

Reddy C.M., Drenzek N.J., Eglinton T.I., Heraty L.J., Sturchio N.C. and Shiner V.J., *Stable chlorine intramolecular kinetic isotope effects from the abiotic dehydrochlorination of DDT*, Environmental Science and Pollution Research, 2002; v9, 183-186

INTENTION, GOAL, SCOPE, BACKGROUND: Identifying different sources and following reaction pathways of chlorinated organic contaminants in the environment can be challenging, especially when only their concentrations are available. Compound-specific stable chlorine measurements of some contaminants have recently been shown to provide additional information and an increased understanding of their biogeochemistry. These studies, however, have been generally limited to volatile molecules. **OBJECTIVE:** Here, the stable chlorine isotope ratios of the semi-volatile pesticide, 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT) were investigated. Specifically, the intramolecular stable chlorine isotopic compositions of DDT and the kinetic isotope effect (KIE) for the abiotic dehydrochlorination of DDT to 2,2-bis(p-chlorophenyl)-1,1-dichloroethene (DDE) were determined. **METHODS:** Selective chemical oxidation of DDT to dichlorobenzophenone (DCBP) and analysis of each compound was used to calculate the stable chlorine isotope ratios of the alkyl and aromatic chlorines in DDT. To determine the KIE for dehydrochlorination, DDT was reacted in a basic solution to yield DDE at 52 degrees C, 60 degrees C, and 72 degrees C for 3, 5, and 5 days, respectively. **RESULTS AND DISCUSSION:** Significant intramolecular stable chlorine isotopic differences were observed in one sample of DDT where the alkyl and aromatic $\delta^{37}\text{Cl}$ values were -5.76 ± 0.45 and $-2.21 \pm 0.24\%$ @1000, respectively. Dehydrochlorination of DDT to DDE in basic solutions at 52, 60, and 70 degrees C resulted in a substantial intramolecular KIE where the alkyl chlorines of DDE shifted by approximately 3%@1000 relative to the alkyl chlorines in DDT. However, no temperature dependence was observed. The KIE, calculated by an iterative program, was 1.009. **CONCLUSIONS:** Intramolecular differences in the stable chlorine isotope ratios were observed in DDT and this is the first such finding. Dehydrochlorination of DDT yields a measurable and distinct intramolecular stable chlorine KIE. **RECOMMENDATION AND OUTLOOK:** The results of this study demonstrate the existence of significant intramolecular differences in chlorinated organic compounds. Many other chlorinated semi-volatile and volatile organic contaminants are synthesized from multiple sources of chlorine, and we recommend that similar studies be performed on many such molecules in order to attain a clear understanding of their intramolecular chlorine isotopic differences. The existence of a measurable KIE for the dehydrochlorination of DDT to DDE shows the potential strength of using isotopic measurements to investigate the biogeochemistry of these important compounds. For example, the isotopically depleted aqueous chloride produced by dehydrochlorination of DDT to DDE may be a useful tracer of these reactions in freshwater environments.