Environmental Media Phase-Tracking Units in the Classroom

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ABSTRACT

When teaching phase partitioning concepts for solutes in porous media, and other multi-phase environmental systems, explicitly tracking the environmental media phase with which a substance of interest (SOI) is associated can enhance the students' understanding of the fundamental concepts and derivations. It is common to explicitly track the customary mass, length, and time based units. The expansion described here is to also track the specific media phases to which these fundamental units apply. This additional step forces students to think more carefully about concentrations and other terms. This paper presents a consistent system of notation for teaching these concepts and some examples of how this system is used. The examples presented here are based on solid-liquid partitioning and a linear Freundlich adsorption isotherm, but could also be applied to other environmental media, such as air and biological tissue, as well as other partitioning models. This approach is most appropriate for advanced undergraduate and graduate students.

INTRODUCTION

Whenever a substance of interest (SOI) is exposed to environmental media (e.g., soil, water, air, biological tissue) in trace amounts, the SOI is redistributed among the media phases (e.g., solid, liquid, gas) and the SOI concentrations associated with each media phase eventually reach a dynamic equilibrium with each other. This distribution of the SOI among the various media phases is often called partitioning. The ways in which the SOI may be associated with environmental media phases include:

- Adsorption onto solids (e.g. soil or sediment
- Dissolution in liquids (e.g. water)
- Volatilization in gases (e.g. air)
- Incorporation into tissue (e.g. uptake and absorption by plants or animals)

If the amount of the SOI in the environment exceeds the collective holding capacity of the various media phases to which it is exposed, it will exist in free phase form, which for liquid SOIs is often called non-aqueous phase liquid (NAPL). The terminology described here applies only to trace amounts of the SOI associated with environmental media, not to free-phase SOI.

Understanding partitioning behavior is a key factor for evaluating the trace substance transport and fate and for understanding the meaning of concentrations as reported by chemical analysis laboratories. Given this importance, it can be useful and instructive to track the environmental media phases with which the SOI is associated. It is customary to track the fundamental units of mass, length, and time when teaching these concepts. The expansion described here is to also explicitly track the media phases with which the units are associated. These expanded units can enhance student understanding of the terms in and development of the relevant equations.

This paper presents a consistent notation system for tracking the media phases with which the SOI is associated through the various equations and concepts needed to evaluate solutes in environmental systems. This system is applied to evaluation of chemical analysis results and various equations of interest. The analysis here

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focuses on concepts and equations of interest when evaluating ground water, and hence covers only solid/liquid partitioning, but the style of phase-tracking notation presented here could easily be expanded to cover gas and biota partitioning also. The notation presented here is cumbersome and would not be used routinely after the concepts have been mastered, but the author still returns to this notation when dealing with some complex problems. This approach is most appropriate for advanced undergraduate and graduate students.

BASIC TERM DEFINITIONS

In order to distinguish SOI associated with the various environmental media, we can define the following terms for a system including a trace SOI, solid particulate matter, and water. When terms are used inside square brackets, they are designating units. Terms not in square brackets are designating the actual value for the sample or system. When a fundamental quantity, such as mass or volume of a specific phase is used as an actual value, the units, which would have the same nomenclature as the quantity itself, are not written.

SOI mass (M = mass):
- M_s = total mass SOI
- M_{sd} = mass SOI dissolved in water
- M_{sp} = mass SOI adsorbed to particulates

Environmental media mass:
- M_w = water mass
- M_p = particulates (solids) mass

Volumes (L = length):
- L_w^3 = water (liquid) volume
- L_p^3 = particulates (solids) volume
- L_g^3 = gas volume
- L_b^3 = bulk (total) sample volume
- L_{void}^3 = void (non-solid) volume = L_g^3 in dry sample = L_w^3 in saturated sample

Note that the terminology "void" in this context can create some confusion because this space is always filled with some combination of gas and liquid. I have

nevertheless used the term "void" here since it is such common terminology.

These units can then be used to track specific phase associations for common media characterization terms, including:

- $\rho_w \left[\dfrac{M_w}{L_w^3} \right]$ = water material density

- $\rho_{bw} \left[\dfrac{M_w}{L_b^3} \right]$ = water bulk density

- $\rho_p \left[\dfrac{M_p}{L_p^3} \right]$ = particulate material density

- $\rho_{bp} \left[\dfrac{M_p}{L_b^3} \right]$ = particulate bulk density.

Note that particulate bulk density is usually called total suspended solids (TSS) for water samples with trace amounts of particulate.

- $n \left[\dfrac{L_{void}^3}{L_b^3} \right]$ = total porosity.

- $R_s \left[\dfrac{L_w^3}{L_{void}^3} \right]$ = saturation ratio.

- $\theta_v \left[\dfrac{L_w^3}{L_b^3} \right] = n \left[\dfrac{L_{void}^3}{L_b^3} \right] R_s \left[\dfrac{L_w^3}{L_{void}^3} \right]$ = volumetric moisture content.

- $\theta_g \left[\dfrac{M_w}{M_p} \right]$ = gravimetric moisture content.

- $TS \left[\dfrac{M_p}{M_p + M_w} \right]$ = total solids content

(commonly used for sediment samples).

Some useful relationships among these media phase characterizations that also illustrate use of the phase-tracking units, include:

$$\theta_v \left[\frac{L_w^3}{L_b^3} \right] = n \left[\frac{L_{void}^3}{L_b^3} \right] R_s \left[\frac{L_w^3}{L_{void}^3} \right] \tag{1}$$

$$\rho_w \left[\frac{M_w}{L_w^3} \right] \theta_v \left[\frac{L_w^3}{L_b^3} \right] = \rho_{bp} \left[\frac{M_p}{L_b^3} \right] \theta_g \left[\frac{M_w}{M_p} \right] \tag{2}$$

$$\rho_{bp} \left[\frac{M_p}{L_b^3} \right] = \frac{\rho_p \left[\frac{M_p}{L_p^3} \right] L_p^3}{L_b^3} = \frac{\rho_p \left[\frac{M_p}{L_p^3} \right] \left(L_b^3 - L_{void}^3 \right)}{L_b^3}$$
$$= \rho_p \left[\frac{M_p}{L_p^3} \right] \left(1 \left[\frac{L_b^3}{L_b^3} \right] - n \left[\frac{L_{void}^3}{L_b^3} \right] \right) = \rho_p \left[\frac{M_p}{L_p^3} \right] \left\{ (1-n) \left[\frac{L_p^3}{L_b^3} \right] \right\} \tag{3}$$

$$\rho_{bw} \left[\frac{M_w}{L_b^3} \right] = \rho_p \left[\frac{M_p}{L_p^3} \right] \theta_g \left[\frac{M_w}{M_p} \right] \left\{ (1-n) \left[\frac{L_p^3}{L_b^3} \right] \right\} \tag{4}$$

For saturated porous media only, we may write:

$$\rho_{bp} \left[\frac{M_p}{L_b^3} \right] = \frac{M_p}{M_w \Big/ \rho_w \left[\frac{M_w}{L_w^3} \right] + M_p \Big/ \rho_p \left[\frac{M_p}{L_p^3} \right]}$$

$$= \frac{1 \left[\frac{M_p}{M_p} \right]}{\dfrac{\theta_g}{\rho_w} \left[\frac{M_w}{M_p} \frac{L_w^3}{M_w} \right] + \dfrac{1}{\rho_p} \left[\frac{M_p}{M_p} \frac{L_p^3}{M_p} \right]} = \frac{1 \left[\frac{M_p}{M_p} \right]}{\left(\dfrac{\theta_g}{\rho_w} + \dfrac{1}{\rho_p} \right) \left[\frac{L_b^3}{M_p} \right]} \tag{5}$$

and

$$\rho_{bw} \left[\frac{M_w}{L_b^3} \right] = \frac{M_w}{M_w \Big/ \rho_w \left[\frac{M_w}{L_w^3} \right] + M_p \Big/ \rho_p \left[\frac{M_p}{L_p^3} \right]}$$

$$= \frac{1 \left[\frac{M_w}{M_w} \right]}{\dfrac{1}{\rho_w} \left[\frac{M_w}{M_w} \frac{L_w^3}{M_w} \right] + \dfrac{1}{\rho_p \theta_g} \left[\frac{M_w}{M_w} \frac{L_p^3}{M_p} \frac{M_p}{M_w} \right]} = \frac{1 \left[\frac{M_w}{M_w} \right]}{\left(\dfrac{1}{\rho_w} + \dfrac{1}{\rho_p \theta_g} \right) \left[\frac{L_b^3}{M_w} \right]} \tag{6}$$

As can be seen in Equations (1) through (6), using the phase-tracking units provides a roadmap to the development of these relationships. Writing units without the phases provides a more compact notation, but also makes it more difficult to learn the principles underlying these relationships. Note that where the numeral 1 appears in the equations, it is essentially non-dimensional, but the dimensions of the values that cancelled out to create the value of 1 are retained in the notation to be consistent with the other terms.

CONCENTRATION MEASUREMENT INTERPRETATION

Correct interpretation of reported SOI concentrations based on environmental media samples must account for the manner in which the concentrations are measured and reported. Environmental media samples commonly include more than one phase. For example, a water sample will have some solid particulate matter, a soil sample will commonly include some moisture, and a sediment sample includes substantial fractions of both solids and water. Definitions for these single phase and whole sample concentrations are:

Individual Phase SOI Concentrations:

- $C_d \left[\dfrac{M_{sd}}{L_w^3} \right]$ = SOI concentration dissolved in liquid

- $C_p \left[\dfrac{M_{sp}}{M_p} \right]$ = SOI concentration adsorbed on solid particulates

Whole Sample SOI Concentrations:

- $C_w\left[\dfrac{M_{sd}+M_{sp}}{L_w^3}\right]$ = Whole water sample SOI concentration

- $C_{soil}\left[\dfrac{M_{sd}+M_{sp}}{M_p}\right]$ = Whole soil sample SOI concentration (dry weight)

- $C_{sed,d}\left[\dfrac{M_{sd}+M_{sp}}{M_p}\right]$ = Whole sediment sample SOI concentration (dry weight)

- $C_{sed,w}\left[\dfrac{M_{sd}+M_{sp}}{M_p+M_w}\right]$ = Whole sediment sample SOI concentration (wet weight)

The common laboratory practice of extracting the SOI from the whole sample (or aliquot of the whole sample) as delivered to the laboratory and then reporting the total mass extracted normalized by a selected feature of the sample will produce a whole sample concentration. Laboratories rarely, however report individual phase concentrations. The customary choices for normalizing the extracted mass, shown in the definitions above, are sample volume for water samples, sample dry weight for soil or sediment samples, either sample mass or sample volume for vapor samples, and whole sample weight for tissue samples. Laboratories sometimes report sediment sample concentrations in terms of total (wet) sample weight, but this is less common than reporting in terms of dry weight.

Use of media-tracking units helps to elucidate development of equations for computing values such as the dissolved and adsorbed fractions from the whole sample concentrations and for partitioning theory, as described below.

Dissolved and Adsorbed Fractions

The dissolved and adsorbed fractions of the SOI in an environmental sample are key values that help characterize the SOI behavior in the environment. Writing the adsorbed mass fraction, f_p, and dissolved mass fraction, f_d using media tracking units, as shown below, illustrates the development of some commonly used relationships for calculating f_p and f_d.

$$f_p\left[\frac{M_{sp}}{M_{sd}+M_{sp}}\right]=\frac{\rho_{bp}\left[\dfrac{M_p}{L_b^3}\right]L_b^3 C_p\left[\dfrac{M_{sp}}{M_p}\right]}{L_w^3 C_d\left[\dfrac{M_{sd}}{L_w^3}\right]+\rho_{bp}\left[\dfrac{M_p}{L_b^3}\right]L_b^3 C_p\left[\dfrac{M_{sp}}{M_p}\right]}$$

$$=\frac{\rho_{bp}\left[\dfrac{M_p}{L_b^3}\right]C_p\left[\dfrac{M_{sp}}{M_p}\right]}{\theta_v\left[\dfrac{L_w^3}{L_b^3}\right]C_d\left[\dfrac{M_{sd}}{L_w^3}\right]+\rho_{bp}\left[\dfrac{M_p}{L_b^3}\right]C_p\left[\dfrac{M_{sp}}{M_p}\right]}\quad(7)$$

$$f_d\left[\frac{M_{sd}}{M_{sd}+M_{sp}}\right]=\frac{L_w^3 C_d\left[\dfrac{M_{sd}}{L_w^3}\right]}{L_w^3 C_d\left[\dfrac{M_{sd}}{L_w^3}\right]+\rho_{bp}\left[\dfrac{M_p}{L_b^3}\right]L_b^3 C_p\left[\dfrac{M_{sp}}{M_p}\right]}$$

$$=\frac{\theta_v\left[\dfrac{L_w^3}{L_b^3}\right]C_d\left[\dfrac{M_{sd}}{L_w^3}\right]}{\theta_v\left[\dfrac{L_w^3}{L_b^3}\right]C_d\left[\dfrac{M_{sd}}{L_w^3}\right]+\rho_{bp}\left[\dfrac{M_p}{L_b^3}\right]C_p\left[\dfrac{M_{sp}}{M_p}\right]}\quad(8)$$

Water samples

Water samples may be defined as samples for which, $L_b^3\cong L_w^3$ or $\theta_v=1$. This property distinguishes water samples from samples with higher solids content, such as sediment and soil samples, for which this approximation does not hold. For such samples, concentrations are typically reported as total extractable SOI mass divided by the sample volume, under the assumption given above that the sample volume and water volume are essentially identical. Even when the particulate content of the sample does not appreciably impact the sample volume, however, the mass of SOI adsorbed onto the particulate matter in the sample may still be significant, depending on how strongly the SOI partitions to the solid phase. For water samples, the customary name for the particulates concentration, ρ_{bp}, is total suspended solids (TSS).

Since the reported SOI mass in a whole water sample will include both the mass dissolved in the water and the mass that was adsorbed on the particulate matter in the sample as collected, SOI concentrations in a whole water (unfiltered) sample, C_w, may be written as:

$$C_w\left[\frac{M_{sd}+M_{sp}}{L_b^3}\right]=C_d\left[\frac{M_{sd}}{L_w^3}\right]\theta_v\left[\frac{L_w^3}{L_b^3}\right]+C_p\left[\frac{M_{sp}}{M_p}\right]\rho_{bp}\left[\frac{M_p}{L_b^3}\right]\quad(9)$$

Using the conditions given above that characterize a water sample, Equation (9) may be written as:

$$C_w\left[\frac{M_{sd}+M_{sp}}{L_w^3}\right]=C_d\left[\frac{M_{sd}}{L_w^3}\right]+C_p\left[\frac{M_{sp}}{M_p}\right]\rho_{bp}\left[\frac{M_p}{L_w^3}\right]\quad(10)$$

Note that in using this equation, the specific units of ρ_{bp} and C_p must be selected or adjusted to produce the same units used to report C_w. SOI concentrations measured in filtered samples are commonly assumed to represent the dissolved concentration, C_d, though this is not strictly speaking true because particulates smaller than filter opening size remain in the sample.

C_p is rarely measured directly, but when both filtered and unfiltered sample concentrations are measured, C_p can be calculated from Equation (9) or (10) as:

$$C_p\left[\frac{M_{sp}}{M_p}\right]=\frac{C_w\left[\dfrac{M_{sd}+M_{sp}}{L_w^3}\right]-C_d\left[\dfrac{M_{sd}}{L_w^3}\right]}{\rho_{bp}\left[\dfrac{M_p}{L_w^3}\right]}\quad(11)$$

Soil or sediment samples

Concentrations in soil or sediment samples are typically reported as total SOI mass extractable from the solid and liquid phases of the sample divided by either the dry or wet weight of the sample. Soil and sediment samples are customarily normalized by the dry sample weight, though sediment samples are sometimes normalized by sample wet weight. The laboratory report will normally describe the basis on which sediment sample concentrations are reported.

Sediment samples typically contain an appreciable amount of water, though not enough for the approximation with regard to sample volume described above for water samples to apply. Note that some government agencies have maximum water content criteria for samples to be considered "sediment" samples. Samples with water content greater that the criteria value, but not high enough for the water sample approximation to apply, fall into an undefined sample category that could be termed slurries. The concepts presented here apply regardless of the actual sample water content. Since the SOI is extracted from both the solid and liquid phases of the sample, reported concentrations given in terms of dry weight, C_{soil} or C_{sed}, may be written as:

$$C_{soil}\left[\frac{M_{sd}+M_{sp}}{M_p}\right] = C_{sed,d}\left[\frac{M_{sd}+M_{sp}}{M_p}\right] = \frac{\frac{C_d}{\rho_w}\left[\frac{M_{sd}}{L_w^3}\frac{L_w^3}{M_w}\right]M_w + C_p\left[\frac{M_{sp}}{M_p}\right]M_p}{M_p} \quad (12)$$

Reported sediment concentrations reported in terms of total wet sample weight may be written as:

$$C_{sed,w}\left[\frac{M_{sd}+M_{sp}}{M_p+M_w}\right] = \frac{\frac{C_d}{\rho_w}\left[\frac{M_{sd}}{L_w^3}\frac{L_w^3}{M_w}\right]M_w + C_p\left[\frac{M_{sp}}{M_p}\right]M_p}{M_p+M_w} \quad (13)$$

When moisture content, $M_w = \theta_g\left[\frac{M_w}{M_p}\right]M_p$, data are available, Equations (12) and (13) may be written:

$$C_{soil}\left[\frac{M_{sd}+M_{sp}}{M_p}\right] = C_{sed,d}\left[\frac{M_{sd}+M_{sp}}{M_p}\right] = \frac{\theta_g\left[\frac{M_w}{M_p}\right]}{\rho_w\left[\frac{M_w}{L_w^3}\right]}C_d\left[\frac{M_{sd}}{L_w^3}\right] + C_p\left[\frac{M_{sp}}{M_p}\right] \quad (14)$$

and

$$C_{sed,w}\left[\frac{M_{sd}+M_{sp}}{M_p+M_w}\right] = \frac{\frac{\theta_g}{\rho_w}\left[\frac{M_w}{M_p}\frac{L_w^3}{M_w}\right]C_d\left[\frac{M_{sd}}{L_w^3}\right] + C_p\left[\frac{M_{sp}}{M_p}\right]}{1\left[\frac{M_p}{M_p}\right] + \theta_g\left[\frac{M_w}{M_p}\right]}$$

$$= \frac{C_{sed,d}\left[\frac{M_{sd}+M_{sp}}{M_p}\right]}{(1+\theta_g)\left[\frac{M_p+M_w}{M_p}\right]} \quad (15)$$

Some laboratories reports total solids content, TS, rather than moisture content, θ_g. TS and θ_g are related as follows:

$$\theta_g\left[\frac{M_w}{M_p}\right] = \frac{1\left[\frac{M_p+M_w}{M_p+M_w}\right] - TS\left[\frac{M_p}{M_p+M_w}\right]}{TS\left[\frac{M_p}{M_p+M_w}\right]} \quad (16)$$

and

$$TS\left[\frac{M_p}{M_p+M_w}\right] = \frac{1\left[\frac{M_p+M_w}{M_p+M_w}\right]}{1\left[\frac{M_p}{M_p}\right] + \theta_g\left[\frac{M_w}{M_p}\right]} \quad (17)$$

DISSOLVED/ADSORBED PHASE DISTRIBUTION COEFFICIENT

In an ideal world of environmental measurement and monitoring, we would directly measure the SOI concentrations associated with each media phase. In practice, that is often not feasible. Further, we often need to predict future behavior. To extend our ability to estimate media-specific concentrations beyond direct measurements and to forecast the future, the theory of sorption-desorption and the concept of a dissolved/adsorbed phase distribution coefficient is used (Karickhoff, Brown et al. 1979).

Consider a saturated control volume in which there are two environmental media, water and solid particulate matter. If a trace SOI is introduced, some will dissolve, some will adsorb to the solid matter (particulates), and there will be a constant interchange of sorption and desorption within the system. The kinetics of this process may be written in terms of either the adsorbed or dissolved state as (Thomann and Mueller 1987):

$$\frac{dC_p}{dt}\left[\frac{M_{sp}}{M_pT}\right] =$$
$$k_s\left[\frac{1}{T}\right]\frac{n}{\rho_{bp}}\left[\frac{L_w^3}{L_b^3}\frac{L_b^3}{M_p}\right]C_d\left[\frac{M_{sd}}{L_w^3}\right]\left[\frac{M_{sp}}{M_{sd}}\right] - k_d\left[\frac{1}{T}\right]C_p\left[\frac{M_{sp}}{M_p}\right] \quad (18)$$

$$\frac{n}{\rho_{bp}}\left[\frac{L_w^3}{L_b^3}\frac{L_b^3}{M_p}\right]\frac{dC_d}{dt}\left[\frac{M_{sd}}{L_w^3T}\right] =$$
$$-k_s\left[\frac{1}{T}\right]\frac{n}{\rho_{bp}}\left[\frac{L_w^3}{L_b^3}\frac{L_b^3}{M_p}\right]C_d\left[\frac{M_{sd}}{L_w^3}\right] + k_d\left[\frac{1}{T}\right]C_p\left[\frac{M_{sp}}{M_p}\right]\left[\frac{M_{sd}}{M_{sp}}\right] \quad (19)$$

where k_s, k_d = sorption and desorption rates.

Note that for this two-state system, the phase transition for mass leaving the dissolved state to become adsorbed is recognized through the unit conversion

$\left[\frac{M_{sp}}{M_{sd}}\right]$ applied to the dissolved phase concentration, C_d, in

Equation (18) and mass leaving the adsorbed state to become dissolved is recognized via the unit conversion

$\left[\dfrac{M_{sd}}{M_{sp}}\right]$ applied to the adsorbed phase concentration, C_p, in Equation (19).

When the adsorption and desorption rates in Equations (18) and (19) reach equilibrium, the time derivatives will equal zero, and from either Equation (18) or Equation (19) we may then define an equilibrium distribution coefficient, K_d:

$$\frac{C_p}{C_d}\left[\frac{M_{sp}/M_p}{M_{sd}/L_w^3}\right] = \frac{k_s}{k_d}\left[\frac{1/T}{1/T}\right]\frac{n}{\rho_{bp}}\left[\frac{L_w^3}{L_b^3}\frac{L_b^3}{M_p}\right]\left[\frac{M_{sp}}{M_{sd}}\right] =$$

$$K_d\left[\frac{M_{sp}/M_p}{M_{sd}/L_w^3}\right] \tag{20}$$

Note that the lower case k_s and k_d terms are rates, while the upper case K_d is an equilibrium constant. Also, the "d" in k_d stands for desorption, while the "d" in K_d stands for distribution. K_d may vary with SOI concentration or the sample solids content and is a function of both the media properties and the SOI properties. See Thomann and Mueller (1987) and Fetter (1999) for further discussion of K_d. The subsequent discussion in this paper is based on a linear Freundlich isotherm in which K_d is constant (Fetter 1999).

The units of K_d can cause confusion because they can be reported in terms of whatever specific units were used for the dissolved and particulate concentrations. Examples might include mg/L or mg/L for C_d and mg/kg or mg/kg for C_p. This does not cause problem as long as K_d is applied to systems in which the same units are used or the units are converted. For example, it is sometime convenient to convert the dissolved concentration to units of mass per mass, making K_d effectively dimensionless.

For many organics, K_d values have been shown to be strongly correlated with the presence of organic carbon associated with the solid fraction (particulates). This observation has been used to motivate development of partitioning data in terms of K_d normalized by the organic carbon content of the particulates. A customary assumption when using this approach is that the SOI mass associated with the particulate matter, M_{sp}, is equal to the SOI mass associated with the organic carbon, M_{oc}. The phase-tracking units for this concept can be written as:

$$K_{oc}\left[\frac{M_{sp}/M_{oc}}{M_{sd}/L_w^3}\right] = \frac{K_d\left[\dfrac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]}{f_{oc}\left[M_{oc}/M_p\right]} \tag{21}$$

where f_{oc} = organic carbon mass/particulate mass and K_{oc} = distribution coefficient in terms of organic carbon mass.

The partition coefficient concept, as written in Equation (20) may be used to simplify Equations (9) and (14) as follows. For water samples:

$$C_w\left[\frac{M_{sd}+M_{sp}}{L_w^3}\right] = C_d\left[\frac{M_{sd}}{L_w^3}\right]\left(1\left[\frac{M_{sd}}{M_{sd}}\right] + K_d\left[\frac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]\rho_{bp}\left[\frac{M_p}{L_w^3}\right]\right) \tag{22}$$

or

$$C_w\left[\frac{M_{sd}+M_{sp}}{L_w^3}\right] = C_p\left[\frac{M_{sp}}{M_p}\right]\left(\frac{1\left[\dfrac{M_{sd}}{M_{sd}}\right]}{K_d\left[\dfrac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]} + \rho_{bp}\left[\frac{M_p}{L_w^3}\right]\right)$$

$$= C_p\left[\frac{M_{sp}}{M_p}\right]\left(\frac{1\left[\dfrac{M_{sd}}{M_{sd}}\right] + K_d\left[\dfrac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]\rho_{bp}\left[\dfrac{M_p}{L_w^3}\right]}{K_d\left[\dfrac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]}\right) \tag{23}$$

where we have made use of the approximation for water samples that, $L_b^3 \cong L_w^3$.

For soil or sediment samples:

$$C_{soil}\left[\frac{M_{sd}+M_{sp}}{M_p}\right] = C_{sed.d}\left[\frac{M_{sd}+M_{sp}}{M_p}\right] =$$

$$C_d\left[\frac{M_{sd}}{L_w^3}\right]\left(K_d\left[\frac{M_{sp}/M_p}{M_{sd}/L_w^3}\right] + \frac{\theta_g}{\rho_w}\left[\frac{M_w}{M_p}\frac{L_w^3}{M_w}\right]\right) \tag{24}$$

or

$$C_{soil}\left[\frac{M_{sd}+M_{sp}}{M_p}\right] = C_{sed.d}\left[\frac{M_{sd}+M_{sp}}{M_p}\right] =$$

$$C_p\left[\frac{M_{sp}}{M_p}\right]\left(1\left[\frac{M_{sp}}{M_{sp}}\right] + \frac{\dfrac{\theta_g}{\rho_w}\left[\dfrac{M_w}{M_p}\dfrac{L_w^3}{M_w}\right]}{K_d\left[\dfrac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]}\right) \tag{25}$$

Equations (7) and (8) for mass fractions presented earlier can also be simplified, as follows:

$$f_p\left[\frac{M_{sp}}{M_{sd}+M_{sp}}\right] = \frac{\rho_{bp}\left[\dfrac{M_p}{L_b^3}\right]K_d\left[\dfrac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]}{\theta_r\left[\dfrac{L_w^3}{L_b^3}\right] + \rho_{bp}\left[\dfrac{M_p}{L_b^3}\right]K_d\left[\dfrac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]} =$$

$$\frac{K_d\left[\dfrac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]}{\dfrac{\theta_g}{\rho_w}\left[\dfrac{M_w}{M_p}\dfrac{L_w^3}{M_w}\right] + K_d\left[\dfrac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]} \tag{26}$$

and

$$f_d\left[\frac{M_{sd}}{M_{sd}+M_{sp}}\right] = \frac{\theta_r\left[\dfrac{L_w^3}{L_b^3}\right]}{\theta_r\left[\dfrac{L_w^3}{L_b^3}\right] + \rho_{bp}\left[\dfrac{M_p}{L_b^3}\right]K_d\left[\dfrac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]}$$

$$= \frac{\dfrac{\theta_g}{\rho_w}\left[\dfrac{M_w}{M_p}\dfrac{L_w^3}{M_w}\right]}{\dfrac{\theta_g}{\rho_w}\left[\dfrac{M_w}{M_p}\dfrac{L_w^3}{M_w}\right] + K_d\left[\dfrac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]} \tag{27}$$

Note that, as always, consistent specific units must be used.

SOLUTE TRANSPORT EQUATION DEVELOPMENT

These notational concepts can also be useful for understanding the development of equations that describe transport and fate of dissolved substances in water. Development of the advection dispersion equation for solute transport in saturated porous media is discussed below as an example. This development follows that presented in many standard references (Ogata 1970; Bear 1979; Fetter 1999), but explicitly shows the phase-tracking units, as described above.

Considering a representative elementary volume (REV) written in terms of Cartesian coordinates, we may write the mass balance for solute transport in fundamental terms of input, output, and transformation within the REV as:

$$\dot{M}\left[\frac{M_s}{T}\right] \equiv \frac{dM}{dt}\left[\frac{M_s}{T}\right] =$$
$$F_{s,in}\left[\frac{M_s}{T}\right] - F_{s,out}\left[\frac{M_s}{T}\right] + G\left[\frac{M_s}{L_b^3 T}\right] dxdydz\left[L_b^3\right] \quad (28)$$

where: M = dissolved SOI mass, $F_{s,in}$ and $F_{s,out}$ = solute mass transport per unit time into and out of the REV, G = solute mass generation or decay per unit time and volume in the REV, and dx, dy, dz = differential lengths of the REV in the x, y, and z axis directions.

Again considering an REV, a general expression for both dissolved and adsorbed SOI mass rate of change within the REV may be written as:

$$\dot{M}\left[\frac{M_s}{T}\right] = \begin{pmatrix} \theta_v\left[\frac{L_w^3}{L_b^3}\right]\frac{\partial C_d}{\partial t}\left[\frac{M_{sd}}{L_w^3 T}\right] + \\ \rho_{bp}\left[\frac{M_p}{L_b^3}\right]\frac{\partial C_p}{\partial t}\left[\frac{M_{sp}}{M_p T}\right] \end{pmatrix} dxdydz\left[L_b^3\right] \quad (29)$$

Combining Equations (28) and (29), and incorporating K_d, produces:

$$F_{s,in}\left[\frac{M_s}{T}\right] - F_{s,out}\left[\frac{M_s}{T}\right] + G\left[\frac{M_s}{L_b^3 T}\right] dxdydz\left[L_b^3\right] =$$
$$\left(\theta_v\left[\frac{L_w^3}{L_b^3}\right] + \rho_{bp}\left[\frac{M_p}{L_b^3}\right]K_d\left[\frac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]\right)\frac{\partial C_d}{\partial t}\left[\frac{M_{sd}}{L_w^3 T}\right] dxdydz\left[L_b^3\right] \quad (30)$$

Derivation of a useful equation for solute transport then focuses on developing usable expressions for the terms of the left hand side of Equation (30). It should be noted that the units for the differential terms should be read as the differential changes in the specified units.

Flux (Transport Rate) Terms

The transport rate is frequently written as a specific (per unit area) transport rate multiplied by the relevant cross-sectional area and is normally viewed as dealing only with dissolved phase SOI (effectively lumping transport associated with colloidal particles that can travel

with the water through the stationary solid matrix in with the dissolved fraction):

$$F\left[\frac{M_{sd}}{T}\right] = J\left[\frac{M_{sd}}{TL_b^2}\right]A\left[L_b^2\right] \quad (31)$$

The specific flux rate is composed of two components, advective and dispersive transport. An expression for advective flux may be written as follows (Fetter 1999):

$$J_A\left[\frac{M_{sd}}{TL_b^2}\right] = C_d\left[\frac{M_{sd}}{L_w^3}\right]J_w\left[\frac{L_w^3}{TL_b^2}\right] =$$
$$C_d\left[\frac{M_{sd}}{L_w^3}\right]\theta_v\left[\frac{L_w^3}{L_b^3}\right]U_w\left[\frac{L_b}{T}\right] \quad (32)$$

where: J_A = solute advective transport rate per unit area, C_d = solute concentration in water, J_w = water flux rate, and U_w = average linear ground water velocity. The mass and water flux rates are normalized by bulk area, while the concentration is normalized by water volume.

The average linear ground water velocity is typically estimated using Darcy's Law, for which tracking of environmental media phase related units can also provide some beneficial insights. Water flow rate per unit area may be written using Darcy's Law and media phase units as:

$$q\left[\frac{L_w^3}{L_b^2 T}\right] = \frac{Q\left[L_w^3/T\right]}{A\left[L_b^2\right]} = -K\left[\frac{L_w^3}{L_b^2 T}\right]i\left[\frac{L_b}{L_b}\right] \quad (33)$$

where: q = specific discharge (volumetric flow rate per unit area), Q = volumetric ground water flow rate, A = cross-sectional area transverse to flow direction, K = hydraulic conductivity, and i = hydraulic gradient.

In the absence of phase-tracking units, the units for q and K are both customarily written as L/T, which both appear to be linear velocities, and appear to be identical to the units for the actual average linear velocity. This custom creates confusion regarding the true meaning of q and leads to explanations in essentially all ground water textbooks about why q is not really a velocity and the assignment of special names, such as Darcy velocity, to help avoid such confusion. Using phase-tracking units clarifies the differences between these two terms. For example, the average linear ground water velocity computation follows naturally from the units when written as:

$$U_w\left[\frac{L_b}{T}\right] = \frac{q\left[L_w^3/L_b^2 T\right]}{\theta_v\left[L_w^3/L_b^3\right]} \quad (34)$$

Dispersive flux follows Fick's first law, which may be written for open water as:

$$J_D\left[\frac{M_{sd}}{L_b^2 T}\right] = -D\left[\frac{L_b^2}{T}\right]\frac{dC_d}{dx}\left[\frac{M_{sd}}{L_w^3 L_b}\right] \quad (35)$$

where: J_D = dispersive solute flux rate per unit area and D = the open water dispersion coefficient (includes molecular diffusion and mechanical dispersion components). In open water, the assumption that bulk volume, L_b^3, and water volume, L_w^3, are identical usually applies. For application to porous media, however, the bulk and water volumes are not identical. Introducing the

media moisture content, we write dispersive flux in a porous media as:

$$J_D\left[\frac{M_{sd}}{L_b^2 T}\right] = -\theta_v\left[\frac{L_w^3}{L_b^3}\right]D^*\left[\frac{L_b^2}{T}\right]\frac{dC_d}{dx}\left[\frac{M_{sd}}{L_w^3 L_b}\right] \quad (36)$$

where: D^* = the dispersion coefficient adjusted for flow path tortuosity in the porous media.

Introducing moisture content into the dispersive flux equation this way is mathematically equivalent to the more commonly used rationale relating porosity to reduction in the cross-sectional area available for flow, but has the advantage of providing a consistent tracking for units on all terms, since porosity is commonly considered to be dimensionless.

In Cartesian coordinates, the unit area flux terms may be used to write the fluxes into and out of the REV as:

$$(37)$$

$$(F_{in} - F_{out})\left[\frac{M_{sd}}{T}\right] = -\left(\frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}\right)\left[\frac{M_{sd}}{L_b^2 T L_b}\right]dxdydz\left[L_b^3\right]$$

where
$$J = J_A + J_D$$

Source or Decay Term

First order decay is among the most commonly used representations for G in Equation (28) and may be written as:

$$G\left[\frac{M_s}{T L_b^3}\right] = -k\left[\frac{1}{T}\right]\left(\theta_v\left[\frac{L_w^3}{L_b^3}\right]C_d\left[\frac{M_{sd}}{L_w^3}\right] + \rho_{bp}\left[\frac{M_p}{L_b^3}\right]C_p\left[\frac{M_{sp}}{M_p}\right]\right) \quad (38)$$

where k is the first order decay rate constant. Introducing the distribution coefficient K_d into Equation (38) yields:

$$G\left[\frac{M_s}{T L_b^3}\right] = -k\left[\frac{1}{T}\right]\left(\theta_v\left[\frac{L_w^3}{L_b^3}\right] + \rho_{bp}\left[\frac{M_p}{L_b^3}\right]K_d\left[\frac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]\right)C_d\left[\frac{M_{sd}}{L_w^3}\right]$$

$$(39)$$

These expressions use the volumetric moisture content, which for saturated conditions is equal to the porosity. Using the phase-tracking units clarifies the common, though not always clearly understood, assumption that the dissolved and adsorbed SOI decay at the same rate.

Solute Transport Equation

Substituting Equations (37) and (39) into Equation (30) and dividing through by θ_v yields:

$$-\frac{1}{\theta_v}\left[\frac{L_b^3}{L_w^3}\right]\left(\frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}\right)\left[\frac{M_{sd}}{L_b^2 T L_b}\right] -$$

$$k\left[\frac{1}{T}\right]\left(\frac{\theta_v + \rho_{bp}K_d}{\theta_v}\right)\left[\frac{M_{sd} + M_{sp}}{M_{sd}}\right]C_d\left[\frac{M_{sd}}{L_w^3}\right] \quad (40)$$

$$= \left(\frac{\theta_v + \rho_{bp}K_d}{\theta_v}\right)\left[\frac{M_{sd} + M_{sp}}{M_{sd}}\right]\frac{\partial C_d}{\partial t}\left[\frac{M_{sd}}{L_w^3 T}\right]$$

Evaluation of the units for each term shows that the transport term deals with only dissolved phase SOI, while the decay term and total mass rate of change term (right hand side of the equation) deal with both dissolved and adsorbed phases of the SOI. This is consistent with the assumptions made during the equation development.

At this point in the derivation, a new term R, called the retardation coefficient, is commonly defined:

$$R\left[\frac{M_{sd} + M_{sp}}{M_{sd}}\right] = 1\left[\frac{M_{sd}}{M_{sd}}\right] + \frac{\rho_{bp}\left[M_p/L_b^3\right]K_d\left[\frac{M_{sp}/M_p}{M_{sd}/L_w^3}\right]}{\theta_v\left[L_w^3/L_b^3\right]} \quad (41)$$

Equation (40) may then be written as:

$$-\frac{1}{\theta_v}\left[\frac{L_b^3}{L_w^3}\right]\left(\frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}\right)\left[\frac{M_{sd}}{L_b^2 T L_b}\right] -$$

$$k\left[\frac{1}{T}\right]R\left[\frac{M_{sd} + M_{sp}}{M_{sd}}\right]C_d\left[\frac{M_{sd}}{L_w^3}\right] \quad (42)$$

$$= R\left[\frac{M_{sd} + M_{sp}}{M_{sd}}\right]\frac{\partial C_d}{\partial t}\left[\frac{M_{sd}}{L_w^3 T}\right]$$

In both textbooks and classrooms, the retardation coefficient R is all too commonly presented as simply the dimensionless ratio between the average linear velocities of the ground water and the SOI mass, with a value given by Equation (41). Equation (41), however, provides little, if any, insight into the fundamental physical/chemical basis for the phenomenon of solute mass retardation. If the specific media with which the SOI is associated are tracked, as shown in Equation (41), R can be seen to have dimensions related to the media phases and further can be seen to be the ratio between the total mass and the dissolved mass. Both of these concepts provide some insight into the physical/chemical reason for the retardation of the solute mass transport rate compared to the water transport rate. Additionally, comparison with Equation (27) shows that there was no need to define a new term R, as it is equal to the reciprocal of the more fundamental term, the dissolved mass fraction, f_d.

Considering now a flow field oriented with the x-axis, we may simplify Equation (42) by considering advection only in the longitudinal direction (along the flow path) and dispersion in the longitudinal and transverse directions. Substituting the expressions for flux rates from Equations (32) and (36) and into Equation (42) produces:

$$D_L\left[\frac{L_b^2}{T}\right]\frac{\partial^2 C_d}{\partial x^2}\left[\frac{M_{sd}}{L_w^3 L_b^2}\right] + D_T\left[\frac{L_b^2}{T}\right]\frac{\partial^2 C_d}{\partial y^2}\left[\frac{M_{sd}}{L_w^3 L_b^2}\right] - U_{wx}\left[\frac{L_b}{T}\right]\frac{\partial C_d}{\partial x}\left[\frac{M_{sd}}{L_w^3}\right]$$

$$-k\left[\frac{1}{T}\right]R\left[\frac{M_{sd} + M_{sp}}{M_{sd}}\right]C_d\left[\frac{M_{sd}}{L_w^3}\right] = R\left[\frac{M_{sd} + M_{sp}}{M_{sd}}\right]\frac{\partial C_d}{\partial t}\left[\frac{M_{sd}}{L_w^3 T}\right] \quad (43)$$

Dividing through by R yields:

$$D_L'\left[\frac{L_b^2}{T}\frac{M_{sd}}{M_{sd} + M_{sp}}\right]\frac{\partial^2 C_d}{\partial x^2}\left[\frac{M_{sd}}{L_w^3 L_b^2}\right] +$$

$$D_T'\left[\frac{L_b^2}{T}\frac{M_{sd}}{M_{sd} + M_{sp}}\right]\frac{\partial^2 C_d}{\partial y^2}\left[\frac{M_{sd}}{L_w^3 L_b^2}\right] \quad (44)$$

$$-U_x'\left[\frac{L_b}{T}\frac{M_{sd}}{M_{sd} + M_{sp}}\right]\frac{\partial C_d}{\partial x}\left[\frac{M_{sd}}{L_w^3}\right] - k\left[\frac{1}{T}\right]C_d\left[\frac{M_{sd}}{L_w^3}\right] = \frac{\partial C_d}{\partial t}\left[\frac{M_{sd}}{L_w^3 T}\right]$$

where: $U' = \dfrac{U}{R}$ and $D' = \dfrac{D^*}{R}$.

Using f_d instead of R, the term definitions in Equation (44) change to $D' = f_d D$ and $U' = f_d U$. Using these terms aids intuitive understanding of the impact of partitioning, since the key parameters for dissolved solute transport are adjusted by the dissolved mass fraction, rather than a somewhat abstract retardation coefficient. An additional educational advantage of tracking units this way is that students are able to more easily grasp the concept that while the terms in Equations (40) through (44) appear to address only dissolved mass, they actually address both dissolved and adsorbed mass.

CONCLUSIONS

Tracking units for dissolved SOI fate and transport evaluation in terms of not only the fundamental unit characteristics, but also the environmental media with which the SOI is associated, while cumbersome, provides substantial value when the concepts and equation derivations are being learned. Experienced practitioners understand these units intuitively without writing them out explicitly, but writing the units explicitly can assist the learning process for others. The proposed notation system provides a consistent framework for tracking the environmental media phases when evaluating data and developing, evaluating, and using associated equations and coefficients.

Acknowledgments

The methods presented here benefited from being tested on numerous students, for whose patience in the early stages of development I am grateful, and the manuscript benefited from careful reading by and insightful comments from two anonymous reviewers.

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