

Research Brief 183: Sequestration of Dioxin by Clays

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Background

On December 30, 2009, EPA's Office of Solid Waste and Emergency Response published draft preliminary remediation goals (PRGs) for dioxin TEQ in soil, requesting comments from the public. The draft interim PRGs of 72 parts per trillion (ppt) for residential uses and 950 ppt for commercial or industrial uses are considerably lower than the PRGs established in 1998 of 1,000 ppt and within the range of 5,000 and 20,000 ppt, respectively. EPA is also considering an alternative concentration of 3.7 ppt dioxin TEQ in residential soil and 17 ppt dioxin TEQ in commercial/industrial soil based on a cancer risk level of 10^{-6} .

The draft interim PRGs are intended to evaluate dioxin (TCDD) and other dioxin-like compounds, including PCDDs, PCDFs, and PCBs, which may collectively be evaluated using the recommended PRGs for dioxin after adjustment to account for relative toxicity using TEFs to calculate dioxin TEQ concentrations.

While EPA address the challenges of identifying appropriate PRGs for PCDDs ("dioxins") and PCDFs ("furans") in soils, Dr. Stephen Boyd at the Michigan State University SRP is investigating the chemical and physical mechanisms that influence the sorption of these compounds to soils. Dioxins have exceptionally low solubilities in water, and so in soils or sediments they occur bound (or sorbed) to some type of geosorbent - soil organic matter, naturally occurring char, or soil minerals such as clays. Although soil organic matter is generally considered the predominant sorptive compartment (geosorbent) for organic contaminants, recent research by Dr. Boyd and colleagues has shown that certain classes of organic contaminants have equal or greater affinities for clays. Additionally, naturally occurring clay deposits, commonly called "ball clays", are known to be contaminated with dioxins, suggesting clays as a natural repository or sink for environmental dioxins, and showing that dioxins and clays often occur together in the environment. Based on these considerations, and building on the simple fact that clays are far more prevalent, e.g. up to 50%, in soils, aquifer materials, and sediments compared to organic matter, which is often less than 1%, Dr Boyd is studying the contribution of clays to dioxin sequestration.

Smectite clay is a category of clay minerals. They have a planar three-layer crystalline structure (one alumina layer sandwiched between two silica layers), and swell when immersed in water, allowing contaminants to enter the interlayer spaces that are created.

Smectites carry a net negative charge that is neutralized by the presence of **exchangeable cations**.

Advances

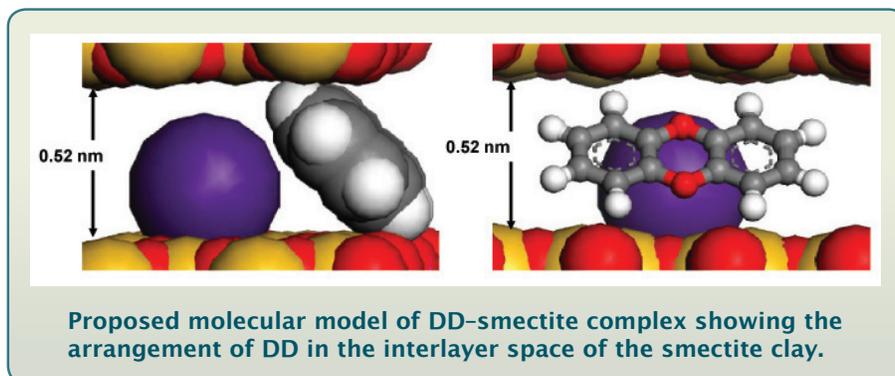
Dr. Boyd and co-workers recently found that one major category of clays, smectites, are highly effective adsorbents for dibenzo-p-dioxins (DD), retaining up to 1% sorbed DD. To understand the affinity of hydrophobic dioxins for hydrophilic smectites, the researchers first compared dioxin adsorption by clays containing different exchangeable cations (Cs^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Fe^{3+} , and Al^{3+}). Sorption was substantially affected by the exchangeable cation, with strong sorption by clays containing Cs^+ and K^+ as exchangeable cations. They determined that the exchangeable cations affect DD sorption by their:

- direct interaction with the DD molecules
- influence on the amount of exposed hydrophobic clay surface between exchangeable cations
- influence on the interlayer swelling.

The large differences in sorption induced by different exchangeable cations imply that: (1) the clay interlayer is an important sorption site; and (2) the clay itself - not organic matter associated with the clay - dominates the sorption of dioxins.

Dr. Boyd and his colleagues demonstrated that smectite clays with negative charges originating from tetrahedral Si-O layers displayed much higher adsorption capacity for DD than clays with charges originating from the octahedral Al-O layers. In tetrahedrally charged clays, the negative charge is spread over fewer surface oxygens, leaving larger clay surface domains unaffected by negative charge, hence more hydrophobic, and manifesting slightly smaller and more optimal interlayer spacings. These interlayer regions provide a sub-aqueous environment for sorbed dioxin, and dehydration of

the intercalated hydrophobic dioxin molecules is an energetically favorable process that helps drive sorption. In addition, favorable electrostatic interactions between the positively charged interlayer cation and the dioxin ring oxygens which possess negative charge character promotes sorption.



They also found that planar compounds show a higher affinity than non-planar or compounds that have bulky substituents, and that clay minerals show a much greater affinity for dioxins over PCBs.

As a next step in this investigation, Dr. Boyd is examining the bioavailability of dioxins bound to clay minerals, and has begun experiments to examine the effects of clay sequestration of dioxins on their availability to a mammalian model (mouse) and biodegradative bacteria.

Significance

The Boyd research team combined structural and sorption data with FTIR and Raman spectroscopy as well as molecular simulations to examine the molecular scale mechanisms and forces responsible for dioxin sequestration. This research has shown that clays may be as or more important than organic matter in the immobilization of dioxins in soils. Dioxins might be expected to accumulate in clay minerals, possibly with inherent selectivity for certain congeners. Such sequestration of dioxins in clay minerals would have important implications for Superfund site stewardship and for bioavailability of dioxins to bacteria and higher organisms.

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To learn more about this research, please refer to the following sources:

Liu, Cun, Hui Li, Brian J. Teppen, Cliff T. Johnston, and Stephen A. Boyd. 2009. Mechanisms associated with the high adsorption of dibenzo-p-dioxin from water by smectite clays. *Environmental Science & Technology* 43(8):2777-83. DOI:10.1021/es802381z

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