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Title: Effect of Natural Dynamic Changes on Pollutant-Sediment Interaction

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Objectives/Hypothesis

The overall objective of this research was to determine whether irreversible adsorption and desorption occur in natural sediments and dredge materials as a mechanism which needs to be considered in cleanup. When the idea was proposed there was considerable skepticism about the existence of such a process in real practical sediments and dredge materials. Therefore the first year was used for proof-of-concept and review purposes.

Approach

After considerable trial and error, modeling and testing with different sediments, solution conditions, separation protocols and hydrocarbon selection a base experiment was developed which demonstrated the feature of hysteresis that was proposed might exist (Fu, et al, 1994). Essentially, a base experiment consisted of adding a sediment to solution at about 1:10 (wt:vol) ratio and adding, e.g., C-14 labeled naphthalene to initiate adsorption. Then after a day the solution was poured off and desorption initiated by adding fresh solution without naphthalene. The desorption process was repeated many times.

Results

During these experiments, adsorption was observed to conform to expected hydrophobic-based K_{ow}/K_{oc} ratios. The desorption path, however, was quite hysteretic, i.e. irreversible.

Several compounds and conditions were tested and details of the desorption process were studied, including mass balance and extraction methodologies (Kan, et al., 1994). Many other factors were studied, such as adsorption and desorption time from minutes to months, several different compounds, varying OC content, and mass balance details. Numerous commonly used mechanisms of slow release, etc., were used to try to explain the observed hysteresis and none were found able to account for the reported experimental observations.

As a related issue, the general approach of calculating partitioning and solubility called “Universal Functional-Group Activity Coefficient (UNIFAC)” was obtained from John Prausnitz at Berkeley and tested. It was found that if a few corrections were made to the aromatic chlorine interaction terms that a much larger group of compounds of common interest to this research and general environmental work could be included. These corrections were made, coordinated with Prausnitz and published (Kan and Tomson, 1995). This work was co-sponsored by the Gas Research Institute division of Environmental Health and Safety as it relates to the fate of PCBs in gas pipelines.

In an attempt to elucidate the mechanism(s) of irreversible adsorption and desorption, M. Hunter developed a true surrogate model system as part of her Ph.D. thesis (1996). This system is composed of non-porous anatase (TiO₂) particles coated with an anionic surfactant. It was found that the fraction of OC added to the anatase in the form of surfactant could be adjusted to within virtually any limits by multiple adsorption steps. Surprisingly, this adsorbed surfactant was not readily desorbed and the multiple layers would resist multiple desorption steps. This is suggestive of Langmuir-Blodgett multiple layer adsorption onto glass slides, etc.. These observations and discussion have been accepted for publication in *Envi. Sci. and Tech.* (Hunter, et al, 1996).

This model surrogate system was used to further investigate the process of irreversible adsorption and desorption. The majority of the work with this system was done either with 2,2',6,6'-tetrachlorobiphenyl (a PCB isomer) or with naphthalene. It was found that when the desorption process was continued via many more desorption steps that this constant level was much lower than predicted by normal partitioning theories. Desorption time was varied from minutes to months with no effect beyond an hour or two. A second aspect was investigated with this model system, that of capacity. Multiple adsorption steps with more PCB were done in an attempt to “swamp” or saturate the irreversible or low solubility compartment. Results of these several hundred experiments are contained in a paper submitted to *Envi. Sci. and Technology* (Kan, et al., 1996).

The nature of the irreversible, or low solubility, compartment was further studied using Lula sediment and naphthalene. With the Lula sediment it was found that there existed a well defined size of this irreversible compartment at about 10 :g-Naph/g-sediment. This constant compartment size was found whether the adsorption was done in one, two, or several adsorption steps. After the irreversible compartment was “filled” additional adsorption of naphthalene was found to be completely reversible with a common adsorption and desorption isotherm, as expected from K_{OC} relations. Also, during these studies, the fraction of the adsorbed naphthalene that ended in the irreversible compartment appeared to be about constant, at around 30-50% of the amount that was expected to adsorb. In any adsorption step the reversible portion could be modeled by a standard isotherm.

From all of these studies a reasonable consistent *ad hoc* model was proposed wherein adsorption takes place on the OC of the sediment and then a small portion of the OC rearranges to entrap a portion of the adsorbed hydrocarbon. This entrapped portion

would be in a more stable thermodynamic environment and thereby desorb at a lower concentration. Even though this mechanism is reasonable, there is no evidence that it is correct nor of the key parameter that cause the effect. Also, the presently funded research group at Rice is doing testing with sediments samples that have been contaminated in the field for years and directly determining whether there exists a desorption compartment that has the properties observed in the laboratory.

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Students Supported

M.A. Hunter

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