



Interactions between dissolved organic matter and organic contaminants

J Tronczynski*

« L'interaction est irréductible et indispensable pour comprendre le comportement du système. »

I Prigogine

The interactions between dissolved organic matter and organic contaminants affect their solution speciation and their distribution between the aqueous and solid phases. This partitioning governs the transport and influences the transformations and toxicity of contaminants. Thus, detailed understanding of fate and effects of contaminant in aquatic ecosystems is dependent upon the knowledge of contaminant speciation in these environments.

The distribution of species in solution that results from chemical or physical interactions between solvent(s) and solutes is generally referred to as chemical speciation [1]. In practice, in natural aquatic environments, it is not only interaction between solvent(s) and solutes that should be considered, but also interactions between sorbent (*ie* suspended particles and sediments), solvents (*ie* salt and freshwater) and solutes (*ie* elements or compounds). Speciation is usually determined independently for each environmental compartment. However, it should be borne in mind that interactions are interdependent and that for their full understanding a fundamental description of physical and chemical properties of sorbent, solute and solvent is needed [2].

First, this implies that interactions between dissolved organic matter (DOM) and contaminants in natural systems not only affect the solution speciation of the solutes, but can also influence distribution of contaminants between aqueous and solid phases present. Second, for description in fundamental terms of the interactions underlying mechanisms, physical and chemical properties of dissolved organic matter in seawater or freshwater and contaminants should be known. Heterogeneous nature itself, and spatio-temporal variability of dissolved

organic matter concentration and composition, preclude a summary of its possible intermolecular interactions with contaminants that might be reasonably presented here. Hence, only dominant or most obvious interactions are presented and most of them have observable environmental effects in natural systems and were recognized by field data and sometimes supported by experimental data in relatively simple well-controlled laboratory systems.

■ Hydrophobic organic contaminants and dissolved organic matter

• Limitations and assumptions

The present discussion is limited almost exclusively to non-ionic persistent hydrophobic organic compounds (HOC), that are often important environmental contaminants such as PCBs and PAHs. The distinction between "truly" dissolved and colloidal phase of organic matter present in natural aquatic systems is of primary importance with respect to the interactions with organic contaminants and of environmental implications involved. This is because, such a phase has the physico-chemical properties of a solid but is generally analyzed with, and is transported like, the soluble fraction. It is recognized that the hydrophobic effect (expulsion) is the dominant interaction of DOM and HOC in a natural situation. It assumes that solute-solvent interactions are not specific

and that involved energies are weak [3].

• Truly dissolved organic matter and HOC

The interaction for truly dissolved organic matter in saltwater or freshwater with dissolved contaminants (solutes) can be viewed as their distribution between the two non-miscible solvents. The thermodynamic description of this phenomena in aquatic environments is the distribution of solute between two naturally occurring solvents (water and its DOM), ideally obeying partition law. This law is defined simply as the ratio between the activities of solute in the bulk phases in equilibrium [4]. The mathematical expression for this partition is the thermodynamic equilibrium constant, or partition coefficient, denoted as $K_p = a_1/a_2 = c_1/c_2 K'_p$ where a is activity and c is the concentration of a solute in respective solvents, and K_p , K'_p are partition coefficient and apparent partition coefficient, respectively. This equation only predicts linear partitioning as long as the activity coefficients remain relatively constant (*ie* $a_1/a_2 = \text{constant}$). This assumes no significant solute-solvent interactions and that they are not specific and weak [4]. It is recognized that these assumptions tend to be most valid for persistent nonpolar hydrophobic organic compounds [5, 6].

In other words, in this model the uptake of HOC by DOM can be viewed as a process of their dissolution into an amorphous organic matter, driven by hydrophobic effect, which restricts the entry of

*Ifremer, Centre de Nantes, rue de l'Île d'Yeu, BP 1049, 44037 Nantes Cedex 01. Tel : 40 37 41 36 ; Fax : 40 37 40 73.

the nonpolar solutes into the aqueous phase [3], and accommodates them in the organic phase [7]. Nonpolar HOC with low solubilities and with low environmental dissolved concentrations, such as PCBs, are expected to behave ideally in the water phase and to exhibit linear partition with the dissolved organic phase.

However, many interesting organic compounds of environmental concern deviate considerably from ideal behavior in water and various solvents [9]. Examples of these compounds include hydrophobic ionizable organic compounds (eg: phenols and anilines) and hydrophobic ionic organic compounds (eg: linear alkylbenzenesulfonate, LAS). Hydrophobic ionizable organic compounds can exist in the aqueous phase as a neutral and ionized species. Hydrophobic ionic organic compounds bear a permanent charge in addition to a hydrophobic group [2]. For both groups of compounds the simple partition constant is not obeyed, and strong interactions with DOM are likely to occur. Additionally, many of these chemicals are highly functionalized and specific chemical interactions and electrostatic effects may dominate their speciation in the water column. Their ultimate behavior is strongly dependent on environmental variables (temperature, pH, salinity...).

• Colloidal organic matter and HOC

The interactions between colloidal organic matter and organic solutes can be viewed as interfacial process such as adsorption to a two-dimensional surface as well as a dissolution of compound into the bulk of a polymeric natural organic phase usually containing some minerals [8, 9]. In other words, in sorption to colloidal organic matter there may be an array of possible interactions starting with surface adsorption and ending with partitioning into bulk organic phase. The mechanisms involved in sorption by organic colloids of an organic compound may likely be accounted for chemical reactions (hydrogen bonding, complexation...), physical interactions (van der Waals forces, electrostatic attraction...) or hydrophobic effects.

Sorption isotherms of nonpolar HOC with colloidal organic matter indicate linear partitioning [10-13]. The slopes of the isotherms derived from the Freundlich equation correspond to linear sorption ie $1/n = 1$ and $C_s = K_D C_d^{1/n}$ where C_s and C_d are sorbed and dissolved concentrations and K_D is a sorption constant and $1/n$ an empirical constant. For sorption of HOC by marine organic colloids, empirical constant $1/n = 1$ would likely indicate no competition for sorption sites or that specific sorption sites are homogeneous [14]. These observations would also suggest that the mechanism involved is similar to sorption of hydrophobic organic contaminants with sediment or suspended organic

matter. It was demonstrated for HOC that tendencies to sorb to the separable solid phase and to the colloids are very similar when normalized to the organic carbon content ie $K_{DOC}(\text{colloids}) = K_{OC}(\text{particles})$ [13].

Conversely, other studies demonstrated much higher K_{DOC} values for colloids suggesting that DOM may be a better sorptive substrate for some HOC than soil or sediment organic matter [10, 12]. Furthermore, the strong evidence on high variability of sorption capacity of organic colloids was given in experimental [15] and field studies [10, 11]. These results suggest an influence of structure and composition of organic colloids on HOC binding. It appears that molecular weight, polarity and degree of aromaticity are important parameters in determining sorptive capacity of organic colloids [15]. Some authors suggest that steric constraints on the diffusion of HOC into organic matter depend on disparity in size and molecular shape of HOCs and organic colloidal sorbent. However, because of differences in experimental methods used for determining sorption and inherent limitation involved in colloidal, dissolved, and particulate phase separation and uncertainties in determination of dissolved nonpolar HOC concentrations, it is not possible to conclude on differences in sorption capacity or to preclude equilibrium partitioning model. However, it may prove that in addition to colloidal concentration and solute properties more information on sorbent properties is required to adequately predict the partition of HOC in natural waters [15].

Despite experimental limitations, many studies have clearly recognized the importance of the dissolved organic matter in determining chemical speciation of HOC as well as inorganic elements. Some authors have proposed that our basic understanding of environmental partition of nonpolar HOC should be revised due to the presence of organic colloids acting as an efficient sorbent and carrier for HOC [16]. From a geochemist's or environmental chemist's point of view, naturally occurring organic colloids would act as solid sorbents in environmental partitioning of organic contaminants and would behave as solute in their transport considerations as they have no appreciable settling velocity and they are moved by advective and diffusive processes.

It appears that apparent discrepancies between experimental data, field data and theory of sorption, supported by evidence of not ideal behavior of nonpolar HOC in partitioning, that is : i) sorbent mass dependent partitioning ; ii) high variability of partition constant for the same solute ; iii) non-reversibility of sorption [7, 17] may be to some extent solved by three-phase equilibrium models. These models involve in sediments : organic colloids of interstitial-water, dissolved phase and sorbed organic matter

phase and in water column : non-settling colloids (microparticles and/or macromolecules), dissolved phase and suspended particulate organic matter phase [13, 16]. These authors suggest that anomalous observations in sorption experiments or field data stem from experimental artifact linked to difficulty (impossibility) of the solid and aqueous phases separation that will correspond to the thermodynamic definition of these phases. In fact, particle size distribution of natural sediments and particulates exist probably in a continuous spectrum and certainly does not correspond neither to conventional cutoffs used for distinguishing between dissolved and solid phase nor to typical centrifugation or filtration separation capabilities.

■ Environmental implications

It is recognized now, that for an understanding of the fate of hydrophobic organic contaminants in natural aquatic systems their interactions with dissolved organic matter are of primary importance.

In a water column, it appears that the interactions of DOM with organic contaminants primarily influence their transport into or out of aquatic ecosystems. Strong evidence exists that dissolved humic material or other sorptive components of the dissolved organic carbon decrease efficiently binding of organic contaminants with suspended particles [18]. It implies that dissolved organic matter reduces sorption of HOC by suspended particles and changes transport and environmental distribution of these compounds, by decreasing their tendency to be removed by settling particles to bottom sediments and increasing the amount and likely residence time of contaminants that will remain within the water column [16, 18]. In highly energetic environments like estuaries, it also means that a more important fraction of dissolved contaminants may be transported further from their sources.

In sediments, mobility and perhaps diagenetic activity of hydrophobic organic contaminants may be enhanced by the presence of dissolved colloidal organic matter in the interstitial water of sediment [13]. This indicates also that precaution should be taken when interpreting the sedimentary record of the persistent organic contaminants.

Sorption of hydrophobic organic contaminants by dissolved organic matter may change their chemical activities in the environmental compartments. Intuitively, chemical activities of bound chemicals by organic colloids *versus* activities of free or truly dissolved molecules are likely different in many important environmental processes, such as photo- or biodegradation. The apparent (or effective) environmental kinetic constants of these reactions for bound contaminants are changed. This also imposes

experimental difficulties on laboratory research of these constants.

The larger fraction of hydrophobic organic contaminants remaining in the water column is of biological concern. The questions arise if these compounds are more available for uptake by aquatic organisms or if their bounding by DOM changes their toxicological properties and hence ecotoxicological effects.

Finally, it appears that three environmental exchanging compartments (water, solid particles and colloids) should be utilized in order to formulate effective model of solid-solution partitioning of organic contaminants and hence to formulate a predictive model of their transport in natural waters. More research on particle dynamics and development of new nondestructive techniques for the study of colloidal particles may provide a necessary understanding of their role in the partitioning as well as coupling between equilibrium and kinetic treatments of HOC sorption and physical transport. ■

References

- 1 Stum W, Morgan J (1981) *Aquatic Chemistry*, Wiley, NY
- 2 Westall JC (1987) Adsorption mechanisms in aquatic surface chemistry. In: *Aquatic surface chemistry* (Stumm W, ed) Wiley & Sons, NY
- 3 Tanford C (1980) *The Hydrophobic Effect*, Wiley, NY
- 4 Leo A, Hansch C, Elkins D (1971) Partition coefficients and their uses. *Chem Rev* 71, 525-554
- 5 Chiou CT (1985) Partition coefficients of organic compounds in lipid-water systems and correlation with fish bio-concentration factors. *Environ Sci Technol* 19, 57-62
- 6 Karickhoff SW (1984) Pollutant sorption in aquatic systems. *J Hydraul Eng* 10, 707-735
- 7 Voice TC, Rice CP, Weber WJ Jr (1983) Effects of solids concentration on sorptive partitioning of hydrophobic pollutants in aquatic systems. *Environ Sci Technol* 17, 513-518
- 8 Mingelgrin E, Gerstl Z (1983) Reevaluation of partitioning as a mechanism of nonionic chemicals adsorptions in soils. *J Environ Qual* 12, 1-11
- 9 Sigelo AC, Hoering TC, Helz GR (1982) Composition of estuarine colloidal organic material: Organic components. *Geochim Cosmochim Acta* 46, 1619-1626
- 10 Carter CW, Suffet IH (1982) Binding of DDT to dissolved humic material. *Environ Sci Technol* 16, 735-740
- 11 Means JC, Wijayarathne R (1982) Role of natural colloids in the transport of hydrophobic pollutants. *Science* 215, 968-970
- 12 Wijayarathne R, Means JC (1984) Affinity of hydrophobic pollutants for natural estuarine colloids in aquatic environments. *Environ Sci Technol* 18, 121-123
- 13 Brownawell BJ, Farrington JW (1986) Biogeochemistry of PCBs in interstitial waters of a coastal marine sediment. *Geochim Cosmochim Acta* 50, 157-169
- 14 Chiou CT, Peters LJ, Freed VH (1979) A physical concept of soil-water equilibria for nonionic compounds. *Science* 206, 831-832
- 15 Gauthier TD, Seitz WR, Grant CL (1987) Effects of structural and compositional variation of dissolved humic materials on pyrene K_{OC} values. *Environ Sci Technol* 21, 243-248
- 16 Gschwend PM, Wu S (1985) On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. *Environ Sci Technol* 19, 90-96
- 17 DiToro DM, Horzempa LM (1982) Reversible and resistant components of PCB adsorption-desorption: Isotherms. *Environ Sci Technol* 16, 594-602
- 18 McCarthy JF, Jimenez BD (1985) Interactions between polycyclic aromatic hydrocarbons and dissolved humic material: Binding and dissociation. *Sci Technol* 19, 1072-1076

10èmes JOURNEES INFORMATION EAUX

POITIERS
23, 24, 25 septembre 1992

60 conférences sur les thèmes :
Eaux potables - Eaux résiduaires urbaines
Eaux industrielles - Ressources en eau
Déchets urbains et industriels...
Exposition de Matériel

Renseignements et inscriptions :
Association des Anciens Elèves
Traitement des Eaux et des Nuisances
40 av du Recteur Pineau
86022 Poitiers cedex
Tél. : 49 46 67 61 - Fax : 49 45 37 68