INTERACTIONS OF XENOBIOTICS AND NOM IN WATER

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Natural organic matter (NOM) is present in surface, pore and ground waters. In all these areas interactions of xenobiotics with NOM can be observed. The interactions can be divided in two different groups: a partitioning process of hydrophobic substances and a more specific binding of substances with functional groups. It is well known that these interactions influence the fate and transport of xenobiotics. For example changes in solubility, bioavailability and toxicity have been determined for several xenobiotics. The measurement of these interactions, especially the sorption to dissolved organic matter (DOM), is still an analytical challenge. There are various methods described in literature. However, most of them are prone to disturbe the sorption equilibrium during the measurement and hence, the sorption coefficients obtained have to be considered with care. Two methods that have no separation step and are therefore less prone to this interference are the fluorescence quenching technique and the solid phase micro extraction (SPME). The fluorescence quenching technique is based on the effect, that the analyt loses his fluorescence activity after sorbing to NOM. After recording the steady state fluorescence spectra at different NOM concentrations the fluorescence intensities were evaluated according to the Stern-Volmer equation.

$$\frac{I_F^0}{I_F} = 1 + K_{SV} \cdot \beta(DOC)$$

Here I_F represents the corrected fluorescence intensity in the absence (0) and presence of NOM (in mg/L DOC) and K_{SV} the binding constant (in L/mg). The fluorescence quenching method is limited to fluorescing compounds and due to the inner-filter correction to a NOM concentration below 35 mg/L DOC.

A promising technique that is applicable for a broad variety of compounds is the SPME. Due to the small amount of analytes extracted it is reasonable to assume that the disturbance of the equilibrium is negligible. Moreover, in case of independent sorption processes this method makes it possible to determine the sorption constants of a mixture of xenobiotics simultaneously.

In our approach we compared the results of both methods for the same xenobiotic/NOM systems to get more information about the quality and limitations of the two methods and of the sorption process itself. The results showed that the sorption constants determined by the fluorescence quenching method (K_{SV}) were 3 to 13 times higher than the sorption constants determined by SPME (K_{DOC}). This difference can be explained by different interaction processes. Therefore we proposed *inner* and *outer sphere* interactions. In the fluorescence quenching approach all analyte molecules, even the ones weakly attached to the *outer sphere* of NOM, were quenched and hence detected as 'bound'. In the SPME approach, on the other hand, the analytes weakly attached to the outer sphere of NOM could readily exchange with the aqueous phase and are extractable by the SPME fiber. As a result they were not detected as 'bound'. This theory corresponds with fluorescence line narrowing spectroscopy experiments at low temperature that showed that in presence of humic acid a change of the site distribution and relative intensities of the ground state vibrations in the

fluorescence spectrum of pyrene has occurred, which can be related to an altered microenvironment of pyrene in the presence of humic acid.

This different results of the two methods indicate that the choice of the analytical method is dependent on the aim of the measurement. For photochemical research K_{SV} might be more useful whereas for the estimation of transport and bioavailability the constants determined by SPME are of higher relevance.

Further measurements showed that the sorption constants increase with decreasing pH. In case of hydrophobic xenobiotics without functional groups this can be explained by the increased hydrophobicity of the protonated NOM. In case of xenobiotics with protonated functional groups, like phenols, the reduced solubility and reduced hydrogen-bond interactions with water are also responsible for a better sorption.

To investigate the soprtion of phenols to DOM further measurements with the SPME were performed with a set of various phenols. The phenols showed a negligible sorption to natural DOM and a small sorption with log K_{DOC}-values between 2 and 3 to the commercial humic acid Aldrich-HA. A much stronger binding was observed to the protein bovine serum albumin (BSA) with log K_{DOC}-values between 2 and 6. The determined sorption constants showed a good correlation with the octanol/water partitioning coefficient (log K_{OW}). A further correlation was performed with the linear solvation energy relationship model (LSER). These model, developed by Kamlet and coworkers, based on the assumption that chemical properties depend on solute-solvent interactions. It can be described by the following equation:

$$\log K_{DOC} = m \cdot V_X + r \cdot R_2 + s \cdot \pi_H^2 + a \cdot \sum \alpha_H^2 + b \cdot \sum \beta_H^2 + c$$

The single terms of the equation that contain a constant (m, r, s, etc.) and a solvation parameter (V_x, R_2, etc.) describe specific interactions between the phenols and DOM. The cavity term ($m \cdot V_x$) is a measure for the difference between water and DOM in forming a cavity for the phenol. The

influence of hydrogen-bonds on the sorption is described by the terms ($a \cdot \sum \alpha_2^H$) and ($b \cdot \sum \beta_2^H$). The values of the solvation parameters needed for the correlation were taken from literature and the constants were calculated by multiple linear regression.

The results showed that the difference in cohesion between water and DOM is the main driving force for the sorption of the phenols. This is indicated by a positive value of m. The water has a strong tendency to form its preferred liquid structure and therefore in comparison to DOM it is harder to form a cavity for the phenol. As a result the phenols were expelled out of the water phase and adsorb to the DOM. The contributions of lone-pair electron interactions ($r \cdot R_2$) and dipole-dipole interactions ($s \cdot \pi_H^2$) are relatively small. The sorption of phenols is reduced by hydrogen-bond interactions (negative a and b). The type of hydrogen-bond interactions, where the phenols act with the strong hydrogen-bond acid water as a hydrogen-bond base, are mainly responsible for the reduction of the sorption and strongly determine the values of the sorption constants. The hydrogen bond-basicity of the phenols increases with increasing pKa-values. As a result the hydrogen-bonds with water molecules become stronger and the sorption to DOM is decreasing.

The regression coefficients of R = 0,950 and R = 0,911 for Aldrich-HA and BSA show a good correlation between the sorption constants and the solvation parameters. As a consequence, the LSER model allows an estimation of sorption constants of different phenols.

Literature

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