

Headspace Analysis: A New Application for Isotopic Characterization of Dissolved Organic Contaminants

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Petroleum products and industrial solvents are among the most ubiquitous contaminants of soil and groundwater and the source of several common and hazardous volatile organic chemicals (VOCs). Volatilization is a key determinant of the fate of VOCs in the subsurface environment, impacting contaminant partitioning between the aqueous, gaseous, and nonaqueous liquid phases. This study uses stable carbon isotope analysis to investigate the isotopic effects involved in volatilization of trichloroethylene (TCE) and toluene from both free product (or pure phase) and aqueous solutions. Results indicate that, during volatilization from the aqueous phase and from free product, the isotopic composition of TCE and toluene remains unchanged within reproducibility limits. These results have two important implications for contaminant hydrogeology. First, they suggest that carbon isotopic signatures may be useful in tracking contaminant transport between the vapor, aqueous, and NAPL phases since they remain conservative during phase changes. Second, they demonstrate the utility of headspace extraction (sampling of the vapor phase or headspace above an aqueous solution) as a preparatory technique for isotopic analysis of dissolved VOCs. Headspace isotopic analysis provides a straightforward and rapid technique for $\delta^{13}\text{C}$ analysis of dissolved organic contaminants at concentrations as low as hundreds of ppb.

Introduction

Volatile organic chemicals (VOCs) are characterized as having boiling points less than 160 °C, vapor pressures exceeding 500 Pa, and relatively low solubilities in water (usually less than 10 g/L) (1). Originating from intentional disposal or accidental release of petroleum products and halogenated hydrocarbon solvents, VOCs are among the most prevalent class of compounds found in both the unsaturated and saturated zone underlying contaminated sites throughout the industrialized world (2, 3). Several VOCs, such as trichloroethylene (TCE), pose a serious threat to human health and have aqueous solubilities that exceed their drinking water limits by several orders of magnitude.

Subsurface contamination by VOCs can be described as a three-phase multicomponent flow and transport process,

ultimately controlled by the physicochemical properties of the chemical and the properties of the subsurface materials or environment (4, 5). In the saturated zone, advection and dispersion are largely responsible for the creation of a VOC plume, while sorption and degradation are the primary processes of attenuation. In contrast, current understanding of contaminant transport and transformation in the unsaturated zone is less well developed. In particular, the impact of abiotic processes of volatilization and gas–liquid partitioning in porous media is particularly difficult to constrain due to the complex dynamics and variable environmental conditions controlling contaminant vapor behavior at actual field sites (3, 6–11). The rate and extent of contaminant volatilization is not only affected by properties of the chemical (i.e., vapor pressure) and the geologic media (i.e., porosity) but also by climatic variations such as rainfall and evapotranspiration. Furthermore, contaminant transport mechanisms such as diffusion, dispersion, and convection are influenced by moisture content variations with depth and time (8, 9).

The role of gaseous transport of VOCs in the unsaturated zone is much debated. Sleep and Sykes modeled the transport of VOCs in variably saturated media and concluded that volatilization was an important process, perhaps more important than dissolution, in dissipating residual amounts of volatile organics immobile in the unsaturated zone (3). Similarly, Cho and Jaffe (7) and Ostendorf and Kampbell (12) studied the dynamics of VOC behavior in unsaturated soils (focusing on TCE and residual aviation gasoline respectively) and found that volatilization was an important long-term transport mechanism. In contrast, at other sites the influence of volatilization on unsaturated zone transport has been found to be relatively minor as compared to mass loss due to biodegradation, illustrating the site-specific nature of its role in the subsurface (13, 14). Similarly, volatilization of BTEX from the saturated zone has not been identified as a significant means of mass loss (15, 16), although it is recognized that gas exchange can occur rapidly at the water table interface (17). In warm and dry environments, volatilization may play a more important role in contaminant transport. Vapor can escape upward by diffusion, and if there is an impervious layer above ground (i.e., a road), the vapor can laterally migrate relatively long distances (8, 18). Clearly, constraining the relative importance of volatilization, biodegradation, sorption, and hydrodynamic processes remains a significant challenge in hydrogeologic site assessment.

Stable carbon isotope analysis is an emerging technique with significant potential for tracing contaminants and elucidating the processes controlling their fate and transport in hydrogeologic environments. Hydrocarbons commonly enter the subsurface with a distinct isotopic composition, or $^{13}\text{C}/^{12}\text{C}$ ratio, characteristic of their source. The variations in isotopic composition of free product chlorinated ethenes and BTEX compounds originating from different sources have been found to be on the order of several per mil (19, 20). In situations where these isotopic compositions of a given carbon contaminant are conserved, isotopic analysis may be used to identify their source. In contrast, in situations where isotopic signatures are altered by subsurface processes acting on the compounds of interest, valuable information about attenuation processes, such as abiotic or biotic degradation, may be obtained. To date, most isotopic investigations involving contaminated field sites have focused on biotic degradation processes and, through $\delta^{13}\text{C}$ measurements of soil CO_2 and dissolved inorganic carbon (DIC), on

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distinguishing the relative contributions to the subsurface CO₂ pool from degradation of organic contaminants versus respiration of natural soil organic matter (21–23). Recently, however, a number of researchers have developed techniques to measure the $\delta^{13}\text{C}$ values of dissolved contaminants directly through continuous-flow compound-specific isotope analysis (CSIA) (19, 24, 25). CSIA is the key to routine application of $\delta^{13}\text{C}$ analysis to dissolved organic contaminants at ppm to ppb levels in groundwater and provides a rapid, sensitive, and efficient means of using isotopic signatures to define subsurface processes.

This paper describes a new application of CSIA to the isotopic characterization of volatile organic compounds. The isotope dynamics of VOC volatilization from the dissolved phase and from free product are investigated in a series of laboratory experiments. The results have important implications for using isotopes to identify and monitor processes controlling the fate and transport of dissolved VOCs. Furthermore, this study demonstrates that headspace extraction (removal of the vapor phase above an aqueous solution) is a simple and rapid preparatory technique for isotopic analysis of VOCs from contaminated groundwater. Headspace analysis has been successfully used as an extraction technique for quantitative analysis of dissolved alkanes (26), but to our knowledge this is the first demonstration of its applicability to isotopic analysis of dissolved organic solvents.

Experimental Approach

Experimental Design. Two different volatilization experiments were performed for two common and hazardous groundwater contaminants—trichloroethylene (TCE) and toluene. The first experiment was designed to determine if carbon isotope fractionation occurred during solvent volatilization from free product. The second experiment was designed to examine if carbon isotope fractionation occurred during volatilization of dissolved solvents from the aqueous phase.

Isotopic analysis of solvent vapor and liquid was performed by gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS). The University of Toronto GC/C/IRMS consists of a Varian 3400 gas chromatograph interfaced with a microcombustion furnace in line with a Finnigan MAT 252 gas source isotope ratio mass spectrometer. After separation and elution of individual organic compounds from the GC, each compound is individually combusted to CO₂. The isotope ratio mass spectrometer provides real time measurement of the $^{13}\text{C}/^{12}\text{C}$ ratio in each CO₂ peak and uses an external CO₂ reference gas to obtain highly precise isotopic compositions, or $\delta^{13}\text{C}$ values, for each carbon compound. The $\delta^{13}\text{C}$ value for a carbon compound is expressed as:

$$\delta^{13}\text{C} \text{ ‰} = 1000 \left[\left(\frac{^{13}\text{C}/^{12}\text{C}}{\text{sample}} \right) / \left(\frac{^{13}\text{C}/^{12}\text{C}}{\text{std}} \right) - 1 \right]$$

The GC column used for toluene analysis is a 30 m × 0.25 mm i.d. Bentone 34 di-*n*-decyl phthalate fused-silica SCOT capillary column. TCE analyses were performed using a 30 m × 0.25 mm i.d. DB-624 capillary column. A range of split settings on the split/splitless injector was required to control the moles of carbon entering the system and to avoid oversaturating the source. While internal reproducibility based on triplicate sample injections is generally between 0.1 and 0.3‰, differences between samples (error bars) are assigned a value of no less than 0.5‰ to incorporate not only variation due to reproducibility but variation due to different split settings.

Free Product Volatilization Experiments. Free product volatilization experiments were performed for both TCE and toluene. For each experiment, a series of six 150-mL glass serum vials containing an equal amount of solvent was

prepared. Before adding the solvent, each vial was flushed for 3 min with helium gas. A microliter aliquot of solvent was then added via syringe, and the vial was quickly capped with a Mininert valve then slightly overpressurized with helium. This overpressurization was to ensure that no leakage occurred during sampling and that sampling did not underpressurize the vial, as this has been observed to cause isotopic fractionation of volatile hydrocarbons such as methane. Because of the relatively small volume of He injected (3 cm³) and the large headspace volume (~160 mL for free product experiments and 80 mL for aqueous experiments), this overpressurization should not significantly affect the extent of volatilization in the vials. Over a time period of 24 h during which the vials were quiescent, each vial was sampled sacrificially at a specific time ($t = 0, 1, 2, 4, 8,$ and 24 h). Sampling a vial involved analysis of both phases in the vial, i.e., removal of an aliquot of the vapor phase for isotopic analysis followed by removal of an aliquot of free product for isotopic analysis (see specifics for each experiment below). In this way, any $\delta^{13}\text{C}$ changes due to solvent volatilization could be monitored by measuring temporal changes in $\delta^{13}\text{C}$ values of both the vapor and the NAPL phases. It was previously determined that variability in $\delta^{13}\text{C}$ values of vapor and free product from a series of replicate vials was always less than analytical reproducibility (<0.5‰).

The toluene free product volatilization test involved the addition of 270 μL of toluene to the base of each 150-mL vial, approximately 10 times the volume of free product required to saturate the vial headspace. At each sampling interval, 100 μL of vapor was removed from the vial through the Mininert septum using a 500- or 1000- μL gastight syringe. Vapor samples were run on the GC/C/IRMS split/splitless injector set at a split of 100:1. For free product analysis, 0.4 μL of toluene was removed from the vial, and analyses were performed at a split setting of 1000:1. Both vapor and free product analyses were performed at an isothermal setting of 90 °C.

The TCE free product volatilization test was performed by adding 0.6 mL of TCE to the base of each 150-mL vial, approximately 10 times the volume of free product required to saturate the vial headspace. At each sampling interval, 300 μL of vapor was removed from the vial through the Mininert septum using a 500- or 1000- μL gastight syringe and analyzed on the GC/C/IRMS system at a split setting of 10:1. For free product analysis, 0.2 μL of TCE was removed from the vial and run on the GC/C/IRMS split/splitless injector at a setting of 500:1. Both vapor and free product samples were run with a temperature program of 40 °C for 6 min followed by an increase to 70 °C and a holding time of 7 min.

Dissolved Phase Volatilization Experiments. The free product experiments described above were designed to investigate any potential isotope effects involved in NAPL volatilization, a common transfer process for VOCs trapped in the unsaturated zone. Volatilization of dissolved VOCs from water trapped in the unsaturated zone or from the water table can also be a significant pathway of movement in the subsurface. To investigate isotope effects involved in the water–gas phase change, separate dissolved phase volatilization experiments were performed for both TCE and toluene. In addition, because preparation of aqueous samples involved dissolution of TCE and toluene, these experiments provided a check on isotopic effects associated with dissolution of these VOCs from free product phases.

For each solvent, a time series of six glass serum vials was filled with an equal amount of distilled water, and the remaining headspace was flushed with helium. After being flushed, a microliter aliquot of solvent was added to the water via syringe to achieve the desired aqueous concentration.

Each vial was quickly capped with a Mininert valve or PTFE/silicone septum and then overpressurized with helium. Over a time period of 24 h, each vial was sampled sacrificially at a specific time ($t = 0, 1, 2, 4, 8,$ and 24 h). Sampling a vial involved analysis of both phases in the vial, i.e., removal of an aliquot of the vapor phase for isotopic analysis followed by pentane extraction of the aqueous phase preparatory to isotopic analysis. In this way, any $\delta^{13}\text{C}$ changes due to solvent volatilization could be monitored by measuring temporal changes in $\delta^{13}\text{C}$ values of both the vapor and aqueous phases. The volatilization experiment was repeated for each solvent at two different aqueous concentrations to test contaminant behavior at a range of dissolved concentrations typical of highly contaminated field environments.

The toluene experiments were performed at dissolved concentrations of 100 and 5 ppm. The vapor evolved from the 100 ppm toluene solution was extracted with a 500- or 100- μL gastight syringe inserted through the septum of the Mininert valve and was analyzed using a split of 100:1 and an injection volume of 300 μL . The vapor from the 5 ppm toluene solution was analyzed using a split of 6:1 and an injection volume of 200 μL . As for the free product experiments, vapor analyses were run at an isothermal setting of 90 $^{\circ}\text{C}$.

The dissolved TCE tests were performed using TCE solutions of two different concentrations—25 and 5 ppm. After sealing each vial with a PTFE/silicone septum, vapor evolved from the 25 ppm TCE solution was extracted with a gastight syringe injected through the PTFE/silicone septum and analyzed using a split of 10:1 and sample size of 300 μL . Vapor from the 5 ppm TCE solution was analyzed using a sample size of 1000 μL and a split setting of 10:1.

Isotopic analysis of dissolved phase toluene required a preparatory pentane extraction step prior to injection into the GC/C/IRMS. The aqueous phase was transferred to a 30-mL glass serum vial and crimp-sealed with no headspace using a PTFE/silicone septum. Pentane extraction at a water: pentane ratio of 20:1 was performed to extract and concentrate the organics in the pentane phase after the technique of Dempster et al. (19). After extraction, a microliter aliquot (0.6 μL for 100 ppm samples, 3 μL for 5 ppm samples) of the pentane-toluene organic layer was removed for injection into the GC/C/IRMS. A split setting of 6:1 and a temperature program of 40 $^{\circ}\text{C}$ for 4 min followed by an increase to 90 $^{\circ}\text{C}$ and a holding time of 10 min was used for isotopic analysis. As for toluene, pentane extraction of aqueous phase TCE was required prior to isotopic analysis of dissolved phase TCE. A water: pentane ratio of 100:1 was used for the 25 ppm TCE solution, and a water: pentane ratio of 400:1 was used for the 5 ppm TCE solution. After pentane extraction, an aliquot of the pentane-TCE layer was removed via syringe for injection into the GC/C/IRMS; 2 μL was removed from the 25 ppm solution and 5 μL was removed from the 5 ppm solution. All TCE analyses in the dissolved phase experiments used a temperature program of 40 $^{\circ}\text{C}$ for 6 min followed by an increase to 70 $^{\circ}\text{C}$ and a holding time of 7 min.

Optimization of Headspace Analysis for Isotopic Analysis of Trace Level (ppb) Dissolved Contaminants. A series of experiments was carried out to optimize the partitioning of the dissolved VOCs into the headspace of the vials and, thus, to maximize the sensitivity of isotopic characterization by headspace analysis. Optimization of the partitioning of the VOCs into the headspace was achieved by the following four steps. First, large liquid-to-headspace ratios were used to ensure equilibration. Second, the samples were saturated with NaCl in order to increase the ionic strength of the solution, thereby reducing the solubility of the VOCs and driving them into the headspace. Third, the samples were heated to 60 $^{\circ}\text{C}$ for a minimum of 1 h to further reduce VOC solubility and drive the VOCs into the headspace. Finally,

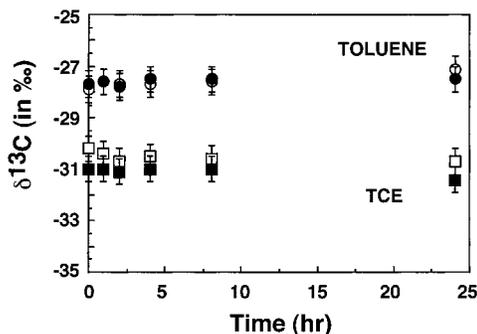


FIGURE 1. $\delta^{13}\text{C}$ values for vapor phase TCE and toluene and $\delta^{13}\text{C}$ values for free product TCE and toluene plotted against time. Vapor $\delta^{13}\text{C}$ values are shown in open symbols, and free product $\delta^{13}\text{C}$ values are shown in closed symbols. The $\delta^{13}\text{C}$ values for vapor and free product TCE and toluene are identical within reproducibility over the 24-h time series of the experiment. Error bars represent 0.5‰ accuracy and reproducibility.

the samples were hand shaken vigorously for 5 min after heating in order to increase NaCl dissolution and strip more of the gas into the headspace of the vial.

Results and Discussion

TCE and Toluene Volatilization Experiments. Results show that volatilization of toluene free product causes no significant fractionation of stable carbon isotopic signatures. As demonstrated in Figure 1, the $\delta^{13}\text{C}$ values of toluene free product are identical to the $\delta^{13}\text{C}$ values of vapor phase toluene within a routine accuracy and reproducibility of 0.5‰ (shown by error bars). Over the 24-h time period of the test, no temporal trends are discernible for toluene, and one phase is not consistently more enriched or depleted than another. Volatilization of TCE free product, however, seems to have a small isotope effect associated with it. Although vapor and liquid TCE $\delta^{13}\text{C}$ values are still identical within reproducibility (0.5‰) as shown in Figure 1, vapor TCE $\delta^{13}\text{C}$ values are consistently about 0.3–0.8‰ more enriched in ^{13}C than $\delta^{13}\text{C}$ values obtained in the liquid phase. Such an inverse isotope effect has been observed for other organic molecules (27, 28) but has yet to be successfully explained.

Experimental results also demonstrate that volatilization of TCE and toluene from the dissolved phase is an isotopically conservative (i.e., nonfractionating) process. Figure 2 shows that the $\delta^{13}\text{C}$ values for dissolved phase toluene and TCE and the vapor phases formed from these solutions are also identical within an accuracy and reproducibility of 0.5‰ over the 24-h time period of the test. Interestingly, unlike the free product results (Figure 1), $\delta^{13}\text{C}$ values for TCE vapor are not consistently more enriched than the dissolved TCE $\delta^{13}\text{C}$ values. A comparison of Figures 1 and 2 demonstrates that the dissolved $\delta^{13}\text{C}$ values show slightly greater temporal variability than the free product $\delta^{13}\text{C}$ values. This may be due to the additional sample handling associated with preparing and pentane extracting compounds in dissolved solution prior to GC/C/IRMS analysis.

Finally, it is important to note that the free product isotopic compositions of TCE and toluene were -31.1‰ ($n = 35$) and -27.5‰ ($n = 12$), respectively, while those in aqueous solutions prepared from the pure phase were -31.0‰ ($n = 12$) and -28.0‰ ($n = 12$), respectively. These results indicate that dissolution, like volatilization, is also not significantly isotopically fractionating.

Optimization Results. As set up in the Stable Isotope Laboratory, GC/C/IRMS analysis typically requires a peak height of 0.2 V, corresponding to approximately 10 ng of carbon injected onto the column. Based on Henry's law calculations, 1 cm^3 of vapor phase associated with a 240 ppb

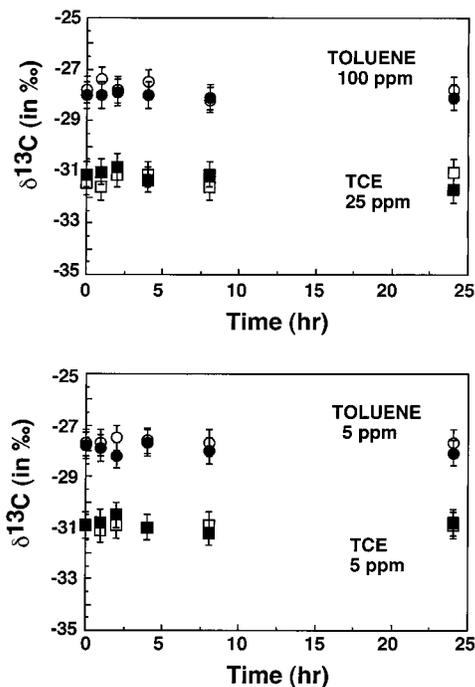


FIGURE 2. $\delta^{13}\text{C}$ values for vapor phase TCE and toluene and the $\delta^{13}\text{C}$ values for dissolved TCE and toluene are plotted against time for two different concentrations of each solvent. Vapor $\delta^{13}\text{C}$ values are shown in open symbols, and dissolved $\delta^{13}\text{C}$ values are shown in closed symbols. The $\delta^{13}\text{C}$ values for vapor and dissolved TCE and toluene are identical within reproducibility over the 24-h time series of the experiment. Error bars represent 0.5‰ accuracy and reproducibility.

aqueous solution of toluene or a 690 ppb aqueous solution of TCE will supply this amount of carbon. Using the four headspace optimization steps described previously, isotopic compositions accurate and reproducible within 0.5‰ were obtained for aqueous solutions at concentrations as low as 100 ppb for toluene and 400 ppb for TCE. The combined effect of the optimization steps must therefore be an increase in mass transfer to the headspace by approximately 2-fold, 2.4 for toluene and 1.7 for TCE, respectively. According to laboratory tests and to reported results by Peng et al. (29), the Henry's law constant for TCE and toluene can be approximately doubled by heating an aqueous solution of toluene or TCE to 50 °C. Tests carried out in the Stable Isotope Laboratory for TCE also indicate that salt saturation can increase the partitioning of TCE into the vapor phase by as much as five times as compared to volatilization from deionized water. Therefore, the extent of the optimization achieved in this study is consistent within an order of magnitude with theoretical predictions, but it may, in fact, be possible to achieve even lower detection limits than those attained in the course of this study.

Implications for Contaminant Hydrogeology. This study is the first to define the isotope effects involved in dissolution from free product and in volatilization from both free product and aqueous solutions, both of which are key transport and attenuation processes for volatile organic compounds in the subsurface. Isotopic fractionation during volatilization will be controlled by differences in the energy required to liberate molecules containing heavy versus light isotopes from the liquid phase. Fractionation of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ molecules is well-known. However, unlike water molecules, where the presence of the heavy isotopes ^{18}O and ^2H make a significant difference to the overall mass of the molecule, the presence of ^{13}C versus ^{12}C in a TCE molecule makes only a 0.8% difference in mass. As such, the presence of ^{13}C versus ^{12}C

will likely have only a small impact on the physicochemical properties of the molecule, and there should be little energetic difference in volatilization of ^{13}C TCE versus ^{12}C TCE. In the case of toluene, there is a similarly small impact on mass due to the presence of ^{13}C versus ^{12}C (1.09%), and hence the lack of fractionation associated with volatilization is not unexpected. While experimental results for TCE and toluene only are reported in this paper, similar results are expected for compounds with similar physicochemical properties. Additional experiments on PCE and cDCE for instance have also shown no evidence of significant fractionation and hence support the assumption that TCE can be used as an experimental proxy for chlorinated hydrocarbons. Further experiments with mixtures of these two compounds as well as a laboratory-prepared gasoline/TCE mixture (unpublished data) demonstrated that the isotopically conservative nature of volatilization is retained in situations involving mixtures of compounds (30).

These conclusions are supported by recent results in the literature. Harrington et al. (28) showed no isotopic fractionation >0.2‰ during volatilization of benzene, toluene, and ethyl benzene. While Balabane and Letolle (27) showed a significant fractionation associated with distillation of benzene and toluene, such as a result is not unexpected in an experiment designed to focus on extremely high or extremely low vapor/liquid ratios. In contrast, both this study and the experiments of Harrington et al. (28) were designed to characterize isotopic effects associated with equilibrium partitioning between the volatile and the liquid phase. This focus was selected in order to maximize the relevance of the experimental results to the field where generally water and contaminant movement in the subsurface is slow enough and contact times between vapor and liquid are long enough that an equilibrium model is the most appropriate.

The fact that dissolution and volatilization are isotopically conservative means that $\delta^{13}\text{C}$ signatures are potentially be used to track the transport of contaminants between the gaseous, aqueous, and free product phases since none of these transformations will involve a change in $\delta^{13}\text{C}$ of >0.5‰. Application of these results to field situations will also depend on the isotopic effects associated with other key subsurface processes affecting contaminants such as adsorption, biodegradation, and abiotic degradation. Experiments to characterize these isotopic effects are presently underway, but preliminary results indicate that unlike volatilization and dissolution, large fractionations (>10‰) are often associated with both biotic and abiotic degradation (31–33). This experimentally based framework is essential if isotopic variation in $\delta^{13}\text{C}$ signatures of dissolved contaminants recently reported in the field (25) is to be successfully interpreted.

The second major contribution of this study is that it demonstrates that headspace analysis is a rapid and robust technique for determination of $\delta^{13}\text{C}$ values for dissolved VOCs. A number of extraction techniques have recently been adapted for isotopic analysis of dissolved organic compounds, including pentane extraction (19), purge-and-trap (34), and solid-phase microextraction (SPME), which is based on the equilibrium partitioning of organic compounds between an aqueous sample phase and an organic polymer extraction phase (24, 35). While all these preparatory techniques are effective, a number of features recommend headspace analysis for certain applications. In order for SPME and purge-and-trap techniques to analyze environmental samples containing free product or high concentrations of organic compounds, samples must be diluted because of solubility and linear response problems (36). In contrast, both headspace analysis and pentane extraction are robust and versatile techniques that can accommodate a wide range of dissolved VOC concentrations. Second, headspace extraction

is an extremely simple and clean technique for, like SPME, it effectively separates the volatile organic fraction from a mixture and so provides a "cleanup" step prior to isotopic analysis (37). In contrast, pentane extraction indiscriminately extracts all volatile and nonvolatile hydrophobic organics from a complex mixture. Since it is the heavy organic fraction that poses the greatest threat for injector and/or column contamination, elimination of these compounds during sample preparation is desirable. Similarly, solvents themselves may chromatographically interfere with the compounds of interest or may form emulsions with fine silt and/or bacteria in field samples (38). Finally, headspace extraction requires only tens of milliliters of water for analysis of dissolved VOCs in the ppb range whereas pentane extraction requires hundreds of milliliters of groundwater at comparable concentrations. In short, while all of the above techniques are sensitive, reproducible, and accurate, headspace analysis is not only simple and rapid but also is particularly well suited in situations where there are high concentrations of contaminant or the concentrations are variable as well as in situations where small volumes of water are available. While detection limits using headspace analysis are slightly higher (hundreds of ppb) versus 10–100 ppb for SPME (23) pentane extraction and purge-and-trap, the other important advantages of headspace analysis make it an excellent method for isotopic analysis of environmental water samples.

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