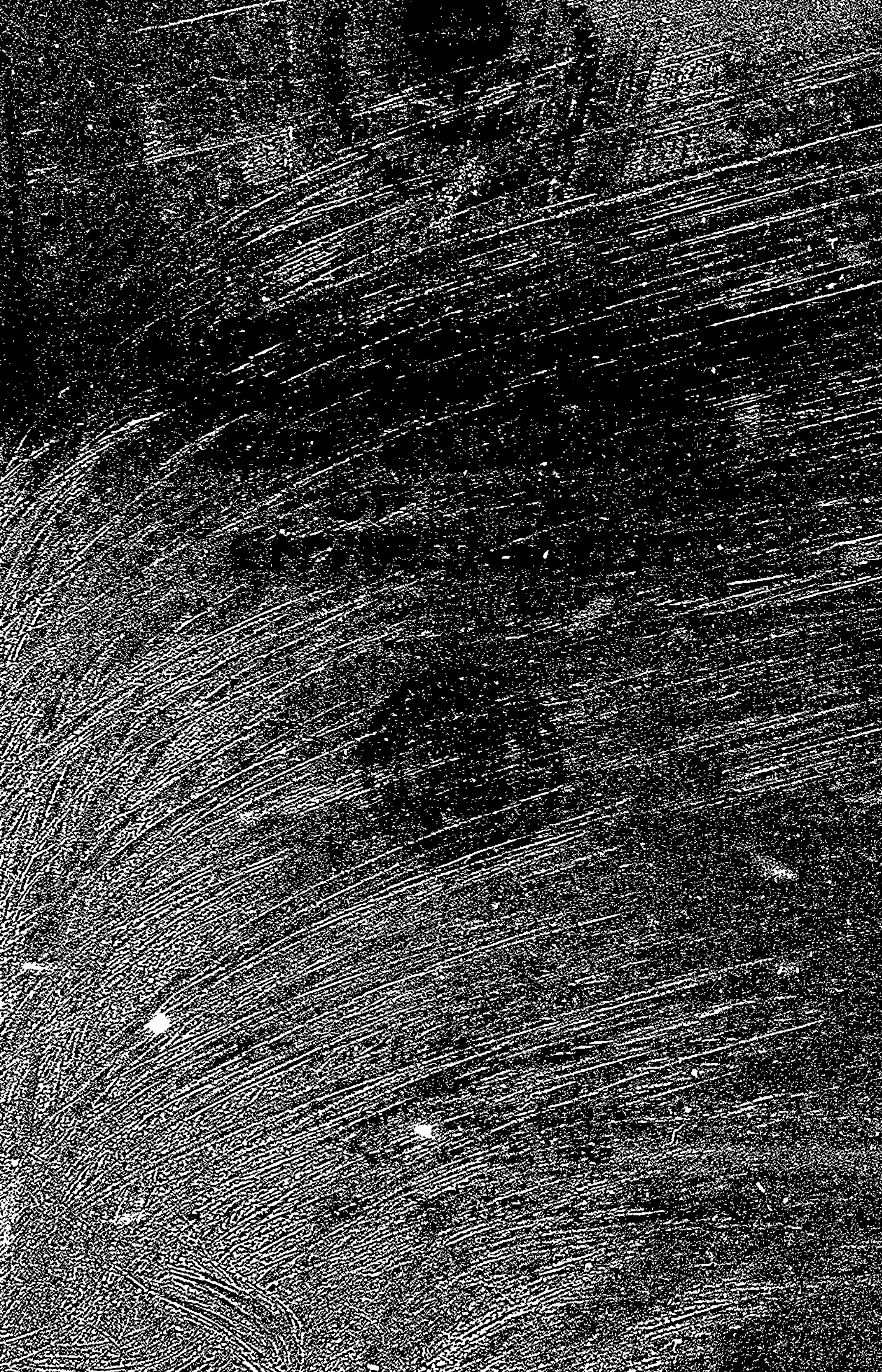

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INTRODUCTION
TO
MONITORING AND SURVEILLANCE
OF THE
ENVIRONMENT

". . . when you can measure what you are speaking about and express it in numbers, you know something about it . . ."

Lord Kelvin

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A NOTE FROM THE AUTHORS:

This text, on Monitoring and Surveillance, is intended for the undergraduate college student and the professional technician. With these readers in mind, we have presented the material both from a practical standpoint and from a philosophical academic approach.

The "reason for" as well as a "how to" approach is important in environmental measurements. The best environmental measurements are made by knowledgeable professionals who are dedicated to environmental protection. To give emphasis to this approach, we have included problems at the end of each chapter which require work in the field, either in making actual measurements or in working with the professionals who make measurements. This integration of practical and theoretical material provides a useful application of the knowledge to actual environmental measurements.

The only way to learn is to do.

The text has been structured to allow key word identification along the side of the written material. Quick reference and mental ordering follow from these key words. This space also provides room for notes and diagrams as desired by the user.

We are grateful to Mrs. Pamelia Murdock and Mrs. Carol Nelson for typing the manuscript, to Mrs. Alice Zimmerman for artwork, and to the many people in academic and governmental circles who contributed ideas and directions to this effort.

Robert L. Champlin

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POLLUTION

The Environment

In recent years a significant interest has developed both in the scientific and public sectors of our society concerning our environment. We have recognized our absolute dependence upon the dynamic system and interrelationships of food, water, and air. In perspective, these revelations generally occurred only after several specific parts of the system had deteriorated to such an extent that awareness became mandatory. This awareness signaled a demand for clean-up and protection of our natural resources. Standards of performance were set and laws were passed to control pollution. These laws and standards, fortunately, go beyond immediate minimum requirements for survival and aim toward the strengthening of the factors involved in the quality of our lives.

Professional Technician

The strict enforcement of pollution standards and the proper management of our resources will require a complex and accurate surveillance system. This system will depend in large part on a new group of professional technicians who are highly trained in monitoring the environment. This monitoring responsibility will involve the selection and installation of automatic monitoring equipment, the standardization of instruments and systems, and the collection and evaluation of the data. Since no automatic sensing system will be adequate to fully monitor our environment, additional data from individual samples will be needed.

This book is aimed primarily toward the training of the professional technician who has the responsibility for this basic environmental data.

Monitoring Responsibilities

The basic responsibility for monitoring is to indicate what is going on in the environment. This monitoring can be broken down into these steps:

1. selection of proper parameters for testing and evaluation,
2. analysis of presently available data,
3. selection of proper sites for additional sample collection,
4. selection of proper collection systems based on need for continuous or non-continuous data,
5. selection of testing systems to produce data based on parameters and management needs,

6. standardization of systems and testing in order to assure accuracy of data,
7. collection and presentation of data,
8. evaluation of data for enforcement of standards or development of better management,
9. evaluation of the total system to see if the data available and data collected is meeting the surveillance requirements.

Although this general outline seems simple, each step involves and requires considerable knowledge and experience for proper success. This book will present the knowledge necessary for proper development of these steps.

Pollution

The primary reason for monitoring is to stop pollution. Our planet is polluted. Everyone is aware that we have changed and polluted our environment. We read about pollution problems in our daily newspapers and magazines such as: oil slicks on our oceans and coastal waters, fish kills in our rivers and lakes, polluted water supplies, and heavy eye-irritating smog in all of our large cities. We see programs on television showing the garbage we dump in the oceans and its effect on ocean life. We see mine drainage that colors our waters and destroys life. We see wrecked automobiles, refrigerators, tires, paper, and garbage all over the country side. We see a loss of beauty in our city and rural life.

The general public and many active conservation groups demand an end to this pollution. Ecology clubs and biology groups warn of impending disaster from pollution. Everyone demands a change in our environmental attitude, a change in our stewardship of natural resources. Responding to this dynamic concern for our environment, our legislatures have passed laws to control and prevent pollution.

But What Is Pollution?

How do you define pollution? How do you put a number on pollution? What makes a river polluted? When is a river not polluted? What causes pollution and how do you prevent it or control it? If money is used to control pollution, how do you know you have been successful and the money was well spent?

These are common basic questions that you must answer in order to understand your job and responsibility.

Popular concepts or definitions of pollution are based on human response. Our five senses of touch, sight, smell, sound, and taste respond individually and collectively to tell us about pollution. We see dirty rivers and floating scum on lakes. We smell foul odors downstream from where sewage is dumped into our rivers. We see piles of dead fish along river banks and lake beaches. Our water tastes funny. We see heavy smoke coming from our waste stacks. We see dirt on our buildings. We smell pungent odors in the air. We see, smell, taste, and feel the general smog that lies over our cities. We hear loud noise from jet aircraft and trains and cars and music. We feel rundown and unhappy. All of our senses respond as a monitor system and say, "this is not the way it used to be," "there is pollution here".

But How Do You Measure Pollution?

All of the human senses are good monitors of the environment. They are our first line of defense in survival but their response is subjective. There is no number associated with our responses. For example, as we clean up a river, when does it become non-polluted? If we depend on the human response system, there would be a variety of answers. Some people would say the river was polluted unless it was absolutely clear, others would not be so restrictive. Said another way, is our eye a good enough instrument to test for pollution or non-pollution? Can we put a number on dirtiness with the human eye - a number which everyone would agree was correct? Obviously, the eye is not a suitable instrument for pollution analysis. It will sense gross or heavy pollution, but instruments which indicate a reproducible number, an objective response, are needed. All of our human responses or senses are subjective and will indicate only gross pollution.

So we need an instrument or test which gives an objective number to pollution.

But When Is Something Polluted?

When do we measure and say, "This is polluted."? When we see a river, for example, the Colorado River in the Grand Canyon, and it is carrying a heavy load of silt, do we consider the river as polluted? In this particular example, most of the silt is due to natural erosion processes and shows little relation to man and his society. A similar problem would be produced if a farmer used too much water with poor soil conservation practice and washed heavy silt (for example, the same amount as in the Colorado River) into a stream. In both cases assume that the concentration or amount of silt per volume is the same. Are both rivers polluted or just the one where man caused the silt?

In the Southwestern part of the United States, severe natural dust storms are common. The dust reduces visibility and settles over everything. A similar problem occurs when a smoke stack emits a heavy concentration of particles which obscures visibility and settles over everything. In both cases, assume that concentrations in the amount per volume of air are the same. Are both situations pollution, or is just the case involving man considered pollution?

In our forest lands we see large areas completely destroyed by fire and further on we see large areas clear cut by logging companies. Are both considered land pollution, or just the one caused by man?

Man Pollution

In general, we define pollution for those cases where man is involved. In the previous examples, only the river where man caused the silt would be pollution, only the air where man caused the dust or smoke would be pollution, and only the land where man caused the damage would be pollution. The reason we define pollution in this manner is simple. We caused the pollution and therefore we can correct it. In the other situations, the pollution is a natural pollution which we cannot control so we do not consider it as true pollution; or as correctable pollution.

In our discussion so far, we have decided that pollution means damage caused by man which we must measure objectively by some instrument or test.

But "How Much" Is Considered Pollution?

If you select one parameter of pollution, for example silt from agricultural runoff, how much silt is necessary before you consider it pollution? Or said conversely, how low a value of silt is necessary before you consider the river non-polluted with respect to silt? Some people consider the lower limit zero. That is, no silt means no pollution. This is a commendable level of pollution control, but far from acceptable, reasonable, justifiable, or technologically practical to achieve. Hopefully, we can approach this level and restore our environment to its best quality, but zero levels of pollution are not possible.

Old Standards

If not zero, then what level should we set as our standard and how do we set the level? Standards are always set on principals involving resource use. If a resource, like a river, is not used, then it is all right to pollute it to any level. This has been our past policy of resource use. If the water is used for agriculture, industry, or cities, then the river standards must reflect and protect these uses. If industry needs a certain quality water and the available water is far below the needed quality, then the water is polluted with respect to that industry's use. In practice, the first standards that are set involve human health. Standards for drinking water have been in use for many years. These standards limit the quantities of poisons and pathogens in order to protect the public health. Here the standard was set on human use. From these basic survival standards, water standards were set for agriculture and industry.

New Standards

Even with these kinds of standards, our rivers have become overloaded with all sorts of waste and now the public has demanded a new standard - an aesthetic standard. The public now demands a return to a natural stream, to a natural air, and to a natural land area. This standard goes far beyond the normal use criteria of the past and demands a return to a quality environment. The return to a natural system does not mean the river or air might not be polluted by nature, but it does mean that man's influence will be minimal.

There are other reasons for protecting our environment. We have learned in the last few years that the living system on Earth is dynamically interlocked with the land, the air, and the water. In the past, man's impact was small enough so if he made environmental mistakes, only small effects were noticed. We have now arrived at the point where there is enough technological potential and mass of people where environmental mistakes can prove enormously disastrous. We must protect our environment and our resources in order to assure our survival.

Ecology

An example of ecology is our oxygen supply. The oxygen level in our atmosphere is approximately 21% by volume. When the Earth was formed, the oxygen level was zero. We have gone from zero free oxygen to 21% free oxygen over some three or four billion years. This oxygen is supplied to the atmosphere by green plants on land and in oceans. If we mismanage some of our poisons, it is possible to significantly reduce the oxygen-production part of our system. There is nothing sacred about 21% oxygen. Knowledge about the Earth and its living systems is showing us that there is a significant risk of survival unless we protect our environment and reduce the rate of use of our resources.

In summary, pollution is generally considered that caused by man or correctable by man. It must be measured objectively by an instrument or test in order to put a number on it. Standards for levels of pollution are set on values of use. These uses have developed to the point where aesthetics and ecologic values are considered as the proper standards. This level reflects our desire for a quality environment and also our knowledge that survival depends on our resource stewardship.

But What Measures Pollution?

There are hundreds of parameters which indicate the state of the environment. It is not feasible or necessary to measure all of these parameters in order to determine pollution. Generally a few selected parameters are measured. These few selected parameters are measured frequently and are used as indicators of pollution. If pollution is indicated, then many more parameters are selected for testing in order to complete the picture of the pollution problem.

In the past, surveillance systems have been based on one or at best just a minimum number of parameters. For example, for many years the Biochemical Oxygen Demand (BOD) test has been used as the only parameter indicating river pollution. This test measures only one parameter of the water and must be used in conjunction with several other parameters in order to indicate pollution. Parameter selection and evaluation will be presented in detail in the specific environment chapters.

Parameter Classification

Parameters of the environment are generally classified as physical, chemical, and biological parameters. This classification is one of convenience. In developing a knowledge of the environment, it is important to keep in mind that all the physical, chemical, and biological systems of nature function together and influence each other. You cannot simply look at the physical system and make statements about the environment. All systems must be evaluated. For example, in a river the velocity of flow (a physical parameter) can affect the chemistry and biology of the river. A fast flowing river can carry a lot of silt from erosion which can change the chemistry of the river. This heavy silt load can also affect the biological systems of the river by reducing plant life and consequently reducing fish life. Selecting parameters from all three systems is necessary in order to properly evaluate pollution.

Another example of the interaction of systems concerns the air environment. For many years visibility (a physical parameter) was used to indicate the state of the atmosphere. Visibility is a good parameter for determining aircraft traffic procedures but is inconclusive for pollution evaluation. If the visibility is reduced because of rain, there is no pollution. If the visibility is reduced because of smoke or cement dust, then there is pollution. Visibility might indicate a reduction in how far you can see, but what is causing the reduction, its chemical and biological effect on materials, plants, and animals, must also be evaluated. A few examples of physical, chemical, and biological parameters are presented in Table 1-1.

But Why Is There Pollution?

Pollution means "too much". It means that man has added so much waste material of one form or another to his environment that he has changed the basic structure of his environment. How did we get into this position?

Pollution History

Historically man has always used the rivers and the lakes and the atmosphere and the land as his garbage dump. "Out of sight and out of mind" has been our philosophy. Until recently this technique of waste disposal has worked satisfactorily. In effect our wastes were so diluted by injecting them into passing rivers or air masses that no environmental change was noticed. Some textbooks in engineering still reflect this philosophy of dilution by including sewage treatment designs which use the river as part of the treatment plant. For example, if a river has dissolved oxygen, why not use it to oxidize sewage. Unfortunately, most of our rivers do not have any more dilution water or treatment capacity, and pollution has degraded our rivers far below their natural conditions.

TABLE 1-1
ENVIRONMENTAL PARAMETERS

Physical	Chemical	Biological
Temperature	pH	Coliform Bacteria
Color	Dissolved Oxygen	Fecal Bacteria
Odor	Alkalinity	Viruses
Total Solids	Acidity	Pathogens
Wind Speed	Hardness	Algae
Water Velocity	Chromium	Fish
Sediment Load	Arsenic	Wildlife
Particle Size	Sulfur Dioxide	Waterfowl
Solar Radiation	Lead	Birds
Visibility	Mercury	Plants
Suspended Solids	BOD	Man
	COD	
	Total Carbon	
	Oil and Grease	

Sinks

In chemical terms, man was using the rivers and airs and oceans and lakes and lands as a sink for waste. He assumed these sinks had infinite capacity for diluting wastes and therefore little treatment was necessary prior to dumping. Pollution has occurred because we have overloaded the system. Our infinite sinks only have a limited capacity to absorb our wastes. Our sinks are finite, not infinite.

Population

The major reason for this overloading of our environmental systems is population and industrial concentration. In midyear 1970, the population of the United States was 205,395,000 people (1-1). The annual population increase at that time was 1.2%. Since that time there has been a slight downward trend in the rate of increase. Population predictions indicate that in the year 1980 the population ought to reach 232,400,000; in 1985, 249,240,000; and in 1990, 266,319,000. The United States has a land area of 3,537,000 square miles and a water area of 78,000 square miles. If you divide the population (1970) by the land area, you get an average density figure of 58 people per square mile.

(1-1). Statistical Abstract of the U.S. Bureau of Census.

Urban Versus Rural

This average value is very misleading. Since about 1920 there has been a steady increase in the urban population over that of the rural population. In 1920 the urban population was 51.2% of the total or about one-half of our people lived in cities and one-half lived in rural areas. In 1960, 70% of our population lived in the city areas and only 30% lived in rural areas. In the early 1800's, only 24 cities had populations in excess of 2,500. In 1960 there were 5,400 communities with a population in excess of 2,500. These 5,400 communities contain 70% of the United States population. From 1900 to 1960 the population of the United States increased from 75 to 180 million people, an increase of 105 million people. Of the 105 million people, 96.6 million were absorbed by our city areas, an increase of 92%. These figures and comparisons show the remarkable change in living style that has occurred in the United States. A better idea of people and their concentrations can be seen from the data of Table 1-2.

TABLE 1-2
POPULATION FIGURES FOR SOME LARGE U.S. CITIES (1970)

City	City Population (Thousands)	City Density (People/ Sq.Mi.)	Metro Population (Thousands)
Chicago	3,367	14,774	6,979
Dallas	844	2,504	1,556
Denver	515	5,060	1,228
Detroit	1,511	10,827	4,200
Houston	1,233	2,715	1,985
Kansas City	507	1,603	1,257
Los Angeles	2,816	6,069	7,032
Miami	335	9,849	1,268
Milwaukee	717	7,431	1,404
Minneapolis	434	7,490	1,814
Newark	382	15,934	1,857
New York	7,896	24,674	11,576
Omaha	347	4,453	541
Philadelphia	1,949	15,106	4,818
Phoenix	582	2,345	968
Pittsburgh	520	9,371	2,401
Portland	383	4,348	1,009
St. Louis	622	10,201	2,363
Salt Lake	176	3,141	558
San Diego	697	2,226	1,358
San Francisco	716	15,457	3,110
Seattle	531	5,801	1,422
Washington, D.C.	757	12,066	2,861

Table 1-2 shows that population density in our larger cities ranges from about 1,600 people per square mile upwards to nearly 25,000 people per square mile in New York City. This is dramatically different from the average value of 58 people per square mile. The significance of these densities is reflected in all of our city problems; crime, pollution, racial problems, housing, tax base, and so forth.

Outer-Inner Cities

Because of these high density concentrations, the inner city has become less attractive for a living environment. The suburban or the area surrounding the inner city has become the new development. Table 1-2 shows the metro population figures. In effect, the inner city system is presenting a new set of problems for government. The outer cities are usually self-governing and independent of the inner cities. Unfortunately, most of the problems which need solutions, including pollution, are area-wide problems. Cooperation between inner and outer cities is generally poor. This compounds the problems and creates a very complex system for pollution control. This is especially true in the financing area. Should suburban areas contribute tax money to the inner city? There have been many approaches used to solve this taxing or money supply problem. None seem totally acceptable at the moment. It seems reasonable that a new governmental structure - a metropolitan government - is the answer. This concept has met with limited success.

But How Do You Stop Pollution?

Historically, the general steps we have gone through in pollution control are as follows:

1. An awareness of pollution and its effects by professionals in the field,
2. An awareness by the general public of pollution through personal experience and information from concerned professionals,
3. A demand by the general public for improvement of their environment,
4. A reaction of legislatures to these environmental concerns which resulted in laws, both State and Federal, and,
5. An application of the laws to the problems of control. If environmental quality did not improve, then new laws were enacted.

These new laws set standards, required monitoring and surveillance systems and set enforcement procedures.

Ambient Standards

First attempts at control set standards for ambient conditions. That is, standards were set for rivers and for air masses. These were the areas where there was pollution so it was reasoned if we set standards on them that should solve the problem. This approach ran into problems. First, in areas where many industries were contributing to the pollutional load, the question was asked, "Who is to reduce their contribution and by how much?". In effect, each industry should reduce its load until the sum of all the industries' waste would be below the maximum standard. But each industry only wanted to do its share. In order to identify this share, industry asked for a complete environmental statement.

A second problem in this approach was the standard itself. Here the question was asked, "Do you set the same standard all across the country for ambient conditions?". If you set all standards as equal, then an industry located in a heavily industrialized area would have to meet a more restrictive standard of discharge than the same industry in a sparsely industrialized area. The former is only one of the many industries contributing to the pollutional load while the latter may be the only industry. Obviously, the latter industry was favored by this approach. This approach could lead to more decentralized industry and concurrent population centers, but it would be a slow process. Many governors, who were looking for industry for their states, favored this approach.

Minimum Ambient Standards

Another question on standards came from areas where the ambient conditions were all ready above, sometimes significantly above, the minimum standards. People in these areas did not want their environment degraded to the minimum standards. A compromise for this upper level was worked out. This allowed some degradation but not down to the minimum levels. In effect then, minimum standards on air and water have been set and in areas where the ambient conditions are above the minimum, more restrictive values or standards have been applied. These upper value standards were generally based on an anti-degradation clause.

This high level standard approach reduced some of the favoritism toward industry in less concentrated areas. Still the pollution problem was not fully solved. Many industries dragged their feet in expending money for pollution control. They were still asking, "How much should I reduce and are my neighboring industries doing their share?". In order to answer these questions and apply the principle of equal justice, new laws were enacted. These new laws restated the policy of ambient standards and they set policies and goals for standards of discharge. They are called effluent standards.

Effluent Standards

Effluent standards are standards on the actual quality of each kind of discharge. These specific standards are being promulgated and approved for each kind of discharge. This approach is far-reaching and more equal in application than previous laws. In this approach, everyone who discharges a waste will be required to meet a standard. Small industries with small volumes of waste will have to meet the same standards of larger, similar industries. If it is cheaper to treat larger volumes, then the larger industries would be favored by this approach. However, this is at present our best approach to control pollution in an equitable manner.

Laws and Policy

In order to understand the general direction taken by our federal government, the beginning statements of our Air Quality and Water Pollution Laws are presented.

CLEAN AIR ACT (1-2)

Air Pollution

"TITLE I--AIR POLLUTION PREVENTION AND CONTROL

"FINDINGS AND PURPOSES

"SEC. 101. (a) The Congress finds--

"(1) that the predominant part of the Nation's population is located in its rapidly expanding metropolitan and other urban areas, which generally cross the boundary lines of local jurisdictions and often extend into two or more States;

"(2) that the growth in the amount and complexity of air pollution brought about by urbanization, industrial development, and the increasing use of motor vehicles, has resulted in mounting dangers to the public health and welfare, including injury to agricultural crops and livestock, damage to and the deterioration of property, and hazards to air and ground transportation;

"(3) that the prevention and control of air pollution at its source is the primary responsibility of States and local governments, and

"(4) that Federal financial assistance and leadership is essential for the development of cooperative Federal, State, regional, and local programs to prevent and control air pollution.

"(b) The purposes of this title are--

1-2. Clean Air Act (42 U.S.C. 1857 et seq.) includes the Clean Air Act of 1963 (P.L.88-206) and amendments made by the "Motor Vehicle Air Pollution Control Act"--P.L.89-272 (October 20, 1965), the "Clean Air Act Amendment of 1966--P.L.89-675 (October 15, 1966), the "Air Quality Act of 1967"--P.L.90-148 (November 21, 1967), and the "Clean Air Amendments of 1970"--P.L.91-604--(December 31, 1970).

"(1) to protect and enhance the quality of the Nation's air resources so as to promote the public health and welfare and the productive capacity of its population;

"(2) to initiate and accelerate a national research and development program to achieve the prevention and control of air pollution;

"(3) to provide technical and financial assistance to State and local governments in connection with the development and execution of their air pollution prevention and control programs; and

"(4) to encourage and assist the development and operation of regional air pollution control programs."

In summary, the following points should be noted. In paragraph 2, Section 101a, health, agriculture, property and transportation are mentioned as "use" functions. Welfare is also mentioned....Welfare and productive capacity....is also mentioned in paragraph 1 of Section 101b. This type of standard indicates a more restrictive form of standard than used in the past.

Another important point is contained in paragraph 3 of Section 101a. Here it says that the States have primary responsibility for prevention and control. In order to insure uniformity throughout the United States, within general limits, the States have to submit their standards and procedures to the Federal Government for approval.

The Federal Water Pollution Control Act has the following goals and policy.

Water Pollution

"THE FEDERAL WATER POLLUTION CONTROL ACT" (1-3)

"TITLE I--RESEARCH AND RELATED PROGRAMS

"Declaration of Goals and Policy

"SEC. 101. (a) The objective of this Act is to restore and maintain the chemical, physical, and biological integrity of the Nation's waters. In order to achieve this objective it is hereby declared that, consistent with the provisions of this Act--

"(1) it is the national goal that the discharge of pollutants into the navigable waters be eliminated by 1985;

1-3. Public Law 92-500, 92nd Congress, October 18, 1972.

"(2) it is the national goal that wherever attainable, an interim goal of water quality which provides for the protection and propagation of fish, shellfish, and wildlife, and provides for recreation in and on the water be achieved by July 1, 1983;

"(3) it is the national policy that the discharge of toxic pollutants in toxic amounts be prohibited;

"(4) it is the national policy that Federal financial assistance be provided to construct publicly owned waste treatment works;

"(5) it is the national policy that areawide waste treatment management planning processes be developed and implemented to assure adequate control of sources of pollutants in each State; and

"(6) it is the national policy that a major research and demonstration effort be made to develop technology necessary to eliminate the discharge of pollutants into the navigable waters, waters of the contiguous zone, and the oceans."

Some specific points in this declaration should be emphasized. First, the objective is "....to restore and maintain the chemical, physical, and biological integrity of the Nation's waters....". This integrity is further stated in subsections 1, 2, and 3 of Section 101a. The elimination of pollution, the attainment of a water quality level necessary for natural fish production, and the prohibition of toxic pollutant discharges are very high standards for our use function. These statements go way beyond the usual health, property, and agriculture standards to one involving the best quality environment possible.

Another important point is the wording used in 1 and 2 compared with the other subsections. In subsections 1 and 2, the word used is "goal" while the word used in 3, 4, 5, and 6 is "policy". A goal is something we hope to reach while a policy is more absolute. Even though Congress used the word "goal," they expect the results of this law to approach this goal very closely. With the amount of money appropriated under this law, the public has a right to expect results. The results will be indicated by monitoring and surveillance systems, manned by a professional staff of technicians, a staff with the highest personal integrity toward their responsibility.

But Where Do You Measure Pollution?

In general, monitoring should be done where wastes discharge into the environment. As pointed out before, monitoring of the ambient conditions in nature is also important, but primary monitoring and control should be at the point where discharges enter the environment.

Source

The first way to group pollutants is with respect to source. Two general types of sources are of concern.

Point Source

The first is called a "point source." The "point source" type discharge is defined as a waste discharge entering the environment from a single point. Examples of this type of discharge are many and varied. For example, the smoke from a power plant is discharged from a stack (point source) into the air environment. An effluent discharge line from a city sewage plant discharges the treated sewage into the river from a single pipe or outfall channel. A car discharges its waste from the exhaust pipe (a point source). A ship discharges its waste into the ocean environment as a point source.

Non-Point Source

The second kind of pollution source is the "non-point source" or "general source." This kind of source discharges pollution into the environment over a large area and not from a point source. There are several examples of this kind of source pollution. Agricultural runoff, consisting of silt and nutrients from fertilizer, may be discharged into a river over a wide area. Sometimes this kind of pollution winds up in a canal which discharges as a point source into the river, but the discharge into the canal could be from a large land area. Irrigation return flow discharging into a river from ground water routes is also an example of a general pollution source. Dust in the air from general agricultural practice is also a common form of general source pollution.

The general plan for pollution control is directed first toward the point sources. This type of pollution source is the easier to control. Monitoring can be done. Effluent standards can be set. Regulation and enforcement can be used. For fixed point sources, like smoke stacks or sewage effluent lines, the approach is fairly straight forward. For some point sources, like automobiles, the solution is not an easy one.

Automobile--Mobile Point Source

Automobiles which contribute significantly to our air pollution problem are a point source, but they are also a mobile or moving point source. This type of problem is much harder to control. The present approach is the requirement of certain control devices in the car, or said another way, the attainment of certain emission standards at the time of manufacture. There is still a question of what happens after a period of use. Are the standards still being met? Periodic checkups at pollution control centers, in order to insure proper compliance, seems like the proper approach. General pollution sources and mobile pollution sources will remain our biggest challenge in the future.

Kind

Another way to define group pollution sources for monitoring purposes is by kind. In this grouping scheme, all industry is grouped together, all municipal sources are grouped together, all transportation systems are grouped together, all agricultural sources, all mining, and governmental sources are grouped together.

Financial

There are several reasons for this type of grouping. First, it separates the sources into groups with different approaches to financing the pollution control. Pollution control systems for municipalities are financed by the public, either through Federal and State support or local bonding or use-taxes. This money is public money. Industry, on the other hand, must build its pollution control systems from its own funds. These expenditures are obviously passed on to the consumer, but do not originate with the public. In effect, the people who use the products of industry pay a pollution control tax when they buy the product.

Parameter

A second reason for this type of pollution-source definition is parameter grouping. In effect, all municipalities have similar kinds of effluents. The pollution from a city contains waste and can be characterized by parameters such as BOD (Biochemical Oxygen Demand), bacterial counts, suspended solids, etc. Some cities may have unique problems which produce unique pollution, but in general, most cities have similar type effluents. Industry can also be subdivided into groups with similar discharges. For example, the waste water effluent from one oil refinery is similar to most other oil refineries. The stack emissions from a cement plant are similar to other cement plants if they use the same manufacturing process. The emissions from sulfuric acid plants are similar. The emissions and effluent from power plants, using the same kind of fuel source, are similar. The emissions from transportation systems are generally the same. All cars emit similar pollution. Other pollution groupings of governmental sources, agriculture, or mining, give similar results.

This kind of grouping gives the pollution monitor an idea of what to expect and what kind of controls and efficiency are necessary to meet effluent standards. Examples of these kinds of pollution will be given in the specific environmental chapters.

Media

A third way of grouping pollutants for monitoring purposes is by media. Is the pollutant discharged into the water medium, air medium, or on the land medium? Most of our laws are structured to prevent water pollution, to prevent air pollution, or to prevent land pollution. This has been convenient for separating our problems, but our environment works as a unit. Pollutants which are discharged into the water can affect the other media of air and land, and vice versa. Monitoring can measure pollutants or environmental parameters in the individual media, but surveillance systems, or the broad overall view, must consider the entire environment, and interactions within it.

President Nixon, in a message to Congress, indicated "....for pollution control purposes the environment must be perceived as a single, interrelated system. An effective approach to pollution control would:

--Identify pollutants

--Trace them through the entire ecological chain, observing and recording changes in form as they occur.

--Determine the total exposure of man and his environment.

--Examine interactions among forms of pollution.

--Identify where in the ecological chain interdiction would be most appropriate."

Monitoring Objectives

In summary, there are six basic reasons or objectives for monitoring our environment.

1. Characterization of Existing Conditions

Background surveys of existing conditions will furnish two kinds of data. First, natural background values must be established. These values will furnish the basic data for setting zero pollution levels. Since most parameters vary according to the seasons, data must be collected in non-polluted areas over long periods of time for proper evaluation. The second kind of data would indicate the present state of pollution levels. It is important in pollution control work to know: where we are now and how much we have to improve in order to meet quality standards.

2. Identification of Trends

Trend information is essential in evaluating the pollution control program. This information will indicate whether control activities are lowering pollution values or if new, more restrictive programs must be started in order to meet quality standards. Enough data, of sufficient accuracy, must be collected for proper evaluation of trends.

3. Evaluation of Standard Compliance

After quality standards have been set for effluents or emissions, it is most important to monitor these discharges in order to assure compliance with the standards. The data collected in monitoring for compliance evaluation must be of the best accuracy possible. Some of these data will be used in enforcement and violation proceedings. There must be no question with regard to the validity of the data.

4. Emergency Conditions

Monitoring systems must provide a warning of emergency conditions. These conditions can involve direct health-related problems. For example, in many cities, air pollution alert systems are in effect. If the cumulative effects of pollution emissions reach health hazard levels, then various sources of pollution are restricted in operation. Hopefully, emission or effluent standards can prevent this level of problem as a general rule, but various accidental situations can occur causing immediate problems. Accidental spills of toxic material into a river is another example. Monitoring systems must sense and report these kinds of problems.

5. Environmental Quality Forecasting

In recent years, many mathematical approaches have been developed to forecast problems in the environment. These mathematical programs are solved using computers. This informational approach is called "modeling" or "systems analysis." This approach uses mathematical equations to describe nature. The constants used in these equations require environmental data for evaluation; thus monitoring supplies the basic data necessary for proper mathematical modeling.

6. Research

There is a considerable amount of basic knowledge about the environment that we do not know. Research methods are being developed to analyze the environment as a whole. Past research has developed around single media, like air or water and then only in chemical aspects or biological aspects, or hydraulic flow problems or quantity demands and so forth. The mathematical modeling approach has indicated how little we know about our environment in individual ways as well as in combined ways.

Synergism

We are using new words in environmental research - synergism or synergistic effects. Synergism is a combined or cooperative effect of several systems. Each system adds to the total system but the total effect is more than the sum of the parts. This is true of smog formation and eutrophication. In each case the compounds leading to the total problem do not create a serious problem by themselves, but their combined effect is serious. The opposite situation is also possible. This is called an antagonistic effect. Here each system adds to the total, but the total effect is less than the sum of the parts.

Since we live in a dynamic world where all processes are interlocked and interdependent, our research must reflect this dependence. The characterization of specific pollutants, their movement and effect on our environment in conjunction with their synergestic and antagonistic effects is essential knowledge. Much of this information will be gained from monitoring and surveillance systems.

Problems:

1. Plot population and population density graphs for the last hundred years for several large cities and metropolitan areas.

2. Visit a populated area and identify all the pollution problems. Visit the water treatment, waste water treatment, and garbage plants.

3. Walk along a river as it passes through a city. Locate point sources of pollution and identify possible sources for the pollution.

4. Collect samples of a river above and below agriculture, industrial, and municipal areas. Does the river quality appear to be changed?

5. Collect samples of natural plant life in the city and in the adjoining countryside. Is there a difference in kind and amount of plant life?

6. Where would you place monitoring stations to indicate pollution in the city and adjoining areas?

7. Who is responsible for pollution?

8. What do you consider the best way to arrange a city? Where should people live, work, and play? Sketch a general model of the city.

9. Should growth and population density be controlled?

10. Who should pay for pollution control?

Additional Reading:

Man's Impact on Environment
Thomas R. Detwyler
McGraw-Hill Book Company

Metropolis in Crisis
edited by Jeffrey K. Hadden
Louis H. Masotti
Calvin J. Larson
F.E. Peacock Publishers

MONITORING AND SURVEILLANCE SYSTEMS

Monitoring Limits

There is no limit to the demands for more and more environmental data. Some scientists profess that we should measure everything -- everywhere -- always. This is The Ultimate goal in monitoring. Supposedly with this infinite amount of data we could completely understand nature, we could predict or forecast everything, and life would contain no surprises. This ultimate approach is not possible or practical. We could not possibly handle, evaluate, or use the mountains of data and secondly we could not afford such a program. Monitoring programs must be functional and usable The data must be accurate, pertinent, concise, and collected for a purpose.

Fortunately, many organizations have been collecting data on several environmental parameters for many years. Much of this data is directly usable in pollution control work. Duplication of this data by new monitoring systems is unnecessary.

Available Data

Many governmental agencies with various missions monitor environmental parameters. The National Weather Service monitors and forecasts weather patterns. This information is directly usable in our air pollution programs. The United States Geological Survey (U.S.G.S.) monitors the quantity and general quality of water in our rivers. The Atomic Energy Commission monitors radioactivity around their plants and reactors. Several state groups monitor the environment also. In order to introduce the variety and kinds of information presently available, a summary of some of this data and the collecting organizations' mission is presented. Governmental departments and agencies summarized in this chapter are:

1. The United States Department of Agriculture
    Soil Conservation Service
2. The United States Department of Commerce
    National Oceanic and Atmospheric Administration (NOAA)
3. The United States Department of Defense
    Defense Supply Agency
    Army
    Navy
    Air Force
4. The United States Department of Interior
    The Fish and Wildlife Service
    The United States Geological Survey (USGS)
5. The Atomic Energy Commission (AEC)
6. The United States Environmental Protection Agency (EPA)
7. State Monitoring Programs
    Ohio Department of Natural Resources
    Ohio River Valley Water Sanitation Commission (ORSANCO)
    New York State Dept. of Environmental Conservation (ENCON)

1. The United States Department of Agriculture

The United States Department of Agriculture has several sections and programs related to the environment and pollution control. The most important of these is the Soil Conservation Service (SCS).

"The mission of the Soil Conservation Service is to assist in the conservation, development, and productive use of the nation's soil, water and related resources so that all Americans may enjoy:

--Quality in the natural resource base for sustained use,

--Quality in the environment to provide attractive, convenient, and satisfying places to live, work, and play,

--Quality in the standard of living based on community improvement and adequate income." (2-1)

In order to meet the needs of the United States, the Soil Conservation Service has initiated a Framework Plan - Soil and Water Conservation for a Better America. This plan has several new and emphasized programs which reflect the growing awareness of pollution control and environmental monitoring.

Some of these areas of emphasis are:

Developing an improved system that uses benchmark standards for quantity and quality for monitoring natural resource conditions and the environment.

Finding new approaches for treating difficult and persistent erosion and sediment problems.

Making pollution prevention and abatement an integral part of the conservation program.

Providing technical assistance in waste management.

Supporting programs that lead to a better distribution of the nation's population.

Helping to develop a stream classification system and standards for stream management.

Assisting state and local governments with legislation, ordinances, regulations, and other planning criteria that lead to prudent land use and treatment.

(2-1). Kenneth E. Grant, Administrator, U.S. Soil Conservation Service, Framework Plan.

Working more intensively with state and local governments on conservation plans, projects, and measures in rural and urban areas.

Helping to improve national and state land use policies.

Improving soil and water conservation technology by encouraging needed research and development.

Encouraging states to enact water use laws that lead to more efficient water use.

Encouraging preservation of areas with unique characteristics for agriculture, recreation, wildlife use, and historical sites.

Seeking new approaches to programs that lead to the development, improvement, and protection of privately owned wetlands and coastal marshes.

Helping communities develop and implement plans for the management and protection of lands subject to flooding.

Relating conservation programs to the needs of people for a better environment, community improvement, and economic opportunity.

Developing a system for rapid storage and retrieval of resource data.

Erosion. Erosion of land due to wind and surface runoff is a very serious continuing problem in the United States. This erosion reduces the available top soil necessary for good agricultural production and produces a sediment load in our rivers and air which is unacceptable. In addition to sediment from farm and ranch land, other sources are construction sites, surface strip mines, roads, and semi-desert areas. Under the Framework Plan, a national effort is underway to reduce this soil erosion.

Sediment Sediment monitoring systems are under development by the Soil Conservation Service. These systems will evaluate sediment-yield as a function of land and use, sediment density, and density changes. The studies will also monitor changes in water quality in reservoirs and lakes due to sediment. Changes in stream channels and flow hydraulics will also be monitored.

Animal Waste A second major pollution problem being monitored by the Soil Conservation Service is animal waste. Livestock production methods now concentrate the animals in small land areas called feed lots just prior to sale. The concentrated waste products from these operations are enormous. Surface and ground waters may be polluted by these operations.

Salinity

A third pollution area of concern to the Soil Conservation Service is the increased salt concentrations in irrigation return flows. These are particularly significant in arid regions. High salt concentrations in irrigation water damage growing crops and may permanently damage the soil. Proper water management should reduce this pollution.

Interpretation

Under this Framework Plan, an expanded emphasis has been placed on surveying and monitoring activities. A Soil Survey Interpretation system is presently being made by District Offices of the Soil Conservation Service. This soil survey will use physical and chemical soil tests to key various kinds of soils to possible use. These groups include:

a. Sanitary Facilities
   1. Septic tank adsorption fields
   2. Sewage lagoons
   3. Sanitary landfill (trench)
   4. Sanitary landfill (area)
   5. Daily cover for landfill

b. Community Development
   1. Shallow excavations
   2. Dwelling sites
   3. Commercial buildings
   4. Roads and streets

c. Source Material
   1. Roadfill
   2. Sand
   3. Gravel
   4. Top soil

d. Water Management
   1. Pond reservoir area
   2. Embankments, dike, and levees
   3. Excavated sands
   4. Drainage
   5. Irrigation
   6. Terraces and diversions
   7. Grassed waterways

After the Soil Survey ~~and~~ possible use functions have been completed, the information will be reviewed and coded for computer use at Iowa State University in Ames, Iowa.

Classification — The second step in this land use program is the Soil Classification Survey by counties' areas. County soil surveys are a continuing program of the Soil Conservation Service. This program identifies and publishes a complete soil classification of the counties. By using the Survey Interpretation system at Ames, a tie between kind of soil and possible use can easily be made. This kind of surveying and monitoring activity will greatly aid land planning activities and pollution control work by showing what land is usable for various needs and predicting changes in water quality from that use.

2. The United States Department of Commerce — The United States Department of Commerce has two monitoring and data programs which are significant for those in pollution control work. These programs involve the atmosphere and the oceans and are coordinated by the National Oceanic and Atmospheric Administration (NOAA). NOAA was created in 1970 within the United States Department of Commerce "to improve man's comprehension and uses of the physical environment and its oceanic life."

a. Objectives of NOAA are:

1. To explore, map, and chart the global oceans, their underlying geological structure, and their mineral and living resources. This knowledge can be used in the management and conservation of these biological and mineral resources.

2. To monitor the characteristics of the physical environment including the atmosphere, the oceans, the sun, the solid earth, gravity, and geomagnetism and to predict changes in these characteristics.

3. To monitor and predict trends and gradual changes in climate, tides, marine life distributions and the effects of human civilization on the environment and oceanic life.

To achieve these objectives, NOAA has regrouped and reshaped several existing units into seven new sections.

b. Organizational Sections of NOAA

1. The National Ocean Survey (2-2) brings together the activities of the ESSA, Coast and Geodetic Survey, U.S. Lake Survey, National

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(2-2) Communication from National Oceanic and Atmospheric Administration - United States Department of Commerce.

Data Buoy Development Project, and the National Oceanographic Instrumentation Center. It prepares nautical and aeronautical charts, conducts precise geodetic, oceanographic, and marine geophysical surveys; and predicts tides and currents. It prepares and publishes navigational charts and related materials for the Great Lakes, and conducts investigations of the physical aspects of the lake waters. It is responsible for the development of a national system of automatic ocean buoys for obtaining essentially continuous marine environmental data. It also provides the national focal point for technology related to instrument measurement, evaluation, and the reliability of sensing systems for ocean use.

The National Ocean Survey provides important information to those in pollution control work. Data charts on currents and tides along our coastlines and in the Great Lakes provide information for computation and calculation of pollution mixing zones, and dilution and dispersion patterns. In our many estuaries (where fresh water rivers meet the oceans) the changing pattern of tides and currents can greatly increase the pollution problem. This is due to stratification of the waters because of varying densities. Stratification problems also occur in lakes and will be discussed in the chapters on the Water Environment.

2. The <u>National Marine Fisheries Service</u> is composed of the Bureau of Commercial Fisheries and Marine Game Fish Research Program. It seeks to discover, describe, develop, and conserve the living resources of the global sea, especially as these affect the American economy and diet. The Fisheries Service conducts biological research on economically important species, analyzes economic aspects of fisheries operations and rates, develops methods for improving catches and, in cooperation with the U.S. Department of State, is active in international fisheries affairs. With the U.S. Coast Guard, the National Marine Fisheries Service conducts enforcement and surveillance operations on the high seas and in territorial waters. It also studies game fish behavior and resources, seeks to describe the ecological relationships between game fish and other marine and estuarine organisms, and investigates the effects on game fish of thermal and chemical pollution.

The National Marine Fisheries Service is a primary source of information on pollution in our oceans and estuaries. They also monitor levels of heavy metals in fishes and cooperate by contract with the Environmental Protection Agency in monitoring pesticides in estuaries.

Marine
Monitoring

A new program of monitoring was started in July 1972. This program called MARMAP - <u>Marine Resources Monitoring Assessment</u>

and Prediction - will seek to evaluate all living marine resources off United States waters. Progressively wider ocean areas will be surveyed in later cruises. The mission of this program is "to explore in the most extensive detail in history samples of the countless fish eggs and larvae (ichthyoplankton) strewn through the seas in profusion - mostly to nourish other live forms, a few to survive and renew seed stocks for future generations." (2-3) Pollution as it affects sea life, ecological degradation of the seas, and unpredictable fluctuations in marine stocks are primary goals for this project.

Standards

Another important part of this project is the development of a standard, a common standard, which can be used to relate all future changes in water quality and ocean life. This baseline standard will include information from MARMAP and all other organizations involved in ocean monitoring, including several international organizations and almost a dozen universities. The information will be organized, standardized, and converted into usable presentations.

Measurements of physical, chemical, and biological parameters will be made concurrently during this project. Weather data and ocean currents will also be monitored.

Information

As with all monitoring systems, information will be operational as well as historical. The data will be released under four kinds of reports (2-3).

1. Red Flag Reports - to provide immediate notice of real or incipient damage to marine resources because of overfishing and changes in the marine environment or in the composition of fishing stocks caused by natural or manmade pollution.

2. Summary Recommendations - to provide the scientific information in support of the need for legislation or regulations related to protection (or use) of living marine resources or for pollution control.

3. Status of Resources Reports - to include facts about various prevailing conditions to disseminate maps and fact sheets, summaries, and forecasts.

4. Real Time Output - to circulate material describing distribution and abundance of various marine species catch data, statistics, analytical documents, and fishery advisory bulletins.

(2-3). MARMAP - Census of the Sea, Ann Weeks, NOAA - U.S. Department of Commerce, October, 1972.

Red Flag Report No. 1

The first report - MARMAP Red Flag Report No. 1 - was released by the U.S. Department of Commerce on January 18, 1973. This report entitled "Fish Larvae Found in Environment Contaminated with Oil and Plastic" indicates that oil and plastic pollution is widespread in the northwest Atlantic Ocean. Tar clumps, not visible from the ship, were concentrated by the fine mesh collection nets. Heaviest concentrations were found in the western boundary region of the Sargasso Sea, off northern Florida, and southern New England. These tar balls ranged from grain size to fist size and appear to have been formed from bunker oil jettisoned from ships. Laboratory analysis has shown that more than half of the plankton samples (young fish and their food) collected were oil contaminated.

Plastic contaminants were also found in all survey regions. The plastic scraps were white or opaque spheres or discs, speck to pea-sized and were identified as polystyrene. There is a possibility that these particles may threaten the survival of the varied small fish which consume them.

This study introduces the importance of environmental monitoring and the scale of our global pollution. Figure 2-1 and 2-2 show results of the initial phase of this program (2-4).

3. The <u>National Weather Service</u>, formerly the ESSA Weather Bureau, reports the weather of the United States and possessions, provides weather forecasts to the general public, issues warnings against tornadoes, hurricanes, floods, and other atmospheric and hydrologic hazards, and provides a broad array of special services to aeronautical, maritime, astronautic, agricultural, and other weather-sensitive activities. These services are supported by a national network of observing and forecasting stations, communications links, aircraft, satellite systems, and computers. Some 300 NWS offices across the land ensure prompt and useful dissemination of weather information.

The National Weather Service is a vast operating section, employing some 5,300 full-time employees at over 400 sites throughout the world (2-5). Several of their monitoring and data collection systems are directly related to pollution and pollution control activities.

(2-4). News Release NOAA 73-17. February 13, 1973. U.S. Department of Commerce.

(2-5). Operations of the National Weather Service, October 1972.

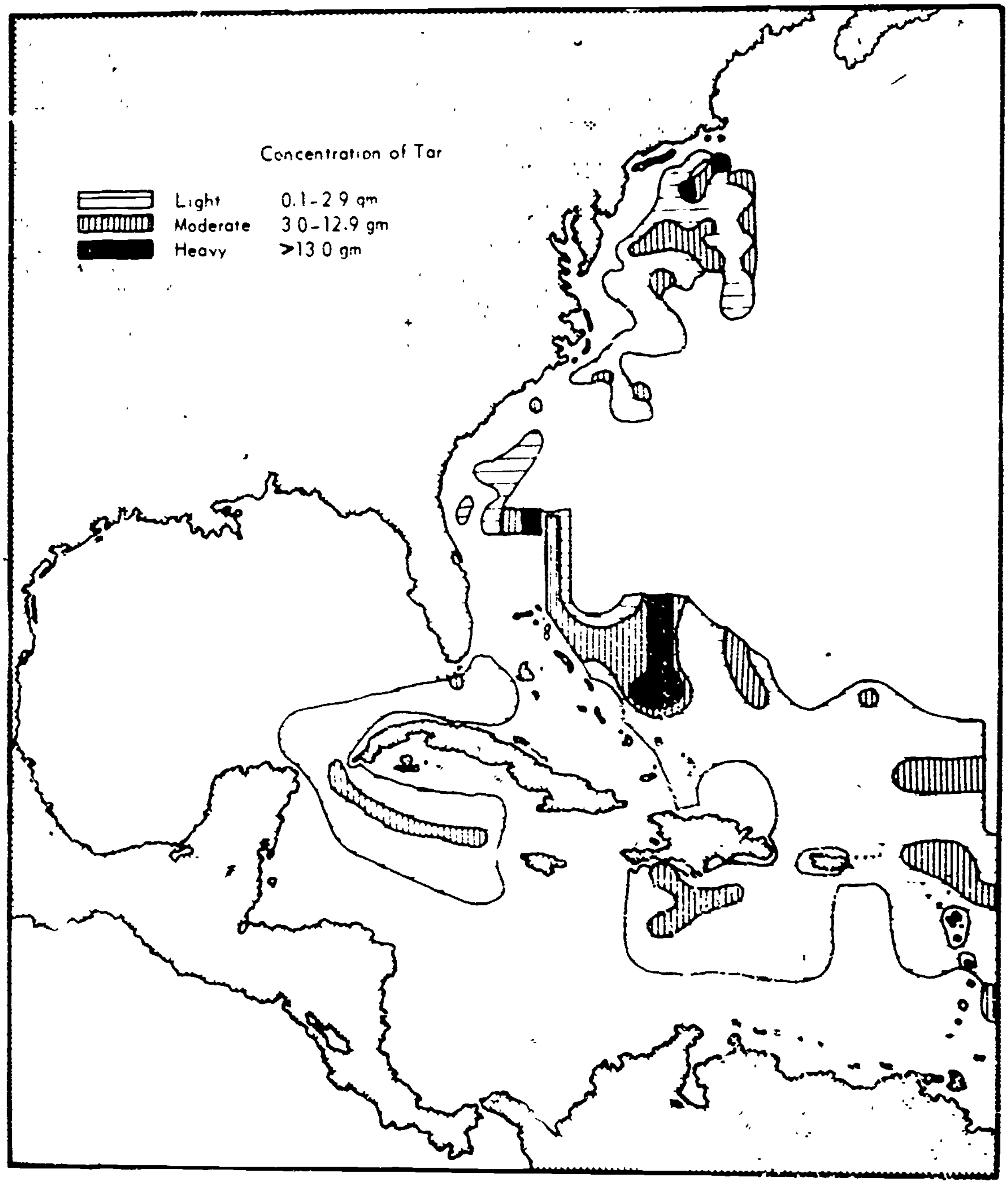

FIGURE 2-1 TAR CONCENTRATIONS

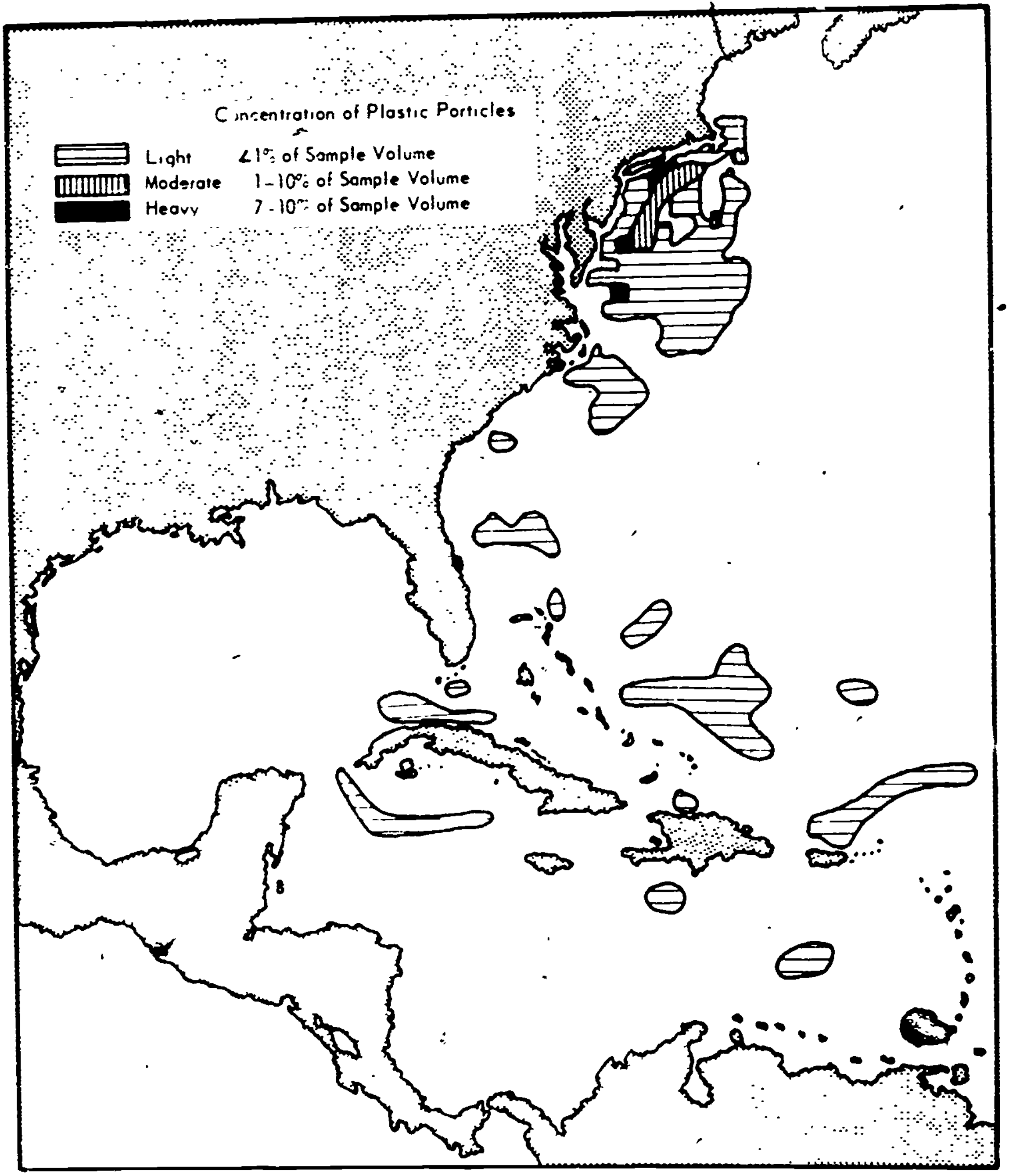

FIGURE 2-2 PLASTIC PARTICLE CONCENTRATION

Forecasting

Forecasting: One of the primary functions of the Weather Service is forecasting or predicting weather. Forecasts, based on numerical and manual techniques, are made at the State Forecast Offices (Figure 2-3). These forecasts are distributed throughout the United States by a long-line teletypewriter system (Figure 2-4). This data distribution system is called the "meteorological network" or the "Service C Teletypewriter Network." This data furnishes the public with an overall picture of the general weather conditions expected over a large area for about 48 hours. Predictions or forecasts from short periods (12 hours up to 30 days) are available. These reports give valuable information on air flow patterns and precipitation regions.

Severe Weather

In addition to daily forecasts, two important severe weather forecasts are made by the Weather Service. The first, the Severe Local Storms Unit (SELS), is responsible for preparing and releasing information on expected severe local storms. The second, the Hurricane Warning Offices (HWO), warns the public along U.S. Coastal areas of unusually high water due to tides and waves caused by severe weather. Severe storms may cause severe pollution by damaging holding ponds and tanks and thereby releasing pollutants to streams. Municipal and industrial waste treatment plants can become damaged, overloaded and flooded by storms, causing temporary pollution problems.

River Forecast Center

Another valuable forecast service is provided by the River Forecast Center (RFC). This unit, staffed by professional hydrologists, prepares short-term (1-5 days) through 30-day forecasts and long-term seasonal water supply forecasts. The unit analyzes precipitation and weather patterns and predicts the amount of water which should occur in various river reaches. This kind of prediction is called "streamflow forecasting." This kind of data will aid in planning, management, and pollution control of the total water resource.

Environmental Quality

Another valuable forecast service is provided by the Environmental Quality Weather Service. This service provides special urban and rural weather observations, forecasts, and advisories on aspects of air pollution, wildfires, and prescribes agricultural burning operations. This service is divided into two programs.

Urban Air Pollution

a. Urban Air Pollution Weather Services. This service forecasts periods when atmospheric stagnation will occur. Atmospheric stagnation, where the ability of the air to transport and dilute pollutants is seriously reduced, may cause severe pollution problems requiring curtailment of industry, automobile traffic, and general activity. These advisories

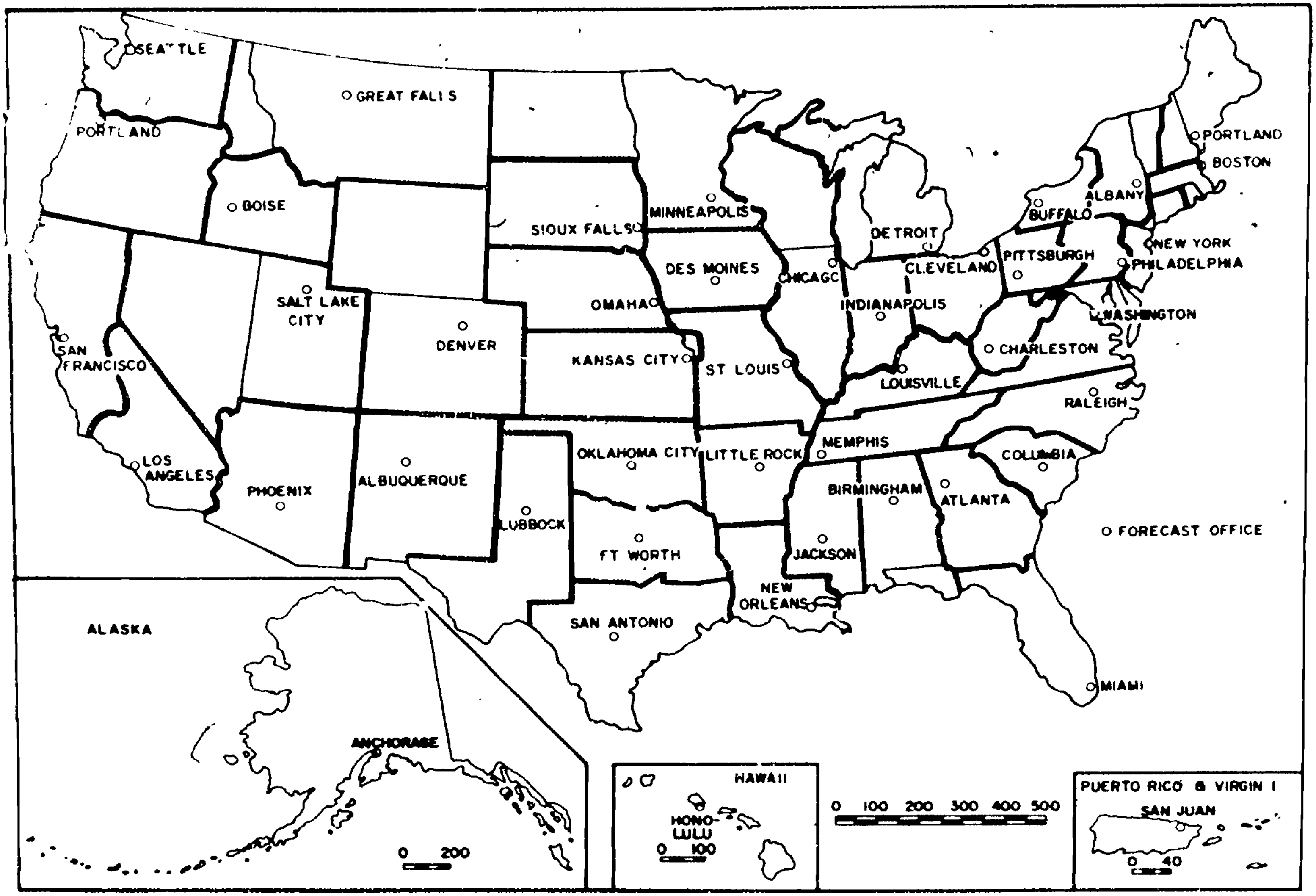

FIGURE 2-3 STATE FORECAST OFFICES AND AREAS

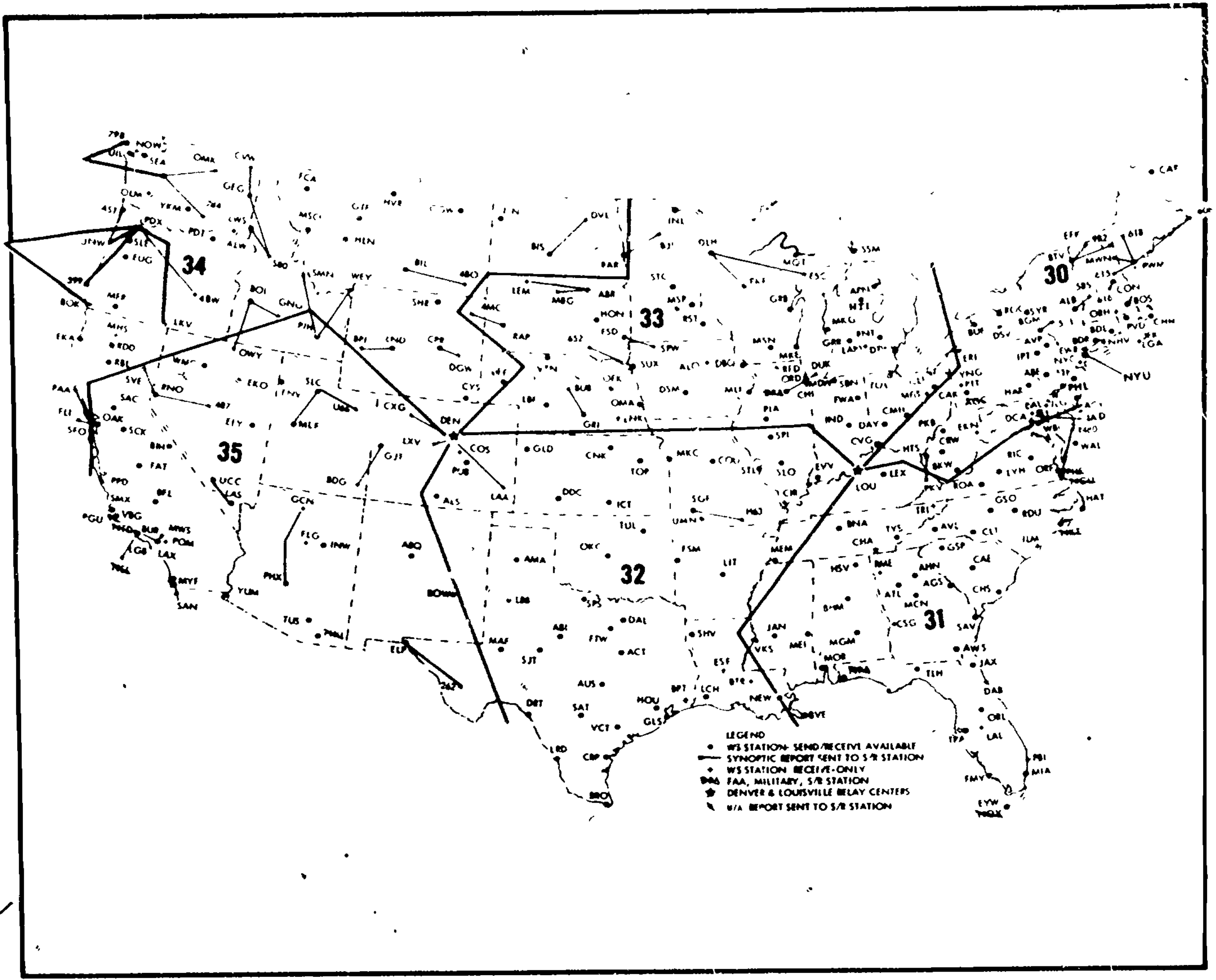

FIGURE 2-4 SERVICE C TELETYPEWRITER SYSTEM

are directly related to the health and well-being of the populace. Figure 2-5 shows advisory areas.

Fire Forecast

b. The Fire Weather Forecast and Warning Service. This service provides advisories on forest fire potentials and provides weather information for smoke management programs. Forecasts are issued to help determine when agricultural or forest debris can be burned without degrading local air pollution standards. Figure 2-6 indicates those weather offices involved in fire weather programs.

Environmental Monitoring

Another important monitoring system is provided by the National Weather Service.

Environmental Monitoring Program. This program is a cooperative effort with the Environmental Protection Agency, Defense Civil Preparedness Agency, and the Atomic Energy Commission. This system provides data on:

a. Solar Radiation - the amount and distribution of solar radiation reaching the earth's surface is measured.

b. Atmospheric Turbidity and Precipitation Sampling - the amount and kind of material in the atmosphere and in precipitation samples is measured.

c. Ion Exchange Materials - radioactive materials from the atmosphere (fallout) are measured.

d. Ozone - ozone concentrations are measured at six National Weather Service offices.

All of these programs give long-term trends in the atmosphere and indicate man's influence on the various parameters.

4. The Environmental Data Service combines the ESSA Environmental Data Service and the National Oceanographic Data Center. It acquires, processes, and disseminates environmental data collected by government agencies and private institutions, and develops improved methods of processing and presentation. EDS operates the national data centers for geodetic, geomagnetic, seismological, meteorological, aeronomic, and oceanographic data, and provides administrative support for the corresponding World Data Centers A, which receives data from cooperative investigations and other international sources.

Data

This service provides the data bank for the various services of NOAA. Each service has its own data center with presentations, programs, and storage systems directly related to the use and mission of the service.

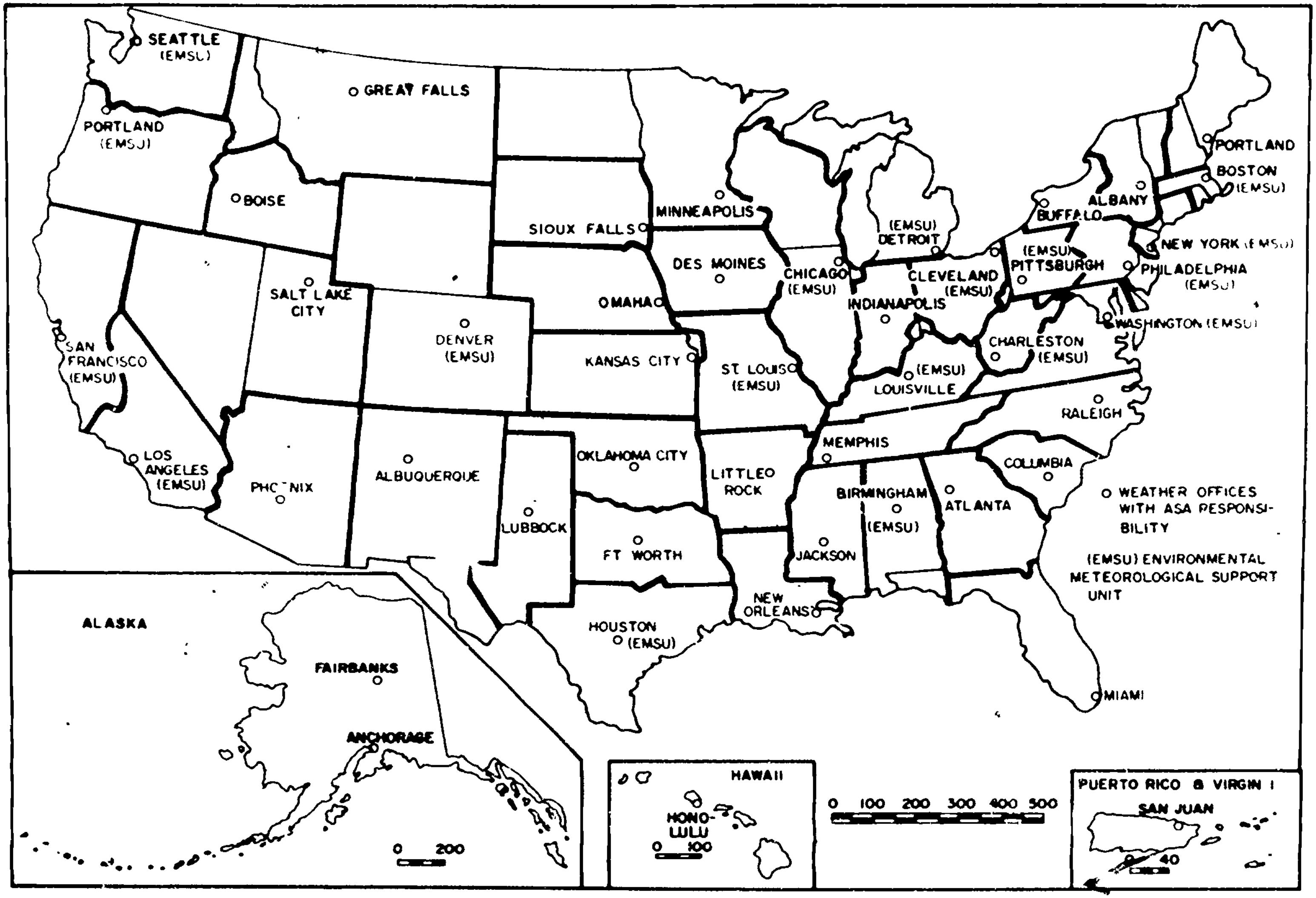

FIGURE 2-5 AIR STAGNATION ADVISORY AREAS

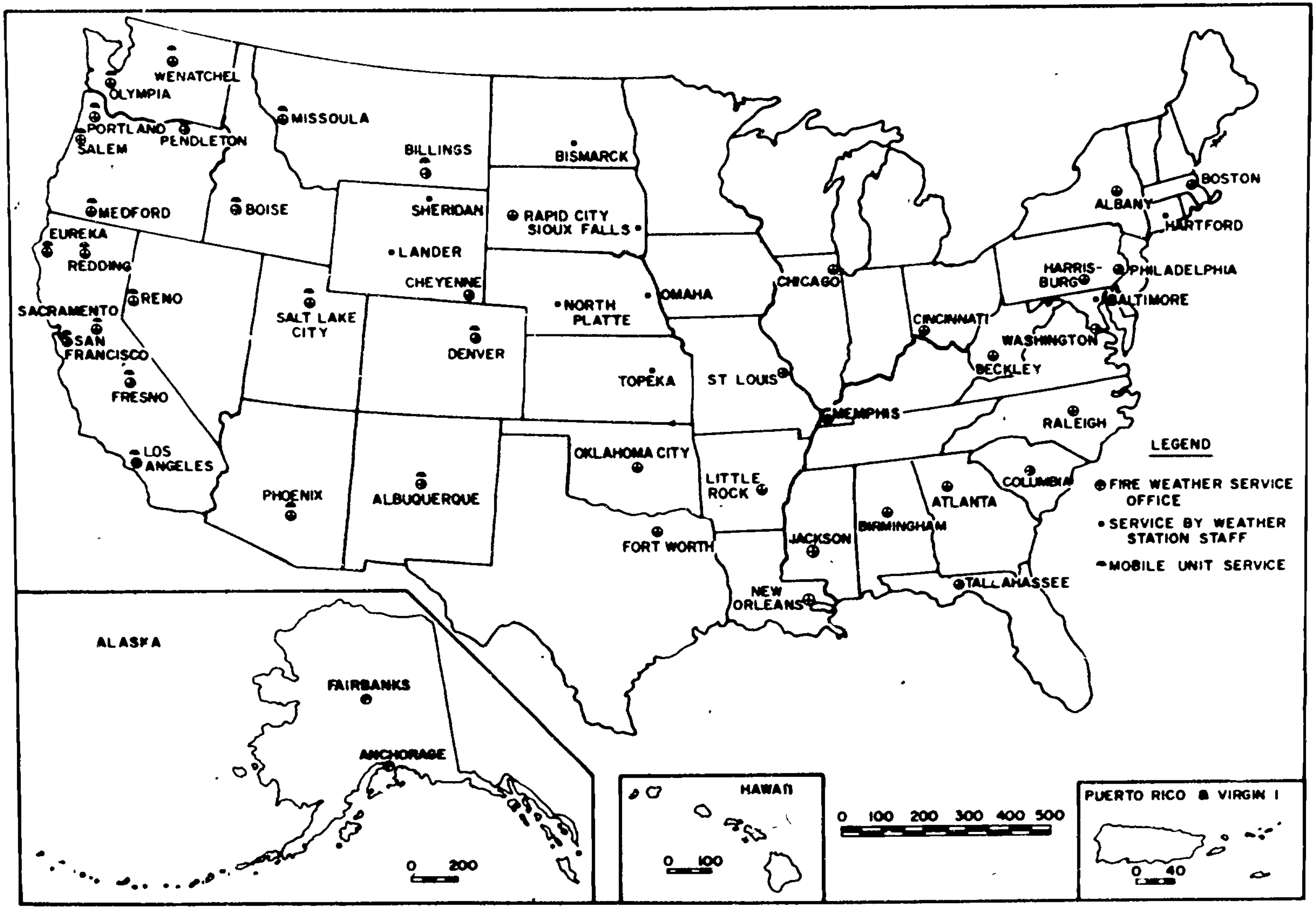

FIGURE 2-6 OFFICES PARTICIPATING IN FIRE WEATHER PROGRAM

There are three other sections in the NOAA organization. These sections have less direct impact on pollution work but are presented for informational purposes.

5. The National Environmental Satellite Service, formerly the National Environmental Satellite Center of ESSA, operates the national weather and environmental satellite systems. It develops new techniques for the acquisition of environmental data and the application of such data to atmospheric, solar, oceanographic, and other geophysical problems.

6. The Environmental Research Laboratories, from ESSA, conduct the fundamental investigation needed to improve man's understanding of the physical environment. Its programs include investigations of ocean processes and their interactions with earthquakes and tsunamis (this branch of NOAA operates the Pacific seismic sea wave warning system); geomagnetism; severe local storms and hurricanes; weather modification; and the environmental effects of global pollution. The Laboratories also are concerned with the development of marine minerals technology with emphasis on the assessment of the environmental impact of systems which disturb the ocean bottom.

7. The Office of Sea Grant administers and directs the National Sea Grant Program. This program provides support for institutions engaged in comprehensive marine research, education, and advisory service programs, supports individual projects in marine research and development, and sponsors education of ocean scientists and [illegible]gineers, marine technicians, and other specialists at sel[illegible]lleges and universities.

3. The United States Department of Defense

The United States Department of Defense has consolidated all environmental quality activities under the Assistant Secretary of Defense (Health and Environment).

a. Environmental Policy (2-6)

It is the policy of the Department of Defense that:

1. Pollution of the environment by the installations, facilities, equipment, vehicles, and other property owned and/or operated by the DoD shall be controlled.

2. All Department of Defense components will demonstrate leadership in pollution abatement and will cooperate in the development of pollution abatement programs with local

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(2-6). Environmental Quality Program, Department of Defense (1972).

communities. Defense components will take positive action to accelerate the pace of corrective measures to conform to environmental quality standards.

3. Where resources to accomplish pollution control are limited, priority of effort will be afforded in accordance with the following order: (1) those situations which constitute a direct hazard to the health of man; (2) those having economic implications; and (3) those which affect the recreational and esthetic value of our natural resources.

4. Maximum effort will be made to incorporate environmental pollution preventive measures in the basic design for weapon systems, military material, tests and exercises, and projects for rehabilitation or modification of existing structures and new construction.

5. Department of Defense components will cooperate fully with the Environmental Protection Agency and other Federal agencies, and will comply with such published standards and criteria relating to pollution abatement for Federal agencies as are promulgated by those agencies or by State and local agencies.

6. Environmental pollution surveillance resources of each DoD component will be utilized to the extent that circumstances permit in interservice support of other DoD components.

7. The use of municipal or regional waste collection or disposal systems shall be the preferred method of disposal of liquid and solid wastes from DoD activities.

8. Pollution abatement at overseas installations will, to the extent practicable, conform to the foregoing policies particularly with respect to cooperation with community programs.

In carrying out the environmental policies of the Department of Defense, four agencies or departments have formed special groups to deal with environmental matters.

b. Program Units

Defense Supply Agency

1. <u>Defense Supply Agency</u> (DSA). The Environmental Quality Program of this agency is administered by the Environmental Protection office within the office of the Director, Installations and Service, Field Support Division. The program involves air pollution, water pollution, land pollution, noise pollution, solid waste, toxic and hazardous materials and research and development activities. Primarily this program insures that facilities of the Defense Supply Agency meet all local and federal pollution

standards. Air pollution emissions originating at their facilities are monitored by the U.S. Army Environmental Hygiene Agency.

Army

2. Department of the Army. The Department of the Army has two environmental organizations grouped under Military Activities and Civil Works.

Military Activities

a. Military Activities. The Deputy Chief of Staff for Logistics has primary responsibility for coordination of environmental preservation and improvement activities within the Army. To meet this responsibility, an Environmental Office was established in early 1971. This office has general responsibility for air pollution, water pollution, land management including soil and water conservation, herbicides and pesticides, noise pollution, thermal pollution, radiation pollution, solid waste, and toxic and hazardous materials. These responsibilities are primarily concerned with Army facilities and operations.

Research

The Environmental Office also maintains a Research Program for Pollution Control. New monitoring methods and technology for measuring water, air, soil, and noise pollution associated with military activities are being developed. This program is also developing advanced waste treatment technology for its wastes, non-polluting substitutes for heavy metals, and new disposal systems for pesticides.

Civil Works

b. Civil Works. The Corps of Engineers Civil Works program has responsibility for flood prevention, navigation, beach preservation, protection from hurricanes and other marine storms, and regulatory management of the nation's waterways. The regulatory program was broadened by the National Environment Act to increase the authority under Section 13 of the River and Harbor Act of March 3, 1899, to include discharge of pollutants into the navigable waters of the United States of their tributaries. Permits for discharge were required under this authority. This authority and permit system has been replaced by Public Law 92-500 and transferred to the Environmental Protection Agency.

Water Programs

The Civil Works Directorate has capability for air pollution control and emission testing. This capability is is somewhat limited in scope and activity. The water programs are the primary responsibilities of the Corps of Engineers. These programs include:

Data Collection

1. Collection and Study of Basic Data. The Corps of Engineers builds many structures for controlling floods, maintaining navigable waterways, and preserving beaches. These structures have definite impact on the environment. In order to monitor this impact, several parameters, including physical, chemical, geological, and biological variables are measured at specified river stations, reservoirs, lakes, estuaries and coastal waters. This impact data will enable researchers to predict environmental changes which will occur from new projects.

Aeration

2. Mechanical Aeration of Lakes. Large lakes have a tendency to stratify. This stratification leads to a reduction in water quality and thereby usefulness. In order to improve water quality, the Corps is investigating the use of under-water air diffusion technology. Monitoring and diffusion testing is continuing in this area.

Nitrogen

3. Nitrogen Supersaturation. The overflow discharge from dams has caused water quality changes in downstream areas. Nitrogen gas from air is dissolved into the water under high pressure. This excess nitrogen gas (supersaturation) is absorbed by fish. When the fish move to lower pressure areas, the dissolved gas comes back out of solution as a gas and forms small bubbles in the circulatory system of the fish. This condition occurs annually in the Columbia and Lower Snake Rivers and is being monitored by the Corps.

Sediment

4. Sedimentation and Dredging Operations. All rivers carry sediment or silt. In areas where the water velocity is reduced, this material sediments out and reduces the flow area of the river. The Corps is responsible for assuring that channels remain open for navigation. In order to keep channels open, dredging operations are carried out. This dredging operation produces a large volume of spoil or waste material which creates a disposal problem and increases water pollution temporarily during the dredging operation.

Sediment is a major problem in most of our rivers. This sediment not only clogs channels but reduces the effective size of our reservoirs. It reduces aquatic plant and animal life, increases costs for water use and reduces the amount of top soil useful for agriculture. Sediment studies are being carried out at St. Anthony Falls

Laboratory of the University of Minnesota. These studies include collection of suspended and bed load data, degradation data, aggradation and delta formation, investigations of sediment transport, and development of new sediment sampling equipment.

Aquatic Plants

5. Aquatic Plant Control Program. Infestations of obnoxious aquatic plants are found along our southern coasts. The Corps of Engineers has a research program to control these plants because of their impact on commercial ship operations. Three methods of control are being tested and monitored.

a. Biological - this program evaluates the use of plant insects and pathogens and herbivorous fish for control of heavy plant growth. Herbivorous fish seem to be an excellent means for control.

b. Mechanical - this program is testing the use of laser energy for eradicating aquatic plants. Some success is noted in the results. A second approach is using the plant life as a food source. This program is under development.

c. Chemical Control - this control program uses herbicides to reduce plant life. Monitoring is carried on to indicate what kinds of herbicides produce the desired control and do not damage the general ecosystem.

Thermal Effects

6. Thermal Effects. The Civil Works study of thermal effects on rivers and lakes include monitoring of temperature regimes, thermal destratification and changes in water quality. Monitoring before and after impoundment determines the project's effect on the ecosystem. Remote sensing is being evaluated as a method for improved collection and operation.

Physical Environment

7. Survey to Describe the Physical Environment. Surveys are conducted to determine the combined effects of winds, waves, tides, and currents on the natural shorelines. Data obtained from these surveys relate environmental parameters to beach erosion and the economic factors of recreational, agricultural, and industrial use.

Divisions

The Corps of Engineers is divided into divisions which include major river basins or parts of river basins. These division offices are primary sources of valuable information on monitoring systems presently in operation. Each division is somewhat different in operation due to different kinds of rivers. An example of some direct monitoring activities and cooperative effort carried on by the Lower Mississippi Valley Division is as follows (2-7):

a. Stages and discharges on all significant streams (District personnel),

b. Water quality data (chemical, biological, physical) on District reservoirs and tributaries to and outlets from the reservoirs (contracts with universities and U.S. Geological Survey),

c. Salinity data in coastal Louisiana (District personnel),

d. Water Quality data (temperature, pH, DO, conductance) in coastal areas (District personnel),

e. Sedimentation studies in reservoirs and streams (District personnel),

f. Potable water monitoring in recreation areas (State health departments),

g. Sewage treatment plant effluent from recreation areas (District personnel),

h. Bank-line and hydrographic surveys to monitor changes in river configuration (contract and District personnel).

Navy

3. Department of the Navy. The Department of the Navy has established an Environmental Protection Division in the office of Chief of Naval Operations. This office directs and coordinates pollution abatement programs for the Navy. Two major aspects of the Navy program are Air Pollution and Water Pollution.

Air Pollution

The Air Pollution program meets requirements for shore installations, aircraft, and related facilities and ships. The shore installations requirement is monitored by a Source Emission Testing Team. This team monitors emissions on the base and recommends appropriate measures for air pollution control.

(2-7). Personal correspondence, E.P. Blankenship, Executive Assistant, Lower Mississippi Valley Division Corps of Engineers, Department of the Army.

The primary air pollution problems associated with aircraft are the waste products of combustion (smoke and chemical by-products). New engines and cleaner-burning engines are under development. The problem of engine testing or runup is being solved by installation of scrubber systems at these sites.

Air pollution from ship operation is being reduced by change of fuel. The old fuel oil, a heavy residual type, is being replaced by the Navy Distillate Fuel which is a clean-burning light fuel oil.

Water Pollution

The Water Pollution program at shore installations involves the usual sanitary sewage as well as some industrial type waste depending on base mission. Both of these discharges are now being monitored and higher standards are being met. The Water Pollution program aboard ship is more complex. New ships must be equipped with marine sanitary devices which will adequately treat sanitary waste on board before release.
Treatment units which will satisfy this requirement are not available, but under development. A second approach which might have merit is a collection, holding, and transfer system on smaller vessels. This system would contain or hold the wastes until they could be transferred to land-based sewage plants or to treatment barges.

Oil Spills

A major effort is underway by the Navy to reduce oil spills. Oil-water separators which will discharge clean water overboard and retain the contaminated oil products are being used on ships. Monitoring devices are employed by the Navy to control and evaluate this program.

Air Force

4. <u>Department of the Air Force</u>. The Department of the Air Force has an Environmental Protection group in the Civil Engineering section. This group has responsibility for all pollution problems associated with Air Force operations.

Air Pollution

In addition to reduction of air pollution at Air Force installations, a major effort is underway to reduce air pollutant emissions from aircraft. This effort includes installation of smokeless combustors on all new aircraft, and a large research and development program for aircraft engine emission control. This research effort is also involved in development of new monitoring equipment specifically designed to meet the requirements of air pollution testing on a mobile point source.

Water Pollution

The Air Force is also involved in water pollution control programs. Basic policy requires secondary treatment for sanitary sewage or connection to local or regional sewage disposal facilities. All installations have been instructed to survey their water usage and identify areas where water can be reclaimed. Use of wastewater treatment plant effluent for irrigation has been in practice for many years. Several specific water pollution problems common to most Air Force installations are under study. Liquid photographic wastes, electroplating wastes, and aircraft washrack wastes are examples.

Monitoring capabilities for air pollution and water pollution testing are being developed for use by the base Corps of Engineering personnel.

4. The United States Department of the Interior

The United States Department of the Interior has several programs directly related to environmental monitoring and pollution analysis. Two of the most important programs involve the Fish and Wildlife Service and Geological Survey.

a. The Fish and Wildlife Service. The Fish and Wildlife Service and its Bureau of Sport Fisheries and Wildlife have programs for research, development, and management of fish resources. The Bureau studies environmental impact statements and water-use projects proposed by Federal or private agencies for the probable effects on fish and wildlife. Emphasis is placed on conservation of our water resources in order to preserve and protect our future needs for fish and wildlife enjoyment.

Research and monitoring programs of the Bureau are aimed at understanding the effects of toxic materials on survival, reproduction, physiology and other factors relating to fish. The Bureau also monitors residue levels of chlorinated hydrocarbon insecticides, heavy metals and other contaminants in fish under the National Pesticides Monitoring Program in cooperation with the Council on Environmental Quality (2-8). Studies are also underway on the effects of pesticides on our fish and wildlife resources.

Geological Survey

b. The Geological Survey. The Geological Survey is one of the most important sources of information on water in

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(2-8). F.V. Schmidt, Deputy Director of Bureau of Sport Fisheries and Wildlife, Personal Communication.

the United States. It is the principal Federal water-data agency. The major objective of the Survey is to appraise the mineral and water resources of the United States and assure that data and information needed to manage these resources is available. The monitoring and surveillance systems of the Survey provide data which pertains directly to all areas of water resource management from quality parameters to quantity flows. At present it provides over 70% of the water data collected in the United States.

The Geological Survey was established in 1879. In 1894 Congress authorized the Survey to gauge streams for quantity of flow and determine the water supply of the United States. Since this authorization, the Survey has been monitoring, collecting data, and publishing results for resource planning. This library of data is invaluable for providing historical perspective to our water resources.

Water Quality

At the present time, the Survey is collecting water quality data at nearly 5,700 sites throughout the United States. About 3,700 of these sites are surface sites (2-9). Special purpose water quality activities include monitoring of toxic metals, pesticides, and radiochemical constituents at selected sites. The Survey maintains about 60 stations throughout the country in what is called the hydrologic benchmark network. These sites are located in natural or near-natural areas that are not expected to undergo significant development in the future. Baseline data from these sites will include streamflow, water quality, sediment discharge, and stream biota. This baseline system should allow a perspective to natural conditions from which pollution and man's influence can be gauged. In addition to these monitoring systems, the Survey acquires processes and publishes information from 18,000 streamflow stations, and 28,000 ground water observation wells. More than 860 aerial investigations were in progress in 1972, covering some three quarters of a million miles.

Pollution Monitoring

There is a basic difference between direct pollution monitoring and the monitoring systems of the Survey. The Survey provides the baseline information necessary for identifying general problem areas. It indicates trends in water quality changes, and furnishes a historical perspective. Direct pollution monitoring is action oriented. It is aimed at solving specific pollution

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(2-9). G.W. Whetstore, Assistant Chief Hydrologist, Geological Survey, Personal Communication.

problems. Once the problem is solved, monitoring becomes less frequent. This action-oriented approach does not mean that the data need to be less accurate or reliable. In most cases, the opposite is true. Many of the pollution problems will result in court cases. This will require the best, most reliable data from samples properly selected, and tested by approved methods. Use of the Survey's data and pollution monitoring will be discussed more fully in the Water Environment sections.

5. Atomic Energy Commission

The Atomic Energy Commission has an Environmental Protection Branch under the Division of Operational Safety. This branch maintains an environmental monitoring and surveillance program. The program is limited to the vicinity of each of its production, manufacturing, and research installations where significant quantities of radioactive material are handled (2-10). The main purpose of this program is not to monitor environmental quality as such but to maintain surveillance of site operations with regard to any potential effect of such operations on the environment. Each process is monitored to maximize control and containment of radioactivity. Liquid effluents and gaseous emissions are monitored prior to discharge in order to control the release of radioactive materials. Non-radioactive discharges are also monitored for pollutants.

Surveillance

In addition to the on-site monitoring programs mentioned, the Environmental Protection Branch also tests the environment near their plants where possible contamination may occur. For example, the Hanford Site located in southeastern Washington State uses waters from the Columbia River for cooling. The waste water from cooling contains some radioactive material and is discharged to the ground (2-11). Small quantities of nuclides which are not decayed or absorbed in the soil may reach the river. Because of the seasonal fluctuations of the Columbia River, the concentration of nuclides (amount per volume) will vary.

(2-10). Arthur Schoen, Chief, Environmental Protection Branch, Atomic Energy Commission, Personal Communication.

(2-11). P.E. Bramson and J.P. Corley, Environmental Surveillance at Hanford for CY-1971. August 1972. Battelle Pacific Northwest Laboratories.

In addition to seasonal changes in the amount of diluting water, scouring of sediments in reservoirs behind each dam causes seasonal variations in nuclide concentrations. This is particularly true for Sc-46 (scandium) and Zn-65 (zinc). The Environmental Protection Branch monitors these concentrations and their effects on downstream users.

6. The United States Environmental Protection Agency

The United States Environmental Protection Agency (EPA) has the major responsibility and need for monitoring and surveillance systems in the United States. Some of this responsibility has been delegated to State Environmental Agencies, but the state programs are reviewed by the Federal agency.

Water Quality

Short-Term Surveys

a. Water Quality. Two types of monitoring and surveillance systems are used for water quality programs - short-term surveys and long-term surveillance networks. Short-term surveys are purpose or problem-oriented. Frequently it is necessary to establish data for enforcement proceedings. A city or industry is suspected of pollution or violation of their discharge permit. A monitoring team of specialists samples and tests the effluent, perhaps in a mobile laboratory, and generates data necessary for enforcement. Once the problem is solved, the frequency of testing is reduced.

Intensive surveys are also used for basin management and modeling studies. In these studies, the change in water quality or how rapid changes occur is important. This requires continuous or at least frequent sampling at the site.

Long-Term Surveys

The long-term surveillance systems provide two kinds of data. First, each state is required under Public Law 92-500 to monitor the quality of navigable waters.

Sec. 106(e) (Public Law 92-500)

"(e) Beginning in the fiscal year 1974 the Administrator shall not make any grant under this section to any State which has not provided or is not carrying out as a part of its program--"(1) the establishment and operation of appropriate devices, methods, systems, and procedures necessary to monitor, and to compile and analyze data on (including classification according to eutrophic condition), the quality of navigable waters and to the extent practicable, ground waters including biological monitoring: and provision for annually updating such data and including it in the report required under section 305 of this Act."

Resource Monitoring

This system provides the long-term data necessary to indicate trends and improvement in water quality. The stations or sites involved are permanent and carefully selected to provide baseline data. Many of the stations are cooperative stations with the United States Geological Survey. A few of these stations are continuous monitoring stations measuring pH, dissolved oxygen, water and air temperatures and conductance. Most of the stations are non-continuous or "grab" sample stations. Samples are taken daily or weekly, and field tested for parameters which vary with time, for example dissolved oxygen. The samples are then shipped to district offices for analysis. The Environmental Protection Agency is setting up some regional laboratories which will aid in the testing and analysis.

Point Source Monitoring

The second kind of data required by Public Law 92-500 involves monitoring of point-source discharges. All discharges into surface streams require a Permit to Discharge. This permit identifies the location and kind of discharge. When the permit is issued, effluent standards will be stated and testing frequency identified. The responsibility for monitoring these discharges rests with the municipality or industry. The States under review by the Environmental Protection Agency must check these discharges and monitoring systems for compliance with the Permit to Discharge. Monitoring of effluent also indicates the efficiency of the treatment plant. This provides a valuable operational tool for treatment plant improvement and stability.

Data

STORET

The water quality data collected by the various agencies and EPA must be properly tabulated and presented for analysis in order to be useful. To meet this need, a computer-oriented information system was devised. This system is called STORET. STORET is the acronym used to identify the Water Quality Control Information System for STOrage and RETrieval of data and information. All water quality information from the states, the USGS, Health Departments, Water Boards, Water and Waste Water Treatment Plants, EPA, and special studies is stored in this system. Data and information available from STORET are: water quality, water quality standards, fish kills, municipal and industrial waste discharge, waste abatement needs, and costs and implementation schedules.

Most states have direct access to STORET through local commuter terminals. A variety of informational programs and presentations are available. This system is not an archive-oriented system, but rather a user-action oriented system.

STORET should develop into the largest bank of usable water quality information in the United States. More complete details of STORET are presented in the Water Environment sections.

Air Quality

b. Air Quality. Three types of monitoring and surveillance systems are used in state air quality programs: 1) background stations, 2) pollution sources requiring abatement procedures and, 3) emission surveys.

Background Monitoring

1. Permanent background sampling stations are in operation in every state. These stations sample and measure a number of background parameters, for example, suspended particulates and sulfur dioxide. Samples are further analyzed in state laboratories and the results are sent to the headquarters in Cincinnati, Ohio, where they will be included in the National Sampling Network.

Point Sources Monitoring

2. Pollution sources requiring abatement notices and proceedings need direct field surveys. These short-term monitoring activities require accurate data and may lead to enforcement procedures and actions.

Annual Emission Survey

3. As a part of the Implementation Plan, yearly emissions surveys are conducted. Using these surveys and emission standards, an evaluation of pollution control is made. If poor control is indicated, then new more effective control strategies are made. This survey also checks and evaluates source monitoring equipment.

In addition to these state monitoring programs, each owner or operator of stationary sources must install, maintain, and use emission monitoring devices and report to the state the nature and amount of emission discharge.

7. State Monitoring & Surveillance Programs

Many states have separate and cooperative monitoring programs which provide valuable data for pollution control evaluation and planning. The State of Ohio has two programs of merit - the Ohio Department of Natural Resources program, and the ORSANCO Quality Monitor.

Natural Resources

The Ohio Department of Natural Resources program consists of a Stream Monitor Control Center and 13 remote automatic sensing stations. These 13 stations are located throughout the State on various rivers. Each station is tied to the Center through a telegraph grade phone line. Every hour the Center interrogates each station with respect to five water quality parameters: river stage, specific conductance, dissolved oxygen, temperature, and pH. The data is received at the Center and recorded on the teletype (hard copy) and punched tape. This data can then be converted into more usable forms, either manually or by computer.

Each of the parameters is compared with standards adopted by the Ohio Water Pollution Control Board for various streams. If standards are violated, the printout indicates the violation. At this point, verification is required. Field representatives check to see if a violation actually occurred or if the equipment malfunctioned. This monitor-telemeter system has detected many violations with resulting pollution abatement and water quality improvement.

ORSANCO

The Ohio River Valley Water Sanitation Commission (ORSANCO) has developed a robot-monitoring system on the Ohio River and its tributaries. The system is use-oriented and issues monthly reports as a service to those concerned with water quality conditions in the Ohio River. The reports summarize measurements from the ORSANCO robot-monitor system. The robot-monitor system,consisting of 19 field stations, a central receiving center, and computer, is located in Cincinnati, Ohio. This robot system is one component of a larger network which includes 32 manually operated stations and covers the entire Ohio River Basin. Five parameters are measured: dissolved oxygen, pH, temperature, conductance, and chloride.

User Committee

In addition to the monitoring data, the ORSANCO Water Users Committee, composed of managers of water treatment plants on the Ohio, Allegheny, and Monongahela Rivers, report water quality problems for inclusion in the monthly reports: for example, taste and odor, high turbidity, oil slicks, and coliform bacterial levels. These observations from user groups contribute significantly to the overall effectiveness of this monitoring system.

Environmental Conservation

The State of New York is also a leader in the field of monitoring (2-12). The New York State Department of Environmental Conservation (ENCON) operates a monitoring and surveillance program which evaluates water pollution

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(2-12). Donald B. Stevens, Director, Ronald E. Maylath, Chief, New York's Water Quality Surveillance Program. Presented at the Water Pollution Control Federation Meeting, San Francisco, California, (1971).

abatement activities. The surveillance system contains approximately 300 manual surface water stations with 120 stations operated by ENCON and the remainder cooperative with industry and municipalities. These stations are sampled with varying frequency depending on pollution potential. The testing period varies from bi-weekly to a few times a year. Thirty-seven parameters are measured at each of the stations. Ground water stations are being added to the network as finances become available.

Automatic Monitors

In addition to the manual network system, approximately 100 automatic monitors are being added to the network. These automatic monitors will not replace the manual monitors but will augment the system so as to provide "real time" data. "Real time" data is information *acquired* and *usable* at a time *close* to the actual time the test was made. Much of the monitoring information available is past history, and reaction to indicated pollution is slow. The use of automatic monitors with a telecommunications link to computer analysis is of real value in maintaining water quality.

Aerial Surveillance

A third type of monitoring performed by ENCON is by aerial surveillance. The results of the manual and automatic monitors are in the form of numbers, but in some situations numbers do not adequately describe the quality of the water. Various photographic systems are used to give added water quality data. Quantitative thermal imagery and radiometry detect temperature characteristics of the water and ultraviolet scanning detects oil slicks. Several visual observations by department personnel while flying have located a number of water quality accidents and illegal waste discharges.

Data

The data collected by ENCON and its cooperative stations is compiled with electronic data processing equipment in the Water Quality Data Library. The information is also stored in the STORET system of the Environmental Protection Agency.

Problems:

1. Select a river basin for study. Locate and tabulate all the sources of environmental information available for that river basin.

2. Select a small stretch of the river, perhaps 10 to 20 miles, and study and report on pollution, pollution control activities and water quality in that stretch of river.

3. Write a report on what additional monitoring is necessary for that stretch of river and why.

4. Select a large lake or reservoir in your local area and find all the sources of environmental information indicating the water quality in the lake. (Upstream pollution will effect the lake.)

SAMPLING

Proper Sampling

Proper sampling of the environment is the most important step in monitoring. Analytical methods for determining the amount of various parameters are highly developed and extremely accurate; but, if the sample does not properly represent the environment, the data is worthless. No amount of expensive analytical equipment can correct a poor sample. A sample must reflect or be representative of nature.

Standard Methods

A second fundamental of monitoring is standard methods. Only methods which have been tested and approved for accuracy and reliability can be used for sampling or testing. Methods which might appear satisfactory, but have not been tested for reliability, produce questionable data.

1. Objectives for Monitoring

The first step in a sampling program is the development of the objective. The general objectives for monitoring as identified in Chapter 1 are:

1. Characterization of existing conditions,
2. Identification of trends,
3. Evaluation of standard compliance,
4. Emergency conditions,
5. Environmental quality forecasting and,
6. Research.

Test Parameters

Each of these objectives has a slightly different requirement for sampling, and many overlapping features. Some sampling programs will fit more than one objective; for example, data collected to meet the objective "characterization of existing conditions" could furnish information for objectives 2, 5, and 6. If possible, economic considerations warrant the inclusion of as many objectives into each sampling program as possible. After the objective or objectives for monitoring have been identified, then the test parameters must be selected. These parameters relate directly to the objective. For example, if "evaluation of standard compliance" is the objective, then a prescribed set of parameters and their limits has been established. These parameters are the test parameters. Municipal waste water effluent must meet secondary standards identified as:

pH = 6.0 to 9.0,
fecal coliforms = #200/100 ml,
B.O.D. = 30 ppm, and
suspended solids = 30 ppm.

Another example of standards is the National Air Quality Standard for particulate matter, 260 $\mu g/m^3$ for an average time of 24 hours. Other parameters not identified in the Standards may be evaluated for showing a broader environmental picture, but in general monitoring would concentrate on parameters and limits established in the Standard.

Selection of parameters for other objective functions may not be so restrictive. For example, a wide variety of biological, chemical, and physical parameters would be included in a test program for evaluating "existing conditions". The complete picture of all parameters would be necessary to establish "existing conditions".

2. Site Selection

After determining the objective, the test parameters and the lack of necessary data, the sampling station or site must be selected. Again the objective or objectives for monitoring will help select the site. If "existing conditions" is the objective, then a site must be selected which reflects the general condition of the air or water. It should not be located near a point source of pollution because a nearby source will influence the sample and subsequent tests. If background, non-polluted conditions are sampled, the site must not be located near any city or industrial complex.

Point Source

If "standard compliance" is the objective, then the site is at the discharge point identified by the Standard. A smoke stack discharging particulates into the air is required to meet a Particulate Standard. The site would be in the stack. If the Standard is for industrial wastewater discharge, then the site would be in the effluent discharge line from the industry. Many cities and industries monitor their processes at each stage of treatment to evaluate performance and efficiency programs. In pollution work, the final effluent is the point where Standards apply.

If "identification of trends" is the objective, a site in the river or air mass downstream from a point source or group of point sources might be selected. This site should indicate the effect on the river or air of pollution and pollution control standards. For this kind of sampling, it is important that the site be selected far enough downstream or downwind so that complete mixing is accomplished.

Zone of Mixing

When a point source is discharged into a stream, it takes some time and space before the discharge is uniformly mixed throughout the body of the stream. This space is called the Zone of Mixing. If samples are taken within this zone, then improper evaluation will result. For example, if the sample were taken in the waste stream side of the river before it is fully mixed, a high value for pollution parameters will result. If the sample is taken on the clean side, little pollution would be noted. These decisions are made in the field either by looking at the appearance of the river or by testing both vertically and horizontally across the river. When all tests at one cross section give the same values, then you are below the Mixing Zone.

Time Variation

Another space criteria for selecting the site for evaluation of trends and existing conditions is time. Space downstream or downwind from a point source also means time as well as dilution. Chemical, physical, and biological changes can occur in time or space downstream from a source of pollution. Organic material can be oxidized by bacteria, gas concentrations can change, silt can settle out, and reduced chemical compounds can be oxidized, precipitated or adsorped. These processes are Nature's way of pollution treatment. Again it is important to set the objective for the monitoring before setting the site.

The waste discharges from industry, municipalities, and agricultural vary both in quantity and quality. These variations occur hourly, daily, weekly, and seasonally. For proper monitoring, an evaluation of these variations must be made. For example, the waste water flow from a city is very low in the early morning hours. This flow represents some infiltration from the ground water and some waste discharge. The concentration of pollutants and quantity of flow at this time are only 30 to 40% of the daily average. If samples are taken at this time, obvious errors of evaluation will result.

Sudden storms or over-irrigation of some agricultural lands can cause sudden variations in silt pollution. If samples are taken during this period, high values of pollution would be indicated.

In other cases, the flow and quality of a river may remain fairly constant for several months. Winter-time flows or late summer flows usually fit this case. Monitoring of these flows for "trends" or background objectives could be done infrequently. The presence or absence of variation should always be proved by sampling and testing and never assumed.

Frequency

The objective for monitoring will help decide the frequency of testing. Some objectives require only an average parameter concentration while other objectives require information on peak concentrations, duration of the peak, and frequency of recurrence of peaks. The latter normally is associated with the objective of "standards compliance".

3. <u>Continuous Monitoring</u>

There are two general types of monitoring with regard to frequency - <u>continuous monitoring</u> and <u>non-continuous monitoring</u>. Continuous monitoring (sampling and/or testing at very short time intervals) will indicate peak concentrations, duration of peaks and variations of peaks. There are two ways of securing this information. First, some parameters lend themselves to immediate analysis; for example, air or water temperature, pH, visibility, turbidity, wind velocity and direction, water flow height, water conductance, and dissolved oxygen. These parameters depend on a simple electronic or mechanical indicator device for immediate response and analysis. There are many other parameters which do not lend themselves to immediate analysis. In order to meet the requirements of continuous monitoring for these parameters, <u>individual</u> samples can be taken at short time intervals and stored as individual samples for later testing. Alkalinity, acidity and salt content are water parameter examples of this kind. In air pollution work, tape samples are used for this kind of sampling. These samples pull a pre-determined volume of air through a piece of clean tape. Particulates will be trapped in the tape. After sampling, the tape is moved forward for a new test and the previous test is stored for later analysis.

Sample Storage

There are several cautions involved in storing samples for later testing and analysis. Many parameters <u>change</u> with time. For example, the amount of dissolved carbon dioxide (gas) in a water sample can change with time. If a sample is collected, stored and analyzed at a later time, the amount or carbon dioxide found and recorded may bear little resemblance to what was actually in the original water.

> The primary requirement of monitoring is to produce data that reflects or represents the <u>natural</u> condition.

In the above case, the data would be questionable and probably worthless. There are several examples of parameters which may change with time. Dissolved gases, organic material especially in the presence of bacteria, and material which precipitates or adsorbs on the container are examples of parameters which may change with time. These kinds of changes can be minimized but <u>never</u> completely eliminated.

Sample Integrity

One method of minimizing changes in organic material and bacteria requires storing the samples at about 4°C. At this temperature, the bacterial activity is very slow and little change in organic material should occur. Freezing the sample would result in damage to the bacterial cells. Changes in dissolved gases can be reduced by filling the container completely full, sealing it, and storing it at the same temperature as the water from which it was taken. The amount of dissolved gas in a water depends on the water temperature.

4. Non-Continuous Monitoring

Non-continuous monitoring (sampling and/or testing at longer time intervals) will indicate average concentrations or concentrations which exist at the time of sampling. This type of sampling is frequently called "grab" or "catch" sampling, since the sample is "grabbed" at a particular time. This kind of sampling does not indicate short-time variations but may indicate long-term trends.

Again, special caution must be exercised in securing the sample so that it is representative and time changes must be minimized before analysis.

Composite Samples

Another type of non-continuous monitoring is the composite, or, integrated sample. This type of monitoring gives an average value over a period of time. An example of this kind of sampling is the average 24-hour BOD. In this case, samples are taken every few minutes using a sample volume proportional to the flow rate. This sample volume is placed in a container and stored at 4°C to minimize bacterial action. At the next increment of time a new sample is taken, the volume being proportional to the flow at this time. This volume is added (composited) with the other sample. This process continues for the sampling period (24 hours). At the end of this period, the composite is analyzed for BOD. An average BOD value, approximately the average BOD for that 24-hour period, is recorded.

Records

Proper records are essential in monitoring. In continuous monitoring systems, the starting point on the graph or punched tape data storage system must be aligned for the correct time. If the time of the test is questionable, a valuable piece of information is lost. Evaluation of pollution sources with correlation of peaks will depend on proper times. Enforcement of pollution standards depends on timing. For maximum values and average values for specified periods of time, an accurate set of data with proper times is essential.

In non-continuous monitoring or "grab sampling" and testing, the technician will record the time of sampling as part of a general information system.

Information System

The general information system records sampling time and date, proper numbers for sample identification, sample site and general observations. Frequently these general observations will provide essential information for proper evaluation of raw data. For river sampling, these observations should include general weather conditions and air temperature, general appearance of the river (turbid, brown, clear, fast, slow, patterns of colors, oil on surface, floating debris, etc.), conditions at the site, construction projects nearby, livestock grazing near the river, boating and recreational sports, and any situation the technician feels will be important for evaluation of test data. This personal on-site inspection of conditions is invaluable for developing a "feel" for the river. After several months of sampling, the technician will "know" the river. Unusual conditions will be recognized easily and reported. Additional sampling, required to explain these conditions, may be necessary.

Summary

In summary, the following rules must be followed for a successful monitoring program:

1. The sample must reflect or represent the actual field or natural conditions,

2. The physical, chemical, and biological integrity of the sample must be maintained, and

3. Proper records, including general observations, must be made.

Communicate

It is obvious from the discussion that monitoring depends on a highly-trained professional technician. Close association between this technician, the analytical laboratory staff, and the surveillance manager is important for all monitoring objectives. The monitoring technician must know what problems the analyst is having in testing. General field observations can give the laboratory staff significant insight into pollution problems and proper test procedures. The surveillance manager must know sampling problems and unusual conditions for proper evaluation of the total monitoring system.

Monitoring and surveillance is
a team effort.

Problems:

1. Secure a monitoring site location map from the local U.S. Geological Survey Office. Select a stretch of river and evaluate the monitoring sites. Are they continuous or non-continuous data stations? What parameters are measured in the field and what are measured in the laboratory? Who checks the instruments or takes the "grab samples"? Arrange a trip to one of the sites with the technician. How are samples numbered and shipped to the laboratory? How often are samples taken? What are the objectives for monitoring? Write a report on your monitoring evaluation.

2. Contact your regional Environmental Protection Agency (Monitoring and Surveillance Section) and secure a monitoring site location map. Locate sites selected for pollution control information. Evaluate these monitoring sites (Problem 1). Determine any differences in objectives between the U.S. Geological Survey and the Environmental Protection Agency for monitoring. Do these differences affect sampling or parameter selection? Is frequency of sampling the same? Write a report on your evaluation.

Additional Reading:

1. Standard Methods for the Analyses of Water and Waste Water 1971 American Public Health Association, 13th Edition N.Y.

2. Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases. Eugene Brown, M. Skougstad and M.J. Fishman.
Book 5 Laboratory Analysis
United States Geological Survey

3. A Practical Guide to Water Quality Studies of Streams. 1969. F.W. Kittrell
U.S. Government Printing Office (FWPCA)
No. CWR-5

4. Annual Book of ASTM Standards (Part 23)
Water; Atmospheric Analysis
American Society for Testing and Materials
1916 Race Street, Philadelphia, Pa. 19103

DATA ANALYSIS AND PRESENTATION

The process of monitoring the environment produces data. These data or numbers measure the magnitudes of pollution parameters, indicate the exact position of the sampling site, and record the time of sampling. In order for these data to be useful, they must be analyzed, evaluated, and properly portrayed for users. This process is sometimes called data reduction or editing. The process consists of four essential steps:

1. Collection of Raw Data,
2. Classification of Raw Data,
3. Generalization of Data, and
4. Presentation of Data.

1. Collection of Raw Data

The collection of raw data and numerical facts is the first step in the scientific and operational evaluation of the environment. These numerical facts must be recorded in some permanent manner for evaluation and storage. Even subjective comments concerning the monitoring site should be written down. Use a good ballpoint pen with a waterproof ink. Pencilled notes are easily smeared, and damaged. Notes made in ink also carry more weight in court proceedings than pencilled notes. Pencilled notes can be erased and changed. Since enforcement proceedings may result from monitoring, data must be accurate and dependable.

The Monitoring Site

Continuous Monitoring

a. The Monitoring Site. Numerical facts are generated in two places: the monitoring site and the analytical laboratory. Several kinds of facts are recorded at the monitoring site. If the station is automatic or semi-automatic, instruments measure and record various parameters. But all instruments and recorders must be frequently adjusted and standardized. This standardization consists of adjusting the zero value of the instrument and the value of some known parameter concentration. After instrument adjustment, these values are then set for proper recordings on the recorder, and the recorder is adjusted to the proper time. The time and date of this standardization must be recorded by the technician on a permanent log and on the actual recording sheet if possible. The correct values must be indicated on a data sheet at the end of the monitoring period as well as at the beginning of a new sheet for the next period. Otherwise it is impossible to check on how far the instrument has drifted from standardization during the monitoring period. If significant drift is noted, more frequent standardization is needed.

Non-Continuous Monitoring

Different kinds of records and responsibilities are associated with non-continuous monitoring. Non-continuous parameter monitoring can occur at sites where a few parameters are measured continuously and also at sites where only "grab" sampling is warranted. Under these conditions, the technician must sample the river or lake or air. The sample must be representative of the natural condition and must be collected in a numbered or labeled container. The container must be properly prepared to prevent contamination of the sample. The site location or number, the number of the container, the time, the date, and the method of collection must be recorded by the technician. If the sample is shipped to a laboratory for analysis, the method of shipment and the method of sample preservation must be recorded.

In addition to preparing the samples for shipment, several parameters are generally measured and recorded at the site. In the water medium these may include dissolved oxygen, water and air temperature, and pH. These measurements are made with instruments which must be standardized before use. Measured values are recorded at the site on permanent records. Although data systems do not use general comments made by the technician, these recorded subjective observations, many times, contain information which can be added to the numerical facts to form the true picture of "what is going on in the environment".

Record general site information.

The Analytical Laboratory

b. The Analytical Laboratory. The second source of data is the analytical laboratory. This laboratory receives the samples with the proper labeling and site information as sent by the technician. Analysis schedules are arranged by the laboratory supervisor and are performed by the professional staff. All data are properly recorded and associated with the site, time, and date of sampling. General comments made by the monitoring technicians are noted and additional tests are scheduled if the information warrants or indicates it. These laboratories must use approved and standardized analytical methods.

The monitoring technician should visit this laboratory and see how samples are received and tested, how paperwork is used, and how general information is used by the laboratory supervisor.

Quality Control

In any collection and analysis system, quality control procedures must be used. These procedures insure the reliability of the data. All laboratories have quality control techniques. These are based generally on the supervisor introducing "known" samples into the analysis schedule. Any variation from the known parameter concentration indicates poor laboratory work. Another technique used introduces a split sample. A sample is split and both are introduced for testing. Obviously, all test results should be duplicated.

These kinds of techniques can also be used at the monitoring site. For example, two samples can be collected in two separate containers at approximately the same time. These can be labeled and sent through the analysis procedures (both field and laboratory). Duplicate values should be produced. Any variation must be rechecked. If procedures do not produce reliable data, change them until they do. Instruments can also be checked. Field checks can be made by comparison to test instruments standardized in the laboratory. For example, pH can be measured by the regular field instrument and the test instrument for comparison.

Quality control costs money but repays the monitoring program in reliability.

The raw information derived from the monitoring program (field and laboratory) is now ready for data analysis as part of the overall surveillance program.

2. Classification of Raw Data

Data generated at the monitoring sites and the analytical laboratory are collected and stored in a data center. It is important that this raw information be stored for possible future reference. Support for legal proceedings may require this data, and future changes in use functions may require a classification based on the raw data. Economic considerations would indicate that at some point in time storage costs would not justify the retention of very old data. Microfilming and other reduction procedures are helping this program.

After data is collected and before it is stored in archives, it is classified.

Informational Need

a. Informational Need. Determining the informational need is the first step in data classification. Again this need has already been established from the monitoring objectives. For example, if "Evaluation of Standard Compliance" is the monitoring objective, then only parameters defined in the standard would be classified. Broader parameter groups would be classified for other objectives; for example, trends, forecasting, and research.

Ordering of Data

b. Ordering of Data. Once the informational need has been established then the pertinent data is ordered. This ordering of data on any parameter includes site location, time, and magnitude. There are three general ways of ordering these three kinds of data:

1. Site Ordering,
2. Time Ordering, and
3. Single Parameter Ordering.

Examples of these orders should provide sufficient insight into their structure and use. Consider the following situation:

> Two stations on a river,
> four measured parameters, pH, temperature (water) dissolved oxygen and flow stage (water depth), and samples taken every two weeks.

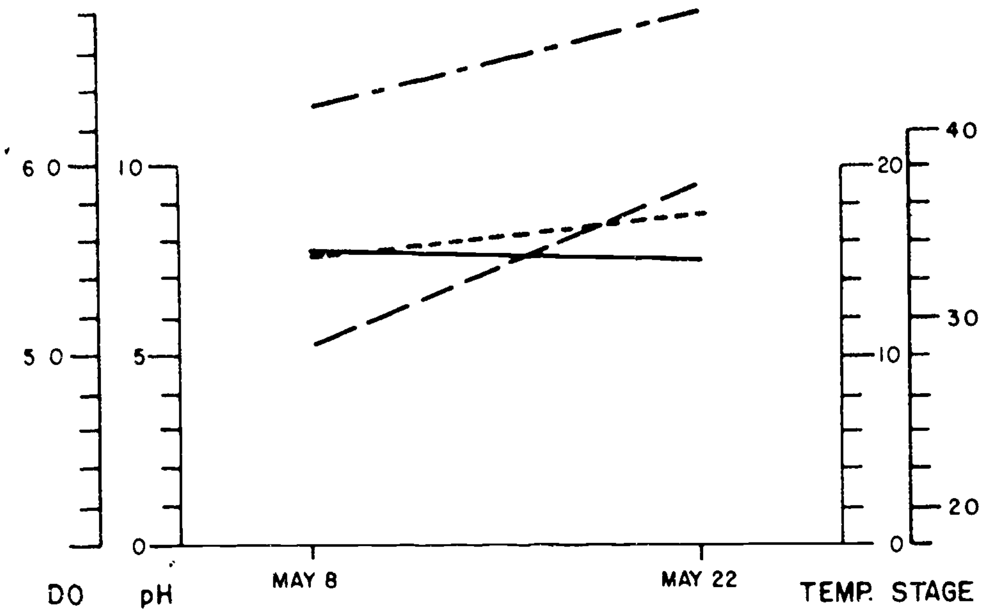
Site Ordering

1. Site Ordering. Ordering by sites (Table 4-1) puts all sites in order and stores all times and parameters by site.

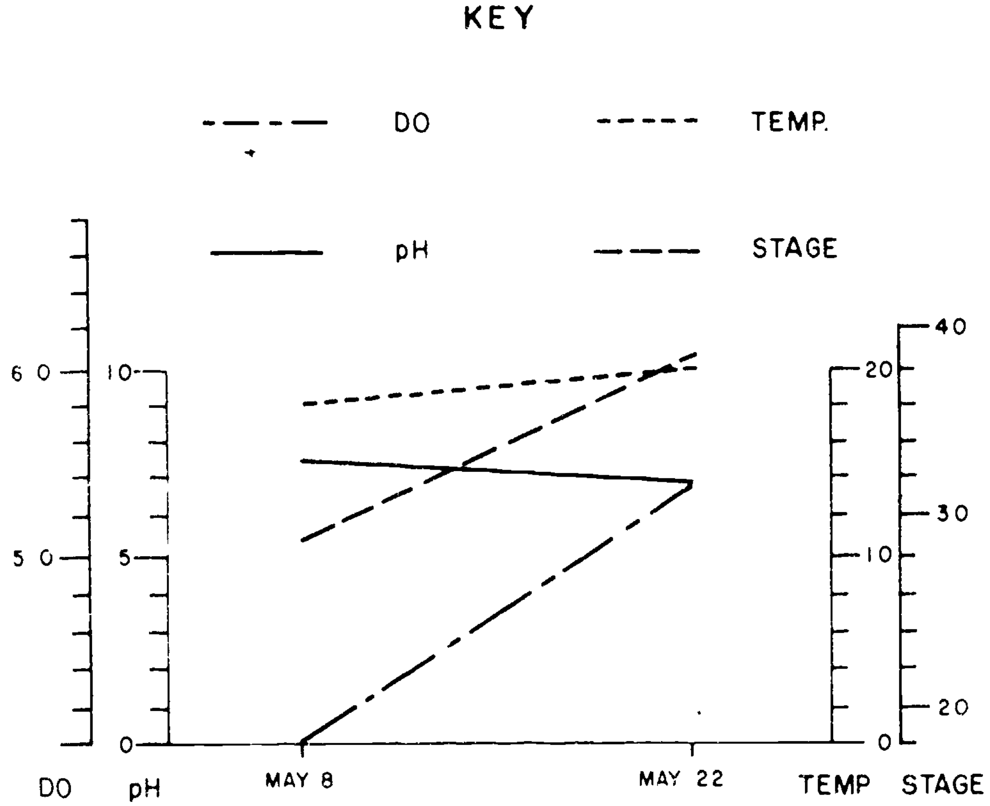
TABLE 4-1
SITE ORDERING

Site 3622		May 8, 1973	May 22, 1973
	pH	7.7	7.4
	temp	15°C	17°C
	DO	6.3 ppm	6.8 ppm
	flow stage	28.6 feet	37.4 feet
Site 3621 (downstream from 3622)	pH	7.4	6.9
	temp	18°C	20°C
	DO	4.1 ppm	5.3 ppm
	flow stage	28.9 feet	38.2 feet

This kind of ordering shows, at one site, how the parameters vary with time. Trends and site variations are easily compared. Graphs of this ordering use parameter magnitude for the ordinate (y) axis and time for the abscissa (x) axis. Figure 4-1 illustrates a plot of the above data by site ordering. Several parameters can be presented on one chart with different units for ordinates scales. This allows



SITE 3622



SITE 3621

Figure 4-1
Site Ordering

useful comparisons of parameters.

Time Ordering

2. Time Ordering. Ordering by time (Table 4-2) puts all times in order and stores all sites and parameters by time.

TABLE 4-2
TIME ORDERING

May 8, 1973		Site 3622	Site 3621
	pH	7.7	7.4
	temp	15°C	18°C
	DO	6.3 ppm	4.1 ppm
	flow stage	28.6 feet	28.9 feet
May 22, 1973		Site 3622	Site 3621
	pH	7.4	6.9
	temp	17°C	20°C
	DO	6.8 ppm	5.3 ppm
	flow stage	37.4 feet	38.2 feet

This kind of ordering shows, at one time, how the parameters vary with site (space). This ordering shows what happens down a river at a given time. Variations show the influence of tributaries, pollution sources and surface and ground runoff. Graphs of this ordering use parameter magnitudes as the ordinates (y) and sites (downstream) as abscissas (x). Several parameters can be presented on one chart with different units for ordinate scales. This allows useful comparisons of data and formulation of possible mechanisms. Figure 4-2 shows a plot of the data by time ordering.

Parameter Ordering

3. Parameter Ordering. Ordering by single parameter (Table 4-3) puts all single parameter values in order and stores all times and sites by parameter. Other parameters are also stored. In this example, only temperature is illustrated.

This kind of ordering shows how one parameter value varies with time and space. Figure 4-3 shows plots of [illegible] four parameters with values in the box. These figures can be read several ways. If the figures are read vertically from bottom up, variation in time is seen. With continuous or more data, contours can be drawn which look like mountains and valleys. If read at angles from the origin, a "feel" for river changes downstream with time are seen.

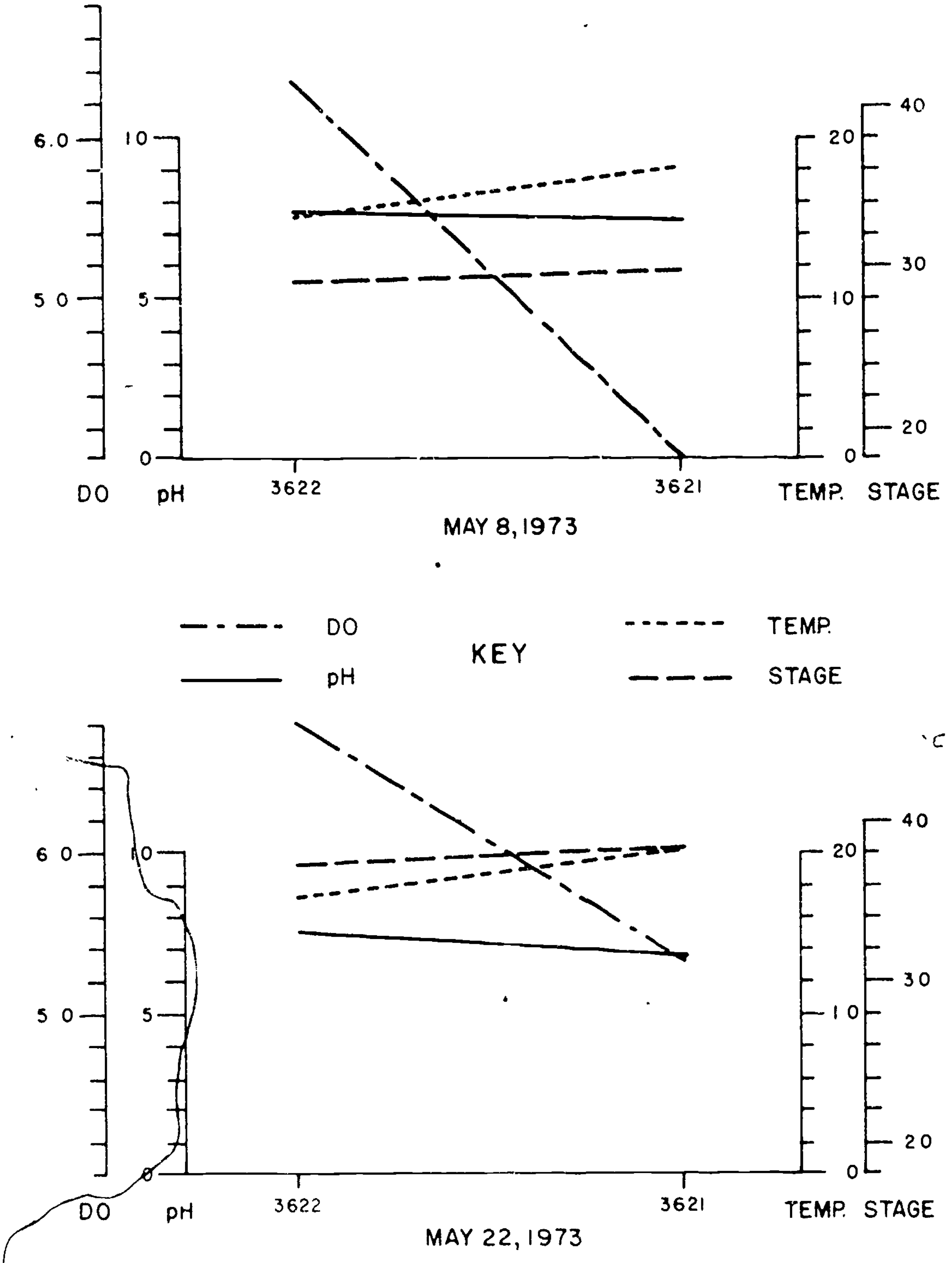


Figure 4-2
Time Ordering

TABLE 4-3
PARAMETER ORDERING

	Site 3622	Site 3621
Temperature 15°C	May 8, 1973	
Temperature 17°C	May 22, 1973	
Temperature 18°C		May 8, 1973
Temperature 20°C		May 22, 1973

Most data is stored by site and further stored in each site by time. For "need" classifications and "use" functions, however, the data may be classified by time and parameter also.

3. Generalization of Data

Generalization of environmental data is the technique of deriving from limited monitoring the true picture--

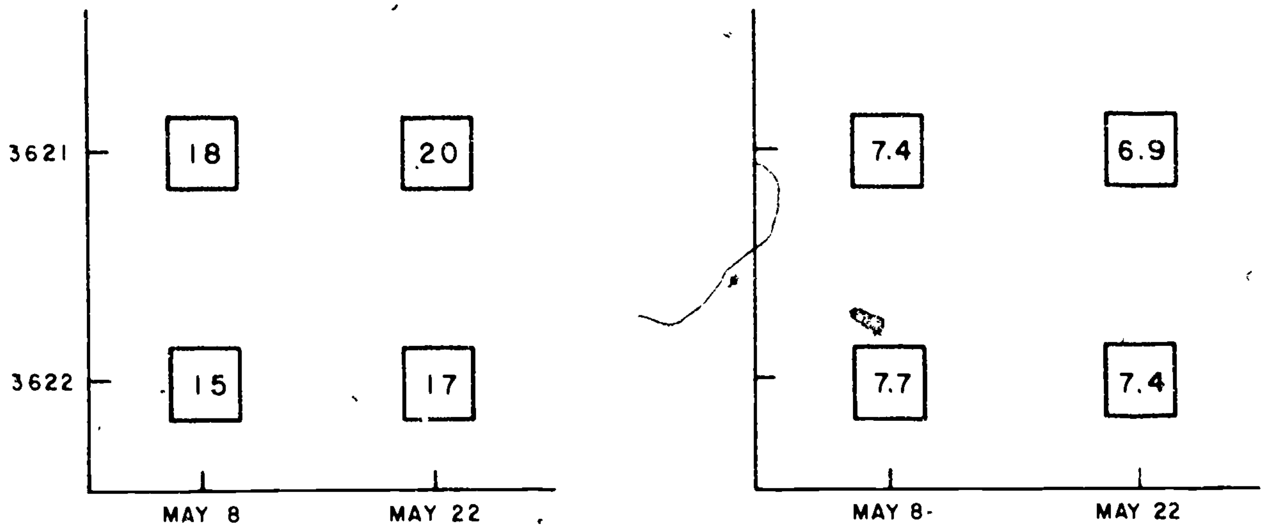
of the environment,
of pollution problems and their effects and,
of the results of pollution control efforts.

This does not mean the drawing of broad, poorly defined conclusions. It does mean subjecting the limited data to the proper mathematical and statistical analysis. Generalization always assumes that the data truly represents the environment and similar sampling and testing (same site and time) would produce the same numerical data.

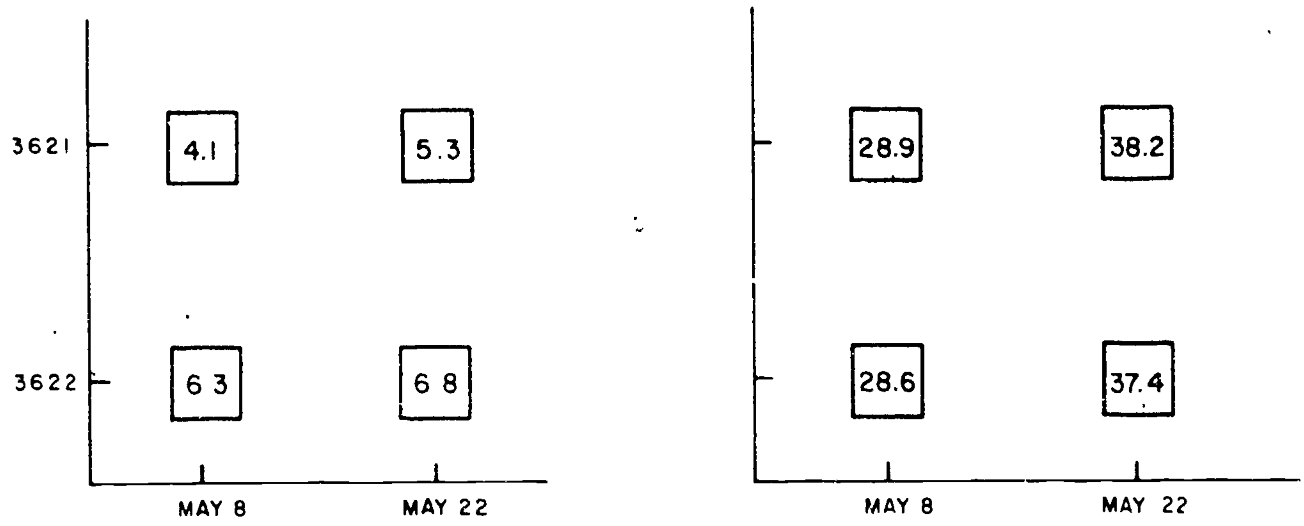
The monitoring program must insure
data represents the environment.

There are two approaches or directions for generalizing data: reduction and expansion. In both cases, the purpose of the generalization is presentation -- presentation of data in a way a human can understand. Decisions on enforcement, analysis of trends, evaluation of backgrounds or existing conditions all require some smoothing out of excess fluctuations or some averaging of data.

Reduction is the process of reducing excess data to average values. These average values obviously mask peaks and fluctuations. It should be noted that reduction can produce longer time averages but the reverse is not true. Instantaneous or



(a) TEMPERATURE (C) (b) pH



(c) DISSOLVED OXYGEN (DO) (ppm) (d) FLOW STAGE (FEET)

Figure 4-3
Parameter Ordering

short time average concentrations cannot be determined from long sample averaging time. In other words, instruments or sampling which produces data only at 6-hour periods cannot show fluctuations occurring at 3-hour intervals or anytime less than 6 hours. Samples times of once per month only indicate values at the time of sampling. Even composite samples average concentrations over a period and do not give intermediate data points.

Expansion is the process of using limited data and expanding the data to produce average values. This process involves the mathematics of statistical analysis. A complete presentation of this kind of analysis is not possible in this text but several good books are available for study. Since most environmental data is non-continuous with respect to time and space, the process of statistical analysis is an important tool for evaluation.

Averaging

a. Averaging. One common method of generalization is averaging. An average value is a value which may represent or replace a group of values. There are four kinds of averages or ways to indicate this central tendency: arithmetic means, geometric means, medians, and modes. Arithmetic means may be calculated by:

$$\overline{X} \text{ (Arithmetic mean)} = \frac{\Sigma X}{n} \qquad 4.1$$

where X represents each individual value and n represents the total number of values. This method is the most common kind of averaging.

Geometric means may be calculated by:

$$\log M \text{ (Geometric mean)} = \frac{(\Sigma \log X)}{n} \qquad 4.2$$

where X represents each individual value and n represents the total number of values. Logarithms are base 10. Geometric means are useful for averaging certain kinds of data. Arithmetric means are sensitive to values which are high or low compared to the normal values. Geometric means can reduce the effect of these high or low values and produce a more representative average.

Medians are the middle value of an array. An array is an ordered grouping of the data by value - high to low or low to high. The mathematical form for finding the median is:

$$M \text{ (median)} = \frac{(n + 1)}{2}\text{th observation of array} \qquad 4.3$$

The median will also reduce the effect of values which vary significantly from the middle values.

The mode is the magnitude of the most frequent and therefore most probable value. This method generally requires a grouping of data within certain limits. For example, all values from 1.51 to 2.50 would be grouped under the value of 2, all values from 2.51 to 3.50 would be grouped under the value 3, and so forth. The value having the greatest frequency would be the mode. The bacterial sampling procedure for coliform density called MPN (most probable number) uses the mode for averaging.

Averaging Time

One factor must be kept in mind in working with data - the averaging time. The effects of averaging time is best illustrated by an example of continuous, non-continuous and composite monitoring (Figure 4-4).

Figure 4-4 illustrates monitoring techniques and the resulting data from one site. The true parameter variation is shown in Figure 4-4(a). In Figure 4-4(b) and (c) the parameter variation at the site is the same as in (a), but it is monitored differently. In (b) the site is monitored at 30-day intervals. The value at day 30 is 500 in both cases (a) and (b). Figure 4-4(c) uses the data of (a) but indicates values as they would result from a composite sample. For convenience the flow rate at this site was assumed constant. Averages were computed and are illustrated to the right of the monitoring data.

Continuous Data

Figure 4-4(a) illustrates continuous monitoring and continuous data with respect to time. During this 90-day period, the parameter concentration varies from 0 to 800 in different ways. The average concentration for the first 30 days is 500. This average is computed by finding the area under the curve in the left hand figure and setting it equal to the average value times 30 days:

$$\begin{aligned} A\ (\text{Area left}) &= \text{Ave} \times 30, && 4.4 \\ \text{for example, } 15{,}000 &= \text{Ave} \times 30, \text{ and} \\ 500 &= \text{Ave}. \end{aligned}$$

The average for the second 30 days is 290 and the average for the third 30-day period is 560. If the averaging time is the first 60 days then the average value is 395. If the averaging time is the last 60 days, the average value is 425. If the averaging time is 90 days, the average value is 450.

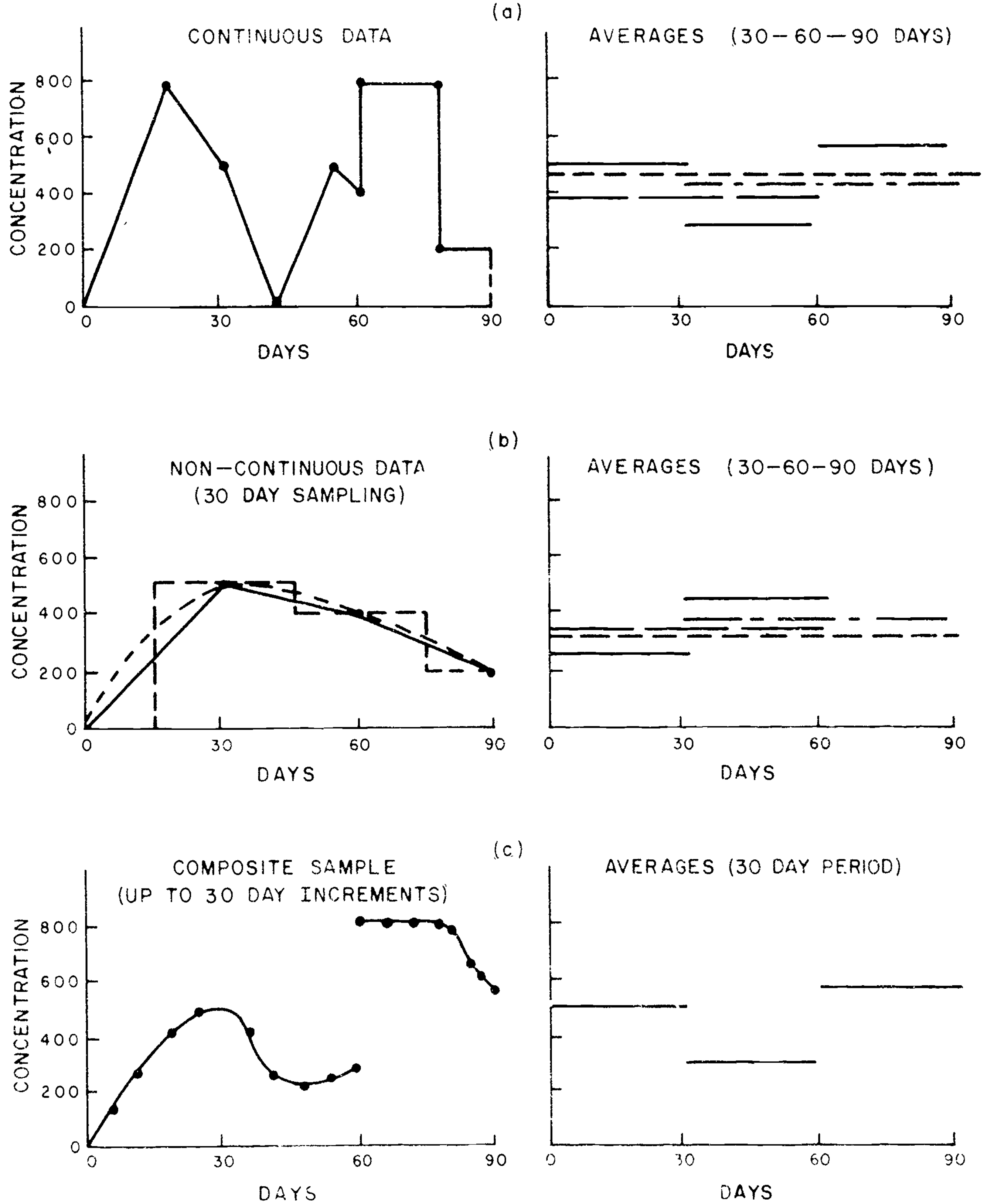


Figure 4-3
Monitoring Data and Averages
(Site Ordering)

If the average values of the right hand figure of Figure 4-4(a) is the only information available, there would be no way of knowing the true variation given in the left figure. If the maximum allowable concentration was, for example, 600 (Standard), no violation would be indicated by 30-day averaging times. Data can be reduced to show various kinds of averages but variations cannot be reconstructed from averages.

Non-Continuous Data

Figure 4-4(b) illustrates non-continuous monitoring at the same site at the same times. The data points at the beginning and end of each 30-day period coincide with the actual conditions from figure (a). The data points are connected by a straight line since no other information is available. The straight line for the first 30 days indicates the concentration varies linearly and uniformly from 0 to 500. The actual data points from (a) show how untrue that assumption is. Long averaging times do not indicate shorter time variations.

Averaging of data in Figure 4-4(b) gives 250, 450, and 300 for each successive 30-day period. Sixty day averaging gives 350 and 375 for the first and last 60 days. The 90-day average is 333. Compare these values with the true averages of figure (a). Note that when fluctuations in (a) are higher than the straight line between 0 and 500 of figure (b) the average in (b) is too low. If the fluctuations are lower (second 30-day period in (a)) then the average in (b) is too high.

A variation in the straight line approach is sometimes used. In Figure 4-4(b), the intermediate points between real data points are assumed to change in steps. The "0" value is assumed to be true for 15 days. The 500 value is assumed to be true for the next 30 days. This assumption is no better than the straight line approach. Both methods give the same average values since the area under the curves are the same. Other kinds of curves could be used between data points, but they will not necessarily improve the average values. Smooth curves through the data points (dotted lines) would give average values closer to true value in the first 30-day period, but would be farther away from the true value in the second 30-day period.

Composite Data

Figure 4-4(c) illustrates composite sampling during the same periods. At the end of each 30-day period, a new composite is started. The values are computed by incremental areas from the "0" time to the data point. At the end of each 30-day period, the true average for the period is reached (see Figure 4-4(a)). These average values are shown in the right figure of Figure 4-4(c). These curves do show how variations are occurring. If the composite curve is increasing, the actual data points are higher than the average for that increment. For example, in the first 30-day period, the composite values continue to increase after Day 18 even though the true variation of figure (a) is decreasing. The rate of increase or slope of the curve is decreased, however. As mentioned in Chapter 3, the integrity of a sample stored for 30 days could be very questionable.

Time Ordering

The data shown in Figure 4-4 was based on Site Ordering. When data is Time Ordered, caution should be exercised in graphing. For example, Figure 4-5 shows three data points indicating a parameter concentration at three different sites at approximately the same time. Since continuous monitoring in space and time is practically impossible, there is a question on how to connect the points on the graph. If this figure is

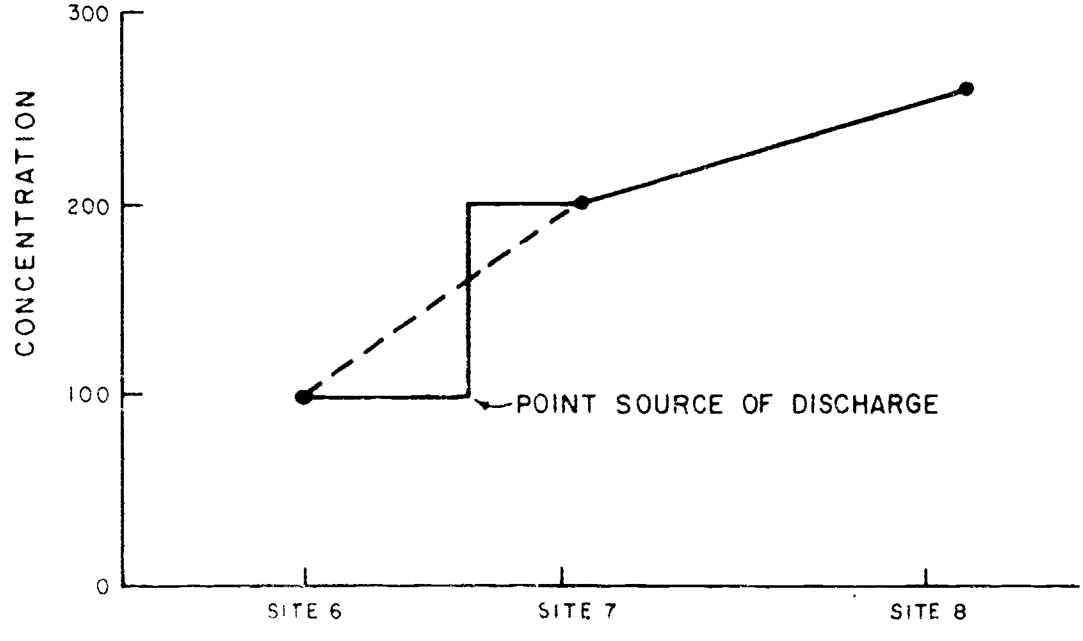


Figure 4-5
Parameter Concentration
(Time Ordering)

graphing a river at approximately the same time, how do the changes occur? The monitoring technician must be aware of what is going on between the sites. For example, a tributary or point source of discharge between Site 7 and 8 could be causing the change in concentration. This would be graphed as a step function and not as a straight line between the points.

If the change in concentration is due to surface or ground water runoff, the change could be gradual between the two sites. This could be represented by a straight line variation. Assume this is the case between Site 7 and 8.

Curve Fitting

b. Curve Fitting. A second method of generalizing data is by fitting the data to a mathematical curve. There are several environmental parameters which vary according to simple equations. Examples of these equations are given in Table 4-4. The procedure is simple. Plot the data points on arithmetic scales (y vs. t). Compare the shape of the curve with those in Table 4-4. Select a curve for testing. Plot data on graph paper using the straight line functions of the data instead of the data. This should produce an approximate straight line if the equation fits. Functional graph paper is also available. This paper is constructed in logarithmic or semi-logarithmic functions or logarithmic-probability functions. The data can be plotted directly on this kind of graph paper for straight line evaluation.

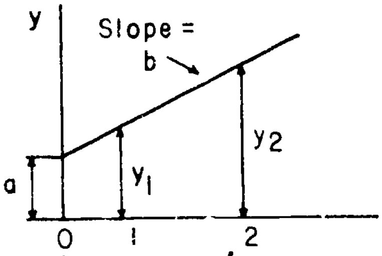
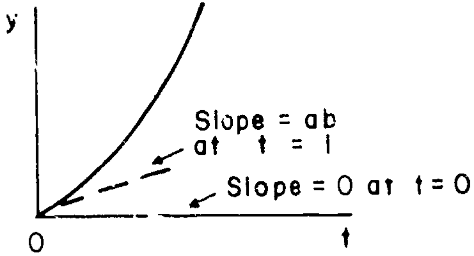
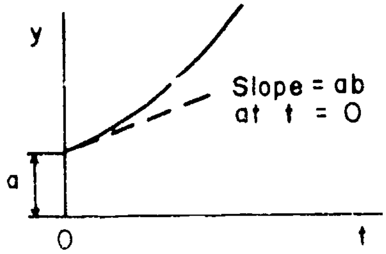
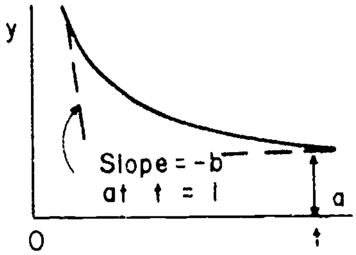
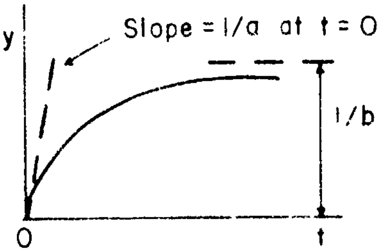
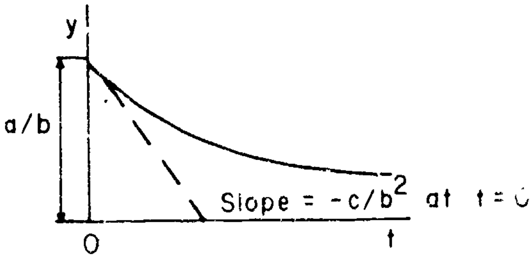
Several hints are useful in curve fitting, especially for straight lines. Choose y as the variable (dependent) to be found from different magnitudes of t (time, independent). Another hint is to pass the line through the arithmetic means of y and t. This intersection is the most probable value of the y and t relationship. A simple computation of these means fixes an intersection point for the line. The only other decision is the slope. Many times an adjustment of slope by eye is sufficient.

Curve fitting is applicable to reduction and expansion of data. Excessive data can be reduced to a simple equation and limited data can be expanded to fit simple equations.

Trends and Cycles

c. Trends and Cycles. Frequently data from long periods of monitoring will show trends or cycles. This kind of generalization or time averaging is useful in environmental evaluation. The procedures for generalizing data for this kind of presentation is straight forward. For

TABLE 4-4
MATHEMATICAL CURVES

EQUATION	SHAPE	STRAIGHT LINE FORM
1. $y = a \quad bt$		$y = a + bt$
2 $y = at^b$		$(\log y) = (\log a) + b(\log)t$
3. $y = ae^{bt}$		$(\log y) = (\log a) + (b \log e)t$
4 $y = a + b/t$		$y = a + b\ (1/t)$
5 $y = t/(a + bt)$		$(t/y) = a + bt$
6 $y = a/(b + ct)$		$(1/y) = (b/a) + (c/a)t$

example, if the change or trend in CO_2 concentration in the atmosphere is needed, average yearly values would be computed and plotted against time. Figure 4-6(a) shows that the CO_2 concentration in the atmosphere is steadily increasing with a definite trend.

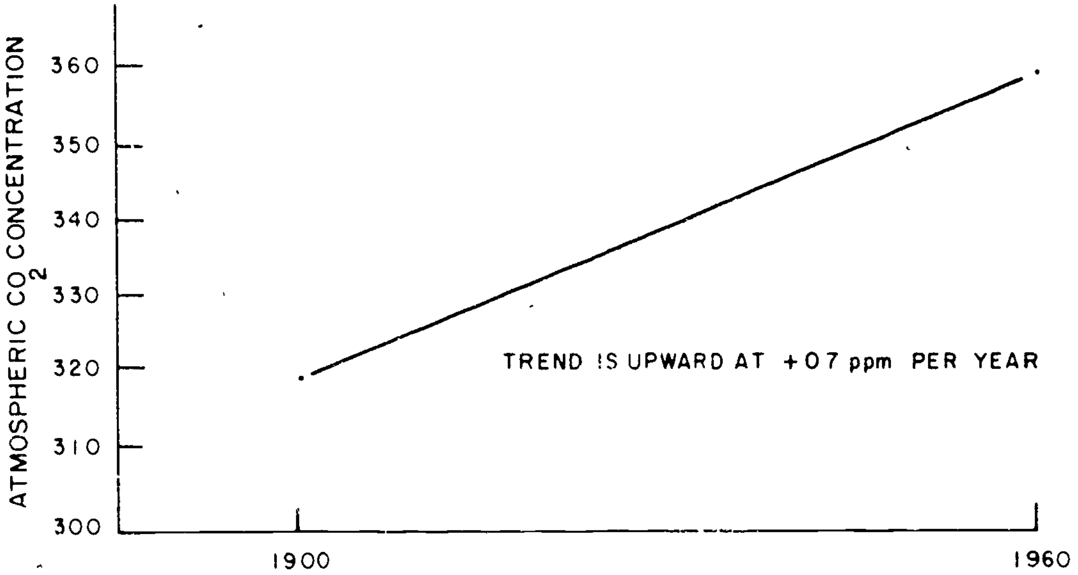
Cycles are also useful to indicate changes in environmental parameters. Wet and dry weather cycles are common examples of cycles. The Water Quality parameter of color shows a similar yearly cycle in mountain streams. Figure 4-6(b) illustrates a color cycle.

Distribution and Variation

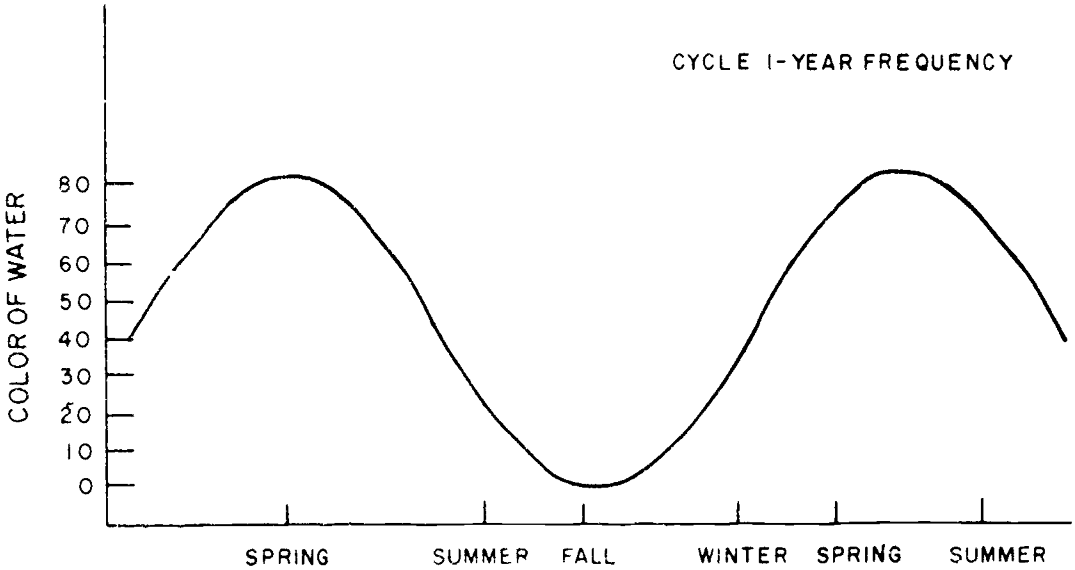
d. Distribution and Variation. Frequently in monitoring programs data will vary, at least for certain periods, around a central value. The distribution and variation of data around this central value is an important evaluation tool. For example, if an average value is 75 and the data varies from 6 to 250 around this value, the data is quite variable. If, however, the data varied from 74 to 76, the variation would be less significant and the average value would be more representative of actual conditions. The analysis of data to determine its distribution and variation involves the mathematics and theory of Statistics. It is beyond the objective o this book to present these concepts; however, a brief description of the procedure and results is warranted.

The analysis of the distribution and variation of a set of data starts with ordering the data by parameter magnitude in an array. Generally simple magnitudes are selected and data is grouped in these magnitudes. For example, if 9 and 10 are simple magnitudes, data from 8.5 to 9.49 would be grouped under a magnitude of 9. The number of times data falls in this group is the frequency of that magnitude. After this grouping by magnitude and frequency the data is plotted. Figure 4-7 shows a normal type frequency distribution (a) and a skewed frequency distribution (b).

It is a curious fact that many arrays of observations and measurements trace a bell-shaped normal curve like Figure 4-7(a). Mathematically, these kinds of arrays have certain characteristics. The largest number of observations occur near the center of the array. Smaller and smaller numbers of observations (frequency) differ from the central magnitude by larger and larger amounts. Values greater than the central value occur about as often as smaller values (symmetrical). These kinds of curves are called probability curves. Probability is synonymous with frequency.

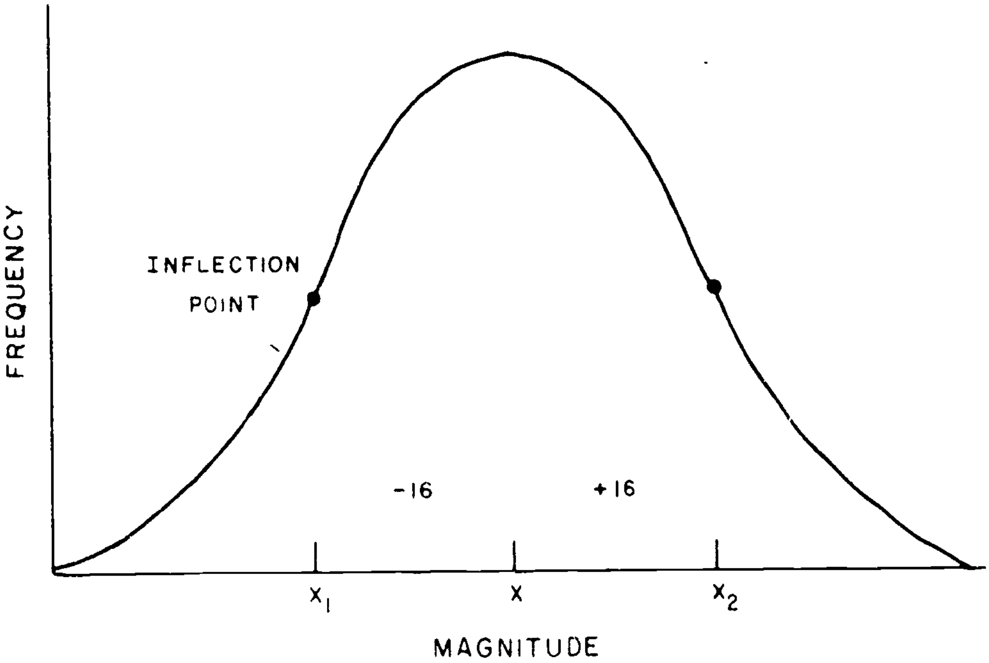


(a) Average CO_2 Concentration (ppm)

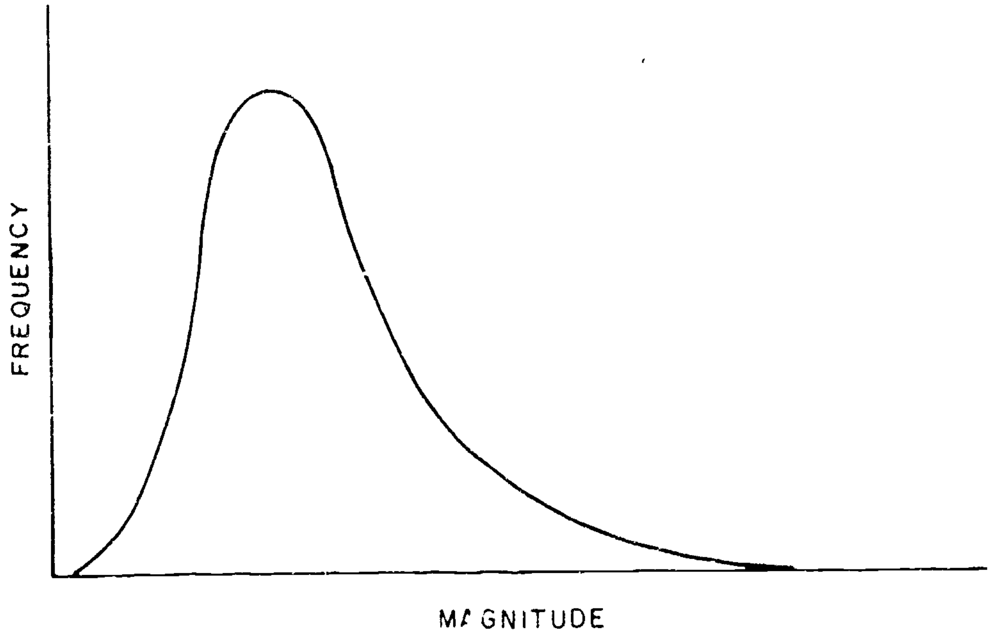


(b) Color of River Water

Figure 4-6
Trend Cycles



(a) Normal Frequency



(b) Skewed Frequency

Figure 4-7
Frequency Distribution

Probability

The area under the curve measures the total number of observations. The ratio of any portion of the area bounded by vertical lines to the whole area therefore gives a ratio of relative frequency or probability of occurrence of values lying between the magnitudes indicated by the vertical lines. These areas or probabilities are found in all basic books on Statistics.

On the normal distribution curve the shapes change from concave to convex at two points. These points are called the inflection points. Deviations of data between these two points is frequently given along with the central average value. If the data fits a normal curve, the probability would indicate that 68.2% of the time sampling would give a value between the lower magnitude (x_1) associated with the left inflection point and the higher magnitude (x_2) (Figure 4-7a)). Other probabilities are easily computed from the statistical tables.

4. Presentation of Data

The fourth step in preparing data for evaluation is presentation. Evaluation is a human function; therefore, the presentation should be aimed at maximizing the response of the human senses. The old adage of "A picture is worth a thousand words" can be changed to:

"<u>A picture is worth a thousand numbers</u>".

The eye can scan a chart or graph of data much more quickly and accurately than a set of numbers. The graphs should be simple with easy-to-understand units. Graphs or charts are sometimes prepared to indicate general situations or problems. Precise data points are not presented, only the general trend or problem is apparent. In other cases, very precise, accurate drawings are needed.

Several engineers and scientists are working on methods for better presentation and storage of data. As mentioned before, data which cannot be used or evaluated is useless. In recent years, the tremendous increase in data systems and data collection has produced serious problems in proper evaluation. Computers have made a significant step in the analysis and classification of data. Several computer systems have graphing equipment for portrayal of data. Weather maps have been graphed by this method for many years. Graphing programs are now available with the STORET system used by the Environmental Protection Agency.

In any presentation for evaluation, the objective or objectives of the monitoring program must be stated. Each objective requires a little different presentation and timing. "Evaluation of Standard Compliance" and "Emergency Conditions" are objective functions which require immediate response. For "Standard Compliance" precise data showing peaks and variations are required. Graphs using a horizontal line to indicate maximum permissible concentrations are useful in presentations. Emergency conditions may require immediate response with reduced demand for accuracy of data or presentation.

For other objectives, for example, "Characterization of Existing Conditions", "Identification of Trends", "Environmental Quality Forecasting" and "Research", more time is available for presentation and evaluation. Precise data graphs, prepared under various ordering, averaging, and curve fitting procedures will provide sufficient data. "Trends", "Forecasting" and "Research" generally require an extension of current data into the future. Extension of data into future times is an educated game of guessing.

Forecasts and Predictions

Making environmental predictions requires a considerable amount of knowledge. All areas and aspects of the environment must be considered in making the predictions. Even with the best available knowledge, only limited predictions can be made. From past experience, several kinds of gross predictions are obvious. Building cities in areas where air inversions occur is poorly advised. Los Angeles is the prime example. High density population centers will not provide a quality environment.

Environmental Impact Statements

Most of these predictions are now obvious, but small-scale predictions are not so obvious. In recent years, federally funded projects have required "Environmental Impact Statements". These statements are attempts at forecasting or predicting the effects of federal projects. Some of the reports are good, others are poor and lack substance.

Even when the statement indicates severe possible impact, no direct action is generally possible except at the Executive level. Significant public pressure and Congressional displeasure can also influence the project. Several eminent scientists have made predictions which indicate we are in serious environmental trouble. The most serious environmental problems are the ones which are irreversible. This means that after discovery of the problem the trend cannot be reversed. The situation has proceeded so far it cannot be reversed. When certain species of animals become extinct, this is irreversible. Some predictions indicate that man is environmentally an endangered species. Hopefully, the trend initiating the prediction is changeable, reversible and only temporary.

Problems:

1. Arrange a monitoring trip to several sites with a technician from the U.S. Geological Survey. Follow and list the procedures used for quality control of data. Identify how data is generated, checked, and recorded. Select a group of consecutive river sites and select a few parameters for study. Order the data by site, time, and parameter. Generalize the data. Find medians, means, and modes for each parameter over a two-year period. Graph the parameters versus time and check for trends and cycles. Write a report on your findings. Include graphs and data presentation. Remember to define objectives functions.

2. Arrange a trip to an industrial site or a municipal sewage plant. Find and list the general data collected on effluent discharge. Identify quality control procedures used to verify data. Collect the data from the last two years and select a few parameters for study. Order the data by site, time and parameter. How does this kind of data differ from river site data? Generalize the data. Define objective functions. Find several different kinds of averages. Check for trends and cycles of various time periods. Write a report on your findings. Include data, graphs, and various presentations.

5

FUNDAMENTALS OF ELECTRICITY, ELECTRONICS, AND INSTRUMENTATION

INTRODUCTION AND PURPOSE

In order to control and protect environmental quality, observations and measurements must be made to ascertain whether or not environmental quality is deteriorating. Many techniques are available to make these observations and measurements. There are chemical techniques as in specific impurity measurements, mechanical techniques as in viscosity measurements, optical techniques as in turbidity measurements, electrical techniques as in conductivity measurements, etc. In a great many of these techniques, some part of the process involves electricity or electronics either directly as in conductivity measurements or indirectly as in turbidity measurements where the light transmission through a turbid media is measured by an electrical signal from a photo-electric cell. Because of this frequent use of electricity and electronics in environmental quality monitoring (and also the occasional use in environmental quality control such as in electrostatic precipitators) an understanding of the basic properties of electricity and electronics is essential to an understanding of these monitoring (and control) techniques.

It is the purpose of Chapter 5 to review basic electrical concepts, electrical circuit concepts and to review electronics as it pertains to environmental instrumentation. These various topics will be reviewed from the standpoint of developing understanding of electrical phenomena for the environmental technician and are specifically <u>not</u> presented as basic training for the electronic technician or engineer, nor is it meant for the training of the environmental technician in the repair and maintenance of his own electronic instrumentation. However, it is hoped that the understanding gained from this material will aid the environmental technician in properly operating his equipment, help him in determining when his equipment is working properly and give him confidence in his calibration procedures.

ELECTRICITY

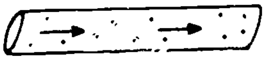
ELECTRICAL CONCEPTS AND DEFINITIONS

The elemental particle which is the basis for all electrical phenomena is the electron. Its mass is 9.1×10^{-31} kilograms. It is one of the principle particles forming the atom and in normal atoms is found in conjunction with a proton which is a much larger particle but with opposite electrical charge from the electron. The charge on the electron is defined as negative while the charge on the proton is defined as positive. The simplest atom (hydrogen) is conveniently viewed as a tiny planetary system with the sun represented by the proton, and the electron as a planet

rotating around the proton like a planet around the sun. This representation of the hydrogen atom is known as the Bohr atomic model and is a very useful model for many applications. All other a are more complicated than the hydrogen atom and contain many electrons and protons (in equal numbers) and also a variety of other atomic particles which are not important to our consideration of electricity.

The electrical charge on one electron or one proton is very, very small and for most electrical applications is inconveniently small. Therefore, electrical scientists many years ago defined a more convenient unit of charge called the coulomb. A coulomb of charge consists of 6.21 x 10^{18} electrons (or protons) and even though this number seems to be a very strange one, the coulomb is a very convenient unit of charge as will be seen by the following discussion of electrical current.

In normal atoms there are equal numbers of protons and electrons. However, in some materials (electrical conductors) the electrons can be removed from the atoms by various means, some as simple as heating the material up from absolute zero temperature. For example, in copper at room temperature (300°K) there are about 10^{29} free electrons per cubic meter. Surprisingly enough, the free electrons can move about within the material, experiencing very little friction due to interaction with the atoms forming the material. Imagine these electrons all moving in one direction down a long cylindrical rod (a wire) of the material. If 6.21 x 10^{18} electrons (i.e., one coulomb of charge) move past each point in this wire in one second, one ampere of electrical current is, by definition, said to flow. Thus the unit of electrical current is the ampere and one ampere, I, is equal to the flow of one coulomb of charge, Q, along a wire of one second of time, t.



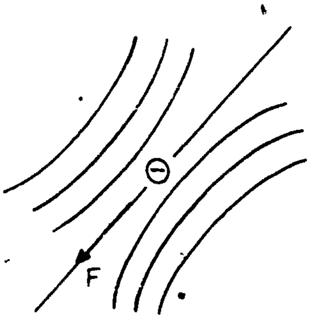
$$I = \frac{Q}{t}$$

The above discussion raises the next question; how are the free electrons in the wire made to move? There are several means available to apply a force to an electron; however, the only imporant one at this juncture is to use the force of attraction between positive and negative charges or similarly the force of repulsion between like charges. The basic law describing these two types of forces is called Coulomb's Law. This experimentally established law states that the force, F, between two separated charges, Q_1 and Q_2, is equal to a constant, k, times the product of the charges divided by the square of the distance, r, separating them. If the force is measured in Newtons, the charges are in coulombs and the distance is

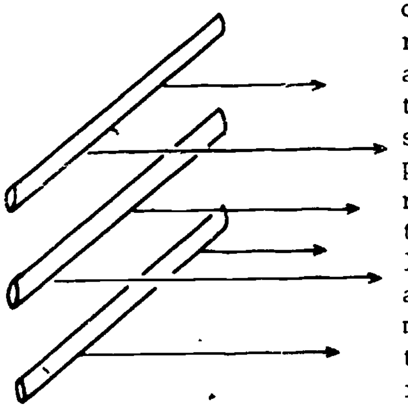
$$F = K \frac{Q_1 Q_2}{r^2}$$

measured in meters then the constant K is 9×10^9 Newton Meters^2 per Coulomb^2 if the charges are located in air or vacuum. K will be different for other materials. If Q_1 and Q_2 are the same type of charge, i.e. either both positive or both negative, then the force is one of repulsion, if they are of opposite type of charge then the force is one of attraction.

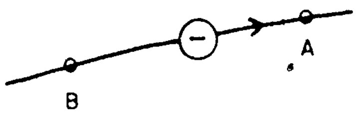
Next consider the situation of an electron being located in the proximity of several protons which are held fixed in position. The electron experiences a coulomb force as per Coulomb's Law directed toward each proton. The net force on the electron is a combination of all of the individual forces. To determine the path along which the electron will move due to these combined Coulomb forces would obviously be a tiresome calculation. Electrical scientists have therefore developed the concept of an electric field to simplify this problem. The electric field is drawn as a number of non-intersecting lines distributed throughout a volume of space. The direction of these lines is the direction of the net Coulomb force while the number of lines per square meter of area perpendicular to the lines (the density of lines) is the strength of the net Coulomb force. Thus once the electric field is determined the direction and strength of the force on a charge located in the field is known.



To digress momentarily for a practical example, these Coulomb forces of attraction are the basis for the operation of electrostatic precipitators used in pollution control in exhaust stacks. A grid of wires in the precipitator is charged positive (by the removal of electrons) and electrons are sprayed on the solid particles in the exhaust. These negatively charged solid particles are attracted to the positively charged wire grid and thus removed from the effluent. The electric field for the wire grid is simply lines running outward from the grid across the stream of the effluent meaning a force exists on the negatively charged solid particles which is more or less perpendicular to the direction of flow of the effluent.



Returning to electrical theory, next consider moving one coulomb of charge along an electric field line <u>against</u> the



$$V = V_A - V_B$$

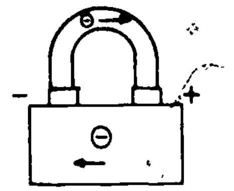
force. Work must be done in moving this charge against the force. Thus the charge will have a potential energy, V_A, at the end of the movement which is larger than the potential energy, V_B, at the beginning. The difference between these two potential energies is called the voltage, V, between these two points. If one joule (one Newton-meter) of work is done in moving one coulomb of charge between two points, the difference in potential between these two points is one volt.

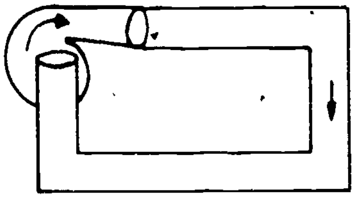
As a practical example, consider combining lead and sulphuric acid properly to form a lead-acid battery. This chemical combination separates positive and negative charges within the battery to form a potential energy difference (voltage) between the terminals. If 12 joules of work are done moving one coulomb (6.21 x 10^{18} electrons) from one terminal of the battery to the other, the battery is said to be a 12-volt battery. An interesting fact is that it does not matter whether we move the charge directly in a straight line between the battery posts or move it over some longer route, we will still do the same amount of work over either path.

In terms of accomplishing something useful, consider connecting a wire containing free electrons to the terminals of the battery; let the wire be tungsten as in the filaments of a headlight. The free electrons will experience coulomb forces and move along the wire toward the postive terminal of the battery. The change in energy of these electrons as they move along the wire will be converted to heat and this heat will cause the filament to emit light.

There are many other ways of generating a voltage between two terminals; electric generators, solar cells, thermoelectric cells, fuel cells and others. How they operate is not important at this point. What is important here is that there are such devices. They are commonly called power supplies, power sources, or occasionally voltage sources.

Reconsidering our headlight example for a moment, as the electrons in the wire move toward the positive terminal of the battery one might conclude that once all electrons in the wire reach the positive terminal the headlight would extinguish - this, of course, does not happen. What actually happens is that as the electrons reach the positive terminal of the battery they combine with positive ions in the battery and migrate back through the battery to the negative terminal. At the same time as electrons move along the wire away from





the negative terminal, new electrons are given up by the chemicals through the negative terminal into the wire replacing those that have moved away. The net result of all of this movement of electrons is that there is a continuous movement of electrons completely around the loop consisting of the wire and the battery. This closed loop type of current flow is true of all electrical current flow. Because of this, it is common to compare electrical current flow with flow of water in a closed system such as a pump with pipes connecting the outlet and the inlet of the pump. Since water is incompressible, if water flows at any one point in this hydraulic loop, it must flow at all points. The complete analogy is, of course, the pump representing the battery, the pipe representing the wire, and the water representing the free electrons. Notice that the water flows from the pump outlet to the pump inlet through the pipe but from the pump inlet to the pump outlet through the pump. Analogously, the electrons flow from minus to plus through the wire but from plus to minus through the battery.

There is occasionally some confusion regarding the direction current flows in a wire. This confusion was caused by Benjamin Franklin, believe it or not! In his early experimentation with electriciy, he knew nothing of electrons and protons. In order to explain some of his experimental results he theorized the existence of electrical charges which moved in the wire. Unfortunately, he arbitrarily guessed that positive charges were the free charges and that these positive charges moved toward the negative terminal of the battery. This, of course, is the exact opposite of what we now know to be the case. However, a considerable amount of electrical circuit theory was developed prior to the discovery of the electron, this theory being based on Ben Franklin's positive current flow. Thus, in circuit theory conventional current is said to flow toward the negative terminal of the power supply. This convention does not cause any problem so long as either conventional current or electron current, but not both, is used in any given circuit analysis problem.

In all of the discussions thus far in which any work was accomplished, charges (electrons) have been moved from one point in a circuit to another changing potential energy in the process. Specifically, if one coulomb of charge is moved through a voltage of one volt, one joule of work has taken place. If charges are moved continuously at the rate of one

$P = VI$

$W = Pt$

coulomb per second along a wire which has one volt connected from end to end, one amp of current is flowing and one joule of work is taking place per second. One joule of work per second is called a watt and is a rate of doing work. The rate of doing work is called power, P, and power is equal to the product of the current times the voltage. If this power is applied over some interval of time when the energy, W, expended will be the power (the rate of doing work) times the time period, t, during which the work is being done.

ELECTRICAL CIRCUITS

CIRCUIT CONCEPTS AND DEFINITIONS

When a voltage is applied from one end to the other of a conductor (a piece of material containing free electrons) coulomb forces are experienced by the free electrons causing them to move along the conductor, this constitutes a flow of electrical current.

$V = IR$

The obvious question to ask is how much voltage is required to cause one amp of current to flow? Ohm, a scientist, experimentally determined this relationship many years ago and determined that the required voltage, V, was proportional to the amount of current, I. The constant of proportionality is called the resistance, R. This relationship is called Ohm's Law. If one volt causes one amp to flow, then the resistance is said to be one ohm.

$I = VG$

$G = \frac{1}{R}$

Ohm's Law can be stated reciprocally by saying that the current flow through a conductor is proportional to the voltage across the conductor. Here the constant of proportionality is called the conductance, G, and is equal to the reciprocal of R, the resistance. If one amp causes one volt drop then the conductance is said to be one mho.

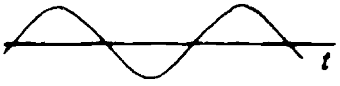
$P = Vi$

$P + I^2R$

$P = V^2G$

If a power supply of voltage, V, supplies a current, I, to a resistance, R, the power heating up the resistance is equal to the product of V times I. By substituting Ohm's Law into this power equation the power is also equal to the current squared times R. By substituting the reciprocal Ohm's Law into the power equation, the power equation becomes the voltage squared times the conductance.

Thus far, the principle type of power supply discussed has been the battery. A battery is characterized by having a terminal voltage which is essentially constant and <u>does not</u> change with time. When this voltage is connected across a resistance the resulting current flow is also constant and does not change with time. Such a current flow is called direct current, frequently abbreviated as DC. It is also commonly, though imprecisely called DC current. Similarly, the battery voltage is imprecisely called DC voltage. There



are many other types of voltage sources that are not constant and do change with time. Of these variable voltage sources there is a very important class whose terminal voltage varies sinusoidally with time, reversing polarity in a periodic fashion. The electrical generators which supply electricity to your home are examples of this type of voltage source. Since the voltage polarity alternates periodically, Ohm's Law says that the current this voltage causes to flow in a resistance likewise alternates periodically, thus this current is called alternating current or AC for short. It is also commonly though imprecisely called AC current and similarly the voltage is called AC voltage.

$f = \frac{1}{T}$

The length of time, T, in seconds required for an AC voltage (or current) to very from zero volts to a positive maximum back to zero volts to a negative maximum and back to zero again is called the period of the voltage or current. The number of periods which occur per second (the reciprocal of T) is called the frequency, f, of the AC voltage or current. If one period (or cycle) occurs in one second, the frequency is called one hertz, abbreviated one hz. The frequency of house voltage is 60 hz; i.e. 60 periods occur each second.

If an AC voltage is applied across a resistance Ohm's Law predicts the AC current flow that results. Frequently the instantaneous current flowing in the resistance is unimportant and what is important is the net effect of the AC current. In a resistance the effect of the current is to heat up the resistance. For this reason it is common to treat the AC current (or AC voltage) as if it were the DC current (or DC voltage) that gives the same heating effect. This is why the AC voltage in your house is called 110 volts AC even though the actual voltage varies from zero volts to plus 156 volts back to zero volts to minus 156 volts back to zero volts 60 times each second. If you were to connect your livingroom lamp to a 110 volt battery it would glow with the same brightness it now does on your normal house AC voltage. The effective value of a voltage is sometimes called the RMS value which stands for root-mean-square, which is a mathematical method of calculating the effective value of an AC voltage.

Ohm's Law can be used with AC voltages and currents in the same manner it is used with DC voltages and current, by using the effective values of the AC quantities. For example, if one volt of AC voltage (effective value) is connected across a resistance and one amp of current (effective value) flows, the resistance is then one ohm, the same as in the DC case; furthermore, the resistance will heat up exactly the same for both one amp of AC and one amp of DC.

Notice that in applying an AC voltage across a resistance, current flows according to Ohm's Law; knowledge of the frequency of the AC was not required in order to determine the current. There are two other important electrical circuit components that also obey Ohm's Law but for which knowledge of the frequency is necessary in order to determine the "resistance." This frequency dependent resistance is called reactance, X.

$X_L + 2\pi fL$

$V = IX_L$

One of these two frequency dependent elements is a coil of wire and operates on the basis of the magnetic field around the coil. It is called an inductance, L. The unit of inductance is the henry. The "resistance" of this inductance to the flow of AC current is called the inductive reactance, X_L. This inductive reactance is proportional to the frequency of the AC times the inductance of the coil. If two pi is used for the constant of proportionality the inductive reactance has the units of ohms and Ohm's Law applies directly.

$X_C = \frac{1}{2\pi fC}$

$V = IX_C$

The other type of frequency dependent circuit element consists of a pair of flat conducting plates separated by a non-conducting material (an insulator) and operates on the basis of the electric field between the plates. It is called a capacitance, C. The unit of capacitance is the farad. The "resistance" of this capacitance to the flow of AC current is called the capacitive reactance. This capacitive reactance is <u>inversely</u> proportional to the product of frequency times capacitance. If the constant of proportionality is the reciprocal of two pi then the capacitive reactance has the units of ohms and Ohm's Law applies directly.

$\omega = 2\pi f$

The product of two pi times the frequency occurs quite often in AC circuit calculations and is commonly given the Green symbol omega, ω, and is called the frequency in radians per second.

$S_1 = \frac{1}{X_L} = \frac{1}{2\pi fL}$

$S_C = \frac{1}{X_C} = 2\pi FC$

$I = VS_L$

$I = VS_C$

The reciprocal Ohm's Law also applies to both inductive reactance and capacitive reactance. The reciprocal of inductive reactance is called inductive susceptance, S_L, and the reciprocal of capacitive reactance is called capacitive susceptance, S_C. The reciprocal Ohm's Law applies to both S_L and S_C.

One other AC circuit element commonly encountered is the transformer. A transformer consists of two coils of wire wound on the same core. The coil connected to the source of power in a circuit is called the primary winding. The coil connected to the load (circuit element consuming power) is called the secondary winding. The principle property of a transformer is that AC power can be transferred from one circuit to another via the magnetic field coupling the primary to the secondary with no direct wire connections required.

If the number of turns in the primary coil differs from

$$n = \frac{N_s}{N_p}$$

$$V_s = nVp$$

$$V_pI_p = V_sI_s$$

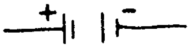
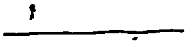
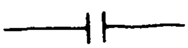
$$I_s = \frac{I_p}{n}$$

the number of turns in the secondary coil the secondary coil will not be the same as the primary voltage. A transformer turns ratio, n, is defined as the ratio of the secondary turns, N_s, to the primary turns, N_p. The secondary voltage is n times the primary voltage. If n is greater than one the transformer is called a step-up transformer and if n is less than one it is called a step-down transformer.

The transformer itself consumes almost no power (ideally no power at all). Therefore, the power is delivered to the primary by the source of power is the same as the power delivered to the load by the secondary. Thus a transformer that steps up voltage must step down current and vice versa.

Standardized symbols have been established for the various circuit elements when used in circuit diagrams. Table 5-1 shows the standardized symbols. The wire connecting the elements is usually drawn as a thin line and is assumed to have such a low resistance that there is zero voltage drop from one end to the other. The common wire, sometimes called groundwire, is frequently not drawn in a schematic diagram. Instead a ground symbol is used to indicate a connection to the common wire.

TABLE 5-1
COMMON ELECTRICAL SYMBOLS

Symbol	Circuit Element
	Generalized Voltage Source
	Generalized Current Source
	Battery
	AC Voltage Source
	Connecting Wire
	Ground Symbol
	Resistance (or conductance)
	Inductance
	Capacitance
	Transformer

Thus far in this chapter various electricl quantities have been discussed such as volts, amps, ohms, etc. Frequently these basic units are much too large or much too small for convenience in calculations or discussion. Rather than repeatedly using powers of ten it is more convenient to use prefixes representing these powers of ten. Table 5-2 lists those in common use.

USEFUL CIRCUIT THEOREMS

By far the most important electrical circuit theorem of all the many theorems has already been introduced, namely Ohm's Law. This law was discussed in conjunction with the very simplest electrical circuit possible, a battery connected across a resistance. If the circuit is drawn out using the various standard symbols previously listed, this circuit drawing is known as a schematic circuit diagram. Ohm's Law describes the current flow in this circuit in terms of the battery voltage and the resistance value.

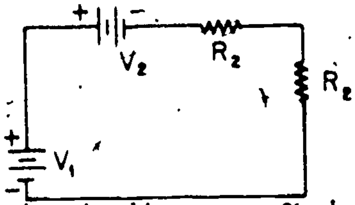
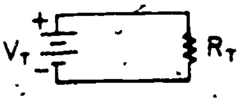


TABLE 5-2
COMMON METRIC PREFIXES

Power of ten	Prefix	Example	Abbreviation
10^{-12}	pico	picoamp	pa
10^{-9}	nano	nanovolt	nv
10^{-6}	micro	microwatt	μw
10^{-3}	milli	milliohm	mΩ
10^{0}	none	amp	a
10^{3}	kilo	kilovolt	kv
10^{6}	mega	megawatt	MW
10^{9}	Giga	gigahertz	ghz

$$I = \frac{V}{R}$$

The battery and the resistance are connected together in this circuit in a "head-to-toe" fashion; such a circuit is known as a "series" circuit. This simple series circuit can be expanded to include more batteries and more resistances by connecting additional elements in a similar head-to-toe fashion. The enlarged circuit is still called a series circuit and can include both AC and DC power sources as well as resistances, inductances and capacitances.



In a series circuit, the current that flows out of one element of the circuit must flow into the next element in the circuit; otherwise, electrons would either be disappearing or being generated at the connection between the two elements--the principle of conservation of mass says this is impossible. Therefore, the same current flows through all elements in a series circuit.

The first question to ask regarding a series circuit containing several resistances and several voltage sources is, how much current flows? A scientist named Kirchoff studied this problem many years ago and derived a theorem answering this question. The theroem is known as Kirchoff's First Law. Kirchoff's First Law states that in a series circuit the sum of the volate "drops" across all of the resistors in the circuit is equal to the algebraic sum of all of the voltage sources in the circuit. This means that to determine the current flow in a series circuit, replace all the resistors in the circuit with a single resistor, R_T, which is equal to the sum of all the series resistors and replace all the batteries in the circuit with a single battery, V_T, equal to the <u>algebraic</u> sum of all the series batteries, then use Ohm's Law on this "equivalent" circuit to determine the current flow. Notice that if several of the batteries individually would force current to flow in the same direction, these battery voltages should be added together; those batteries that would force current in the opposite direction should be subtracted to obtain the total voltage, V_T. All resistances are positive, therefore, they always add only.

$$R_r = R_1+R_2+R_3$$

$$V_T = V_1-V_2$$

$$I = \frac{V_T}{R_T}$$

Another way of determining the current in a series circuit containing several power sources and several resistances is to use the part of Kirchoff's First Law that states that the total resistance is equal to the sum of the individual resistances, and another theorem called the Superposition Theorem. The Superposition Theorem states that the total effect of several power sources can be determined by calculating the effect of each power source separately as if it were the only power source in the circuit and then algebraically adding the individual currents to determine the total current.

$$I = \frac{V_1}{R_T} + \frac{V_2}{R_T}$$

All series circuit theorem apply equally well to AC circuits as they do to DC circuits, except that in AC series circuits only like kinds of "resistances" can be added together directly. That is to say, only resistances can be added to resistances, only inductive reactances can be added to inductive reactances, and only capacitive reactances can be added to capacitive reactances.

$$R_T = R_1+R_2$$

$$X_{L_T} = X_{L_1}+X_{L_2}$$

$$X_{C_T} = X_{C_1}+X_{C_2}$$

In AC circuits it is common to call the "resistance" to the flow of AC current the impedance to the flow, this impedance, Z, being the "resistance" to AC current flow by any one of the three types of circuit elements, resistance, inductive reactance, or capacitive reactance, or the impedance to current flow caused by any combination of the three types of elements.

$X_T = X_{L_T} - X_{C_T}$

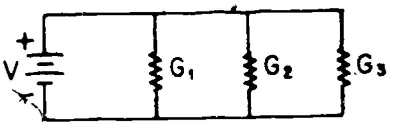
If both inductive reactances and capacitive reactances occur together in a series circuit, the net impedance is determined by adding all inductive reactances together then subtracting the sum of all capacitive reactances from this. If the sign of the total is positive, the net impedance is inductive reactance. If the sign is negative, the net impedance is capacitive reactance.

$Z = \sqrt{R_T^2 + X_T^2}$

$I = \frac{V_T}{Z}$

If the resistances and reactances are combined in the same circuit, they cannot be combined directly. In a series circuit the total impedance to AC current flow is determined by taking the square root of the sum of the total resistance squared plus the net reactance squared. The current flow is determined by applying Ohm's Law to the total impedance and the total voltage.

Another very important type of electrical circuit is one in which more than one resistance is connected across the same battery. This type of circuit is called a "parallel" circuit. Ohm's Law still applies to this circuit but the current through each path must be calculated separately and the current supplied by the battery, I_T, is the sum of the currents through each conductance.



$I_1 = VG_1$

$I_2 = VG_2$

$I_3 = VG_3$

$I_T = I_1+I_2+I_3$

$G_T = G_1+G_2+G_3$

$I_T = VG_T$

Kirchoff studied the parallel circuit many years ago and formulated this type of circuit calculation in a law known as Kirchoff's Second Law. This law states that at any point in an electrical circuit the current flowing into the point is equal to the current flowing out of the point. This means that if the current, I_T, from the battery flows into the point connecting the various parallel resistors, then the sum of the currents flowing out of the junction point into the individual resistor must be equal to this incoming battery current. This infers that to determine the current flow from the battery in a parallel circuit, replace all the conductances in parallel by a conductance equal to the sum of the individual conductances, then to determine the battery current, apply the reciprocal Ohm's Law to the resulting total conductance.

$Y = \frac{1}{Z}$

In applying Kirchoff's Second Law to AC parallel circuits, it is convenient to perform the calculations in terms of the reciprocal impedance quantities. The reciprocal of the impedance is known as the admittance, Y. In combining parallel elements together, again as in series circuits, only like admittances can be added together; only conductances can be added to conductances; only inductive susceptances can be added to inductive susceptances, and only capacitive susceptances can be added to capacitive susceptances.

$S_T = S_C - S_L$

If both inductive susceptances and capacitive susceptances occur in a parallel circuit, the admittance is determined by adding together all of the capacitive susceptances then subtracting all inductive susceptances from this sum. If the sign of the total is positive, the net admittance is capacitive susceptance. If the sign is negative, the net admittance is inductive susceptance.

$Y = \sqrt{G_T^2 + S_T^2}$

$I = VY$

If conductances and susceptances are combined in the same circuit they cannot be combined directly. In a parallel circuit the total admittance to AC current flow from the power source is determined by taking the square root of the sum of the total conductance squared plus the net susceptance squared. The power source current is determined by applying the reciprocal Ohm's Law to the total admittance.

$G_t = G_2 + G_3$

$R_t = R_1 + \frac{1}{G_t}$

$I = \frac{V}{R_t}$

While many electrical circuits are either series circuits or parallel circuits, frequently more complex circuits are encountered which are a combination of both series and parallel sections. If such circuits consist of only one kind of circuit element, such as resistance only, then these circuits can be analyzed using the series and parallel methods previously described on one branch of the circuit at a time. For example, if a circuit has one resistor in series with two resistors in parallel, the battery current can be determined by first combining the two parallel conductances then combining the resulting total conductance with the single series resistance and then applying Ohm's Law. More complex circuits merely require more calculations. If a series-parallel circuit contains both resistances and reactances, the calculations are more complicated and will not be discussed here.

ELECTRONICS

ELECTRONIC AMPLIFICATION

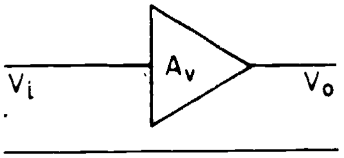
Quite frequently in making environmental quality measurements, the electrical quantities (voltage or current) generated by the basic device sensing the environment are very small and difficult to detect. In order to increase the detectability of these electrical quantities, electronic amplifiers are necessary. If the electrical quantity generated by the measuring device (known as the "transducer") is fed into an amplifier, the amplifier is controlled by this "input signal" and generates an "output signal" which is proportional to the input signal. The constant of proportionality is called the "gain", A, of the amplifiers.

There are four basic types of electronic amplifiers. One

$V_{out} = A_v V_{in}$
$I_{out} = A_i I_{in}$
$I_{out} = A_G V_{in}$
$V_{out} = A_R I_{in}$

is the voltage amplifier, which requires a voltage signal input and amplifies this voltage signal to a larger voltage output. The second type is the current amplifier which requires a current signal input and amplifies this current signal to give a larger current output. A third type of amplifier is the transconductance amplifier. This type of amplifier requires an input voltage signal. This voltage signal is amplified and converted to an output current which is proportional to the input voltage. The last general type of amplifier is the transresistance amplifier. This amplifier requires an input current signal. This current is amplified and converted to an output voltage which is proportional to the input current.

By far the most common kind of electronic amplifier encountered in environmental quality monitoring is the voltage amplifer. This will be the only type of amplifier discussed in detail. The schematic symbol for a voltage amplifier is an isoceles triangle with the base drawn vertically. The input voltage, V_i, is connected between the base of the triangle and the common wire between the input and the output. The output voltage, V_o, is taken from between the apex of the triangle and the common. The voltage gain of the amplifier, A_v, is usually written inside the triangle. The voltage gain can either be a positive number or a negative number. If the voltage gain is positive then the output voltage has the same sign as the input voltage. However, if the voltage amplification is negative then the output voltage will have the opposite sign from the input voltage.

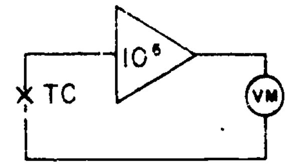


$V_o = A_v V_i$

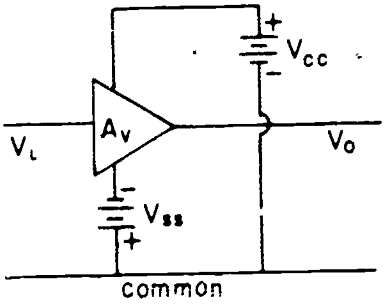
It would appear from this description of the voltage amplifier that it has properties very much like those of a transformer. However, recall that in a transformer when the output voltage is increased over the input voltage then the output current is decreased over the input current. In other words, the power passed through the transformer is unaffected by the transformer. This is not true in electronic amplifiers. In all practical cases where the amplifier is properly designed the power available from the output of the amplifer is substantially larger than the power available from the source connected to the input to the amplifier. That is to say that not only does the amplifier amplify the input voltage, but also gives rise to power amplification as well.

As an example of using a voltage amplifier consider measuring the temperature of an effluent emptying into a stream by using a thermocouple, TC. A thermocouple is made by spotwelding two different metals together. A small voltage, V_{tc}, is generated by the thermocouple proportional to the temperature of the thermocouple. This voltage is only a few microvolts

(10^{-6}) volts) over the range of temperatures encountered in effluents. Therefore, in order to read the TC voltage on a relatively inexpensive voltmeter, VM, with a few volts scale, it is necessary to amplify the TC voltage with an amplifier having a voltage gain of around one million. The voltmeter scale of course would not be printed in volts, but rather in temperature. Thus, by proper calibration of the thermocouple, voltage amplifier, and voltmeter, the reading on the meter would indicate the temperature of the effluent within the accuracy of the calibration. (Note: for this type of temperature measurement to be repeatable, the ends of the two TC wires connected to the amplifier and the common must be maintained at a fixed reference temperature.)



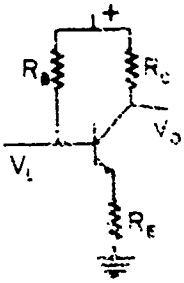
The diagrams and discussions on electronic amplifiers thus far have been misleading in one respect; that is that it would appear that amplifiers are sources of energy within themselves -- this is not true. Amplifiers are passive devices and are not power sources at all, but rather they are control valves controlling the flow of power from power supplies to the output of the amplifier. The power supplies are called bias supplies and by convention are now shown in the diagrams. If these bias supplies were drawn in the diagram they would consist of a battery of power supply Vcc positive with respect to the common and a battery or power supply, Vss, negative with respect to the common. If the amplifier output voltage is positive, this means that the input voltage is causing the amplifier to valve power from the positive power supply to the output. If the amplifier output voltage is negative. then the input voltage is amplifier to valve power from the negative power supply to the output. This type of valvelike control is true of all types of amplifiers. So long as the power supplies are adequate, they have no direct bearing on the performance of the amplifier and therefore they are commonly left out of the schematic diagram and the discussion.

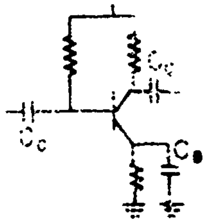


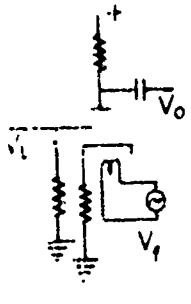
In many amplifier applications it is necessary to pass signals that change very slowly with time. That is to say, these signals appear to be essentially DC signals. Amplifiers that have this requirement do not use any capacitors in the circuit and are called DC amplifiers. While they will amplify DC signals they will also amplify AC signals sometimes to very high frequencies. However, because they do amplify DC signals they are called DC amplifiers. On the other hand, there are a large number of amplifiers that will not amplify very, very low frequencies or DC. These amplifiers do contain capacitors through which the signal must pass and are called AC amplifiers. These types of amplifiers have a property known as low frequency cut-off. This means that for AC signals below a certain frequency the amplifier performs very poorly and does not have the voltage gain, Av, for signals with frequencies below this cut-off frequency.

All amplifiers have a limit as to how high a frequency they will amplify. The frequency beyond which the voltage amplification begins to deteriorate is called the high frequency cut-off. Above this frequency, the voltage gain is poor. Amplifiers should not be used for frequencies below the lower cut-off frequency or above the upper cut-off frequency.

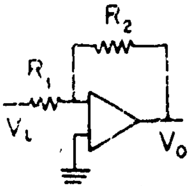
While the amplifier has been represented as a simple device whose schematic symbol is an isoceles triangle, there are actually very few amplifiers that can be bouthg that merely require the connecting of bias power supplies, the input, and the output. Much more commonly the amplifier consists of an amplifying device that requires several additional circuit components such as resistors and capacitors in order to function as an amplifier. For example, a transistor is considered an amplifier but in order to function properly it must have not only bias power supplies but biasing resistors and coupling capacitors in order to function properly. This combination of resistors, capacitors and the transistor is the amplifier. If the transistor amplifier is a DC amplifier there are no capacitors. If it is an AC amplifier then there will be both coupling capacitors, C_C, and by-pass capacitors, C_B, which serve to allow the amplifier to function properly and amplify AC signals but not DC signals. When a circuit is drawn containing a wire marked (+) or (-), this means that the wire is connected to a bias power supply of that polarity with respect to the common.





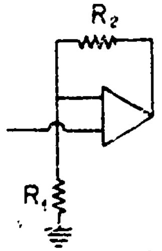


In older equipment built before the advent of the transistor, vacuum tubes were commonly used as the amplifying element in amplifiers. These devices required bias resistors and coupling capacitors similar to those required in transistor amplifiers. In addition to this, vacuum tubes required an electrically heated filament in order to operate properly. This required an additional bias supply known as the filament power supply, V_f. Vacuum tubes are rarely found in modern day environmental measurement and control equipment.



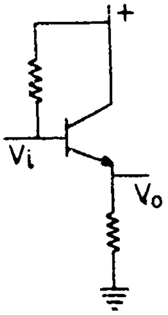
$$A_v = -\frac{R_2}{R_1}$$

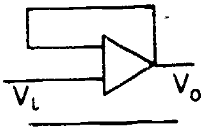
In the very newest of electronic environmental monitoring equipment an amplifying device known as an operational amplifier is used for the amplifying element. Operational amplifiers can be used very much like the ideal amplifier represented by the isoceles triangle by merely connecting the bias power supplies, the input, and the output, the system is an amplifier. However, used in this fashion the voltage gain, A_V, is very large and in fact, so large that it tends to be of limited use. By the addition of external resistors, this voltage gain can be reduced to whatever value is desired. By the proper connection of these gain control resistors, it is possible to build an amplifier with a positive amplification factor or with a negative amplification factor.



$$A_v = \frac{R_1 + R_2}{R_1}$$

One very important kind of circuit that can be built using any of the devices described above is a device with a voltage gain of positive one. These amplifiers are known as source follower amplifiers since the voltage gain is one, then obviously the amplifier is not a voltage amplifier. However, it is a very substantial power amplifier and it is used in applications where the signal source has inadequate power to operate the desired load. Thus, the amplifier actually supplies power to the load while the source merely controls the amplifier.





DIGITAL ELECTRONICS

In a great many environmental monitoring units, the parameter being monitored is either displayed on a panel meter or recorded on a pen recorder or in some cases, both. However, as electronic technology advances and the requirement for automatic computer processing of data increases, the information is displayed in forms of digits, much like a digital clock or a digital thermometer and quite frequenlty it is also recorded in digital form. The digital display generally is in the form of the conventional arabic numerals, 0 through 9. However, it is inconvenient to record in this form, therefore a different numbering system is used for digital recording. This numbering system is called the binary numbering system and consists of two digits, a 0 and a 1. This obviously is convenient for recording in that it represents, for example, in recording data in punched paper tape, no punch at a particular location on the tape represents a zero and a hole punched at that location would represent a one. Unfortunately, the reading of this kind of numerical data is more difficult for humans who are familiar with the conventional decimal counting system.

Recall that in the decimal numbering system, the first figure to the left of the decimal point is called the units figure. The second figure is called the tens figure. The third figure is called the hundreds figure and so on. In terms of powers of ten, this means the first position to the left of the decimal is multiplied by 10^0, the next position is multiplied by 10^1, the next position multiplied 10^2, etc. The reason for this power of 10 method of representing the number is because there are ten symbols used in the decimal numbering system, 0 through 9. A numerical quantity can be represented in a very similar fashion by using the binary system which has only two symbols, 0 and 1. The first symbol to the left of the decimal in the binary is muliplied by 2^0 because there are two symbols. The second position to the left of the decimal is multiplied by 2^1. The third position is multiplied by 2^2. The fourth position is multiplied by 2^3, etc. Thus, if we were to count from 0 to 9 using binary symbols, a 0 would be represented by four zeros to the left of the decimal point. A one would be represented by a 1 in the first position to the left of the decimal followed by 3 zeros. A 2 would be represented by a zero next to the decimal point, then a 1 then two zeros, etc.

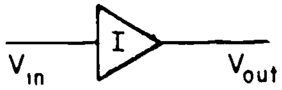
5×10^0
6×10^1
7×10^2
765

1×2^0
1×2^1
1×2^2
111
(Decimal 7)

0000	0
0001	1
0010	2
0011	3
0100	4
0101	5
0110	6
0111	7
1000	8
1001	9

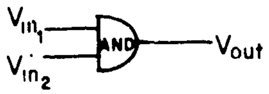
There are several different kinds of recording devices for the recording of these types of digital numbers, such as punched paper tape, punched paper cards and magnetic tape recorders. Since the information from the measuring equipment generally is in the form of a voltage proportional to the value of the parameter, this voltage must somehow be converted to this binary number in order to be recorded or to the decimal in order to be displayed in decimal form. This process of converting this voltage, which is known as an analog voltage, to the digital form is called analog-to-digital conversion of ADC, for short. For the sake of completeness it is worth nothing that it is possible to convert the digital signal back to an analog voltage

by the process known as digital-to-analog conversion, or DAC, for short. The process of analog-to-digital conversion is rather sophisticated and beyond the scope of this text. It will suffice to say that for the purposes here the way to make the analog-to-digital conversion is to buy a device known as an ADC. This device is biased according to the specification requirements and the input is connected to the input terminal and voltages representing the digital number are produced at the output terminals.

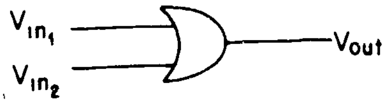


Truth Table

V_{in}	V_{out}
0 Low	1 High
1 High	0 Low



V_{in_1}	V_{in_2}	V_{out}
0	0	0
1	0	0
0	1	0
1	1	1

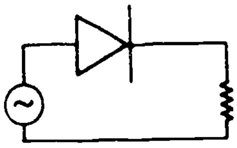


V_{in_1}	V_{in_2}	V_{out}
0	0	0
1	0	1
0	1	1
1	1	1

Occasionally, these various types of digital signals must be processed or manipulated in some manner. Electrically speaking a binary 1 is represented by a high voltage while a binary 0 is represented by 0 volts. The simplest kind of electronic processor for manipulating these digital voltages is the inverter circuit. The symbol for the inverter is a simple amplifier. The inverter performs a function that if a zero signal is applied to the input, a one signal will occur at the output and vise-versa. A truth table can be written for this kind of device comparing input to output for both input possibilities, a 0 and a 1. Another common type of digital circuit is known as the AND gate. This device has two inputs or more and is characterized by the occurrence of a 1 at the output if all of the inputs are 1, and a 0 at the output for all other input possibilities. The symbol for the AND gate is a half moon. The OR gate is another digital device similar to the AND gate except that a 1 occurs at the output of the OR gate whenever any of the inputs are 1 and a 0 occurs at the output if all the inputs are 0. The last fundamental device for digital signal processing is known as the flip-flop. This device is characterized by holding either a 1 or a 0 at the output whenever the input is pulsed accordingly. This, if a 1 is pulsed into the input, the output will indefinitely remain 1 until such time as a 0 is pulsed into the input, then the output will remain at 0. The flip-flop is used as an information storage device.

There are many, many other types of digital circuit elements; however, they can all be generated by combinations of the four elements just described. For example, if an AND gate is followed by an inverter, this combination device is known as a NAND gate. Likewise, an OR gage followed by an inverter is known as a NOR gate.

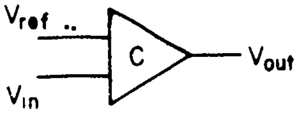
MISCELLANEOUS ELECTRONIC CIRCUITS



There are a variety of other specialized electronic circuits that should be described for the sake of completeness. One such circuit is the rectifier circuit. The basic element used in a rectifier circuit is a diode. This device will conduct current in the direction of the arrow but not in the other direction. It is used to convert alternating current to direct current.

A general class of electronic circuits that is of considerable importance in instrumentation is the oscillator circuit. Oscillator circuits are characterized by having no input but merely bias supplies and an output. The oscillator converts power from the bias power supplies to an output signal. The output signal can be a sine wave or a square wave or other types of waves such as triangular waves, sawtooth waves, etc. These circuits are constructed using various kinds of amplifiers, resistors, and capacitors. Another related circuit is the pulse generator circuit. This circuit generates an electrical pulse of some pre-determined duration at the occurrence of the proper input signal. These circuits are sometimes called mono-stable multivibrator circuits or single-shot multivibrator circuits. They are used where it is important to actuate some other electronic component or circuit on a momentary basis.

Another important circuit used to generate warning signals when dangerous thresholds are exceeded is the voltage comparator circuit. It contains two inputs, the signal input and a reference voltage input. Whenever the input signal exceeds the reference voltage, the output is a high voltage, and whenever the input signal is less than the reference voltage, the output is zero volts.

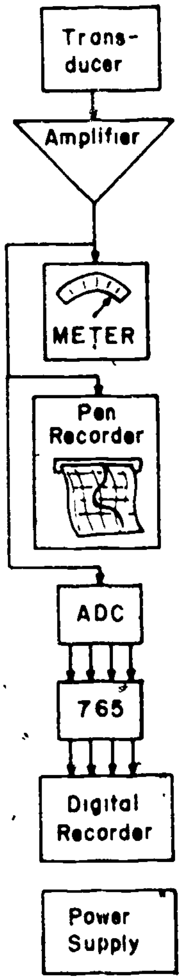


The list of specialized electronic circuits is unlimited; however, one factor to be recognized in these types of circuits is that they are generally sophisticated combinations of all of the various components and circuits previously described. The number of such types of circuits is limited only by the imagination of the electronics circuits designers.

ELECTRONIC ENVIRONMENTAL MONITORING SYSTEMS

There are a great many different kinds of environmental monitoring systems for monitoring all kinds of environmental parameters such as temperature, wind speed, particulate matter in air, pH of water, and on and on in an unlimited list.

However, any or all of these systems can be described in a general way by a block diagram indicating the principal elements required for any instrumentation system. The first element in the block diagram is a device known as the transducer. This transducer is the device which converts the parameter value being measured into an electrical signal. For example, a thermocouple converts the temperature into a voltage, or the pH electrodes used in pH measurement converts the pH of the water into an electrical signal, etc.



Generally speaking, the transducer output is inadequate to operate a recording instrument directly, therefore the electrical output of the transducer must be electronically processed in order to make it useful. This normally is done by an electronic amplifier, any one of the types that have been described previously. In the simplest of monitoring systems, the next element of the system would be a simple panel meter calibrated to read the parameter value being monitored. This output device can be extended to include a pen recorder for continuous monitoring of the parameter value.

If the monitoring system is to include some type of digital display or digital recording for the output, then it is necessary to connect the amplifier output to an analog-to-digital converter. The digital output of the ADC can then be used to operate the digital display or the digital type recorder for continuous digital monitoring.

The last block that is required of all environmental monitoring systems is the power supply. Power supplies for monitoring systems vary widely depending upon the monitoring system requirements. If the monitoring site is to be located near a source of commercial power, then the power supply can be a simple commercial power supply which converts the 110 volts AC line power to the voltage and currents required to operate the environmental monitor and its recording equipment. This type of power supply is by far the most inexpensive and reliable of any of the various types of power supplies available.

In the event the monitoring site is remotely located, so that there is no AC line power available, then the most common kind of power supply for this application is batteries, generally speaking some kind of rechargable storage battery, such as lead-acid battery similar to your car battery or a nickel-cadmium battery which is more reliable than the lead-acid type. When monitoring systems are operated on batteries of this type, the batteries must then be maintained and re-charged on some periodic basis. In the event that this type of remote monitoring is required to operate for long periods of time unattended, it is then necessary to use auxiliary battery charging equipment. The two types that are in common use are the solar panel which will recharge the batteries during the daytime from sunlight and the thermoelectric generator, which is a device that converts the heat generated by burning propane into an electrical current to recharge the batteries.

Quite often equipment is made highly portable so that it can be carried from one location to another for grab-sample type of recording. This type of portable equipment falls into two categories. One is the light-weight, hand carried kind of equipment, while the other is what is classified more precisely as mobile monitoring equipment which is mounted permanently in some type of vehicle. For the lightweight hand carried type of equipment, the power supply is generally the nonrechargeable battery pack, much like your transistor radio battery, while the mobile monitoring equipment is usually operated by the battery of the vehicle.

TRANSDUCERS

Before concluding this chapter on electricity, electronics and instrumentation, some description of the various types of transducers used in environmental monitoring should be included. These transducers fall generally into three classes; those used to measure micrometeorological parameters; those used to measure air pollution parameters; and those used to measure water pollution parameters. These various types of transducers will be discussed in sequence.

The first type of transducers to be discussed will be those used for monitoring micrometeorological information. The important parameters in this area are temperature, wind speed, wind direction, humidity and solar radiation.

There are three common transducers used for measuring temperature. They are the thermocouple, the semi-conductor thermistor and the platinum resistance thermometer. The thermocouple is constructed by welding two dissimilar metals together. A voltage is generated within this thermocouple junction which increases more or less linearly with increasing temperature; however, for precise temperature measurements using a thermocouple, a very precise reference temperature transducer is a small resistance device made from semi-conductor materials such as silicon or germanium. The resistance of this type of transducer decreases with increasing temperature. Thus, by running a constant current through the thermistor a voltage is generated which decreases with increasing temperature. In using thermistors care must be taken to account for the heat generated within the thermistor due to the current flowing in the thermistor. The platinum resistance thermometer is the more or less standard for accurate temperature measurements in meteorological temperature measurements. The platinum resistance transducer is similar to the thermistor in that the resistance of the platinum element varies with temperature. However, for the platinum resistance element, the resistance increases with increasing temperature. Thus, by running a constant current through the platinum resistor the voltage generated across the resistor increases with increasing temperature.

There are two types of wind speed transducers in general use. One operates by attaching a small electrical generator to the shaft of the rotating anemometer. A voltage is generated by this generator proportional to the rate at which the anemometer rotates which is proportional to the wind speed. This type is the most convenient to use electronically. The other type is a device which has a contact mounted on the shaft of the rotating anemometer. This contact opens and closes as the shaft rotates and the number of closures that occur per second is a measure of the wind speed. This type is quite convenient for use in digital wind measuring systems.

As in wind speed measurements there are also two general types of wind direction transducers used to measure wind direction. One connects a variable resistor to the shaft of a wind vane. The resistance increases with increasing angle from North. A constant current is run through this resistance generating a voltage which increases with increasing wind direction from zero to 360°. The second type of wind direction transducer is one in which there are multiple contacts connected to the wind vane shaft and the direction is determined by which contact is closed. Normally 16 contacts are used. This technique suffers from a lack of resolution as to the precise wind direction.

Accurate humidity measurements are very difficult to obtain because of the fact that there are very few accurate humidity transducers. The two that are in somewhat common use are the carbon-film transducer which is simply a resistor which absorbs moisture from the air and the resistance changes with this absorbed moisture so that the conductance of the carbon film element increases with increasing humidity. And again, a current is run through this resistance generating a voltage which is proportional to humidity. The other type of humidity transducer is one in which a mirror is cooled thermo-electrically until the dew point is reached and the mirror collects moisture affecting its reflectivity at the dew point. The dew point temperature, which is a measure of humidity, is then measured by one of the aforementioned temperature measuring methods. One other technique that has been used to some degree is the wet bulb-dry bulb temperature measurement where the temperature of a wet bulb thermometer is measured and compared with the temperature of the dry bulb, the difference being a measure of humidity.

The most common type of solar radiometer is the so-called sun battery. This is a semi-conductor device which converts sunlight directly to an electrical voltage. Optical filters are placed over the solar panels in order to distinguish the light intensity at various wavelengths throughout the visible, infra-red and ultra-violet spectrum. One other technique occasionally uses a device called a thermopile. This device absorbs heat rays from the sunlight and is heated up to a temperature related to the amount of sunlight incident on the thermopile. The temperature of the thermopile is then measured as a measure of solar radiation.

Air quality monitoring transducers fall into two principal categories: Those which measure gaseous constituents in the air and those which measure particulate matter. A third parameter which is occasionally considered as an air pollutant is noise. However, strictly speaking, the air is only the carrier of this type of pollutant.

There are a number of techniques available for monitoring various kinds of polluting gases. Only the principal ones will be described here. A very common method is called colorimetry. In colorimetry, the gas sample is passed through an aqueous solution the color of which will be determined by the concentration of the gas being measured. Electrical signals are generated using appropriate light sources and photocells. The photocells generate a voltage proportional to the concentration of the gas being monitored. Gas chromatography is another very common technique in which the vapor is burned and the optical spectrum of the resulting flame is measured by photocells. A device known as a flame ionization detector is a common device used for gas chromatography.

In measuring particulate matter in the air, a very common technique is a simple light source and photocell, the combination of which is known as an opacity light meter. The total particulate volume can be measured in this manner using a large cross section light source and photocell. The size distribution of the particles can be determined by using a much smaller light source and photocell and noting the amount of absorption associated with each particle as it passed through the light beam. Another method is one in which the air sample is passed through a thin mechanical filter, usually a piece of paper tape containing chemicals. The particles are collected by the paper tape causing the paper tape to darken and the amount of darkening is measured by a light bulb and photocell.

Noise is of course, the very simplest kind of air pollution to measure in that the transducer is nothing more than a conventional microphone.

The most important parameters to measure in determining water quality are dissolved solids, dissolved salts, particles held in suspension, pH, temperature and dissolved gases.

The most common technique used for measuring dissolved solids is the colorimetric method described above. The measurement of dissolved salts is done by running a current through the water sample and measuring the voltage across the electrodes inserted into the water sample. The voltage will be proportional to the amount of dissolved salts.

Water containing particles in suspension is known as turbid water. The turbidity is measured using the opacity light meter as previously described. pH is measured by inserting pH electrodes in the water. A voltage is generated by the electrodes proportional to the pH. A similar technique is used in measuring most dissolved gases. Specific electrodes are sensitive to specific types of dissolved gases. Temperature measurements are made in much the same manner as temperature measurements described previously.

PROBLEMS

1. What is the force exerted on an electron that is located one micro-meter from a proton? In what direction is the force?

2. An incandescent lamp (light bulb) is used as a light source for an optical system. The light bulb has a resistance of 25 ohms. What is the conductance of this light bulb? What current will flow when the bulb is connected across a 12.6 volt automotive battery? What power is supplied by this battery?

3. What is the inductive reactance of an inductor of 10 henries when operating at 60 Hz? How much current will flow across the AC voltage in your home? What size capacitor will have the same capacitive reactance as this value of inductive reactance?

4. What is the total resistance of the parallel combination of a 10 ohm resistor, a 20 ohm resistor and a 30 ohm resistor?

PART II

THE WATER ENVIRONMENT

PROPERTIES OF THE WATER ENVIRONMENT

The Water Environment is a dynamic system. The water, in its various forms, is constantly moving and changing as it interacts physically and chemically with the Earth. These interactions and changes form a cycle involving the quality and quantity of water called the Hydrologic Cycle. Before examining the cycle, some of the physical and chemical properties of water are presented.

1. Physical Properties

a. Structure. Water molecules are composed of two hydrogen atoms and one oxygen atom bonded covalently. The water molecule has a dipole moment of 1.85 debyes and a triangular structure with a bond angle of about 105°. The dipole moment is caused by the difference in electronegativity between oxygen atoms and hydrogen atoms. In this case, oxygen is more electronegative and electrons tend to be associated more closely with the oxygen atom than with the hydrogen atoms. In effect, the oxygen can be visualized as partially negative and the hydrogen atoms as partially positive. This partial ionization effect gives water molecules, under quiescent conditions, the ability to form a quasi-structure. In this structure, the adjacent water molecules adjust their positions so that the partially negative oxygen atom of one water molecule is "close" to the partially positive hydrogen atom of another water molecule, and so forth. The water molecules therefore can be found singly or in groups and ionized as hydrogen or hydroxide ions.

Phases

Water exists in three states: vapor, liquid, and solid (ice). A phase diagram is useful for demonstrating the equilibrium conditions (Figure 6-1).

Three areas are shown in Figure 6-1: solid, liquid, and vapor. Within these single phase areas, the system is defined by both a temperature and pressure (bivariant). Separating these single phase areas are lines where two phases can exist in equilibrium. For example, the curve AB indicates an equilibrium between liquid water and water vapor. This curve is univariant in that only one variable of pressure or temperature is independent. Select one and the other is fixed by the curve. Only one pressure goes with any temperature.

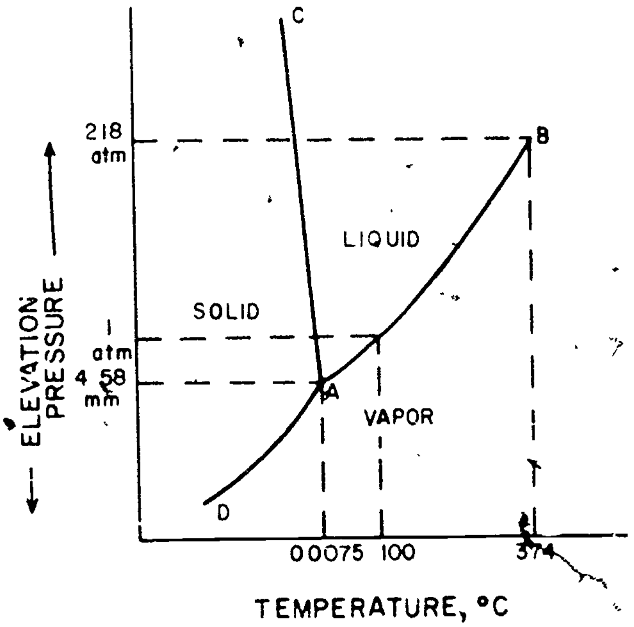


Figure 6-1
The Water System

Boiling

The curve AB illustrates the pressure and temperature where water will boil. If, for example, the applied pressure due to the atmosphere equals the pressure of the water vapor, the water will boil. Therefore, water will boil at lower temperatures in areas of lower pressure (mountains).

Sublimation

The curves of AC and AD give the univariant phase systems for solid-liquid and solid-vapor. The curve AC (solid-liquid) shows that increased pressure will reduce the temperature where ice and water are in equilibrium. The line AD is the sublimation curve for ice. Ice can change directly from a solid to a gas (sublimation).

Point A is a unique invariant point. It is the point where vapor, liquid, and ice (all three) can exist in equilibrium. This point is at a temperature of $273.16^{\circ}K$ ($.0075^{\circ}C$) and 4.579 mm (millimeters mercury) pressure. It is called the triple point. This is not the point where ice melts. That point is generally above A and along the line AC: for example, one (1) atmosphere of pressure and a temperature of 273.15°K (0°C). The slope of line AC indicates that water expands on freezing. Very few common substances have this property. Most materials are more dense as solids than as liquids.

Point B is a unique point where line AB ends. Beyond this point (at pressures and temperatures beyond B), there is no way of distinguishing two phases. Only one phase exists. This point is called the critical point. No similar point is known to exist on line AC.

Impurities

Figure 6-2 shows the effect of adding non-volatile substances (salts) to water. In effect, the freezing point temperature is decreased and the boiling point temperature is increased for a given pressure. The solid phase (ice) and the water vapor are <u>pure</u> water. Icebergs have pure ice crystals with salt crystals adsorbed on their surface. Non-volatile materials (salts) remain in solution on boiling, unless the physical turbulence of the boiling splatters droplets of water and dissolved salt from the container. The turbulence of ocean waves, especially near beaches, also produces the same effect.

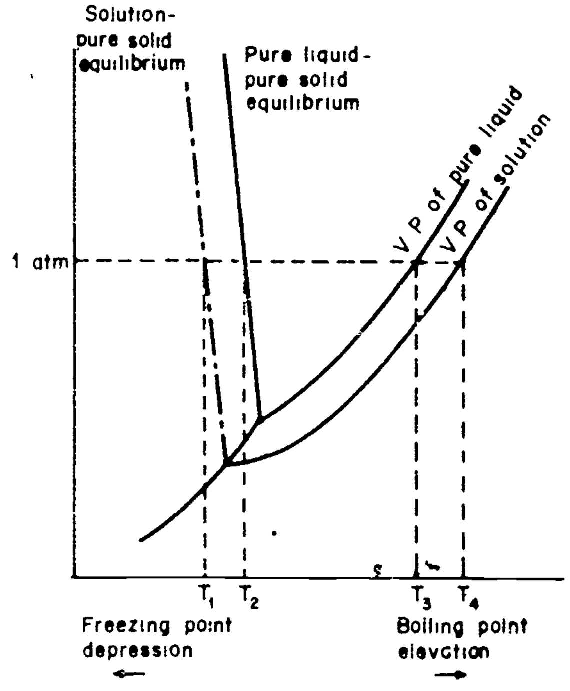


Figure 6-2
Water System (Salt Addition)

Density

b. Density and Viscosity. Water density varies with temperature and phase. Ice has a density of 0.93, or it is only 93% as heavy as water at 4°C (39.2°F). Ice is lighter than water. Freezing of water increases the volume and reduces the density. The density of the liquid phase also has a unique feature. Water has its greatest density at 4°C (39.2°F) and not at zero degrees. Density variations due to temperature in deep bodies of water, result in stratification and possible seasonal overturning of lakes and reservoirs with subsequent wide variations in quality. Table 6-1 gives density and temperature relationships. Note that the density of water is less than one (1) below and above 4°C.

TABLE 6-1
Density and Viscosity of Water
(From International Critical Tables)

Temperature (°C)	Temperature (°F)	Density (grams/cm^3)	Absolute Viscosity (centipoises)
0	32.0	0.99987	1.7921
2	35.6	0.99997	1.6740
4	39.2	1.00000	1.5676
6	42.8	0.99997	1.4726
8	46.4	0.99988	1.3872
10	50.0	0.99973	1.3097
12	53.6	0.99952	1.2390
14	57.2	0.99927	1.1748
16	60.8	0.99897	1.1156
18	64.4	0.99862	1.0603
20	68.0	0.99823	1.0087
22	71.6	0.99789	0.9608
24	75.2	0.99733	0.9161
26	78.8	0.99681	0.8746
28	82.4	0.99626	0.8363
30	86.0	0.99568	0.8004

Viscosity

Viscosity is important in flow considerations. Conceptually, viscosity is related to the internal resistance of a fluid to motion, or it is proportional to internal friction. All real fluids possess viscosity and exhibit friction under motion. Viscosity is due to cohesion between water molecules. This internal cohesion breaks down at higher velocities and higher temperatures; so, viscosity is only significant at low velocities, for example in ground water flows. Values for viscosity are given in Table 6-1. As noted, viscosity decreases with temperature, and therefore flow is easier at higher temperatures (less friction).

Vapor Pressure

c. Vapor Pressure and Surface Tension. Vapor pressure is one of the controlling factors in evaporation. It occurs at all water-air interfaces. As dry air is introduced to a water surface, water evaporates to form vapor. At some point (saturation and equilibrium), the vapor molecules condense back to water at the same rate as the water evaporates (equilibrium). The pressure exerted by these water vapor molecules at equilibrium is the vapor pressure. Table 6-2 gives values of vapor pressure. When applied (atmospheric) pressure equals the vapor pressure, the liquid boils.

TABLE 6-2
Vapor Pressure and Surface Tension

Temperature, F°	32	41	50	59	68	77	86
C°	0	5	10	15	20	25	30
Vapor Pressure mm Hg	4.58	6.54	9.21	12.8	17.5	23.8	31.8
Surface Tension dyne/cm.	75.6	74.9	74.2	73.5	72.8	72.0	71.2

Surface Tension

Surface tension is an apparent tension on the surfaces of liquids. This occurs when the liquid surface is in contact with a gas or a solid. This tension force depends primarily on the cohesion between water molecules. There are several significant conditions where surface tension is important. The capillary rise of water through fine soils and plants depends on surface tension effects. The formation of liquid drops and bubbles depends on surface tension. Many long-chained organic molecules adsorb on the liquid surface, and reduce the cohesion and subsequently the surface tension. This effect is used to improve the wetting and cleaning efficiency to detergents. Values for surface tension are given in Table 6-2. Surface tension decreases with increasing temperature.

Gas Solubility

d. Gas Adsorption and Desorption. The solubility of a gas depends on:

1. its partial pressure,
2. the water temperature, and
3. the concentration of impurities in the water.

Gas Law

The basic equation for solubility is known as Henry's Law, or

$$Cs = K P, \tag{6.1}$$

where Cs equals the saturation concentration of the gas in the water, P equals the partial pressure of the gas in the gas phase and K equals the coefficient of absorption. The coefficient of absorption is a function of temperature, and decreases with increasing temperature. At the boiling point, no gas is dissolved in solution.

Although Henry's Law describes the situation at equilibrium, this does not mean it always applies. In natural water systems, equilibrium conditions are always approached but not necessarily attained. The rate at which equilibrium conditions are approached depends on:

1. the amount of under-or over-saturation,
2. the temperature, and most importantly,
3. the amount of interface between the gas and the liquid.

Kinetics

The kinetics (rates) depend on how far you are away from equilibrium, the temperature, and how much turbulence or increased surface area you have. Rapidly moving streams, bubbling over rocks, absorb oxygen very quickly. Deep stagnant lakes do not absorb oxygen quickly. The more the surface area (liquid to gas), the faster the rate of change.

Reactive Gases

Many gases absorb significantly in water because they chemically react with water. The total solubility may be several thousand times the solubility of non-reactive or slightly reactive gases. Sulfur dioxide (SO_2), chlorine (Cl_2) and hydrogen sulfide (H_2S) are examples of gases which chemically react with water, and therefore absorb significantly. Carbon dioxide (CO_2), a normal component of air, and ammonia (NH_3) are examples of slightly reactive gases. Examples of non-reactive (with water) gases are methane (CH_4), nigrogen (N_2), oxygen (O_2), and hydrogen (H_2).

Desorption of gases from water (kinetics) follows the same rules as absorption. The rate depends on the amount of over-saturation, the temperature, and the amount of turbulence (surface area).

e. Light Absorption. Absorption of light into water is important for three reasons:

1. plants derive their energy from sunlight,
2. ultraviolet wave lengths kill bacteria and bleach organic color, and
3. heat is absorbed by the water.

Penetration

The amount of light that penetrates the water depends on the angle of the sun (angle of incidence). As the angle becomes more acute (morning and evening), less light is absorbed and more is reflected. The period of daylight is less in water than on land. Waves change the angle of incidence and generally increase reflection.

Selectivity

A second consideration of light absorption is selectivity. Water absorbs certain wave lengths more than others. Red wave lengths absorb significantly in water. This is why water appears blue-green in color. Dissolved and suspended material increase the absorption of light and reduce its penetration. Changes in water quality with depth can significantly change light absorption and penetration.

Heat Capacity

f. Heat Capacity. Most of the energy absorbed from the sun by the water is converted into heat. However, since certain wave lengths are absorbed selectively, the heat is not uniformly added to the water with depth. The upper layers adsorb more heat than lower layers. Water is a poor conductor of heat. If vertical motion is absent, temperatures and densities will vary with depth and stratification will occur.

Specific Heat

The specific heat of water is about four times that of air. For example, one BTU of heat will change the temperature of one pound of water 1°F. Only 0.24 BTU's of heat will change the temperature of one pound of air 1°F. If a water surface is calm, the air above the water will be at the same temperature as the water. Winds will remove the heat of the water and will distribute the water temperature uniformly. The water acts as a moderator or buffer to variations in air temperatures. The changes in weather along coast lines are moderated by the ocean.

Mixing

When the air is warmer than the water, the water warms up. Since it is less dense, no vertical motion occurs without wind. When the air is colder than the water, the water loses heat, becomes more dense, and settles. Vertical motions are induced and mixing occurs. If water evaporates, it also cools and becomes more dense and settles. Again convective currents are induced and mixing occurs.

2. Chemical Properties

a. Ionization of Water. Water is weakly ionized as shown by

$$H_2O = H^+ + OH^- . \tag{6.2}$$

More correctly, the hydrogen ion should be shown as attached to a water molecule as the hydronium ion as shown by

$$2H_2O = H_3O^+ + OH^- . \tag{6.3}$$

The equilibrium constant for this reaction can be represented by

$$[H_3O^+]\ [OH^-] = K[H_2O]^2 = Kw . \tag{6.4}$$

Note the inclusion of H_2O in the constant Kw. The equilibrium constant for this reaction is 10^{-14} at 25°C. If both the hydronium (H_3O^+) ion concentration and the hydroxide (OH^-) ion concentration are equal, then their concentrations would be 10^{-7} moles/liter.

Kinetics

The equilibrium represented by equation 6.4 is rapidly achieved (kinetics) in all aqueous conditions, and is always assumed to hold. In solutions where the hydronium ion concentration is greater than the hydroxide ion concentrations,

$$[H_3O^+] > [OH^-] , \tag{6.5}$$

the solution is acidic. In solutions where the hydronium ion concentration is less than the hydroxide ion concentration,

$$[H_3O^+] < [OH^-] , \tag{6.6}$$

then the solution is basic. If the hydronium ion concentration is equal to the hydroxide ion concentration,

$$[H_3O^+] = [OH^-] , \tag{6.7}$$

then the solution is neutral.

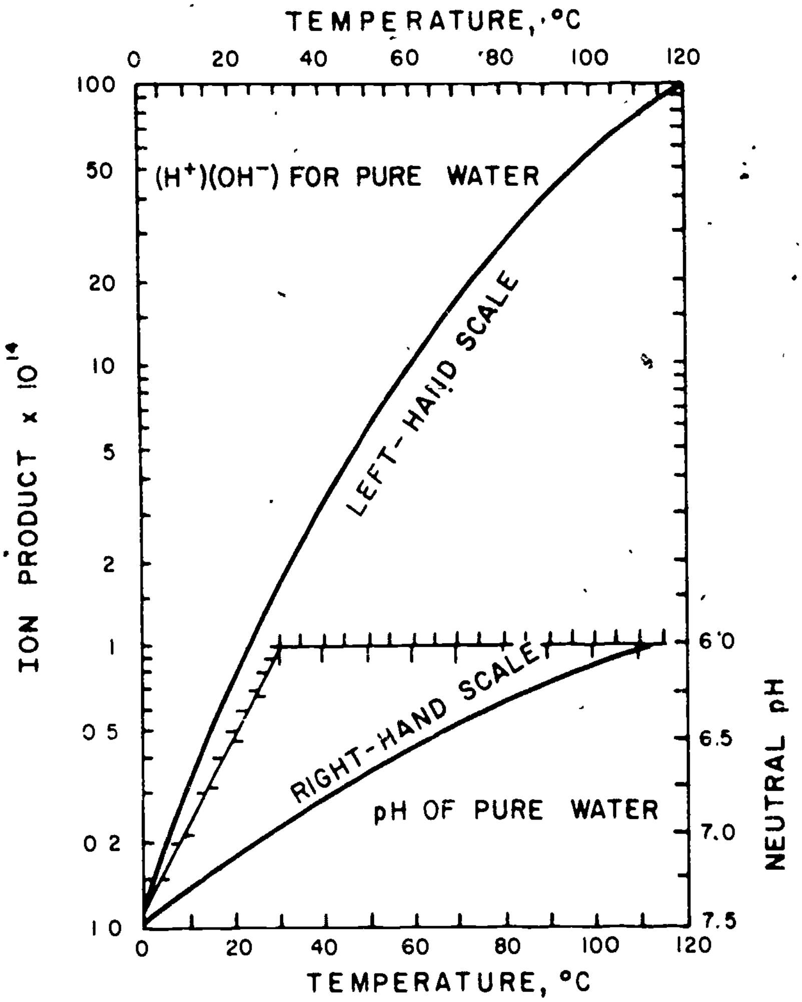


Fig. 6-3 ION PRODUCT AND pH VALUE OF PURE WATER AT DIFFERENT TEMPERATURES

Gases and Water

b. <u>Gas Reactions in Water</u>. As mentioned in the physical properties of water, some gases absorb significantly in water because they react with the water, for example (H^+ is shown for simplicity),

SO_2 (sulfur dioxide gas) + $H_2O = H_2SO_3 = 2H^+ + SO_3^{-2}$, 6.10

sulfurous acid sulfite

SO_3 (sulfur trioxide gas) + $H_2O = H_2SO_4 = 2H^+ + SO_4^{-2}$, 6.11

sulfuric acid sulfate

and

NH_3 (ammonia gas) + $H_2) = NH_4OH = NH_4^+ + OH^-$. 6.12

ammonium hydroxide ammonium

In most aqueous solutions, the ionized forms are found. Equations 6.10 and 6.11 are acid reactions since H^+ is produced. Equations 6.10, 6.11, and 6.12 proceed very far to the right. Since Henry's Law (Equation 6.1) must also apply, it is easily seen why these gases absorb significantly. As as absorbs, it reacts with water and is ionized. Henry s constant is not satisfied and therefore more gas is absorbed, and the process continues.

Some gases react with water, but only sparingly; for example,

CO_2 (gas) + $H_2O = H_2CO_3 = H^+ + HCO_3^-$. 6.13

carbonic acid bicarbonate

This reaction proceeds only to the extent of about 1% to form the carbonic acid. Since all atmospheres contain naturally about 0.035% (350 ppm) CO_2 by volume, all water should show some carbonic acid. Rainwater adsorbs CO_2 and is therefore not neutral but slightly acidic. Note again that two equilibriums are indicated for reaction 6.13. The first is governed by Henry's Law (Equation 6.1). The second involves the ionization of carbonic acid. If the carbonic acid reacts with a base (neutralization), then the reaction would continue as before and more and more CO_2 (total) would be absorbed.

Solids and Water

c. Solid Reactions in Water. Water is frequently in contact with solids. These minerals or mixtures of minerals also react in water (ionize), for example

$CaSO_4$ (solid gypsum) = $Ca^{+2} + SO_4^{-2}$, 6.14

"ions in solution"

with $Ks = 10^{-6.4}$ (25°C) = $[Ca^{+2}]\ [SO_4^{-2}]$, 6.15

$CaCO_3$ (solid limestone) = $Ca^{+2} + CO_3^{-2}$, 6.16

with $Ks = 10^{-8.3} = [Ca^{+2}]\ [CO_3^{-2}]$, and 6.17

$Fe\ (OH)_3$ (solid iron ore) = $Fe^{+3} + 3OH^-$ 6.18

with $Ks = 10^{-38} = [Fe^{+3}]\ [OH^-]^3$. 6.19

Kinetics

The possible extent of these reactions is identified by the equilibrium constants (solubility constants Ks). Most reactions involving gas absorption and ionization proceed rapidly. Reactions involving solids, however, may be very slow in reaching equilibrium. For example, dissolution of gypsum is quite fast because of the loose, soft surfaces found in nature. Limestone dissolution is slower, depending on the kind of surface; for example, marble is very hard and reacts very slowly.

Several of the mineral types can be considered solid bases, for example, limestone. These solid bases can react with acids and thereby increase the rate of dissolution as well as the amount of dissolution. One common example is shown in the following set of reactions:

CO_2 (gas) + $H_2O = H_2CO_3$, 6.13

$H_2CO_3 = 2H^+ + CO_3^{-2}$, 6.13

$H^+ + CO_3^{-2} \rightarrow HCO_3^-$, and 6.20

$H^+ + CaCO_3$ (solid) = $Ca^{+2} + HCO_3^-$. 6.21

Summation of these equations gives:

CO_2 (gas) + $H_2O + CaCO_3$ (solid) = $Ca^{+2} + 2HCO_3^{-1}$. 6.22

This equation (acid from gas + base from solid) shows the reaction in water to form more neutral species. Hardness ions of calcium and magnesium may enter way in this way. The bicarbonate ion is one of the most common components of alkalinity in natural waters.

Phase Contact

These gas-solid reactions or acid→base reactions imply contact with the atmosphere, water, and mineral. This physical contact of the three-phase system may not always occur. For example, in deep lakes the bottom water is in contact with the minerals but the top is not. The reverse is true for the atmosphere. Although equilibrium equations and constants indicate what should occur, kinetics and physical contact of phases will dictate the true state. Most ground waters have higher mineral content (ionized) than surface waters.

In analyzing water systems, all phases (gases, liquids, and solids) must be considered.

Surfaces and Water

d. Surface Reactions in Water. Most natural surface waters contain solid materials of various kinds, shapes, and sizes. These materials affect the water in different ways. Heavy silt loads change the viscosity and density of the water and affect the natural hydraulics of flow. In slow moving river areas, material can deposit as silt banks and eventually affect the course of the river. In other cases, these loads can deposit in lakes and reservoirs and reduce the storage capacity, and cover up bottom aquatic life, thereby reducing or changing the biota.

Colloids

If the material is very small, it is classified as colloidal. The distinguishing feature of this kind of material is its surface area. Even though the weight of such material may be small, the surface area can be enormous. A cube, one centimeter on a side, has a surface area of approximately 0.006 square feet. If this cube is cut into smaller cubes of 1×10^{-6} centimeters on a side, the surface area is now increased to 6500 square feet. As can be seen, colloidal chemistry is surface chemistry.

Three properties are important in colloidal chemistry:

1. dissolution - ionization of minerals
2. adsorption - adsorption on the colloidal surface of substances in solution, and
3. electrokinetics - charges developed on the surfaces of colloidals.

Dissolution

1. Dissolution. The rate of solution of solids, like that of gases, is proportional to the degree of undersaturation of the solid in solution. It also varies directly with the surface area and inversely with the volume of solution. In effect, the larger the surface area per unit volume, the faster the dissolution toward equilibrium. Minerals in colloidal size should approach equilibrium much faster.

Adsorption

2. Adsorption. Ordinary physical adsorption usually is rapid. Adsorption is reversible and the equilibrium between the surface and the solution is quickly achieved. The adsorption is generally selective. Ions common with the mineral structure fit the crystal structure and will be selected. Some organic material is adsorbed on surfaces due to its hydrophobic nature. Detergents are a prime example. These substances decrease surface or interfacial tension and accumulate on surfaces. Activated carbon is used as a common reactive surface for organic removal. Some organic material is hydrophilic and remains in solution as a stabilized ion or colloidal. Starches and proteins are examples of hydrophilic organic structures.

Catalysts

Surface areas also serve as cataylsts. Many natural processes are rate controlled by the influence of surface areas. Colloidals serve as heterogenous catalysts. They influence reaction rates in solution (solid-liquid). The surface adsorbs the reacting species, reduces the activation energy, and structurally orients the reactants for reactions. Biological colloidal units such as bacteria, algae, etc., also respond as surface catalysts.

Electrokinetics

3. Electrokinetics. Colloidal particles are normally charged with respect to the medium. The charge and charge density depends on the material and the concentrations of various adsorbing ions in solution. This charge gives the colloidals the property of continuous suspension. Like-charges repel and therefore colloidals with similar charges will repel each other and remain suspended and not settle. Most naturally occurring colloidals are negatively charged. In water treatment units, negative colloidals are removed by applying positively charged ions and colloidals.

Water is known as the universal solvent for good reason. Practically everything dissolves in water to some extent. Gases, solids, liquids, organic, inorganic materials, all are changed by water. In analyzing and monitoring a river, lake, ocean, treatment unit, irrigation project, or any water system, all phases must be considered.

<u>All phases must be consciously evaluated.</u>

Neglect of the atmosphere (air or special environmental gases) or the solid phases (suspended or bottom) can cause serious errors in water management programs.

3. Hydrologic Cycle

The Hydrologic Cycle is a descriptive term applied to the general circulation of water from the oceans to the atmosphere, to the land and back to the oceans. A schematic diagram of the Hydrologic Cycle is shown in Figure 6-4. The cycle is <u>dynamic</u>. It is constantly changing in response to solar heat and atmospheric or wind movements.

The cycle can be simply described beginning with the water in the oceans. Water in the oceans is evaporated into the atmosphere. This water vapor is carried in the atmosphere and is precipitated back to earth as rain or snow. This precipitation results from a cooling of the air. When the air becomes supersaturated with water vapor, more water vapor than equilibrium values for given temperature, then precipitation results. This cooling is caused chiefly by moving the air vertically to cooler temperatures, either by passing the air over a mountain range or moving it up over a weather front. Recent weather modification research has developed methods of increasing precipitation yields by adding small nuclei to storm clouds. These nuclei form surfaces for more rapid condensation of water vapor. Natural nuclei, especially from forest areas, also provide surface areas for condensation.

A portion of the water falling on land is retained temporarily in the soil, in surface depressions, in vegetation, or in snow until it flows into streams or groundwater areas or is re-evaporated. The water not retained moves through surface or groundwater channels to rivers, lakes, and reservoirs and eventually back to the oceans. During this movement the water is subjected to evaporation.

Although the general description of the cycle is simple, the actual mechanics and variations of the cycle are quite complex. On a world-wide basis, the volumes of moisture involved in each phase of the cycle are somewhat constant.

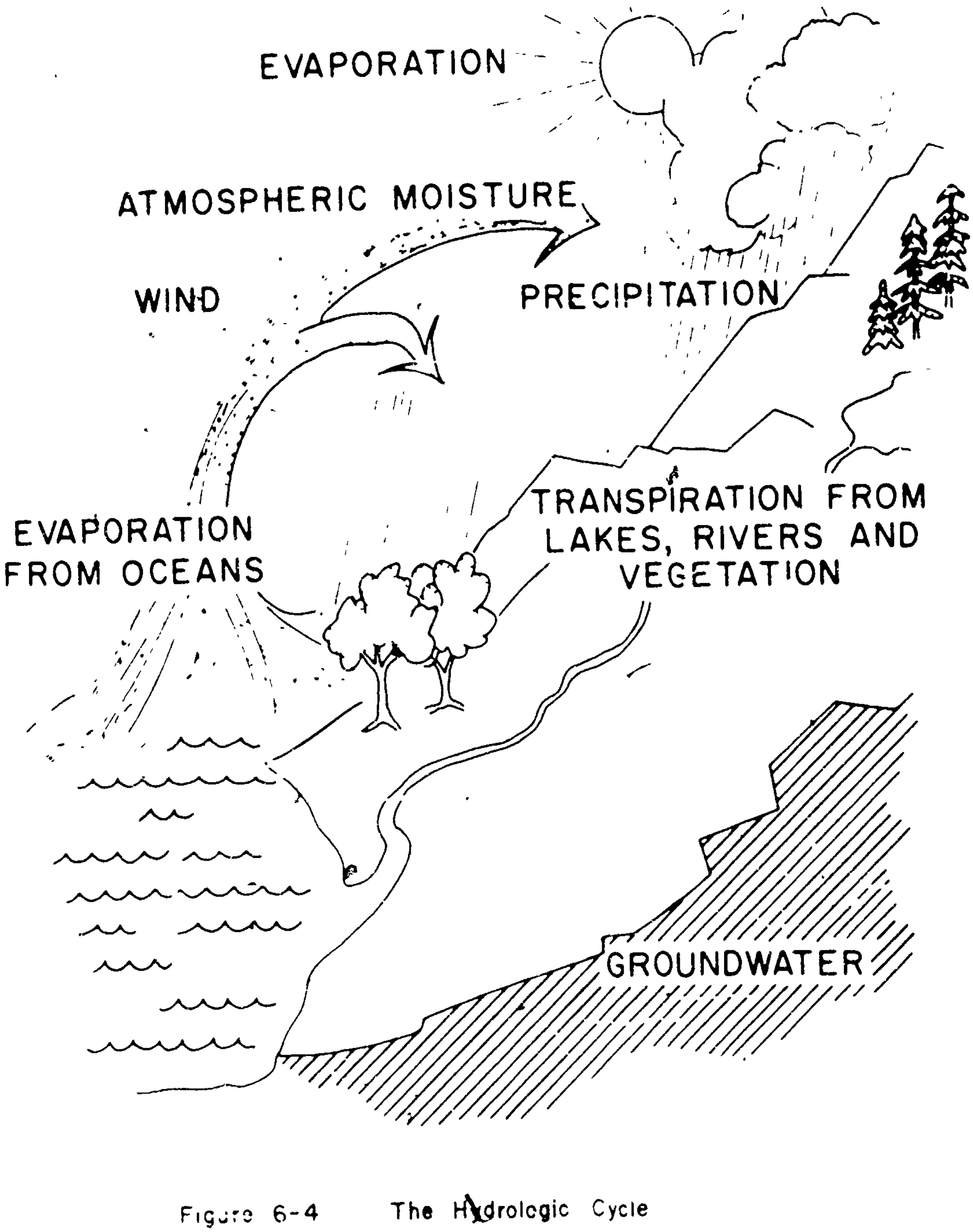


Figure 6-4 The Hydrologic Cycle

In limited areas, however, the variations can be extreme. Excessive precipitation can cause flooding and insufficient precipitation can cause drought.

The Hydrologic Cycle describes the changes and variations

of the amount of water (quantity),

and

of the things in the water (quality).

In a true environmental sense, both quantity and quality are important. In all pollution control programs, the concentration of a pollution parameter is the significant measurement. Concentration is the amount per unit volume; both quality and quantity are involved. If a very strong waste material is diluted by a much, much larger amount of good water, the concentration is reduced and possibly no pollution is present. Most pollution problems have evolved from a lack of or reduction in dilution water.

a. Water Resources. The nation's water resource is derived from the water vapor or atmospheric moisture passing over the land. This water vapor is estimated to contain about 40,000 billion gallons of water per day. About 10% of this water precipitates, 4200 billion gallons of water per day, on the mainland or conterminous part of the United States. Some 70% of this 4200 billion gallons is re-evaporated back to the atmosphere either by direct evaporation or by plant evaporation (transpiration). The remaining 30% constitutes our water resource, 1260 billion gallons per day. Alaska has an additional 580 billion gallons per day available for future use.

Annual rainfall over the mainland is about 30 inches, ranging from less than four inches in the desert southwest, to more than 200 inches in the pacific northwest. About 26 inches is rain and about four inches is snow. The area east between the Mississippi River and the Rocky Mountains averages about 28 inches. The area west of the Rocky Mountains averages about 18 inches. The areas with the least rain generally also have the greatest variability in rain. Some of the drier states experience ranges from 50% to 250% of the average.

Seasonal variations in precipitation are important to pollution control. In the New England states there is little seasonal variation in precipitation. All seasons produce similar precipitation amounts. In the midwest states, summer storms produce two-thirds of the available moisture. In the southern states, summer storms and cyclonic storms (hurricane types) produce the moisture. In the western United States, snow is the major source of precipitation. In summer periods, little or no moisture may occur.

These seasonal fluctuations change the nature of the rivers, lakes, and streams. Snow is a form of a reservoir. In the spring, the reservoir releases the flow over a short period of time and major flooding generally occurs. Western reclamation projects have been designed to hold this flow and release it to downstream users at a more useable rate. Sudden thunderstorms across the midwest also produce localized flooding. Figure 6-5 illustrates variations in the average annual precipitation. Figure 6-6 illustrates the average annual runoff from precipitation.

Quality

b. Water Quality. The water quality of streams and rivers also changes in response to changes in quantity. This can be simply stated.

> Water quality depends on the history of the water.

Where the water has been will determine its quality. In Rocky Mountain areas snow-melt water is close to distilled water in chemical content. The water has not been in contact with the mineral solids. The high flow rates and flooding, however, cause the rivers to overflow and pick up debris and silt (sediment) along the river banks (flood plain). This rapid flow can also cause serious erosion of river channels. During other times of the year, river flow originates from mountain springs and water quality approaches a western groundwater type, i.e. highly mineralized.

Figures 6-7 and 6-8 illustrate the average dissolved solids (ions) and sediment load (solids or silt) carried by streams in the various sections of the country. Variations of soil type and vegetative cover are apparent from a study of these figures. In Figure 6-7, areas of high precipitation, the Northwest, Northeast, and Southeast, have little dissolved solids. The large quantities of precipitation on these areas have long since dissolved away the more soluble minerals. Sediment loads (Figure 6-8) vary with soil and vegetation. Heavy vegetation and forests reduce soil erosion. Areas with poor soils and vegetative cover and high surface runoff produce heavy sediments in the streams. New England,

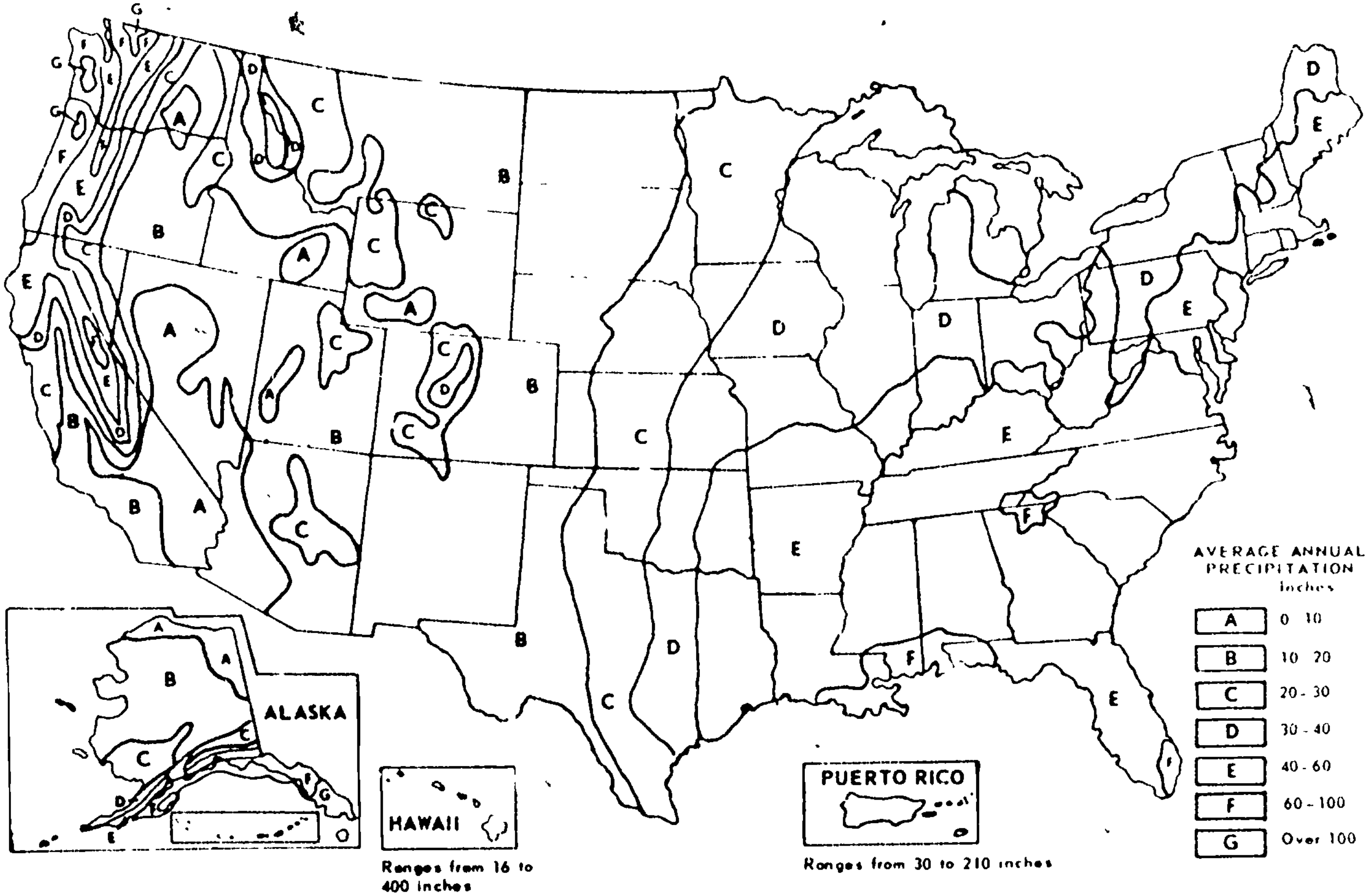
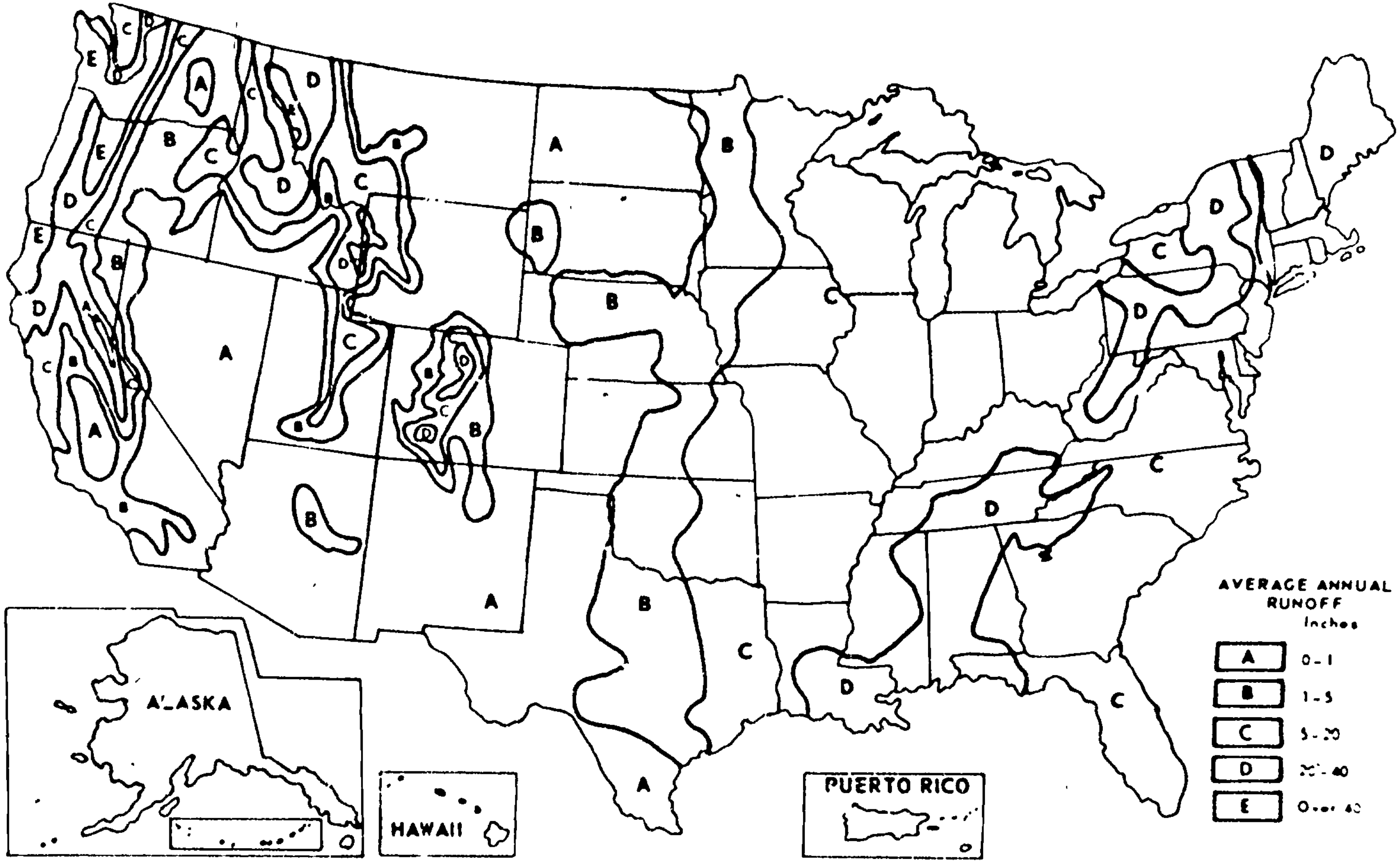


Figure 6–5 Average annual precipitation.



Regional data not available.

Regional data not available

Figure 6-6 Average annual runoff

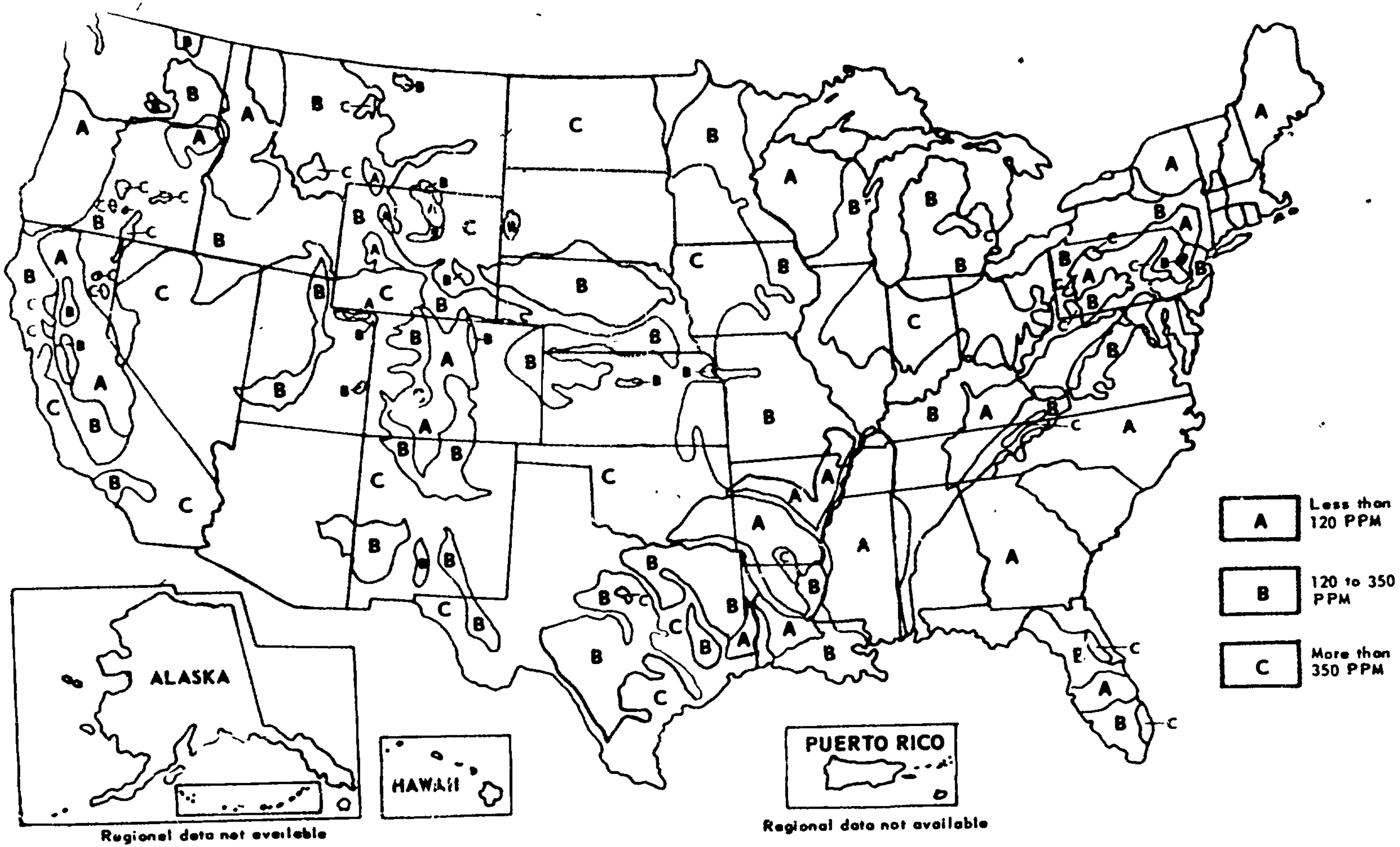
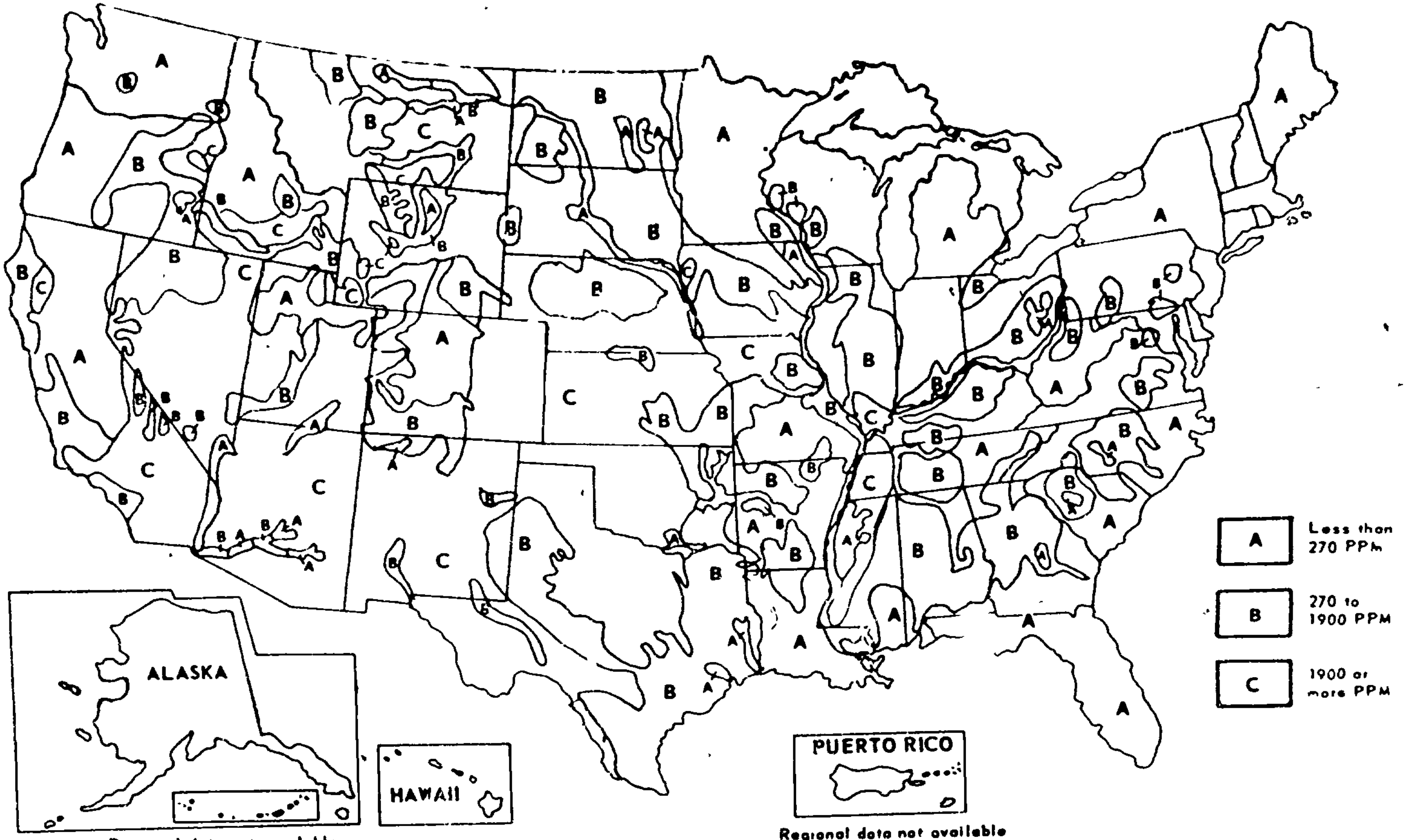


Figure 6-7 Concentration of dissolved solids in streamflow.



Regional data not available

Regional data not available

Figure 6-8 Concentration of sediment in streams parts of the Midwest and Northwest, show low sediment in streams. The Southwest semi-desert area shows high sediment content.

Basins

c. Basins. The most convenient approach to water management is the basin or region method. Basins or water resource regions contain areas where all streams tend to converge toward a single source or sink. The total conterminous United States contains two major water resource regions - east of the Continental Divide, and west of the Continental Divide. The Continental Divide passing through the Rocky Mountains divides flows toward the Atlantic Ocean or Gulf of Mexico or the Pacific Ocean. All rivers east of the Divide flow toward the Atlantic Ocean or Gulf of Mexico. All rivers west of the Divide flow toward the Pacific Ocean.

Regions

These two major regions have been sub-divided into smaller regions. The Water Resource Council of the United States has divided the United States into 20 water resource regions. Figure 6-9 illustrates these regions. Table 6-3 gives runoff, withdrawal and consumptive (used and not returned) values for these regions. Projected values for 1980 and the year 2000 are also given.

Several basins reuse their water several times as it proceeds downstream. Cities and industry take out water, treat it, use it, re-treat it, and discharge it back to rivers. The waters of the Ohio River and its tributaries are a good example of this kind of reuse.

These water resource regions and their sub-basins provide the basic areas for monitoring and surveillance systems.

Constancy of Flow

1. Streams and Rivers. Sub-regions or basins contain different kinds of streams. One basis of stream classification is constancy of flow. Perennial or continuous streams contain water at all times except in severe droughts. Intermittent streams carry water most of the time but cease to flow occasionally because evaporation and seepage from the stream bed is greater than inflow. Ephemeral streams carry water only during periods of snowmelt or after rains. Perennial streams receive flow from groundwater sources during dry periods. Most large rivers are perennial; small streams are frequently intermittent or ephemeral.

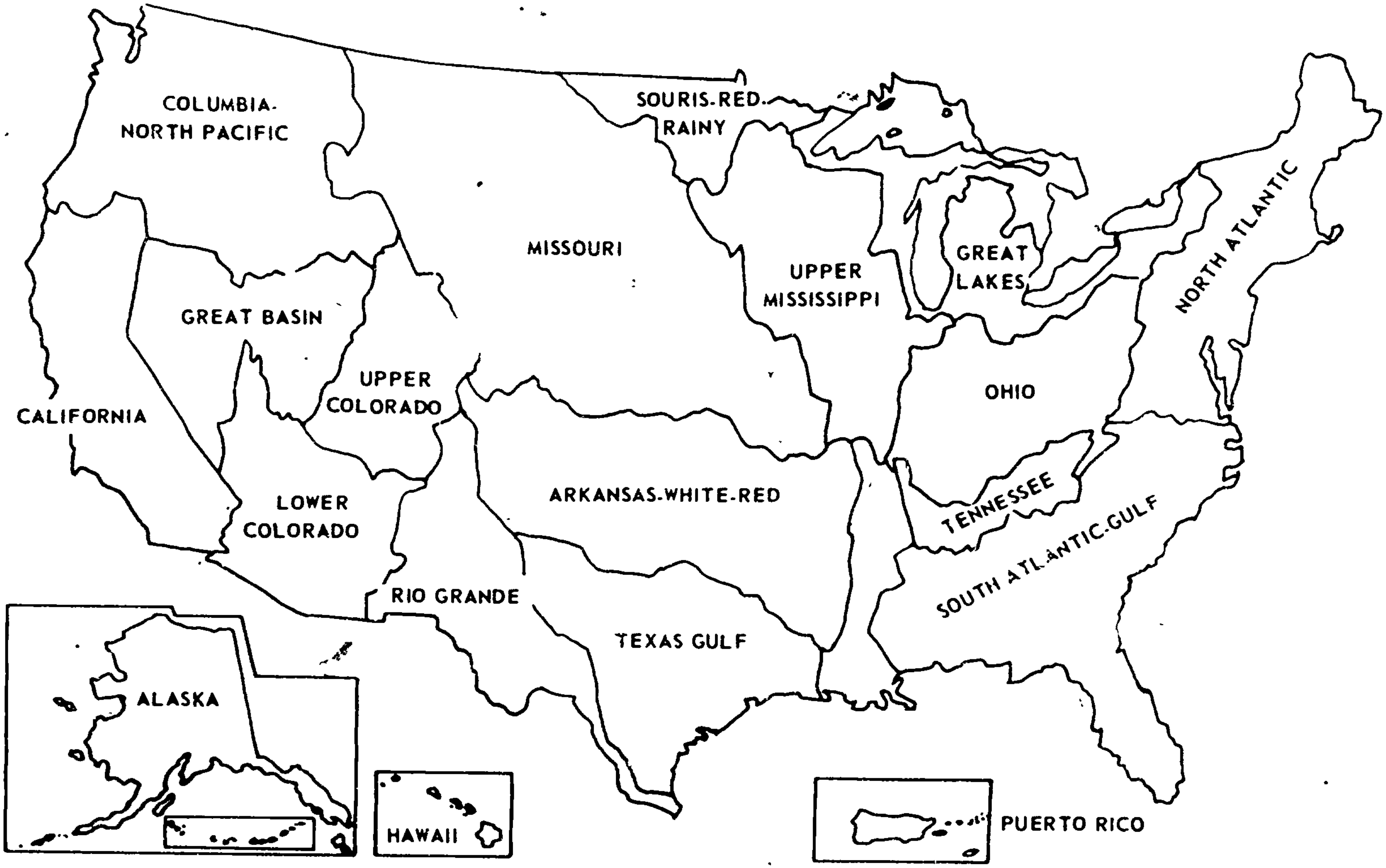


Figure 6–9 Water resources regions used in the first National Assessment.

Figure 6–9 Water resources regions used in the first National Assessment.

Intermittent streams can contain flow originating entirely from a waste discharge. This presents a situation where no diluting water is present and serious pollution is possible. Classification of these streams to high-use functions (Standards) is many times economically expensive and possibly not justified.

Age

Another method of classifying streams is by age. This does not indicate age or time in the usual sense. It indicates an age based on slope. Young streams actively erode their channels. Velocities are sufficiently high to carry all the sediment contributed by tributaries. Mature streams have reduced slopes. The mature stream does not erode its own channel, but the stream does have sufficient velocity to carry sediment from steeper tributaries. Old streams have wide flood plains, a broad meander belt, and gentle slopes. The Mississippi is an old stream. Upper tributary rivers are less old. The delta region of the Mississippi River extends many miles into the Gulf of Mexico. Swift rivers carrying heavy silt loads will deposit part of that sediment load when they join slower-moving, older rivers.

River Structure

Streams also form different tributary forms depending on flow and soil type. Dendritic, or tree-like, streams result in regions where the rock and mineral structure is homogeneous and there is no variation in the resistance to flow. Dendritic patterns are found in the granite mountains of the Sierra Nevada and the Rocky Mountains. Rectangular drainage patterns occur in the Adirondack region in New York State where geological joints and faults join at right angles.

Trellis drainage patterns develop in areas where the underlying rock is strongly folded or sharply dipping. The longer streams follow the fold or weaker rock strata while shorter tributaries cross the fold or dip. The State of Pennsylvania has several Trellis drainage patterns. Radial flow occurs from dome or volcanic structures. The flow radiates outwardly. Occasionally radial flow also occurs toward a depression or center. The flow radiates inwardly. Turkey Mountain in New Mexico and Mount Hood, Oregon, have radial flow.

Lakes

2. Reservoirs and Lakes. Reservoirs and lakes are important units of the Hydrologic Cycle. Lakes are classified by age. Again, the term age refers to appearance and not time. In the natural (non-man influence) conditions, most lakes age over a period of time. New lakes, geologically, are called Oligotrophic Lakes. These lakes, in an ecological sense, have low accumulation of dissolved nutrients, sparse plant and animal life, high dissolved oxygen content, and low organic content. As dissolved minerals flow into these lakes, over a period of time, nutrients are added, more plants and animals develop, organic material increases, and dissolved oxygen is reduced. In the extreme, a swamp develops and the lake is an Eutrophified Lake.

Eutrophication

This natural process of eutrophication has been significantly speeded up by man's influence. The major reason for aging has been the addition of nutrients to these lakes. The nutrients come from industrial and municipal waste water sources. They also come from surface runoff of fertilized agricultural areas. It has been estimated that Lake Erie has been aged by a million years by man's pollution.

Evaporation

Evaporation is significant from the surface of lakes or reservoirs. Figure 6-10 shows the rate of evaporation from lakes. Evaporation rates vary from a minimum of 20 inches to over 140 inches per year from the surface. Organic molecules like duodecanol have been added to the surface or reservoirs to reduce evaporation. This evaporation cools the water and increases the salt concentrations due to reduced volume.

Lakes and reservoirs reduce flow velocity and therefore the sediment-carrying ability of the stream. All reservoirs have reduced capacity from silting. Lake Mead (Hoover Dam) is gradually filling up with silt carried by the Colorado River. The reservoir should be full of silt before the turn of the century.

Reservoirs

Reservoirs and dams also act as buffers to changes in quantity and quality. Empty reservoirs will reduce flood peaks significantly. In a quality sense, sudden upstream changes in quality can be diluted by reservoirs to a point of non-pollution. Reservoirs have been used to dilute downstream pollution for many years. The new legislation (Public Law 92-500, Section 102 b-6), however, limits use of dilution water for quality control:

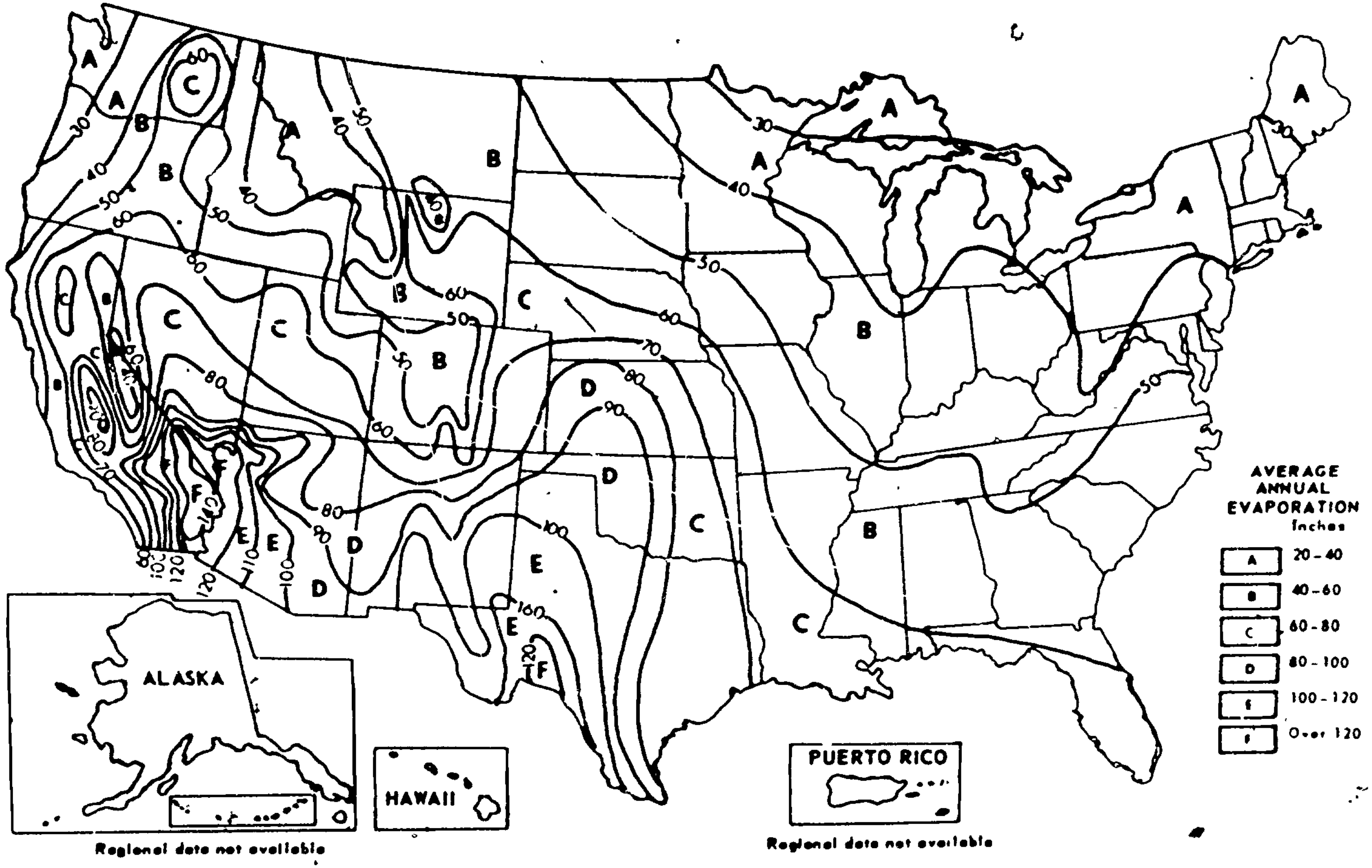


Figure 6-10 Average annual lake evaporation.

"(6) No license granted by the Federal Power Commission for a hydro-electric power project shall include storage or regulation of streamflow for the purpose of water quality control unless the Administrator shall recommend its inclusion and such reservoir storage capacity shall not exceed such proportion of the total storage required for the water quality control plant as the drainage area of such reservoir bears to the drainage area of the river basin or basins involved in such water quality control plan."

Reservoirs also allow natural processes of recovery to proceed. Excess organic matter can be oxidized, organic color molecules can be oxidized and bleached, and excess thermal energy or heat can be dissipated.

Wind

Reservoirs also produce water quality problems. These problems relate directly to stratification due to changes in density. Figure 6-11(a) shows an idealized cross section of a lake with the effects of wind. As can be seen, as a wind moves across a lake, a head is produced which causes a return flow underneath the primary currents. As water becomes colder and colder with depth, this shearing area is reduced toward the surface. Bottom areas become stagnant and water quality changes occur.

Stratification

These changes can be significant. Figure 6-11(b) shows changes in oxygen and carbon dioxide with depth in a stratified lake during the summer. Although fluid exchange across the thermocline is reduced, solid material can cross the barrier. Algae is a good example. Dead algae settle across the barrier and move toward the bottom of the lake. Aerobic bacteria (oxygen-consuming) oxidize the algae and thereby reduce oxygen levels and increase carbon dioxide levels. If sufficient oxygen is not available, septic or anaerobic conditions will exist and noxious gases of ammonia (NH_3), hydrogen sulfide (H_2S), and mercaptans will be produced.

Lake Overturn

Another sequence of events significantly affects water quality in lakes. Water is most dense at 4°C (39.2°F). Above and below this temperature the water is less dense. Because of this variation, lakes may overturn in the spring and fall. In a mechanistic sense, the spring overturn sequence follows these steps:

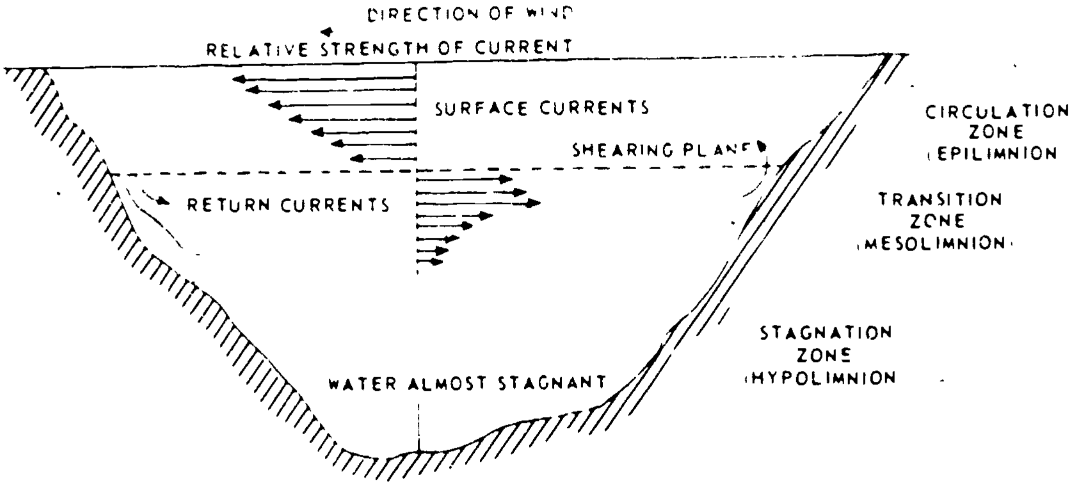


Fig. 6–11 a Direction and relative horizontal velocity of wind-induced currents in a lake or reservoir (idealized). (After G. C. Whipple, G. M. Fair, and M. C. Whipple, *Microscopy of Drinking Water*, 4th ed. Wiley, New York, 1948)

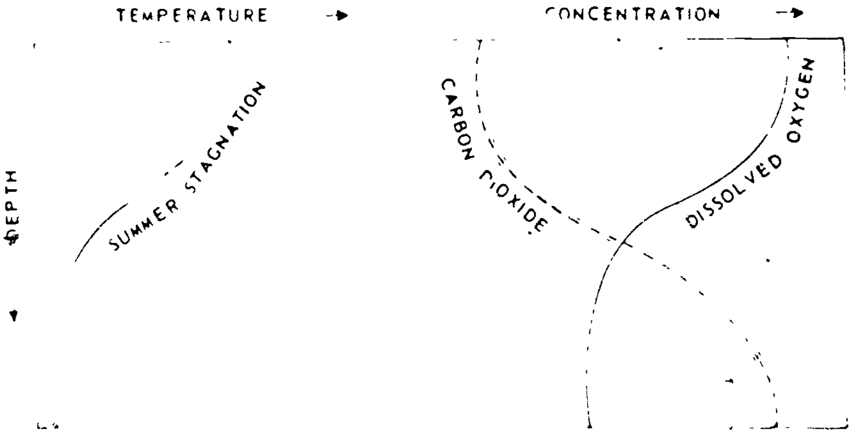


Fig. 6–11 b Vertical gradients of temperature and water quality in lakes, reservoirs, and other deep bodies of water (idealized)

Spring

1. lake water temperature < 4°C (winter),
2. surface water warms up to 4°C (spring),
3. surface water now is heavier (4°C) than lower water, and
4. a wind shifts the instability and the lake overturns.

Fall

In a mechanistic sense, the fall overturn sequence follows these steps:

1. lake water temperature > 4°C (summer),
2. surface water cools off to 4°C (fall),
3. surface water is now heavier (4°C) than lower water, and
4. a wind shifts the instability and the lake overturns.

Following this period of overturn, water quality will change. Turbidity or silt concentrations will increase, dissolved oxygen will increase due to surface exchange, nutrients deposited on the bottom or in the bottom zone are redispersed throughout the lake, and temperatures become constant with depth. Spring turnover redistributes nutrients back to the surface for reuse in plant growth during the summer. If spring or fall temperatures move back and forth through 4°C, and the water responds adequately to these changes, then several overturns may occur.

In summary, monitoring requires selection of a specific area or basin for study, clear-cut selection of objective functions, and inclusion of all phases of solids, gases, and liquids involved in the water system. Specific natural changes which affect water quality must be noted; for example, lake overturns, rapid snow melt, reservoir depths, temperature changes, and stratification.

Problems:

1. Select one of the river regions (20). Secure a topographic map from the local state or U.S. Geological Survey and trace a complete river basin (all area that contributes runoff to the river). Secure hydrologic data from the state hydrologist or Water Resource Department and evaluate the precipitation over the basin. How is the precipitation measured? Who does the measuring? How is the data collected, stored, and evaluated? Measure the area of the basin. Multiply the area of the basin by the precipitation and evaluate the surface runoff. Write a report on your findings.

2. Select one of the river regions (20). Contact the local Environmental Protection Agency or United States Geological Survey and secure maps and data on the basin. Locate all stations in the basin that indicate flow quantity (reservoirs and dams record flow). Plot flow versus reach (distance) down the mainstream of the river. Plot quality parameters on parallel coordinates to quantity downstream and find how quality changes downstream. Write a report on the study.

LEGAL AND ADMINISTRATIVE REQUIREMENTS

The development of a water pollution control program is a continual process. Laws and administrative procedures are constantly being reviewed, evaluated and revised. This process is going on right now, particularly in response to the recent legislation. It is important for those involved in water pollution work to know how the process works. This is important for two reasons. First, the general goals, policies, and requirements as stated by Congress must be known (law). Secondly, the specific operational procedures as stated by the U. S. Environmental Protection Agency must be known (administration).

In October 1972, the "Federal Water Pollution Control Act Amendments of 1972" became law. This law consolidated and extended the environmental ideas and policies of many years into an effective, concentrated effort for solving our water pollution problems. This law, Public Law 92-500 (86 Stat. 816), is administrated by the Administrator of the United States Environmental Protection Agency. The general goals and policies of this law were presented beginning on page 12 of this text. Several more specific sections of the law are presented to illustrate parts of the program.

1. WATER QUALITY MONITORING

Several sections of Public Law 92-500 pertain directly to the monitoring and surveillance program. The first set of information pertains to water quality monitoring and surveillance systems for navigable waters, ground waters, the contiguous zone and the oceans. This system will establish "where we are", "where we should be" and "how fast we are getting there".

TITLE 1--RESEARCH AND RELATED PROGRAMS

"Research, Investigations, Training, and Information

"Sec. 104. (a) The Administrator shall establish national programs for the prevention, reduction, and elimination of pollution and as part of such programs shall--

"(5) in cooperation with the States, and their political subdivisions, and other Federal agencies establish, equip, and maintain a water quality surveillance system for the purpose of monitoring the quality of the navigable waters and ground waters and the contiguous zone and the oceans and the Administrator shall, to the extent practicable, conduct such surveillance by utilizing the resources of the National Aeronautics and Space Administration, the National Oceanic and Atmospheric Administration, the Geological Survey, and the Coast Guard, and shall report on such quality in the report required under subsection (a) of section 516; and

Under Title I of Public Law 92-500, all Federal appropriations for State pollution control programs are tied to a monitoring capability--

"Grants for Pollution Control Programs

"Sec. 106 (e) states--

Beginning in fiscal year 1974 the Administrator shall not make any grant under this section to any State which has not provided or is not carrying out as a part of its program--

"(1) the establishment and operation of appropriate devices, methods, systems, and procedures necessary to monitor, and to compile and analyze data on (including classification according to eutrophic condition), the quality of navigable waters and to the extent practicable, ground waters including biological monitoring; and provision for annually updating such data and including it in the report required under section 305 of this Act;

Under Title III--"Standards and Enforcement", Section 303--"Water Quality Standards and Implementation Plans" Part (e) gives information on the State planning process--

"(e) (1) Each State shall have a continuing planning process approved under paragraph (2) of this subsection which is consistent with this Act.

"(2) Each State shall submit not later than 120 days after the date of the enactment of the Water Pollution Control Amendments of 1972 to the Administrator for his approval a proposed continuing planning process which is consistent with this Act. Not later than thirty days after the date of submission of such a process the Administrator shall either approve or disapprove such process. The Administrator shall from time to time review each State's approved planning process for the purpose of insuring that such planning process is at all times consistent with this Act. The Administrator shall not approve any State permit program under title IV of this Act for any State which does not have an approved continuing planning process under this section.

Operational rules, based on Public Law 92-500 and developed by the Environmental Protection Agency, are published in the Federal Register. Most libraries have copies of the Federal Register. On May 28, 1973, the Register (Vol. 88, No. 99) published proposed rules for Water Quality Management Plans. Under these rules Subpart C--"Monitoring and Surveillance"--gives the tie of monitoring to the State plans as stated in Section 303 (e) of the law.

Subpart C--Monitoring and Surveillance

131.300 Relationship of monitoring and surveillance to plans.
131.301 Coverage of monitoring and surveillance program.
131.302 Use of monitoring surveys for plan development.
131.303 Frequency of monitoring surveys.
131.304 Output of monitoring surveys.
131.305 Water quality data from fixed stations; input to information system.
131.306 Provision and use of point source discharge information input to information system.

2. POINT SOURCE MONITORING

The National Pollutant Discharge Elimination System (NPDES) is formulated in Title IV--Permits and Licenses--Section 402 of Public Law 92-500. Parts (a) (1) and (2) read:

"National Pollutant Discharge Elimination System

PERMITS

"Sec. 402. (a) (1) Except as provided in sections 318 and 404 of this Act, the Administrator may, after opportunity for public hearing, issue a permit for the discharge of any pollutant, or combination of pollutants, notwithstanding section 301(a), upon condition that such discharge will meet either all applicable requirements under sections 301, 302, 306, 307, 308, and 403 of this Act, or prior to the taking of necessary implementing actions relating to all such requirements, such conditions as the Administrator determines are necessary to carry out the provisions of this Act.

"(2) The Administrator shall prescribe conditions for such permits to assure compliance with the requirements of paragraph (1) of this subsection, including conditions on data and information collection, reporting, and such other requirements as he deems appropriate.

Under Title IV--Permits and Licenses, Section 401--Certification--Part (d) reads:

EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS FOR PERMITS

"(d) Any certification provided under this section shall set forth any effluent limitations and other limitations, and monitoring requirements necessary to assure that any applicant for a Federal license or permit will comply with any applicable effluent limitations and other limitations, under section 301 or 302 of this Act, standard of performance under section 306 of this Act, or prohibition, effluent standard, or pretreatment standard under section 307 of this Act, and with any other appropriate requirement of State law set forth in such certification, and shall become a condition on any Federal license or permit subject to the provisions of this section.

This section identifies that all permits will have stated effluent limitations and monitoring requirements.

Under Title III, Standards and Enforcement, Section 308, "Inspections, Monitoring and Entry gives--

"Inspections, Monitoring and Entry.

"Sec. 308. (a) Whenever required to carry out the objective of this Act, including but not limited to (1) developing or assisting in the development of any effluent limitation, or other limitation, prohibition, or effluent standard, pretreatment standard, or standard of performance under this Act; (2) determining whether any person is in violation of any such effluent limitation, or other limitation, prohibition or effluent standard, pretreatment standard, or standard of performance; (3) any requirement established under this section; or (4) carrying out sections 305, 311, 402, and 504 of this Act--

RECORDS

"(A) the Administrator shall require the owner or operator of any point source to (i) establish and maintain such records, (ii) make such reports, (iii) install, use, and maintain such monitoring equipment or methods (including where appropriate, biological monitoring methods), (iv) sample such effluents (in accordance with such methods, at such locations, at such intervals, and in such manner as the Administrator shall prescribe), and (v) provide such other information as he may reasonably require; and

ACCESS RULES

"(B) the Administrator or his authorized representative, upon presentation of his credentials--

(i) shall have a right of entry to, upon, or through any premises in which an effluent source is located or in which any records required to be maintained under clause (A) of this subsection are located, and

(ii) may at reasonable times have access to and copy any records, inspect any monitoring equipment or method required under clause (A), and sample any effluents which the owner or operator of such source is required to sample under such clause.

"(b) Any records, reports, or information obtained under this section (1) shall, in the case of effluent data, be related to any applicable effluent limitations, toxic, pretreatment, or new source performance standards, and (2) shall be available to the public, except that upon a showing satisfactory to the Administrator by any person that records, reports, or information, or particular part thereof (other than effluent data), to which the Administrator has access under this section, if made public would divulge methods or processes entitled to protection as trade secrets of such person, the Administrator shall consider such record, report, or information, or particular portion thereof confidential in accordance with the purposes of section 1905 of title 18 of the United States Code, except that such record, report, or information may be disclosed to other officers, employees, or authorized representatives of the United States concerned with carrying out this Act or when relevant in any proceeding under this Act.

"(c) Each State may develop and submit to the Administrator procedures under State law for inspection, monitoring, and entry with respect to point sources located in such State. If the Administrator finds that the procedures and the law of any State relating to inspection, monitoring, and entry are applicable to at least the same extent as those required by this section, such State is authorized to apply and enforce its procedures for inspection, monitoring, and entry with respect to point sources located in such State (except with respect to point sources owned or operated by the United States).

On November 11, 1972 the Federal Register (Volume 38, No. 98) published proposed guidelines for the National Pollutant Discharge Elimination System (NPDES). Subpart G--Monitoring, Recording, and Reporting—the following proposed rules are given:

SUBPART G--Monitoring, Recording and Reporting

124.61 Monitoring

MONITORING

Procedures of any State or interstate agency participating in the NPDES for the monitoring of any discharge authorized by an NPDES permit shall be consistent with the following:

(a) Any discharge authorized by an NPDES permit may be subject to such monitoring requirements as may be reasonably required by the Director, including the installation, use, and maintenance of monitoring equipment or methods (including, where appropriate, biological monitoring methods).

(b) Any discharge authorized by an NPDES permit which (1) averages more than 50,000-gallons-per-operating day, (2) the Regional Administrator requests, in writing, be monitored, or (3) contains toxic pollutants for which an effluent standard has been established by the Administrator pursuant to section

307(a) of the Act, shall be monitored by the permittee for at least the following:

(i) Flow (in gallons per day); and,

(ii) All of the following pollutants:

(a) Pollutants (either directly or indirectly through the use of accepted correlation coefficients or equivalent measurements) which are subject to reduction or elimination under the terms and conditions of the permit;

(b) Pollutants which the Director finds, on the basis of information available to him, could have a significant impact on the quality of navigable waters;

(c) Pollutants specified by the Administrator, in regulations issued pursuant to the Act, as subject to monitoring; and,

(d) Any pollutants in addition to the above which the Regional Administrator requests, in writing, be monitored.

(e) Each effluent flow or pollutant required to be monitored pursuant to paragraph (b) of this section shall be monitored at intervals sufficiently frequent to yield data which reasonably characterizes the nature of the discharge of the monitored effluent flows and pollutant. Variable effluent flows and pollutant levels shall be monitored at more frequent intervals than relatively constant effluent flows and pollutant levels which may be monitored at less frequent intervals.

RECORDING

124.62 Recording of monitoring activities and results.

Any State or interstate agency participating in the NPDES shall specify the following recording requirements for any NPDES permit which requires monitoring of the authorized discharge:

(a) The permittee shall maintain records of all information resulting from any monitoring activities required of him in his NPDES permit;

(b) Any records of monitoring activities and results shall include for all samples: (1) The date, exact place, and time of sampling; (2) the dates analyses were performed; (3) who performed the analyses; (4) the analytical techniques/methods used; and, (5) the results of such analyses; and,

(c) The permittee shall be required to retain for a minimum of 3 years any records of monitoring activities and results including all original strip chart recording for continuous monitoring instrumentation and calibration and maintenance records. This period of retention shall be extended during the course of any unresolved litigation regarding the discharge of of pollutants by the permittee or when requested by the Director of Regional Administrator.

124.63 Reporting of monitoring results.

REPORTING

Any State or interstate agency participating in the NPDES shall require periodic reporting (at a frequency of not less than once per year) on the proper NPDES reporting form of monitoring results obtained by a permittee pursuant to monitoring requirements in an NPDES permit. In addition to the NPDES reporting form, the Director in his discretion may require submission of such other information regarding monitoring results as he determines to be necessary.

(Comment. Reporting frequency, as with monitoring frequency, depends upon the nature and impact of the discharge Annual report submission is sufficient for small cooling water discharges. Discharges for which more frequent, even monthly, reporting is desirable include variable discharges, major, including municipal, discharges, and discharges for which new treatment or control methods are being applied. Reporting frequency should correspond with administrative capability to evaluate the reports as they come in.)

124.64 NPDES monitoring, recording, and reporting requirements.

NPDES

Any State or interstate agency participating in the NPDES shall adopt procedures consistent with any national monitoring, recording, and reporting requirements specified by the Administrator in regulations issued pursuant to the Act.

As part of the permit program effluent standards will be established. One standard applies to toxic pollutants. Title III, Section 307(a) (1) and (2) of Public Law 92-500 states:

"Toxic and Pretreatment Effluent Standards

TOXIC
POLLUTANTS

"Sec. 307. (a) (1) The Administrator shall, within ninety days after the date of enactment of this title, publish (and from time to time thereafter revise) a list which includes any toxic pollutant or combination of such pollutants for which an effluent standard (which may include a prohibition of the discharge of such pollutants or combination of such pollutants) will be established under this section. The Administrator in publishing such list shall take into account the toxicity of the pollutant, its persistence, degradability, the usual or potential presence of the affected organisms in any waters, the importance of the affected organisms and the nature and extent of the effect of the toxic pollutant on such organisms.

"(2) Within one hundred and eighty days after the date of publication of any list, or revision thereof, containing toxic pollutants or combination of pollutants under paragraph (1) of this subsection, the Administrator, in accordance with section 553 of title 5 of the United States Code, shall publish a proposed effluent standard (or a prohibition) for such pollutant or combination of pollutants which shall take into account the toxicity of the pollutant, its persistence, degradability, the usual or potential presence of the affected organisms in any waters, the importance of the affected organisms and the nature and extent of the effect of the toxic pollutant on such organisms, and he shall publish a notice for a public hearing on such proposed standard to be held within thirty days. As soon as possible after such hearing, but not later than six months after publication of the proposed effluent standard (or prohibition), unless the Administrator finds, on the record, that a modification of such proposed standard (or prohibition) is justified based upon a preponderance of evidence adduced at such hearings, such standard (or prohibition) shall be promulgated.

Section 307(a) (1) of the law requests a list of toxic pollutants. On July 6, 1973, the Federal Register (Volume 38, No. 129) published the list.

TOXIC POLLUTANTS

List of Toxic Pollutants

1. Aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8 - endo-exodimethanonaphthalene) Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo, exo-5,8-dimethanonaphthalene)
2. Benzidine and its salts (para-para'-diaminobiphenyl)
3. Cadmium and all cadmium compounds
4. Cyanide and all cyanide compounds
5. DDD(TDE)1,1 - dichloro-2,2 -bis(para-chlorophenyl)-ethane DDE (dichlorodiphenyldichloroethylene) 1,1 - dichloro-2,2-bis (para-chlorophenyl)-ethylene DDT (dichlorodiphenyltrichloroethane) 1,1,1 - trichloro-2,2-bis (para-chlorophenyl)-ethane

6. Endrin (1,2,3,4,10,19 - hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a - octahydro-1,4-endo-endo-5,8-dimethanonaphthalene)
7. Mercury and all mercury compounds
8. Polychlorinated biphenyls (PCB's)
9. Toxaphene (chlorinated camphene)

Effluent limitations or standards as requested by Section 307a (2) will be forthcoming.

A second important standard relates to Secondary Treatment for municipal sewage. Section 304d (1) of Public Law 92-500 states:

SECONDARY TREATMENT INFORMATION

> "(d)(1) The Administrator, after consultation with appropriate Federal and State agencies and other interested persons, shall publish within sixty days after enactment of this title (and from time to time thereafter) information, in terms of amounts of constituents and chemical, physical, and biological characteristics of pollutants, on the degree of effluent reduction attainable through the application of secondary treatment.

On April 30, 1973 the Federal Register (Volume 38, No. 82) published the standards for Secondary Treatment.

EFFLUENT STANDARDS

SECONDARY STANDARDS

Unit of measurement	Monthly average	Weekly average
Biochemical Oxygen mg/liter Demand (5 day).	30	45
Suspended Solids---mg/liter	30	45
Fecal Coliform---Number/100ml	200	400
Bacteria pH. --------------	Within limits of 6.0 to 9.0	

The third set of standards of critical importance to pollution control involves point sources other than public owned treatment works. Section 304(b) of Public Law 92-500 states:

> "(b) For the purpose of adopting or revising effluent limitations under this Act the Administrator shall, after consultation with appropriate Federal and State agencies and other interested persons, publish within one year of enactment of this title, regulations, providing guidelines for effluent

limitations, and, at least annually thereafter, revise, if appropriate, such regulations. Such regulations shall--

"(1)(A) identify, in terms of amounts of constituents and chemical, physical, and biological characteristics of pollutants, the degree of effluent reduction attainable through the application of the best practicable control technology currently available for classes and categories of point sources (other than publicly owned treatment works);

The standards associated with this section are presently under development. Interim standards are being used as guides under the title "Interim Effluent Guidance for the NPDES" as issued by the office of Permit Programs, U. S. Environmental Protection Agency.

3. Definitions

In any law or text, important terms should be defined. Common terms used in everyday conversations can mean different things to different people. Clear meaning is essential for legal definitions. Several important terms used in Public Law 92-500 are defined in the Law under Title V - General Provisions under Section 502--"General Definitions." Only a few are included for reference:

"Sec. 502. Except as otherwise specifically provided, when used in this Act:

POLLUTANT

"(6) The term 'pollutant' means dredged spoil, solid waste, incinerator residue, sewage, garbage, sewage sludge, munitions, chemical wastes, biological materials, radioactive materials, heat, wrecked or discarded equipment, rock, sand, cellar dirt and industrial, municipal, and agricultural waste discharged into water. This term does not mean (A) 'sewage from vessels' within the meaning of section 312 of this Act; or (B) water, gas, or other material which is injected into a well to facilitate production and disposal purposes is approved by authority of the State in which the well is located, and if such State determines that such injection or disposal will not result in the degradation of ground or surface water resources.

NAVIGABLE WATERS

"(7) The term 'navigable waters' means the waters of the United States, including the territorial seas.

"(11) The term 'effluent limitation' means any restriction established by a State or the Administrator on quantities, rates, and concentrations of chemical, physical, biological, and other constituents which are discharged from point sources into navigable waters, the waters of the contiguous zone, or the ocean, including schedules of compliance.

"(13) The term 'toxic pollutant' means those pollutants, or combinations of pollutants, including disease-causing agents, which after discharge and upon exposure, ingestion, inhalation or assimilation into any organism, either directly from the environment or indirectly by ingestion through food chains, will, on the basis of information available to the Administrator, cause death, disease, behavioral abnormalities, cancer, genetic mutations, physiological malfunctions (including malfunctions in reproduction) or physical deformations, in such organisms or their offspring.

TOXIC
POLLUTANT

"(15) The term 'biological monitoring' shall mean the determination of the effects on aquatic life, including accumulation of pollutants in tissue, in receiving waters due to the discharge of pollutants (A) by techniques and procedures, including sampling of organisms representative of appropriate levels of the food chain appropriate to the volume and the physical, chemical, and biological characteristics of the effluent, and (B) at appropriate frequencies and locations.

BIOLOGICAL
MONITORING

Problems:

1. Secondary standards are applied to industry as well as municipalities. Find the standards in Public Law 92-500 and follow their implementation through the Federal Register. Select just one industry, for example steel, cement, chemical, etc.

2. Are all industrial standards for one industry the same?

3. Is the timing for meeting secondary standards the same for old plants as well as new plants?

4. How can you justify meeting standards with old plants?

5. If an industry cannot meet the new standards and stay in business competitively, then his standards should be reduced (less strict). Comment on this proposition.

PARAMETER SIGNIFICANCE AND VARIATION

INTRODUCTION

Monitoring techniques for water quality parameters in streams, lakes, oceans, or waste discharges depend basically on an objective function. These functions were identified and discussed in Chapter One. They are:

1. Characterization of Existing Conditions,
2. Identification of Trends,
3. Evaluation of Standard Compliance,
4. Emergency Conditions,
5. Environmental Quality Forecasting, and
6. Research.

Each objective formation may require some differences in parameter selection (because of significance) and testing frequency (because of variability in space and time). This chapter will discuss various parameters, their significance and variation in light of objective functions.

WATER PARAMETERS

There are three basic kinds of tests performed on water: physical, chemical and biological. The parameters identified by these tests are known as physical, chemical or biological parameters. There is a seemingly endless list of these parameters. This text has narrowed the list to those considered more important in water evaluation. A brief list of these parameters, grouped under the test classification, is presented.

It is not possible in this text to describe or explain the analysis for each parameter. Many texts are available for reference. Four basic texts are:

1. "Standard Methods for the Examination of Water and Sewage" published by the American Water Works Association and the American Public Health Association,
2. "Methods for Collection and Analysis of Water Samples" United States Geological Survey paper No. 1454,

3. "Methods for Chemical Analysis of Water and Wastes" Published by the U. S. Environmental Protection Agency,

4. American Society for Testing and Materials, Part 23 Water; Atmospheric Analysis. Published by the Society, 1916 Race Street, Philadelphia 3, PA.

TABLE 8-1

A PARTIAL LIST OF WATER PARAMETERS

Physical

Temperature, turbidity, color, odor, taste
Solids (suspended, dissolved, fixed, volatile)
Oil and Grease and
Total Carbon (TC)

Chemical

pH, alkalinity, calcium and magnesium
Chlorides and sulfates, dissolved oxygen
Nitrogen, minor elements. phosphate and
Chemical Oxygen Demand (COD).

Biological

Total Coliforms
Fecal Coliforms
Plankton
Biochemical Oxygen Demand (BOD)

PHYSICAL PARAMETERS

The physical parameters are the most easily understood grouping. They reflect measurements which practically everyone can visualize.

TEMPERATURE

Temperature measurement is the most important physical parameter. It is freqeuntly overlooked by field technicians. With this one measurement water variables are known, such as viscosity, vapor pressure, surface tension, and gas solubility. Kinetics of chemical and biological reactions can also be identified. For example, a bacteria can describe its rate of metabolism and growth by an increase of 10 to 15°C. The same is true for most chemical reactions. Therefore, an analysis of possible pollution probl[illegible] must be built from temperature data. Most natural waters have temperatures ranging from 0°C (liquid) to around 30°C.

TURBIDITY

Turbidity measurements are based on the passage of light through a sample of water. The less light passing through the higher the turbidity. This test gives an indication of how much silt or finely divided material is in the water. Turbidity measurements normally are used by water plants to meet enforcements standards concerning drinking water. Turbidity is restricted by these Standards for two reasons: 1) customers want clean water (appearance), and 2) bacteria or viruses may be protected from disinfection by being inside the turbid particles. This could be a health hazard. In general, turbidity measurements are not made on sewage, or highly polluted water since the measurement is somewhat meaningless. Turbidity values range from less than 1.0 turbidity unit to several thousand in sewage.

COLOR

Color measurements reflect the intensity of light absorption in water. The absorption depends on specific wave lengths. For example, a blue water is blue because it absorbs the red wave lengths from light. A water is yellow because it absorbs the violet wave lengths from light. Natural waters generally have some color due to contact with vegetation, particularly decaying materials. In the Rocky Mountains, the snowmelt runoff in the spring washes yellow colored decaying material, both dissolved and colloidal, into the streams. The same is true in the New England area. Drainage from swamp areas is highly colored with brown to yellow coloring. Industrial wastes can add dyes or colors of all kinds to water. Sewage is also colored. Fresh sewage is normally gray. If the sewage has become septic it will turn black.

Color is limited by drinking water standards because customers do not want a colored water. It looks bad and may stain clothes and fixtures. In streams color is limited from pollution sources because of visual pollution effects and reduced use capability downstream. Values for color range from about zero in clear streams to 70 or 80 in spring snowmelt runoff waters to several hundred in some industrial waste discharges.

ODOR

Odor is caused by a gas molecule reacting in the nose on an olfactory nerve. If the odor comes from water it, therefore, is from volatile material. Most odor in water is associated with organic material, algae and bacteria. Specific algae produce specific odors. For example, Asterionella (a diatom) produces an acromatic odor. Synura (a protozoa) produces a cucumber taste. Bacteria can also produce odors. For example, under anaerobic conditions (no dissolved oxygen), sulfur compounds are reduced (chemical reduction) to sulfides. Hydrogen sulfide is thereby also produced along with its characteristic rotten egg odor. Odor is measured by adding odor free water to a sample until the odor is just noticeable. For example, if a 10 ml sample is diluted by 100 ml of odor free water to the point where the odor is just barely noticeable, then the odor number or threshold is 100/10 = 10, or a 10 to 1 dilution will erase the odor. This test is performed by the human nose and therefore is not absolute and subject to variation.

Heating a water releases more volatile material and increases the odor. Most odor values range from no odor to a few hundred. Only the lower values are of much use in quantitizing measurements. Odor is restricted in the drinking water standards.

TASTE

Taste in water is normally attributed to the chloride and sulfate ions. Some organic material which produces odor also is involved in taste sensations. The test is similar to the odor test; that is, a human sensor is used. The test is subjective but useful in some situations. Water containing chloride concentrations around 1000 milligrams per liter is not suitable for drinking water.

SOLIDS

Solids testing is important in characterizing a water. The test essentially measures the amount of solids left after the water evaporates. This solid residue can be further heated to about 600°C and organic material will be volatized. If the sample is filtered before testing, then only the dissolved ion type material is reflected by the test. An analysis of this type shows how much material is suspended (filtered out) and how much is dissolved (passes the filter). By heating to around 600°C each of these functions can be further catagorized into volatile (organic) and fixed (inorganic) fractions.

High velocity runoff from erodible soil would show large amounts of suspended material and less dissolved material. Organic wastes from cities and industries would show large amounts of volatile matter either suspended or dissolved or both. Water at lower reaches of basins normally shows higher salt content than at higher reaches because of many uses during the flow passage. Slow moving streams carry less suspended matter than fast moving streams. Salt content (dissolved) can range from less than 10 to 35,000 mg/l in the ocean. Suspended material normally ranges from zero to a few thousand.

OIL AND GREASE

Oil and grease in water are measured two ways: by volume (so much per volume) and by surface (so much in the surface). Oil or grease can be dissolved or homogenized in the water to some extent and is measured by volume. Oil or grease can also float on the surface and produce a surface pollution. Most oil and grease found in water comes from human activity, including normal household sources and industrial oil wastes. They are limited in streams to very low values, normally less than 10 or 15 mg/l and no visible discoloration of the surface. Oil spills and the possible resulting pollution are rapidly being reduced by concentrated efforts of enforcement agencies with significant industrial cooperation.

TOTAL CARBON

In recent years tests have been developed to quickly indicate the amount of carbon (organic material) in water. One of these is the Total Carbon (TC) test. The test consists essentially of evaporating the water and volatilizing the carbon to carbon dioxide gas and measuring the amount of carbon dioxide. The test is a collective test indicating only the total carbon (or carbon dioxide) present. Specific compounds are not identified. Since each type of organic compound has different chemical properties a test of this kind only gives gross values. It is a good test for getting overall values of organics and is replacing the volatile solids test mentioned under solids testing.

CHEMICAL PARAMETERS

Chemical parameters are more difficult to understand than physical parameters. Procedures for determing concentrations are normally complex, involving several steps and percise reagents or expensive analytical equipment. After securing the basic data a complete evaluation is also complex. If one considers all the inter-relationships of each parameter including all phases of air, water, and solids the situation would require a computer for solution. Fortunately, many species in any given sample are not significant, either because their concentration is too low or because they do not react dynamically with the system. The general scheme of chemical parameters in water can be visualized if insignificant species are not considered.

pH

The term pH has been discussed somewhat in Chapter 6. The mathematical definition is

$$pH = -\log [H_3O^+] \tag{8-1}$$

the brackets refer to the hydronium ion concentration. In fact, it is more precise to refer to the hydronium in activity, but in most fresh water systems this is unnecessary. pH is an intensity term which describes the balance of acids and bases in a water. It is not a capacity factor like alkalinity which indicates an amount. pH is temperature dependent, as are all chemical parameters. Neutral pH is 7.0 only at 25°C (see Chapter 6).

pH is a very significant chemical parameter. Nearly all chemical reactions are pH dependent. The concentrations of various ions in solution depend on the pH. In like manner the biological systems found in water operate within the neutral pH range from about 4 to 9. Outside of these ranges they die.

Most natural waters have pH values from 4 to 9. In the West pH values are basic around 8; in New England waters are slightly acidic around 6.5. The pH is determined by the soil or mineral content the water has contacted. In the West many of the minerals are solid bases which make the water slightly basic. In New England, very few minerals are present and carbon dioxide from the air and decomposition processes makes the water slightly acidic. Other areas of the country generally lie in between these extremes.

ALKALINITY

Alkalinity is another useful chemical parameter. In effect the alkalinity is a sum of all the bases in a water. Or said another way, it indicates how much acid can be added to a water before the pH exceeds the general biological limit of about 4 (neutralization). Alkalinity is a collective term, that is, it is not specific to any one species. Alkalinity is a capacity term not an intensity term like pH.

Alkalinity is a significant water variable. It indicates the stability of a water system with regard to acids and bases. The more alkalinity the more stability, or said another way, the less change in pH for added acids and bases. Since biological systems depend on narrow pH ranges, pH stability is important. Normal values of alkalinity range from around 10 or 20 to around 300 ppm as $CaCo_3$. In the West, you find the higher values because of the mineral content in the soil. In New England very low values are common due to the lack of mineral content in the soils.

CALCIUM AND MAGNESIUM (HARDNESS)

Calcium and magnesium ions are generally always present in water. The sum of these two ions is called the water hardness. Occasionally other ions are included in the hardness term but generally only the calcium and magnesium ions are significant, based on concentration. Calcium and magnesium ions are derived from various minerals, specifically limestone ($CaCO_3$), magnesite ($MgCO_3$), brucite $Mg(OH)_2$, dolomite ($CaMg(CO_3)_2$) and gypsum ($CaSO_4$).

These ions are significant in many areas of water use. They effect the suitability of the water for municipal use, industry, and agriculture. Hard water may incrust (deposit $CaCO_3$) or reduce the effectiveness of soaps. Normal values of hardness vary from about 10 or 20 to about 300 mg/l as

$CaCO_3$. Again the higher values are in the West and low values are in the East due to mineral content in the soil. Higher mineral content gives higher hardness.

CHLORIDES AND SULFATES

Chlorides are widely distributed in nature. They are found in many different kinds of minerals and in ocean waters. Human urine and industrial wastes also add to the chloride concentrations. Chlorides react only moderately (change) after their dissolution into water. Its concentration increases with general water use in agriculture, industry, or municipality. Generally the amount of chloride in water is low, seldom above 80 mg/l. Its major significance rests with its taste in drinking water (limited to 250 mg/l) and its properties affecting agriculture.

Sulfates are also common in nature. Gypsum ($CaSO_4$) is very soluble and increases both the hardness (Ca ion) and the sulfate ion. There are several oxidation states of sulfur ranging from sulfide to sulfur (solid) to sulfite to sulfate. The form in which sulfur is found depends generally on the availability of dissolved oxygen. The more oxygen the higher the oxidation level (for example sulfate).

Sulfides are odorous (H_2S, hydrogen sulfide) and are found where anaerobic conditions prevail (no oxygen). The presence of sulfides in a water indicates pollution. Sulfates are significant in drinking water primarily because of their laxative effects. Values over 500 mg/l can cause laxative effects unless the body has been acclimated to it.

DISSOLVED OXYGEN

The amount of dissolved oxygen in a water depends on the temperature, altitude, and chemical state in the water. As temperature increases the oxygen level is reduced (see Table 8-2) from 14.62 mg/l at $0^\circ C$ to 9.17 mg/l at $20^\circ C$. Since the amount of oxygen in water depends on its partial pressure above the water (Henry's Law), an increase in altitude should reduce the oxygen level. This change is about 3.7% per thousand feet. The third dependence of oxygen relates to the activity or salt concentration in the water. As salt concentrations increase, for a given temperature, the oxygen values decrease (see Table 8-2).

Dissolved oxygen gives significant information on the state of a stream or lake. Values approaching saturation (Table 8-2) generally indicate little bacterial activity. In other cases, the water may be very polluted. Algae can produce saturated values during daylight hours overcoming bacterial demands for oxygen. This shows that one parameter does not evaluate a water's condition. Low values of oxygen indicate that the oxygen is being consumed either by chemical

TABLE 8-2
EQUILIBRIUM VALUES OF DISSOLVED OXYGEN IN FRESH AND SEA WATER IN AN ATMOSPHERE CONTAINING 20.9% OXYGEN AT SEA LEVEL

Dissolved Oxygen (mg/l) for Stated Concentrations of Chloride (mg/l)

Temperature, °C	0	5000	10000	15000	20000
0	14.7	13.8	13.0	12.1	11.3
1	14.3	13.5	12.7	11.9	11.1
2	13.9	13.1	12.3	11.6	10.8
3	13.5	12.8	12.0	11.3	10.5
4	13.1	12.4	11.7	11.0	10.3
5	12.8	12.1	11.4	10.7	10.0
6	12.5	11.8	11.0	10.4	9.8
7	12.1	11.5	10.8	10.2	9.6
8	11.8	11.2	10.6	10.0	9.4
9	11.6	11.0	10.4	9.7	9.1
10	11.3	10.7	10.1	9.5	8.9
11	11.0	10.4	9.9	9.3	8.7
12	10.8	10.2	9.7	9.1	8.6
13	10.5	10.0	9.4	8.9	8.4
14	10.3	9.7	9.2	8.7	8.2
15	10.0	9.5	9.0	8.5	8.0
16	9.8	9.3	8.8	8.4	7.9
17	9.6	9.1	8.7	8.2	7.7
18	9.4	9.0	8.5	8.0	7.6
19	9.2	8.8	8.3	7.9	7.4
20	9.0	8.6	8.1	7.7	7.3
21	8.8	8.4	8.0	7.6	7.1
22	8.7	8.3	7.8	7.4	7.0
23	8.5	8.1	7.7	7.3	6.8
24	8.3	7.9	7.5	7.1	6.7
25	8.2	7.8	7.4	7.0	6.5
26	8.0	7.6	7.2	6.8	6.4
27	7.9	7.5	7.1	6.7	6.3
28	7.7	7.3	6.9	6.6	6.2
29	7.6	7.2	6.8	6.5	6.1
30	7.4	7.1	6.7	6.3	6.0

or biological reactions. Some groundwaters show little oxygen because of non-contact with the atmosphere. Dissolved oxygen in combination with many other parameters can indicate a stream's condition.

NITROGEN

Nitrogen occurs in water in various states: organic nitrogen, albuminoid nitrogen, ammonia nitrite and nitrate. Organic nitrogen occurs in all living systems, primarily as protein. This total amount of nitrogen is called "organic nitrogen". A protein of this total liberated by the action of alkaline permanganate is called "albuminoid nitrogen". In normal decomposition the organic nitrogen compounds break up to ammonia (NH_3). If oxygen is present the process can continue as the nitrogen is further oxidized to nitrites and nitrates. The nitrogen cycle in combination with other parameters gives good information on water quality. High values of organic nitrogen indicate high numbers of living systems. This probably indicates recent pollution. In clean waters, albuminoid nitrogen is about 50% of the total organic nitrogen. In polluted waters the percentage is much higher. As the nitrogen compounds reach the higher oxidation states (nitrate) it can be assumed that organic pollution is not present or the bacterial population is inhibited.

MINOR ELEMENTS

Many other elements exist in water. Their importance can be significant even in small concentrations. Toxic metals, for example barium, can cause problems in very low concentrations to living systems.

Phosphate compounds are common in water. They form part of the fertilizer system which is necessary for plant growth. In small amounts they may limit growth since most other necessary growth factors are present in water. This has led to the idea that phosphate is the limiting nutrient in plant growth in water system. In some cases, this may be true. Phosphates enter water from three major sources; phosphate rocks, detergents found in sewage, and agricultural runoff. Control of phosphate is important in pollution programs. Concentrations around 1 mg/l and above can cause more growth problems.

CHEMICAL OXYGEN DEMAND

In water there is organic material. At the present time the classification of this material is time consuming and expensive, but it is still important to come up with some indication of its presence. Under physical parameters, the Total Carbon test was mentioned. Chemically there is also a test which indicates organic matter. In this test organic material is oxidized in a boiling acid solution of dichromate. The amount of dichromate used indicates the amount of chemically oxidizable organic matter present. This test has some merit and can give important values for stream analysis. The Chemical Oxygen Demand (COD) test is a collective parameter like the Total Carbon test. No delineation of organic types is possible. And, since that is important, the test is not fully satisfactory. High values of COD indicate high amounts of organic material which probably means pollution. COD values are generally less than Total Carbon values since some carbon compounds resist oxidation.

BIOLOGICAL PARAMETERS

Biological parameters are the most complex parameters involved in the water environment. They are living systems adapting and moving through complex inter-relationships with each other, the water, and the material in the water. It is fascinating to study the wide variety of organisms in a water, but the procedures are time consuming and expensive, and require highly competent help. These kinds of studies are normally used only for research objectives. Fortunately there are several organisms found in water which indicate its quality. Their presence and number indicate whether a stream is fairly clean or heavily polluted. Some of these parameters are: total coliforms, fecal coliforms, and plankton. There also is a collective parameter showing a relationship between the organic material and the bacteria, the Biochemical Oxygen Demand (BOD) parameter.

Biological Indicators are indirect measurements of the quality of a water. Game fish have been used as biological indicators for many years. These fish are sensitive to pollution, so their presence normally indicates a clean stream. On the other hand, bacteria found primarily in the human intestine would indicate sewage pollution if found in a stream.

TOTAL COLIFORMS

The total coliform group is composed of two major parts, fecal coliforms and soil coliforms. The fecal coliform group, composed primarily of Escherichia coli, is present in the intestines of all warm blooded animals. The soil coliform group, primarily Aerobacter aerogenes, is found in soil, on grain and in decaying vegetation. The presence of total coliforms indicates possible contamination by sewage. The presence of pathogens, disease organisms, is also possibly indicated.

The test procedures for total coliforms are relatively easy using the membrane filter technique. Most water plants have this equipment available since drinking water standards limit the number of total coliforms in the water to an average of 1 per 100 ml.

FECAL COLIFORMS

The fecal coliform group contains only that part of the total coliform group which comes from intestinal waste. Their presence indicates, generally, human sewage pollution, and not soil or vegetation contact. New test procedures for fecal coliforms have been developed in recent years using the membrane filter system. The test is more complicated than the total coliform test but is still relatively easy to learn.

Fecal coliforms are restricted in the new guidelines for domestic sewage effluent discharges, and they are becoming an important new indicator of pollution.

PLANKTON

Plankton is a term which normally refers collectively to the algae in a water. The presence of large amounts of algae indicates pollution. The form of the pollution is interesting. Algae, during daylight hours, functions as a plant; that is, it uses carbon dioxide for carbon, sunlight for energy, and minerals from the water to grow, producing more algae and oxygen. In recent years research has shown that primarily phosphates and sometimes nitrates are the limiting factors for algal growth. Where the concentration of these is large sudden algae growth, a bloom, is possible.

Algal blooms normally contain only a few genera. They can impart nauseous odors to the water, kill fish, poison livestock and mussels and seriously interfere with water use.

Major sources of phosphates and nitrates are from sewage and agricultural runoff. Modern sewage treatment plants, under construction, will remove phosphates from the sewage. Older plants will increase their treatment to also remove phosphates in the future. Some lakes (Lake Erie) have serious problems associated with algae blooms.

BIOCHEMICAL OXYGEN DEMAND

Biochemical Oxygen Demand (BOD) is one of the most popular parameters in water analysis. It is also one of the most misunderstood. In order to understand its significance, a brief description of the test itself is necessary. The test consists of adding a small portion of the sample to be tested to a bottle. To this is added a volume of water (BOD water) which contains oxygen, buffers to control pH, and nutrients. The bottle is then placed in an incubator (20°C) for five days. At the end of this period, the amount of oxygen left in the bottle is measured. The difference between the amount of oxygen at the start and the amount left is the amount used or the Biochemical Oxygen Demand (BOD).

In the test procedure, bacteria feed on the organic matter and use oxygen. The test indicates organic matter indirectly by the oxygen consumed. The organic matter indicated is only that part which is degradable by bacteria. Many organic forms are non-biodegradable and are not indicated. Several features of this test must be recognized. First, a seed (bacteria) is necessary for a proper test. In some cases organic material is present in water (industrial waste for example) with few bacteria. Therefore a seed must be supplied for proper results. Second, some organic material is not metabolized or at least is metabolized very slowly by the bacteria. In this case, low BOD values do not mean the absence of organic material. Aromatics fit this case, again perhaps from an industrial waste discharge. The test is a collective parameter and does not indicate specific compounds. Third, the test bottle is not stirred, under standard procedures. This reduces the rate of metabolism during the test. Many people use this test to indicate what will happen in a stream to the oxygen reserve. Streams are mixed (stirred) and direct correlations between the test and the stream are impossible. The test however is very popular. If evaluated properly it provides an important parameter for consideration. BOD values are less than COD values which are less than TC values. Raw sewage has a BOD of about 200 to 250 mg/liter. Some easily metabolized wastes, for example sugar waste from a sugar refinery, have BOD values of several thousand.

PARAMETER INTERRELATIONS

The number of parameters involved in water testing is broad. This is necessary. The uses of water are many and varied; likewise, the waste materials that pollute our streams are also many and varied. Several of the parameters complement each other and give a comprehensive picture of a stream. In this light, it must be emphasized that

-- All stream parameters must be considered
for proper stream evaluation --

There are no general rules that apply in all cases. A thorough understanding of the hydrologic cycle, stream hydraulics, chemical dynamics, and biological interrelationships is necessary for complete evaluation. This should not detract from the idea that the basic fundamental relationships can easily be identified and evaluated.

A model is presented to illustrate some of these basic relationships (Figure 8-1). The model consists of a small water basin with different types of natural source waters, both farm and irrigation lands and a mountainous region. The two source waters join and flow into a reservoir which supplies water to the city and an industrial complex in this case a poorly operated pulp and paper mill. Waste discharges from the paper mill and the city are discharged back into the river.

Monitoring stations are identified on the model (Figure 8-1). These stations will show how the quality of the river is effected by its history. The sites have been selected so that proper hydraulic mixing has been achieved and the stream is of uniform quality upstream from the monitoring station. The stations are below the mixing zone. Table 8-3 summarizes the test data from the various monitoring stations.

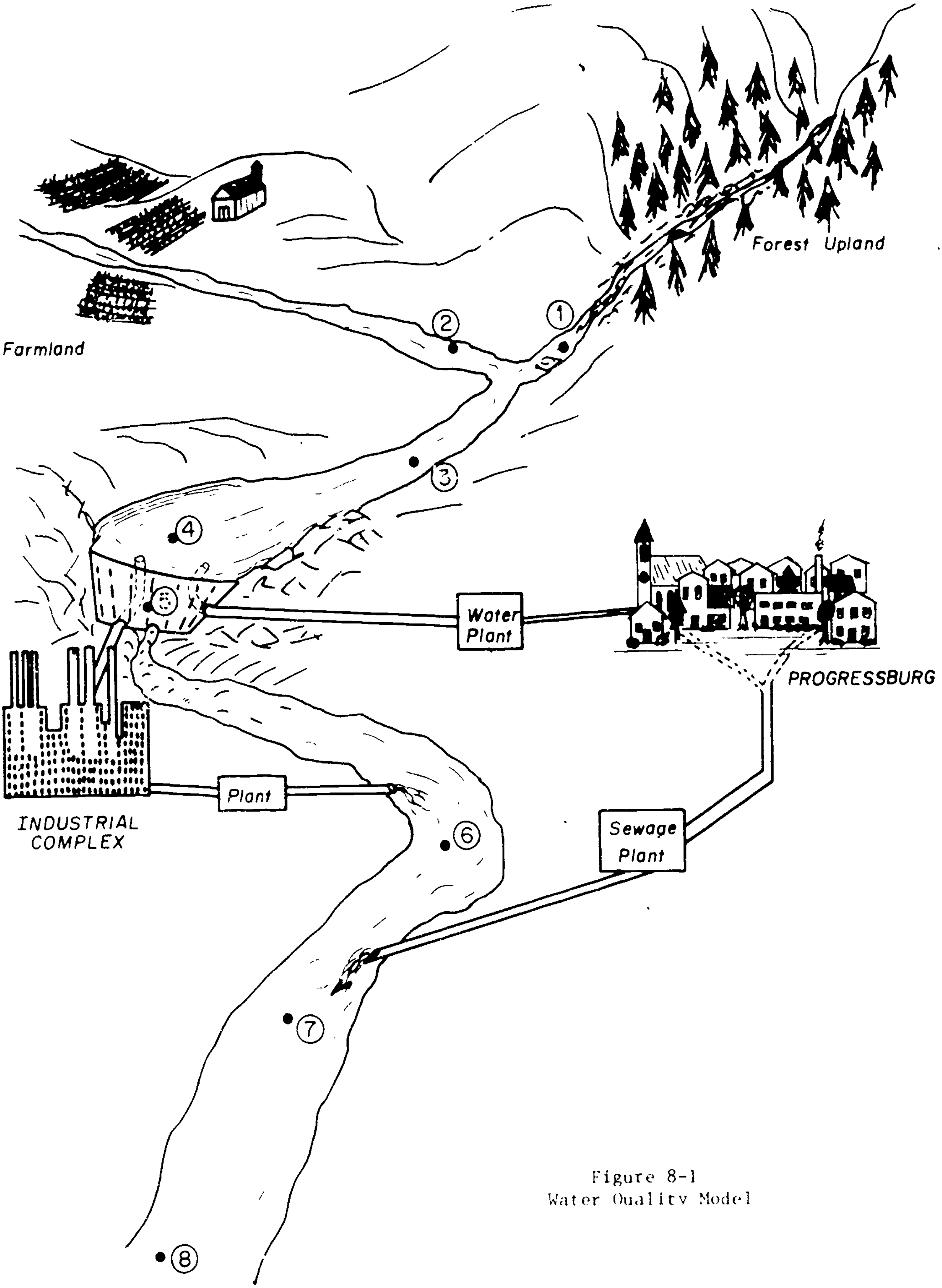


Figure 8-1
Water Quality Model

TABLE 8-3
MODEL PARAMETERS

	Sampling				Oxygen (mg/1)		
	Time						
Stations	Date	Hour	Temp.	pH	Dis-solved oxygen	Saturation Values	Color Units
1	June 6	9 a.m.	10°C	7.1	11.3	11.3	50
2	June 6	10 a.m.	15°C	7.5	9.0	10.2	30
3	June 6	11 a.m.	12°C	7.2	10.7	10.8	42
4	June 6	1 p.m.	15°C	7.2	10.0	10.2	30
5	June 6	1 p.m.	10°C	7.5	8.1	11.3	10
6 ave.	June 6	3 p.m.	17°C	8.4	3.0	9.7	100
7 ave.	June 6	4 p.m.	19°C	7.8	1.2	9.4	130
8 ave.	June 6	5 p.m.	17°C	7.7	4.8	9.7	105

TABLE 8-3 (Cont.)
MODEL PARAMETERS

			Solids (mg/1)					
Stations	Odor	Total	Total		Suspended		Dissolved	
			Fix	Vol	Fix	Vol	Fix	Vol
1	0	100	90	10	50	2	40	8
2	5v	150	130	20	25	15	105	5
3	2v	130	110	20	30	10	80	10
4	1v	160	155	5	10	0	145	5
5	0	185	170	5	30	2	155	3
6 ave.	15v	800	420	380	150	120	270	260
7 ave.	20v	1000	450	550	160	210	290	340
8 ave.	disagreeable 15.	700	430	270	140	150	290	120

MONITORING

The selection of a monitoring site or station is the first step in developing a surveillance system. The site should complement the overall network and provide useful information for the objectives sought. Ordinarily, a stream site is selected to show what is happening upstream and how it is affecting the water quality. In a lake or reservoir area, a site is selected to indicate quality changes due to activities around and on the lake. Vertical sampling is important as quality parameters generally vary with depth. Groundwater sites, normally in wells, are used to determine the normal aquifer flow rate, mineral content, dissolved gases, and general water quality. Groundwater sampling is on the increase. There are two general reasons for this. Available supplies from surface waters are being reduced and disposal wells for pollutants are becoming popular. This possible kind of pollution must be monitored.

SITE SELECTION

A. Stream Sites

The proper selection of a stream site involves many steps:

1. Walk the entire stretch of stream in question. Boats or air boats are also useful in this step. Learn the stream hydraulic structure, flow patterns, bank erosion, high and low water marks, vegetative cover, agricultural patterns, access roads and population habits.

2. Map all waste discharge points and tributary confluences.

3. Measure general stream flow rate and flow from all tributaries and waste discharge points. Discharge rates from stream quantity monitoring stations and city or industry stations should be consulted.

4. Measure quality parameters from tributaries and waste discharges.

5. Select sites based on objectives sought using data from steps 1 through 4. The sites should be easily accessible. A two-hour hike to the site can cause operational problems. The site should be below the mixing zone so one

TABLE 8-3 (Cont.)
MODEL PARAMETERS

Station	Coliforms/100 ml Total	 Fecal	mg/l BOD	 COD
1	10	0	0	0
2	280	50	20	25
3	150	20	10	15
4	80	10	---	---
5	30	6	10	15
6	35	7	400	700
7	5×10^5	4×10^5	450	800
8	3×10^3	6×10^2	200	800

It is assumed that it is spring and daily variations, due to city and industrial use, have been averaged for the data presented. Obviously, the city uses little water and applies little waste to it during the night period. The industry is also only working during the day. The basin is close to sea level elevations. Analysis of the data presented in Table 8-3 must be done vertically as well as horizontally. This means each parameter must be viewed in space (up or down the river system - vertically in the table) and each station must be viewed through all the parameters at one time (horizontally across the table).

STATION #1

Monitoring Station #1 is characteristic of a spring mountain type stream. The temperature is still fairly cold from snowmelt water. The dissolved oxygen is at saturation indicating good turbulent mixing in the stream with little organic material. Color and turbidity units indicate a washout of color from forest humus and a fast flowing stream carrying spring washoff silt. The solids data indicate little organic material (volatile) and about an even split between suspended material and dissolved material. The chemical data show very little in the water. The pH is near neutral and considering the hardness, this is a very soft water. Biological parameters show a relatively unpolluted stream.

-- All in all Station #1 data show an unpolluted natural mountain stream --

STATION #2

Monitoring Station #2 is characteristic of a stream containing drainage from an irrigated farm land area. The dissolved oxygen is a little less than saturation probably due to some decomposition processes. There is some BOD confirming decomposition. Color is still high from vegetable organic material and there is a distinct vegetable odor (v) in the water. The slower moving stream shows long turbidity values compared to the mountain stream, which seems reasonable. The solids breakdown indicates a buildup of dissolved material and a reduction in suspended material. Water contact with the soil should introduce some more dissolved species and slow movement and the soil filtering action should reduce suspended material.

The chemical analysis shows a soft water with a little more basic pH and alkalinity, again probably due to soil contact. The biological parameters indicate increased coliform counts, predominantly soil coliforms from agricultural soil runoff. No nitrates are evident showing good soil and fertilizer practice.

-- All in all, Station #2 data shows a clean stream eminating from an agricultural area --

STATION #3

Monitoring Station #3 is downstream from the confluence of the two streams. The quality parameters should show an averaging of the separate streams. The averaging will depend on the quantity of flow. If the mountain stream is the major stream then Station #3 should look similar to Station #1. If the agricultural stream has the most flow then Station #3 will reflect that. In addition to straight averaging, it should be recognized that chemical reactions, rates of reactions and biological systems can change when dissimilar waters are mixed.

In this case, it appears from the data that each river is contributing about 50% of the flow. Most parameters appear to be diluted by the joining.

-- All in all, Station #3 indicates a general 50-50 mixture of the mountainous and agricultural streams, a relatively clean, softwater stream with very little material in it --

STATION #4
AND
STATION #5

Monitoring Stations #4 and #5 are in the supply reservoir. This is not a large reservoir and it is influenced by the incoming stream. Station #4 is at the top of the reservoir and Station #5 is at 50 feet depth. The temperature is higher than those of #1 and #2 indicating larger surface area and more warming on the surface. Station #5 is colder showing that the reservoir is stratified. If the reservoir is not too large, it may have overturned earlier in the Spring. The water in the lower section of the reservoir seems to be the older water. New water (considering the temperature) would enter somewhat below the surface but above the 50 foot depth of Station #5.

There appears to be some mixing vertically between the entering stream and the surface. The color is higher at the top than the bottom. Turbidity and suspended material seem to be settling out toward the bottom. Turbidity and suspended solids are increasing with depth. There is a slight increase in BOD with depth but a value of 10 mg/1 is insignificant.

-- All in all, the reservoir shows a dilution of the stream parameters, a warming on the surface with stratification below. Chemical parameters are modified by the incoming stream and the present older water in the reservoir --

STATION #6

Monitoring Station #6 shows the significant influence of a paper and pulp mill. This particular one is poorly operated and its waste discharge is seriously polluting the stream. Several parameters have changed significantly. The temperature has increased to 17°C. Since most reservoir intakes are below the surface an increase in heat content of from 2 to 7°C has occurred. All the chemical parameters indicate a large increase in dissolved and suspended material. Suspended solids have increased to 530. About half of these increases is organic material. This is expected from an organic type plant. Sulfates show an increase due to its use in processing pulp. Dissolved oxygen is down indicating some biological and chemical demand. Wastes from pulp plants normally contain chemicals in reduced form. Some oxygen is used chemically to oxidize these in addition to oxygen requirements of bacteria.

The biological parameters show an interesting situation. The BOD test shows an increase in biodegradable organics. The coliform group population, however, is very small. This indicates that organic material is being discharged into the stream but concurrent coliform bacteria are not. The COD test indicates that about one-half of the organic material is not biodegradable or at least only slowly. Many wood products fall into this category.

-- All in all, Station #6 shows a polluted stream. The waste discharge from the

industrial plant is significantly
changing the clean stream --

STATION #7

Monitoring Station #7 is downstream from the cities' effluent sewage discharge line. It shows the cumulative effect of the industrial plant and the city. The temperature has increased again, the dissolved oxygen is practically gone, the BOD has increased to 450 mg/l, the bacterial (fecal and total coliforms) population has increased to 500,000/100 ml from the sewage discharge and the stream is badly polluted. With the values given, a complete absence of oxygen could be expected downstream. This would produce obnoxious odors (mercaptors) and turn the river water black. Organic nitrogen is now present in significant amounts. Ammonia is present indicating only partial oxidation to nitrates. Fish life is dead (very little oxygen left). Fixed solids are up slightly and organic solids (volatile) are up to 550 mg/l.

-- All in all, the city discharge has
further degraded the stream. This
stream is badly polluted --

STATION #8

Monitoring Station #8 is several miles downstream from Station #7. No general discharges, other than runoff, occur in this stretch of the river. The data indicate a beginning recovery of the stream. Dissolved oxygen is increasing (back to 4.8 mg/l). The water is cooling off. Solids are decreasing due to biological and physical (settling) action. Bacterial counts are down and the BOD is reduced. There still is a high value of COD showing that some organic material is non-biodegradable. Most of this material came from the industrial plant. Nitrogen is shown now toward the oxidized state. If no more pollution is discharged into the stream further recovery should be expected.

-- All in all, the stream is in the recovery
stage, but is still badly polluted --

The model shown here can be varied and examined under many conditions. Depending on background knowledge, it can develop from the more simple to the most complex analysis. Many of the more complex analysis models point up a lack of basic knowledge in stream dynamics. New research, particularly in stream biology is badly needed.

Problems:

1. Select a small river basin (or lake) for parameter study. Walk the river and identify on a map all pollution sources as to type of waste and location. Collect all recent data on quality and quantity parameters for the river and the pollution sources including basin standards. Draw a map of the river basin and show major pollution sources, miles between sources, flowrates and monitoring stations.

2. Develop a comprehensive picture of how the basin works and answer the following questions:

   a. How does the flow in the river change during the year? Why?

   b. Select 4 parameters and plot how they change from the top of the basin to the bottom of the basin. Why are they changing?

   c. Do changes depend on the time of year?

   d. Draw a dual plot of dissolved oxygen (saturated) and dissolved oxygen (monitored) (y) as a function of river distance (x). Why do oxygen variations occur (be specific)?

   e. Did you find any violations of stream standards? Who is to blame for any violations?

   f. What is the condition of the river? Is it a clean river? Who has major responsibility for the river's condition (be specific)?

MONITORING

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SITE SELECTION

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3. Measure general stream flow rate and flow from all tributaries and waste discharge points. Discharge rates from stream quantity monitoring stations and city or industry stations should be consulted.

4. Measure quality parameters from tributaries and waste discharges.

5. Select sites based on objectives sought using data from steps 1 through 4. The sites should be easily accessible. A two-hour hike to the site can cause operational problems. The site should be below the mixing zone so one

sample position will represent the whole cross section. If this is not possible, compositing, vertically and horizontally across the stream will be necessary. Stream testing at various distances below discharges points will establish the mixing zone length. This length will change depending on stream hydraulics. When the stream is flowing full, more mixing is present and the mixing zone is shorter. During low flow rates, the reverse is true and mixing zone may be extended downstream. Obviously a site should be selected which is below the mixing zone under most conditions.

MODEL

Figure 9-1 shows a surveillance system with possible sites for a model stream. This figure was also used in Chapter 8. The sites shown in Figure 9-1 were selected to show the influence of various uses on water quality, and Stations 9 and 10 were selected to meet discharge permit requirements established under Public Law 92-500. It should be noted that each stream site has a control site above it. An evaluation between these sites should establish changes in water quality.

CAUTION

A caution is necessary to site selection. Occasionally the main river may be at a higher stage than a tributary stream. If a site, for example Station #2 - Figure 9-1, is too close to the confluence, then it may be influenced by the main river and not measure the tributary quality.

LAKES

B. Lake Sites

Figure 9-2 shows a model of a surveillance system for a lake or reservoir. Again, in this case, the sites are selected to mark changes in water quality due to use. Stations 1 and 2 measure the quality of tributaries entering the lake. Stations 3 and 4 monitor the effects of public swimming and camping on lake quality. Station 5 (at the dam site) measures the quality of water leaving the lake. This may be in the exit stream or in a discharge to a user, for example, irrigation, industry or a city.

The lake sites should also be sampled at various depths. If these samples show little change their

What's going on at the surface is not necessarily the same at lower depths.

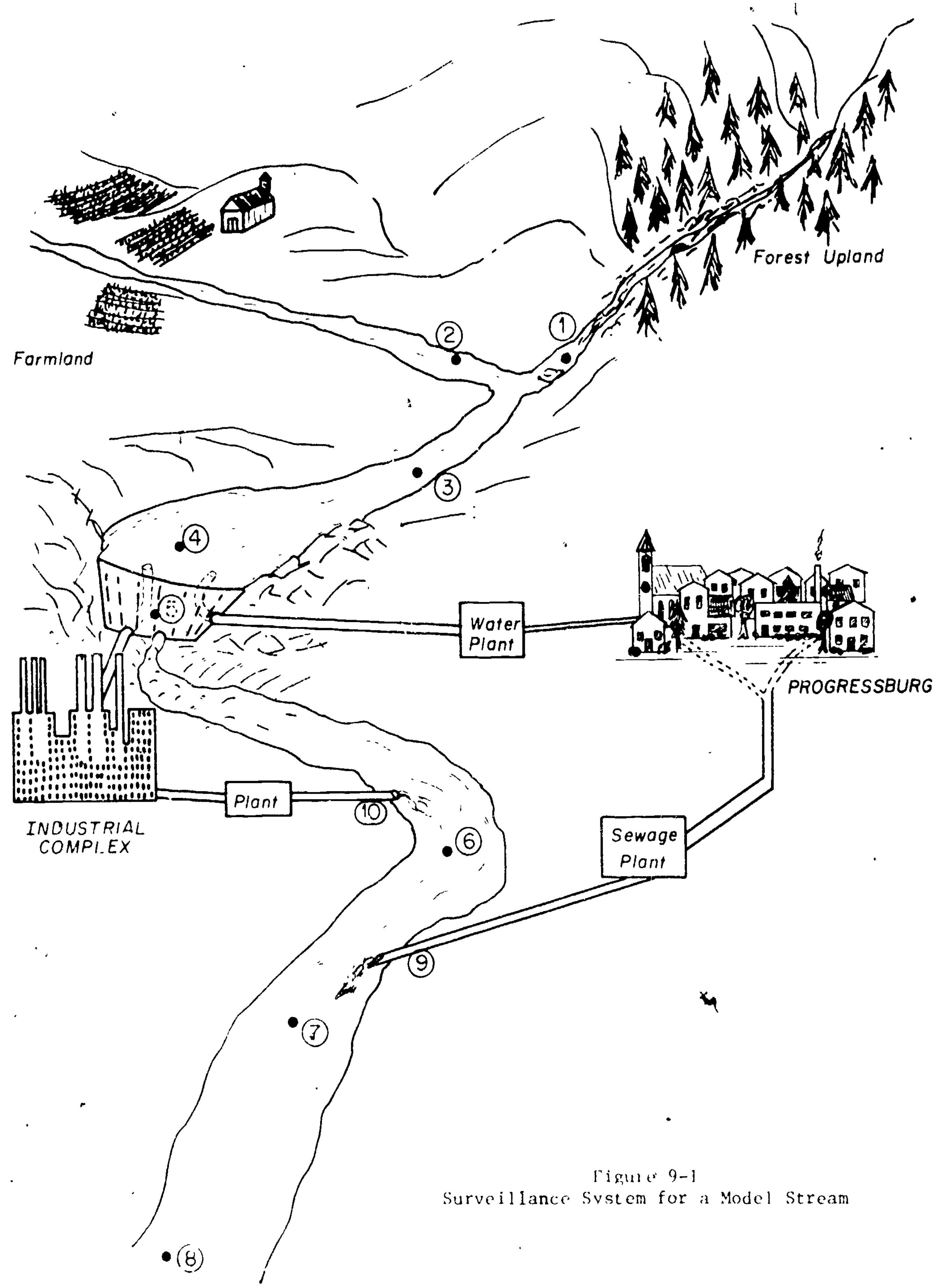


Figure 9-1
Surveillance System for a Model Stream

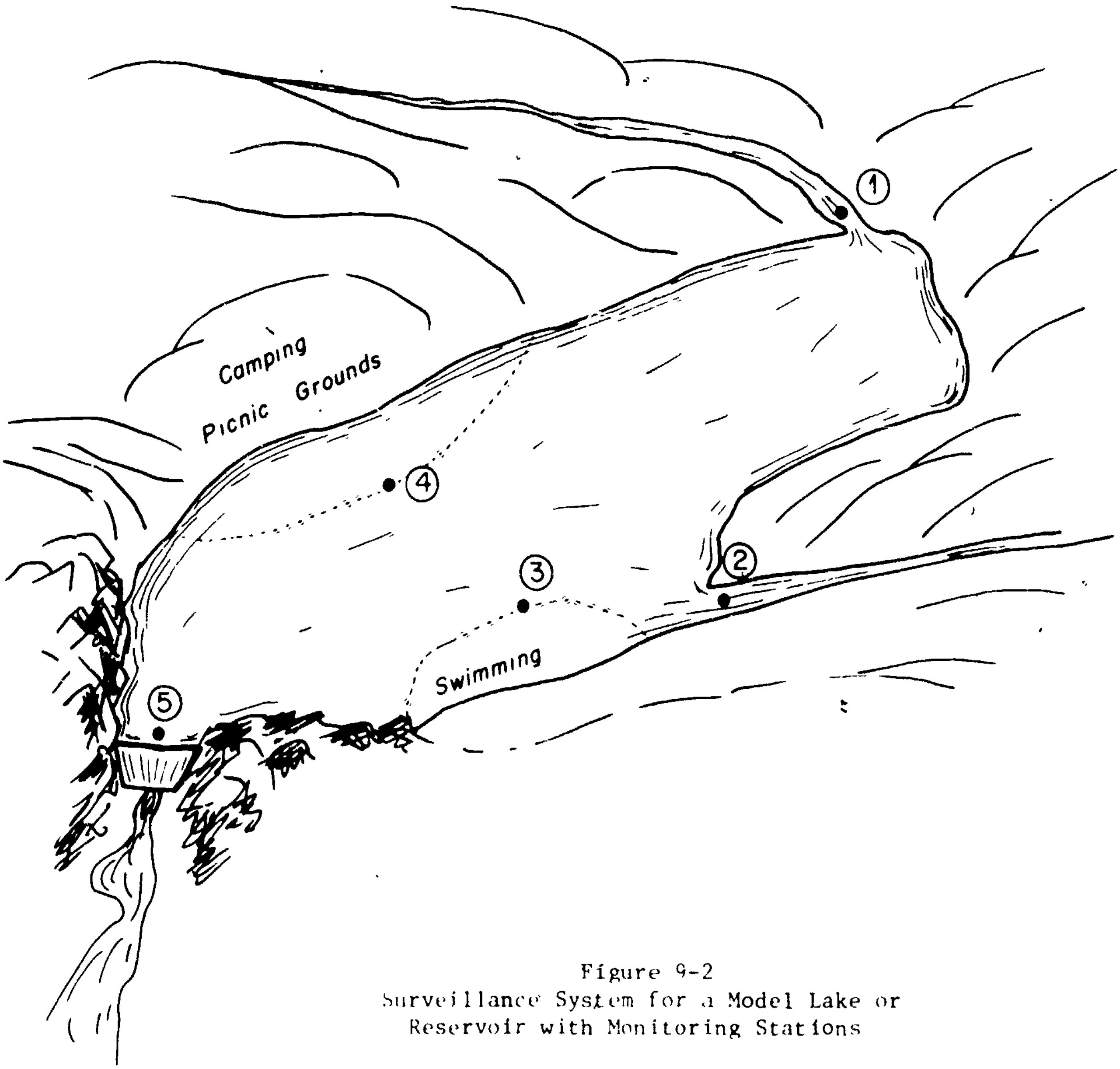


Figure 9-2
Surveillance System for a Model Lake or
Reservoir with Monitoring Stations

sampling frequency can be reduced. Camping, boating, and swimming are seasonal sports: therefore, off season sampling frequency can be reduced.

GROUNDWATER

C. Groundwater Sites

Figure 9-3 shows a model of a groundwater surveillance system. This model contains a normal river basin with agriculture, a city with an infiltration-evaporation system for sewage disposal, and a sanitary landfill for garbage disposal, and an open pit mine. Below the surface the model shows a confined aquifer (water trapped between nonporous rock layers) and a groundwater table (not confined) which slopes toward and discharges into the stream.

Four stations were selected for surveillance. Station #1 is the control site for the basin. It reflects the quality of the groundwater at the upper reaches of the basin. Station #2 indicates the effect of agriculture on the groundwater. Agricultural drainage, particularly from feed lots operations can drastically change groundwater quality.

Station #3 monitors the effects of the city disposal systems. Evaporation and percolation through the soil is presently being promoted as the ultimate sewage treatment process. Transmission of organics and bacteria through the soil must be monitored. Sanitary landfill operations can also affect groundwater quality. In periods of high water tables, water contact with the garbage is possible. Dramatic changes in water quality could result.

Station #4 monitors the effects of surface mining. Open pits provide a method for serious changes in water quality. Frequently, these pits form ponds where minerals are dissolved, acids produced, and dissolved oxygen reduced. Flow from these areas into streams or groundwater tables must be monitored.

At all stations some monitoring of the confined aquifer is also necessary. In general, little water will flow between the normal groundwater table and the aquifer, but wells drilled to tap the aquifer may provide a mechanism for polluting it. Sampling sites for groundwater may be farm wells, city or industry wells or wells specifically drilled for monitoring.

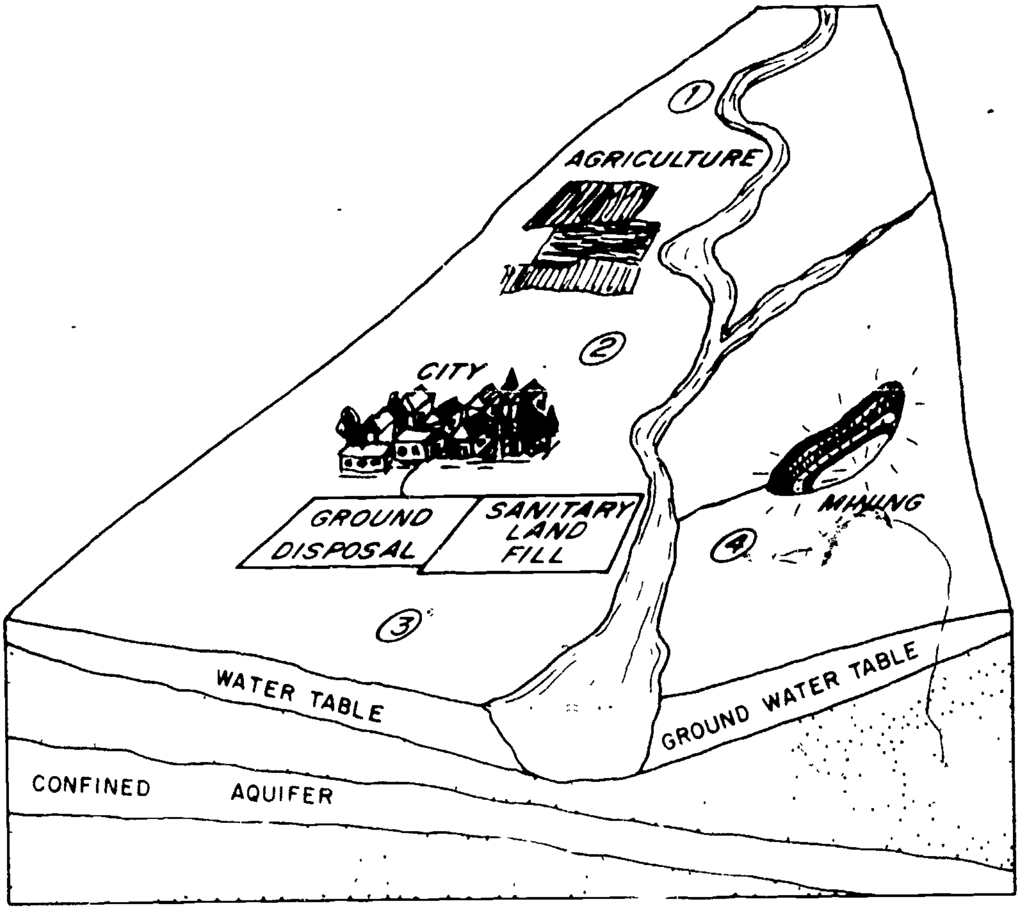


Figure 9-3
Surveillance System for a Ground Water Model

SAMPLING FREQUENCY

Samples of surface or groundwaters should be obtained at intervals such that no important change will go unnoticed. This requirement predicts the frequency of sampling. In some cases, daily or weekly sampling is sufficient since little change has occurred. In other cases, quality parameters are changing continuously and monitoring should reflect these changes. In the final analysis, the frequency of sampling is based on economics. It would be nice to have all parameters measured everywhere always, but this is impossible. A compromise between objectives to be met and money available always sets boundaries on sampling frequency.

The J. S. Geological Survey has followed the practice of collecting samples daily as the minimum frequency necessary for chemical parameters. This compromise may be sufficient for most streams and lakes but obviously is inadequate for waste discharges which vary continuously.

This chapter will develop some of the monitoring techniques for:

A. Periodic sampling, and for
B. Continuous sampling.

PERIODIC SAMPLING

A. Periodic Sampling

When water quality parameters change slowly, periodic or "grab" sampling is sufficient.

Equipment for grab sampling is varied. General considerations require a wide mouthed bottle for actual sampling. This provides easy flow of water into the container with little turbulent and change in dissolved gas content. The container material should not react with the water. Obviously a material which reacts with the water will change the water quality. Another requirement is ease in handling reduced breakage, and low cost. The trend in recent years has been away from glass containers and toward polyethylene teflon or plastic containers.

Before use, all bottles must be thoroughly cleaned and rinsed with distilled water. New bottles should be cleaned and then soaked for several days to remove possible surface contamination. If the bottles are used for bacterial testing, then they must be sterilized. The cleaning, rinsing in distilled water and the sterilizing processes prevent cross contamination of the sample with some other source. If chlorine is present in the sample and bacterialogical examinations are to be run, then

0.1 ml of 10% sodium thiosulfate is added to each sample bottle of 120 ml capacity. This reduces (chemically) the chlorine and prevents bacterial kill due to the chlorine.

Grab sampling from a boat or the bank proceeds in these steps (see Figure 9-4):

1. If water is polluted or pathogens are possible, use a rubber glove,

2. Hold bottle by its base,

3. Remove stopper and protective hood (foil) if sterilized (keep hood sterile),

4. Plunge bottle into stream mouth down, about 6 to 12 inches. Avoid surface scums and floating material (example, oil),

5. Point bottle into flow and tip up to fill. Fill bottle with at least 150 ml of sample. If dissolved oxygen is not a test parameter, then some air space is left at top of bottle. If dissolved oxygen is a test parameter, then fill bottle completely and seal to prevent in or out flow of gases. Keep flow smooth; reduce turbulence, for gas testing,

6. Remove bottle from water, cap and replace sterile hood (foil), if required, back on the top of the container, and

7. Tag and record pertinent information concerning site, time, date and sample number.

Grab sampling from a bridge follows these basic steps (see Figure 9-5):

1. Use a nylon rope and a weighted frame containing the sample bottle,

2. Remove cap and sterile hood if required,

3. Lower bottle and frame from bridge (downstream side) into stream,

4. Pull bottle toward bridge to fill,

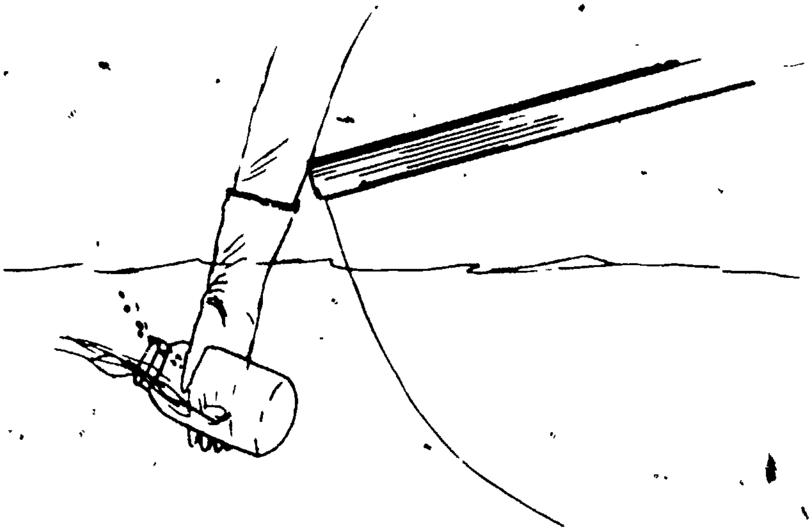


Figure 9-4
Grab Sampling from a Boat or Shore

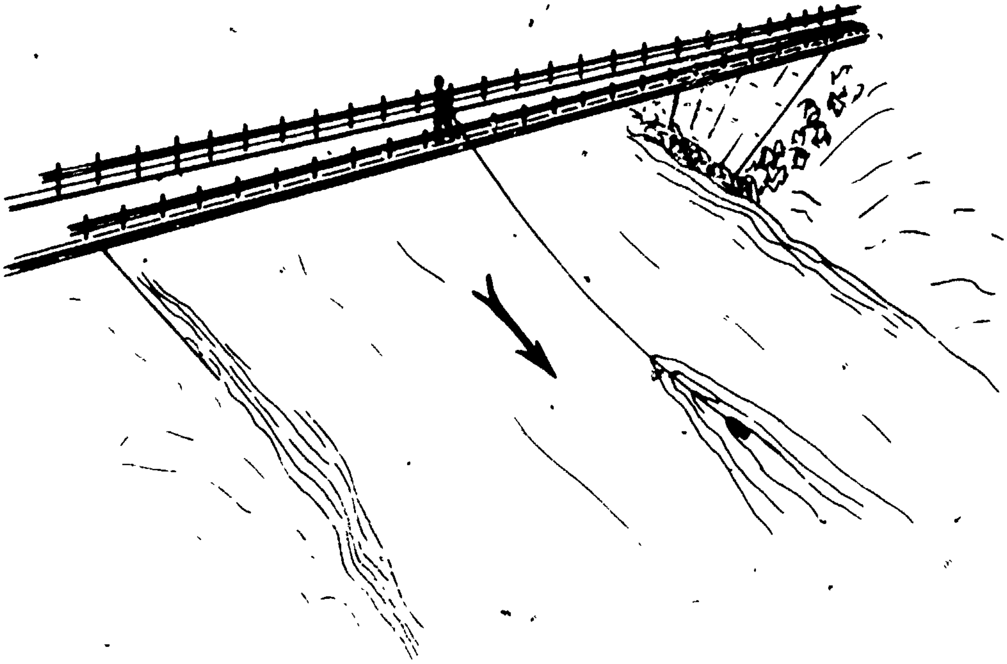


Figure 9-5
Grab Sampling from a Bridge

5. After filling, pull bottle to bridge surface (watch out for bridge structure),

6. Reseal and cap with sterile foil hood,

7. Tag and record pertinent information concerning site, time, date and number.

CAUTION

Some note should be made about safety concerning sampling. There are two major hazards in sampling: the environment and disease. Environmental hazards include snakes, falling in the water, animals, ice, electric power lines, rotting timbers on old bridges, falling off bridges, motors and equipment and traffic. Disease hazards are always possible in handling water samples. Rubber gloves should be used and hands should be washed with soap before eating in the field. Bacterialicidal soap is useful.

FIELD TESTS

Field tests must include:

1. Temperature,
2. pH,
3. Dissolved oxygen, and
4. Specific conductance

These parameters can change with time. The parameter, pH, is sensitive in many waters to biological action and to gas interchanges with the atmosphere. For this reason, it should be measured in the field. Acidity and alkalinity are also recommended for field testing.

There are several other parameters which can change with time. As a matter of fact, all parameters change with time and unless they are measured in the field or preserved for later laboratory testing, their magnitude will be in doubt.

SAMPLE CHANGES

The changes that take place are physical, biological, and chemical. It must be remembered that the water in the sample bottle is now in a new environment. New adjustments to this environment will occur. Adsorption on the container or on soil particles may occur. The container may contaminate the sample with material that may not be cleaned off. Metal ions may precipitate as hydroxides or oxides or form complexes which adsorb surfaces. The pH may change affecting the kinetics (speed up or slow down) of reactions. Dissolved oxygen, or its absence, may affect the valence states of oxidizable, or reducible species. Biological reactions can drastically change the water sample. In the new environment (water in sample bottle), algae may grow changing the pH balance and thus affecting the entire chemical structure of the water. Algae may die, increasing the bacterial population feeding on them and again change the entire chemistry of the water. Since parameter data must reflect what is going on at the sample site, sample preservation must be considered.

SAMPLE PRESERVATION

There is some difference between analysts as to proper sample preservation techniques. In general, the techniques are intended to:

1. Retard biological reactions,
2. Retard the hydrolysis and polymerization of chemical compounds, and
3. Reduce the volatility of molecules by ionizing them.

These techniques cannot be done all at once. For example, reduction of volatile compounds requires a high pH (add NaOH). A high pH will kill bacteria and algae and obviously not preserve them. Biological parameters are preserved by refrigeration or cooling. Therefore, in order to test for all parameters, several samples must be taken and preserved in different ways. Proper marking of tags is essential for later analysis.

Table 9-1 gives the general preservations that are used to retard changes in samples. In general refrigeration at a temperature of 40°C or less is the best technique.

Table 9-2 gives specific preservatives for sample protection.

Both Table 9-1 and 9-2 are the techniques approved by the Regional Analytical Quality Control Coordinators of the U. S. Environmental Protection Agency. They are reported in the text, "Methods for Chemical Analysis of Water and Wastes 1971," published by the U. S. Government Printing Office stock number 5501-0067.

TABLE 9-1
GENERAL SAMPLE PRESERVATIVES

Preservative	Action	Applicable to:
$HgCl_2$	Bacterial Inhibitor	Nitrogen forms, Phosphorus forms
Acid (HNO_3)	Metals solvent, prevents precipitation	Metals
Acid (H_2SO_4)	Bacterial Inhibitor	Organic samples (COD, oil & grease, organic carbon, etc.)
	Salt formation with organic bases	Ammonia, amines
Alkali (NaOH)	Salt formation with volatile compounds	Cyanides, organic acids
Refrigeration or freezing	Bacterial Inhibitor	Acidity - alkalinity, organic materials, BOD, color, odor, organic P, organic N, carbon, etc., biological organisms (coliform, etc.)

As mentioned, there is some difference between analysts as to sample preservation. The U. S. Geological Survey recommends breaking samples into filtered and unfiltered (at the field site) and then refrigerating or adding preservatives after filtering. With turbid waters, this technique has its merits; because the surface areas, associated with the turbidity, can rapidly change the properties of the sample.

CONTINUOUS
SAMPLING

B. Continuous Sampling

In recent years, automated or continuous sampling equipment has come on the market. This equipment can only monitor a few parameters and must be supplemented with periodic sampling. The equipment can, however, provide useful information ~~for~~ pollution abatement programs. For example, if a stream parameter, continuously monitored, should suddenly change, then

TABLE 9-2
SPECIFIC SAMPLE PRESERVATION

Parameter	Preservative	Maximum Holding Period
Acidity-Alkalinity	Refrigeration at 4°C	24 hours
Biochemical Oxygen Demand	Refrigeration at 4°C	6 hours
Calcium	None required	7 days
Chemical Oxygen Demand	2 ml H_2SO_4 per liter	7 days
Chloride	None required	7 days
Color	Refrigeration at 4°C	24 hours
Cyanide	NaOH to pH 10	24 hours
Dissolved Oxygen	Determine on site	No holding
Fluoride	None required	7 days
Hardness	None required	7 days
Metals, Total	5 ml HNO_3 per liter	6 months
Metals, Dissolved	Filtrate: 3 ml 1:1 HNO_3 per liter	6 months
Nitrogen, Ammonia	40 mg $HgCl_2$ per liter - 4°C	7 days
Nitrogen, Kjeldahl	40 mg $HgCl_2$ per liter - 4°C	Unstable
Nitrogen, Nitrate-Nitrite	40 mg $HgCl_2$ per liter - 4°C	7 days
Oil and Grease	2 ml H_2SO_4 per liter - 4°C	24 hours
Organic Carbon	2 ml H_2SO_4 per liter (pH 2)	7 days
pH	Determine on site	No holding
Phenolics	1.0 g $CuSO_4$/1 + H_3PO_4 to pH 4.0-4°C	24 hours
Phosphorus	40 mg $HgCl_2$ per liter - 4°C	7 days
Solids	None available	7 days
Specific Conductance	None required	7 days
Sulfate	Refrigeration at 4°C	7 days
Sulfide	2 ml Zn acetate per liter	7 days
Threshold Odor	Refrigeration at 4°C	24 hours
Turbidity	None available	7 days

indications are that some problem has developed. This might be a problem in the instrument and therefore not real. This must be verified by a field check. If the change is real then a field check would also decide on the pollution problem.

PLANT OPERATION

Continuous monitoring also is useful in waste treatment plant operations. Variations and trends give the operators significant data on plant efficiency and stability. With the advent of the U. S. Environmental Protection Agency's Permit System, established under Public Law 92-500, monitoring, both periodic and continuous, will increase in waste treatment plants.

Several planners have visualized automatic monitoring equipment at sites throughout river basins. The data produced from each site would be stored at each site and also delivered in real time (not delayed) by telecommunications to a central computer. This computer would be programmed to perform surveillance functions and notify proper administrative personnel if significant variations had occurred.

At this time only a very few of these surveillance systems are operational in the United States. The equipment reliability and cost has delayed use. Future engineering development will improve this picture.

There are two basic elements in continuous monitoring: The sampling unit and the test unit.

THE SAMPLING UNIT

The sampling unit is a delivery system. It provides contact between the water and the parameter sensor. Several methods have been used for this system. One system places the sensors on a platform or in a container in the water itself (in situ monitoring). Power lines and information lines are attached to the shore or a bridge. This system is an operational nightmare. Changes in water heights, freezing of sensors, clogging of sensors, damage from floating objects and vandals and difficulty in instrument maintenance are common problems.

Some work also has been done in lake monitoring using the in situ method. Instruments are attached to buoys and powered by batteries. These, too, have produced operational problems resulting in high maintenance and replacement costs.

In situ monitoring and analysis is the best system if it works. Unfortunately, operational problems have reduced its use to short term problem solving functions. A second method is to pump the water from the stream or lake through a pipe to the sensors. The sensors would be located in a structure on shore. The structure would have suitable power and controlled temperatures. Valuable instruments are protected and maintained a fairly constant temperature. Vandal problems are not eliminated but somewhat reduced.

A general schematic of this second method is shown in Figure 9-6. In cold weather climates, the intake line is normally placed under the low water line and ground surface. This reduces freezing problems. Maintenance of the shelter, flow lines and pumps is required.

In general, the lines from the site to the shelter have dimensions greater than one inch. This provides more flow of water than is needed but reduces clogging and, hopefully, parameter variations due to pumping.

CAUTION

> In all cases, a comparison must be made between data automatically numbered and tested, and data from normal test procedures. This will insure that what is being recorded is accurately what exists.

The water from the sample line flows through a sensor chamber to a waste line. This chamber has several electrodes in it which measure various parameters. If spectrophotometric techniques are used, additional lines are used leading from the sensor chamber before finally being vented to the waste line.

SENSOR CHAMBER

Electrode sensors and probes rest on a platform support with the sensing elements extending into the flow-through chamber. Some installations have single flow-through cells for each sensing system. If the sensors (electrodes) are mutually independent then this is not necessary. Figure 9-7 illustrates the general scheme. Spectrophotometer monitoring depends on the specific absorption of a narrow band of wave length.

SPECTROPHOTOMETRIC LINES

In order to develop this "color" (wave length) sometimes chemicals are added which produce the specific absorption. If the absorption is

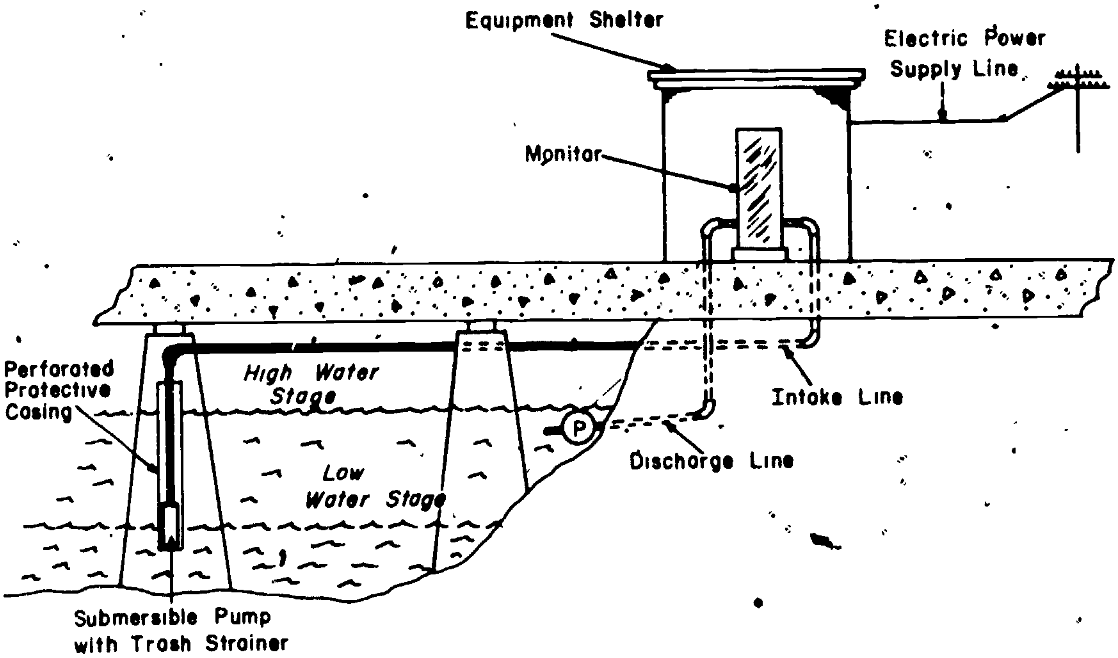


Figure 9-6
Sampling System

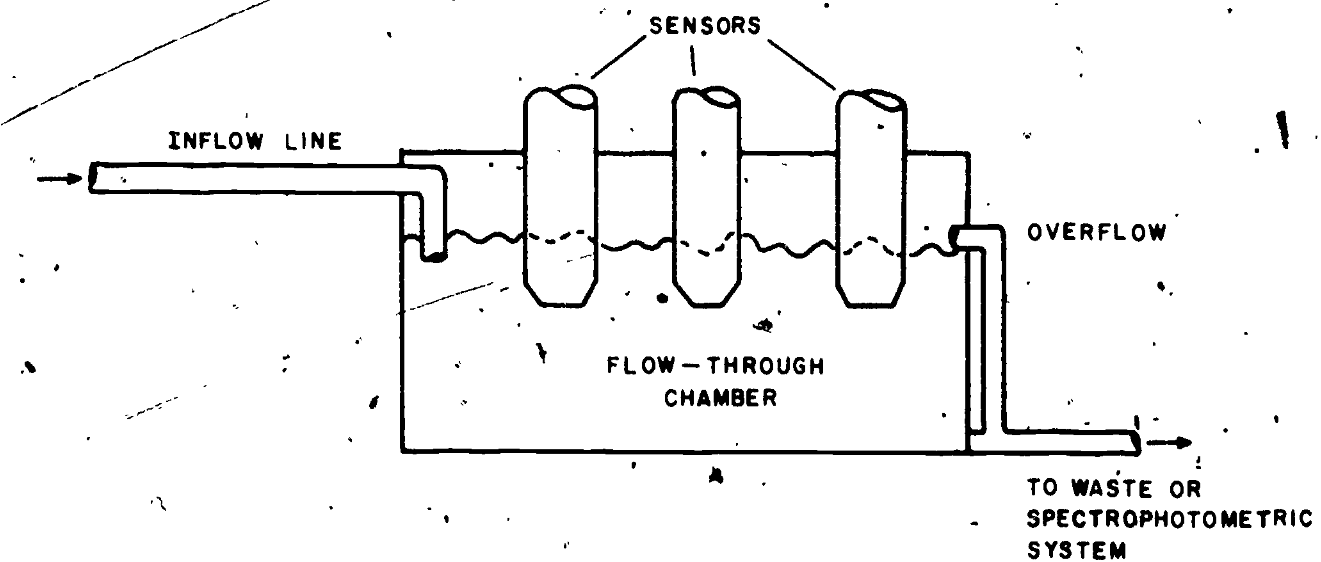


Figure 9-7
Sensor Chamber

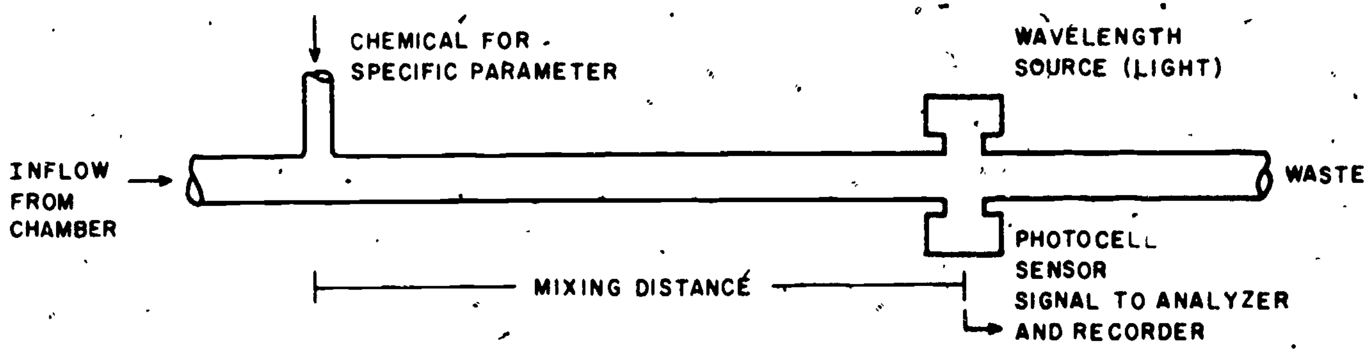


Figure 9-8
Spectrophotometric Monitoring

proportional to concentration, Beer's-Lambert Law, then a photoelectric light cell can sense and measure the concentration. Since all parameters, which are measured in this way, require different chemicals and wave lengths, separate flow lines to each of these sensors is required. Figure 9-8 shows the general scheme for this kind of monitoring.

ELECTRODES

Electrodes are used, almost exclusively, for determining free ion concentrations in solution. Examples of these electrodes, shown in Figure 9-9, consist, generally, on a membrane surface, an internal solution and a probe.

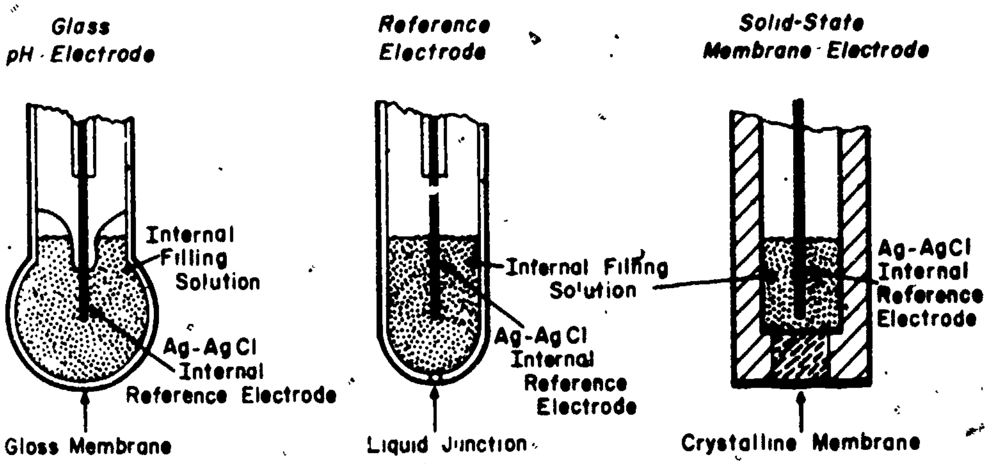


Figure 9-9
Electrode Systems

Membranes are used to separate interfering ions from the ion to be monitored. For example, in Figure 9-9, the pH electrode membrane passes hydrogen ions through the membrane and blocks other interfering ions. The internal solution transmits the electrical potential to the metal electrode and a voltage is produced. If this is connected to a reference electrode (Figure 9-9), then a voltage proportional to the hydrogen ion concentration is produced and a pH reading can be made. Reference electrodes have a constant potential and therefore can be used as a standard. In general, the higher the hydrogen ion concentration, the higher the voltage between the pH electrode and the reference electrode.

Many specific ion electrodes are now coming on the market. These offer an important tool to the water quality specialist which is needed for proper monitoring.

CLOGGING

Electrode systems have problems in measuring environmental parameters. The main problem is one of clogging. Most membranes are easily clogged from silt, algae, bacterial slimes and chemicals. This causes a change in potential and thereby data information. The problem varies from location to location and from season to season. Monitors of this electrode type normally require maintenance every week in order to produce good data.

ANTI-CLOGGING

Many companies are developing anti-fouling systems for their electrodes. One of these is a wiper blade which periodically clears the membrane surface. Others use vibrating bars to keep the surface free of suspended material. Automatic flushing with chlorine water or with water jets are also methods for cleaning the sensor membranes. Ultrasonic vibrations have also been used with poor results. Membranes degrade, glass breaks and sensors are ruined. None of these methods are completely reliable and periodic maintenance and recalibration are required.

TEMPERATURE EFFECTS

Electrodes are also expensive and breakable. Many are made of glass and require gentle handling. Floating material can easily damage them when they are used in situ.

Temperature can also cause problems. The reactions at the electrode surface are temperature dependent; therefore, the instrumentation must have a temperature probe which readjusts the sensoring instrument.

PROBES

Dissolved oxygen, conductivity and temperature are usually measured or monitored by the use of various types of probes. Probes have similar problems as do electrodes. They are somewhat fragile, need repeated calibration, and maintenance requirements must be carried out periodically. However, they are subject to fewer interferences and usually are used alone, that is, they do not require a standard reference electrode.

The spectrophotometric system also has problems. The system depends on:

1. Determining a specific wave length for a specific ion (may require adding a chemical to produce a complex necessary for absorbance),
2. Shining this wave length across the water sample, and
3. Reading the amount absorbed by the specific ion or its complexed form.

TURBIDITY PROBLEMS

If turbidity is present, there may be interference in step number 3. The specific wave may absorb on the turbid particles and show up as "high" values for the specific ion being monitored. This problem can somewhat be compensated for by using the double-cell method, Figure 9-10. In this case, a reading of turbidity (A) is also made and subtracted from the total reading (B). The result should be the specific ion. This is not a fool proof method since some chemical "colored" complexes will adsorb on the silt and not absorb the specific wave lengths. Pretreatment, including filtration, is the preferred method for these situations.

ANALYZER

The analyzer unit takes the signal, usually a voltage or current, from the sensor and amplifies it for comparison and readout. A discussion of electronic analyzing is included in Chapter 5. Changes in voltage or current signifies changes in parameter concentration. Since the electronic elements are sensitive to temperature, they must be calibrated against known concentrations. One mistake which is common involves calibration. Frequently, the electronics are calibrated without the sensors. Obviously the whole system must be calibrated and maintained and not just the electronic instrument.

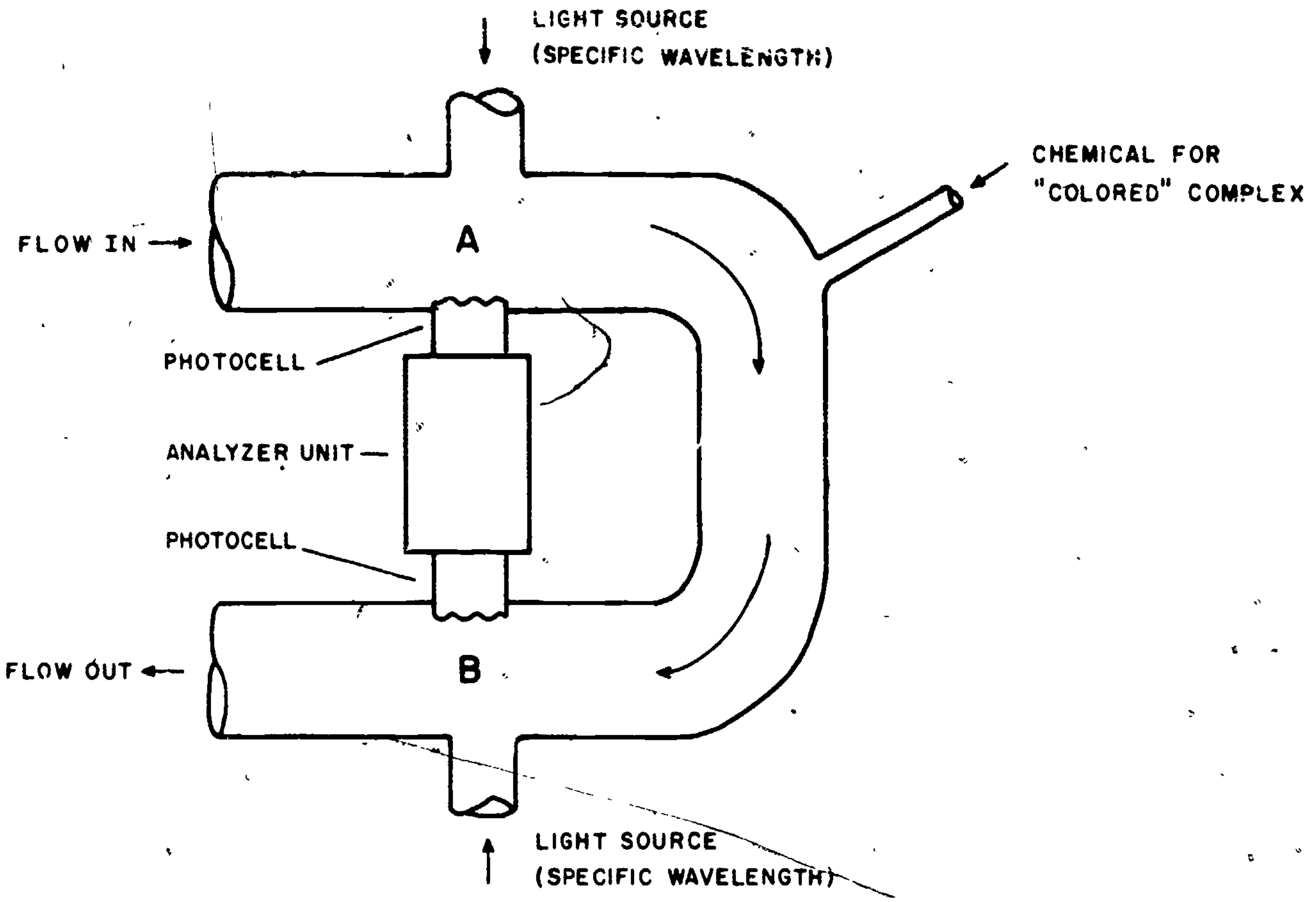


Figure 9-10
Double-Cell Method for Turbid Samples

Maintenance of analyzer can be quite costly. New solid state systems are decreasing this. Analyzers should be placed close to the sensor. Sensor signals are small in magnitude; and therefore, lengthy circuits can change or modify these signals by introducing large resistances and interfering magnetic fields.

RECORDERS

Recorders permanently portray the parameter data. If the data are graphically, they might be quite continuous. If they have single values, they are less than continuous. Many continuous monitoring systems make measurements frequently, but only record every 5, 10, or 30 minutes.

The permanent record of data points can be portrayed in many ways—strip charts, circular charts, punched tape or magnetic tape and of course data can be forwarded in real time by telemetry systems. It is important that data records be stored for future use. Obviously, there is a limit to this, but if legal action is necessary then the original information will be required. Magnetic tape and telemetered data are suspect because of interferences. Hard data, punched tape or graphically charts are the best.

CAUTION

In using a recording system timing is important. The data on the tape or chart must be keyed to time, date and place. Reams of data without space and time correlation are worthless.

Strip or circular charts produce volumes of paper information. They must be set at a speed which will show significant parameter changes. This also produces yards of paper for analysis. They do, however, present a pictoral display which a human can see. This is a plus. Reduction of data from these kinds of charts is monumental.

Other systems try to produce the original data in a form where computers can analyze it. These systems like punched tape and magnetic tape are much preferred because of the reduced time in the analysis function.

Future developments in electrode hardware, in in situ monitoring, in analyzer instrumentation and in recorder systems should increase the use of automatic monitoring systems. The first and operational cost of these systems is high, however, and their reliability and convenience must prove itself.

Problems:

1. Select a river basin (see Problems Chapter 8) and select new monitoring sites which are necessary for proper surveillance of the basin. Consider monitoring objectives, pollution sources, mixing zones, access points, tributaries, control sites and so forth.

2. Discuss and plan the type of monitoring required, for example, continuous, noncontinuous, frequency, collection, testing, parameters and so forth. Be sure to plan for the people and places (be specific).

3. Take some samples below a municipal sewage effluent discharge point (review safety concerning sampling, for example pathogens). Pack one sample in ice and leave the other at ambient temperature. After 24 hours test both samples for fecal coliforms. Compare and explain any differences noted.

ROBOT SURVEILLANCE NETWORKS

Two surveillance networks, based in Ohio, illustrate the advantages and problems associated with robot monitoring. These two are the Ohio River Valley Sanitation Commission (ORSANCO) and the Ohio Department of Natural Resources (ODNR) Monitoring System.

ORSANCO

ORSANCO has been monitoring the Ohio River and its tributaries for some 25 years. During the first several years, the system was operated manually using the usual laboratory and field testing methods. In 1960, a robot monitoring system was put into operation. This system increased testing frequency, produced data in real time and reduced operating costs.

SYSTEM

The system consists of approximately 30 robot stations (Figure 10-1). These stations are in the Ohio River itself and also the major tributaries. Each station is equipped with multiple sensors, including: pH, oxidation-reduction potential, chloride, dissolved oxygen, conductivity, temperature and solar radiation. Each station monitors only the parameters which are significant to the site.

The monitors are housed in municipal water treatment plants and power generating stations along the river. These sites provide a convenient shelter with heat, a ready source of flowing water for tapping, and a power source for monitor operation.

Each of the robot stations is tied into ORSANCO headquarters by a transmitter system involving leased teletype-grade telephone lines. Each station is interrogated once every hour. In response, the station transmits the quality data being measured at that moment (real-time data). The data are punched on tape for storage, placed in computer programming and portrayed for visual use.

TELEMETERING

This telemetering system provides many advantages over the on-site recording methods. On-the-site recording of water quality data is not real-time data. If the charts are read once per week, for example, then the data reflects water quality for water now many miles downstream; perhaps the water is now in the ocean. The advantage of real-time data is obvious. Spills or accidental discharges and sudden water quality changes can be monitored. Downstream users of the water can be informed of possible problems and can adjust their operations to fit the problems.

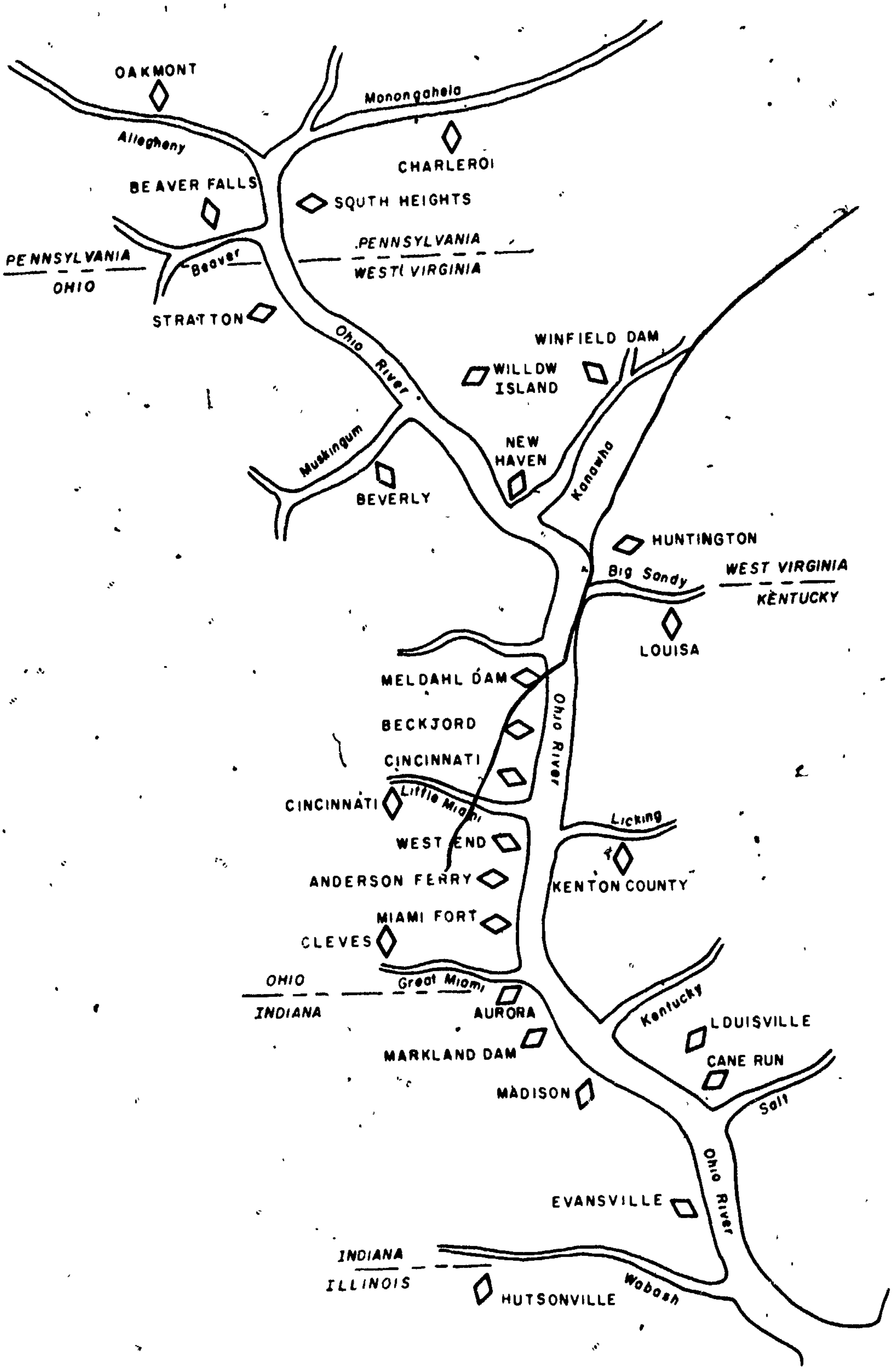


Figure 10-1 Robot Monitoring Station

Recently an oil spill occurred on the river. Downstream users were warned of the spill. Times for passage of the spill were calculated for each user. The user then shut off his inflow until the spill had passed. Costly equipment and distribution systems were protected by this warning system.

The system could furnish continuous data, at least within minutes, but a balance between enough data versus too much data was selected. The period selected was one hour. This time period is sufficient to monitor spills and sudden changes, but is not excessive with regard to data and processing.

DATA RELIABILITY

The data arriving at the processing center must be validated.

Is it accurate data or erroneous data?

Equipment malfunctions will produce erroneous data. It is therefore important to check the equipment. Every transmission from a monitoring site includes a test signal which monitors the equipment itself. Reduction in power or poor sensing due to reduced flow will produce improper test signals. Data included with improper test signals are not processed.

The data itself is tested. Limits of acceptability are used in this test. The first part of this test determines if the value is within the usual range of possibility. For example, a water temperature of 1°C is August does not seem possible and the data point would be in question. The value is not within the usual boundaries of water temperatures. The second test further refines the boundaries to usual values found in August. Again, the value is not possible and the data is not processed. The third test monitors the rate of change of values. If hourly data shows rapid fluctuations in water temperatures, then the data again would be questioned and removed from processing.

PRINTOUT

Processing of data can produce any kind of a printout which is deemed necessary. These printouts can show trends, maximum and minimum hourly values for daily, weekly, monthly or yearly data, and maximum hourly variations.

Once the computer has processed the data, then it is evaluated. Two major evaluations are performed using the Ohio River Basin data. First, the data is compared to establish criteria and standards. These criteria and standards involve: Stream Standards approved by EPA for the various stream segments, and Users Standards determined by the various users of the river (Drinking Water Standards).

The second evaluation involves planning. This evaluation determines long term trends. For example, if the water quality is being steadily degraded, then better standards for waste discharge must be set. These standards may involve both quantity and quality of water. The effects of waste discharge involve the pollution parameter and its concentration. Concentration is a function of the quantity of flow.

MAINTENANCE

The key to proper robot monitoring is maintenance and standardization. The ORSANCO system is maintained by contract with the Schneider Instrument Company. This company also supplies the majority of the monitoring equipment. This kind of dual capacity has led to good operation and performance.

Water personnel at plants and power stations clean the sensors and flow through cells weekly. The Schneider Company services each monitor on a two week interval. This service includes a complete instrument standardization.

The ORSANCO system has provided a model for robot monitoring of a river basin. The monitoring is costly, but less on a per item basis than usual field and laboratory methods. Good servicing and maintenance has kept the system in operation. Some robot monitoring systems have failed because of poor equipment and maintenance.

The robot system will not maintain itself.

A second surveillance network is the Ohio Department of Natural Resources (ODNR) Monitoring System. This system involves many streams throughout the State of Ohio. Some of the main monitoring stations are:

1. Blanchard River at Findlay.
2. Auglaize River at Fort Jennings.
3. Auglaize River at Defiance.
4. Tymochtee Creek at Crawford.
5. Sandusky River at Fremont.
6. Auglaize River at Spencerville.
7. Blanchard River at the Findlay Reservoir, Intake.
8. Tymochtee Creek at Marseilles.
9. Sandy Run River near Lake Hope.
10. Scioto River below Shadeville.
11. Cuyahoga River at 3rd Street in Cleveland.
12. Mahoning River below Lowellville at State line.
13. Tuscarawas River below Navarre.

These stations are tied to telegraph grade phone lines to the Ohio Department of Natural Resources. Stream Monitor

Control Center in Columbus, Ohio.

Every hour the Center interrogates each station with respect to five parameters: river stage (depth of flow), specific conductance, dissolved oxygen, temperature and pH. The data is punched on tape and printed on a teletype. Processing can be accomplished manually or by computer programming.

Data evaluation consists of comparison to Stream Standards. The Ohio Water Pollution Control Board has adopted two Standards for Ohio streams. These are "Aquatic Life 'A'" and "Aquatic Life 'B'". Each of these Standards sets limits on Dissolved Oxygen, pH and Temperature.

> Stream standards are constantly being revised. Check present state standards for current criteria and permissible values.

The stations were selected for specific reasons or objectives. The Blanchard River site (1) at Findlay measures the effect of several waste discharges including Findlay's sewage effluent. Station 2 on the Auglaize River at Fort Jennings measures the river quality before it is joined by the Blanchard River and the Ottawa River. Station 3 measures the quality of the Auglaize River after it is joined.

All the stations are specific to objectives of monitoring either the natural river (base line data) or the river after waste discharges have been introduced (pollution).

Several violations have been monitored. A substantial drop in dissolved oxygen signaled a pollution increase. Wildlife Division personnel established the cause.

The pollutor was fined and required to correct the situation. Another violation was caused by a leak in an industrial primary treatment lagoon. Monitoring established a decrease in dissolved oxygen content. Further testing established the problem and the industry modified its waste stream to eliminate the leak.

Future requirements will accelerate the use of robot monitors with telecommunication systems. More parameters will be measured, and some sophisticated analyses will be performed. The key is good maintenance.

Data is only as good as its monitor.

Problems:

1. Check with the State Office of Environmental Quality and locate a nearby robot monitor.

2. Visit the robot monitor (with a professional technician) and report on the following:

   a. What is the physical location of the monitor. Include structure dimensions, power, lights, heat. river location (variations in height), monitor lines, pumps, flow through rates and so forth.

   b. What parameters are measured?

   c. What technique is used for each parameter?

   d. How often is a measurement made?

   e. What recording device is used? (Make a copy of a recording).

   f. Are the data telemetered to a central location?

   g. What maintenance and standardization work is required?

AVAILABLE WATER DATA

To accurately and consistently predict our water environment the ultimate goal, as discussed previously, should be to measure everything -- everywhere -- always. Again, let us state that it is not feasible. Our funds and resources are limited and the monitoring programs now in existence are limited. However, extensive and accurate data does exist and can be of great help in water quality and pollution control work. To understand the background or history of a study or problem area is of great importance.

AGENCY OBJECTIVES

Several federal and many state and local agencies regularly obtain and record water quality data. The scope or objective of the individual agencies should be examined before the data is incorporated in any study. The agency objective may affect the type of results obtained on water quality. The agency may be looking for composite or average values or for maximum or minimum values. Examples of average values would be data on a raw water for a city drinking water. Maximum or minimum values would be used to determine violations of standards such as water quality standard. Frequency of testing will again depend on the agency and its monitoring objectives. Testing frequency will also depend on the situation being monitored. For instance, testing on a raw water source for a public drinking water will be more frequent than a zone in a stream designated for maintenance of rough fish and boating. If either situation is subjected to the possibility of pollution from waste discharges, the frequency of testing may well have to be increased.

WHAT PARAMETERS

The monitoring objectives will also determine the parameters which are tested. Some agencies may be only concerned with salinity, sediment load or temperature. Stream quality measurements will be dictated by the state water quality standards and the number and type of waste discharges into the stream. Table 11-1 shows the frequency of different parameters as they are used in state water quality parameters.

LONG-TERM VS. SHORT-TERM STUDIES

Monitoring may be of two types. Long-term studies have permanent stations located at strategic points. Information produced in this type of study provides the user with general trends or changes in the water quality. Short-term studies are based on a shorter time frame and are used in collecting data on a smaller area. Short-term studies are usually more detailed and can be used to fill in information where the long-term study indicates a problem. Short-term studies are

TABLE 11-1
HOW FREQUENTLY PARAMETERS ARE USED IN WATER QUALITY CRITERIA OF STATE STANDARDS

Uniform (100%)	Frequent (99-50%)	Less Frequent (49-20%)	Least Frequent (19-0%)
Dissolved Oxygen	Radioactivity	Arsenic	Bottom Deposits
		Barium	Chromium (trivalent)
pH	Parameters listed in: Public Health Service Drinking Water Standards	Cadmium	Electrical Conductance
Coliform			
Temperature		Chromium (hexavalent)	Ammonia
	Total Dissolved Solids		Acidity
Floating Solids (Oil-Grease)			Alkalinity
		Fluoride	
		Lead	
Settleable Solids		Selenium	Carbon Chloroform Extract
		Silver	
		Suspended Solids	Hydrogen Sulfide
Turbidity and/or Color			Pesticides
		Chloride	Sodium
		Copper	Iron
Taste-Odor		Nitrate	Plankton
		Phenols	Foaming Substances
Toxic Substances		Phosphate	
		Sulfate	Boron
		Cyanide	Manganese
		Median Tolerance Limit	Hardness
			Biochemical Oxygen Demand
			Methylene Blue Active Substances
			Zinc

often done on request when problems are indicated.

When reviewing and using data not obtained by yourself it is always important to know the validity and reliability of the results. Standard methods in sampling and laboratory procedures are very important if one is to rely on the results of others. Water data should be viewed both in this light and the reasons or objectives the data was collected.

QUALITY & QUANTITY

A question may be raised at this point. Are flowrate and volume (storage) important parameters to obtain in water quality studies? The answer is a most definite yes. Quantity and quality are both factors which must be considered. Seasonal variations in flow may greatly affect the quality parameters. Volume and concentration are always related. Downstream influence may depend not only on quality but on quantity as well. The need for tying quality with quantity is quite important.

Now that we have seen that many factors should be considered before interpreting data, we should take one step back to see what data is available and where to find it. In the remainder of this chapter the following sources of water data will be discussed.

1. United States Geological Survey,
2. United States Environmental Protection Agency, and
3. Other federal, state and local agencies.

UNITED STATES GEOLOGICAL SURVEY (USGS)

The <u>United States Geological Survey</u> (USGS) which is under the U. S. Department of the Interior is one of the major sources of water data in the United States. The USGS has been gauging streamflow in the United States since 1894 and has been keeping records of water quality since 1941. Data collected make up input to the National Water Data System and the National Stream Quality Accounting Network.

USGS PUBLICATIONS

Data have been published yearly on a state-by-state basis in two publications. Part 1. Surface Water Records deals with streamflow and Part 2. Water Quality Records is a compilation of water quality parameters.

WATER YEAR

Both the Surface Water Records and Water Quality Records are based on the water year which runs from October 1 to September 30 of the next year. For example, water year 1972 ran from October 1, 1971 to September 30, 1972. Both parts may be obtained by contacting the District Chief, Water Resources Division, U. S. Geological Survey from the state in question. The Water Surface Records and Water Quality Records are later compiled into a Water Supply Paper (WSP). The USGS arranges the WSP on a basin system. All information from each basin (see Figure 6-9) is compiled into the WSP. The Water Supply Papers can be obtained from the Government Printing Office in Washington, D. C. Publications on methods of streamflow measurements and sampling and techniques of chemical and other quality parameters are also available.

OBJECTIVES (USGS)

The data collected and presented by the USGS is primarily for providing general on baseline data which can be used to depict general trends in water quality.

This fulfills the needs of the long-term network or general watchdog. The Survey for the most part is not problem-oriented. Parameters in which they are mainly interested are temperature, specific conductance, sediment, a salinity analysis and some specific ions. Other parameters such as radiochemicals, pesticides, minor elements and biological parameters are also monitored at some locations.

A major part of the USGS monitoring system is done on a cooperative basis with state and federal agencies. Here the agency requests information be collected on a certain stream and provides funds to the USGS for this monitoring service. These cooperative studies may be on a long-term or short-term basis. The parameters and testing frequency depends, of course, on what the requesting agency needs from this location. Monitoring stations established on request from other agencies may provide more detailed information than network stations. It is important to remember that every station will provide the same type of data.

SPECIAL NETWORK (USGS)

The USGS maintains a special network of stations across the United States in remote, undeveloped areas. They are designated hydrologic bench-mark stations and are selected because they are free from impact by man. The results are used to see what effects nature itself has on hydrologic data. The data may also be used in separating natural and manmade effects in basins with similar charcteristics which have been developed.

AVAILABLE DATA

Examples of water data available from the USGS are shown in Figure 11-1 and Figure 11-2. Figure 11-1 is from the Surface Water Record and shows the streamflow data for the station and Figure 11-2 is from the Water Quality Records and presents the water quality data collected for the year. Note the dates of the water year which are quite different from the calendar year. Most results are listed in units of milligrams/liter (MG/L) or micrograms/liter (UG/L).

Location of the station is given by the station number and by latitude and longitude. In addition, a written description of the location is given. Stations are listed in the records in a downstream order by starting with the upstream stations and working progressively downstream. Stations on tributaries are listed in the order the tributaries enter the mainstream. Both the Surface Water Records and the Water Quality Records are divided into river basins for ease of correlating data for a particular

YELLOWSTONE RIVER BASIN

06277500 GREYBULL RIVER NEAR BASIN, WYO

LOCATION.--Lat 44°24'24", long 108°11'10", in NE¼NW¼SW¼ sec 8, T 51 N., R 94 W., Big Horn County, on right bank at upstream side of bridge on State Highway 0200, 3.0 miles upstream from Dorsey Creek, and 8 miles west of Basin.

DRAINAGE AREA.--1,115 sq mi

PERIOD OF RECORD.--April 1930 to current year. Monthly discharge [illegible] for some periods, published in WSP 1309

GAGE.--Water-stage recorder. Altitude of gage is 4,000 ft (from topographic map). Prior to Sept. 30, 1930, nonrecording gage at site 250 ft downstream at datum 2.92 ft higher. Oct. 1, 1930, to Sept. 20, 1934, nonrecording gage and Sept. 21, 1934, to Apr. 14, 1936, water-stage recorder, at site 250 ft downstream at datum 1.92 ft higher. Apr. 15, 1936, to Aug. 13, 1951, at site 100 ft downstream at present datum. Aug. 14, 1951, to June 17, 1970, at site 300 ft downstream at present datum.

AVERAGE DISCHARGE.--42 years, 181 cfs (131,100 acre-ft per year).

EXTREMES.--Current year: Maximum discharge, 2,550 cfs June 9 (gage height, 5.79 ft), maximum gage height, not determined, Feb. 28 (backwater from ice); minimum daily discharge, 13 cfs May 4, 5.
Period of record: Maximum discharge, 19,400 cfs June 16, 1963 (gage height, 8.83 ft), from rating curve extended above 2,200 cfs on basis of contracted-opening measurement of peak flow; no flow at times in 1931-34, 1936, 1939.

REMARKS.--Records fair except those for winter period, which are poor. Slight regulation by Sunshine Reservoir beginning May 1940 (capacity, 53,000 acre-ft). Diversions above station for irrigation of about 63,300 acres, of which about 2,600 acres lies below station. Water-quality records for the current year are published in Part 2 of this report.

REVISIONS (WATER YEARS).--WSP 826: 1936. WSP 1309: 1930-31, 1932-33(M). WSP 1709: Drainage area.

DISCHARGE, IN CUBIC FEET PER SECOND, WATER YEAR OCTOBER 1971 TO SEPTEMBER 1972

DAY	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP
1	164	183	48	74	68	600	119	70	675	111	140	54
2	320	179	48	74	80	280	115	50	785	70	110	43
3	289	190	54	70	80	270	111	14	720	56	80	43
4	243	213	60	62	86	280	119	13	748	26	50	38
5	234	186	62	64	90	290	122	13	910	18	30	39
6	213	161	48	68	96	250	127	16	1,050	17	30	35
7	172	165	40	70	98	200	122	24	1,130	54	38	38
8	155	183	35	74	100	150	119	48	1,400	70	40	37
9	139	209	40	78	100	150	114	21	1,880	57	23	41
10	149	193	45	76	100	170	108	17	1,490	35	27	38
11	146	197	40	78	98	180	146	20	1,380	26	26	41
12	139	186	44	76	98	190	149	19	1,190	19	25	39
13	136	183	47	68	98	190	149	18	867	17	26	34
14	149	172	50	62	86	170	149	17	641	19	30	35
15	161	160	52	60	90	172	136	24	576	19	96	41
16	168	170	50	64	100	168	136	37	576	22	34	30
17	186	150	50	68	110	186	136	19	552	45	17	26
18	728	140	52	74	100	201	139	22	584	28	17	35
19	353	130	56	70	90	190	142	34	552	21	180	42
20	230	140	60	68	84	183	[illegible]	76	598	22	95	28
21	222	150	58	76	84	155	96	70	320	18	60	22
22	193	140	56	76	90	139	76	112	252	34	70	24
23	179	130	69	70	100	139	78	48	279	100	78	26
24	183	140	62	66	110	139	78	28	320	78	388	24
25	179	120	64	64	110	127	76	28	252	30	172	18
26	172	100	52	60	120	122	94	32	175	20	98	22
27	168	94	52	74	150	108	76	30	108	30	72	22
28	136	80	56	78	400	101	60	35	74	25	60	21
29	103	70	60	78	800	103	49	154	61	20	43	21
30	127	56	64	72	------	103	[illegible]	266	96	20	90	21
31	175	------	68	72	------	119	------	439	------	50	139	------
TOTAL	6,311	4,570	1,633	2,184	3,816	5,825	3,342	1,813	20,151	1,177	2,384	974
MEAN	204	152	52.7	70.5	132	188	111	58.5	672	38.0	76.9	[illegible]
MAX	728	213	68	78	800	600	149	439	1,880	111	388	54
MIN	103	56	35	60	68	101	49	13	61	17	17	[illegible]
AC-FT	12,520	9,060	3,240	4,330	7,570	11,550	[illegible]	3,600	39,970	2,330	4,730	1,940

CAL YR 1971 TOTAL 75,099 MEAN 206 MAX 2,210 MIN 16 AC-FT 149,000
WTR YR 1972 TOTAL 54,184 MEAN 148 MAX 1,880 MIN 13 AC-FT 107,500

PEAK DISCHARGE (BASE, 1 300 CFS)

DATE	TIME	G.HT.	DISCHARGE
10-18	1800	4.98	1,340
6-9	1200	5.79	2,550

Figure 11-1 Surface Water Records (USGS)

YELLOWSTONE RIVER BASIN

06278500 GREYBULL RIVER NEAR BASIN, WY

LOCATION.--Lat 44°24'24", long 108°11'10", in NE¼NW¼SW¼ sec. [illegible], T. 51 N., R. 94 W., Big Horn County, at gaging station at bridge on State Secondary Highway 0200, 3.0 miles upstream from Dorsey Creek, and 8 miles west of Basin.

DRAINAGE AREA.--1,115 sq mi

PERIOD OF RECORD.--Chemical analyses: January 1951 to September 1953, July 1965 to September 1972.

CHEMICAL ANALYSES, WATER YEAR OCTOBER 1971 TO SEPTEMBER 1972

DATE	TIME	DIS-CHARGE (CFS)	DIS-SOLVED SILICA (SIO2) (MG/L)	DIS-SOLVED IRON (FE) (UG/L)	DIS-SOLVED CAL-CIUM (CA) (MG/L)	DIS-SOLVED MAG-NE-SIUM (MG) (MG/L)	DIS-SOLVED SODIUM (NA) (MG/L)	DIS-SOLVED PO-TAS-SIUM (K) (MG/L)	BICAR-BONATE (HCO3) (MG/L)	CAR-BONATE (CO3) (MG/L)	DIS-SOLVED SULFATE (SO4) (MG/L)	DIS-SOLVED CHLO-RIDE (CL) (MG/L)
OCT 12...	1030	142	14	210	65	25	90	3.1	272	[illegible]	220	[illegible]
NOV. 09...	1145	220	15	90	58	28	66	1.8	250	0	190	[illegible]
DEC. 07...	1030	39	16	40	87	42	94	2.7	325	[illegible]	300	[illegible]
JAN 03...	1130	72	15	90	78	33	82	2.4	302	0	250	[illegible]
FEB. 03...	1140	76	18	0	77	30	78	2.2	248	0	250	5.8
MAR. 01...	1200	698	9.6	570	43	13	43	5.3	153	0	[illegible]	4.6
APR. 05...	1110	140	11	170	59	30	89	2.6	247	[illegible]	[illegible]	6.8
MAY 04...	1145	13	12	100	83	47	140	3.0	322	0	400	[illegible]
JUNE 02...	1300	1280	16	100	29	6.8	23	2.1	112	0	[illegible]	[illegible]
JULY 07...	1600	49	19	20	64	25	130	3.3	289	0	290	[illegible]
AUG. 15...	1110	172	17	50	49	15	61	3.3	202	0	140	[illegible]
SEP 07...	1445	40	18	190	62	25	130	3.5	279	0	190	[illegible]

DATE	DIS-SOLVED FLUO-RIDE (F) (MG/L)	DIS-SOLVED NITRATE (NO3) (MG/L)	DIS-SOLVED BORON (B) (UG/L)	DIS-SOLVED SOLIDS (SUM OF CONSTI-TUENTS) (MG/L)	DIS-SOLVED SOLIDS (TONS PER AC-FT)	DIS-SOLVED SOLIDS (TONS PER DAY)	HARD-NESS (CA,MG) (MG/L)	NON-CAR-BONATE HARD-NESS (MG/L)	SODIUM AD-SORP-TION RATIO	SPE-CIFIC CON-DUCT-ANCE (MICRO-MHOS)	PH (UNITS)	TEMPER-ATURE (DEG C)
OCT 12	4	5	80	564	.77	216	270	35	2.4	850	8.4	[illegible]
NOV 09	4	9	60	492	.67	292	260	55	1.8	[illegible]	[illegible]	[illegible]
DEC 07	4	1.2	80	715	.97	75.3	390	123	2.1	[illegible]	[illegible]	[illegible]
JAN 03	[illegible]	2.2	80	619	.84	120	330	82	2.0	[illegible]	[illegible]	[illegible]
FEB 03	[illegible]	2.2	80	589	.80	121	320	117	1.9	[illegible]	[illegible]	[illegible]
MAR 01	3	[illegible]	50	[illegible]	.43	597	160	34	1.5	[illegible]	7.9	[illegible]
APR 05	4	1	50	598	.81	226	300	[illegible]	2.3	[illegible]	8	10.0
MAY 04	5	9	120	852	1.16	20.9	400	136	3.0	1200	[illegible]	[illegible]
JUNE 02	[illegible]	1.3	40	192	.26	664	100	[illegible]	1.0	301	[illegible]	19.0
JULY 07	6	[illegible]	[illegible]	686	[illegible]	91.0	260	[illegible]	3.5	1010	[illegible]	16.0
AUG 15	[illegible]	1.9	60	394	.54	181	180	[illegible]	2.0	609	[illegible]	9.5
SEP 07	6	9	[illegible]	678	.92	[illegible]	260	41	1.5	975	8.2	19.5

SUSPENDED SEDIMENT DISCHARGE MEASUREMENTS, WATER YEAR OCTOBER 1971 TO SEPTEMBER 1972

DATE	TIME	TEMPER-ATURE (DEG C)	DIS-CHARGE (CFS)	SUS-PENDED SEDI-MENT (MG/L)	SUS-PENDED SEDI-MENT DIS-CHARGE (T/DAY)
FEB 03	1145	0	76	24	4.9

Figure 11-[illegible] WATER QUALITY RECORDS (USGS)

stream. Besides stream data the USGS also publishes a large amount of water data from wells and groundwater sources.

U.S. ENVIRONMENTAL PROTECTION AGENCY (EPA)

The United States Environmental Protection Agency (EPA) is the second major source of water quality data that should be examined in detail. The EPA is the primary agency for collecting data on water quality and pollution control. The various state environmental agencies have been given some responsibilities but any program initiated by the states is subject to EPA review.

OBJECTIVES (EPA)

The Environmental Protection Agency is involved with many kinds of monitoring. Monitoring of stream quality is one major area. EPA delegates much of this responsibility to the states but covers areas where the states or other federal agencies have not taken charge and need is felt for monitoring. Much of the EPA run monitoring system is based on surveillance of discharges which are under permits to discharge. Many of their stream quality stations are downstream from discharges. Monitoring of discharges is done by EPA as well as local and state agencies. The proceeding studies are mainly of a long-term variety. Maintaining surveillance on water quality vs. water quality standards and treatment plant effluent quality vs. effluent limitations are major job of EPA. In some cases short-term studies are also run by EPA. These short-term studies are usually done on request or because a problem situation must be studied and resolved.

STORET

The Environmental Protection Agency maintains a large computer stored data file called STORET. The term STORET stands for STOrage RETrieval of water quality, municipal and industrial waste facility inventory, water quality standards compliance, fish kill, oil spill, construction cost, and other related data. This comprehensive management system increases the availability of data collected by EPA and other agencies. Many different agencies contribute data to STORET. The variety of sources for STORET is extensive as seen in Table 11-2. As can be seen the list includes federal agencies, state agencies and some municipal water and wastewater treatment facilities. Input to STORET from these many sources provides a variety of information (the number of parameters is upwards of 1600). The STORET system has several capabilities of output data. Retrieval of raw data is possible. Several outputs providing statistical analysis of data are also possible. Furthermore, STORET is capable of comparison of water quality to federal or state standards and digital plotting of charts and graphs. Because of this versatility STORET is quite useful for studies requiring

TABLE 11-2
TYPICAL INPUT SOURCES FOR STORET
(REGION VIII)

AGENCY	STATE
Forest Service - Ogden	Utah
Air Force Academy	Colo.
Boulder-City-County Health Dept.	Colo.
EPA (Short term studies)	Region VIII
EPA - Denver Field Investig.	USA
Crystal Dam (USBR)	Colo.
Link-Templeton-Alsup - Jordan R. 3C Grant	Utah
Montana State	Montana
USGS	Region VIII
Bureau Sport Fisheries	So. Dak.
North Dakota Health Dept.	No. Dak.
EPA Data	Region VIII
Bureau of Reclamation - Pueblo	Colo.
Colo. River Basin EPA	Colo, Utah, Wyo.
Denver County Health Dept.	Colo.
Forest Service - Missoula	Montana
Black Hills - 3C Grant	So. Dak., Wyo.
South Dakota Health Dept.	So. Dak.
Utah Health Dept.	Utah
Colo. State Health Dept.	Colo.
EPA - Seattle	Montana
EPA - Snake River	Montana, Wyo.
EPA - South Platte River	Colo.
Corps of Engineers, Omaha, Neb.	Mont., No. Dak. So. Dak.
Forest Service - Black Hills	So. Dak.
EPA - Seattle	Montana
EPA - Kansas City	Mont., No. Dak., So. Dak.
Bureau Sports Fish & Wildlife	So. Dak.
Manitoba Canada	---------------
Wyoming State	Wyoming
Bureau of Mines	Region VIII
Bureau of Sport Fisheries (National Program) (Fish Hatcheries)	Region VIII
Denver Metro Sewer District	Colo.
Denver Board of Water Commissioners	Colo.
City of Grand Forks	No. Dak.
City of Pueblo	Colo.
Bureau of Sport Fisheries Kansas City	Region VIII
Colorado Game, Fish & Parks	Colo.
Rocky Mountain Arsenal	Colo.
Forest Service-Custer	Region VIII

water quality. Data is continuously being updated and revised as new data is stored. STORET offers a more complete inventory of water data than any other single source in the United Sates.

WATER QUALITY INVENTORY

To obtain such data, the Regional office of EPA must be contacted. In particular, the Surveillance and Analysis Division or Surveillance Branch may be of the most help. Data at this time is offered to anyone or any agency that requests the information. The first request when starting a study would probably be for a water quality inventory of a basin. This printout will include all stations in the area and give mean (average) values and other statistical data on parameters monitored at each station. An example is shown in Figure 11-3. Here one station out of a water quality inventory is presented. It is the same station as shown in example data from the USGS, however, mean values for the given time period have been displayed.

On the printout, the station information is given first. The primary station number, latitude and longitude, station name, state code, agency code and type of station code are presented. On the listing included are parameter number, name, type of units, number of tests, the mean value of the data, statistical analysis of the data (variance, standard deviation, coefficient of variance, standard error, maximum value, and minimum value), the beginning date of the study and the ending date of the study. From the water quality inventory stations may be located and it may be determined that original data is needed. Printouts of this nature can also be obtained upon request. This may take the form of all parameters for a station or a partial listing as desired by the user.

OTHER DATA SOURCES

1. State

We have seen that USGS and (EPA) STORET are the two major single souces of available water data. There are many other sources of water data. Many state pollution control agencies have monitoring and surveillance programs to gather data on water quality. The extent of these state programs run from minimal to complete systems. Much of the information goes into STORET. Other state agencies such as state engineer's office and game and fish, agriculture and geological agencies may also collect water data. State agencies may very well be an important source in the future when states begin to implement their own permit and monitoring system over waste discharges. In any water quality study state agencies should be consulted for available water data.

Figure 11 3 Example Data from EPA (STORET Water Quality Inventory)

```
STORET  DATE  73/04/20                                                                06277500
                                                                                      44 25 00.0 108 11 00.0  2
                                                                                      GREYBULL R NR BASIN, WYO
                                                                                      56

                                                                                      [illegible]          06111204
                                                                                      0000

PARAMETER                                          NUMBER   MEAN     VARIANCE  STAN DEV  COEF VAR  STAND ER  MAXIMUM   MINIMUM   BEG DATE  END DATE
00010   WATER      TEMP       CENT                     70  9.85795    72.0730   8.48958   .861191   1.01470  28.0000    .000000  65/06/24  72/09/07
00060   STREAM     FLOW       CFS                      94  309.558     564769   751.511   2.42769   77.5124  5830.00    8.00000  51/01/16  72/08/15
00080   COLOR      PT-CO      UNITS                     6  3.66667    10.6667   3.26599   .890724   1.33333  10.0000    1.00000  65/09/24  67/03/06
00095   CNDUCTVY   AT 25C     MICROMHO                110  980.927    73201.7   270.558   .275819   25.7967  1730.00    301.000  51/01/16  72/09/07
00400   PH                    SU                      109  8.03294    .092773   .304587   .037917   .029174  8.70000    7.10000  51/01/16  72/09/07
00410   T ALK      CACO3      MG/L                    106  225.991    2234.60   47.2716   .209175   4.59142  361.000    92.0000  51/01/16  72/09/07
00440   HCO3 ION   HCO3       MG/L                    110  273.164    3456.26   58.7899   .215219   5.60540  440.000    112.000  51/01/16  72/09/07
00445   CO3 ION    CO3        MG/L                     98  1.85714    13.8351   3.71955   2.00283   .375731  15.0000    .000000  51/01/16  72/09/07
00900   TOT HARD   CACO3      MG/L                    112  295.000    5309.98   72.8696   .247016   6.88553  482.000    100.000  51/01/16  72/09/07
00902   NC HARD    CACO3      MG/L                    111  68.3333    1224.21   34.9887   .512030   3.32098  146.000    .000000  51/01/16  72/09/07
00915   CALCIUM    CA,DISS    MG/L                    105  70.9048    280.264   16.7411   .236106   1.63376  115.000    25.0000  51/01/16  72/09/07
00925   MGNSIUM    MG,DISS    MG/L                    105  27.9314    78.3341   8.85066   .316871   .863736  52.0000    6.10000  51/01/16  72/09/07
00930   SODIUM     NA,DISS    MG/L                     80  110.587    2152.12   46.3910   .419496   5.18667  283.000    23.0000  65/07/19  72/09/07
00931   SODIUM     ADSBTION   RATIO                    79  2.76455    1.02714   1.01348   .366598   .114025  6.50000    .900000  65/07/19  72/09/07
00932   PERCENT    SODIUM     %                        76  43.3947    54.9633   7.41373   .170844   .850413  63.0000    31.0000  65/10/18  72/09/07
00935   PTSSIUM    K,DISS     MG/L                     80  3.47371    .818449   .904682   .260437   .101146  6.90000    .900000  65/07/19  72/09/07
00940   CHLORIDE   CL         MG/L                    105  8.84088    25.5209   5.05182   .571415   .493007  28.0000    .700000  51/01/16  72/09/07
00945   SULFATE    SO4        MG/L                    110  288.784    12030.9   109 685   .379818   10.4581  628.000    .254000  51/01/16  72/09/07
00950   FLUORIDE   F,DISS     MG/L                     90  .451074    .038929   .197304   .437409   .020798  1.10000    .000000  51/01/16  72/09/07
00955   SILICA     DISOLVED   MG/L                     90  15.9733    6.01014   2.45156   .153478   .258417  23.0000    9.60000  51/01/16  72/09/07
01020   BORON      B,DISS     UG/L                     99  80.5050    1396.69   37.3722   .464223   3.75605  190.000    .000000  51/01/16  72/09/07
01045   IRON       TOTAL      UG/L                     50  106.800    11740.6   108.354   1.01455   15.3236  440.000    .000000  51/01/16  71/10/12
01046   IRON       FE,DISS    UG/L                     12  120.000    23472.7   153.208   1.27673   44.2274  570.000    .000000  66/10/06  72/09/07
01055   MANGNESE   MN         UG/L                      1  100.000                                           100.000    100.000  65/12/22  65/12/22
32730   PHENOLS               UG/L                     15  6553.33    8544128   2923.03   .446038   754.724  10000.0    1000.00  65/07/19  66/08/31
70300   RESIDUE    DISS-180   C  MG/L                  90  661.289    38013.3   194.970   .294833   20.5516  1230.00    198.000  51/01/16  72/09/07
70301   DISS SOL   SUM        MG/L                     54  641.389    26795.8   163.694   .255218   22.2759  1040.00    192.000  53/09/02  72/09/07
70302   DISS SOL   TONS/DAY                            79  401.730     915265   956.695   2.38144   107.637  7520.00    21.0000  51/01/16  72/08/15
70303   DISS SOL   TONS PER   ACRE-FT                  89  .897972    .070969   .266400   .296668   .028238  1.67000    .270000  51/01/16  72/09/07
71845   AMMONIA    NH4        MG/L                      1  2.20000                                           2.20000    2.20000  65/09/24  65/09/24
71850   NITRATE    NO3        MG/L                     90  1.22107    .896482   .946827   .775406   .099804  4.00000    .000000  51/01/16  72/09/07
71855   NITRITE    NO2        MG/L                      1  1.00000                                           1.00000    1.00000  65/09/24  65/09/24
71870   BROMIDE    BR         MG/L                      3  .400000    .012100   .110001   .275003   .063509  .510000    .290000  65/07/19  65/09/24
71885   IRON       FE         UG/L                     25  100.000    8475.00   92.0598   .920598   18.4119  390.000    10.0000  65/07/19  67/08/04
80154   SUSP SED   CONC       MG/L                      2  7166.50   .906E+08   9522.60   1.32877   6733.50  13900.0    433.000  65/06/24  66/03/21
80155   SUSP SED   DISCHARG   TONS/DAY                  2  65165.0   .840E+10   91690.5   1.40705   64835.0   130000    330.000  65/06/24  66/03/21
```

2. Local

Local and county agencies also collect water data. Many municipal water plants monitor surface water supplies regularly and have extensive available data. Wastewater treatment plants also do monitoring of discharges and stream conditions. Also, colleges and universities frequently obtain water data which is available to the researcher.

3. Federal

Other federal agencies are also involved in monitoring of our nation's waters. Among these are the Bureau of Reclamation, Corps of Engineers, Forest Service, Bureau of Land Management and the Soil Conservation Service. Each agency has its own objectives in the water data they collect and these objectives effect the type of data collected. Special studies run by each agency account for much of the data. Again, most of this data goes into STORET but these agencies should be contacted to be sure that all data on the area of interest can be obtained.

PART III

THE AIR ENVIRONMENT

Problems:

1. Contact the Regional Office of the Environmental Protection Agency and ask for the quality data (from STORET) on a small section of a river basin (see Problems Chapter 8). Specifically request statistical information on maximums, minimums and averages for 5 parameters. Ask for a graphic portrayal of the information.

2. Study the information received and determine the condition of the river at several points. Does it meet river standards?

3. Compare this information with that derived from problems in Chapters 8, 9, and 10.

METEOROLOGY

1. Introduction

Air has been described as one of the most important of three survival commodities. When we consider air, water, and food as units of survival for civilization, we soon realize that we cannot exist without these for minutes, days, or weeks respectively.

Our air environment has been aptly described as an "unheeded component." When the atmosphere contains only the usual and commonplace components, we do not focus attention on it - it is so familiar and unnoticed that we rarely think about it. The air we breath has an interesting relationship to our everyday lives. We do not enjoy an unlimited choice in selecting our air environment: This is true when we think of it in comparison with water and food. We usually pay close attention to the water we drink and food we consume both in quantity and in the taste or quality. We may deny ourselves water or food for a limited period of time, but we cannot refrain from breathing except for a very few minutes. Upon exertion, man's metabolism requires increased volumes of air for survival - so man cannot limit such use if he is to survive, be productive and lead a useful life.

Receptors

Problems associated with air pollution cannot exist unless there is a receptor that responds unfavorably to the pollutant. The receptor may be a human being, a plant (vegetation), an animal, or material of some kind. Air pollution effects may be classified as:

a. physiological
b. material
c. visibility reduction
d. agriculture
e. psychological

Transport

For a receptor to respond to a pollutant, the substance must be transported from a source to the receptor. The only medium of transportation is the atmosphere and the atmosphere has characteristics which effect the time, concentration and manner by which the unwanted material reaches the receptor.

Without an atmosphere, no air pollution could exist. The exchange or transport of pollutants moves gaseous and particulate matter from source to receptor. In some cases, the atmosphere serves as a decay reservoir where pollutants decay into other compounds or react to form other components.

After the initial effects are exerted on man, vegetation or materials, there are more indirect effects such as murky skies, dirty buildings, offensive smells - the aesthetic evidence which limits enjoyment of our environment.

Many laws include these considerations in defining air pollution. The source characteristics are important to fully understand and predict the behavior of the emitted materials. The amount and nature of pollutants are primary considerations. If the released quantities and types of materials are known, it becomes easier to plot a detection strategy to measure effects on receptors. Sampling can be done at the source in some instances, and this becomes a valuable tool for working toward control.

Dispersion

Atmospheric dispersion is a powerful ally to dilute and remove pollution, but it introduces difficulties when we cannot accurately measure and relate the materials to the source. The mixing of emissions from several stacks or sources introduces uncertainties and confusion for researchers who must identify the measurements with the original point of release. Ambient atmospheric measurements are required to make comparisons with receptor effects. When unidentified and unexplained effects on a receptor (human beings, vegetations or materials) occur, the pollutant material and extent or level must be known at a point where the effect is noted. Little would be gained if the point source concentration only were known. The intervening air space with all its variables would not give enough information to really determine which pollutant is present and at what concentration the effects were noted. The ambient atmosphere between the source and receptor can be measured and, if meteorological data are collected at proper times, the relationships between source and receptor will begin to appear.

2. Meteorological Factors

a. Primary Meteorological Factors. The spread of contaminants in the atmosphere is dependent on: speed and direction of air movements (wind), characteristics of air turbulence which disperses airborne material, underlying surface characteristics (terrain features) and, vertical air temperature throughout the lower layers of the atmosphere.

Wind Direction

1. Wind Direction. Air movement, generally horizontal and parallel with the earth's surface is known as wind. Wind direction is described as the direction from which the movement occurs. Thus, a north wind identifies air in motion coming from the north or moving from the north toward the south.

Wind Speed

2. <u>Wind Speed</u>. Air in motion, near the earth's surface is retarded by friction effects which vary with surface roughness. These friction effects diminish with height and the more significant influences are within a zone known as the "planetary boundary layer" extending one-half mile to one mile above the surface.

Standard Height

The usual increase in wind speeds with height has made it necessary to designate what is known as a <u>standard height</u> for surface wind measurements. This height is <u>ten meters</u> above the earth's surface.

Most recorded and reported wind data from official agencies can be assumed to have been measured at this vertical level unless otherwise identified (Figure 12-1).

Slippage

Moving air layers are influenced by adjacent layers and the degree of slippage or "coupling" between them. When vertical movements are negligible, the coupling is reduced and marked increases of speed between horizontal layers occur.

Diurnal Variation

Daily changes in wind speeds are known as diurnal variations, and are most noted in the lower few hundred feet of atmosphere. Maximum diurnal speeds are exhibited in the early afternoon due to instability and higher vertical diffusion, and minimum speeds occur in the early morning hours.

In the next higher layers (above 200 to 300 feet), a change takes place where the minimum speeds occur near midday and are maximum during the night due to less coupling during stability and minimal vertical diffusion.

Seasonal Variations

Wind speed averages are usually higher in winter than in summer and there is an observed tendency for maximum wind speeds in the spring months.

Strong winds are only slightly diverted by surface or topographical influences. Light to moderate winds (under about 13 miles per hour) are affected appreciably by local temperatures, pressure distortions and surface friction from terrain features.

Wind Turbulence

3. <u>Wind Turbulence</u>. Irregular wind motions (with respect to direction) are known as turbulence. This irregular motion is important to air pollution study since it is a <u>primary</u> diffusion factor for airborne materials.

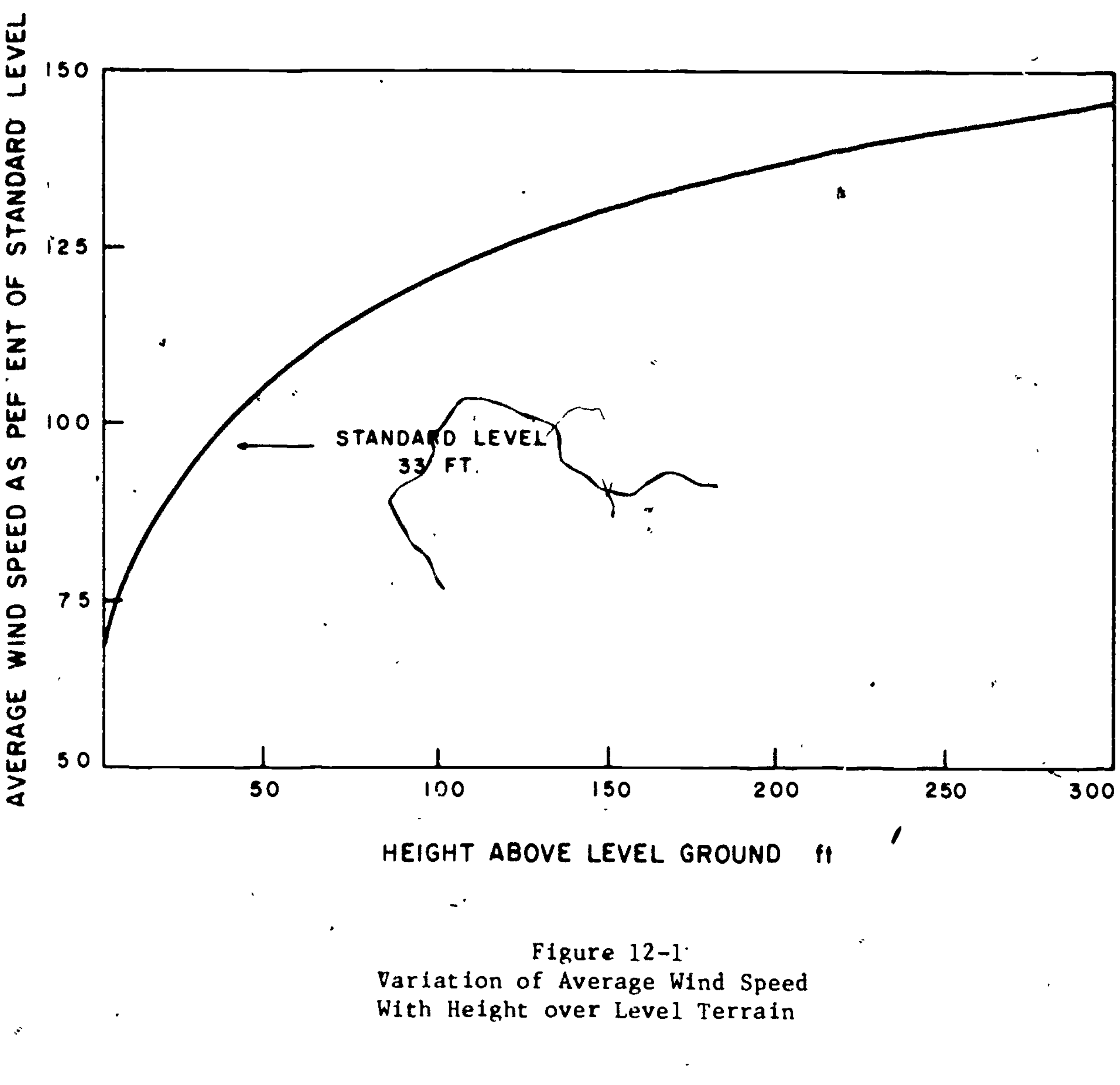


Figure 12-1
Variation of Average Wind Speed
With Height over Level Terrain

Mechanical Turbulence

Mechanical turbulence is the result of air movement over irregular surfaces producing surface friction. Increased wind speed or surface friction produces greater mechanical turbulence. This explains the reduction of stagnant or unstable air conditions with high winds. The surface friction influences decrease with height, so mechanical turbulence effects are decreased in value in the upper atmospheric layers.

Thermal Turbulence

Thermal turbulence is produced by convection or vertical air movements produced by temperature differentials. Warm, rising air, accompanied by wind fluctuations produce mixing eddies. Uneven surface heating increases thermal turbulence, and variations in solar heating will vary the intensity with time of day, altitude, fog, or other atmospheric filtering effects. This turbulence is at a maximum in early afternoon on clear, sunny days and is minimal on clear winter days in the early morning. These maximum or minimum effects are best noted during periods of light winds or calm.

Horizontal turbulence from wind and surface irregularities exceeds vertical turbulence components over long time periods and large areas. In small areas influenced by local conditions, either effect may be noticeable. Generally, periods of vertical effects lengthen with increasing height above ground surfaces.

b. Secondary Meteorological Factors.

Secondary Turbidity

1. Turbidity. This factor is sometimes known as meteorological visibility or the distance at which objects of certain dimensions and color can be recognized. This visibility characteristic refers to atmospheric conditions which reduce its transparency. Some indication of particulate pollution is possible, but there are many problems associated with the direct use of visibility as a precise or quantitative measurement.

Optical equipment has been devised to accurately measure the degree of turbidity or amount of attenuation from such atmospheres, but the relationship of such measurements to actual amounts, nature and kinds of airborne particulates is difficult, if not impossible to measure.

Humidity

2. Humidity. Airborne moisture is almost universally excluded as an air pollutant in most definitions. The amount of water contained in the air as droplets, steam or water vapor does not usually exert adverse effects by itself. It is an extremely important component, however, due to its relationship in air reactions. Many of the damage effects of air pollutants are dependent on moisture as a part of interactions with other airborne materials or pollution receptors. For example, the degree or speed of corrosion from sulfur-bearing gases is closely related to relative humidity.

A stack plume containing warm water vapor discharged into an atmosphere with a high relative humidity is much more persistent and visible than when it is released into a low humidity atmosphere. The released vapors condense and combine with the atmospheric moisture and become highly visible in the first instance and they evaporate and dissipate rapidly in the second case.

Precipitation

3. Precipitation. Rainfall or snow are the most important natural air cleansing mechanisms. Water soluble contaminant gases and particulates greater than one micron in size are washed out of the atmosphere by rainfall and are diluted or deposited on receptor surfaces. Small particles may be accumulated in raindrops or mist and are removed by rainout rather than washout.

Scavenging

While particulate settling influences material that is located in the lower atmospheric layers, precipitation scavenges the air space to the extreme height from which it falls.

Two interactions of particulates and moisture are effective in precipitation scavenging of atmospheres. The direction actions depend on interception, inertia, electrostatic attraction and collisions from random particulate movements. The indirect mechanism is that of incorporation of fine particles in cloud droplets. Scavenging becomes relatively unimportant for particulate sizes under two microns when total removal amounts are considered.

Solar Radiation

4. Solar Radiation. Solar radiation can be an important influence in the creation or solution of air pollution problems. Ultra-violet light is a controlling factor in the production of photochemical smog from reactive contaminants.

World-wide weather measurements have included solar radiation for many years, and the use of such information for investigating photochemical air pollution is extremely useful.

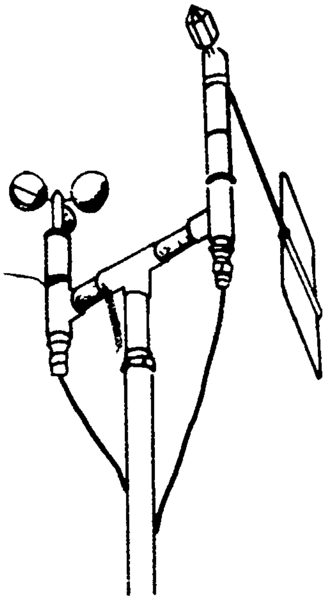
Reductions of ground-level absorption of solar radiation from polluted air layers is a growing concern in seeking long-term, world-wide climatology relationships.

The normal earth surface warming, convection, and vertical turbulence is largely dependent on diurnal solar influences. Without such radiation effects, stagnation and emergency air pollution episode conditions would be more prevalent.

3. Meteorological Measurements

Wind-Speed-Surface

a. Surface Wind Speed. Air movement or wind speed and direction are measured by relatively simple instrumentation. Long-term and short-term recording devices are in common use by most air quality control agencies or investigators. Weather bureau data include such measurements which are usually available in towns and cities of the United States. Wind vanes and rotating-cup anemometers are fairly simple, rugged, and can be readily adapted to recorders for securing continuous readings over extended time periods.

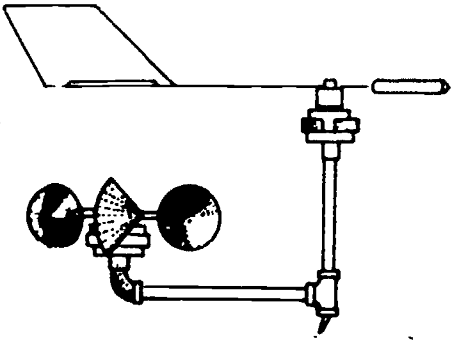


MICROVANE & 3 CUP ANEMOMETER

Errors Where surface terrain features are not consistent from established weather stations to sampling areas, significant errors can result in using such data. Portable units, located in the actual sampling area are warranted in most cases where such features of terrain and wind influence are found.

Transport Patterns Wind direction and speed are basic items which are necessary to give a means of predicting and measuring transport patterns of pollutants from source to receptor.

Mechanical Instruments Mechanical instruments are designed to translate motion of a propeller or windmill wheel to wind speed. Some devices drive small generators, which produce current proportional to velocity of the driving wind, and others operate similar



speedometer with a permanent magnet fixed to an axis.

Induced current from the rotation of vanes is then measured and related to with speed. Direction vanes are simple and readily adaptable to record changes even in very low intensity winds. Some recorders have delay modules to prevent confusion from horizontal turbulence or eddy influences which last only a few seconds or minutes and do not represent a significant directional change.

Wind Speeds - Aloft

b. Wind Speeds Aloft. Wind direction and velocity aloft can be accurately measured by using ordinary balloons inflated with hydrogen or helium. These are observed with an optical instrument known as a theodolite which affords a means of measuring direction drifts at different heights. Triangulation computations then will reveal wind direction and speeds at the observed heights.

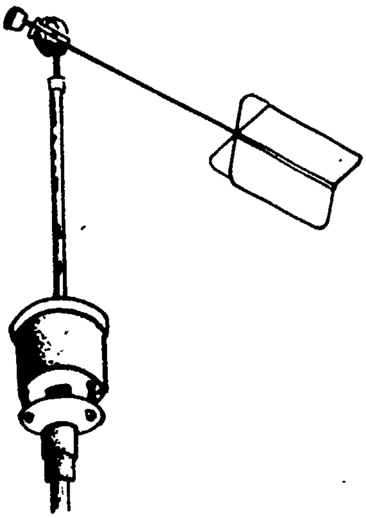
In highly polluted atmospheres, this technique has limited value due to poor visibility and loss of the balloons from view within short periods of time from their release.

Tetroon Balloons

Tetroon balloons are constructed in the shape of a tetrahedron and weighted to give a zero rise condition at a selected height. These are released and allowed to drift in a horizontal fashion to measure direction and velocity at pre-determined atmospheric levels. These balloons can be accurately tracked over considerable time periods and may be operated at low enough levels to remain visible in relatively polluted atmospheres. They are especially useful in determining air flows where surface obstructions complicate simple flow patterns. While the balloon-theodolite system may not have such special advantages, it continues to be widely used due to cost and operational factors. Long sweeps of tetroon balloons require electronic tracking such as radar and transponders attached to the balloon in order to secure responses over extended paths of flight.

Turbulence

c. Turbulence. Instruments for measuring turbulence must be extremely sensitive with rapid response and low inertia characteristics. Sensitive vanes and special anemometers are designed to measure horizontal turbulence with little or no overshooting and lags between the rapid fluctuations of air movements.



BIVANE

A bi-directional wind vane known as as "bi-vane" is used to measure vertical fluctuations of wind direction. One such device utilizes synchro receivers coupled to synchro generators which rotate on horizontal and vertical shafts to chart record separate traces of azimuth and elevation angles of fluctuating winds. Others have potentiometers which respond to minute deflections of vertical and horizontal pressures by gearing to a recording circuit. Some recorders use counting principles to indicate turbulence events for air pollution studies.

Turbidity-Visibility

d. Turbidity and Visibility Measurements. Visibility indexes are often measured by establishing a series of prominent objects at varying known distances from an observation point. The National Air Sampling Network of the Federal government used a letter designation for this purpose for several years at their stations in the United States.

Where objects at suitable distances are not present, an estimate of visibility can be made by observing the outline and clarity of nearer objects. Haze, smoke, and particulate pollutants give blurred and indistinct visible outlines and details which may be related to an index of visibility.

Turbidity has been measured by many types of instruments which depend on light transmission. The usual methods use a source of intense and carefully-focused light which is directed toward a receiver (usually a photocell) which records the intensity of the transmitted beam. The transmission distance and beam intensity can be tailored to give the desired sensitivity and capability. Long paths are applicable to relatively clean atmospheres and slight variations of transmittance (and turbidity) can be detected. These instruments have an advantage of being able to document absence or presence of particulate contaminants over long continuous periods along specified paths. When the path is chosen between sources of particulate pollution and sensitive areas such as residential districts, expected citizen response and comparisons with other sampling methods can be determined.

Humidity

Hygrometers

e. Humidity Measurements. There are various means of expressing atmospheric moisture but the most frequently used in air pollution work is relative humidity. Wet and dry bulb temperatures may be measured and compared to psychrometric charts. Hygrometers consist of two identical thermometers, one of which has a cloth covering over the sensing bulb. When this covering is kept saturated with water, a temperature differential is noted which can be compared to chart values for a humidity reading. Air movement is supplied by a fan to evaporate moisture from the cloth to give steady state, accurate readings. A sling psychrometer incorporates the two thermometers on a handle to allow it to be whirled at a rate to give proper cooling of the wet bulb. Hand aspirated psychrometers are also available, which employ a rubber hand pump for ventilating the wet bulb.

Sling Psychrometer

Hair

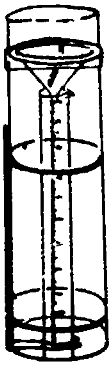
Hair hygrometer instruments use human hairs as a sensor to register changes in ambient moisture. Human hair elongates when exposed to increased relative humidity and shortens slightly as it decreases. This change is magnified and read on an indicating instrument or recorded by a pen tracing on a moving chart. These instruments will respond quite rapidly and are capable of recording about 90% of the humidity change within approximately three minutes after exposure at temperatures between zero and 30 degrees centigrade. The response rate is much slower at lower temperatures.

Infrared

Very accurate humidity measurements can be made by using an infrared hygrometer. This is a complex and sophisticated instrument which gives the mass of water vapor per unit volume of air. The relative absorption of infrared radiation through the air over a specified distance compared to the known water vapor absorption band is measured by a photocell and amplifier system. No phase change or moisture absorption occurs with this instrument and it will respond accurately in all temperatures without changes of sensitivity. If air pollutants are present which have a spectrographic absorption band near the water reference band, erroneous readings may result.

Precipitation Measurements

Rain Gage



PLASTIC RAIN GAUGE

f. Precipitation Measurements. A simple rain gage may be utilized if certain basic principles are applied. A funnel-shaped collector having a uniform cross section, located with its top opening horizontal is often used. A vertical sided cylinder is often used as part of the top opening to prevent splash-out, and best results are obtained with steep funnel walls for the same purpose. The bottom outlet should be comparatively small, especially in dry areas, to prevent evaporation loss. The collector should have a small cross-sectional area (often about one-tenth that of the funnel mouth) to give a magnification for measuring depth of the collected water. Most gages have transparent, calibrated water vessels to allow direct readings.

Weight Gages

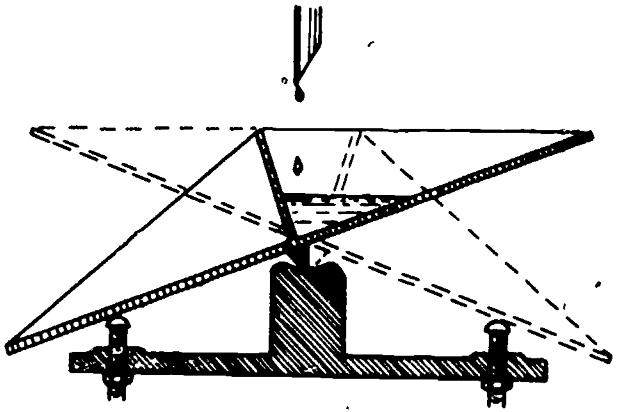
Weighing precipitation gages funnel the moisture into a bucket with a 12-inch rainfall capacity. A mechanical weighing mechanism converts the collected amount to inches or millimeters and may activate a pan on a moving chart. Since freezing does not affect the weight, this device is suitable for all climates, and due to its capacity, is able to measure high precipitation levels before being serviced by emptying the collection bucket. Where freezing occurs, anti-freeze can be used to facilitate ease of emptying the vessel.

Float Gages

Automatic siphoning or float rain gages sense the amount of water collected by means of a float which converts motion to a recorder chart pan. When the recorder registers the top, the collector is emptied by an automatic siphon which discharges into a larger reservoir collector in the instrument base. This device is useful to give time-of-day information as well as total rainfall data. Freezing weather necessitates the use of heaters, which must be controlled to prevent evaporation loss from excess heating. In extremely low temperatures, evaporative losses may be significant from such heaters and other instruments may be more accurate.

Tipping Bucket Gages

A tipping bucket rain gage counts small individual amounts of precipitation. The collection funnel transfers the water to a divided container with two compartments which pivot on a horizontal axis. The compartment is positioned to tilt and empty its contents after



TIPPING BUCKET RAIN GAUGE

a measured amount is collected. Each event is recorded by number and frequency to measure the total and amount and rate of rainfall received.

Radar Methods Recently, reflective radar methods have proven to be useful in measuring surface rainfall and hourly precipitation rates. Where precipitation information is needed for washout studies, weather radar techniques are being utilized with increasing frequency.

Solar Radiation Measurement

g. Solar Radiation Measurement. Instruments which measure radiant energy from the sun are known as actinometers. These may be very simple, with small bimetallic strips or complex "solarimeters" with sensitive thermocouples in suitable exposure chambers. Other actinometers depend on chemical reactions with photo-sensitization characteristics which depend on and measure sunlight effects.

4. Temperature and Wind Structures

Atmospheric temperatures normally decline with increase in height. The rate of temperature change with altitude is known as the lapse rate or temperature lapse rate. A plot of air temperature at various heights is called a temperature-height curve or, simply, a temperature profile. Temperature profiles are very useful in air pollution studies as they indicate a meteorological quality known as air stability. Stability may be defined as a measure of assistance or resistance to vertical air motion.

Stability

Atmospheric stability is a characteristic of a given layer or layers of air that partially control vertical motion throughout the layers. Vertical motion is resisted in stable layers and assisted in unstable layers. A temperature profile is a graphic representation indicating whether an atmospheric layer is stable or unstable.

Lapse Rates

The lapse rate of a parcel of dry air as it moves upward in a stable air environment is known as the adiabatic lapse rate. The lapse rate for saturated air is smaller than for dry air, due to the release of latent heat from the contained moisture as the rising air cools.

intensity as the ground cools during the night and a maximum is reached just before dawn. After sunrise, the ground again warms and the inversion is destroyed, again beginning at the warm ground surface and extending upward for the next few hours. This simplified cycle may be influenced or changed by strong winds, clouds or precipitation which may prevent formation of strong night inversions. Unequal heating from building surfaces, urban development, and terrain factors also tend to complicate the process.

Negative and positive lapse rates sometimes occur at the same time at various vertical heights, with resulting areas of inversion and positive lapse conditions as shown in Figure 12-2.

5. Wind Structures and Stack Plumes

Under neutral or unstable atmospheric conditions, the pollution from a single stack will exhibit highest ground level concentrations relatively near the stack. This usually is found within a downwind distance equal to approximately 20 stack heights. If the pollution results from a single or several closely grouped stacks, the problem may be more serious with increased wind speeds. The opposite is true for the same amount of emissions from large numbers of stacks over a wide area and the dilution or dispersion will be improved from such sources with turbulence and increased wind speeds.

Effluents

Effluents from stacks may be composed of particulates, gases, or combinations of both. The kinds of pollutants contained in the plume dictate the type of sampling and evaluation by the investigator. For particulates, long-term deposits may be of primary interest, and for gases (especially when toxic) short-term exposures may be the governing factor. Particle size information is sometimes important to predict or measure ground-level concentrations. When extremely small sizes are emitted, the studies and predictions are similar to those for gases, and if large particles predominate, areas close to points of release will be most important due to rapid fallout of heavy large components.

When an effluent is released from a stack or chimney, mixing with the surrounding atmosphere begins and dilution increases as it moves away from the stack. The first mixing is influenced by the motion, temperature, and velocity at the point of release. Later, atmospheric parameters begin to influence the mixing process.

Low Density Plumes

Low density plumes released under conditions of little or no wind tend to rise to high elevations and areas near the stack remain relatively unaffected. Large particle or heavy

Superadiabatic When temperature decreases more rapidly with altitude than the adiabatic rate, it is said to have a superadiabatic lapse rate. This ascending air becomes warmer and less dense than the surrounding air and accelerates upward from the increased buoyancy. This reinforced vertical motion is a mark of unstable equilibrium when compared to the "normal" or adiabatic rate.

Stable Air If the lapse rate is less than adiabatic, or "negative," rising air parcels cool, become more dense than the surrounding environment and may tend to sink or return to a starting point. This is stable equilibrium and vertical motions are decreased. Stability or instability are therefore referenced to a neutral equilibrium condition exhibited by an adiabatic lapse rate.

Isothermal In isothermal layers the lapse rate is zero. When temperature increases with height, the lapse rate is negative, and the resulting condition is called an inversion.

Inversion Under relatively cloudless conditions in rural areas, a normal daily temperature lapse cycle may begin with an adiabatic surface condition. That is, the temperature decreases with height near ground surfaces. When solar heating of ground surfaces begins, the rate becomes superadiabatic and thermal turbulence occurs from rapidly rising air parcels. Just before sunset for an hour or two, the air near the ground cools rapidly, decreasing the lapse rate and developing a surface inversion. This layer inversion grows in depth and

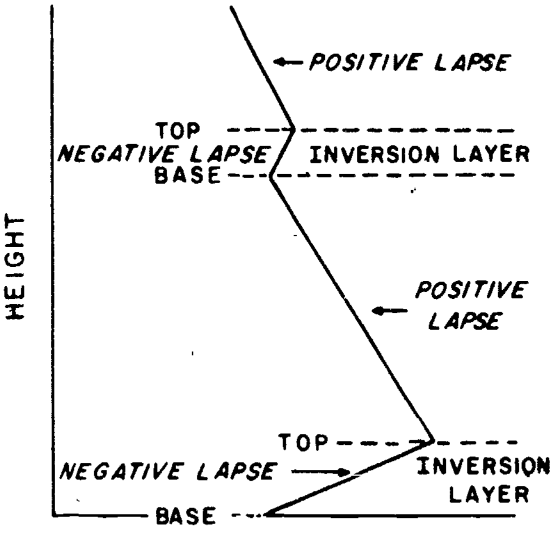


Figure 12-2
Inversions - Aloft and at Ground Surface

TABLE 12-1

PLUME TYPES AND RELATED PARAMETERS

	DESCRIPTION	TEMPERATURE AND PROFILE STABILITY	OCCURRENCE	ASSOCIATED WINDS AND TURBULENCE	PROBABILITY OF GROUND CONTACT
Looping	Plume irregular; movement random and serpentine. Dissipates relatively rapidly.	Strong or superadabiatic lapse; unstable.	Usually during day, clear skies and strong solar heating. Not favored by cloudiness, snow cover or strong winds.	Light to moderate winds together with strong thermal turbulence (convection).	Diffuses rapidly; good probability of high concentrations sporadically contacting ground relatively close to stack.
Coning	Cone-shaped with horizontal axis. More regular and less random than looping. Diffuses and becomes larger as it moves downwind. Dissipates farther downwind than looping plume.	Weak lapse or temperature gradient between dry adabiatic and isothermal; neutral or stable.	Usually during windy conditions, day or night. Cloudiness favored in day. May also occur as a lull condition. Most frequently noted in hilly terrain.	Brisk to strong winds. Turbulence is largely mechanical rather than thermal.	Diffuses less rapidly than looping plume. Fair probability of ground contact some distance downwind. Concentration will be less than but persist longer than that of looping.

TABLE 12-1 (Cont.)
PLUME TYPES AND RELATED PARAMETERS

	DESCRIPTION	TEMPERATURE AND PROFILE STABILITY	OCCURRENCE	ASSOCIATED WINDS AND TURBULENCE	PROBABILITY OF GROUND CONTACT
Fanning	Ribbon-like, horizontal with regular flow. Little or no vertical movement. If stack exit is high it resembles a meandering river, widening but not thickening as it moves downwind. Under greater wind speed and level terrain plume may reach miles downwind. If stack exit is low and winds light, plume rises slowly and drifts as a horizontal layer.	Inverted or near isothermal lapse rate; very stable.	Frequent, mostly at night, any season. More frequent over flat terrain. Usually associated with surface inversions. Favored by light winds, clear skies and snow cover.	Very light to light winds; no turbulence.	Diffuses poorly, concentration remaining high good distance downwind. Probability of ground contact low. (Changes in turbulence or stability can result in ground contact), High ground level concentrations or adverse conditions may occur through fanning because of (a) short stacks, (b) harmful radiation or radioactive fallout, (c) multiple stacks in calm, stable weather, (d) plume travels over terrain much higher and more irregular than terrain of origin.

TABLE 12-1 (Cont.)
PLUME TYPES AND RELATED PARAMETERS

	DESCRIPTION	TEMPERATURE AND PROFILE STABILITY	OCCURRENCE	ASSOCIATED WINDS AND TURBULENCE	PROBABILITY OF GROUND CONTACT
Lofting	Well defined underside with poorly defined diffusive upperside. Result of two opposing stability conditions.	Plume exits into air layer having temperature lapse and is neutral or slightly stable. Just below exit, temperature is inverted and air is very stable.	Transition type occurring in change of lapse to inversion condition. Not uncommon. Occurs mostly near sunset on fair days. Persistence, somewhat dependent on stack height and depth and strength of stable layer below plume. Usually persists for approximately an hour but may persist for most of the night.	Moderate winds and turbulence found in exit layer; very light winds and little or no turbulence in layer below plume.	Probability of ground contact low unless inversion layer is shallow and stack exit is low. Concentration greatest at base of plume but contact usually prevented by stability of inversion layer. This condition considered by some as best for dissipation since pollutants are dispersed in upper air without great probability of ground contact.

TABLE 12-1 (Cont.)
PLUME TYPES AND RELATED PARAMETERS

	DESCRIPTION	TEMPERATURE AND PROFILE STABILITY	OCCURRENCE	ASSOCIATED WINDS AND TURBULENCE	PROBABILITY OF GROUND CONTACT
Fumigation	Plume flat, restricted on upper side; ragged irregular and diffuse on underside. Result of two opposing stability conditions.	Plume often exits in layer experiencing a superadabiatic lapse with attending instability. Above exit layer temperature and air layer is stable.	Transition type occurring in change of inversion to lapse condition. Can occur when nocturnal inversion is being broken up by warming of surface layers by morning sun. Lapse layer usually begins at ground and works upward, less rapidly in winter than in summer. May also occur under sea breeze circulations in late AM or early PM.	Winds light in both layers; Thermal turbulence very evident in lower layer, no turbulence in upper layer.	High probability for ground contact, especially with short stack and a persistent inversion layer.

density gas plumes will release these components near the stack under such conditions. The opposite effect is noted as winds increase, light densities may deflect more rapidly to ground surfaces and heavy materials will be transported further downwind.

6. Plume Types and Meteorological Factors

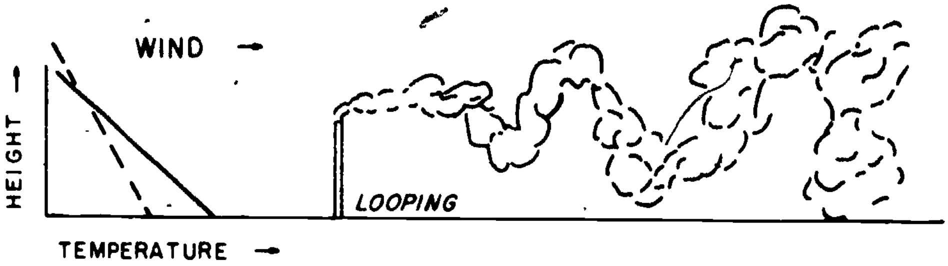
Turbulence characteristics influence the physical form and distribution of gas plumes. Five types of plumes which are classified with respect to their physical configurations are represented schematically in Figure 12-3. The various conditions of vertical stability are shown by the solid temperature-height line and dry adiabatic lapse rates are depicted by the dashed line.

Diffusion Calculations

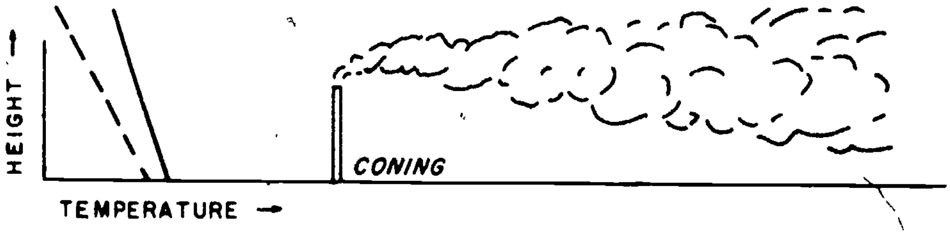
Atmospheric diffusion computations have been devised by various investigators. F. Pasquill of the British Meteorological Office introduced a method and formula for computing dispersion from both elevated and ground level sources. His results were shown in terms of height and width of the airborne plume. A similar method was published by P.J. Meade at the World Meteorological Organization in Geneva in 1960, and F.A. Gifford, Jr., transformed Pasquill's height and width parameters to vertical and horizontal values using standard deviation concentration distribution techniques.

An in-depth treatment of the diffusion equations are not within the scope of this text, but it is important to consider the use of atmospheric effects, since these factors are the bases for such calculations. Wind speed, combined with horizontal and vertical dispersion, allow calculations of centerline concentrations at certain specified downwind distances. Stack heights and stability categories are also important factors in such calculations.

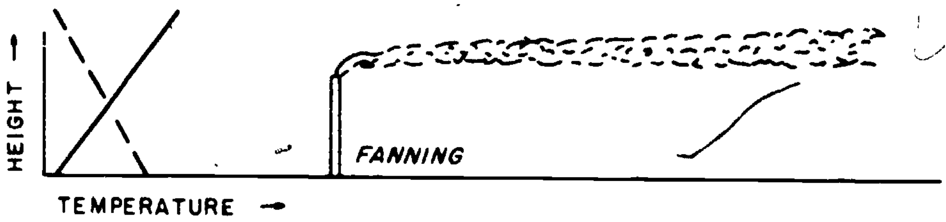
Table 12-1 summarizes Plume characteristics and related parameters illustrated in Figure 12-3.



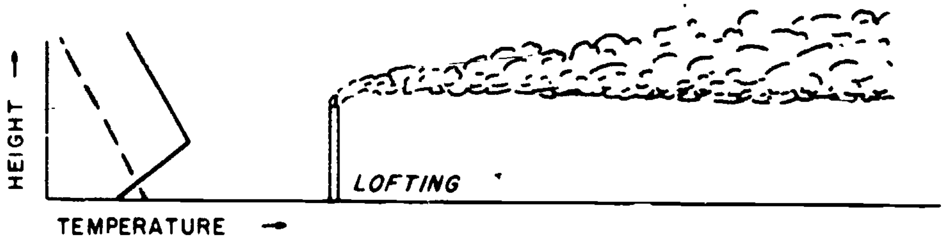
STONG LAPSE CONDITION (LOOPING)



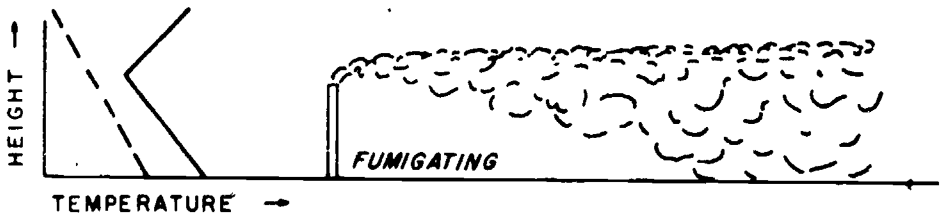
WEAK LAPSE CONDITION (CONING)



INVERSION CONDITION (FANNING)



INVERSION BELOW, LAPSE ALOFT (LOFTING)



LAPSE BELOW, INVERSION ALOFT (FUMIGATION)

Figure 12-3
Plume Types and Lapse Conditions

Problems:

1. Visit the local airport (one with a weather station) Examine all measuring devices available at the site, including weather vanes, anemometers, visibility, humidity, radar, precipitation, and temperature devices, balloons, rockets and so forth.

2. Collect data derived from these devices and write a short report on the information gathered, including test frequency, robot instruments, recording, telemetering and so forth.

3. Find a discharge plume near your area and watch for plume characteristics. Characterize lapse rates based on the plume appearance.

PARAMETERS OF THE AIR ENVIRONMENT

Significance of Pollution

The effects of a polluted air environment are sometimes grouped under five general headings. These are: a) physiological effects, b) material damage, c) visibility reduction, d) agricultural damage, and e) psychological effects.

1. Effects

a. Physiological Effects on Man and Animals. Human deaths recorded at Donora, PA, Poza Rica, Mexico, London, England, and the Meuse Valley of Belgium have shown that localized, high-level pollution can kill. Other studies by many researchers imply less dramatic, but long-lasting and well-documented effects of pollutants on health of humans and animals.

Chronic bronchitis in Los Angeles, London, and New York, along with the rising incidents of lung carcinoma in metropolitan populations are associated with air pollution. Animal fluorosis from dust containing fluorides has been found to result from exposure to emissions from industrial processes in the Pacific northwest states.

Material Damage

b. Material Damage. A frequent and widespread effect of air pollution is the direct damage to structural metals, fabrics and surface coatings. Protective actions, and surface cleaning is estimated to result in an economic loss of several billion dollars annually in the United States. Acid mists, particulate products of combustion, and sulfur-bearing materials as well as secondary pollutants all contribute to such losses. Oxidation of textiles and rubber products causes extensive and rapid damage from the effects of ozone and some of its related oxidant compounds.

Visibility Reduction

c. Visibility Reduction. This effect is the one most noted by early writers and the most easily observed by layman and expert alike. The reduction in visibility or "smog-haze" effects result in scattering of light from surfaces of particles in the air. The amount of such light scattering depends on density of the aerosol, particulate size of the pollutant, thickness of the air mass and other physical factors. Smoke, as a primary particulate pollutant or secondary photochemical smogs may be causitive agents. In some instances, visibility reduction due to pollution gives rise to severe curtailment of transportation and municipal activities. When ultra-violet and other normal radiation effects are reduced by such layers, adverse effects on vegetation and man are observed.

Agricultural Damage

d. Agricultural Damage. Food, forage and ornamental plants show damage from air pollutants. Reduced values result from growth stunting, decreased yields, destruction of flowers and leaf damage. Certain species are so sensitive to specific airborne materials that they can be relied upon for monitoring and identification of pollutants. In California, estimates have been made which run into several millions of dollars per year for damage to edible commercial crops.

The materials usually associated with this damage are organic oxidants, acid mists, secondary reactive pollutants, sulfur oxides, and fluorides.

Psychological Effects

e. Psychological Effects. Periodic public exposure to air pollution has brought forth fear as an important element in human reaction to such environmental conditions. Where actual measurements are lacking, psychosomatic illnesses can be related to the threat of the unknown. This phenomenon should not be ignored as citizen responses, political actions and mental health of affected persons are important factors in shaping control actions. Mass hysteria from episode conditions serve to give emphasis to positive actions and reactions in public and governmental programs for controlling pollution.

2. Parameters of the Air Environment

While there are many materials which can be considered, measured, and related to the significance of air pollution, there are six basic pollutants for which national ambient standards have been developed. These are considered to be basic indicators or parameters of general air quality and are used nationwide as indices of overall ambient air quality. Not all of these materials appear in every section of the country in sufficient quantity to be considered a problem, but at least one or more are found in measurable concentrations almost anywhere on earth.

These materials will be treated individually to afford opportunity to consider each in their respective roles as indicators of overall air quality.

Particulates

a. Particulates. Particulate air pollution as used in this text refers to any matter dispersed in the air, whether solid or liquid, where the individual particles are larger than small molecules but larger than 500 microns in diameter. Such particles stay in the air anywhere from a few seconds to several months. They have a number of physical properties in common, and are generally classified in a single category referred to as aerosols.

Since particulate matter consists of such a wide variety of substances, chemical properties of the material cannot be specific. Biological and mechanical properties are usually grouped in terms of the effects produced on a receptor.

1. Properties of Particulates. Three general physical properties are reasonably well accepted as applying to all particulate matter. These are: surface properties, motions, and optical properties.

Surface Properties

The principle of adsorption applies to the impact of particles and molecules of a gas. Upon collision between such materials and accumulation of gas molecules on or near the particle surface, a fraction of the surface may be covered or coated with gas molecules and adsorption results. If this action is caused by a chemical interaction between the gas and the surface, it is known as chemisorption. Absorption usually refers to the action where a gas is dissolved into the particle.

Motions

All particles, regardless of composition, have the common property of motion. Small particles less than 0.1 micron in size exhibit large random motion by collision with individual molecules. Those larger than one micron have settling velocities and their motions may not be entirely dominated by the motion of the air.

The settleable portion of particulates in motion may be measured by using dustfall techniques. This method of evaluation is not considered representative as an index of overall particulate air pollution, since it does not consider the finer, more mobile sizes. Dustfall itself is a nuisance, so its measurement does give some concept of the deposition of airborne dirt from a contaminated atmosphere.

Optical Properties

The behavior of particles towards light is defined as another class of physical properties. This characteristic or behavior of particles influences visibility, and the optical effects allow a means of perception in the atmosphere.

2. *Reactions of Atmospheric Particulates*. Both particle-particle and particle-gas reactions can and do occur in aerosol mixtures or particulates and gases. The particle-to-particle reactions have been studied only to a limited extent since it is more generally a mechanical reaction and does not significantly alter the overall composition of the air mixture. It is understood, however, that this reaction occurs more readily in size ranges under 0.1 micron where collisions are frequent, but due to the small size, are difficult to study and evaluate. When particles are large enough to identify and study, collisions are much less frequent in the atmosphere because of the low concentrations. Confusion and inaccurate evaluations can result when analyses of particles collected on filters do not consider their abilities to react when placed in close proximity with other reactive particles.

Sources of Particles

3. *Sources of Particulates in Atmospheres*. Large particles result from trituration and small particles are produced principally by condensation. Considerable overlap occurs as small particles can be produced as spray from nebulizer mechanisms and very small particles can result from rupture of bubbles. The production of very small particles below a few microns by dry grinding is rare.

Combustion

An interesting complex source of particulates is that of combustion because four distinct types of particulates can result. Vaporization due to heat produces very fine materials which condense and form particles in ranges between 0.1 microns and 1.0 microns. The energy of the combustion process produces very small particles (less than 0.1 microns) which may be short-lived, unstable molecular masses. Mechanical comminution reduces fuel or ash to particle sizes larger than 1.0 microns which are entrained in the mechanical process streams. When the fuel is an aerosol during the burning process, a very fine ash may escape at or during the process. Soot particles may be formed during partial combustion of fossil fuels.

Wind Erosion

Wind erosion, spraying, grinding, and blasting frequently produce 10 microns and larger particles. The usual sources of dust are from pedestrians, vehicles, and wind action. Partially-burned trash, ash and smoke from burning refuse incinerators and soot from poorly adjusted space heating systems contribute particulates in urban areas.

Particles in size-ranges of 1.0 to 10 microns are usually considered to have been produced locally by point sources or soil becoming airborne by pulverization from plant processes.

Since the small particles between 0.1 microns and 1.0 microns cannot readily be formed by ordinary size reduction processes, they usually are found in aerosols composed of significant amounts of condensation products. In these "small particle size mixtures," combustion products and photochemical aerosols predominate. In most studies, the increase of less than 0.1 micron particles is not chemically formed, but appears to be more directly associated with combustion.

Sulfur Dioxide

b. Sulfur Oxides.

1. Properties. Sulfur dioxide is a colorless, non-explosive, non-flammable gas that most people can taste in atmospheric concentrations of about 0.3 ppm to 1.0 ppm or about 0.9 to 3.0 milligrams per cubic meter. When it is found in levels above 3 ppm, it has an irritating, pungent and characteristic odor. In the air, photochemical and catalytic reactions change it partially to sulfur dioxide or to sulfuric acid. The oxidation which converts sulfur oxide (SO_2) to sulfur trioxide (SO_3) depends on several factors. Time, moisture, and sunlight all affect the degree of this change. Other factors, the amounts of catalysts (nitrogen oxides and hydrocarbons) and the available alkyline and sorptive materials affect the process.

Cause and Effect

The cause and effect relationship of sulfur oxides on receptors is complicated by its interactions with other pollutants, with moisture in the air, and with oxygen. Temperature and sunlight also cause variations in this relationship. Laboratory exposures of animals, materials, and plants yield informative and useful data, but direct application of such findings to ambient conditions in outside atmospheres with all the inherent variables must be done with considerable understanding.

Sources of Sulfur Oxide

2. Sources of Sulfur Oxide. Sulfur oxides in the atmosphere arise mainly from fuel combustion. Liquids and solid fossil fuels usually contain inorganic sulfide and sulfur-bearing organic compounds. The ratio of formation of sulfur

dioxides and sulfur trioxides from the fuel combustion is about 50 parts of sulfur dioxide to one part of the trioxide.

Most urban atmospheres contain sulfur oxides in low concentrations. Since they are highly toxic to vegetation, animals, and man, sensitive detection methods must be used to give short-period averages and maximum concentrations. Other contaminants from combustion processes or urban activities are almost universally present, so analytical and sampling procedures must be chosen to give minimum interferences from such contaminant gases.

Reactions of Sulfur Oxide

3. Reactions of Sulfur Oxides. Experimental laboratory demonstrations show that sulfur dioxide can act as an oxidizing or as a reducing agent at normal room temperatures. With hydrogen sulfide, the gaseous sulfur dioxide reacts to form water and elemental sulfur. As a direct reducing agent, heat is required and it reacts slowly to form sulfur trioxide. In catalytic reactions, this change can occur at ordinary temperatures. Nitrogen oxides will function as catalysts in this reaction.

Effects

4. General Effects of Sulfur Oxides. Sulfur oxides adversely affect human health, agriculture, visibility, materials, and climate. Damage to exposed metal increases with high humidity and temperature. If particulate matter is present, the deleterious effects are also increased.

Corrosion

Corrosion is accelerated by conversion of sulfur oxide to sulfuric acid. This change may occur in the atmosphere or on the metal surface. The corrosion produced consists largely of sulfate salts of the exposed metal. Sulfate salt formed in the air by sulfuric acid and suspended particulates will also corrode many metals.

Low relative humidity (below 70%) slows the corrosion effects considerably, but in atmospheres with very high humidity, noticeable corrosion occurs even when levels of sulfur oxide are quite low.

Metals Damaged

Carbon steels are most affected, followed by zinc, copper, aluminum and stainless steel. Limited economic data is available to document the economic significance of corrosion from sulfur oxides. The maintenance and replacement of overhead wires indicated that high pollution areas tend to need more frequent maintenance, especially where direct wind lines intersect such structures.

In the communication and power transmission industries, corrosion of contact surfaces from sulfur oxides necessitates the use of low reactive metals for such mechanisms. Gold, palladium, and silver are used depending on the pollution levels. Silver contacts are most readily tarnished with gold being the least affected.

Masonry and Stone Damage

Limestone, marble, roofing slate, and mortar are attacked by sulfur dioxide in the presence of moisture which converts it to sulfurous or sulfuric acid. Any building stone containing carbonate is damaged by the reaction whereby carbonates are converted to soluble surfaces which are readily leached away by rain water. Granite and some sandstones contain little or no carbonates and therefore are not significantly affected by airborne sulfur oxides.

Damage to Buildings

Building surfaces containing dolomites and limestone are susceptible to acid attack. Dolomite contains magnesium and calcium carbonates which are vulnerable. When calcium sulfate is formed on masonry surfaces, it is more bulky than the parent stone and appears to be bulbous and lumpy. Roofing slate often contains calcareous sandstone or carbonates and shows damage on their undersides and between laps where films of moisture are held.

Old buildings suffer from cracking and cleavage of planes and of stones which slowly open and lift fragments from the surface due to crystalization of calcium and magnesium salts formed by sulfur oxide reactions. Such crystalization may increase the volume of these "wedges" by as much as four times.

Valuable monuments and archaeological materials as well as buildings suffer real damage from high levels of combustion emissions containing sulfur oxides. It has been noted that the stone obelisk known as Cleopatra's Needle has suffered more deterioration in London's atmosphere in the past 70 years than the earlier 3,000 years of its history before being removed from Alexandria, Egypt.

Animal and Vegetable Fibers

Animal fibers used in textile manufacture, such as wools, and furs, are more resistant to acid damage than certain cellulose vegetable fibers and synthetics. Cotton, hemp, jute, linen, synthetic rayons and nylons are sensitive to acid combustion products containing sulfurous and sulfuric acids.

Fabric Dyes

Some fabric dyes are reduced or destroyed even without exposure to sunlight. Studies of the National Air Sampling Network effects packages show the maximum fading of some dyes when sulfur oxide levels were highest.

Experiments with other gaseous pollutants indicate that sulfur dioxide working together with other airborne gases produced textile fading and deterioration effects greater than that observed with any of the components by themselves.

Paper and leather absorb and are adversely affected by SO_2. Leather disintegrates and loses its strength while paper becomes discolored, brittle, and fragile.

Paints

Some oil-based paints dry slower by 50 to 100% in atmospheric concentrations of 1 ppm of sulfur dioxide. Other paints show reduced gloss and increased moisture sensitivity in sulfur dioxide atmospheres. Ammonium sulfate crystals form in Brunswick green pigments causing them to appear blue in air concentrations of 0.1 to 0.2 ppm of sulfur dioxide.

Health Effects

5. Health Effects: Toxicological effects of sulfur oxides are of primary concern, both for humans and animals. Most available data are from grossly polluted atmospheres which may not be directly comparable or related to low-level, long-term conditions. Even extensive experimentation with small laboratory animals in controlled atmospheres must be used with the realization that ambient air mixtures and varying physical conditions of the air environment will produce additional factors.

Changes in lung pathology of small experimental animals (especially mice, rats, hamsters and guinea pigs), all appear to generally agree that high concentrations (300 to approximately 1000 ppm) significantly alter the respiratory system and lead to marked life-shortening. Constriction of bronchial passages and resulting airflow reductions are generally reported for most small animal exposures to high level concentrations.

In certain sensitive humans, bronchospasm can be induced by exposures for 30 minutes to 1 or 2 ppm of sulfur dioxide and almost all persons will experience respiratory irritation at 5 ppm or above.

London Episodes

The London episodes document a rise in daily death rates when there is an abrupt rise of sulfur dioxide to levels as low as 0.25 ppm (715 micrograms per cubic meter) when smoke is present at about 750 micrograms per cubic meter. After this episode, it appears that when sulfur dioxides were found in excess of 1500 micrograms per cubic meter for one day and particulate levels exceeded 2000 micrograms per cubic meter, an overall death rate of 20% more over baseline levels was documented. Similar exposures in New York during a 24-hour sulfur dioxide concentration gave almost identical results.

Vegetation Effects

6. Vegetation Effects. Injury to plants is thought to be due to the apparent accumulation of absorbed sulfur oxides which are transformed to sulfuric acid and then to sulfates. Some studies indicate that high levels overwhelm the usual defense mechanisms, resulting in accumulated sulfite which attacks plant cells from sulfurous acid formation. This absorption rate depends on airborne concentration and determines the amount of acute injury.

Low Vs. High Level Exposures

Low level concentrations over a time period will be resisted better than the same amount of pollution in high concentration for a shorter period. Some plant species can be used to plot mathematical relationships of exposure time, concentration and damage from airborne sulfur dioxide.

Susceptability

Different plants respond with different susceptability to acute injury from sulfur dioxide. Alfalfa has been noted as a sensitive indicator with noticeable damage occurring at slightly over 1.0 ppm for a one-hour exposure.

Chronic plant injury results from low-level, long-term exposures where excessive amounts of sulfate accumulate in leaf and plant tissues. Growth suppression and yield reduction in crops have been blamed on low-level exposures which are below the amount capable of causing visible injury.

Carbon Monoxide

c. Carbon Monoxide.

1. Properties. Carbon monoxide is a major pollutant in the United States with an estimated annual emission rate of about one hundred million tons. It is slightly lighter than air (97%), colorless, odorless, and tasteless and is formed from combustion or oxidation with insufficient oxygen to form carbon dioxide. Carbon dioxide in the atmosphere is converted to CO in high temperatures under reducing conditions. This process is known as dissociation of carbon dioxide to carbon monoxide.

Sources

2. Sources. About 64% of all carbon monoxide formed in the United States is considered to result from transportation sources. The automobile is the greatest single source. Burning refuse, forest fires, and structural fires are major sources. Industrial sources include foundries, petroleum refineries, and paper mills. Stationary sources such as steam-electric generating plants and industrial, commercial, and domestic heating facilities also produce this contaminant.

Reactions

3. Reactions. If there were no scavenging or reaction processes affecting carbon monoxide, the atmospheric levels would be expected to rise each year from its continued production at such high rates. Measurements in non-urban areas have indicated that this expected buildup does not occur and some theories are advanced indicating that upper atmosphere oxidation (where short-wave, ultra-violet radiation is greatest) converts carbon monoxide to dioxide. This theory has been offered to explain the apparent reduction of rates of accumulation at an upper concentration limit in spite of long-period, high-level global emissions.

Effects

4. Effects. Carbon monoxide has long been recognized as having a high toxicity potential in urban atmospheres. Investigations of current levels and the health involvement such as respiratory, cardiovascular, anemia, and renal effects continue to be made by governmental and regulatory agencies. In-plant monoxide exposure studies have resulted in reductions of threshold limits over the past years from 100 parts per million to 50 parts per million for eight-hour daily exposures. Many urban sampling stations show levels which approach and sometimes surpass this level, especially during periods of heavy vehicular traffic.

Detection

With no warning properties which allow ready detection by the senses such as smell, or sight, carbon monoxide is insidious and may produce significant impairment and damaging symptons.

Human Effect

The most significant human effect is related to impairment of oxygen transport by the blood. Carbon monoxide has a great affinity for red blood cells and combines readily to reduce their oxygen-carrying capacity. Exposure and resulting carbon monoxide toxicity is directly dependent on the concentration of monoxide in the inhaled air and duration of the exposure.

The usual symptons of injury are headache, dizziness, nausea, muscular weakness and with increasing exposure, collapse, unconsciousness and death. Exertion, with higher-than-normal breathing rates, hasten the symptons and blood levels of carboxy hemoglobin (Hb CO).

Many individuals show impairment with a level of Hb CO in blood of 5%, which corresponds approximately to an air level of 30 parts per million monoxide at normal human activity. When exposures are terminated, the red cells slowly lose their absorbed monoxide and the oxygen-carrying characteristic is restored.

Hydrocarbons

d. Hydrocarbons.

1. Properties. Hydrocarbons are organic compounds whose molecules consist of atoms of hydrogen and carbon only. Those considered in this text are gas-phase compounds which may be encountered in the atmosphere. Those having a carbon number of one to four are gaseous at normal temperatures, those with a carbon number above five are liquids or solids when found in the pure state.

Hydrocarbons are usually listed in three major divisions: 1) aromatic, 2) aliphatic and, 3) alicyclic. Aromatics have a "benzene structure" which is a six carbon ring with three double bonds. Where no such ring structure exists, the compound is said to be aliphatic. If the organic ring structure is not identifiable as a benzene ring, the compound is considered to be alicyclic. There are many subdivisions in each of these major divisions.

2. Sources. Four major sources of hydrocarbons are well documented: 1) petroleum, 2) coal, 3) natural gas 4) biological products. The loss of this contaminant into the atmosphere occurs during production, storage, transport, processing, and use of the original organic material.

Petroleum

In the petroleum industry, potential emission sources are leakage in oil field operations, gasoline storage tanks, refining, loading of gasoline, flares, pumps, compressors, and waste-handling equipment. During marketing and distribution of gasoline, hydrocarbon vapors are released from automobile tank-filling operations, service station tank filling, tank-truck loading, and piping of gasoline to pumps and storage. The main source of organic solvents is from petroleum. Smaller contributions come from drug, chemical, and pharmaceutical manufacturing.

Cleaning

Degreasing and cleaning of parts sometimes causes volatile vapor losses and emissions. Plastic and rubber product manufacturing involves use of solvent-bearing adhesives which lead to organic emissions.

Manufacturing

Paint, varnish, coatings and lacquers have high percentages of solvents which evaporate during drying cycles after application.

Fuel Burning

The combustion of fuels when equipment is poorly adjusted leads to significant emissions of hydrocarbons. Automobiles and stationary internal combustion engines are major sources in urban areas.

Waste Burning

Open burning of waste materials can cause high organic emissions from incomplete combustion. The largest source is the disposal of municipal garbage by open burning. Agricultural and forest burning are also significant sources, especially during uncontrolled forest and prairie fires.

3. Reactions. Hydrocarbons in the atmosphere are important to air pollution control agencies because of their characteristic of participating in secondary reactions with other compounds. The exact chemistry of such reactions is sometimes unclear, but there are definite observable reactions with oxygen atoms, ozone molecules and free radicals in the presence of sunlight.

Sunlight Effects

It is thought that hydrocarbons and sunlight alone do not react appreciably, but the presence of nitrogen oxides and hydrocarbons give rise to photochemical smog.

Ozone Production

One significant product of photochemical origin is ozone (O_3), a toxic and highly-reactive form of oxygen. This material is a secondary contaminant and is known as a photochemical oxidant. The amounts of ozone and photochemical materials produced depend on the levels of hydrocarbons present, the levels of nitrogen oxide, and certain meteorological factors including sunlight and temperature.

Methane

While methane is a hydrocarbon, it is considered photochemically non-reactive and must be subtracted as a major contributor to air pollution. In atmospheres where a high percentage of hydrocarbons present is measured as methane, a monitoring system must be chosen to detect the mechane levels so that the real significance of total hydrocarbons reactions can be realized.

Ethylene

A major hydrocarbon found in automobile exhaust is ethylene. It is considered to be a significant photo-oxidant and presents one of the greatest hazards to plants.

4. <u>Effects</u>. The effects of hydrocarbons alone would not be particularly significant. The pro-motion of photochemical reactions and formation of other derivatives cause the more noticeable effects.

Human Responses

Eye irritation is one of the most noticeable and important effects of photochemical air pollution. Formaldehyde and other aldehydes are involved in eye-irritation effects.

Aliphatics

Hydrocarbons themselves have rarely been implicated as having direct physiological effects on humans, even in rather high concentrations. The toxicity of the reaction products is of much greater importance than hydrocarbons themselves. In high concentrations, ethylene, propylene and acetylene may produce anaesthetic effects, but in ambient air, the likelihood of sufficient quantities for this response is remote.

Alicyclics

Alicyclic hydrocarbons are similar in their characteristics and are considered to have a relatively low order of human toxicity, except in overwhelming exposures.

Aromatics

Vapors from aromatic hydrocarbons are irritating to the mucous membrances and are considered biochemically active. Industrial uses of benzene and toluene have proven toxicity potentials. Long-term exposures even at low levels, are to be avoided. Ambient atmospheres do not usually contain sufficient levels to give physiological damage except in rare instances near plant exhaust systems or near drying operations. Levels below 25 parts per million are considered to be safe for continued human occupancy.

Vegetative Effects

Damage to green-house plants from illuminating gas leads to the discovery that ethylene has adverse effects on growing vegetation. Certain sensitive plants are damaged by concentrations of ethylene as low as 0.001 to 0.5 parts per million. The principle effect is growth inhibition. Other characteristic effects of ethylene are dry wilt of orchids and closing of carnation blossoms (13-1). Two other hydrocarbons, acetylene and propylene, have been implicated in adverse plant effects, but 60 to 500 times the concentration is needed to give a comparable result.

e. Oxides of Nitrogen. The term NO_x is widely used to represent a composite of the two nitrogen oxide compounds, nitric oxide (NO) and nitrogen dioxide (NO_2), which are the most important in air pollution considerations.

Other oxides of nitrogen include nitrous oxide (N_2O), nitrogen sesqui oxide (N_2O_3), nitrogen tetroxide (N_2O_4), and nitrogen pentoxide (N_2O_5). Of these, only nitrous oxide is found in significant concentrations in the atmosphere.

1. Properties. Nitric oxide (NO) is an odorless, colorless gas which is formed during high-temperature combustion processes by combination of atmospheric oxygen and nitrogen.

The reaction depends on the concentrations of each gas present, pressure, temperature, and time of passage through temperature ranges. Nitric oxides

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(13-1). Air Quality Criteria for Hydrocarbons, U.S. Department of HEW, March 1970, National Air Pollution Control Administration Publication No. AP-64.

are more prevalent when combustion is followed by rapid cooling of the gas stream. Nitrogen dioxide has a brown-orange color with a pungent, irritating odor. It is highly oxidizing and corrosive and is considered toxic to humans.

Natural

2. Sources. The greatest proportion of NO_x is the nitric oxide (NO) form from bacterial action. It is estimated that 500 million tons per year is produced world-wide from natural biological processes. Emissions of NO_2 and NO from man-made sources are estimated at about 50 million tons per year.

Man-Made

There are notable differences in urban and rural NO_x concentrations. Generally city atmospheres contain 10 to 100 times as much as non-urban atmospheres.

The most important man-made source of NO_x is associated with fuel combustion. The burning of coal, oil, natural gas, and motor vehicle fuel accounted for 18 million tons of NO_x during the year 1968. Power plants emitted about 4 million tons, industries 4.8 million tons, and space heating produced about 1.2 million tons. It was estimated that of the 1968 levels, 8 million tons came from transportation sources, with motor vehicles responsible for 7 million tons.

The combustion of waste and refuse by burning produced about 2.5 million tons of NO_x during 1968.

The production of nitric acid and its use in industrial chemical processes accounts for about 0.2 million tons per year.

Sunlight Reactions

3. Reactions. The atmospheric reaction of NO_x with hydrocarbons in the presence of sunlight is a complex reaction. To greatly simplify this cycle, one can consider that NO_x is an efficient absorber of visible and ultra-violet light from solar radiation. This radiation has enough energy to alter or disrupt chemical bonds in NO_2 to form nitric oxide (NO) and oxygen in the atomic form (O). The atomic oxygen (O) reacts with atmospheric molecular oxygen (O_2) to form ozone (O_3) which is a strong oxidant in the ambient air. The ozone will then combine with reactive hydrocarbons (olefins and aromatics) to produce photochemical pollutants.

4. Effects. Some textile dyes are faded and discolored by the reaction of No_x in the air.

Material Effects

Such materials situated near combustion processes exhibit marked changes due to high-temperature production of these oxides. Dyes containing amino compounds are especially vulnerable to this damage. Violet, green, and blue shades of acetates show fading when exposed in rooms with gas heaters.

White fabrics woven from nylon, acetate, and certain permanent-press materials have shown mysterious yellow streaks when stored or on display. Laboratory experiments show that NO_x will produce this result, and resistive additives are being woven with the fabrics to prevent such damage.

Metals

Electrical contacts, relays, and springs, have a high failure and corrosion rate in areas where NO_x and dust levels coincide. The deposition of nitrate-bearing dust has been found to be an important causative factor.

Vegetation

Even though the involvement of NO_x in photochemical reactions is well documented, effects on plants by NO_x have been difficult to prove. Some plant damage near nitric acid plants has been noted but no widespread characteristic patterns are known.

Laboratory studies have noted certain interesting effects due to high-level exposures (one part per million or more), but evidence of injury from low-level chronic exposures are not particularly conclusive. Some yield reductions have been attributed to NO_x when plants are fumigated with low concentrations. It is generally thought that other effects such as temperature, soil moisture, nutrition, etc., may be more easily measured than the effects of NO_x on most commercial crops.

Human Effects

There are only limited data available on toxicological effects of oxides of nitrogen in human exposures. The information that is available deals primarily with levels much greater than can be conceived in ambient air even in grossly polluted areas. High experimental exposures produce transient effects of increased breathing difficulties and reduced breathing capacity.

Occupational exposures to extremely high levels produce pulmonary edema and decreased vital capacity. These symptoms result from 30-minute exposure to approximate 90 parts per million NO_2.

f. Oxidants.

1. Properties. With respect to air pollution, ozone (O_3) is the principle oxidant gas now being monitored to detect the presence of "total oxidants." Surface air usually contains total oxidant levels from 0.01 to 0.03 parts per million. These concentrations are not detectable by the human senses. Increases in altitude give considerable increases in ozone levels.

Oxidants are detrimental to biological systems. Generally, oxidation refers to chemical reactions where oxygen combines with other atoms to form compounds known as oxides. Oxidation is used also as a term to describe the loss of electrons by an atom or molecule.

2. Sources. Photochemical oxidants are produced by reactions between hydrocarbons and nitrogen oxides in air in the presence of sunlight. Ozone and peroxyacyl nitrates (PAN) along with other organic nitrogen compounds which are identified as photochemical smog, are produced by this process. Ozone is the primary product of this photochemical process and virtually none is formed naturally.

Oxidation-
Reduction

3. Reactions. Ozone is a highly-reactive substance and will readily give up its extra oxygen atom upon contact with another substance to become ordinary oxygen (O_2). The material that receives the extra oxygen is said to have been "oxidized." The ozone is said to have been "reduced."

When nitrogen oxides are present in the form of nitrogen dioxide (NO_2), and react with sunlight, NO_2 and atomic oxygen (O) are formed. Ozone is then formed by the reaction of atomic oxygen and naturally occurring atmospheric oxygen (O_2). This cycle continues by the reaction of NO and NO_3 to form new nitrogen dioxide and ordinary oxygen. This is a balancing reaction and the cycle perpetuates itself as long as sunlight energy and the necessary reactant substances are present.

Certain types of hydrocarbons enter this cycle of reactants and it is theorized that oxygen atoms attack the hydrocarbons to form oxidized compounds and free hydrocarbon radicals which react with NO to form NO_2. This reaction results in a buildup of O_3 and NO_2 and a depletion of nitric oxide (NO).

Health Effects

4. Effects. Humans will usually detect ozone when the concentration reaches about 0.05 parts per million. Since there are more irritating effects at these levels, odor is not a common compliant. Throat irritation occurs at 0.10 parts per million and increases with further elevated concentrations.

Large doses of ozone can produce emphysema, bronchitis, and pulmonary edema. Some researchers indicate that cell changes in heart muscles and other parts of the body as well as in the respiratory system occur from exposures to ozone.

Plant Effects

In the 1950's, early air pollution researchers began to notice plant damage in the Los Angeles basin. Further research and experiments at the University of California showed that bean and tomato seedlings, grapes and grape leaves, petunias, and lettuce were injured by (PAN). Ozone is one of the most reactive of the gaseous air pollutants and it is responsible for causing leaf yellowing and plant aging. The degree of damage by any one pollutant is difficult to assess in open, natural areas due to the known effects of single contaminants such as sulfur oxides, fluorides, and chlorides.

Acid Mists

g. Other Pollutants. Many other pollutants have significance in certain special areas where special processes are in use. Acid mists emitted from sulfuric acid manufacturing plants are highly irritating, offensive, and damaging to property and plants.

Sulfides

Hydrogen sulfide (H_2S) is a highly-toxic material found in certain "sour" crude oils and natural gases in the Rocky Mountain areas of Wyoming, Montana, and Mexico. The conversion of H_2S to SO_2 by burning at refineries, wellsites, and oil field tank batteries gives rise to significant sulfur oxide levels. Sulfur recovery units are utilized to efficiently remove sulfides from these crude oils and natural gases to produce elemental sulfur and allow the use of the oil and gas for further refining or fuel use.

Decomposition of organic wastes produces hydrogen sulfides and mercaptans. These materials are also found in odorous gases which are by-products of the Kraft pulp industry.

In many cases, odor is a sufficient pollution index to evaluate the hazard. In the case of hydrogen sulfide, however, the sense of smell cannot be relied upon to give reliable information on its occurrence. This is due to the paralysis of the olfactory nerve and loss of smell response upon high exposures to this material.

Fluorides

The reduction of aluminum ores and phosphate milling give rise to the release of fluorides. Animal toxicity in the Pacific northwest has prompted the use of emission controls in aluminum smelters.

Chemical processes and metal smelters are potential sources for airborne lead and arsenic. These materials are significant due to their known health effects on humans and animals.

Uranium tailings and waste piles which are unstabilized allow radioactive materials to become airborne. Special interest has been directed to the presence of radium compounds because of their long-lived activity in these discarded piles.

Problems:

1. Select and measure several air parameters. Visibility, material damage (put out new material and watch for changes), particulate (settleable) are some of the easier ones to measure.

2. Decide on the source of the pollution problem. Is this an easy job?

3. Vary the sites selected for sampling and discuss possible changes in results, for example, are particulates higher near highways or in a rural area?

4. What specific pollutants are common in your area and what are their sources?

5. Has a control program been instituted to reduce pollution?

VARIATIONS IN TIME AND SPACE

Air quality monitoring is not a static process if it is successful in giving answers that can be used for controlling or reducing emissions. The fallacies of dependence on single time or "grab" samples have been discussed in this text, and it is equally important to avoid sampling and measuring which merely restates known facts about the atmosphere. Long-term sampling to establish trends and patterns of ambient pollutants is useful to predict effects, identify sources and detect reductions associated with control measures. When short-term, high-level standards are exceeded or when the contaminant is hazardous, single samples may be adequate to recommend correction programs.

Seasonal weather patterns including wind and temperature variations must be included in any survey which attempts to assign yearly averages. The use of background figures from one season or even for a year may not be accurate enough to really evaluate low-level emissions during years when weather systems are exceptionally dry or wet in comparison with so-called normal conditions. The rain-out or snow-out of gross particulate pollutants often brings noticeable citizen responses and can serve to damage surfaces excessively when compared to dry dispersed depositions over longer time periods.

Channeling and reversals of winds in basins or airsheds can concentrate and re-expose receptors to increasing amounts of pollutants that may be ordinarily unnoticed and below established standards.

Vehicular pollution emissions in metropolitan areas usually follow cyclic patterns associated with peoples' work habits. In some central urban locations pollution peaks coincide with morning and evening traffic, while others are overwhelmed by influences of commercial traffic in the mid-day business periods.

Fugitive dust from construction and vehicle travel on unpaved roads can overwhelm particulate samplers during dry weather or windy conditions.

GLOBAL POLLUTION

Dispersion of pollutants may create problems such as changes in global climate or atmospheric conditions. Some theorists hypothesize that an increase in carbon dioxide levels could raise global temperatures sufficiently to raise the ocean level due to the melting of polar ice deposits.

From 1958 through 1968, the rate of increase of atmospheric carbon dioxide averaged about 0.7 parts per million. During the years 1969 and 1970, the measured increase at the same observatory (Mauna Loa) has been 1.35 parts per million per year. Accurate studies of climatic change must be carefully made in order to verify or discount these predicted effects on global climate.

There are wide variations in pollution levels between cities of comparable size and between regions having similar geographic characteristics. These differences are often related to the types of fuels used and population distribution patterns.

Overall air pollution emissions increase along with increases in population and production. In areas of low population density and limited numbers of point sources, correction effects are dramatic and quite easily documented. This is especially true due to the overall good air quality and excellent visibility in the intervening air spaces. On the other hand, the introduction of relatively minor sources will be noticed as increased pollution even by the most casual observer.

LEGAL CHANGES

Changes in environmental laws are being instituted to provide greater protection for the environment. This development is seen in the enactment of the National Environmental Policy Act (NEPA), wherein the Congress states "it is the continuing policy of the Federal Government to create and maintain conditions under which man and nature can exist in productive harmony."

CITIZEN INVOLVEMENT

Another factor influencing monitoring and detection is found in the provision for citizen responses to standards setting and rule making by governmental agencies. The need for pollution control programs themselves must be explained to and understood by legislatures and civic governing bodies. New obligations are placed on citizens to become knowledgeable regarding pollution effects, standards and legal requirements.

CITIZEN SUITS

The Federal Clean Air Act Amendment of 1970 (14-1) Section 304 provides for citizen participation in the enforcement of standards by citizen suits. These actions are carefully restricted to situations where violations of standards or failures to act on the part of the responsible agencies are alleged. This provision is described in the Senate Committee Report (14-2) as a means to "motivate governmental

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(14-1) Public Law 91-604. 91st Congress H.R. 17255. December 31, 1970.

(14-2) Report of the Committee on Public Works. U. S. Senate No. 91-1196.

agencies charged with the responsibility to bring enforcement and abatement proceedings."

LEVELS OF CONCERN

Levels of concern for environmental quality have been described in four categories by one writer. (14-3) These are (1) bare survival -- control of major physical damage, (2) control of disease or injury -- chronic damage or accidental responses, (3) efficient performance -- adequate maintenance for proper functioning, (4) comfort -- satisfaction and enjoyment of life and property.

If we limit our concerns to bare survival, any failure or change is disastrous. If we are only providing for continuing safety, we also can expect some serious effects from failure. We can tolerate some change of efficiency for limited periods, but most will agree that this needs some reversal and correction. The most rewarding achievement of course, would be to gain the most difficult and elusive goal--that of assured comfort and a satisfying environment.

NATURAL SYSTEMS

It would be a grave mistake to assume that only man pollutes the air. Nature produces enormous quantities of hydrocarbons, nitrogen oxides, sulfur compounds and other pollutants. Under usual conditions, barring forest fires, dust storms and volcanoes, natural systems remove what nature adds and man does not become concerned. However, there are other less dramatic sources (windy conditions, dry desert areas, hurricanes, mineral springs, and decaying organic matter) that cannot be disregarded as major sources in certain areas under special conditions.

(14-3) Winthrop, H. (1968). "Ventures in Social Interpretation" Page 252. Appleton, New York.

Problems:

1. Select sites downstream (air) from an air pollution source. Does the distance from the source affect parameter measurement? What is the change? Is the change linear or logrithmic?

2. Does the season of the year or stability of the air cause changes in parameter values?

3. Could pollution standards be used for zoning considerations in future planning?

MONITORING TECHNIQUES

1. Introduction

In order to secure meaningful and accurate results from sampling, certain basic factors must be recognized.

Basic Considerations

Five considerations are of primary importance: 1) reasons for sampling, 2) type of instrumentation or collection, 3) methods of analysis, 4) laboratory capabilities and, 5) data evaluation and interpretation.

Reasons

When we consider the reasons for monitoring or sampling, decisions must be made so the effort is coordinated to a specific need for information. Sampling effluents from a single source or stack can impose much different conditions than seeking general overall data from an urban area. In any case, sample location should be representative and free of interferences or obstructions. The need for more than one sample is apparent when annual or geometric means are needed for comparisons with limits.

Instruments

It is necessary to carefully select the proper type of sampling device or instrument. A single sample, by opening an evacuated flask in a gaseous atmosphere, may be adequate in some cases, but if longer-term, integrated results are needed, bubbling trains with specific collection solutions would be required. In either case, the exact volume of air sampled must be known. The technique has to be balanced with and related to sampling objectives and available resources.

Analysis

Methods of analysis are chosen before samples are taken. Interfering influences or materials should be known and considered in the choice of analysis methods. Sensitivity is an important factor in order to be able to relate and compare results with standards and regulations.

Laboratory

When highly-toxic and hazardous materials are being sampled, limits are generally imposed in the parts per billion range. This places a significant requirement on the laboratory to be able to detect such low concentrations. The sampling methods are also highly dependent on laboratory capabilities. When low volume evacuated flask "grab" samples are collected in low concentration atmospheres, thresholds of detection become very important, and special methods of sample preparation or preservation may be required. Known samples are often desirable to test analysis systems and insure reproducible and accurate results.

Evaluation

Reporting

The presentation and calculation of resultant data is extremely important. The best methods, sampling, and analysis can be entirely useless if information cannot be intelligently interpreted. All factors culminate in the final report, which may be the only part of the program that is available to the agency staff, pollution source, or enforcement officer. Limited amounts of information from short-term surveys can be hand calculated, tabulated, and explained in a survey report. The report should be accurate and sufficiently detailed to be understood without extraneous explanations. When legal or enforcement actions depend on such surveys, care must be taken to meet regulation and statutory requirements so that results can be used as evidence or proof.

Unless emergency situations develop and time is not available, sampling periods must be chosen to clearly represent actual day-to-day averages rather than maximum or minimum conditions.

Intelligent and accurate application of background conditions is sometimes quite important. Natural conditions, over which no control is possible, must be a part of the interpretation of results.

In instances where multiple sources are situated in close proximity to each other, stack or point source sampling is required to supplement ambient or area sampling.

An excellent reference of recommended practice for planning the sampling of the atmosphere is contained in Part 23, American Society for Testing and Materials Designation 1357-67.

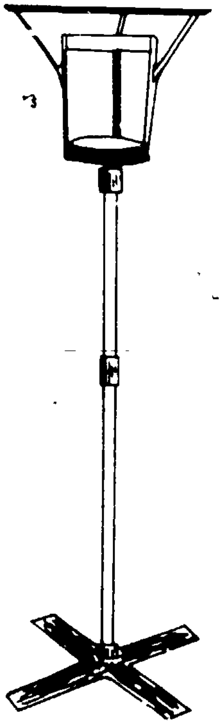
2. Ambient Monitoring Techniques

a. Sampling of Particulate Matter.

Weight Per Area

1. Dustfall. For materials larger than 10 microns in size, dustfall is a most common index, reported in tons per square mile per month or in grams per square meter per month. A container of uniform cross-section placed in a representative area is used. The weight per unit of area is extrapolated from a few square inches or centimeters to a square mile or a square meter. Usual values for urban areas are 10 to 100 tons per square mile per month. In heavily-polluted industrial complexes, values may reach 2,000 tons per square mile per month.

Dustfall measurements do not reflect the lighter, smaller components accurately, and therefore offer limited scientific interpretation or correlation between sampled areas. Trends of dustfall can be noted with respect to industrial or human activity and evidence of major sources of dust can be secured when multiple sample stations are carefully chosen. Small fluctuations in dustfall cannot be used to secure detailed and exacting information on air quality. Open areas, heavy traffic, wind velocity, and surface obstructions add to the complexity of such sampling.



STANCHION WITH DUST FALL JAR HOLDER

Particles greater than 10 microns in size exist in most atmospheres only in very low numerical concentrations. Their settling velocities and impact characteristics are the main factors influencing their deposition in a dustfall jar or container. The configuration of the container, the aerodynamic effect of its edges, the mounting brackets and its location with respect to adjacent structures complicate the collection process.

These conditions must be carefully standardized insofar as possible in order to attach anything more than relative significance to the data.

Cyclonic Collectors

Cyclonic collectors can be used to collect the larger particles above five microns with good efficiency. Some fraction of the smaller particles are also removed, and the relative efficiencies must be known in order to successfully relate samples with other methods of collection.

Some size-selective methods of sampling have been used in attempting to sample respirable versus non-respirable fractions of airborne dust. These devices are employed in industrial hygiene measurements, and are not generally used to give comparisons with gravimetric air pollution standards.

Dustfall Jar

Thus far, the dustfall jar with its inherent limitations is the most widely used technique for air quality evaluation of large (over 10 microns) particles. It has the advantage of being inexpensive, can be operated relatively unattended and can serve to integrate long-term effects.

Low-Humidity Collection

In low-humidity climates where high winds are common, the dustfall container is usually used with a liquid to prevent loss of collected materials. A choice of wetting agents must be made carefully to prevent introduction of errors from deposits of dissolved solids. In cold atmospheres, solutions containing glycol or alcohol can be used to prevent freezing.

High dustfall levels are readily noticed by the general public and even though nation-wide levels from urban areas are declining, the use of dustfall containers still is recognized as a good indicator of artifically-caused, high-dust emissions. However, particles that fall out of the atmosphere cannot be related to a given volume of air sampled and are not generally considered representative of the atmosphere's composition at the sampling point due to the number of particles remaining suspended in the air. In sizes lower than about seven microns, suspension becomes an important factor and other methods must be used to collect and measure the airborne concentrations.

Filtration

2. Filtration. Filtration techniques are universally used to collect particulate matter for sizing, counting, and gravimetrically evaluating dusty atmospheres. If counting and sizing are prime considerations, filter materials must be carefully chosen as particles tend to penetrate most fibrous filters and cannot be microscopically inspected. Membrane or molecular filters are utilized for count or size analyses, and the collected materials can be removed in approximately the same state as they were deposited. Such filtering materials have high collection efficiencies, even for the sub-micron sizes, and are especially well suited for low concentration atmospheres having relatively large percentages of fine particles.

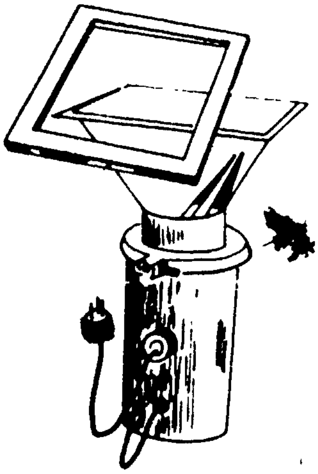
Membrane Filters

Pore sizes of membrane filters are uniform and are offered in sizes from 0.005 to 10 microns. Electrostatic effects make them suitable for collecting materials smaller than the pore size. The internal passages and channels of the filter cross-section also provide surfaces for impaction of particles within the filter.

In general, membrane filters have considerable resistance to airflow when compared to filter papers and glass fiber materials. This resistance is increased in heavily-polluted atmospheres due to surface and penetration buildup and airflows can be significantly reduced. even to the point that ordinary pumps cannot be used for extended sampling periods.

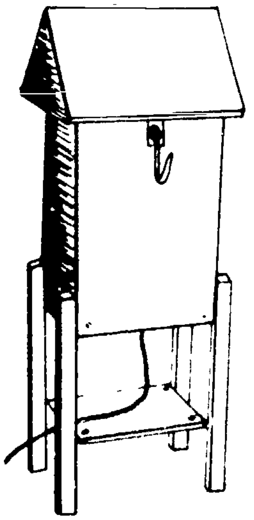
High-Volume Sampler

The most widely-used filtration sample collection device is the high-volume sampler, which consists of a motor and blower originally designed for a household vacuum cleaner. The sampler incorporates the blower, a suitable filter holder and enclosure to prevent direct dustfall and precipitation effects. For the past few years, very little has been changed in the original assemblies, except minor refinements in housings, flowmeters, and devices to make filter changing or motor servicing more convenient.



Usually the motor-blower unit is contained in a shelter having a roof which is suspended to allow airflow around the periphery. The horizontal filter surface faces upward and airflow characteristics generally prevent collection of particles larger than about 100 microns. The filters are mats of fiberglass or some synthetic fiber having relatively open structures and low resistances to airflow. Samplers are normally run for long periods, from 8 to 24 hours, and airflow rates are measured at the beginning and end of the sampling period.

Filters are weighed before exposure and if weighing conditions are standardized, it is possible to determine the total weight of the collected material by a second weighing at the end of the period. The filters should be visually inspected with a light box to detect pinhole leaks or defects in the filter material. Filters are kept at relative humidities of 50% or less, and the exposed filter is allowed to equilibrate to the same condition of dryness to avoid major moisture errors.



When samples are collected under humid conditions, filters should be dessicated for a period of two to four hours and then allowed to stand exposed in the same general laboratory atmosphere as during the initial weighing.

Large chamber analytical balances are useful to avoid folding of the 8 by 10-inch mats, which are usually used. Smaller sizes can be employed, but with reduction in airflows and limitations in capacity. The 8 by 10 size has proven practical to sample even highly polluted atmospheres and still allow sufficient airflow to cool the blower-motor unit.

Glass fiber filters allow the collected materials to be heated, incinerated, extracted, and otherwise analyzed for various constituents. Determinations can be made for organic content, carbon, minerals, or any other substance element or fraction. In relatively contaminated atmospheres, the collected sample is large enough for most laboratory analyses, and in less polluted environs, sampling times may be extended to secure sufficient material for special tests.

Reactions between fractions of the deposited materials are not easily predicted or understood, but when highly reactive pollutants are present, it is reasonable to believe that important changes do occur.

Benzene Soluble Organics

An index known as "benzene soluble organics" is used with high volume sampling. The organic material in the total collected sample is determined and used to estimate the contribution from incomplete fuel combustion. The organic fraction known as polycyclic aromatic hydrocarbons is sometimes used to explore the possibility of cancer-producing characteristics of the collected pollutants.

Calibration

High-volume samplers must be calibrated periodically in order to prevent gross errors in airflow measurements. At best, the usual practice of recording beginning airflows and a like reading at the end of the sampling period is somewhat crude. This technique assumes a linear and uniform deposition of particulates during the sampling interval.

Membrane filters are useful for special applications with the high-volume sampler. The filter backing plate support must be suitable to prevent fracturing and airflows must be high enough to cool the motor for the sampling period.

Acceptable filtration sampling techniques suitable for evaluation purposes are listed in the American Society for Testing and Materials (ASTM) Volume 23, Standard No. D2009. In addition to the commonly-used high volume system, reference is also

Portable Sampling

made to a miniaturized system utilizing small, battery-powered pumps and small membrane filters. Several manufacturers offer such portable pumps with built-in flowmeters and rechargeable batteries. Some have sufficient power reserves to operate continuously for eight hours with a small diameter membrane filter (usually 37 millimeters) before recharging.

This miniaturized method requires careful selection of components to assure quantitative results. The filters which give best results are those that are relatively free from moisture absorption affects and certain vinyl metricel materials are recommended. Equilibrium by dessication and exposure in the weighing laboratory atmosphere is necessary to avoid moisture errors. Even though the filter material is essentially free of significant moisture sensitivity, the collected materials cannot be so classified.

Electro-Balances

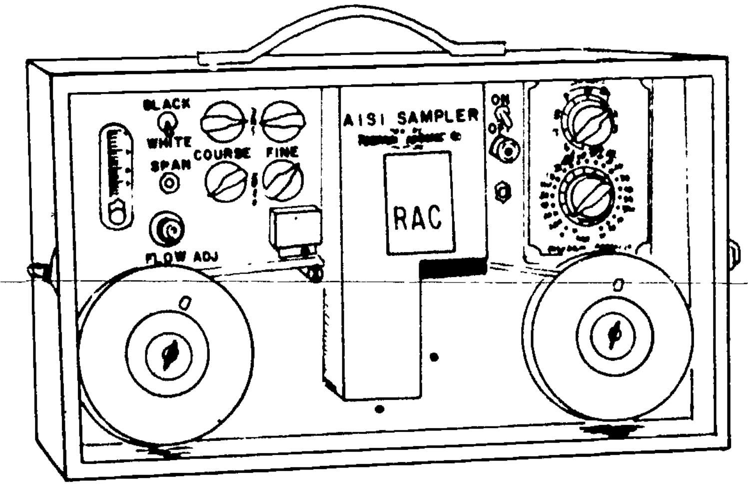
The usual laboratory analytical balance is unsuitable for miniaturized methods and an electrobalance is required to detect the small weight differential in this method. These balances depend on the principle of measuring electrical potential changes for their extreme accuracy. Deflections of a weighing beam attached to a sensitive galvanometer allows this type of measurement. A further advantage is their portability allowing their use in field surveys along with portable pumps.

Small filter holders can be mounted integrally or attached to shelters which can be connected to the pumps with flexible tubing. The small volumes of air sampled do not allow the advantage of subsequent laboratory analyses of the collected materials. This shortcoming is offset by the advantage of sampling where electrical power is not available for the conventional high-volume units. Another feature is the availability of results in the field, since samplers and gravimetric evaluation equipment (electrobalances) are portable and suitable for field use.

Suspended particulates may be collected and evaluated by using a tape sampler and some device for reading or observing the tape after exposure. In the United States, the tape sampler developed by W.C. Hameon and his associates is known as the

Tape Sampler

AISI (American Iron and Steel Institute) sampler. Other tape samplers are available in similar design and function.



Paper tapes are fed through a sampling head to provide for successive exposure areas and automatic changing to unexposed sections. A uniform cross-section of the tape is exposed by clamping in the head which is connected to an air pump which draws a chosen volume of air through the tape. Variable timers are generally incorporated in the sampler to allow a selection of the sample volume per exposed area. Timers can be adjusted, usually from a few minutes to about four hours, and at the end of the pre-set period the tape is automatically advanced for the next sampling interval. Tapes are available to allow continuous sampling for several days even with reasonably short individual collection periods.

Optical Analysis

Analysis is usually optical, by which deposited materials are examined and compared to some scale. Two additional methods are common, reflectance and transmittance. Reflectance can be measured with photometric devices and, in most cases, will provide a means for determining the nature and amount of deposit. When light-colored dusts predominate, the amount of deposit cannot be accurately determined by reflectance techniques, since this property may be increased rather than diminished when materials such as magnesium oxide are sampled.

Transmittance measurements are made by measuring the light passing through both filter and deposit and comparing with transmittance through a clean portion of the filter. Transmittance measures a function of all particles collected, while reflectance measures the blackness of the deposit. Relationships of the two methods are not always comparable.

Particulate pollution is usually not light colored in urban areas and the relative amount of suspended material can be evaluated visually, by reflectance and by transmittance with fair correlation.

Difficulties arise in relating transmittance and reflectance measurements to quantities and numbers of collected particles. The penetration of material in the filter influences reflectance readings and transmittance cannot be relied upon to indicate whether continued deposits are on already-collected particles or lodged in pores and gaps, thus increasing bulk but not thickness.

Sampling Errors

The small cross-sectional area makes constant sampling rates difficult to achieve in moderately or heavily-polluted areas. This may be overcome somewhat by selecting short-term cycles between individual samples.

Soiling Ind x

The determination of soiling index as a measure of particulate pollution is possible with respect to reflectance and transmittance measurements. Black smokes and soot create aesthetic and material damage problems. They are not readily evaluated by gravimetric methods since a black filter with a thin layer of smoke may not exceed a total weight per volume standard, even though it is the result of a very dirty, smoky atmosphere. Soiling index standards are useful to evaluate such conditions and tape samplers are the best known devices to give accurate data. Soiling index standards are usually expressed in coefficient of haze units which is related to optical density.

Coefficient of Haze

A coefficient of haze unit is defined as the quantity of particulate material which produces an optical density of 0.01 when measured by transmission of light at 400 millimicrons when compared to a light transmission of dust-free filter paper taken as 100%. Airborne smoke concentration is expressed in terms of the number of Coh units per 1,000 linear feet of air drawn through the filter tape.

The ASTM (American Society for Testing and Materials), Designation D1704-61 procedure is based on the use of an automatic tape sampler with transmittance or reflectance measurements on the sample spot. A parallel high-volume sample taken in the same atmosphere is evaluated gravimetrically for the mass of particulates.

b. Sampling for Sulfur Dioxide.

1. Pararosaniline Method. Sulfur dioxide in air is almost universally measured by the pararosaniline method described in the Federal Register Volume 36, No. 84, April 30, 1971, Appendix A.

In this procedure, sulfur dioxide is absorbed from the air in a solution of potassium tetrachloromercurate (TCM). Drawing atmospheric air containing SO_2 through this solution results in the formation of a complex known as the dichlorosulfitomercurate complex. This is a stable complex which resists oxidation by airborne oxygen and can be retained ~~and reacted by pararosaniline and formaldehyde~~ to form a colored solution of pararosaniline methyl sulfonic acid. This solution can be measured spectro-photometrically to obtain quantitative results of the original aspirated air sample.

This method is applicable for measuring ambient air for relatively long time periods, usually up to 24 hours.

Concentrations from 25 to approximately 1,000 micrograms per cubic meter can be measured. The lower limit of detection using 10 milliliters of TCM is about 0.75 micrograms per cubic meter of air.

After collection, samples are considered stable and at about 22 degrees centigrade, losses of one percent of sulfur oxide per day will occur. If solutions can be stored at 5 degrees centigrade, no detectable losses of sulfur dioxide occur.

Sampling

The sampling apparatus is described in detail in the Federal Register and consists of a basic bubbler sampling train with glass impingers preceded by a membrane filter to remove particulates and a hypodermic needle which functions as a limiting orifice for accurate airflow control. A trap, flowmeter, and suction pump completes the sampling train, Figure 15-1.

Calibration

The flowmeter and hypodermic flow limiting device must be calibrated by a laboratory precision wet test meter or some equally standardized flow measuring device.

A calibration curve procedure and test solutions may be prepared by using a sulfite solution or

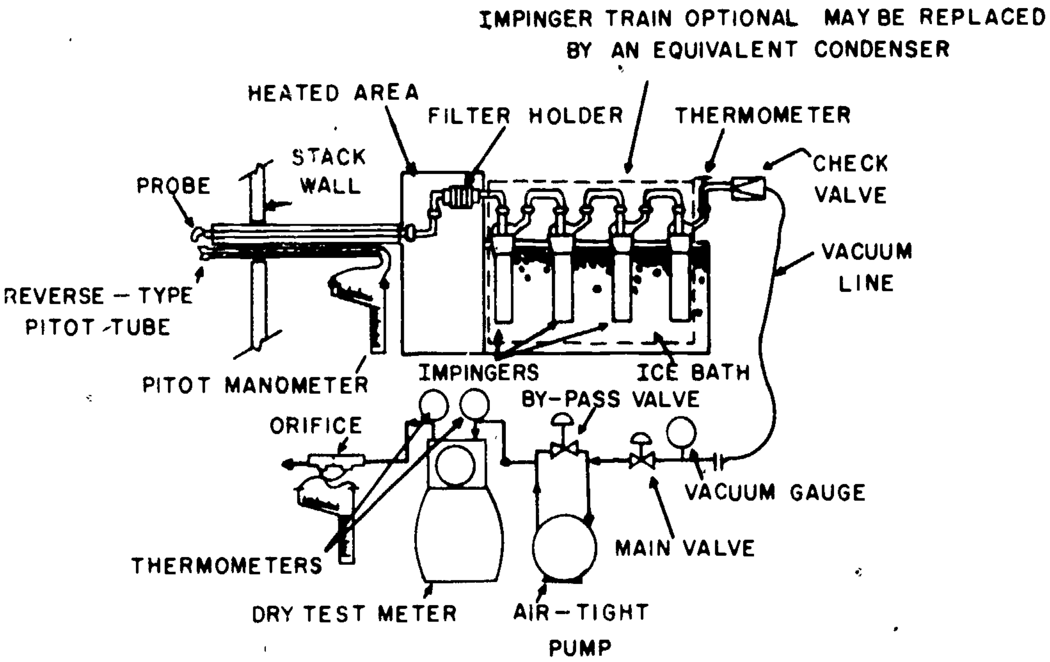


Figure 15-1
Particulate Sampling Train

permeation tubes as described in the Register.

Conductivity Methods

2. Conductivity Methods. Various conductivity instruments are available which draw measured volumes of air through an electrolytic solution contained in a cell which is connected to a recording circuit measuring changes in conductivity from the resultant chemical change. This general reaction is described in the American Society for Testing and Materials Method D-1355-67 and typical instrumentation is listed which utilizes this method. Flow rates are chosen to give wide ranges of sensitivity and absorption efficiencies for these devices.

Lead Peroxide Candle Method

3. Lead Peroxide Candle Method. In 1932, an attempt was made in Great Britain to provide an index of activity for SO_2 by measuring its effects on metals, buildings, and fabrics. The resulting technique was the lead peroxide (PbO_2) method which is based on measuring sulfation caused by gaseous SO_2 in ambient air by exposing lead peroxide paste. This method is somewhat analogous to the sampling of particulates by the dustfall method because it does not require power and can be left unattended for long periods of time.

A detection "candle" is prepared by covering a glass cylinder with gauze which is coated with the reactive reagent paste. This paste is prepared by dissolving 8 grams of lead peroxide in about 5 milliliters of gum tragacanth solution prepared by dissolving the gum in ethyl alcohol and diluting with distilled water. The candle is then exposed by placing it in a louvered shelter to protect the prepared surfaces from rain and high wind effects. A time period of 30 days is usually chosen, depending on the levels being measured and the weather conditions. After exposure, the candle is stripped of the reactive material with sodium carbonate and a standard gravimetric procedure is used to determine the amount of sulfate. Results are reported as milligrams of SO_3 per 100 square centimeters of lead peroxide per day.

While this method cannot be interpreted to give the same degree of precision as the absorption train or conductometric methods, it is convenient to determine general SO_2 levels where the more complicated sampling methods are impractical.

Definite relationships between emission and area concentrations can be secured if site selection is carefully done and if the precision capabilities are known and considered.

The lead peroxide method is a standard reference method described in Part 23 of the Standard Methods published by ASTM.

Miniaturized Method

4. Miniaturized Method. A more compact method was developed by Mr. Norman Huey in 1968, utilizing a plastic petri dish 48 mm in diameter, suspended in an inverted position with the open side facing downward. The inside surface of this dish is coated with the lead dioxide material, along with glass fibers to prevent loss of reactive surfaces. Mr. Huey reported that the plates were 19 percent more reactive than conventional candles and with significantly less deviation between exposed plates than was found to exist between simultaneously-exposed candles.

The Huey plate method offers distinct advantages in easier transport of prepared units and a more simple exposure mechanism in small-angled brackets or holders which can be attached to power poles, buildings, or other vertical surfaces. The petri dish can serve as a shipping container. Low cost of disposable dishes and simplicity of design and sampler placement has made this modification of the conventional lead peroxide universally popular in regulatory and survey programs.

Non-Dispersive Infrared Method

c. Sampling for Carbon Monoxide.

1. The Non-Dispersive Infrared Method. The non-dispersive infrared method (15-1) is based on the absorption of infrared radiation by carbon monoxide. A laboratory or portable spectrograph is required and a radiation source is used to produce energy in the infrared region. Parallel energy beams are directed through reference and sample cells. Instruments are available to measure carbon monoxide in the range from 0 to 50 parts per million in ambient air.

(15-1). Appendix C, Federal Register Volume 36, No. 84, April 30, 1971.

2. The Iodine Pentoxide Method. The iodine pentoxide method (15-2) involves the use of relatively sophisticated laboratory equipment and is not considered applicable as a portable or in-field method. This method depends on the reaction between carbon monoxide and iodine pentoxide at approximately 140 degrees centigrade to produce iodine vapor and carbon dioxide. The measurement of CO in the sample may be determined by measuring either the carbon dioxide or iodine vapor. This method is successful only with interfering substances such as water vapor, aldehydes, unsaturated hydrocarbons and other organic compounds removed. These interfering substances introduce errors by their reaction with the liberated iodine or the iodine pentoxide.

Continuous recorders are available which utilize an iodine pentoxide tube with appropriate temperature control and photometric system to estimate absorbed iodine. Other recorders utilize an electrolysis detector cell with a colorimetric evaluation of the liberated iodine.

3. Colorimetric Methods. Colorimetric methods have been in use in occupational health work for many years to detect relatively high levels of carbon monoxide in workroom atmosphere. A direct-reading, dry-chemical tube containing palladium sulfate and ammonium molybdate is used in a portable squeeze bulb tester. The granules are contained in a sealed glass tube which is broken before the test is made and attached to a calibrated orifice and a suction bulb or pump. A carefully metered amount of air is aspirated through the reagent which reacts to carbon monoxide by changing from light yellow to dark green. The intensity of the color change is compared to appropriate color charts for a quantitative reading.

Interferences

Moisture is absorbed by drying agents in the tube, but very damp atmospheres will cause erroneous readings where large quantities of air must be sampled in low concentrations to give readable results. Acetylene, ethylene, and propylene give positive interferences. Serious errors also result in temperatures below 65 degrees Fahrenheit.

(15-2). Air Pollution, Volume 2, A.C. Stern, Academic Press.

Limitations

Carbon monoxide levels may be accurately estimated by the indicator tube method. Field comparisons of the infrared and detector methods in 1966 by Hochheiser and Santner (15-1) indicate that measurements must consider influences of temperature, humidity, and other interfering substances before the two methods could be considered directly comparable.

d. Sampling for Hydrocarbons.

Gas Chromatography

Gas Chromatography. The most successful and accurate method for quantitative hydrocarbon analysis is the gas chromatograph. In this method, provision must be made for passing carbon monoxide and methane through the column for eluting and evaluating separately. This procedure is necessary to avoid high results and an erroneous comparison with standards which exempt methane.

Since carbon monoxide is combustible, it would lead to positive errors if not evaluated separately. Equipment manufacturers are developing applicable columns and transportable units to allow measurements of hydrocarbon levels in field studies.

A detailed discussion of the chromatograph method is contained in the Federal Register applicable to hydrocarbon measurements (15-2),

e. Sampling for Oxides of Nitrogen.

Saltzman Method

The Saltzman Method. The Saltzman Method (15-3) is considered applicable for detecting levels of nitrogen dioxide (NO_2) over a range of a few parts per billion to approximately 5 parts per million. The sampling train consists of a fritted glass bubbler, flowmeter, and suction pump. The absorbing solution is prepared by dissolving 5 grams of sulfanic acid in water containing 140 milliliters of glacial acetic acid. This solution is then diluted to one liter after adding 20 milliliters of 0.1 percent N- (1-napthyl)-ethlenediaminedihydrochloride. Handling of this solution

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(15-1). Field Comparison Methods of Measuring Atmospheric Carbon Monoxide. Hochheiser and Santner, American Chemical Society, 152nd National Meeting, New York, September 1966.

(15-2). Federal Register Volume 36, No. 84, April 30, 1971, Appendix E.

(15-3). B.E. Saltzman, Analvtical Chemistry 26, 1949 (1954).

should be done with minimum air contact to avoid discoloration by absorption of nitrogen dioxide from the air.

The absorbing reagent is placed in the fritted glass bubbler and air is drawn through at a maximum rate of 0.4 liters per minute until a definite color is developed. The exact amount of air must be carefully recorded. Development of the red-violet color is complete in about 15 minutes at ordinary temperatures.

Colorimetric Evaluation

The developed color may be evaluated by visual comparison with standards or read in a spectrometer at 550 millimicrons wave length, using unexposed reagent as a reference. Colors are relatively stable if stoppered in closed tubes with a usual absorption loss of about 3 to 4 percent per day.

f. Sampling for Ozone and Oxidants.

1. Chemiluminescent Method. A reference method for the measurement of photochemical oxidants in the atmosphere is outlined in detail in the National Air Quality Standards published by the Environmental Protection Agency (15-4).

EPA Method

This is a chemiluminescent method which is corrected for nitrogen oxide and sulfur dioxide interferences. The ambient air and ethylene are drawn through a mixing zone where ozone and ethylene react to form emitted light which is then recorded by a photo multiplier tube. The resulting current is either read directly or transmitted to a recorder display. Several commercial models of this system are available with minor variations of design and configuration. (15-5).

Manual Method

2. Potassium Iodide Method (15-6). This is a manual method which can be utilized for the measurement of total oxidants including ozone in concentrations of a few parts per billion to about 10 parts per million.

(15-4). Federal Register Volume 36, No. 84, April 30, 1971.

(15-5). Photochemical Oxidants and Air Pollution Parts 1 and 2, U.S. EPA Publication No. AP-88.

(15-6). Air Pollution, A.C. Stern, Vol. 2, 1968 Academic Press.

Midget Impinger

Sampling is accomplished by using a calibrated air pump, flowmeter and glass midget impingers containing one percent potassium iodide in a neutral buffer of 0.1 Molar disodium hydrogen phosphate and 0.1 Molar potassium dihydrogen phosphate. During sampling in ambient air containing oxidants, a liberation of iodine occurs in the absorbing reagent. Analysis of this solution should be completed within an hour after sampling.

The absorbing reagent is prepared by dissolving 13.61 grams of potassium dihydrogen phosphate, 14.2 grams of anhydrous disodium hydrogen phosphate, and 10.0 grams of potassium iodide diluted to one liter. It is recommended that this reagent be allowed to stand for 24 hours at room temperature before use. Storage in brown bottles at low temperatures is recommended.

Standard iodine solution consists of a 0.05 normal potassium iodide solution prepared by dissolving 16.0 grams of potassium iodide and 3.173 grams of iodine in distilled water made up to 500 milliliters volume. This solution should also age for about 24 hours before use. If desired, this solution may be standardized by titration with the usual sodium thiosulfate-starch method.

Sampling periods of 30 minutes or less at a flow rate of about 2 liters per minute should allow adequate sampling for analysis. During sampling, direct sunlight exposure to reagents should be avoided. Distilled water may be used as a reference and the exposed reagent solution can be evaluated colorimetrically at 352 millimicrons absorbance.

g. Other Pollutants. Other contaminants besides the six so-called major ambient pollutants are of importance, depending on special considerations such as geographic conditions and occurrence from special sources. Acid mists, hydrogen sulfide, fluorides, ammonia, asbestos, mercury, beryllium and radioactive materials must be considered, evaluated, and controlled in such areas of interest.

3. Source Monitoring Techniques

Source monitoring is an important part of air quality measurement. Ambient or area measurements are useful in determining overall quality, and while most of the effects of air pollutants are related to ambient exposure conditions, the relationship of ambient point source emissions often cannot be accurately made from general air sampling alone.

Ambient Sampling

Maximum ground-level concentrations of an emitted pollutant usually require measurements outside the plant premises. If several sources are located within a small area, the relative contributions from individual points of emission are difficult to estimate from ambient data alone. In some instances where emission points are spaced sufficiently apart, wind direction controlling devices are useful. These devices employ a wind vane actuating system to activate samplers only when the wind is blowing from a pre-selected area of interest. This same device can be used to establish background pollution levels by selecting quadrants from which there are no emission sources.

Emission Sampling

Multiple sources in crowded industrial areas cannot be successfully evaluated without point source or emission sampling. This means that a method must be designed to quantitatively collect samples of emitted materials at or near their origin.

There are several purposes of source testing. Operation of control equipment must be checked for compliance with applicable standards. Federal regulations (15-7) require all states "to provide for monitoring the status of compliance for any rule or regulation." This Register also requires every state to "establish a system for detecting violations of rules and regulations through the enforcement of appropriate visible emission limitations."

Various sampling trains have been devised to collect airborne samples from stacks and ducts. Gases may be sampled with conventional probes which traverse the duct area at sufficient points to assure representative velocities and concentrations. However, when sampling particulates greater than a few microns in diameter contained in an emitted stream, care must be exercised to adjust the system to secure representative samples.

Isokinetic Sampling

The sampling must be conducted so the flow rate at entry to the sampling probe is at the same velocity as the main gas stream. This is called isokinetic sampling (15-8). When the velocity in the probe is different from that of the

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(15-7). CFR Title 40, Section 51.19, Source Surveillance.

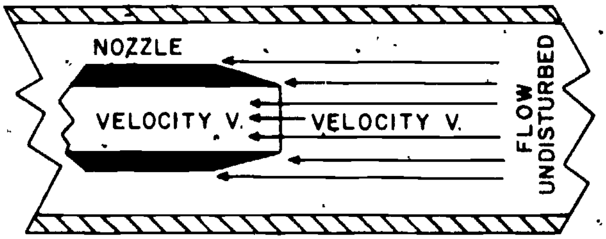
(15-8). Maintenance, Calibration and Operation of Isokinetic Source Sampling Equipment. U.S. EPA Publication APTD-0576.

main stream, the size distribution and total weight concentration of the collected particulate matter will be different from those in the duct or stack. This is due to the mass and velocity characteristics of the particles which cause momentum effects. At sampling velocities less than the duct velocity, all large particles in the probe cross section will be projected into the probe opening, while a portion of the air or gas in the stream will be deflected around the sampler probe. This results in a sample entering the system that contains more large particles than are representative of the sampled stream. Additionally, the weight will be greater due to the disproportionate number of large particles so collected.

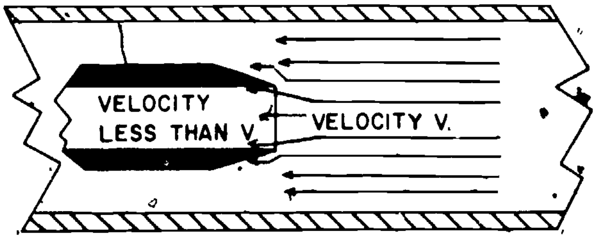
When sampling velocities are greater than the main duct velocity, all the air in the stream intercepted by the probe inlet will be sucked into the sampler, plus some additional air from the probe area inlet. When air is drawn from outside the intercepted stream tube, smaller particles will follow curved streamlines into the probe. Larger particles, due to their inertia, will not be drawn in. This results in a collected sample with fewer large particles than the main stream being sampled, and a total weight concentration of particulate matter which is less than representative.

The streamline effects of improper and correct flow rates are shown in Figure 15-2. Whenever the velocity into the sampling probe is different from that of the main gas stream, the sampling is said to be anisokinetic.

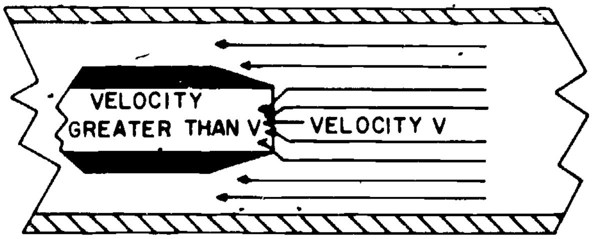
In order to assure uniformity of sampling by official agencies, the U.S. Environmental Protection Agency has approved and specified a collection train system which is described in detail in Title 40, Method 5, Part 60, Standards of Performance for New Stationary Sources, Section 60.42. The basic elements of this system are shown in Figure 15-1.



A ISOKINETIC SAMPLING, CONCENTRATION AND GRADING REPRESENTATIVE



B SAMPLING RATE LESS THAN ISOKINETIC, EXCESS OF COARSE PARTICLES



C SAMPLING RATE GREATER THAN ISOKINETIC, DEFICIENCY OF COARSE PARTICLES

Figure 15-2
Streamlines Around a Sampling Probe

Problems:

1. What is the difference between ambient and source monitoring? Which has the more restrictive standards?

2. Secure the use of High-Volume (Hi-Vol) sampler (contact state or city air pollution division). Measure the particulate matter at a nearby site for 24 hours. Check flowrate and compute ambient particulate concentrations. Consider a normal human uses 7500 liters of air a day (breathed in and out), and compute the weight of particulates inhaled daily by you.

3. Do all of these particles enter your lung? Why not? How could you decide how much does enter the lung?

SURVEILLANCE NETWORKS

It has been said that monitoring is not a substitute for action. However, in order for action to be most effective, knowledge from adequate monitoring is a basic requirement. There are difficult decisions involved with choosing appropriate environmental indices for data requirements. Many monitoring systems are already in existence and are recognized as inadequate. The coverage afforded, geographically and with respect to the many existing pollutants is not complete. Many systems have sensors which are inaccurate or improperly calibrated, so that measurements cannot be compared with other locations.

During 1970, the National Council on Environmental Quality reported that there were some 56 major monitoring programs located in 16 different federal agencies. (16-1) The federal government monitoring programs were estimated by the Office of Management and Budget (OMB) to cost approximately 40 million dollars during fiscal year 1971. This figure does not include any monitoring and surveillance activities by state and local governments, private researchers, contractors or industries.

These existing efforts and the difficulties of securing good information do not minimize the need to continue to make every reasonable attempt to collect and analyze environmental data.

Gauges on national air quality must be collected. The status and trends of such quality must be known in order to direct intelligent attention and effort toward control and improvement.

METROPOLITAN NETWORKS

Urban centers are the main targets for air quality improvement programs. Two eastern states, New York and New Jersey have been successful in lowering sulfur oxide and particulate emissions in certain urban areas by strict enforcement programs. The urban levels were reduced, relocationed and de-centralized industrial siting resulted, but the total weight of emissions continued to rise outside these areas. If sampling stations were located only in the central city areas, these trends or results would not have become apparent and overall air quality would have been assumed to be better.

(16-1) The Second Annual Report of the Council on Environmental Quality, August 1971. U. S. Printing Office. Stock No. 4111-0005.

The importance of monitoring site selection in any community or state cannot be over emphasized. The early National Air Sampling Network (NASN) stations were generally located in central city areas. Most state and local sampling programs were begun to detect effects of major pollutant sources. Thus, the state and local data showed more contamination than the NASN data and direct comparisons were not valid.

EMERGENCY PLANS

All states are required to institute episode emergency procedures to prevent ambient pollutant concentrations at any location from reaching levels which would endanger the health of persons. For this purpose, each source emitting 100 tons per year or more of particulates must be identified and subject to a control plan to reduce emissions during episode conditions.

Monitoring of such emissions must be often enough to determine whether the incident is so persistent that control measures are warranted. Serious economic impacts result from faulty decisions and plant shut-backs or work stoppages. The resulting disadvantage of such curtailment measures must be carefully weighed against the air monitoring data. Close liaison with weather stations regarding air stagnation advisories must be maintained, so that emergency procedures can be timed to be no more or less restrictive than is necessary. Frequency of sample collection and analysis is critical during episode conditions. Guidance must be given for decisions so that additional cut-backs can be instituted or the restrictions lifted entirely, depending on trends of the recorded levels.

IMPACT STATEMENTS

The National Environmental Policy Act (NEPA) contains provisions for environmental impact statements. This limitation is imposed to prevent construction of facilities or systems which would seriously impair the best use of the environment. Certain federal agencies now require such statements to be submitted and approved before construction is allowed. Background data are useful to establish the existing quality so that changes can be calculated.

PERMITS

Certain new sources must secure permits before construction of facilities which have a potential for exceeding applicable air quality standards. On December 23, 1971, a Federal Register was adopted (16-2) which imposed such limitations on fossil fuel-fired steam generators, large incinerators, portland cement plants, nitric acid plants and

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(16-2) Federal Register, Vol. 36; No. 247. December 23, 1971 sulfuric acid plants. On June 11, 1973 another Federal Register (16-3) was proposed for seven more source categories. These stationary sources include asphalt concrete plants, petroleum refineries, petroleum storage facilities, secondary lead smelters, brass and bronze production, iron and steel plants, and sewage treatment plants.

The new construction limitations include requirements that all such sources provide monitoring capabilities to assure continued acceptable operation after start-up. Source testing and monitoring are specified in some instances and in others certain options are allowed.

INDIVIDUAL SITE NETWORK SYSTEMS

Sampling networks having various degrees of sophistications are being established by sources themselves to assure compliance with control strategies. As a minimum, wind direction and velocity readings are usually taken to correlate with whatever ambient collection is applicable. For particulates, dustfall and high volume samplers are generally situated in surrounding environs at varying distances from the source.

With the increasing emphasis on nondegredation policies, results of existing air quality are critically important to be able to calculate significant departures from such levels. The amount of allowable degredation in various areas is an item of national concern due to court actions to prevent degrading of existing high quality environments.

Networks of samplers must be located in undeveloped regions for a sufficient time span to give meaningful and accurate results for these decisions. Seasonal variations, weather changes, etc., must be considered before a studied judgement can be made on the capacity for such airsheds to accommodate industrial and municipal growth. Most authorities agree that the non-degredation concept is not a cessation of all development, but a carefully planned, long-term weighing of environmental values so that benefits and risks will be properly considered.

AREA MONITORING LIMITS

Often sampling station locations are already determined by political boundaries or regions of jurisdiction. In some cases, laws or standards will specify ambient measurement boundaries or will exempt private properties from application of limitations. When observable effects of the pollutant are defined by area limits, certain sampling decisions can be made. It is not always advisable to limit

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(16-3) Federal Register, Vol. 38; No. 111. June 11, 1973 monitoring to areas within boundaries of known or observed effects. It may be equally important to secure borderline or outside background data to give comparisons with the affected zone.

METEOROLOGICAL TOPOGRAPHICAL

Terrain features are vital considerations since many of the disasters associated with air pollution have occurred in valleys where physical characteristics prevented adequate dispersal of contaminants. Episode networks should include such drainage areas, especially if meteorological and source location features are situated so that emergency conditions could occur. Knowledge of prevailing winds, temperatures and lapse rates are useful in establishing specific sampling locations and the interpretation of data collected near point sources.

GRIDS

The planning of sampling points by artificially imposed boundaries or grids may be useful for some purposes. Land use planning by counties, municipalities and other subdivisions may require acquisition of data for site selection and building limitations. Point data from uniform grid locations lends itself to systematic graphic illustration of results, which is sometimes important aid in explaining or interpreting results. Concentration contour lines can be drawn if grids are chosen to give adequate plotting points and such information can be superimposed as topographical or meteorological maps.

GENERAL REQUIREMENTS

Sampling site selection introduces several factors which may require compromises from optimum layouts. Availability of support facilities, logistics of supplies and accessibility may require major adjustments from simple programs and orderly plans. Power supplies for continuous recorders, pumps, heaters, etc., are often lacking in remote areas. Portable generating units or battery powered devices are available, but sampling rates and frequencies may need to be adapted to accept such equipment.

Access roads are sometimes nonexistent on all sides of some point sources, so that allowances must be made for increased distances or authority and permission may be necessary to traverse private properties to establish suitable sites.

DATA

Information collected from testing and monitoring must be handled in such a manner that the original usefulness and application are retained until a final result is achieved. Even after control is secured for a single problem, the information cannot be discarded and forgotten. Considerable attention is being directed to establishing data resource books and retrieval systems which allow continued use of such information.

Statistical summaries are useful to document area-wide and national trends. These facts can then be utilized to concentrate efforts where air quality deterioration is noted and attention can be withdrawn from other areas to more effectively utilize limited monitoring resources.

SIMPLE SURVEYS

The usefulness of air quality data is directly related to its availability and its reliability. Information produced in a monitoring network or at a single station must be reduced to usable form from the raw data. In small systems where manual analyses of single samples are performed, the laboratory or field readings are the basic data unit. The usual handling of this information is to prepare a survey report or evaluation which describes the calculated results and, in most cases, gives some opinion as to the expected impact of the pollutant level. This impact may be an unfavorable comparison with an official standard or regulation and, as such, should clearly outline the relative importance of the findings. This is sometimes called an instantaneous value of the data, but it is not usually the only value which should accrue from its collection. If correction or enforcement is indicated, clear decisions cannot usually be based on single samples or a few results. The short-term use of monitoring data is usually for determining relationships between point sources and the quality of the atmosphere. Two problems may be involved. Identifying an unknown source of a known contaminant, and finding the effects on air quality by a known source.

FEDERAL DATA SYSTEMS

The Federal EPA has established a system for Storage and Retrieval of Aerometric Data (SAROAD) (16-4) which gives station codes and site identification for all permanent sampling points which are established in state and local air pollution control programs. Every city with a population of 2,500 or more has been listed and given an identification number, which is used to report network results as required

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(16-4) SAROAD Coding Manual. U. S. Environmental Protection Agency. Office of Air Programs. Publication No. APTD-0907.

by the Federal Clean Air Act Amendments of 1970.

REPORTING REQUIREMENTS

All states are required to maintain a minimum number of air quality detection stations for the six pollutants for which nationwide standards are established. The exact requirements are based on priorities of each air quality control region which has been designated by the EPA, and depends on population and existing air quality.(16-5) The data collected from these stations are collected and reported quarterly on SAROAD forms, which allow handling by the data bank maintained by the EPA. Samplers are located by the Universal Transverse Mercator (UTM) grid coordinates. This network is designed to provide air quality monitoring during air pollution emergency episode stage and must be capable of indicating when pollutant concentrations have reached, or are approaching, episode or emergency levels.

PUBLIC AVAILABILITY

Federal laws (16-6) require that emission data be made available to the public. Only special information that can be considered to be confidential and which upon release "would divulge methods or processes entitled to protection as trade secrets" is exempted.

The Committee Report on Public Works of the United States Senate (16-7) contains a strong statement in this regard. This document says "The Committee believes that the public right to know what is being emitted overrides the proprietary character of such information."

This requirement imposes grave responsibilities for accurate development and interpretation of monitoring information. All surveys and monitoring efforts should be performed in such a manner that public scrutiny can be tolerated and the collected information will be able to be used for legal purposes if necessary.

AUTOMATIC SYSTEMS

The most advanced and sophisticated data communication systems consist of telemetering devices to transmit information to a central location for input into a reduction system or display. Radio or land lines can be used for transmission. These are expensive systems and the advantage of telemetering must be great enough to warrant their use over more conventional methods such as mail, messenger or phone.

(16-5) Code of Federal Regulations. Part 40, Chapter 1, Section 51.17.

(16-6) Public Law 91-604. December 31, 1970. Section 114(c)

(16-7) Report of the Committee on Public Works. U. S. Senate, No. 11-1196. September 17, 1970.

Automatic recording devices can be maintained at various sites aside from the telemetering capability and, unless the speed of reporting is a major factor, the usual physical scanning, collecting and processing may be adequate.

Some telemetering systems are limited to alarm or emergency warning signals. This can be useful to inform collection centers that additional sampling or more definitive monitoring is needed to describe the problem. Methods of checking and maintenance are necessary to assure reliability and prevention of false alerts.

DATA VALIDATION

Statistical handling of monitoring data is important when adequate numbers of samples warrant such manipulation. This is useful, not only to predict, describe and plot trends, but to determine reliability and significance of results. Wide variations may be lost or given undue attention unless a reasonable statistical test is made to establish their validity.

Problems:

1. Visit a large metropolitan area and contact the air pollution division. Obtain information on all city monitoring programs, including alert status requirements. Are monitors robot or grab type? Is information telemetered for analysis and evaluation? How reliable are the data?

2. Write a short report on your city's air pollution monitoring and surveillance systems. What programs are being planned for better pollution monitoring and abatement?

PART IV

PESTICIDES

17

OCCURRENCE AND DETECTION OF ORGANIC PESTICIDES IN OUR ENVIRONMENT

INTRODUCTION

Much concern has been expressed in recent years about the contamination of our environment with organic pesticides. There are charges and indictments of thin egg shells, inducement of cancer in man, wholesale destruction of wildlife, teratogenic and mutagenic effects, etc. Few of these charges have been proven for man but the effects on wildlife have been documented quite well. Organic pesticides and herbicides, no doubt, may be found in several phases of our environment. It is, however, the significance and the level of occurrence that is controversial about these chemical toxicants. One of the major difficulties with assessing the environmental damage from pesticides and herbicides lies with their analytical detection and confirmation. Much of the charge about the world-wide distribution of the chlorinated hydrocarbons, for example, has been made out of false analytical information. There are many naturally-occurring substances and artifacts that give positive answers as pesticides. It is imperative that the presence of a pesticide in any environment should be confirmed analytically before an indictment is offered. This chapter discusses the occurrence and distribution of organic pesticides in the various environments of man and how to detect and to confirm their presence.

CLASSES

There are many systems in which these chemical compounds may be classified, organized, or typed. The most common is by use or by target: i.e., insecticide, miticide, nematocide, rodenticide, fungicide, herbicide, etc. All of these "-cides" may be placed under the inclusive term - pesticides. An alternative classification is by their chemical nature, i.e., organic, inorganic, chlorinated hydrocarbons, organophosphates, carbamates, etc. A summary of the more important classes appears in Table 1. More and detailed information concerning uses, toxicity, physical and chemical properties, chemical structures, etc., may be found in references (1, 2, and 3).

DISTRIBUTION AND OCCURRENCE

Perhaps we should begin with a discussion of the distribution and occurrence of organic pesticides in the bodies of humankind. Certainly, humans are not an endangered species with respect to the pesticide as alleged by some environmentalists. We are, however, considered as the principal target for various environmental insults and we are at the apex of the food chain pyramid. Most of the surveys for the body burden content of pesticides have been conducted in the United States and Great Britain. Some of

TABLE 17-1
CLASSES OF ORGANIC PESTICIDES[a]

A. Chlorinated hydrocarbons
   1. Class I: oxygenated compounds
      Dieldrin, methoxychlor, endrin
   2. Class II: benzenoid, nonoxygenated compounds
      BHC, DDD(TDE), DDT, perthane
   3. Class III: nonoxygenated, nonbenezoid compounds
      Aldrin, Chlordan, heptachlor, strobane, toxaphene

B. Organophosphorus compounds
   1. Aliphatic derivatives
      Demeton dimethoate, ethion, malathion, phosdrin, phorate
   2. Aromatic derivatives
      Trithion, diazinon, EPN, fenthion, parathion, ronnel

C. Herbicides, fungicides, nematocides, etc.
   1. Phenoxyalkyl acids: 2,4-D; 2,4,5-T; 2(2,4,5-TP)
   2. Substituted ureas: fenuron, monuron, diuron
   3. Substituted carbamates: IPC, CIPC, EPTC, sevin
   4. Symmetrical triazines; simazine, atrazine
   5. Substituted phenols: PCP, DNBP, DNC

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[a] In part from reference 4.

these surveys will be presented here and, in addition, several references will be given for the convenience of the reader who wishes a greater coverage of this information.

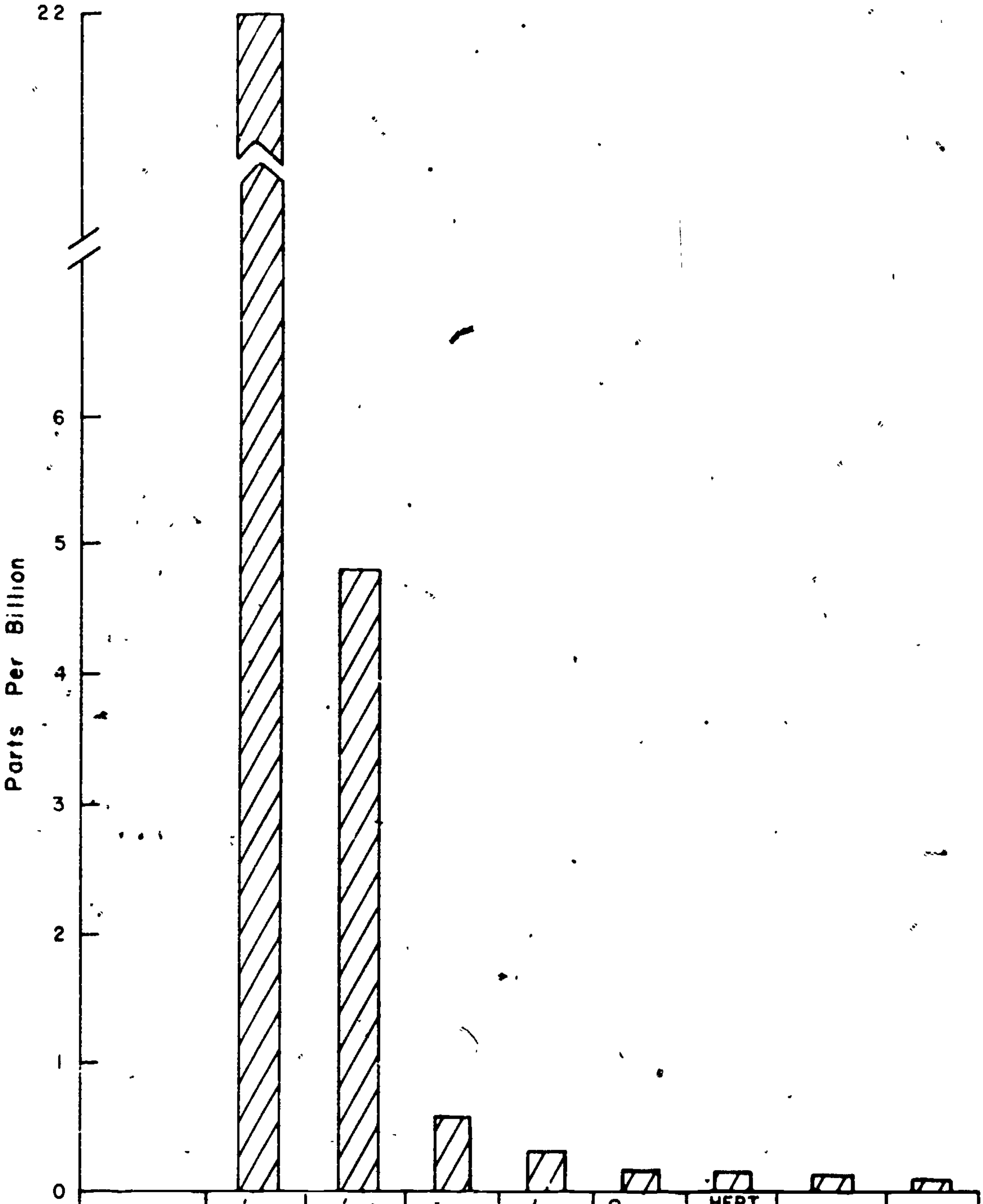
PESTICIDES IN HUMANS

A. Pesticides in Humankind

In 1967, the U. S. Public Health Service activated a survey of organic pesticides in the adipose tissues and blood serum of the general population in 16 states (5). These studies sampled three population groups.

a. occupationally exposed workers,
b. individuals not occupationally exposed but known to be repeatedly exposed, and
c. the general urban population.

One of the earliest reports from this national survey came from Dade County, Florida (6) where 159 autopsy fat specimens from persons accidentally or violently killed were examined for DDT and DDE only. This was an interesting study because of the distribution of these two pesticides amongst the age, race, and sex groups. Figure 17-1 summarizes the median



	p,p′-DDE	p,p′-DDT	DIELDRIN	p,p′-DDD	β-BHC	HEPT. EPOX	LINDANE	α-BHC
Percent Occurrence	99.8	84.0	33.0	7.1	2.6	2.2	0.9	0.4
Range (ppb)	0-383	0-80	0-25	0-27	0-15	0-5	0-24	0-18

Figure 17-1
Median Levels of Total DDT-Derived Residues in 159
Necropsy Tissues, Dade County, Florida, 1965-1967

levels of the total DDT-derived residues in the 159 necropsy tissues. When the means in these various groups were considered, DDE values ranges from 2.5 to 15.1 ppm and from 5.0 to 22.0 ppm for total DDT-derived material. No discussion of the significance of these data is attempted here as the reader is referred to the original paper (6). There are, however, some significant differences in DDT and DDE concentrations associated with demographic variables that the authors were unable to explain.

Another one of the reports from the national survey came from Southern Idaho (7) where, the organic pesticide (chlorinated hydrocarbons, only) content of blood serum from 1,000 samples was examined. Eight different pesticides were detected in this order of decreasing frequency: DDE, DDT, dieldrin, DDD, γ-BHC, heptachlor epoxide, lindane, and -BHC. It is rather significant that 99.8% of the samples contained DDE at a mean concentration of 22.0 ppb, whereas DDT occurred in 84% of the serums at an average of 4.7 ppb. The percentages and average contents of the other six chlorinated hydrocarbons are seen in Figure 17-2. There were some differences in pesticide content due to age and sex, but insufficient data does not permit discussion of these observations. The authors concluded that the Idaho residents in this study do not differ basically from persons in other areas of the United States in their accumulation of serum chlorinated hydrocarbons. A similar and updated study was reported by Wyllie, et al. (8) for the organochlorine pesticide residue in serum and biopsied lipoid tissue of 200 persons in Southern Idaho.

Another survey of the human pesticide monitoring program comes from Utah (9) where 1,417 serum and 103 adipose samples were collected during 1967-1971. This survey was limited to p,p'-DDT, p,p'-DDE, total DDT (DDD, DDE, and DDT), and dieldrin. Residue levels in the Utah residents compared closely with the people in Chicago, Arizona, Florida and Idaho "despite considerable differences in quantities of pesticides used." These statistics are for serum (average values in ppb): DDE-19.8, DDT-6.2, total DDT-28.3, and dieldrin-1.8 and for adipose tissue (average values in ppm): DDE-5.03, DDT-1.53, total DDT-7.31, and dieldrin-0.17. As expected, significantly higher levels of the chlorinated hydrocarbons were observed in persons occupationally exposed to pesticides than in those from the general population. A rather revealing statistic was uncovered in this survey; namely,

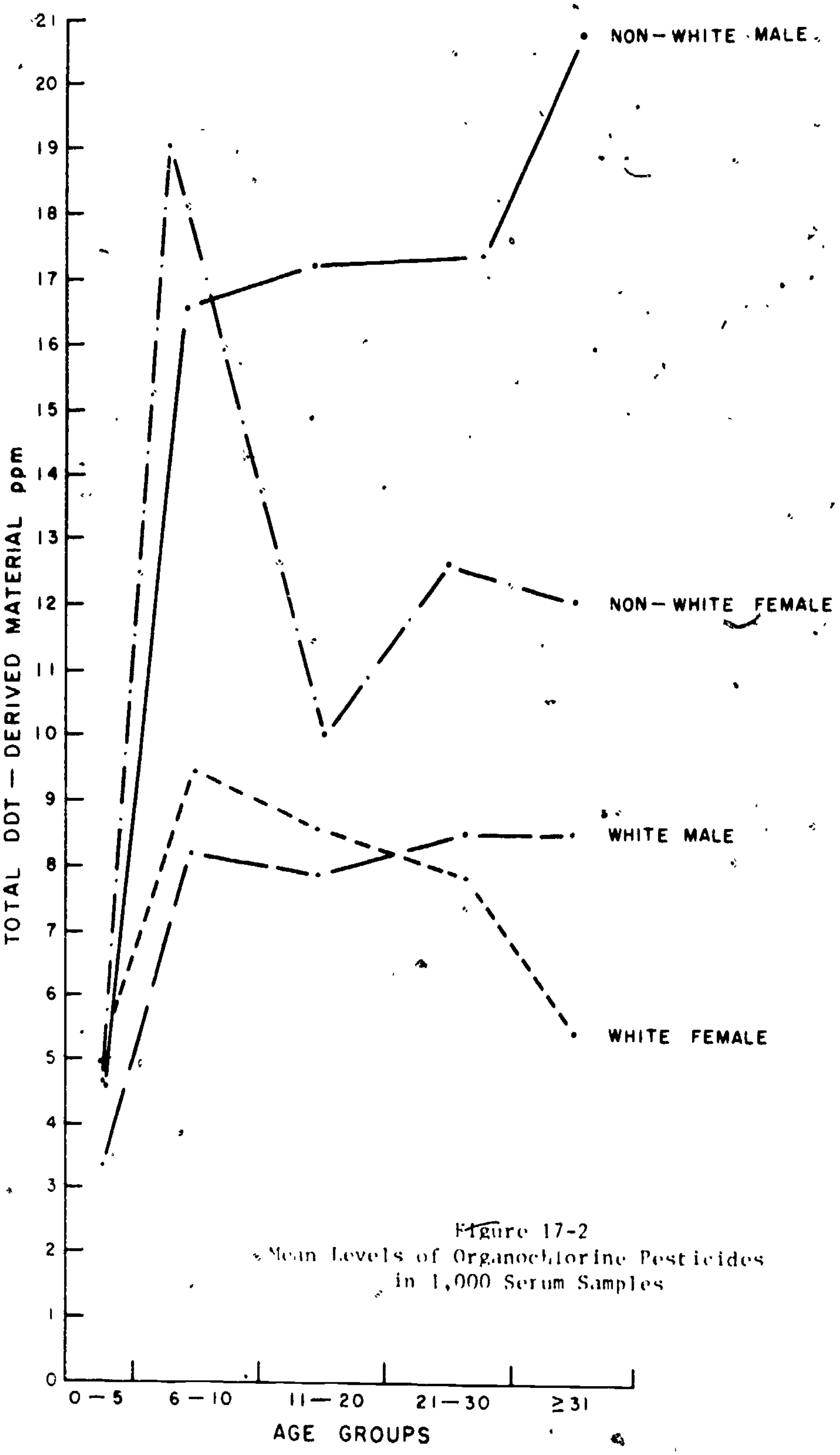


Figure 17-2
Mean Levels of Organochlorine Pesticides
in 1,000 Serum Samples

the mean values of total DDT in adipose tissue decreased over the years of the survey in Utah. In 1968, the mean DDT content was 9.0 ppm whereas in 1969, the value was 7.2 ppm and in 1970 it was 5.3 ppm. This does, of course, suggest a decrease in storage levels of the pesticides but the continuation of this trend is uncertain at this time.

That the occurrence and distribution of chlorinated hydrocarbons in the adipose tissue of humankind are universal is seen in Table 17-2. It would be fortuitous to interpret or to explain these data. There are so many variables that enter into the establishment of pesticide levels in adipose tissue. No inference should be made also toward the levels observed in a particular country. The observation is, however, that the chlorinated hydrocarbons are distributed widely throughout the human race and the levels of occurrence may be related to exposure and usage within a specific country.

There have been many surveys, studies, researches, etc., conducted of the pesticide content of humans. These have reported principally the chlorinated hydrocarbon. Very little information, if any, is available on the level of such pesticides as the phenoxyherbicides, organophosphates, carbamates, ureas, etc. It is not that these pesticides are not physiologically important but, in all liklihood, the analytical procedures have not been perfected for human tissue. Additional references are listed (11,12,13,14 and 15) for the reader who wishes to obtain more and detailed information concerning the pesticide content of humans.

PESTICIDES IN THE MARKET BASKET

B. Pesticides in Our Market Basket

That the human body contains the chlorinated hydrocarbon pesticide is ascertained from the above information. There is very little doubt that these pesticides have their origin in the food we ingest. A study of the pesticidal content in ready-to-eat foods was initiated by the Food and Drug Administration in the early 1960's. In 1967, the U.S. Public Health Service acquired this responsibility and launched the larger scale human monitoring program cited above (16). Much of this information is found in the Pesticides Monitoring Journal (17,18,19,20 and 21).

TABLE 17-2

CONCENTRATIONS OF TOTAL EQUIVALENT DDT IN THE ADIPOSE TISSUE OF MEMBERS OF THE GENERAL POPULATION

Country	Period of Collection of Samples	Type of Sample	Number of Specimens	Mean concentration of total equivalent DDT, ug/g (range of conc.)
Canada	1959-60	Necropsy	62	5.3
France	1961	Necropsy	10	5.3
Hungary	1960	Necropsy	48	12.4*
India	1964	Biopsy and necropsy	86	27.2
India	1964	Biopsy and necropsy	16	12.5
Israel	1963-64	Biopsy and necropsy	254	19.2*
Poland	1966-67	Necropsy	72	13.4[a]
U.K.	1961-62	Necropsy	131	2.2[g]
U.K.	1964	Necropsy and biopsy	100	4.9
U.K.	1966	Biopsy	53	4.6
U.S.A.	1950	Necropsy and biopsy	75	5.3[a]
U.S.A.	1955	Biopsy	49	19.9
U.S.A.	1954-56	Necropsy and biopsy	61	11.7
U.S.A. (Alaska)	1960	Biopsy	20	3.0
U.S.A.	1961-62	Biopsy and necropsy	130	12.9
U.S.A.	1961-62	Necropsy and biopsy	28	10.7
West Germany	1958-59	Necropsy	60	2.3

* = range of values not available
g = geometric mean
a = DDT + DDE

Only a very brief summary is attempted here.

Twelve categories of foods and feeds were examined for pesticidal residues in five major cities of the United States. The so-called "market basket" is composed of:

a. dairy products,
b. meat, fish, and poultry,
c. grain and cereal products,
d. potatoes,
e. leafy vegetables,
f. legume vegetables,
g. root vegetables,
h. garden fruits,
i. fruits,
j. oils, fats, and shortening,
k. sugars and adjuncts, and
l. beverages.

All classes of pesticides were sought with most of the information, however, coming from the chlorinated hydrocarbons. In all of the reports by Duggan and Corneliussen (16,17,18,19,20, and 21), no discussion was offered for the significance of the levels that were found.

Table 17-3 shows the levels of DDT in three of the 12 categories of food over the years 1965 to 1970. No pertinent comment nor interpretation may be offered for these data. DDT appears to be ubiquitous throughout the United States at approximately the same level. There is apparently no regional bias or concentration of DDT into one sector of the United States. Also, there is no discernible trend of DDT to higher or lower levels with time despite the efforts to restrict the introduction of this pesticide into our environment. It is appropriate to compare these levels with the recommended tolerances of DDT on various foods. For example, the FAO/WHO recommends a tolerance of 1.25 ppm for DDT in milk products (fat basis) and 3.5 ppm for such fruits as cherries, plums, citrus and tropical fruits (22). The levels of DDT cited in Table 17-3 are well below these tolerances.

The dietary intake of pesticide chemicals is our next question to explore. Concomitant with the market basket survey, Duggan and Corneliussen obtained the information necessary to answer this

TABLE 17-3
LEVELS OF DDT RESIDUES (ppm) IN SOME FOOD PRODUCTS[a]

Year	Boston	Kansas City	Los Angeles	Baltimore	Minneapolis
Dairy Products (8-13% fat)					
1965	.010	.065	.031	---	---
1966	.029	.039	.073	.035	---
1967	.033	.023	.109	.029	.070
1968	.029	.058	.036	.009	.017
1969	.027	.036	.030	.004	.019
1970	.019	.026	.02	.005	.016
Meat, Fish, and Poultry (17-23% fat)					
1965	.247	.096	.228	---	---
1966	.679	.313	.437	.096	---
1967	.370	.177	.139	.107	.152
1968	.028	.290	.086	.064	.048
1969	.287	.055	.092	.020	.052
1970	.192	.064	.040	.010	.056
Fruits					
1965	---	.008	---	---	---
1966	.010	.008	.011	.010	---
1967	.035	.01	.059	.01	.009
1968	.010	.022	.002	.003	---
1969	.010	.010	.014	---	.003
1970	.001	.084	.005	.011	.004

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[a] From references 16,17,18,19,20 and 21.

question (23,24, and 25) for the United States. All major classes of pesticides were sought in the 12 categories of foods cited above. A very brief summary of this suryey is offered here. Figure 17-3 shows the dietary intake (mg/day) and the distribution of residues by chemical class for the 1967 to 1970 period. As expected the chlorinated hydrocarbons composed the greater percentage of the total intake of residues. For example, in 1970, 17 chlorinated hydrocarbons, 5 organic phosphates, 3 herbicides, and 2 carbamates were found in the diet. The absolute intake of chlorinated hydrocarbons was approximately .044 mg/day (average, total diet) in this same time period. The data in Figure 17-3 suggests also that an overall decline in the total intake of pesticides had occurred in 1967 through 1970. Concurrently, however, with this decline was an increase in the percentage and absolute intake of the organic phosphates. This is undoubtedly due to the shift of useage from chlorinated hydrocarbons to these chemicals. To cite one specific example, the average dietary intake of total DDT over the 6-year survey was .0007 mg/kg of body weight/day which is considerably lower than the FAO/WHO standard of .005 mg/kg/day. In fact, the average intake of all pesticides was below the safe tolerances established by the FAO/WHO (22).

Should the reader desire additional information about the pesticidal content of food and food products, these references may be helpful: For chlorinated pesticides in fluid milk and other dairy products in the U.S. (26), for the rate of decline of chlorinated hydrocarbons in dairy milk (27), for a statistical analysis of pesticidal residue levels in foods in the U.S. from July 1, 1963 to June 30, 1969 (28), for a study on the uptake of DDT, dieldrin, and endrin by peanuts, soybeans, tobacco, turnip greens and turnip roots (29), for pesticide residues in prepared baby foods in the U.S. (30), and for pesticide residues in foods relative to human health (31).

PESTICIDES IN SOILS

C. Pesticides in Our Soils

We have established the fact now that many organic pesticides reside in human tissue. Undoubtedly, these chemicals came into man via his food as noted in the previous section. Since much of man's food is grown in soils that are treated by a variety of pesticides, we should examine this environment for the occurrence, distribution, fate,

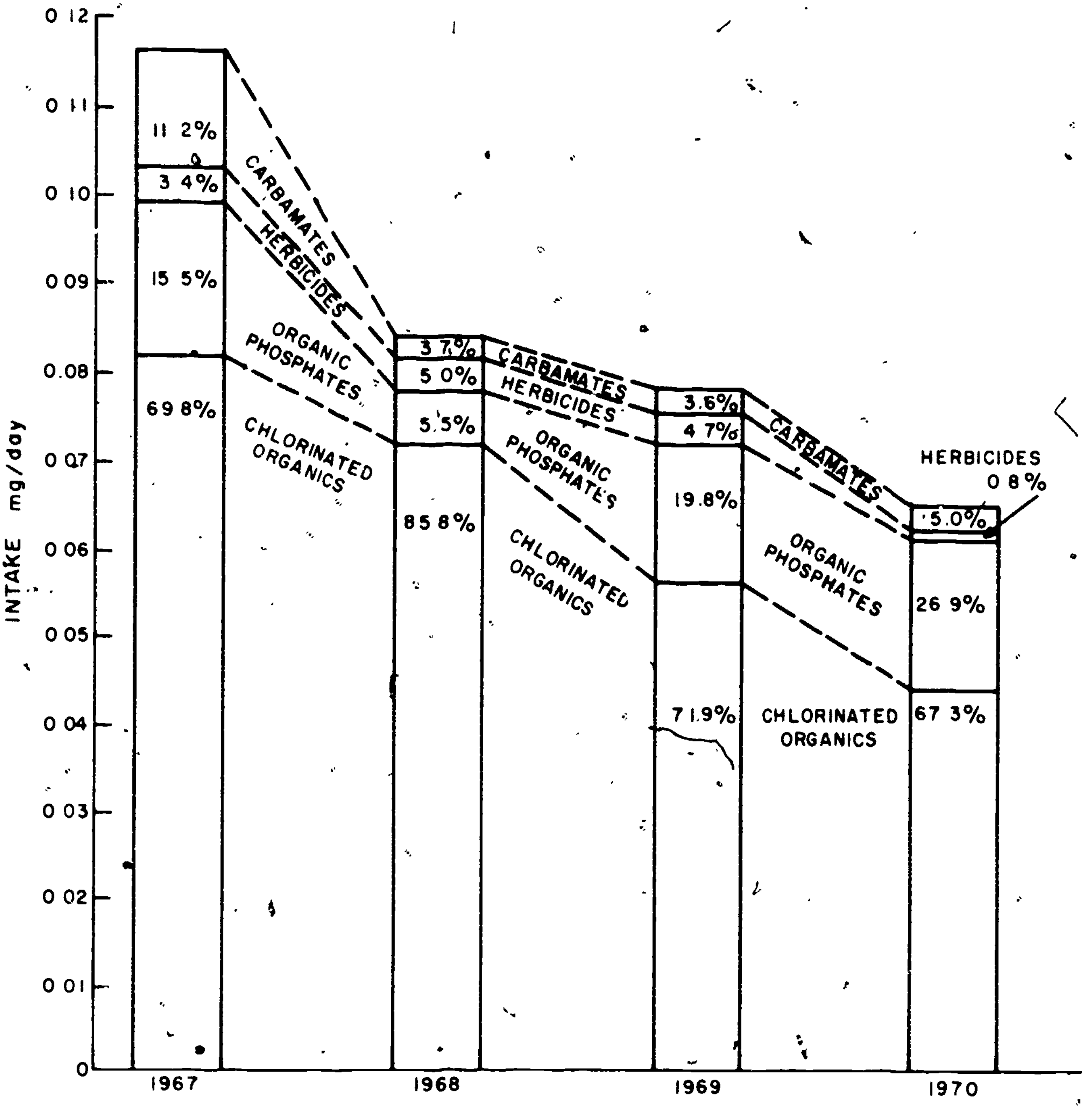

Figure 17-3
Distribution of Pesticide Residues by Chemical Class, 1967-1970

and persistence of these compounds. Much of the information in the literature is concerned with the latter two points - fate and persistence - because known quantities of the pesticides are applied to soils for pest control. It would be superfluous to examine for type and level without concern about the resident time in the soils.

NATIONAL SOIL MONITORING PROGRAM

In concert with monitoring of other environments, the national soil program was initiated in 1964 (32) and was revised in 1967 (33). The initial phases of this program (1964-1967) were concerned with the application of selected pesticides on soils growing soybeans, carrots, peanuts, and potatoes. Emphasis was placed on the uptake and translocation of pesticides by these crops. In 1967, this program was revamped "to determine levels of pesticide residues and major pollutants in soils in major land-use areas and other areas in the United States."

A rather comprehensive paper was published in 1972 that details pesticide residue levels in soils of the United States for FY 1969 from the National Monitoring Program (34). Cropland soils were sampled in 43 of the 50 states whereas non-cropland soils were sampled in only 11 states. Some 33 organic pesticides were detected in the cropland soils with dieldrin as the most widely distributed compound. It was found in 27.8% of the sites with a mean residue of .03 ppm (.01-1.60 range). Total DDT residues (0.31 ppm mean) were observed in 26.1% of the sites. For organophosphates, ethylparathion was detected 10.6% of the time with a mean residue level of 0.06 ppm. 2,4-D was the only chlorophenoxy herbicide detected in 1.6% of 188 samples with a mean residue of less than .01 ppm. Atrazine (a herbicide) was detected in 14.1% of 199 samples with a mean residue of .01 ppm. Eleven organic pesticides were detected in noncropland soils with the DDT residues observed in 16.1% of the samples at a mean residue level of .01 ppm. Dieldrin was observed in 4.0% of these soils at a mean residue level of .01 ppm. Data are presented in this reference (34) for the occurrence of pesticides in individual states. One unique feature of this study is that usage and rate of application data are available. Thus, a correlation between usage, application, and residue level may be established for soil environments. The reader should review this paper very carefully for the comprehensive data on the occurrence of pesticides in soils.

Other monitoring studies have been conducted by Trautmann, et al. (35) for chlorinated hydrocarbons in randomly selected soils and sediments in Wisconsin and in 8 states west of the Mississippi River, by Stevens, et al. (36) for soils from areas of regular, limited, and no pesticide usage and by Wiersma, et al. (37) for pesticides in soils from 8 U.S. cities. Perusal of these references should give the reader a more detailed indication of the occurrence and distribution of organic pesticides in soils of the United States.

In cropland soils, the occurrence of pesticides should not be considered as pollution since they are applied for one purpose or another. The concern about persistent residues in these soils, however, should be indicated here. Many laboratory and field studies have been performed on this subject, but we will cite some information from the aldrin and dieldrin literature. In the case of persistence, aldrin and dieldrin disappear slowly from soils. For example, aldrin, 15.6 ppm was decayed and was converted slowly to .860 ppm dieldrin over a five-year period (38,39). In a field study, aldrin was found to have a half-life value of 5 years whereas dieldrin was assigned a value of 7 years (40). This hould give the reader an order of magnitude concerning the persistence of chlorinated hydrocarbons in soil environments.

Some other notable persistence studies are those of Tarrant, et al. (41) who applied DDT aerially to an eastern Oregon forest and observed that the residue had been decreased by more than 50% in three years; those of Ware, G. B., et al. (42,43) who followed the persistence of DDT in soils, alfalfa, and beef fat after a moratorium had been placed on this pesticide in Arizona during the years 1969 and 1970; and those of Mullins, et al. (44) who examined the persistence of chlorinated hydrocarbon insecticides in the agricultural soils of Colorado.

PESTICIDES
IN PLANTS
AND CROPS

D. Pesticides in Our Plants and Crops

Other important areas of our environment exposed to organic pesticides are the growing plants and crops. We have established that man contains pesticides in his body that are obtained undoubtedly from his market basket. Since many pesticides, especially the chlorinated hydrocarbons, are relatively persistent in soils, we should consider the uptake of these chemicals by edible plants and crops. It is well established that such root crops as carrots, beets, sugarbeets, onions, potatoes, radishes, sweet potatoes, turnips, etc., absorb certain chlorinated hydrocarbons from soils. Furthermore, translocation of these chemicals from soil into the aerial portions of lettuce, cabbage, celery, peas, beans, soybeans, cucumbers, tomatoes, peppers, peanuts, rice, wheat, cotton, alfalfa, etc., has been reported. These observations led to cooperative field and laboratory studies in six states where DDT, endrin, and dieldrin were applied to soils in which soybeans, peanuts, turnip greens, and tobacco were growing (45). The results from these studies will illustrate the occurrence and distribution of pesticides in edible plants and crops.

An indication of the uptake of pesticides may be seen in Table 17-4 where the total DDT content of four crops are given for the cooperative study (45-51). There is, of course, variation in the DDT content of the same crop that is grown in different states. This was especially true of the peanut which may be a reflection of the initial DDT content of the soil before the crop was planted. Other significant observations were reported from this study:

a. The DDT content of crops eaten by man was considered generally "low and insignificant," and below the FAO/WHO tolerances for nuts and root vegetables (22).

b. In some cases the total DDT content of peanut hulls exceeded 1.0 ppm which, if fed to dairy cattle for any length of time, would constitute eventually a residue problem in milk.

c. Dieldrin residues were detected at 0.35 to 0.83 ppm in peanut meats, hulls, and forage. These residues would constitute a possible hazard to man.

d. For soybeans, there may be a low-level residue problem when grown in soils containing relatively high levels of DDT and endrin (8 and 16 lbs. per acre), and

e. There was some translocation of endrin and dieldrin into turnip tops (greens) where the

TABLE 17-4
TOTAL DDT CONTENT (ppm) OF CROPS GROWN IN TREATED SOILS

State	Ref.		Application Rate (lbs/acre)			
			0	2	8	16
Florida	46	Peeled turnips	.03	.01	.01	.01
Florida	46	Turnip greens	.02	.02	.02	.02
Mississippi	47	Soybeans[a]	<.01	<.01	<.01	<.01
N. Carolina	48	Peanuts[b]	<.08	<.08	.08	.13
N. Carolina	48	Tobacco[c]	.16	.15	.16	.18
S. Carolina	49	Tobacco[c]	--	.56	.58	.69
S. Carolina	49	Soybeans[a]	--	.56	.64	.57
Texas	50	Peanuts[b]	.04	.09	.11	.17
Texas	50	Soybeans[a]	.01	.03	.07	.09
Virginia	51	Peanuts[b]	.01	.01	.05	.05
Virginia	51	Turnip greens	.10	.13	.19	.23

[a] Whole bean

[b] In the meat portion

[c] In the green leaf

tolerance is zero.

Consequently, any detectable residue would be illegal.

In summary, it may be stated that organic pesticides are found in man-edible crops where the source is obviously the treated soil. For the most part, these crops appear to be "safe" for ingestion by man directly. However, a subtle and possible hazard exists when other portions of the crop are eaten by cattle, for example, whereupon the pesticide becomes incorporated in the milk. It is these circuitous routes of pesticides to man that may represent a potential hazard.

E. Pesticides in Our Air and Water

The National Pesticide Monitoring Program that was launched in 1967 established a network to survey the major drainage rivers in the United States (52). Initially, 39 rivers were selected for monthly sampling points near their mouths. A revision of this program was announced in 1971 where water samples would be collected quarterly and bed material samples would be collected semi-annually at 161 sites in the conterminous United States, Alaska, Hawaii, and Puerto Rico (53).

These pesticides are sought:

Insecticides

Aldrin
Chlordane
DDD
DDE
DDT
Dieldrin
Endrin

Heptachlor
Lindane
Malathion
Methoxychlor
Methyl Parathion
Parathion
Toxaphene

Herbicides

2,4-D
2,4,5-T
Silvex

A listing of the 161 sampling sites is given in reference (53).

Some of the early river surveys prior to 1967 were conducted by the Federal Water Quality Administration in the U. S. Department of the Interior. Breidenbach, et al. (54) and Weaver, et al, (55) reported upon the chlorinated hydrocarbons in our major rivers for the years 1957-1965. Samples were collected from 99 stations in the month of September when stream flows are usually the lowest. In order of decreasing concentrations, dieldrin (.1 ug/l), endrin, DDT, DDE, DDD, heptachlor and heptachlor epoxide, and γ-BHC were found. Aldrin was found infrequently but when it was, the concentration was low: .006 ug/l.

A five-year summary (1964-1968) of the pesticidal content of the major rivers of the United States (199 sites) was reported by Lichtenberg, et al. (56). Several chlorinated hydrocarbons were found (in order of decreasing frequency): dieldrin, endrin, DDT, DDE, DDD, aldrin, heptachlor, heptachlor epoxide, lindane and γ-BHC, and chlordane. The highest concentration was .407 ug/l of dieldrin in the Tombigbee River at Columbia, Mississippi. Six organophosphorus pesticides were sought but only two were found in one sample in the Snake River at Wawawai, Washington: parathion, .050 ug/l, and ethion, .380 ug/l. Table 17-5 shows a comparison of the maximum pesticide concentrations found in this five-year survey with the permissible water supply criteria in effect at that time (57). All concentrations were far below the permissible criteria.

AIR

The atmosphere environment has been examined on a number of occasions in the United States because of its possible role in the transport of pesticides from one location to another. This medium has often been cited as the mechanism through which pesticides are distributed (presumably) throughout the world. Cohen and Pinkerton (58) were among the first investigators to examine a dust that fell on Cincinnati, Ohio for pesticides. Apparently, a high dust storm had originated in the Southern High Plains region (western Texas) of the United States that was later deposited on Ohio by rainfall. The following pesticides were found (ppm, dry weight): DDT, 0.6; chlordane, 0.5; DDE, 0.2; ronnel, 0.2; heptachlor epoxide, .04; 2,4,5-T, .04, and dieldrin, .003.

A nation-wide survey of the atmosphere was reported by Stanley and co-workers (59) in which the air was sampled at nine localities: Baltimore, Md., Buffalo, N.Y., Dothan, Ala., Fresno, Calif., Iowa City, Iowa, Orlando, Fla., Riverside, Calif., Salt Lake City, Utah, and Stoneville, Miss. Twelve chlorinated hydrocarbons, one phenoxyherbicide, and three organophosphorus compounds were sought. Only DDT was found at all sites with heptachlor epoxide, chlordane, DDD, and 2,4-D esters not found at all. Aldrin and 2,4-D were found in only one sample (of 880). Toxaphene and DEF were found in several samples. These four organophosphate pesticides were found only in samples from Dothan, Orlando, and Stoneville: methyl parathion, parathion, malathion, and DEF. Maximum pesticide levels that were found in air samples are presented in Table 17-6. The highest pesticide levels were found in the agricultural areas of the South. In general,

TABLE 17-5
MAXIMUM PESTICIDE CONCENTRATION FOUND VERSUS PERMISSIBLE WATER SUPPLY CRITERIA FOR 1968[a]

Pesticide	Permissible Criteria	Desirable Criteria	Maximum Concentration Found
Dieldrin	17	absent	0.407
Endrin	1	do	0.133
DDT	42	do	0.316
DDE			0.050
DDD			0.840
Heptachlor	18	absent	0.048
Heptachlor epoxide	18	do	0.067
Aldrin	17	do	0.085
Lindane (BHC)	56	do	0.112
Chlordane	3	do	0.169
Methoxychlor	35	do	b
Toxaphene	5	do	c
Organophosphates plus Carbamates	100	do	0.380
Herbicides: 2,4-D plus 2,4,5-T and 2,4,5-TP	100	do	b
Phenols	1	do	b

[a] After reference (57)

[b] Not determined

[c] Not detected

TABLE 17-6
MAXIMUM PESTICIDE LEVELS (ng/m^3)[a] FOUND IN AIR SAMPLES[b]

Pesticides	Baltimore	Buffalo	Dothan	Fresno	Iowa City	Orlando	Riverside	Salt Lake City	Stoneville
p,p'-DDT	19.5	11.0	177.0	11.2	2.7	1560	24.4	8.6	950
o,p'-DDT	3.0	2.9	88.0	5.5	2.1	500	6.2	1.4	250
p,p'-DDE	2.4		13.2	6.4	3.7	131	11.3		47
o,p'-DDE			3.9			9.6			1.9
γ-BHC	4.5			4.5	4.4			9.9	
Lindane	2.6				0.1			7.0	
γ-BHC	2.2							1.8	
γ-BHC								9.9	
Heptachlor					19.2	2.3			
Aldrin					8.0				
Toxaphene			68.0			2520			1340
2,4-D								4.0	
Dieldrin						29.7			
Endrin									58.5
Parathion						465			
Methyl parathion			29.6			5.4			129
Malathion						2.0			
DEF									16

[a] Lower limit of detection, 0.1 ng/m^3.

[b] After reference (59)

the urban areas of Baltimore, Fresno, and Riverside yielded the lowest levels.

WATER

An excellent study of the chlorinated hydrocarbon pesticides in the rainwater over the British Isles was reported by Tarrant and Tatton (60). It is an excellent study in the sense that British analysts are quite thorough in their confirmation of the presence of a pesticide. This is especially important where the ubiquitous distribution of the pesticide throughout the world is charged. Seven sites were selected over the British Isles for collection of the rainfall samples. These pesticides were found at all nine sites: BHC (5 to 230 picograms/l), dieldrin (1 to 40 pg/l), DDT (6 to 190 pg/l), DDE (3 to 56 pg/l), and TDE (2 to 60 pg/l). In comparison with earlier reports (61,62), the general concentrations of dieldrin at two of the sites (Wellesbourne and London) were lower than before. This was explained as "a consequence of the abandonment of large scale uses of aldrin and dieldrin" in Britain.

Other surveys of aquatic and atmospheric environments for pesticides are:

a. Abbott, et al. (62,63) sought chlorinated hydrocarbons in air samples over England,

b. Barthel and co-workers (64) collected sediments in the lower Mississippi River and its tributaries and analyzed them for chlorinated hydrocarbons,

c. Manigold and Schulze (65) were looking for pesticides in selected western streams of the United States,

d. Holden and Mardsen (66) examined several surface waters and sewage effluents for organochlorine pesticides in England,

e. Croll (67) sought the concentrations of organochlorine pesticides in the ground and surface waters of England and Wales,

f. Schafer, et al. (68) took more than 500 grab samples of raw and finished drinking water from the Mississippi and Missouri Rivers between March, 1964 and June 1967. Ten chlorinated hydrocarbons were sought,

g. Johnson and Morris (69) sampled the rivers of Iowa 1968 through 1970 for chlorinated hydrocarbons,

h. Hindin, et al. (70) collected several ground and surface waters and bottom muds in the Columbia River Basin during the 1961 and 1962 irrigation seasons,

i. Zabik and co-workers (71) determined the effect of urban and agricultural pesticide usage on residue levels in the Red Cedar River in south-central Michigan. Water and bottom samples were collected,

j. Herzel (72) sought organochlorine insecticides in the surface waters of Germany for the years 1970 and 1971.

In summary, there is sufficient evidence to suggest that organic pesticides are in residence in our aquatic environments. Moreover, most of these pesticides have been detected and confirmed as the chlorinated hydrocarbons. The organophosphates, phenoxy acids, carbamates, and ureas are observed infrequently. Concern about the concentrations of pesticides in the water phase leads to the question of safe levels. To date, almost all of the chlorinated hydrocarbon contents have been less than the current water quality criteria for potable water and for fish and other wildlife inhabitants of natural surface waters. Occasionally, an accidental or deliberate discharge will result in a fish kill and other types of wildlife damage. However, none of this has been permanent and no species of aquatic wildlife has been elminated from the face of this good earth. Also, there is evidence to suggest that some pesticides may be transported around the world through dust storms and rainfall. This may account for some of the recent (after 1965) world-wide distribution of pesticides.

PESTICIDES IN FISH AND WILDLIFE

F. Pesticides in Our Fish, Wildlife, and Estuaries

The literature abounds with information concerning the pesticidal content of many species of fish and wildlife. A rather cursory summary of this information is attempted here. However, ample references are listed for the reader.

FISH AND WILDLIFE

The estuarine environment was chosen to launch the 1967 National Monitoring Program for fish and wildlife (73). Initial efforts were directed towards indicator species near top of the food chain, sediments, and these fish: carp, buffalo, black bass, channel catfish, green sunfish, yellow perch, rainbow trout, and squawfish. Sampling sites were selected in the estuaries of all major drainage basins in the United States and Alaska. In 1971 this program was expanded to include these birds: starling, mallard, black duck, and bald eagle (74).

One of the first reports was concerned with the organochlorine residues in starlings from 128 sampling sites throughout the contiguous United States (75). DDT and its metabolites and dieldrin were found in all samples. Other residues, in order of decreasing frequency, were: Heptachlor epoxide, lindane, and BHC. For 126 samples, 60% of the birds had DDT and metabolites less than 1.0 ppm (whole bird, wet) and 80% had less than 2.0 ppm. Approximately 52% of the birds had dieldrin contents less than 0.1 ppm and 83% had less than 0.2 ppm. Some of the birds sampled in Arizona and New Mexico had DDT contents as high as 48 ppm. No comments were made about the significance of these pesticidal contents in the starlings. All of the birds were alive when captured.

BIRDS

The results of a nationwide monitoring of the organochlorine pesticides in the wings of more than 24,000 mallards and black ducks were reported by Heath (76). These wings were submitted to the U. S. Bureau of Sport Fisheries and Wildlife by hunters during the 1965 and 1966 hunting seasons. Previous research had established that the average DDT residues in wings were essentially equal to the median level of such body parts as the breast skin, kidney, breast muscle, etc. DDE was the predominant residue followed in order by DDT, DDD, dieldrin, and heptachlor epoxide. DDE was reported for every state and was notably high in wings from New Jersey, Massachusetts, Connecticut, Rhode Island, New York, Pennsylvania, Alabama, California, and Utah. Dieldrin residues were prevalent in wings from Arkansas, Texas, Utah, California, and several states in the Atlantic Flyway. Some of the average values for DDE were: .24, .09, .16, 2.17, 2.1, .94, and .44 ppm (wet weight). Dieldrin contents were in this range of values: .1, .06, .21, and .05 ppm.

FISH

As part of the National Pesticide Monitoring Program, fish were collected in 1967 and 1968 from 50 sampling stations located in the Great Lakes and in major river basins throughout the United States (77). DDT and metabolites were found in 99% of the samples with levels up to 45 ppm (mg/kg wet weight, whole fish). Dieldrin was found frequently also, 75% of samples, with levels ranging to nearly 2 ppm. Other chlorinated hydrocarbons that were found: aldrin, endrin, lindane, heptachlor, heptachlor epoxide, chlordane, and toxaphene. In order to provide the reader with an indication of the pesticidal contents of fish, Table 17-7 lists some values selected at random from 590 composite samples. One important general observation was made from this study: the bottom feeding fish did not appear to have pesticidal contents any higher than the non-bottom feeders. For example, two smallmouth bass (a bottom feeder) caught in the Potomac River showed dieldrin contents of .01 and .05 ppm whereas two largemouth bass showed levels of .03 and .06 ppm.

One of the more controversial issues has been the pesticidal concentrations in Great Lakes fish. Reinert (78) has published an excellent four-year (1965-1968) survey where DDT and metabolites and dieldrin have been found in all fish sampled from the Great Lakes. Lake Michigan seems to yield fish whose pesticidal content is 2 to 7 times greater than those from the other Great Lakes. For example, an alewife in Lake Michigan contains 3.89 ppm, on the average, of DDT whereas an alewife in Lake Superior contains 0.72 ppm. This report has considerable information on the DDT and dieldrin contents of twelve species of fish from the five Great Lakes.

ESTUARIES

Modin (79) issued a report from California that resulted from the nation-wide program to monitor chlorinated hydrocarbons in estuaries. Samples were: giant Pacific oyster, Bay mussel, Dungeness crab, offshore fish and shellfish. Of the 10 chlorinated hydrocarbons sought, only DDT, DDD, and DDE were routinely found. Dieldrin was not routinely found in the oysters where typical concentrations were 10, 27, 20, 11, 18 ppb (ug/kg). In mussels, 16 ug/kg was reported in one of 27 samples. No dieldrin was reported in the offshore fish and shellfish. One interesting observation was that "expected high levels of pesticides were not found in San Francisco

TABLE 17-7
ORGANOCHLORINE CONTENTS OF SELECTED FISH[a]

Location	Species	Dieldrin ppm[b]	Aldrin ppm	DDT[c] ppm
Delaware River	White suckers	.01, .35, .19, .35	-------------	4.58, .37, 5.50
Lake Huron, Mich.	Carp	.01, 1.3	.04, .03, .15	.16, .58, .74, 67
Illinois River	Bigmouth Buffalo	.02, .52, .32	.04	.54, .16, .16, .19
Lake Huron, Mich.	Channel Catfish	.04, 2.58	.10, .31	2.52, 4.58, 11.49, 3.2
Connecticut River	White Catfish	.28, 1.58, .37	-------------	---------------------
Savannah River	Carp	.06, .62, .52	-------------	---------------------
Miss. River, Luling, La.	Carp	.04, .01, .08, .09	.02, .01, .58	---------------------
Ohio River, Marietta, Ohio	Carp	.04, .02, .02, .03	-------------	---------------------
White River, Ark.	Carp	.07, .01, .34, .04	-------------	---------------------
Missouri River, Nebraska City, Neb.	Carp	.09, .11, .05, .09	-------------	---------------------
Colorado River, Ariz.	Carp	.02, .01, .01	.08	---------------------
San Joaquin River, Los Barros, Calif.	Channel Catfish	.01, .14, .31	-------------	---------------------
Yakima River, Grainger, Wash.	Carp	.05, .06, .08	-------------	---------------------

[a] From reference (77)

[b] Mg/kg wet weight - whole fish

[c] DDT and metabolites

Bay, the terminating point for the Sacramento and San Joaquin Rivers which drain over 6 x 10^6 acres of agricultural land in the Sacramento and San Joaquin Valleys."

Another survey of estuarine organisms comes from the marine waters of Long Island, N.Y. (80). Shellfish were used as the major testing organisms. Pesticides sought were: DDT, DDE, DDD, dieldrin, endrin, aldrin, heptachlor, lindane and heptachlor epoxide. Typical results in the shellfish for DDT + DDE + DDE, 0.019 to .115 mg/kg (wet weight, organic tissue) and for dieldrin, .007 to .020 mg/kg. Some data were given also for lobster: .216 mg/kg DDT, and blue claw crab, .019, .136, .083 mg/kg DDT. Only DDT, DDD, DDE, and dieldrin were found in the survey. Residues found in the shellfish were well below the limits set by the Food and Drug Administration.

Some other references about the occurrence, distribution and levels of pesticides in fish, wildlife, and estuaries are:

a. organochlorine pesticides in hatchery trout (81);

b. chlorinated pesticide levels in the eastern oyster from selected areas of the South Atlantic and Gulf of Mexico (82);

c. The Galveston Bay, Texas, pesticide survey in water and oysters (83);

d. monitoring of the aquatic biota (plants, clams, and fish) at the Tule Lake National Wildlife Refuge (84);

e. insecticide residues in grouse and pheasants of South Dakota (85);

f. pesticide residues in bald and golden eagles (86);

g. organochlorine pesticides in fur seals (87);

h. occurrence of pesticides in whales (88);

i. pesticide residues in channel catfish from Nebraska (89);

j. organochlorine residues and autopsy data from bald eagles, 1966-1968 (90);

k. organochlorine insecticide residues in fish-fall 1969 (National Pesticide Monitoring Program) (91);

l. organochlorine pesticides, PCB, and mercury in bald eagle eggs and changes in egg shell thickness, 1969 and 1970 (92,93);

m. reference (11) has an excellent tabulation of organochlorine pesticide residues in almost all forms of wildlife, and

n. DDT residues in the common surf-zone sand crab along coastal California (94).

SAMPLING OUR ENVIRONMENT

That organic pesticides reside in almost every phase of our environment should be well established from the above discussion. Most of this information was derived from the National Pesticide Monitoring Program where well structured sampling schemes were employed to obtain the elusive "representative" sample. Also, these schemes were designed to yield statistically significant data wherever possible. If one wishes to search our environment for pesticides in a qualitative manner, it is not necessary to obtain a large number of samples with the statistical frequency of a large-scale monitoring program. Samples collected at random would suffice for almost all environments. There are, however, some variables and notes of precaution that the environmental sampler should know. These points are considered in each environment cited below.

HUMAN

A. Humankind

The sampling of humans, dead or alive, should not be attempted by the amateur environmentalist. This should be trusted to the professional only. The analysis of human tissue, blood, organs, etc., for organic pesticides is not particularly difficult. It is, however, the procurement of the human sample which is difficult and should be in the hands of competent personnel.

FOOD

B. Market Basket, Plants, and Crops

The national sampling program for the determination of pesticide residues in unprocessed and commercially processed consumer food commodities and animal feeds is described in detail by Duggan, et al. (16,95). This Market Basket survey is designed to assay pesticide residues in the basic two-week diet of a 16 to 19-year-old male who is statistically the nation's largest eater. There is a total of 117 items in the current market basket under surveillance. Samples of food items are procured by simply purchasing the items at the appropriate retail or wholesale outlets were the food is grown, processed, or sold. The reader should study carefully the references of Duggan, et al. (16,95) for the food items that are analyzed and for preparation of the sample prior to the analytical procedure.

SOIL

C. Soils

The national soils pesticide monitoring and sampling program is presented in detail by Sand and Wiersma, et al. (32,33). Sample collection procedures are described for large-scale study areas where block and plot sampling techniques are needed. This elaboration is needed, of course, to assure statistical significance of the sample. It is not necessary to do this detail for the occasional analysis of soil samples. However, if one wishes to survey a field, forest, lawn, etc., in order to demonstrate the presence of pesticides, it is suggested that several core samples should be collected throughout the area. Also, it is extremely desirable to collect a soil sample reasonably free from pesticides for the analytical control. There are many artifacts in soils that interfere in the analysis and may be mistakenly interpreted as pesticides.

A uniform procedure taking the cores, compositing the sample, and general handling has been developed for the national monitoring program. It is suggested that this procedure is followed. Soil is sampled to a depth of 3 inches with a corer two inches in diameter. All cores should contain the surface cover of the soil, e.g., debris, sod, leaves, etc., which is penetrated through normal sampling. Cores are collected in a large container such as a five-gallon pail. Combined cores are passed through a 1/4 inch screen to facilitate mixing and to remove stones, roots, twigs, etc. Lumps of soil should be forced through the screen. A 1/2-gallon container is filled with the mixed, screened soil and is sealed with an air-tight lid. This "1/2-gallon" of soil constitutes a sample. Needless to say, all containers into which soil is placed should be thoroughly cleaned to avoid extraneous contamination by pesticides.

AIR AND WATER

D. Air and Water

The national monitoring and sampling program was described by Green and Love (52) that was modified and updated later by Feltz and co-workers (53,96). Initially, 53 water sampling stations were chosen for the major fresh water rivers in the conterminous United States. Samples are collected near the river mouths, of course, to take advantage of as much of the drainage area as possible. Where streams have a tidal area, the stations are located above salt water intrusion. Usually the samples are taken from middle of the stream and just below the water surface. If you have a rather broad stream or river, cross-sectional samples may be taken.

All water samples should be collected and stored in glass bottles and never in plastic containers. These sample containers should be cleaned as thoroughly as possible with such cleansing agents as chromic acid or an organic solvent (hexane, for example). Several distilled water rinses of the bottles should follow the cleansing agent. The water sample must have no contact with such cap liners as rubber, cork, and most plastics (Teflon, however, is permissible). A one-liter sample is sufficient usually but there may be occasions when a gallon is more appropriate. Analysis should begin as soon as possible after collection and preferably within two days. Samples should be refrigerated (in the dark) until used.

River sediments may simply be sampled by scraping the upper three inches of the bottom deposits. The sediment samples should be placed in a wide-mouth glass jar and refrigerated and analyzed as soon as possible.

FISH AND WILDLIFE

E. Fish, Wildlife, and Estuaries

The sampling of fish and wildlife in their many natural habitats is a rather difficult task. This point was considered in the national monitoring program by Johnson, et al. (73) and Dustman, et al. (74). For fish, it was decided to select species that were at or near the top of their food chain (in order of preference): carp, buffalo, black bass, channel catfish, green sunfish, yellow perch, rainbow trout, and squawfish. Fish are collected by seining, gillnetting, electric shocking, or by any alternative means other than by chemicals. Approximately one pound of fish is taken for each sample when the whole fish is ground for analysis. If individual tissues are analyzed, it is necessary to collect more than a pound of whole fish. Samples should be wrapped individually in aluminum foil for preservation by freezing until analysis. If there is a long time interval involved in the transportation of samples to the laboratory, dry ice should be used at the rate of 10 lbs. for 10 to 15 lbs. of fish.

Since procurement of a representative sample of each major group of animals is a rather difficult task, the National Pesticide Monitoring Program selected several species of wildlife which occur reasonably close to the top of a food chain (73). The chosen species were: mallard duck, starling, and the bald and golden eagles. Destruction of these birds or any other form of wildlife for the sole purpose of pesticide analysis is not advised. Instead, it is recommended that the procedure of Heath (76) should be followed where only the wings of birds are sampled and analyzed. Furthermore, it is not recommended that stray dead birds be analyzed by the amateur environmentalist because of the possibility that death may have been caused by disease. It is suggested also that the procurement of any type of wildlife should be done in cooperation with your appropriate state agency or with the U. S. Bureau of Sport Fisheries.

The shellfish, oysters and clams are the species most commonly sampled from estuarine environments (73). Once again, it is suggested that the procurement of shellfish or any other estuarine wildlife should be done in cooperation with the appropriate state agency or the U. S. Bureau of Commerical Fisheries.

DETERMINATION AND CONFIRMATION

A. General Information

Analytical determination of organic pesticides in the many environments discussed above is a tedious, but not necessarily a difficult task. Almost all of the analytical techniques employed by the National Pesticide Monitoring Program are complex and cannot be simplified to the level of an electrometric pH value, for example. Furthermore, pesticide analysis requires considerable experience and training. Consequently, it is strongly recommended that any pesticide sampling and analysis of any part of our environment should be under the supervision of a well-trained and competent analyst.

The technical literature is filled with many rather sophisticated techniques for pesticide analysis. Many of these require the use of gas-liquid chromatography and associated instruments which is a highly specialized and expensive procedure. The reader is given references (97,98) for the "official" methods employed by Federal agencies and other laboratories.

A general outline is given below for the detection, determination, and confirmation of only the chlorination hydrocarbon pesticides. This does not suggest that the other types of pesticides are unimportant and do not affect our environments. Selection of organochlorine pesticides should be rather obvious from the discussion above. Almost all of the data from the National Pesticide Monitoring Program is concerned with these pesticides which appear to be the most environmentally prevalent, distributed, and stable.

ANALYSIS

A very generalized schematic diagram for pesticide analysis is seen in Figure 17-4. The sample preparation and extraction steps are different for each sample cited below. However, the cleanup and thin-layer chromatography (TLC) steps are common for all samples after extraction. The "heart" of this analytical diagram is the thin-layer chromatographic step. This technique was selected for many reasons because it provides a rapid method for separation of small quantities of related compounds. The TLC method requires a thin coating of an adsorbent material, usually Silica Gel G, on a glass plate. The mixture of compounds for separation is spotted on the adsorbent layer and the plate is placed in a chromatographic vessel which contains an appropriate solvent system. The solvent migrates throughout the layer which permits separation of the compounds according to their relative affinities for the adsorbent. Once separation is complete, the compounds are developed into visible "spots" by the appropriate chromogenic reagents. Then, the spot is identified into a compound by the distance it has travelled from the origin of insertion on the plate. It is usually the practice to include a known quantity of a pesticide with the sample. This acts as a reference or a standard for the unknown spots. The reader is given reference (99) for greater detail on thin-layer chromatography.

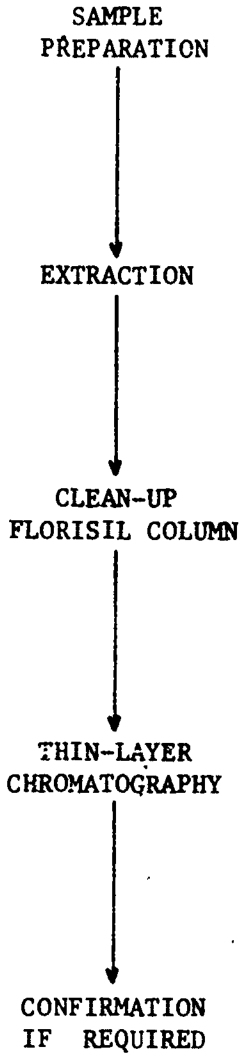

Figure 17-4. Generalized Schematic Diagram for Analysis of Organochlorine Pesticides

B. Special Equipment, Reagents, and Solvents

1. Equipment and Sources

   a. Kuderna-Danish Glassware (24/40 joints)
      Snyder Column - three ball (macro) and one ball (micro)

Evaporative Flasks - 125 ml, 250 ml, and
500 ml
Receiver Ampoules - 2 ml and 5 ml
Ampoule Caps

Kontes Glass Company
Vineland, New Jersey 08360

Dohrmann Instruments
1062 Linda Vista Avenue
Mountain View, California 94040

b. Column Chromatography - Pyrex column 19 mm I.D., 400 mm length with coarse fritted plate on bottom and Teflon stopcock, 250 ml reservoir bulb top of column with flared out funnel shape at top of bulb--a special order.

Kontes Glass Company
Vineland, New Jersey 08360

c. Micro Syringes - (1, 10, 25, 50, and 100 µl)

Hamilton Company
Post Office Box 307
Whittier, California 90608

d. Separatory Funnels - two liter and four liter funnels with Teflon stopcock.

Pyrex or Kimble supplied through many distributors.

e. Thin Layer, Applicator and accessories, including UV source.

Applied Science Laboratories
Post Office Box 440
State College, Pennsylvania 16501

Brinkmann Instruments, Incorporated
Cantiague Road
Westbury, New York 11590

also - from many other suppliers

STANDARDS

2. Standards, Reagents, and Solvents

a. Pesticide standards - highest available purity

City Chemical Company
132 West 22nd Street
New York, New York 10011

Environmental Protection Agency
Perrine Primate Research Branch
P. O. Box 490
Perrine, Florida 33157

Applied Science Laboratories, Inc.
Post Office Box 440
State College, Pennsylvania 16501

also - from the manufacturer

b. Florisil (60/100 mesh) - purchased activated at

1200°F. and stored at 130°C.

Floridin Company
2 Gateway Center
Pittsburgh, Pennsylvania 15222

c. Sodium sulfate (A.C.S.) - granular, anhydrous

d. Pyrex wool - filtering grade

e. Solvents - hexane, diethyl ether, acetone, benzene, xylene, carbon tetrachloride, acetonitrile, methylene chloride, - high purity distilled in glass for pesticide analyses--either Nanograde type or purified in laboratory.

Burdick and Jackson, Incorporated
1953 South Harvey Street
Muskegon, Michigan 49442

Mallinckrodt Chemical Works
2nd and Mallinckrodt Streets
St. Louis, Missouri 63160

Matheson, Coleman, and Bell
Post Office Box 85
East Rutherford, New Jersey 07073

f. Silica gel-G with gypsum binder (No. 8076).

Warner-Chilcott Laboratories
Instrument Division
200 South Gerrard Boulevard
Richmond, California 94801

SCOPE

C. Scope of Method and Special Precautions

TYPES

1. Types of Chlorinated Hydrocarbons Determined

This method covers preparation of the sample and determination of the concentration of various chlorinated hydrocarbon pesticides by thin-layer chromatography in water and waste water.

The following compounds may be determined individually by this method: BHC, lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin, Perthane, DDE, TDE, DDT, methoxychlor, endosulphan, γ-chlordane, and Sulfenone. Under ideal circumstances, Strobane, toxaphene, Kelthane, chlordane (tech.), and others may also be determined.

Various combinations (mixtures) of these compounds in a single sample may not be adequately distinguished, thereby causing high, low, or confused results through misidentification and/or compound obscuring another of lesser concentration. Provisions incorporated in this method will minimize the occurrence of such interferences.

INTERFERENCES

2. Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of thin-layer chromatograms. All of these materials must be demonstrated to be free from interference under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all glass systems is required. Glassware should be cleaned by rinsing successively with chromate cleaning solution, tap water, distilled water, and finally with redistilled acetone. If the type and size of glassware permits, it is heated in a muffle furnace to about 400°C. for 15 to 30 minutes.

Sample treatment required to remove non-pesticide materials which cause interference may result in the loss of certain chlorinated hydrocarbons. It is beyond the scope of this method to describe procedures for overcoming all of the possible interferences that may be encountered. Methods for eliminating or minimizing interferences are described in the sections on Clean-up and Separation Procedures.

3. Preparation of Standards, Reagents, and Solvents

STANDARD REAGENTS

a. Analytical Standards and Other Chemicals

Analytical reference grade standards should be used whenever available. They should be stored according to the manufacturer's instructions. Standards and reagents sensitive to light should be stored in dark bottles and/or in a cool dark place. Those requiring refrigeration should be allowed to come to room temperature before opening. Storing of such standards under nitrogen is advisable.

STOCK SOLUTIONS

b. Stock Standards

Pesticide stock standards solutions should be prepared in 1 ug/ul concentrations by dissolving 0.100 grams of the standard in pesticide-quality hexane or other appropriate solvent, (Acetone should not be used since some pesticides degrade on standing in this solvent) and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles. These standards should be checked frequently for signs of degradation and concentration, especially just prior to preparing standard solutions from them.

STANDARD SOLUTIONS

c. Standard Solutions

Pesticide standard solutions are prepared from the stock solutions using a micro syringe preferably equipped with a Chaney adapter. The concentration of these solutions will vary depending on the TLC system employed and the level of pesticide in the samples to be analyzed. A typical concentration (0.1 ng/ul) may be prepared by diluting 1 ul of the 1 ug/ul stock solution to volume in a 10 ml ground glass stoppered volumetric flask. The standard solutions should be transferred to ground glass stoppered reagent bottles. Preparation of a fresh working standard each day will minimize concentration through evaporation of solvent. These standards should be stored in the same manner as the stock solutions.

REAGENTS

d. <u>Identification of Reagents</u>

All stock and standard solutions should be labeled as follows: name of compound, concentration, date prepared, solvent used, and name of person who prepared it.

Na_2SO_4

e. <u>Anhydrous sodium sulfate</u> used as a drying agent for solvent extracts should be prewashed with the solvent or solvents that it comes in contact with in order to remove any interferences that may be present.

COTTON

f. <u>Cotton</u> used at the top of the sodium sulfate column must be pre-extracted for about 40 hours in soxhlet using the appropriate solvent. A cheap grade of cotton is recommended. Red Cross cotton is not recommended.

SOLVENTS

g. <u>Solvents</u>

Organic solvents must be of pesticide quality and demonstrated to be free of interferences in a manner compatible with whatsoever analytical operation is to be performed. Solvents can be checked by analyzing a volume equivalent to that used in the analysis and concentrated to the minimum final volume. If necessary, a solvent must be redistilled in glass using a high efficiency distillation system. A 60 cm column packed with 1/8 inch glass helices is effective.

ETHER

h. Ethyl Ether - Hexane

It is particularly important that these two solvents, used for extraction of organochlorine pesticides from water, be checked for interferences just prior to use. Ethyl ether, in particular, can produce troublesome interferences. (Note: the information of peroxides in ethyl ether creates a potential explosion hazard. Therefore, it must be checked for peroxides before use.) It is recommended that the solvents be mixed just prior to use and only in the amount required for immediate use since build-up of interferences often occurs on standing.

4. Common Analytical Operations

BLANKS

a. Method Blank

A method blank must be determined whenever a sample or group of samples is analyzed. This is done by following the procedure step by step including all reagents, solvents, and other materials in the quantity required by the method concurrently and under conditions identical to those for the samples. Additional blanks are required whenever a new supply of any of the reagents, solvents, etc., is introduced.

TRANSFER

b. Sample Transfer

The utmost in care and technique must be exercised in order to assure quantitative transfer of extract solutions from one vessel to another throughout the analysis. Careless technique will introduce determinate errors and produce inaccurate results. The internal wall of the vessel must be carefully rinsed several times (usually three) with a volume of the particular solvent appropriate for the analysis involved. Final flushing while pouring into the receiving vessel is recommended.

5. Concentration of Extracts

EVAPORATION

a. Kuderna-Danish (K-D) Evaporation

Snyder column, evaporative flask and calibrated receiver ampul are employed. The evaporative flask should be filled to no more than 60% capacity. Set the K-D assembly over a vigorously boiling water bath or a live steam bath. The evaporation must be carefully attended to avoid loss of pesticides. The water level should be maintained just below the lower joint, and the apparatus mounted so that the lower rounded surface of the flask is bathed in steam. Carry out the evaporation in a hood so that solvent vapors are exhausted. When the solvent no longer actively distills, the K-D apparatus is removed from the bath and allowed to cool. The condensed solvent is allowed to cool. The condensed solvent is allowed to drain into the ampul before dismantling.

FINAL CONCENTRATION

b. Final Concentration

Concentration below 5 ml is usually required when analyzing surface water samples. Final evaporation to a minimum of 0.2 ml may be accomplished in the ampul with the air of a gentle stream of clean dry nitrogen or air in a warm water bath, adjusted to the temperature prescribed by the method. Final evaporation may also be accomplished in the ampul using a micro Snyder column to give a final volume of 0.2-0.4 ml. In the latter case, a small sand-size boiling clip is added to the ampul prior to evaporation. The extract volume is reduced to 0.1 ml below the volume sought so that the internal wall of the ampul may be rinsed. This step is carried out at least three times. Great care must be exercised to prevent the extract from going to dryness.

SAMPLE PREPARATION

D. Preparation of Samples

Each of the samples cited below requires a different technique of preparation prior to solvent extraction. Some samples will need more preparative work than others. Preparation generally is the blending or grinding of the sample into smaller particles where the subsequent extractive step is more efficient and quantitative recovery of the pesticide is assured.

FOODS

1. Foods

Market Basket items (i.e., foods) that normally require further processing by cooking, such as fresh meats and certain raw vegetables, or preparation for eating raw, such as tomatoes, carrots, celery, lettuce, cucumber, cabbage, and fresh fruits, should be delivered to a diet kitchen for preparation under the direction of a dietician. Market Basket items that are normally consumed as purchased such as dairy products, luncheon meats and frankfurters, canned meats, some fruits and vegetables, potato chips, canned fruit juices, concentrated fruit juices, and frozen fruits should be retained for compositing by commodity groups with the foods prepared by the diet kitchen. Guidelines for the preparation and compositing of food are presented by Duggan and Cook (95). It is strongly recommended that Market Basket items should be prepared under the direction of or by an expert dietician.

ROOT CROPS

2, Root Crops

Such root crops as carrots, peanuts, and potatoes may be prepared by the technique of Seal, et al, (100). First, the samples are water-washed and air-dried before chopping into small pieces. Then these pieces are homogenized usually with a solvent in the extractive step cited below.

MILK

3. Milk

All milk samples are processed immediately and the butterfat is removed upon receipt at the laboratory (101). The milk is warmed to room temperature by standing. The butterfat is removed by placing 100 ml into a 200-ml volumetric flask and, with constant mixing, the flask is filled to the mark with a detergent reagent (50 g sodium tetraphosphate plus 24 ml of Triton X-100 per liter of water). This mixture is placed into a water bath at 95° C until the clear butterfat layer separates into the neck of the flask. The butterfat is transferred into vials and held under refrigeration until analysis.

SOILS AND WATER

4. Soils and Waters

There are no special preparative steps for soil, water, fish, shellfish, and animal tissue since they are extracted shortly after taken. In addition, no drying steps are required for soils.

EXTRACTION FOODS

E. Extraction of Samples

1. Foods

Reduce 500 grams of more of a representative food sample into small pieces using a food cutter, chopper, or knife. Weigh a representative aliquot (100 grams) of the finely chopped material into a high-speed Waring Blender. Add 4 ml of extraction solvent (hexane-isopropyl alcohol, 3:1) per gram of sample, measuring the amount of solvent accurately. (For extremely watery foods such as tomatoes, watermelon, etc., decrease the hexane-isopropyl alcohol ratio to 2:1). Blend until the sample is thoroughly macerated (3 to 5 minutes is usually sufficient). Pour the mixture from the blender cup into a separatory funnel containing about 50 ml distilled water, removing the food matrix through the use of a funnel containing a plug of glass wool. Wash the isopropyl alcohol from the solution with five successive volumes of distilled water equivalent to the amount of alcohol present. Discard the water each time. If trace amounts of alcohol can be detected in the wash water by odor, use additional water washes until no odor is present. Drain the hexane into an Erlenmeyer flask containing anhydrous sodium sulfate. Shake and allow to stand for approximately 15 minutes. Filter off the sodium sulfate through fluted filter paper. This hexane extract is ready now for the cleanup through the Florisil column described below.

ROOT CROPS

2. Root Crops

One hundred grams of chopped samples are homogenized for one to two minutes with 200 ml of chromatographic grade acetonitrile with about 10 grams of Celite added (100). This homogenization should occur in a stainless steel cup. The solvent and pulp are separated by centrifugation in this cup. The solvent is decanted through filter paper into a 1-liter flask and held. Another 100 ml portion of acetonitrile is added to the pulp in the cup and the extraction, settling, and filtration are repeated. This second extract is added to the first which is reduced then by evaporatior through a Snyder column on a hot plate to leave a water layer covering the bottom of the flask. One hundred mls of hexane are added through the column to the water layer which is subsequently evaporated completely. Another 200-ml portion of hexane is added through the Snyder column to the water layer in the flask and the contents are refluxed. The water and hexane are transferred to a separatory funnel where the water subsequently is rejected. The hexane extract is filtered through sodium sulfate, made to 300-ml volume, sealed in a glass bottle, and held, if necessary, under refrigeration until determination by thin-layer chromatography cited below. Normally, clean-up with Florisil is unnecessary with carrots and potatoes when the initial extraction is made with acetonitrile.

Slightly different extraction techniques are described by Wheeler, et al. for turnip roots (46) and soybean seeds (102).

MILK

3. Milk

The butterfat is fluidized in a warm oven. One gram (1.00) is transferred with a dropping tube to 25 g of activated Florisil (see above) and mixed thoroughly until a free-flowing powder is obtained (101). Twenty-five grams of deactivated Florisil (take room temperature, activiated Florisil and add water at the rate of 5 ml per 100 grams) is poured into a chromatographic column to form the bottom half of the clean-up system. This is prewashed with 50 ml of a 1:1 mixture of dichloromethane and hexane. The butterfat-Florisil mixture is then introduced into the column to form the top layer which is eluted with 300 ml of a 1:4 dichloromethane-hexane elution mixture at a percolation rate of approximately 5 ml/minute. Eluates are concentrated just to dryness with a rotary vacuum at 45°C. The residue is redissolved in 5.0 ml of hexane and transferred to a glass stoppered tube for subsequent thin-layer chromatographic analysis.

SOILS

4. Soils

A sample of soil, 300 grams wet weight, is placed into a 2-quart fruit jar with 600 ml of 3:1 hexane-isopropanol solvent (34). The jars are sealed and rotated for 4 hours. After rotation, the soil is allowed to settle and 200 ml of the extract solution is filtered into a 500-ml separatory funnel. Isopropyl alcohol is removed with two washings of distilled water. The remaining solution is filtered then through a funnel containing glass wool and anhydrous sodium sulfate. This hexane solution should be put through the Florisil column described below before thin-layer chromatography is attempted.

WATER

5. Water

One liter of sample is drained into a 2-liter separatory funnel, equipped with a Teflon stopcock, and extracted with 60 ml of 15% ethyl ether in hexane, by shaking vigorously for two minutes (97). The mixed solvent is allowed to separate from the water and this water is drawn into a second 2-liter separatory funnel. The organic layer is passed through a small column of anhydrous sodium sulfate (which has been previously rinsed with hexane) and collected in a 250 ml beaker. The extraction is repeated and the solvent treated as above. Approximately 35 ml of sodium sulfate saturated water is then added to the sample and a third extraction is completed with 60 ml of hexane (not hexane-ethyl ether). This solvent too is passed through the sulfate column and collected in the beaker. The column is rinsed with several small portions of hexane and this solvent is blown out and recovered in the collection beaker containing the combined extracts. With a clean sample, the extract may be treated as described below.

If the sample is composed of relatively

clean water, apparently free from oils, coloring matter and other organics, it may be concentrated by transferring the partially evaporated sample extract with small portions of hexane to a 125 ml Kuderna-Danish (K-D) evaporative flask equipped with a 2 ml receiver ampoule. A three ball Snyder column is mounted to the top of the flask and the solvent is evaporated in a steam bath. After no more solvent actively distills the assembled K-D is removed from the bath and allowed to cool slightly. The Snyder column and the flask while still warm are rinsed with a small portion of hexane into the receiver ampoule. The ampoule is disconnected and the concentrated extract is ready for thin-layer chromatography described below.

If the concentrated extract appears "dirty" or is believed to contain materials which may interfere with measurement proceed as described below under Clean-up and Separation Procedures.

FISH

6. Fish, Shellfish, and Animal Tissue

Approximately 50 to 100 grams of fish, shellfish, or animal tissue are placed into a clean Mason jar and homogenized with an Osterizer (103,104,90). It may be necessary to homogenize some animal tissue with a Hobart food cutter. A 30-gram aliquot of the homogenate is transferred to another clean Mason jar and mixed with 90 grams of a desiccant mix composed of 9 parts anhydrous sodium sulfate and 1 part Quso (a micro fine precipitated silica). The mixture is alternately frozen and blended with an Osterizer until a free-flowing powder is obtained. Thirty grams of this powder are extracted for 4 hours with 300 ml of hexane in a Soxhlet apparatus. This extract is filtered through sodium sulfate, made to 300-ml volume, sealed in a glass bottle, and held, if necessary, under refrigeration until determination by thin-layer chromatography cited below. However, clean-up through a Florisil column should occur before the chromatographic step.

CLEAN-UP

F. Clean-up and Separation Procedures

The analytical procedure, from this point forward is common to all of the sample extracts cited above. Unless noted previously, all extracts should be run through the Florisil column before thin-layer chromatography is attempted.

ADSORPTION COLUMN

1. Florisil Column Adsorption Chromatography

The sample extract is concentrated to approximately 40 ml in a water bath at 70°C without air or vacuum. A 15 g charge of Florisil, which has been stored in an air-tight container at 130°C, is placed in a column over a small layer (one-half inch) of anhydrous granular sodium sulfate. After tapping the Florisil into the column, about a 3/4 inch layer of granular sodium sulfate is added to the top. The column, after cooling, is pre-eluted with about 75 ml of hexane. The pre-eluate is discarded, and just prior to exposure of the sulfate layer to air, the sample extract is quantitatively transferred into the column by decantation and subsequent hexane washings. The elution rate is adjusted to about 5 ml per minute with two eluates collected separately in 500 ml K-D apparatus equipped with 2 ml ampoules. The first elution is performed with 200 ml of 5 to 6% ethyl ether in hexane and the second elution with 200 ml of 15% ethyl ether in hexane. The K-D apparatus containing the eluates is connected to three ball Snyder columns and the solvents are evaporated.

ELUATE

2. Eluate Composition

If the Florisil has been properly activated and stored, and if the reagents are carefully prepared, the following eluate compositions will be obtained when the pesticides are present: (The first eluate 5 to 6% ethyl ether in hexane):

lindane

BHC

Kelthane

aldrin

heptachlor

DDE

Perthane

heptachlor epoxide

methoxychlor

toxaphene

Strobane

chlordane (γ & tech)

TDE

DDT

endosulfan I

The second eluate (15% ethyl ether in hexane):

dieldrin

endrin

endosulfan II

lindane (possible trace of total)

Kelthane (possible trace of total)

Standard pesticide mixtures should be used frequently to demonstrate the effectiveness of the Florisil to characterize the eluate composition and provide quantitative recovery.

G. Thin-Layer Chromatography

THIN LAYER

1. Thin-Layer Plates

Previously prepared plates should be purchased and activated in accord with the supplier's directions.

SOLVENTS

2. Developing Sólvent

The developing solvent, carbon tetrachloride, is added to the developing chamber to a depth of 10 mm. Two filter paper wicks, one on each side of the chamber, are placed so that one end contacts the solvent. After the lid is in place, the chamber is allowed to equilibrate for one hour. It is important that the chamber be protected from drafts and large temperature changes.

SPOTTING

3. Sample Spotting

The sample extracts contained in K-D ampoules or extracts retained and transferred to ampoules are carefully evaporated in a bath of warm water at 40°C with a fine draft of clean air to about 50-100 ul. (Utmost care must be exercised to keep evaporation losses to a minimum) and evaporated by the same technique to about 50 ul <u>very</u> carefully. The volume in the ampoule is adjusted to exactly 100 ul with benzine and a measured aliquot is spotted using a micro syringe. The entire sample may be spotted, if necessary, by using several small applications, transferring the entire contents of the ampoule each time as thoroughly as possible with a micro syringe. Utmost care must be exercised in keeping the spot small (less than 1 cm diameter). A gentle stream of clean, dry air of nitrogen may be applied over the spot to facilitate close boundary evaporation, but thin gas flow exposure should be kept to a minimum. With the aid of a spotting template up to nine spots including samples and standards may be spotted 20 mm apart and 10 mm from the bottom of the layer. Samples may be spotted in duplicate depending on the nature of corroborative evidence desired.

STANDARDS

4. Standards

A mixture of standards containing 10 to 20 ug of each pesticide is spotted on each plate to confirm the separation of the respective pesticides by visual observation. Standards for recovery and instrumental measurement are spotted in the 20 to 100 nanogram range and handled just as a sample would be treated in the subsequent steps of the procedure.

LAYERS

5. Layer Development

The spotted layer is placed in the pre-equilibrated chamber so that the bottom edge is in contact with the developing solvent and the lid is replaced. When the developing solvent reaches the upper reference line (10 cm), the layer is removed from the chamber and allowed to air dry at room temperature.

VISUAL

6. Visualization and Sectioning of Layer

After development, the portion of the layer containing the standards (10-20 ug) is sprayed with a fairly heavy even coat of Rhodamine B (0.1 mg/ml in ethanol). The sprayed area is allowed to thoroughly dry (about 5 minutes) and then exposed to and viewed under short wave UV light. The pesticides show up as quenched areas (dark) on a fluorescent background. Mark the location of each pesticide.

The distance of travel for pesticides present in the unknown samples and recovery test standards will be, respectively, the same as those of the sprayed standards. From this information the vertical zone for each sample is divided into five horizontal sections. The sections are identified with Roman numerals as shown in Figure 17-5. Examples of respective Rf and Rr values for various pesticides are listed in Table 17-8.

CONFIRM

H. Confirmatory Techniques

The analytical procedure described above is reasonably specific for the chlorinated hydrocarbon pesticide. That is, the preparation, extraction, and clean-up steps eliminate and separate the pesticides from most interferences and artifacts. There may be occasions when it is imperative to confirm the identity of a pesticide. Many techniques and innovations are available for confirmation and the analyst may choose from various combinations of thin-layer chromatography, gas-liquid chromatography, paper chromatography, infrared, and ultraviolet spectroscopy, nuclear magnetic resonance, and mass spectrometry (105). Many of these are rather complex and require the skill of a specialist. Should the reader perform a sampling and subsequent analysis that requires confirmatory information, he is referred to any one of the State or Federal laboratories mentioned in the National Pesticides Monitoring Program.

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TABLE 17-8
SOME Rf AND Rr VALUES OF PESTICIDES DEVELOPED WITH CARBON TETRACHLORIDE ON SILICA GEL G THIN LAYER PLATE

Pesticides and Metabolites	Rf Value	Rr Value	Section
Dieldrin	0.17	0.33	
Endrin	0.20	.037	II
Heptachlor Epoxide	0.29	.052	
Lindane	0.37	0.69	
DDD	0.54	1.00	III
γ-Chlordane	0.55	1.02	
Heptachlor	0.67	1.24	
DDT	0.68	1.26	IV
DDE	0.72	1.33	
Aldrin	0.73	1.35	

Rf = distance traveled by the compound divided by the distance traveled by the solvent front.

Rr = distance traveled by the compound divided by the distance traveled by standard p,p'-DDD.

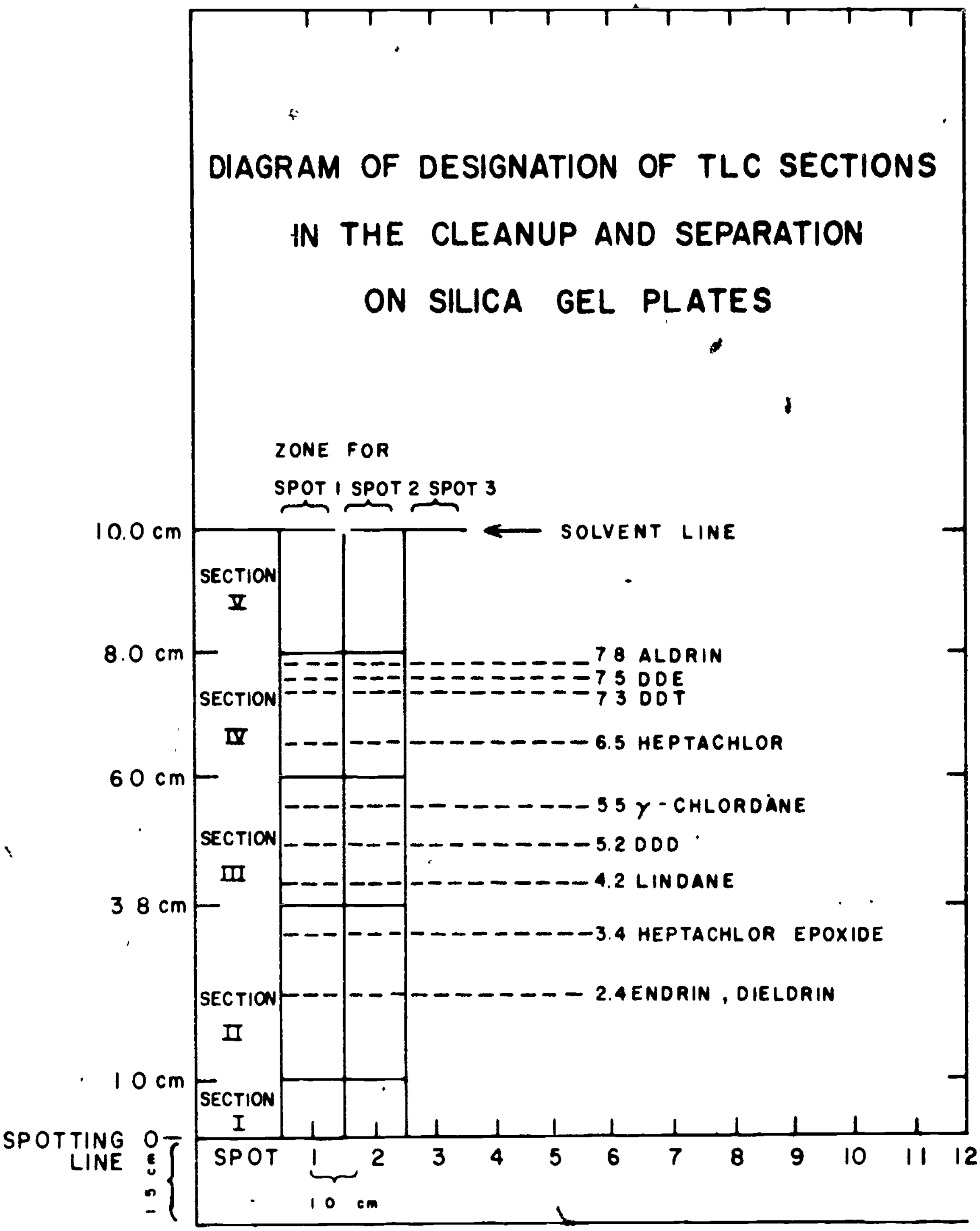

Figure 17-5
Diagram of Designation of TLC Sections on Silica Gel Plates

Problems:

1. Visit a nearby Agriculture or Health Department Office, and collect all available information on various kinds of pesticides used in your area.

2. Write a report on your findings, including; monitoring requirements, kinds, types and amounts of pesticides used. Who uses them? Are they licensed? What are the major sources of pesticides in your area?

3. Check the Federal Register and see if pesticides are limited in water environments.

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