Investigating the Transport and Fate of Polychlorinated Biphenyls with Stable Chlorine Isotopes

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LONG-TERM GOALS

My long-term goal is to investigate and further understand the source, transport, and fate of semi-volatile halogenated organic contaminants (HOCs) in the marine and coastal environment. Such compounds include polychlorinated biphenyls (PCBs), 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT), and toxaphene. Of particular interest is the ability to apportion different sources even when environmental processes have selectively weathered these inputs. In addition, I hope to identify conditions that promote or hinder natural degradation processes that act on HOCs. These results will aid the US Navy in assessing their environmental remediation and responsibilities, especially relative to other polluters.

OBJECTIVES

My objective is to use novel isotopic measurements at the molecular level to gain insight into the behavior of semi-volatile HOCs in the environment. Similar approaches have been successively achieved with volatile HOCs, but little work has been done on semi-volatile HOCs, even though they are persistent, toxic, and can bioaccumulate into marine food webs. I hope to provide information that was previously unattainable with merely the molecular signatures of each contaminant.

APPROACH

In order to understand the isotopic characteristics of different semi-volatile HOCs in their pre-weathered state, numerous semi-volatile HOCs in neat form will be analyzed for both stable carbon and chlorine isotope ratios. The isotope ratios of these compounds should then only reflect their raw materials, synthesis and post-production handling. These data along with the results of laboratory and field studies will be used in apportioning different sources as well as identifying and understanding environmental weathering. “Real-world” sediments from New Bedford Harbor (MA) and San Diego Bay (CA) as well as samples from other locations have been targeted for such investigations. This work has been done mostly in my laboratory, but Dr. Neil Sturchio at the University of Illinois (Chicago) assists me in the stable chlorine isotope measurements. I have also been given sediments from Dr. Barbara Bergen at the United States Environmental Protection Agency (Narragansett, RI). Dr. Li Xu, Mr. Robert Nelson, and Mr. Nicholas Drenzek have all worked with me in my laboratory on various aspects of this project.

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14. ABSTRACT

My long-term goal is to investigate and further understand the source, transport, and fate of semi-volatile halogenated organic contaminants (HOCs) in the marine and coastal environment. Such compounds include polychlorinated biphenyls (PCBs), 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT), and toxaphene. Of particular interest is the ability to apportion different sources even when environmental processes have selectively weathered these inputs. In addition, I hope to identify conditions that promote or hinder natural degradation processes that act on HOCs. These results will aid the US Navy in assessing their environmental remediation and responsibilities, especially relative to other polluters.

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WORK COMPLETED

Over the past year, this grant has supported a variety of efforts in achieving the desired goals of the project, including laboratory experiments, fieldwork, presentation at a national meeting, and publication of the initial results.

To determine the isotopic characteristics of semi-volatile HOCs due only from their raw materials, synthesis and post-production handling (pre-weathering), we analyzed several different compounds for both stable carbon and chlorine isotopes. This study also included an extensive literature search on the reactions used to synthesize these compounds. The results of this work were presented at the American Chemical Society meeting in Chicago last August and a manuscript on this topic was recently accepted in the journal *Organic Geochemistry*. We published another manuscript in *Environmental Science and Pollution Research* on the intramolecular stable chlorine isotopic differences in DDT and the chlorine kinetic isotope effect associated with DDT dehydrochlorination to 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethene (DDE). Also in order to determine whether the stable chlorine isotopic composition of individual PCB congeners vary within a complex mixture of PCBs, my technician, Dr. Xu, and I have separated several PCB congeners by preparative capillary gas chromatography. Most of these samples have now been analyzed, and we are assembling a manuscript on these results.

In addition, we acquired over fifty sediment samples from New Bedford Harbor (MA). This area is severely impacted with PCBs and shows significant evidence of environmental weathering. Dr. Barbara Bergen kindly donated these sediments to me. One of my graduate students, Mr. Nicholas Drenzek, and I have extracted and isolated the PCBs from these samples. Laboratory-based experiments designed to investigate water washing of HOCs from sediments have also been initiated. Mr. Robert Nelson and I are using reversed-phase high performance liquid chromatography coupled to an ion trap mass spectrometer to mimic and determine the isotope effects from water washing.

Last spring, Mr. Drenzek and I went on a two-week research cruise aboard the R/V New Horizon. The objective of this National Science Foundation (NSF) sponsored cruise was to collect sediment samples along the Pacific coast of the United States in order to investigate inputs of terrestrial material to the coastal ocean. However, the chief scientist of the cruise, Dr. Timothy Eglinton (WHOI), allowed us to participate on the cruise and collect sediment near and around San Francisco Bay, San Diego Bay, and the Palos Verde Shelf. The latter location is west of greater Los Angeles, CA and is contaminated with DDT. We are beginning to process some of these samples.

Last, this grant provided support for me to review Chlorine in the Environment a book written by Ruth Stringer and Paul Johnson. This review will soon appear in the journal *Environmental Science and Pollution Research.*

RESULTS

The most significant technical results for this year are the studies on neat, pre-weathered semi-volatile HOCs, and here I will summarize the results from the stable chlorine isotope measurements. The following semi-volatile HOCs were analyzed for their stable chlorine isotopic composition (δ^{37}Cl): Aroclors 1016, 1242, 1254, 1260, and 1268 as well as aldrin, γ-chlordene, chlordane, DDT, dieldrin, hexachlorocyclopentadiene, heptachlor, γ-lindane, mirex and toxaphene. [With the exception of Aroclor 1016, which is ~41% chlorine by mass, the last two digits of each Aroclor represent the approximate percentage of chlorine, by mass, in these mixtures of PCBs that were produced and sold in the U.S.]. Two additional PCBs mixtures from Europe, Phenoclor DP-6 and Clophen A60, were also analyzed.

The δ^{37}Cl values of the HOCs ranged from -5.10 to +1.22‰ (Figure 1) and are within the previously reported distribution for other chlorinated organic compounds (Tanaka and Rye, 1991; van Warmerdam *et al.*, 1995; Holt *et al.*, 1997; Jendrzejewski *et al.*, 1997; Reddy *et al.,* 2000, 2001). Two different lots of toxaphene had the most depleted δ^{37}Cl values of -5.10 and -4.21‰. Both pure *p,p'*- and technical grade DDT were slightly enriched in ^{37}Cl relative to toxaphene, with values of –4.34 and -3.49‰ respectively. All of the other HOCs measured in this study (γ-lindane, heptachlor, γ-chlordene, dieldrin, aldrin, mirex, and hexachlorocyclopentadiene) had chlorine isotopic compositions that fell between chlordane and the Aroclors.

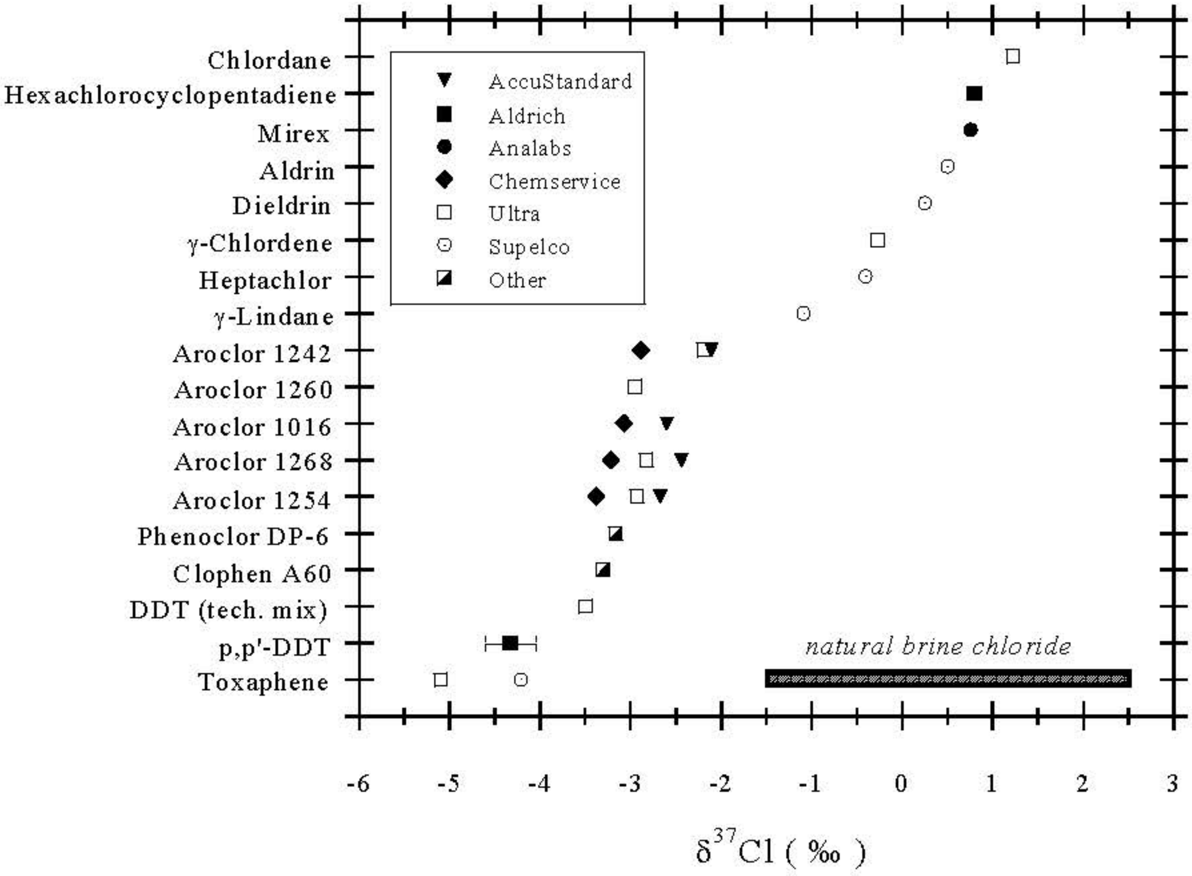

Figure 1. δ^{37}Cl values for the HOCs measured in this study.
[The δ^{37}Cl values of the HOCs range from -5.1 to +1.2‰, while brine ranges from –1.5 to 2.5‰]

At this time, we cannot unequivocally explain the variability in the δ^{37}Cl values of the chlorinated HOCs. Differences in the starting materials or from the synthesis, purification, or post-production storage and handling of the products (or some combination of these factors) may be responsible. However, when considering the isotopic compositions in the context of the chemical reactions involved in their synthesis, there is an observable correlation between the synthetic pathway and δ^{37}Cl values, suggesting that post-production effects were minimal. From a chlorine perspective, it is notable that heptachlor, •-chlordene, dieldrin, aldrin, and chlordane constitute the most enriched samples in this study (-0.40 to +1.22 ‰) and were each synthesized via Diels-Alder reactions using hexachlorocyclopentadiene as a substrate. Mirex, which is also relatively enriched (+0.75 ‰), is formed upon the condensation of two hexachlorocyclopentadiene molecules. It is unlikely that Diels-Alder or condensation reactions would produce a chlorine isotope effect because carbon-chlorine bonds are neither broken nor formed in these processes. Thus, these compounds likely exhibit chlorine isotopic compositions that directly reflect that of their common precursor, hexachlorocyclopentadiene. This is consistent with the δ^{37}Cl value observed in a sample of hexachlorocyclopentadiene that we analyzed (+0.78 ‰). Hexachlorocyclopentadiene is commonly synthesized from the chlorination of cyclopentadiene from sodium hypochlorite (NaOCl), which is generated from the reaction of Cl_2 gas with water in the presence of base (Atkins, 1998). Brine exhibits an isotopic composition of –1.5 to +2.5 ‰ (Long *et al*., 1993), a range which is analogous to that observed for the Diels-Alder-product HOCs measured here. It should also be noted that incomplete yields, substrate recycling, and synthesis via batch processes have the potential to introduce apparent fractionations or impart distinctly different isotopic compositions between batches and/or isomers of technical mixtures. However, we provide evidence here for the maintenance of isotopic consistency throughout the synthesis of these particular compounds. Hence, post-production effects appear to play at most a subordinate role in determining isotopic compositions, as might be expected considering their semi-volatile nature. This may prove advantageous in isotopic tracing studies, in contrast to more volatile contaminants (such as trichloroethylene, 1,1,1-trichloroethane, perchloroethylene and dichloromethane) in which potentially large post-production evaporative fractionations may introduce a relatively wide degree of uncertainty in their initial isotopic compositions (van Warmerdam *et al*., 1995; Beneteau *et al*., 1999; Jendrzejewski *et al*., 2001).

More depleted chlorine isotopic compositions were seen in compounds whose synthesis involved a chlorination step. In these reactions, differences in activation energies associated with the scission of the ^{37}Cl-^{35}Cl bond versus the ^{35}Cl-^{35}Cl bond most likely produce an isotope effect. For example, Aroclor mixtures were synthesized by chlorine substitution onto the biphenyl ring in the presence of a ferric chloride catalyst (Wade, 1995; Erikson, 1997). Electrophilic substitution reactions producing halogenated, conjugated systems (e.g. PCBs) have rate limiting steps at the sigma complex formation producing products that are relatively depleted in ^{37}Cl with respect to the source, presumed to be brine-derived Cl_2 gas.

IMPACT/APPLICATIONS

The semi-volatile HOCs measured in this study exhibit a defined range of chlorine isotopic compositions that appear to correlate with the chemical pathway by which they were synthesized. This observation suggests that post-production processes such as purification, evaporative loss, and storage have a negligible influence on their isotopic compositions. Unlike volatile HOCs, therefore, the integrity of these initial compositions may be preserved, providing a well-constrained signature against which environmental samples can be compared.

TRANSITIONS

None recognized at this time.

RELATED PROJECTS

This project nicely meshes with USEPA and ONR sponsored research that focuses on isotope effects associated with microbial reductive dechlorination of PCBs. This work is being done in collaboration with Drs. Harold May (Medical University of South Carolina) and Kevin Sowers (University of Maryland), both of whom are funded by ONR to study these reactions. I am also investigating reactions that may occur between HOCs and the natural organic matter that is present in soils and sediments; the National Science Foundation funds this work.

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