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### Introductory Note

# Compound-specific isotope analysis: tracing organic contaminant sources and processes in geochemical systems

Compound-specific isotope analysis (CSIA) is quickly changing the face of earth and environmental sciences. The types of questions now being routinely asked and answered by geochemists using CSIA were only in their wish lists a decade ago. Specifically, CSIA is facilitating the application of isotopic analysis at much finer spatial and temporal scales than ever before possible, and opening up detailed isotopic investigation of a whole new range of organic compounds typically present at part per million to part per billion levels in the subsurface. The impact of CSIA is felt most in biogeochemical and environmental research, which are fields undergoing tremendous evolution. Basic and applied questions pertaining to pollutant fate and transport in near-surface environments continue to demand more definitive methods of investigation. Gas and liquid chromatography are among the time-tested instruments utilized in biogeochemical investigations. The marriage of these techniques with high-precision stable isotope mass spectrometry has resulted in the critical ability to trace the sources and pathways of a wide variety of natural and anthropogenic organic compounds.

This special issue of *Organic Geochemistry* explores the common theme of using CSIA for elucidating the sources and fate of organic compounds in surface and groundwater systems. The thirteen papers in this volume examine isotope fractionation in experimental systems (with and without pure microbial strains or soil microcosms) and at field sites. All of these studies pertain to anthropogenic organic contaminants, defined broadly to include processed and unprocessed petroleum hydrocarbons. This collection of papers represents a snapshot of this fast-evolving field. Our hope is that these papers reflect the current state of understanding of compound-specific isotope biogeochemistry of organic contaminants. There is a limited amount of such information, but more will likely emerge in the next few years. If some of the work presented here motivates others to examine or re-examine any of the sys-

tems discussed, then this treatise will have fulfilled one of its goals.

The papers are organized into four basic themes. The first two papers (Harris et al. and Beneteau et al.) focus on the analytical requirements of compound-specific carbon isotope analysis. Harris et al. test the veracity of compound-specific carbon isotope analysis of gasoline range hydrocarbons prepared by solid phase microextraction (SPME) (cf. Dayan et al.). They conclude that SPME is a more efficient technique to couple with CSIA than purge-and-trap methods. However, they observed non-systematic enrichments and depletions of  $\pm 0.2$  to 2.0‰ whose origin remains to be fully elucidated. Beneteau et al. perform similar tests on halogenated compounds extracted with a purge-and-trap apparatus, where they showed reproducibility of  $\pm 0.9\%$  and  $\pm 0.4\%$  for  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$ , respectively. Whereas these reproducibilities are higher than those observed for straight headspace analyses of halogenated solvents, Beneteau et al. make the point that these reproducibilities are nonetheless small compared to typical variations observed among numerous solvent manufacturers. A similar large variation of  $\delta^{13}\text{C}$  values in hydrocarbons is observed by Harrington et al. (below).

The second group of papers includes contributions by Dayan et al., Harrington et al., Huang et al., and Jackson and Pardue, that deal primarily with the physical fractionation of C and Cl isotopes in experimental or analytical systems. Dayan et al. examine carbon isotope fractionation accompanying reductive dehalogenation of chlorinated ethenes by metallic iron. This process involves the successive replacement of Cl by H in chloroethenes, which when carried to completion can lead to the formation of ethene. These authors show that dramatic fractionation of carbon isotopes accompanies reductive dehalogenation, and the calculated fractionation factors,  $\alpha$ , could be useful in quantifying engineered zero-valent remediation. Harrington et al. and Huang et al. examine isotope

fractionation accompanying volatilization of monoaromatic hydrocarbons and chlorinated aliphatic hydrocarbons, respectively. In the work of Harrington et al., 'equilibrium' vapor-liquid  $\alpha$  values measured during volatilization of benzene, toluene and ethyl benzene were all +0.2%. This  $\alpha$  value implies that at large volatile/liquid ratios resulting from substantial evaporation, measurable depletion (several ‰) in  $^{13}\text{C}$  of residual BTEX compounds will result. Harrington et al. further suggest that carbon isotope fractionation accompanying adsorption should be comparable to that accompanying evaporation. Huang et al. evaporated trichloroethene and dichloromethane and measured carbon isotope fractionation consistent in both magnitude and direction with that reported by Harrington et al. Huang et al. measured up to 3.5% depletion in residual  $^{13}\text{C}$  after greater than 99% evaporation. Even larger isotope fractionation was shown for chlorine, but with depletion of the lighter isotope ( $^{35}\text{Cl}$ ) in the residue, in Huang et al.'s experiments. A reasonable conclusion to draw from this set of papers is that while physical fractionation of carbon and chlorine isotopes may be small under vapor/liquid equilibrium conditions, such isotopic fractionation may be magnified at large degrees of evaporation. Such potential Rayleigh reservoir effects must therefore be taken into account in natural or engineered systems. Nevertheless, it is evident that there is ample need for additional experiments that can further clarify the systematic isotopic fractionation resulting from a wide range of physical processes potentially affecting many common organic contaminants in surface and subsurface systems. Finally, Jackson and Pardue addressed the issue of physical mixing of  $\text{CO}_2$  derived from hydrocarbon degradation and that derived from 'background' production (i.e., from indigenous organic matter). They showed consistency between stable isotope measurements ( $\delta^{13}\text{C}$ ) and the more expensive  $^{14}\text{C}$  labeling experiments both in terms of estimated total mineralization and mineralization rates.

The next set of papers examines biological fractionation of C and Cl isotopes in pure cultures (Heraty et al. and Hall et al.) and microbial consortia (Sherwood Lollar et al. and Stehmeier et al.). Heraty et al. show that both  $^{13}\text{C}$  and  $^{37}\text{Cl}$  isotope are enriched in residual dichloromethane during aerobic microbial degradation by the pure microbial strain MC8b. The magnitude of carbon isotope fractionation is much larger than the corresponding chlorine isotope fractionation. Interestingly, the volatilization experiments performed by Huang et al. on dichloromethane shows similar direction and magnitude of fractionation for chlorine but not for carbon. Hence, Huang et al. offer the suggestion that, under certain circumstances, physical and microbial fractionation can be readily distinguished. Hall et al. provides experimental data on carbon iso-

tope mass balance during the degradation of phenol and benzoate in pure cultures. They report  $\Delta^{13}\text{C}$  between the organic substrate and produced  $\text{CO}_2$ , and offer possible physiological controls on the differences in observed fractionation. These authors emphasize the need for similar experiments on other microbial systems and organic substrates to elucidate the origin of isotopic fractionations. Sherwood-Lollar et al. performed experiments on microbial consortia, and showed contrasting behavior between anaerobic trichloroethene degradation and aerobic toluene degradation. They show  $^{13}\text{C}$  enrichment in residual trichloroethene, but no resolvable carbon isotope fractionation associated with aerobic toluene degradation. Sherwood Lollar et al. suggest the utilization of CSIA for monitoring in-situ bioremediation of trichloroethene. The results they present for toluene suggest that a similar application of compound-specific carbon isotope monitoring of bioremediation is less likely to be successful, noting, however, that other groups have shown measurable carbon isotopic fractionation associated with aerobic biodegradation of monoaromatic compounds. One such study is reported by Stehmeier et al., where they show rather small  $^{13}\text{C}$  enrichment in residual benzene during aerobic biodegradation. Whereas it is clear that more experiments are required to establish the governing controls on carbon isotopic fractionation, it is useful to point out that aromatic hydrocarbons, in contrast to aliphatic hydrocarbons, are generally less efficiently assimilated by microbial organisms. One interesting focus of future experiments is the examination of the impact of intra and extra-cellular processes on isotopic fractionation.

The application of CSIA to actual field problems is limited not only by a present incomplete understanding of the isotope systematics, but perhaps more so by the complexity of real biogeochemical systems. The paper by Stehmeier et al. opens the final group of papers dealing with field applications of compound-specific carbon isotope measurements. Stehmeier et al. suggest that carbon isotopic fractionation consistent with biodegradation is generally observed in the shallow and surface hydrocarbon-contaminated field sites that they examined. Nevertheless, their work also highlights the multiplicity of other factors that may complicate carbon isotopic fractionation in realistic field situations, thus requiring some caution in applying results of controlled laboratory experiments to the field. This point is also reinforced in the tetrachloroethene release site studied by Beneteau et al., where variation in the  $\delta^{13}\text{C}$  value of tetrachloroethene was noted in spite of the lack of evidence for biodegradation. Bergamaschi et al. used compound-specific  $\delta^{13}\text{C}$  measurements to examine the possible contributors to trihalomethanes (THM) in waters draining agricultural fields. They conclude that specific contribution of *maize* to the

THM carbon can be discerned with  $\delta^{13}\text{C}$  measurements, but proceeded to caution that diagenetic effects may preclude the direct use of isotopic mixing models in determining THM sources. Conrad et al. examine gasoline range organic compounds in a shallow plume of aviation gas (AVGAS) believed to be undergoing intrinsic bioremediation. They coupled compound-specific  $\delta^{13}\text{C}$  and  $\delta\text{D}$  measurements of  $\text{CH}_4$  and  $\text{CO}_2$  with  $^{14}\text{C}$  measurements to show that AVGAS biodegradation was taking place on the aerobic fringes of the plume. In contrast, similar data collected in the central portion of the plume indicate a dominantly methanogenic origin for  $\text{CH}_4$  and  $\text{CO}_2$ . In the final paper in this special issue, Rowe and Muehlenbachs show that compound-specific  $\delta^{13}\text{C}$  ‘fingerprints’ of C1 to C4 hydrocarbons could be used to determine their mode of formation at depth. They also show that these ‘fingerprints’ could be used ingeniously to identify depth of origin of gas leaks in heavy oil wells, thereby allowing delineation of target depths for remediation.

The papers included in this special issue make it apparent that much remains to be done to make fuller use of compound-specific isotope tracers in determining organic contaminant sources and processes. The future is therefore both tortuous and exciting, especially with the added vectors being provided by compound-specific hydrogen, nitrogen, and chlorine

isotope capabilities. The challenge is to continue to build a systematic foundation from experimental work, yet to remain fully cognizant of the complexities of actual field situations. As with any tool applied to environmental research, there should always be a recognition by practitioners of isotope geochemistry that, at best, we may hold a small piece to a grand environmental puzzle. Isotopic measurements are most useful when used in tandem with careful field observations and other geochemical, geophysical and geological constraints.

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