

WHAT'S KNOWN AND WHAT'S YET TO BE KNOWN WITH RESPECT TO THE SORPTION OF ORGANIC POLLUTANTS ONTO SOILS

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ABSTRACT

Understanding and quantifying the sorption of organic pollutants onto soils is essential to predict their fate and transport in the environment. While many correlations exist between partition coefficients of organic pollutants onto soils and the quantity of soil organic matter, only recently studies have revealed the importance of the nature of soil organic matter. In many instances, the polarity index (PI) (O+N/C) of the organic sorbent should be considered. A regression of K_{ow} , solubility, and polarity index indicated that correlations between those properties and the extent of sorption are very specific to the pollutant class. Nuclear magnetic resonance (NMR) spectroscopy is widely used in routine structure elucidation of natural organic matter and other organic compounds, yet, its application in the field of environmental sciences is relatively untapped. Recent work has proved NMR to be invaluable at identifying conformations and metabolites, interactions with soil constituents, reactivity, and heterogeneous catalytic processes of organic pollutants. Yet, before NMR can be applied to field conditions, in-depth studies must be conducted in simple chemical environments, to provide background information that can be extrapolated, to interpret interactions in more complex environments.

Palabras clave: contaminantes orgánicos, sorción, desorción, técnicas de espectroscopía, NMR, calorimetría

RESUMEN

Es importante entender y cuantificar la sorción de los contaminantes orgánicos en el suelo, para predecir su destino y transporte en el ambiente. Aunque hay muchas correlaciones entre los coeficientes de partición de los contaminantes orgánicos en el suelo con el contenido de materia orgánica, los estudios recientes revelan la importancia de la naturaleza de la materia orgánica. En muchos casos debe ser considerado el índice de polaridad (PI)(O + N/C) del sorbente orgánico. Una regresión de K_{ow} , solubilidad, e índice de polaridad, indican que las correlaciones de estas propiedades con la magnitud de sorción son muy específicas para cada clase de contaminante. La espectroscopía de resonancia magnética nuclear (NMR) es ampliamente usada en la elucidación rutinaria de la estructura de la materia orgánica natural y otros componentes orgánicos. Sin

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embargo, esta aplicación en el campo de las ciencias ambientales no ha sido explotada. En trabajos recientes se ha establecido que la NMR es invaluable para identificar estructuras y metabolitos, interacciones de los contaminantes orgánicos con los constituyentes del suelo y las reacciones y procesos catalíticos heterogéneos de los mismos. Pero antes de que la NMR puedan aplicarse en condiciones de campo, deben realizarse estudios a profundidad en ambientes químicos sencillos, de forma que generen información de base extrapolable para poder interpretar interacciones en ambientes más complejos.

INTRODUCTION

Every day, we all use detergents, cosmetics, solvents, pesticides and petroleum-derived materials. Organic compounds are introduced into the environment intentionally (as pesticides) and unintentionally (as plasticizers, oils, and numerous industrial effluents). The current annual consumption of oil exceeds 3 billion tons and over the last decade the production of synthetic organic chemicals has steadily increased to over 400 million tons per year. According to the Organization of Economic Cooperation and Development, there are about 70,000 synthetic chemicals in daily use. With society's ever expanding utilization of organic chemicals our natural resources are endangered. Today there are more than 12 major laws and many thousands of pages of regulations governing our actions. We want to believe that with 21st century technology we are empowered to control pollution and standards are often set-up to the lowest detectable limits of modern instrumentation.

This is however inadequate; rational environmental standards should take into account the macro-environment as well as the micro-environment and not merely focus on the possible detection level. Spending all our energy in eliminating the last molecule of pollution may be wasteful as well! It takes time to learn what works and what doesn't, but because we can produce new chemicals so rapidly, we have conflicts between functionality and safety. Over the next 20 to 30 years, it has been estimated that government and private industry will need to commit billions of dollars annually for remediation of contaminated sites in the US alone.

To improve society's ability to anticipate, reduce and respond to environmental pollution, we must develop systematic ways of thinking about pollutants and classifying chemicals for their potential environmental impact. A sound mechanistic understanding of the interactions between pollutants and subsurface materials builds the foundation to address current and future practical concerns.

A key process controlling the risk and mitigation of hydrophobic organic chemicals (HOC's) is their interactions with aqueous and solid constituents. Sorption onto colloidal and/or immobile materials greatly affect their mobility, chemical reactivity, bioavailability and toxicity, and in turn, our ability to remediate contaminated sites.

The approach commonly taken to account for sorption in models is to assume an equilibrium distribution of the contaminant between the aqueous (mobile) phase and the soil (immobile) phase. The accuracy of such models depends on the availability of reliable thermodynamic and kinetic information of the individual processes that a pollutant can undergo in a subsurface environment. Many of the techniques used today (i.e., sorption isotherms) provide only macroscopic information on sorption processes and assumes fast local equilibrium. Furthermore, while many correlations exist between partition coefficients of organic pollutants onto soils and the quantity of soil organic matter, only recently studies have revealed the importance of the nature of soil organic matter. In a recent study we reported that the uptake of three acetamide pesticides onto four model organic sorbents was influence by the nature of the organic sorbent (Torrents *et al.* 1997). The organic carbon referenced sorption coefficient, K_{oc} , decreased with increasing the polarity index (PI) (O+N/C) of the organic sorbent.

As far as transport, availability, and susceptibility to biotic degradation is concerned, the dynamics of a pollutant's sorption and desorption is likely to be more important than its sorption at equilibrium. It is well established that compounds are not perfectly accessible to chemical recovery after they are introduced into the environment. This does not imply that non-readily reversible bound fractions are not of environmental concern. The degree and extent to which this occurs has implication on the toxicity, resistance to degradation, and subsurface transport properties of chemicals. The use of equilibrium sorption coefficients may not accurately represent solution concentrations in contact with polluted soils (Isaacson and Frink 1984, Pignatello 1990, Pavlostathis and Jaglal 1991, Locke 1992, Dousset *et al.* 1994, Kan *et al.* 1994.). There is a large body of evidence that indicates that sorption is not rapidly reversible and that desorption K_d 's increase as a function of the sorption equilibration time (Steinberg *et al.* 1987, Pignatello and Huang 1991, Scriber 1992, Pignatello *et al.* 1993) and depends on substrate structure (Brusseau and Rao 1989, 1991) and soil characteristics. Sorbed pollutants can be divided into a "rapidly reversible pool" and a "slowly reversible pool" (Karickhoff and Morris 1985, Wauchope and Meyers 1985).

Predictions of potential hysteresis of organic pollutant desorption is critical for selection and application of remediation technologies. In engineering practices, it is normally assumed that the same models applied to determine the sorption (from solution to the soil surface) of the HOC's can be applied to attain concentrations from desorption (from the soil surface to solution). It is generally accepted that only the pollutants in soil solution/groundwater (soluble) are available for physical removal and microbial degradation. HOC's are generally known for their low aqueous solubility and great tendency to stay sorbed in soil, and therefore unavailable for any possible removal either by physical means or microbial uptake. Depending on the properties of the HOC and the soil, interactions other than hydrophobic interactions can take place and thus increase the degree of hysteresis. The use of surfactants can increase the degree of HOC's desorption and thus their availability for removal. As environmental scientists, we need to improve our basic knowledge to mitigate tomorrow's risks. Advancements on spectroscopic techniques have been proved beneficial in other fields (such as in medical research) and could provide information on sorption mechanisms. Spectroscopic data, when combined with calorimetric determinations and macroscopic sorption studies, will aid to reveal mechanistic information on interactions between solutes and soil constituents. As environmental engineers, our mission is to apply today's knowledge to the control of today's problems. In this paper we focus on the application of spectroscopic techniques to study the sorption of HOC's. In the following paper, the use of biosurfactants to enhance bioavailability of HOC's is evaluated.

Spectroscopic techniques

Sorption mechanisms have rarely been studied at the molecular level. Recent advances in spectroscopic techniques indicate that these methods can reveal mechanistic information on interactions between solutes and soil constituents (Gu *et al.* 1994). In spectroscopic techniques we follow the quantised interaction of energy of molecular atoms (electromagnetic energy) with matter. The level of information that can be gained from each spectroscopic technique is different. **Table I** shows a comparison of the practical aspects of the different spectroscopic techniques that are used to gain molecular level information.

Nuclear Magnetic Resonance (NMR) spectroscopy can provide the most information on direct molecular evidence of specific interactions and mechanisms. Among scientific and other considerations that make NMR an unique technique is that it is a non-destructive technique and can be applied under conditions of interests, liquid or solid state without destroying the sample integrity. In NMR spectroscopy a nuclei with a spinning magnetic

TABLE I. COMPARISON OF PRACTICAL ASPECTS OF SPECTROSCOPIC TECHNIQUES USED (Field *et al.* 1995)

Parameter	Comparison
Cost	MS~NMR >> IR/Raman > UV
Operating difficulty	MS > NMR > UV~IR/Raman
Scope (amount of useful information)	NMR > MS > IR/Raman > UV
Theoretical background knowledge required	NMR >> MS > IR/Raman ~UV

MS=Mass Spectroscopy, NMR=Nuclear Magnetic Resonance Spectroscopy, IR=Infrared Spectroscopy, UV=Ultra Violet Spectroscopy

moment (e.g. ^1H , ^{13}C) will absorb electromagnetic radiation in the radio frequency range. The NMR spectrum provides information on the symmetry, electronic environment of the individual atoms, the quantity of nuclei present and the nature of adjacent atoms in a molecule. Over 30 years ago, the first application of Nuclear Magnetic Resonance (NMR) spectroscopy to natural organic matter was reported (Barton and Schnitzer 1963). The development of Fourier Transform (FT) techniques for data acquisition and developments such as superconducting magnets, modern pulsed-NMR techniques and new polarization transfer methods (to increase spectra resolution for solids) during the past decade has made NMR a valuable tool for environmental applications. NMR with Fourier transform techniques allows the rapid acquisition of the average of many individual spectra to enhance signal-to-noise ratio and thus sensitivity. Further by using labeled sites to increase the sensitivity of certain nuclei, we could specifically follow the chemistry of a molecule in an environmental sample.

^{13}C labeling: Since the natural abundance of ^{13}C in the environment is only ~ 1.0%, ^{13}C -NMR is over 100 times less sensitive than ^1H -NMR. Therefore high sample concentrations and longer experiment times will be encountered. This insensitivity can be overcome by the use of site-specific ^{13}C labeling to enhance the specific carbon signal by 100 times, with 100% enrichment (Levy and Lichter 1980). Site specific labeling can also simplify the NMR spectra for easy analysis of those enriched carbon signals of interest by increasing the intensity ratio of the enriched to the natural abundance levels.

NMR spectroscopy

NMR spectroscopy is a powerful technique that is based on the magnetic properties of the observed nucleus, which is influenced by its local chemical environment via electron density, and the physical interactions with its environment. NMR spectroscopy permits the identification of atomic configurations in molecules.

Electron density is a function of bonding and the electronegativity of the atoms involved. Because the outside of most organic molecules consists of protons within specific chemical environments, ^1H -NMR is sensitive to molecular-surface environments within and between molecules. ^{13}C -NMR is valuable in showing changes in the backbone of organic molecules within and between chemical environments. NMR is extremely accurate and sensitive in detecting small changes in local chemical environments (less than 1 Hz/300 Hz).

Although there have been enormous achievements in the application of NMR in fields such as biochemistry, medicine etc. and routine structure elucidation of Natural Organic Matter (NOM) (Wershaw 1985, Olk *et al.* 1995, Preston 1996) and other organic compounds (Jackson and Line 1997, Mesilaakso 1997, Morton *et al.* 1997,) we have only a glimpse of its capabilities in the field of environmental sciences.

Application of NMR techniques to study hocsorption mechanisms

Both liquid- and solid-state NMR has been used in environmental studies for the characterization of humic materials for over three decades. ^1H and ^{13}C -NMR has been widely used for the structure elucidation of humic materials and organic molecules (Hatcher *et al.* 1981, Harvey *et al.* 1983, Wershaw 1985, Noyes and Leenheer 1989). ^{13}C , ^{15}N , and ^{31}P have also been used to study the chemistry of functional groups present in humic materials (Mikita and Steelink 1981, Haider *et al.* 1992, Thorn *et al.* 1992; Nanny and Minear 1993). NMR is a promising tool, which can be used as an *In-Situ* and non-invasive probe to provide direct molecular scale data of environmental samples, without destroying the sample integrity as when using extraction methods. In addition since NMR has the added advantage of following the exact chemistry of both the pollutant and the complex environmental matrices, it can be used to determine conformational changes, transformations, and bioavailability. This information is vital for successful remediation processes. Recent studies have applied NMR to identify molecular conformations of pesticides and metabolites (Schmidt *et al.* 1995, Morton *et al.* 1997, Jayasundera *et al.* 1999) showed that in very specific chemical environments metolachlor atropisomers and conformations, that are stabilized in the presence of unbound water, can also freely interchange.

A few studies in the recent past have shown the importance of NMR in the study of the fate of pesticides in the environment. ^1H and ^{19}F -NMR was recently used to study hydrogen bonding or dipole-dipole interactions between humic acid and DDT and fluoroaromatic compounds (Anderson 1997). The enzymatic coupling of Bentazon with humus monomers and the formation of reaction products has been studied using ^1H - and ^{13}C -

NMR (Kim *et al.* 1997) while ^{13}C -NMR was also used recently to characterize the bound and sequestered residues of the fungicide cyprodinil in soil (Dec *et al.* 1997). A common conclusion in all these studies has been the necessity for more research in the application and development of NMR to examine the chemical and physical interactions between pollutants and the environmental matrix.

Experimental approach

Specific NMR parameters such as changes in chemical shifts of specific nuclei, T_1 relaxation times, line broadening, and coupling constants can provide information on the type of interactions occurring, such as noncovalent, covalent or partitioning, between organic pollutants and natural environmental samples (Table II). Detailed descriptions and definitions of NMR parameters can be found in any spectroscopic textbook that includes NMR and it is not the intention of this article to cover this material. Bonding of pollutants to mineral surfaces and humic substances induce changes in the NMR chemical shifts and/or changes in NMR spin-lattice relaxation times (T_1), both of which provide information on the types of molecular association and dynamics. While covalent bonds are easily visualized by variations in the chemical shift, non-covalent interactions are not expected to cause a significant change in the chemical shift unless it significantly alters the electron density surrounding the nuclei. However, measuring changes in the spin lattice relaxation times can unravel the nature and extent of non-covalent association. Covalent and noncovalent interactions of HOCs with Dissolved Organic Matter (DOM) have been probed, using solution phase ^{13}C - and ^{19}F -NMR, by other researchers (Hatcher *et al.* 1993, Herbert and Bertsch 1997, Nanny *et al.* 1997).

TABLE II. SPECIFIC NMR PARAMETERS THAT ARE A MEASURE OF INTERACTION MECHANISMS

Type of Interaction	Specific NMR parameter
Covalent binding e.g. addition, oxidation	Chemical Shifts
Non-covalent binding e.g. partitioning, van der Waals, ligand exchange, charge transfer, ion exchange, hydrogen bonding	T_1 relaxation times Spin-Spin coupling Line broadening

Cross polarization/magic-angle spinning (CP/MAS) allows the acquisition of highly resolved ^{13}C NMR spectra from solid samples. This is also another instrumental advantage for environmental samples. Solid-state NMR techniques have been used for *In-situ* investigation of

adsorption and heterogeneous catalytic processes (Ansermet *et al.* 1990, Haw 1992) and to investigate the reactivity and orientation of organic pollutants (OP's) in smectites (Resing *et al.* 1980, Carrado *et al.* 1990). O'Brien *et al.* (1991) studied triethylphosphate adsorption on clays and organo-clays and they were able to distinguish between liquid like molecules and molecules with restricted motion. Jurkiewicz and Maciel (1995) examined the interactions of ^{13}C -labeled acetone, carbon tetrachloride, and trichloroethylene onto clays and Aldrich HA. Hydrogen bonding with no covalent coupling was postulated as the major mechanism. Netzel *et al.* (1997) used solid state ^{13}C -NMR to study the sorption of HOCs to coal fly ash and correlated the chemical shift to the bonding strength. Weissmahr *et al.* (1997) applied ^{13}C -NMR with MAS together with other spectroscopic methods to investigate the adsorption mechanisms of nitroaromatic compounds at clay surfaces.

Chemical shifts: NMR Chemical shifts of a specific atom of a molecule is determined by the electron density around that nucleus and is influenced by the neighboring atoms that form chemical bonds and intermolecular interactions with the chemical environment such as solvents and humic substances. The influence of the surrounding chemical environment on the chemical shifts is qualitatively defined as the resulting change in chemical shift, measured relative to a common reference compound, when a solute is transferred at infinite dilution from one environment (inert reference solvent) to another (Laszlo 1967):

$$\delta_{\text{medium}} = \delta_{\text{sample}} - \delta_{\text{refsol}} \quad (1)$$

where $\Delta\delta_{\text{medium}}$ denotes the contribution of intermolecular interactions to NMR chemical shifts and δ_{sample} and δ_{refsol} are the chemical shifts in the sample and reference systems, relative to a common reference compound.

Chemical shift changes and/or peak broadening are indications of sites of association. Sharp peaks are indicative of a liquid-like environment. As a molecule spends more time at a mineral surface, the static component of the dipole-dipole in the microenvironment will result in site selective line broadening.

Relaxation studies: Spin-lattice relaxation times (T_1) and Spin-spin relaxation times (T_2) are functions of the thermal motion of the molecules, and other chemical and physical interactions. Therefore, T_1 and T_2 measurements can be used to infer interactions within chemical microenvironments. The spin-lattice relaxation is the process of energy exchange between individual nuclear spins and the surrounding liquid or solid lattice. The T_1 measured is an average of those associated and unassociated nuclei.

Relaxation experiments have been used to infer information regarding the size, shape and flexibility of NOM. Olk *et al.* (1995) measured ^{13}C T_1 values in a

study of humification processes. Longer relaxation times and higher UV E_{465}/E_{665} ratios were correlated with the lower molecular weight, lower aromaticity and less rigid fractions. T_1 relaxation studies and paramagnetic relaxation studies have been recently applied, using ^{13}C and ^{19}F respectively, to show the existence of encapsulated hydrophobic regions in humic acids (Chien *et al.* 1997, Nanny *et al.* 1997).

Recent studies used T_1 relaxation measurements to determine non-covalent interactions of molecules such as phenol, acenaphthenone, and F-acetonaphthone with humic acids by measuring the T_1 at a single labeled site in the molecule (e.g. carbonyl carbon of acenaphthenone) (Nanny *et al.* 1997, Dixon *et al.* 1999). These studies however cannot be used to identify the specific sites of the molecule that are directly involved in binding.

When a molecule interacts with NOM or other surfaces it can induce changes to the T_1 relaxation times. A decrease in relaxation time indicates a reduction in molecular mobility as a result of interactions. Bound sites of a molecule will have a faster relaxation rate than the non-bound sites. This variation in T_1 's can be used to assess the degree of non-covalent interactions. Thus different chemicals can interact with NOM via different mechanisms and the relaxation times will vary to a larger extent in systems with a larger degree of chemical interactions. Furthermore, relaxation times could also be used to discern different site-specific interactions and their variability upon the type of NOM.

Figure 1 sketches the expected changes on relaxation times for different pollutants and different organic sorbents. The sites that are directly involved in binding would have shorter T_1 relaxation times since they would be on average less mobile. Sites that are only indirectly involved in binding would have T_1 relaxation times similar to those in solution. Changes in T_1 relaxation times of the different sites within the chemical structure enabled the prediction of interaction sites of acetanilide and metolachlor in colloidal and dissolved organic matter (DOM) (Jayasundera *et al.* 2000). Metolachlor, a nonionic pre-emergence herbicide, consists of polar functional groups. The non-aromatic sites of metolachlor were involved in forming specific interactions initially with polar organic matter such as chitin while the aromatic sites were involved in more non-specific interactions with less polar organic matter such as lignin (**Fig. 2**). Molecular simulations using molecular and quantum mechanics also complement this behavior (**Fig. 3**) and can be used to predict interaction sites of organic pollutants. Binding site information can also be further determined using 1D and/or 2D NOESY (Nuclear Overhauser Enhancement Spectroscopy) experiments. More recently, a very promising technique has been proposed to determine H-bonding by the

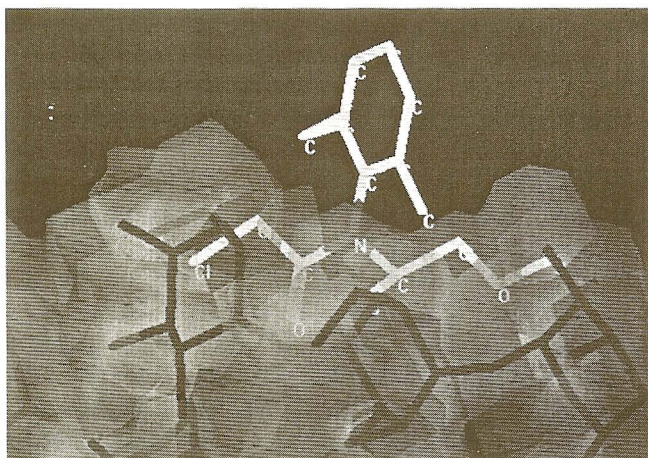


Fig. 3. Predicted metolachlor interactions with chitin using molecular and quantum mechanics simulations

Differential Scanning Calorimetry (DSC) is a technique in which the energy difference between a sample and a reference is measured as a function of temperature while they are subject to a controlled temperature program. The DSC energy is obtained by integrating the DSC signal $d\Delta H/dT = f(T)$, ΔH being the endo or exothermal enthalpy and T the temperature. Endo and exothermic enthalpy results from positive and negative heat of reaction respectively. The magnitude of the enthalpy of desorption can then be related to the different interactions between the organic molecules and the surface. DSC has been used to obtain desorption energies of water and organic molecules from activated carbon

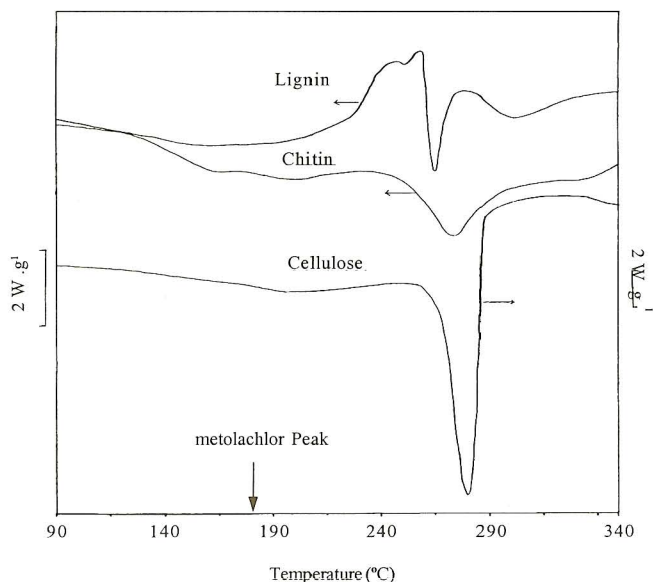


Fig. 4. DSC graphs of metolachlor adsorbed onto different organic sorbents. Cellulose is plotted versus axis on the right in a different scale (Torrents *et al.* 1997)

(Amicarelli *et al.* 1979, Baudu *et al.* 1993) and to quantify the water, volatile matter and pyrolysis of bituminous coal (Rosenvold *et al.* 1982).

The DSC graphs for metolachlor desorption from lignin (A), chitin and cellulose are presented in figure 4 (Torrents *et al.* 1997). The endothermic enthalpy peaks for metolachlor on the different organic sorbents were obtained at temperatures higher than that of metolachlor by itself and indicate binding of metolachlor onto the organic sorbent. The enthalpy of desorption is the result of different interactions between metolachlor molecules and the various organic sorbents and will result in different energies. A narrow peak and low energy obtained when metolachlor desorbed from lignin indicates that a physisorption mechanism was involved. For chitin a wider peak and low desorption energy was found which can be indicative of the contribution of several interactions with different adsorption energies. For cellulose, the peak is larger than that for lignin (A) and also has a higher desorption energy. This too indicates several interactions and stronger binding than that of chitin. The results obtained up to now, indicate that DSC provides both qualitative and quantitative information on the desorption energy of OPs from soil organic matter surfaces. Hence, DSC gives a measure of the strength of the adsorption bonds. By measuring the endothermic enthalpy peaks of metolachlor in different surfaces with different equilibration times, the extent of lability can be understood.

Titration calorimetry (TC) is a useful technique to obtain adsorption enthalpies and is a direct measure of the strength of the bonds between the adsorbate and the surface. This technique has successfully been applied to study cation-exchange processes (Clearfield 1988) and ligand adsorption onto metal oxides (Machesky *et al.* 1989, Benoit *et al.* 1993) and to the sorption of NOM (Gu *et al.* 1994). In TC, the heat evolved (Q) when a known quantity of sorbate (titrant) is introduced to the sorbent (titrate) is directly measured. By knowing the adsorption isotherm data, the exact quantity of molecules adsorbed in relation to the quantity introduced can be determined and this allows the calculation of differential molar enthalpies (ΔH_{obs}) using,

$$\Delta H_{obs} = \frac{-Q}{\mu\text{moles adsorbed}} \quad (2)$$

where Q is the total heat evolved (mJ) and ΔH_{obs} is the measured enthalpy of reaction (kJ mol^{-1}). The adsorption energy of metolachlor to different organic matter surrogates was a function of the surface and a measure of the type and strength of interactions. The adsorption enthalpies together with information gained from spectroscopic techniques can provide valuable information on pollutant interactions in the environment.

CONCLUSIONS

There is an extensive body of literature indicating that equilibrium sorption models have their limitations. Often, when those models are used to set clean-up goals, such as operational time and soil residuals, such goals can not be reach. Desorption is the process that controls the accessibility and environmental risk of the sorbed pollutant. For instance, if the pollutant can be bound to soil organic matter to render a non-labile complex, its toxicity may decrease and thus would its environmental risk.

The use of spectroscopic techniques can provide insight into the broader question of pollutant-surface interactions. It is anticipated that the molecular information gained can shed light on many aspects of surface site reactivity and specific chemical interactions between organic pollutants and mineral and organic surfaces. Such information will increase our ability to predict sorption behavior from properties of both sorbents and sorbates. Important benefits will result from a mechanistic understanding of sorption: 1) innovative and more effective methods can be designed for treating polluted environments, 2) management and clean-up guidelines will have a stronger scientific basis, and 3) the ability to estimate potential environmental hazards of new chemicals even before such compounds are synthesized could be developed; permitting the development of environmental benign processes.

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REFERENCES

- Amicarelli V., Baldassare G. and Liberti L. (1979). Thermoanalytical study of activated carbon regeneration-I. Desorption of phenol and aniline. *Thermochim. Acta* 30, 247-253.
- Anderson S. J. (1997). Proton and ¹⁹F NMR spectroscopy of pesticide intermolecular interactions. In: *Nuclear magnetic resonance spectroscopy in environmental chemistry* (M.A. Nanny, R.A. Minear, J.A. and Leenheer, Eds) Oxford University Press, New York, pp. 51-72.
- Ansermet J. P., Slichter C. P. and Sinfelt J. H. (1990). Solid state NMR techniques for the study of surface phenomena. *Prog. NMR Spectr.* 22, 401-421.
- Barton D. H. R. and Schnitzer M. (1963). A new experimental approach to the humic acid problem. *Nature* 198, 217-218.
- Baudu M., Le Cloirec P. and Martin G. (1993). First approach of desorption energies of water and organic molecules onto activated carbon by differential scanning calorimetry studies. *Wat. Res.* 27, 69-76.
- Benoit P., Hering J. G. and Stumm W. (1993). Comparative study of the adsorption of organic ligands on aluminum oxide by titration calorimetry. *Appl. Geochem.* 8, 127-139.
- Borman S. (1999). Hydrogen bonds revealed by NMR. *Chemical and Engineering News*, American Chemical Society, May 10, 36-38.
- Brusseau M.L. and Rao P.S.C. (1989). The influence of sorbate-organic matter interactions on sorption nonequilibrium. *Chemosphere* 18, 1691-1706.
- Brusseau M.L. and Rao P.S.C. (1991). Influence of sorbate structure on nonequilibrium sorption of organic compounds. *Environ. Sci. Technol.* 25, 1501-1506.
- Carrado K.A., Hayatsu R., Botto R.E. and Winans R.E. (1990). Reactivity of anisols on clay and pillared clay surface. *Clays Clay Miner.* 38, 250.
- Chien Y., Kim E. and Bleam W. F. (1997). Paramagnetic relaxation of atrazine solubilized by humic micellar solutions. *Environ. Sci. Technol.* 37, 3204-3208.
- Clearfield A. (1988). Role of ion exchange in solid-state chemistry. *Chem. Rev.* 88, 125-148.
- Dec J., Haider K., Schaffer A., Fernandes E. and Bollag J. (1997). Use of a silylation procedure and ¹³C-NMR spectroscopy to characterize bound and sequestered residues of cyprodinil in soil. *Environ. Sci. Technol.* 31, 2991-2997.
- Dixon A. M., Mai M. A. and Larive C. K. (1999). NMR investigation of the interactions between 4-fluoro-1-acetonaphthone and the suwannee river fulvic acid. *Environ. Sci. Technol.* 33, 958-964.
- Dousset S., Mouvet C. and Schiavon M. (1994). Sorption of terbutylazine and atrazine in relation to the physico-chemical properties of three soils. *Chemosphere.* 28, 467-476.
- Field L.D., Sternhell S. and Kalman J.R. (1995). *Organic Structure from Spectra*, 2nd Edition, J. Wiley, West Sussex, 74 p.
- Gu B., Schmitt J., Chen Z., Liang L. and McCarthy J.F. (1994). Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. *Environ. Sci. Technol.* 28, 38-46.
- Haider K., Spiteller M., Reichert K. and Fild M. (1992). Derivatization of humic compounds: an analytical approach for bound organic residues. *Int. J. Environ. Anal. Chem.* 46, 201.
- Harvey G. R., Boran D. A., Chesal L. A. and Tokar J. M. (1983). The structure of marine fulvic and humic acids. *Mar. Chem.* 12, 119-132.
- Hatcher P. G., Maciel G. E. and Dennis L. W. (1981). Aliphatic structure of humic acids; a clue to their origin. *Org. Geochem.* 3, 43-48.
- Hatcher P. G., Bortiatynski J. M., Minard R. D., Dec J. and Bollag J. (1993). Use of high resolution ¹³C NMR to examine the enzymatic covalent binding of ¹³C-labelled 2,4-dichlorophenol to humic substances. *Environ. Sci. Technol.* 27, 2098.

- Haw J. F. (1992). Nuclear magnetic resonance spectroscopy. *Anal. Chem.* 64, 243R-254R.
- Herbert B.C., Bertsh P.M. and Novak J.M. (1993). Pyrene sorption by water-soluble organic carbon. *Environ. Sci. Technol.* 27, 398-403.
- Herbert B. C. and Bertsh P. M. (1997). A ^{19}F and ^2H NMR spectroscopic investigation of the interaction between nonionic organic contaminants and dissolved humic material. In: *Nuclear magnetic Resonance Spectroscopy in Environmental Chemistry*, (M. A. Nanny, R. A. Minear and J. A. Leenheer Eds.) Oxford University Press, New York.
- Isaacson P. J. and Frink C. R. (1984). Nonreversible sorption of phenolic compounds by sediment fractions: the role of sediment organic matter. *Environ. Sci. Technol.* 18, 43.
- Jackson M. J. and Line M. A. (1997). Organic composition of a pulp and paper mill sludge determined by FTIR, ^{13}C CP MAS NMR, and chemical extraction techniques. *J. Agric. Food Chem.*, 45, 2354-2358.
- Jayasundera S., Schmidt W. F., Hapeman C. J. and Torrents A. (1999). Influence of the chemical environment on metolachlor conformations. *J. Agric. Food Chem.* 47, 4435-4442.
- Jayasundera S., Schmidt W. F., Hapeman C. J. and Torrents A. (2000). Molecular interactions of Acetamide pesticides with organic matter surrogates – Application of ^1H - and ^{13}C -NMR relaxation parameters. Submitted to *Environ. Sci. Technol.*
- Jurkiewicz A. and Maciel G.E. (1995). Solid state ^{13}C -NMR studies of the interactions of acetone, carbon tetrachloride and trichloroethylene with soil components. *Sci. Total Environ.* 164, 195-202.
- Kan A.T., Fu G. and Tomson M.B. (1994). Adsorption/desorption hysteresis in organic pollutant and soil/sediment interaction. *Environ. Sci. Technol.* 28, 859-867.
- Karickhoff S. and Morris K. (1985). Sorption dynamics of hydrophobic pollutants in sediment suspensions. *Environ. Toxicol. Chem.* 4, 469-479.
- Kim J., Fernandes E. and Bollag J. (1997). Enzymatic coupling of the herbicide bentazon with humus monomers and characterization of reaction products. *Environ. Sci. Technol.* 31, 2392-2398.
- Laszlo P. (1967). Solvent effects and nuclear magnetic resonance. *Progr. NMR Spectrosc.* 3, 231-402.
- Levy G. C. and Lichter R. L. (1980). *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd Ed. J. Wiley, New York.
- Locke M.A. (1992). Sorption-desorption kinetics of alachlor in surface soil from two soybean tillage systems. *J. Environ. Qual.* 21, 558-566.
- Machesky M. L., Bischoff B. L. and Anderson M. A. (1989). Calorimetric investigation of anion adsorption onto goethite. *Environ. Sci. Tech.* 23, 580-587.
- Mesilaakso M. T. (1997). Application of NMR spectroscopy to environmental analysis: detection of trace amounts of chemical warfare agents and related compounds in organic extract, water, and sand. *Environ. Sci. Technol.* 31, 518-522.
- Mikita M. A. and Steelink C. (1981). Carbon-13 enriched nuclear magnetic resonance method for the determination of hydroxyl functionality in humic substances. *Anal. Chem.* 53, 1715-1717.
- Morton M. D., Walters F. H., Aga D. S., Thurman E. M. and Larive C. K. (1997). Nuclear magnetic resonance identification of new sulfonic acid metabolites of chloroacetanilide herbicides. *J. Agric. Food Chem.* 45, 1240-1243.
- Nanny M. A. and Minear R. A. (1993). Organic phosphorus in the hydrosphere: characterization via ^{31}P FT-NMR. In: *Environmental Chemistry of Lake and Reservoirs*. (L. Baker, Ed.), American Chemical Society, Washington DC, 161-191.
- Nanny M. A., Bortiatynski J. M. and Hatcher P. G. (1997). Noncovalent interactions between acenaphthenone and dissolved fulvic acid as determined by ^{13}C NMR T_1 relaxation measurements. *Environ. Sci. Technol.* 31, 530-534.
- Netzel D. A., Miknis F. P., Lane D. C., Rovani J. F., Cox J. D. and Clark J. A. (1997). Adsorption isotherms and ^{13}C solid-state NMR study of hazardous organic compounds sorbed on coal fly ash. In: *Nuclear magnetic resonance spectroscopy in environmental chemistry*. (M.A. Nanny, R.A. Minear, and J.A. Leenheer, Eds.) Oxford University Press, New York, pp. 91-119.
- Noyes T. I. and Leenheer J. A. (1989). Proton nuclear-magnetic-resonance studies of fulvic acid from the suwannee River in humic substances in the suwannee river, Georgia: Interactions, properties, and proposed structures, In: *US Geological Survey Open-File Rept.* 87-557 (R.C. Averett, J.A. Leenheer, D.M. McKnight, K.A. Thorn, Eds.) Denver, CO, pp. 235-250.
- O'Brien P., Williamson C. J. and Groombridge C. J. (1991). Multinuclear solid-state MAS and CPMAS study of the binding of triethyl phosphate to a montmorillonite. *Chem. Mater.* 3, 276-280.
- Olk D. C., Cassman K. G. and Fan T. W. M. (1995). Characterization of two humic acid fractions from a calcareous vermiculite soil: implications for the humification process. *Geoderma* 65, 195-208.
- Pavlostathis, S.G., Jaglal, K. (1991) Desorptive behavior of trichloroethylene in contaminated soil. *Environ. Sci. Technol.* 25, 274-279.
- Pignatello, J.J. (1990) Field observed ethylene dibromide in an aquifer after two decades. *J. Contaminant. Hydr.*, 5, 195-214.
- Pignatello J. J. and Huang L. Q. (1991). Sorptive reversibility of atrazine and metolachlor residues in field soil samples. *J. Environ. Qual.* 20, 222-228.
- Pignatello J. J., Ferrandino F. J. and Huang L. Q. (1993). Elution of aged and freshly added herbicides from a soil. *Environ. Sci. Technol.* 27, 1563-1571.
- Preston C. (1996). Applications of NMR to soil organic matter analysis: history and prospects. *Soil Sci.* 161, 144-166.

- Resing H. A., Slotfeld-Ellingsen D., Garroway A. N., Weber D. C., Pinnavaia T. J. and Unger K. (1980). ^{13}C chemical shifts in adsorption systems: molecular motion, molecular orientations, qualitative and quantitative analysis. Magnetic resonance in colloid and interface science. Fraissard J.P., Resing H.A. Eds, 239-258, Reidel, Boston.
- Rosenvold R. J., Dubow J. B. and Rajeshwar K. (1982). Thermal analysis of Ohio bituminous coals. *Thermochim. Acta* 53, 321-332.
- Schmidt W. F., Hapeman C. J., Waters R. M. and Johnson W. E. (1995). NMR and molecular mechanics of alachlor conformations and conformers: implications to the mechanism of environmental photodegradation. *J. Agric. Food Chem.* 1724-1729.
- Scribner S.L. (1992). Desorption and bioavailability of aged simazine residues in soil from a continuous corn field. *J. Environ. Qual.* 21, 222-228.
- Steinberg S. M., Pignatello J. J. and Sawhney B. L. (1987). Persistence of 1,2-dibromoethane in soils: entrapment in intraparticle micropores. *Environ. Sci. Technol.* 21, 1201-1208.
- Thorn K. A., Arterburn J. B. and Mikita M. A. (1992). ^{15}N and ^{13}C NMR investigation of hydroxylamine-derivatized humic substances. *Environ. Sci. Technol.* 26, 107.
- Torrents A, Jayasundera S. and Schmidt W. F. (1997). Influence of the polarity of organic matter on the sorption of acetamide pesticides. *J. Agric. Food Chem.* 45, 3320-3325.
- Wauchope R.D. and Myers R.S. (1985). Adsorption-desorption kinetics of atrazine and linuron in fresh-sediment aqueous slurries. *J. Environ. Qual.* 14, 132-136.
- Weissmahr K. W., Haderlein S. B., Schwarzenbach R. P., Hany R. and Nuesch R. (1997). *In Situ* spectroscopic investigations of adsorption mechanisms of nitroaromatic compounds at clay minerals. *Environ. Sci. Technol.* 31, 240-247.
- Wershaw R.L. (1985). Application of nuclear magnetic resonance spectroscopy for determining functionality in humic substances. In: *Humic substances in soil, sediment, and water*. (G. R. Aiken, D. M. McKnight, R. L. Wershaw and P. McCarthy, Eds.) Wiley, New York.