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This column presents news, information and summaries of research related to modeling environmental contaminants, including fate, transport and human and ecosystem exposure. Contributions or suggestions for articles are always welcome! Contact the editor for more information or to submit an article or news item.

The Importance of Chemical Mass-transport Coefficients in Environmental and Geo-chemical Models

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Introduction

Thermodynamic principles establish the potential for chemicals to move from place-to-place within a single environmental medium or between phases and across the interface connecting two media compartments. In the environmental and geo-chemical fields these potentials are conventionally quantified by so-called phase partition coefficients. Alternatively, the chemical fugacity difference between phases provides the same quantitative information. However, chemical movement can occur only if a diffusive or other mass transport process is also operative. In the geo-chemical and engineering transport sciences these are conventionally termed mass-transport velocities or more commonly mass-transfer coefficients (MTCs).

Simply put, chemical movement about the Earth occurs by three transport processes; they are termed advective, dispersive and interphase. Advective transport moves chemical mass by virtue of the bulk motion flow (i.e., speed) of the media. It is enhanced by turbulent dispersion, a diffusion-like process, which is superimposed on the flowing media and it also moves chemical mass perpendicular across the flow direction. Inter-phase transport processes move chemical mass across the various media interfaces and associated boundary layers that separate them such as air, water, soil, etc. compartments. Except for the advective and turbulent dispersion, both the thermodynamic potential and a transport mechanism must be present for chemical movement to occur between adjacent compartments when they are composed of different phases of matter.

The presence of anthropogenic substances in all the environmental media on the surface of the Earth is evidence that these transport processes are operative. The observed high concentration in some media indicates that both partitioning and transport are working efficiently and in unison.

The purpose of this essay is to stress the importance of inter-phase processes which are quantified by MTCs. Three lines of evidence illustrating the importance of these parameters in regulating chemical movement are presented. First, the theoretical basis for chemical mobility is presented using the flux concept. This is followed by an example illustrating the immense range of the MTCs. The range is typical of those encountered in environmental and geo-chemical modeling contexts. The third is a serendipitous finding which resulted from round-robin testing of Mackay-type multimedia models.

Flux - The Expression for Chemical Mobility

The elegant, simple, practical and theoretically sound means of capturing chemical mobility is through the concept of the chemical flux. The flux equation has its roots in Ficks' first law of diffusion. It is a mathematical expression for the chemical mass movement rate between media in g/s normalized to a unit of surface area, m^2, of the interface plane connecting the two adjoining media compartments, i.e., $g/m^{2}\cdot s$. A specific example is used to relate it to chemical mobility and the MTC.

For example, the equation for the flux across the interface with the chemical pathway originating in the sediment compartment and moving to the water column above is:

$$N = Ktc\ (\ Cs/Kd - Cw\ ) \qquad \text{Eqn. (1)}$$

Where N is the flux in SI units of $g/m^{2}\cdot s$, Ktc is the MTC in m/s, Cs is the chemical loading on the sediment solids in g/kg, Kd is the sediment-to-water chemical partition coefficient in m^3/kg and Cw is the concentration is the water column in units of g/m^3.

This concept is applied to the boundary layer regions (i.e., films) that exist on either side of the interface plane separating the two compartments or phases. Decades of research and experimental evidence both in the field and laboratory support the theoretical form of Eqn. 1. It is a chemical quantity that has been measured in the laboratory and the field. In addition it has a well established role in chemodynamic modeling (Mackay, 1991; Thibodeaux, 1996 and DiToro, 2001).

Mathematically and physically it is a vector quantity. It has a numerical value as well as an explicit direction of chemical movement. In this case it is positive (+) when directed from the bed and negative (-) when directed into the bed. In addition the flux equation is ideally suited for use in the mass balance which is more correctly termed the Lavoisier, chemical species mass balance. All models that seek to mathematically mimic natural chemodynamic processes use the mass balance in their derivation.

In summary, the importance of the MTC in regulating chemical mobility is established theoretically through the flux concept. Its simple algebraic form illustrates transparently the unison roles of the MTC and chemical partitioning. Clearly, flux and therefore mobility increase with an increase in the numerical value of the MTC and decrease with an increase in the partition coefficient. Various forms of the flux equation similar to Eqn. 1 also apply to chemical movement across the air-water interface as well as the air-water, air-snow/ice, plant-air, soil-air, soil-plant root, biota-water, urban surfaces-air, etc. Often the group (Cs/Kd - Cw) is termed the diffusive "driving force" because when it is zero there is no net flux. It is analogous to the temperature difference that drives heat transfer.

The Numerical Range of MTCs – An Example

The steady-state chemodynamics of aquatic bed-sediment pollutant transport to the overlying water column is used to illustrate the numerical range MTCs enjoy at this interface. In addition the coefficients are the subject of considerable interest worldwide. Numerous bed-sediment locales in streams, lakes, estuaries, ports and the near shore marine aquatic environments contain various metal and organic pollutants and are being considered for remediation. Up-dated versions of traditional water quality models (Connolly et al, 2000) are being used to assess the rates of chemical release and ecosystem exposure as part of the planned clean-up efforts. Key to this effort is assuring that the models employ the appropriate and site-specific MTCs for quantifying the release processes (Erickson, et al. 2005). Earlier reviews of processes and MTCs (Reible et al. 1991 and Valsaraj, et al. 1997) were up-dated recently and form the basis of this section (Thibodeaux, 2005).

The chemical flux concept is used to assess the numerical values of the MTCs representing transport at a riverine site near and entering the Great Lakes, USA. Site-specific chemical and physical data and local environmental conditions were used to make quantitative estimates of MTCs based on available algorithms and theoretical approaches (Thibodeaux, 1996). Individual process coefficients were evaluated using the PCBs at the site in addition to benzene as the representative chemicals.

A variation of Eqn. 1 was used to create a "graphic" to present and aid in visualizing the flux, the magnitudes of the MTCs and the partition coefficients simultaneously. In this example it is reasonable to assume Cw is very small or negligible (i.e., equal zero) in flowing streams so that Eqn. 1 can be simplified to:

$$N/Cs = Ktc/Kd. \qquad \text{Eqn. (2)}$$

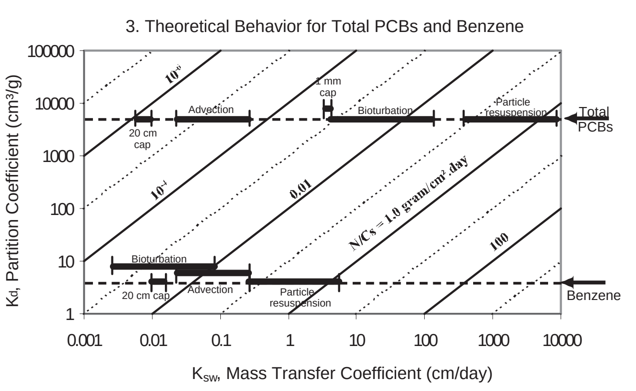
The left side of Eqn. 2 is the bed solid chemical loading normalized flux and Figure 1 is its graphical representation. It is easily constructed by arbitrarily choosing both Ktc and Kd values and using the numerical ratio for the N/Cs values which are shown plotted as the diagonal lines. A key feature of this graphic is that it allows a simultaneous presentation of the ranges of Ktc and Kd illustrating how they operate in unison to establish the chemical mobility or flux from the bed. It is clear from this graphic that the flux decreases from right to left and bottom to top, as the MTC decreases and the partitioning increases.

The numerical ranges of the MTCs for six basic mass-transport processes were determined. Realistic variations on these yielded a total of eleven. These are summarized in Table 1 and also appear graphed in Figure 1. Processes 1 and 2 are for the water side and the others are for the porous bed surface layers. Numbers 3 through 5 represent chemical movement in the water-filled pore spaces. The last one represents sediment particle and pore-water movement by macrofauna. The Kds for this site ranged from 5–8 cm^3/g for benzene and 7000–8000 for total PCBs. In Fig. 1 the ranges of the MTCs are organized in categories to simplify the presentation and the very low values for benzene were omitted. The overall ranges of the MTCs were 0.0021–8600 cm/hr for the PCBs and $1.4E^{-6}$–450 cm/hr for benzene. These ranges of MTCs cover 6–8 Log scales! The typical range of Kds is large as well with reported chemical specific values from $1–1E^6$ cm^3/g.

Table 1 Estimated MTCs (cm/d) at Sediment–Water Interface

Process	Total PCBs	Benzene
1) Particle re-suspension	400–8600	0.26–5.6
2) Benthic boundary layer	13.0–320	18.0–450
3) Molecular diffusion (solutes)		
thin layer (1mm.)[a]	3.5–4.1	5.7–6.7
bio-available layer (5cm)	0.038–0.071	0.062–0.12
In-situ cap (20cm)	0.0059–0.0094	0.015–0.0097
4) Brownian (colloid) diffusion (5cm)	0.0049–0.0092	$3.2E^{-6}$–$6.0E^{-6}$
5) Pore-water advection		
solutes	0.023–0.26	0.023–0.26
colloids	0.0088–0.010	$5.8E^{-6}$–$6.5E^{-5}$
6) Bio-diffusion (5cm)		
particles	4.1–127	0.0027–0.083
pore water solutes	0.0054–0.17	$3.5E^{-6}$–$1.1E^{-4}$
pore water colloids	0.0021–0.064	$1.4E^{-6}$–$4.2E^{-5}$

[a] diffusion distance



The Round-Robin Testing of Four Multimedia Models

A noteworthy point about this part of the essay in illustrating the importance of MTCs is that it came about as a result of pure serendipity.

Under the auspices of SETAC two workshops were held in 1994 to conduct a systematic, international evaluation of the strength, limitations precision, and accuracy of multi-media fate models in current use to address the specific needs of regulators and scientists in various assessment activities (Cowen, et al., 1995). Four models were included in the evaluations: a USA model, a Canadian model, one representing the EU member states and one model from the Netherlands. One objective was to evaluate the commonalities and differences. As part of the evaluation process a "round-robin" exercise using the four models was designed to explore model precision.

The respective model groups were given similar data and information as inputs. The Information given included: a) physical-chemical properties and degradation half-lives for nine chemicals, b) emission rates and input scenarios for the air, water and soil compartments and c) multi-media landscape dimension and properties. Inter-media transport parameters such as MTCs were not specified, but were left to the modelers to select.

This omission specifying identical MTCs for all models provided the serendipitous element of the testing that illustrated their importance.

A comparison of the compiled numerical results of computations for the steady-state mode of simulation for each model revealed some unexpected large differences. The most important differences arose because inter-media transport data were selected independently by each modeling group, and this resulted in large discrepancies for the chemicals with extreme physical-chemical properties. Although similar compartmental mass distributions were predicted for most chemicals there were significant differences in the predicted absolute amounts and therefore concentrations in the various compartments. For air the agreement was judged satisfactory however, there were two chemicals where the model predicted maximum-to-minimum mass ratios (max factor ratio) were approximately 80; these were well beyond the normal 1–3 range. For water the max factor ratios for all chemicals ranged from 2–30. For sediment it was 9–60 and for soil it was 1–10 excluding a 110 outlier. The authors note "It is clear from these results that to be reliable, models must have fairly accurate expression and parameters for describing inter-media transport."

The round-robin exercise was subsequently repeated at the second workshop but with only two chemicals. The inconsistencies in the mass transfer and other parameters were accounted for and it was found that the four models could give essentially the same results within a few percent of the amounts in each compartment at steady state. However, the authors emphasized that "…the models produce essentially the same results only if all relevant mechanisms and parameters are set to the same value." It was recommended that lists of values of MTCs will eliminate these differences.

This study of four multimedia models with round-robin numerical comparison of results appears to be the only comprehensive study documenting the importance of accurately specifying the MTCs for achieving model output precision. For the purposes of this essay it highlights a common misconception about the MTC model parameter and brings into focus the still much adhered to conventional wisdom that partition coefficients are the only parameters key to regulating chemical mobility. So ingrained was this notion in the minds of the workshop attendees that specifying the MTCs was completely overlooked. In the end it proved to be a very fortunate happening because it highlighted their importance. In addition the outcome encouraged the authors of this essay to make plans filling the literature gap on values for MTCs.

Closure and the way forward

This essay is designed to illustrate the importance of MTCs in environmental and geo-chemical models used in tracking the movements of natural and anthropogenic chemicals throughout the Earth's natural media. First it was established that chemical mobility has a theoretical basis in the flux concept where the MTC appears as a key parameter in the rate equation. Transport across the sediment-water interface was used as an example to demonstrate that a wide numerical range of MTCs is possible. Finally the serendipitous outcome of a SETAC sponsored international workshop showed that modelers are not free to arbitrarily select numerical values of MTCs with the expectation that the various models used will have of any degree of numerical precision on calculated concentrations, etc. These findings suggest that the appropriate fluxes or transport rates for these models need to be based on the best knowledge of the controlling transport mechanisms and a consistent, theory-based means for the accurate estimation of the inter-media transport coefficients.

The research needs section of the workshop final report noted: "There has been a fair amount of laboratory research and field simulation work devoted to measuring and correlating the inter-media transfer coefficients. These data should be compiled, evaluated, and condensed for use in describing the various environmental types or units. A research/study project should be undertaken to recommend average numerical values of transport coefficients, including temperature dependence, with ranges, for incorporation into models."(SETAC,1995).

The expectations of and dependence on environmental chemodynamic models for various predictive tasks involving chemicals in the medias will undoubtedly enjoy a bright future. Such models are used as investigative tools to accompany and extend field measurements aimed at the scientific understanding of chemical behavior in nature. On the applied or engineering side a range of model types from complex multimedia ones to the vignette variety will be increasingly used in making concentration-time of exposure prediction for chemical risk assessments. In an attempt to fulfill a part of this need for multiple users the authors are currently organizing an international team of experts to produce a handbook on the subject of environmental MTCs. The plan is well along. Approximately twenty five chapters have been commissioned and about 40 contributors are preparing drafts. The goal is to have the book completed and on the shelves in early 2008.

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