

# Role of clay minerals in controlling the fate of exceptionally toxic organic contaminants in the environment

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## Abstract

Understanding the chemical mechanisms of interaction of dioxins with soils and sediments are critical to understanding their environmental fate, transport and bioavailability. Recently, expandable clay minerals have been shown to have a higher-than-expected affinity for these exceptionally toxic, nonpolar compounds. To gain additional perspective, this study focused on the interaction of dioxin congeners with expandable clay minerals by integrating macroscopic batch sorption experiments, spectroscopic analysis and computational methods. In addition, preliminary data on the bioavailability of dioxin sorbed to clay minerals will be presented. Maximum dioxin sorption occurred on clay minerals exchanged with weakly hydrated monovalent cations (e.g., Cs<sup>+</sup>). Regarding clay specificity, highest sorption was observed on saponite, a trioctahedral smectite with isomorphous substitution in the tetrahedral sheet. Of the cation-smectite variables explored in this study, the nature of the exchangeable cation was the most significant determinant followed by the type of clay. In order to investigate the influence of chlorine substitution, we compared the sorption of dibenzo-p-dioxin (DD) and 1-chloro-dibenzo-p-dioxin (1ClDD). For all of the smectites studied, sorption of 1ClDD was greater than that of DD. Polarized FTIR and Raman spectra of sorbed DD and 1ClDD on the clay minerals revealed information about the orientation of the sorbed species and, in the case of DD on saponite, specific information about the interaction of the sorbed DD species with the interlayer cation. Specifically, Raman spectra of dioxin associated with Cs-saponite showed that the molecular symmetry of the interlayer species was reduced. The exception toxicity of vertebrate animals to chlorinated dioxins occurs through activation of the aryl hydrocarbon receptor (AhR). Working in collaboration with the Center for Integrative Toxicology at Michigan State University, we at the early stages of examining the bioavailability of dioxins sorbed to clay minerals.

## Key Words

Dioxin, bioavailability, FTIR, Raman spectroscopy, sorption, smectite.

## Introduction

Dioxins represent a group of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzo furans, and polychlorinated biphenyl compounds. They are persistent toxic organic pollutants, hydrophobic, and are resistant to degradation and tend to accumulate in soil and sediments. Although soil organic matter (SOM) has been traditionally thought to be responsible for the sequestration of these hydrophobic compounds (Chiou *et al.* 1983), recent evidence has shown that smectites have a greater affinity for dioxin than SOM (Liu *et al.* 2009; Rana *et al.* 2009). Additional support for the link between dioxins and clay minerals has been provided by the observation of elevated levels of PCDDs found in prehistoric clay deposits in the United States, Germany and Spain (Ferrario *et al.* 2000; Rappe 1994). The congener pattern found from these prehistoric clay deposits is unique to clays and is distinct from the congener patterns of anthropogenic dioxins. The overall goal of this study was to gain a molecular level understanding about how selected dioxins interact with clay minerals. The first objective was to combine batch sorption, molecular spectroscopy, X-ray diffraction and computational methods to identify the molecular mechanism(s) of interaction. The second was to examine how the degree of chlorination influence sorption processes. The third objective is a work in progress and that is to assess the bioavailability of sorbed dioxins to mice in oral exposure studies.

## Materials and methods

### *Clay minerals and chemicals*

Dibenzo-p-dioxin (DD) and 1-chloro-dibenzo-p-dioxin (1ClDD) with > 99% purity were purchased from Chem Service, West Chester, PA. Smectite clays (SapCa-2 saponite, SWy-2 montmorillonite, and Upton

montmorillonite) were obtained from the Source Clays Repository of The Clay Minerals Society (Purdue University, West Lafayette, IN). The < 2- $\mu\text{m}$  clay fraction was obtained followed by saturation with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  cations.

#### Batch sorption isotherms

Sorption isotherms of 1CIDD and DD from water were conducted by the batch equilibrium method (Liu *et al.* 2009 and Rana *et al.* 2009). Mixtures of smectite and aqueous solution of DD or 1CIDD were equilibrated for 24h at room temperature ( $23\pm 2$  °C). The equilibrium supernatant concentration of DD or 1CIDD was measured using a Shimadzu SLC-10 high-performance liquid chromatography (HPLC) system equipped with a UV detector; set at the maximum absorption wavelength 223 nm (for DD) and 227 nm (for 1CIDD), and a 15 cm x 4.6 mm x 5 mm Supelcosil ABZ PLUS column. The mobile phase was a mixture of 80% methanol (for DD) or acetonitrile (for 1CIDD) and 20% water with a flow rate of 1.0 ml/min. The amount of DD and 1CIDD sorbed was calculated based on the amount of DD and 1CIDD lost from the solution.

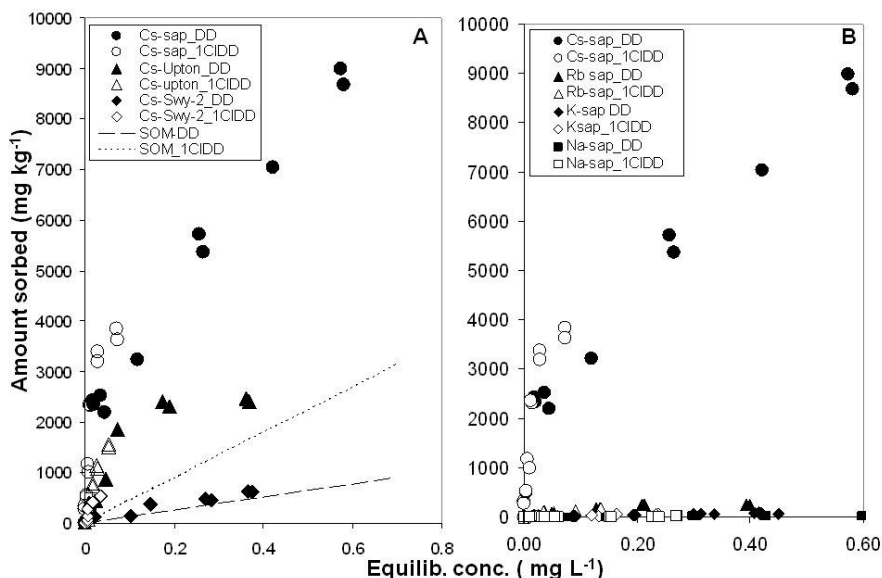
#### Spectroscopic analysis

Self supporting clay films (SSCF) of DD- or 1CIDD- smectite complexes were prepared from suspension obtained from batch sorption experiment.

1. FTIR analysis: Infrared spectra of SSCF and reference DD or 1CIDD in KBr and in polar solvents (ATR-FTIR) were obtained on a Perkin-Elmer GX2000 Fourier Transform Infrared (FTIR) spectrometer equipped with deuterated triglycine (DTGS) and Mercury-cadmium-telluride (MCT) detectors, an internal wire grid IR polarizer, and a KBr beam splitter.
2. Raman Analysis: Raman spectra of crystalline DD, DD in  $\text{CCl}_4$ , and SSCF of clay-DD complex were obtained on an Acton Research Corporation SpectroPro500 spectrograph. A Melles-Griot helium-neon laser with 632.8 nm wavelength and a power output of 35 mW measured at the laser head was used as the excitation source. Raman-scattered radiation was collected in a 180-degree backscattering configuration. The entrance slits to the spectrograph were set to 50 mm. The spectrograph used a holographic super notch filter to eliminate Rayleigh scattering. The detector was a Princeton Instruments liquid N<sub>2</sub> cooled CCD detector. The spectrograph was calibrated daily using a Ne-Ar calibration lamp based upon known spectral lines.

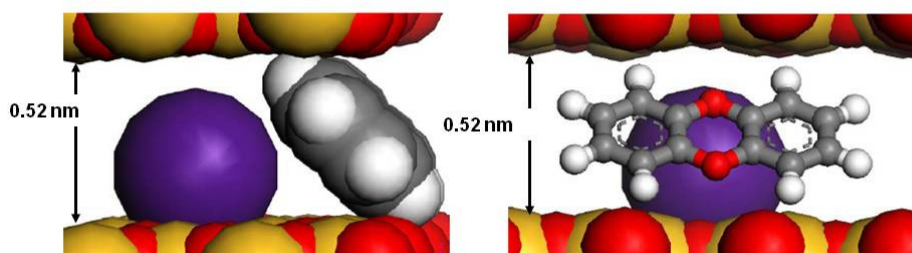
## Results

Sorption isotherms of DD and 1CIDD from water to smectites are shown in Figure 1. In prior work, sorption of DD by Cs-smectite was found to be greater than that of sorption to SOM (Liu *et al.* 2009). Sorption of both DD and 1CIDD on smectite was strongly influenced by the type of smectite and the nature exchangeable cations present in smectite interlayer.



**Figure 1.** HPLC derived batch isotherm representing DD and 1CIDD uptake from water by Cs saturated smectite (saponite, Upton and SWy-2) and SOM (A) and homoionic saponite saturated with different exchangeable cations (B). The amount sorbed by soil organic matter was estimated using the equation:  $\log \text{KOM} = 0.904 \log \text{KOW} - 0.779$  (Chiou 1983). Log Kow for DD and 1CIDD are 4.3 and 4.9 (Schwarzenbach *et al.* 2003), and water solubilities are 0.901 and 0.42 mg/L (ASTDR 1998).

Of the variable studies here (clay type and exchangeable cation), the nature of the exchangeable cation was the strongest determinant of sorption of DD and 1CIDD. Sorption of both DD and 1CIDD on saponite increased as the enthalpy of hydration of the exchangeable cation decreased. In agreement with prior work, Cs<sup>+</sup> exchanged saponite showing the highest affinity for DD and 1CIDD (Liu *et al.* 2009; Rana *et al.* 2009). The high affinity of these dioxin congeners for Cs-saponite could be explained by two possible mechanisms. One possibility is that Cs<sup>+</sup> ions are partially sequestered in the ditrigonal cavities of the clay which further reduces the effective enthalpy of hydration of these ions giving these sites a strongly hydrophobic character which, in turn, favours sorption of the hydrophobic dioxins. A second possibility is that because less water is clustered around the interlayer Cs<sup>+</sup> ions, direct interaction between the Cs ion and dioxin molecule is possible. We have provided evidence recently that in the case of DD sorption by smectite, the second mechanism is operative (Rana *et al.* 2009). A figure illustrating this complex is shown in Figure 2 where sorbed DD adopts a tilted arrangement with respect to the basal surface of the clay.



**Figure 2.** Schematic illustration of possible arrangement of DD molecule in smectite interlayer.

## Conclusion

The sorption of DD and 1CIDD on smectite was influenced by the enthalpy of hydration of the exchangeable cation and by clay type. Based on a comparison of DD and 1CIDD, sorption increased as the octanol water partition coefficients (*K<sub>ow</sub>*) increased. Vibrational spectroscopy revealed that site-specific interactions between DD and the interlayer cation occurred.

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