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Effects of volatilization on the hydrogen isotope composition of selected n-alkanes

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ABSTRACT

The hydrogen isotope composition of n-C$_{15}$ to n-C$_{32}$ n-alkanes was measured by GC–IRMS to investigate the behavior of H isotopes during evaporation. The H isotope fractionation of n-C$_{15}$ to n-C$_{19}$ ranged from −8.5 to −22.5‰, demonstrating the preferential vaporization of the isotopically heavier organic compounds. The H isotope fractionation rates of n-C$_{16}$ to n-C$_{18}$ showed no obvious fluctuations with time (average rates were 1.1, 0.5 and 0.3‰ per day, respectively); this indicated that fractionation followed the Rayleigh model. Although less conclusive, the fractionation of H isotopes in n-C$_{19}$ also apparently followed the Rayleigh trend. Information on fractionation rates may be useful for identifying the dominant attenuation and degradation processes for organic substances in the environment. The results also highlight potential applications of isotope fractionation factors, which were determined by regression analysis, for investigations into the behavior of organic substances in the environment.

1. Introduction

The n-alkanes, a homologous series of non-polar organic compounds, often show high concentrations in atmospheric aerosols, including total suspended particulates (TSP), particulate matter less than 10 μm (PM$_{10}$), PM$_{2.5}$ and PM$_1$ (Guo et al., 2003; Li et al., 2012; Lin, 2004; Young and Wang, 2002). Primary sources for these compounds include fossil fuel combustion and biological emissions (Bi et al., 2008; Ulevicius et al., 2010; Zhou et al., 2009); and the contributions from these two sources have been evaluated using the carbon preference index, carbon number maximum, homologue distributions, and C and H isotope variations (Ladji et al., 2009; Mansuy et al., 1997; Xie et al., 2009; Yamamoto and Kawamura, 2011). Although diagnostic parameters such as these provide important insights into the origins of organic compounds in the environment, attention still needs to be focused on how they degrade and how their concentrations are attenuated. Here we use the term "attenuation" to describe in general terms the decreases in the concentrations of the compounds brought about by evaporation and other loss processes.

Compound-specific isotope analysis (CSIA) has become a powerful analytical tool, and it has been used to investigate how physical processes (vaporization, adsorption) and chemical processes (photo-degradation, biodegradation and chemical oxidation) affect the composition of specific compounds, including the ways in which these substances are modified in the natural environment (Fischer et al., 2007; Harrington et al., 1999; Hunkeler et al., 2003; Ma et al., 2010; Oba and Naraoka, 2008). Isotope fractionation often results from the preferential evaporation of molecules containing heavier H isotopes (Kuder et al., 2009a, 2009b; Poulson and Drever, 1999); but for compounds that have hydrogen bonds, the H isotopes often show the opposite fractionation tendency (Wang and Huang, 2003). The magnitude of H isotope fractionation for short chain n-alkanes (n-C$_7$ to n-C$_{14}$) during evaporation has been found to range from −7.2‰ to −32.8‰ (Wang and Huang, 2001, 2003). These findings suggest that isotope signatures can be used to investigate the attenuation of the compounds'

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concentrations in the environment and thus provide information on the fates of hydrocarbons in that context (Pond et al., 2002).

Isotope fractionation during evaporation is driven by the molecular forces between molecules rather than the breaking of chemical bonds within a molecule, and this phenomenon has been explained in terms of binding energies (Grootes et al., 1969) and molecular structure (Bradley, 1954). Most studies to date have focused on isotope fractionation in the context of natural attenuation, and it has become apparent that the extent of fractionation often increases over time, but there is little quantitative information on the rates at which the isotope fractionation proceeds.

In the present study, we conducted experiments to investigate the H isotope fractionation of *n*-alkanes; in particular, we focused on isotope fractionation rates during the evaporation process because this subject has received relatively little attention to date. The objectives of our studies were (1) to apply CSIA to investigate the behavior of organics by measuring the fractionation of H isotopes from *n*-alkanes and (2) to develop a diagnostic tool for studying the environmental attenuation of organic matter.

2. Experimental methods

2.1. Experimental design

All vaporization experiments were conducted in a laboratory with environmental controls. Room temperature during the experiments was 24 °C ± 1 °C, and relative humidity was 34% ± 2%. A mixed standard, composed of n-C_{15} to n-C_{32} dissolved in *n*-hexane, was used for the experiments without further purification. The purity of the test compounds ranged from 99.9% to 97.9%, and their initial concentrations were known to range from 1012 μg/ml to 1088 μg/ml. Two-milliliter brown glass vials were cleaned with dichloromethane in an ultrasonic bath for 20 min, and then the vials were wrapped with aluminum foil to avoid any potential influences of ultraviolet light on the isotope composition.

Seven pre-cleaned vials were sequentially capped with Teflon® (PTFE)-lined caps immediately after 20 μl of the standard mixture was added into them with a 25 μl microsyringe. Next, the vials were moved into a fume hood, and the caps were removed as simultaneously as possible to allow the *n*-alkanes to start volatilizing. The fume hood was kept running so that the evaporation process would start immediately after opening the vials. Periodically, the vials were capped and then kept in a freezer (4 °C) prior to the measurements of hydrogen isotope composition. To account for the solvent lost to evaporation, the standards were diluted again to 20 μl with *n*-hexane before the next aliquots were taken for hydrogen isotope analysis.

2.2. Gas chromatography (GC)

Quantification of the *n*-alkanes was performed with the use of a Hewlett-Packard 6890 gas chromatograph, equipped with a 30-m, fused-silica, capillary column (HP-5, 0.32 mm i.d., 0.25 μm film thickness) and a flame ionization detector. Ultra-high purity helium was used as the carrier gas, and it was delivered a constant flow rate of 1.0 ml min^{-1}. The sample of 1 μl volume was injected in the splitless mode, and the injection port temperature was 280 °C. The temperature program for the *n*-alkane determinations involved three steps (1) 70 °C for 2 min, (2) heating to 290 °C at 6 °C min^{-1}, and (3) 290 °C for 30 min. The concentration of each compound during the vaporization experiments was determined by its abundance relative to the internal standard *n*-tetracosane-D.

2.3. Hydrogen isotope analysis

Hydrogen isotope analysis of individual *n*-alkanes was performed using a gas chromatography/high-temperature conversion/isotope ratio mass spectrometry (GC–TC–IRMS) system. An HP-6890 gas chromatograph, fitted with a 30 m capillary column (HP-5, 0.32 mm i.d., 0.25 μm film thickness), connected with a high-temperature pyrolysis furnace through a GC combustion-III interface to a Finnigan MAT Delta Plus-XL isotope-ratio mass spectrometer was used for these analyses. Injection was performed in the splitless mode, and the GC temperature program and the carrier gas and flow were the same as those described above for the *n*-alkane analyses. Individual *n*-alkanes separated by GC were successively pyrolyzed to H_2 and C at 1440 °C. The H_2 was then introduced into the mass spectrometer.

Recently, stable hydrogen isotope ratios (calculated as δD in per mil, ‰) have been used to investigate the sources and transport of *n*-alkanes (n-C_{21} to n-C_{33}) in a polluted urban atmosphere (Yamamoto and Kawamura, 2010, 2012). Here δD values were calibrated using a reference H_2 gas, and they were reported relative to Vienna Standard Mean Ocean Water (VSMOW) as is the convention:

$$\delta D = \left[\left(D/{}^{1}H\right)_{\text{sample}}/\left(D/{}^{1}H\right)_{\text{VSMOW}}-1\right] \times 1000. \qquad (1)$$

The standard deviation for the δD analysis of each compound was <6‰.

For the correction of $D/{}^{1}H$, the H_3 factor was determined daily prior to sample analysis by measuring the (mass-3) / (mass-2)($(HD^{+} + H_3^{+}) / H_2^{+}$) ion current ratio of a sample over a range of H_2 pressures in the ion source. Least-squares regression was then used to find the value of the H_3 factor. The mass spectrometer was tuned to ensure that the H_3 factor was always ~8 and the daily variability <0.1. A set of laboratory standards (n-C_{12}, n-C_{14}, n-C_{16}, n-C_{18}, n-C_{20}, n-C_{22}, n-C_{25}, n-C_{28}, n-C_{30} and n-C_{32}) with known δD values was injected after every sixth sample analysis to test the stability of the instrument. The fluctuation of δD values for the standard *n*-alkanes was smaller than 4‰. The δD values reported for the samples were the average of three repeat analyses.

3. Results and discussion

3.1. Hydrogen isotope fractionation during evaporation

The residual n-C_{15} to n-C_{19} *n*-alkanes in the test solutions became depleted in D as a result of evaporation; that is, when 2.4, 0.8, 7.1, 36.5 and 50.6% of initial n-C_{15} to n-C_{19} *n*-alkanes remained, the D depletions were −15.1‰ for n-C_{15}, −22.5‰ for n-C_{16}, −16.0‰ for n-C_{17}, −10.2‰ for n-C_{18} and −8.0‰ for n-C_{19} (Table 1). Larger variations in concentrations clearly