Position-specific carbon isotope fractionation gives insights into mechanistic models for evaporation of organic liquids in the environment

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Abstract

This work describes position-specific isotope effects (IE) measured by intramolecular position-specific 

13C-NMR during the evaporation of 8 different liquids of different polarities under 4 evaporation modes (passive evaporation, air-vented evaporation, low pressure evaporation and distillation). The observed effects are used to assess the question whether for carbon isotopes in organic liquids the use of the Craig-Gordon isotope model is valid. It is shown for five liquids that the overall IE include vapour-liquid IE which are strongly position-specific in polar compounds and less specific in apolar compounds, and a diffusive effect for which is not position-specific. The diffusive effect is diminished under wind and low pressure. After evaporation, the position-specific isotope pattern created by liquid-vapour IE is still quite reasonably preserved in these five liquids, which have, like water, an air-side limitation for volatilisation. Three other liquids in this study with limitations rather or fully on the liquid side differed from this pattern. It is concluded that evaporation of organic pollutants creates a unique position-specific isotope pattern that may be used to assess the progress of remediation or natural attenuation, and that the Craig-Gordon isotope model is valid for the volatilization of organic liquids with air-side limitation of the volatilization rate.

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1. Introduction

Organic liquids such as solvents, fuels and fuel additives are among the most problematic groundwater contaminants since they migrate actively to groundwater and form long-lasting sources. At many contaminated sites, volatilization of compounds based on soil vapour and or dual-phase extraction, or air-sparging is the chosen remediation strategy. CSIA can be a tool for the assessment of remediation success and is applied frequently for following degradation processes involving strongly isotope-fractionating bond-breaking reactions. However, diffusive isotope fractionation during volatilisation can also create isotope fractionation, and thus the CSIA approach for remediation assessment is only possible when the mechanisms of volatilization are well understood and the pertinent isotope fractionation factors are quantified. The earliest and most complete understanding of isotope fractionation during evaporation of a liquid is that for water and its isotopes $^2$H and $^{18}$O. $^1, ^2$ The well accepted model of Craig-Gordon (CG-model)$^1$ states that two isotope effects (IE) – the vapour-liquid IE and the diffusive IE – are implied in water evaporation and that the effects are additive.

Volatilization of liquids to the open air is best represented by a conceptual model based on two stagnant films, a liquid film on the liquid side and a gas film on the air side. One of these films is the bottleneck for defining the overall flux rate. The outcome of the overall limitation depends on in which film the transfer velocity is smaller. Discussing IEs during volatilization requires thus the analysis of the transfer velocities in these films. For the evaporation of water, it is the air film which controls the overall flux rate.$^1$ For this situation, the CG-model has been developed for deuterium and oxygen-18. It has been adopted by Kuder$^3$ for describing the volatilization of organic liquids when their flux limitation is also on the air side. The IE is composite, including two processes: the liquid-vapour IE ($\Delta_{\text{liquid-vap.}}$), and the diffusion effect through the air film $\varepsilon_{\text{diff-air}}$. These effects are additive (eq. 1):$^3$

$$\text{IE} = \Delta_{\text{liquid-vap.}} \cdot \varepsilon_{\text{diff-air}} \quad \text{(eq. 1)}$$

Vapour-liquid IEs for organic liquids were studied in the past by distillation and manometric methods $^4$, and mostly inverse carbon IEs for vapours of hydrocarbons were found (i.e. the vapours were enriched in $^{13}$C compared to the liquids). Harrington and co-workers $^5$, who observed an equal inverse effect in hydrocarbons and trichloroethene over a temperature range from 5 to 70°C, suggested that the remaining contaminant mass therefore would become depleted in $^{13}$C during volatilisation. Bouchard and co-workers $^6, ^7$ found that the opposite is true for hydrocarbons evaporating from a mass of hydrocarbons buried in soil. This was interpreted as being the result of two IEs, of which the normal diffusive IE dominates over the inverse vapour-liquid effect for $^{13}$C. $^7, ^8$ Kuder and co-workers$^3$ were the first to apply the CG-model to passive and vented evaporation of an organic liquid pollutant, methyl tert-butyl ether (MTBE), studied by $^{13}$C and $^2$H.

A number of other studies measured carbon isotope fractionation of organic liquids during volatilization in fume hoods, and fractionation was often quite different from what has been measured and predicted during volatilization from soil. The magnitude of wind and how the vapour is carried away seem to play a role, but no quantitative understanding for this is available.

Intramolecular isotope analysis is a powerful new tool to look at processes where irm-MS-based analysis fails to see any effect. In our case of two additive processes, it can be anticipated that the vapour-liquid IE might be fairly site specific, especially in liquids with polar interactions (e.g. hydrogen bonding). In contrast, the IE for diffusion in a gas phase should not, a priori, be site-specific. Thus, our working hypothesis is that using intramolecular isotope analysis, one can assess progressive evaporation even for compounds where the bulk (all over the compound) IE is nil, and get new insights in the molecular understanding of the evaporation process. In a previous paper $^9$ we have shown how iq-NMR gives access to the position-specific isotope fractionation (PSIF), expressed as $\delta^{13}$Ci and that this indeed does vary with a much greater amplitude than the one seen in the $\delta^{13}$Cg obtained by irm-MS.

In this study, evaporation conditions on 8 model organic liquids (bromoethane, trichloroethene, MTBE, n-heptane, toluene, acetone, propanol and ethanol) were varied: passive evaporation, air-flux assisted evaporation, low pressure evaporations and distillation, and the $\delta^{13}$Ci values were determined by iq-$^{13}$C NMR, with the objective to give a proof-of-concept for the use of iq-$^{13}$C NMR in pollution studies involving volatilisation.
2. Materials and methods

The evaporation simulation was performed from four different experiments using 20mL or 100 mL of pure compound, the remaining substrate (2-7%) was submitted to isotope analysis. The “passive” evaporation (PE) was carried out with 20 mL of compound in a 30 mL vial under fume-hood at constant airflow of \(2.10^5\) L/h at an ambient temperature of approx. 22°C. The “air flux” evaporation (AFE) has been performed with 20 mL of pure chemicals in a 250mL three necks round bottom flask with two opened necks and the third one connected to an inlet blowing air at 500L/h (ref). Evaporation at “low-pressure” (LPE) has been done on 20 mL compound, using a Rotavapor with a 30°C water bath and a vacuum of about 10 mbars. Evaporation upon distillation experiments (DE) was carried out using a spinning band (Cadiot) distillation column on 100 mL of each compound. The temperature is usually near the boiling temperature of the distilled compound for practical purposes. When the IE is normal, the heavier isotope enriches in the liquid, and the still pot becomes isotopically heavier. Condensed vapour taken at the top is then lighter. Distillation has been used for measuring the liquid-vapour IE. As discussed before, the IE is highly specific on the position of the isotope substitution, and it is therefore expected that isotope enrichments during distillation are position-specific.

The protocols for sample analysis were described previously. Quantitative \(^{13}\)C NMR spectra were recorded using a Bruker AVANCE I 400, fitted with a 5 mm i.d. \(^{1}H/^{13}\)C dual” probe, carefully tuned at the recording frequency of 100.61 MHz, or a Bruker AVANCE III connected to a 5mm i.d. BBFO probe tuned at the recording frequency of 100.62 MHz. The temperature of the probe was set to 303K. The offset for \(^{13}\)C was set at the middle of the frequency range observed for each studied compound. An inverse-gated decoupling technique has been used to avoid Nuclear Overhauser Effect (NOE).

Bulk \(^{13}\)C abundance \((g^{13}\)C) was determined by isotope ratio measurement by mass spectrometry (irm-MS) using an Integra2 spectrometer (Sercon Instruments, Crewe, UK) linked to a Sercon elemental analyser (EA) (Sercon Instruments, Crewe, UK). A precise amount of each compound is weighted using a 10^6g precision balance (balance, Ohaus Discovery DV215CD) to ensure to have 0.4mg of carbon in tin capsules (2x5mm, Thermo Fisher scientific). Isotope \(^{13}\)C/\(^{12}\)C ratios were calculated from processed spectra essentially as described previously. Enrichment factors were calculated using the traditional Rayleigh equation.

3. Results and discussion

Due to lack of space, only the results of the evaporation of one organic liquid, toluene, are shown here. These results are shown in Figure 1. The bulk isotope effect is inverse for low pressure evaporation and distillation (+0.3 ‰ and +0.4 ‰, respectively), whereas it is normal for passive evaporation (-0.9 ‰) and air-flux evaporation (-0.7 ‰). This switch from inverse to normal isotope effect is explained by the influence of the diffusive air boundary layer in PE and AFE, which adds the diffusion effect \(e_{diff-air}\) (the second term in equation 1). This diffusion effect is somewhat lower under AFE since the diffusive air boundary layer is smaller.

The position-specific analysis shows that the highest inverse effect is that for the position C-1 under low pressure evaporation. This position, which is the most shielded carbon in toluene (Fig. 1) shows also the smallest normal effect under PE and AFE. It is noteworthy that, for PE and AFE it is the eccentric carbon position the C-5 (the methyl of toluene) that is most susceptible to normal fractionation. The position C-5 shows always a contrasted behaviour compared to the three remaining positions C-2 to C4, which themselves behave rather similarly. It is furthermore interesting to note that the patterns of LPE and AFE are very symmetric: each bar of the histogram decreases by about -1 ‰ from a positive e to a negative one. The decrease of -1 ‰ is somewhat smaller than the theoretically predictable diffusion effect \(e_{diff-air}\) which is -1.3 ‰. This is in perfect accordance with the Craig-Gordon evaporation model which states that wind decreases the diffusion effect. As shown in figure 1, the shift is larger between LPE and PE which involves less wind than AFE.

Thus: we conclude that the position-specific isotope pattern created by the vapor-liquid isotope effect (the first term in eq. 1) is more or less preserved during passive evaporation. The position-specific isotope analysis of all 5 carbon positions shows that the specific pattern developed under distillation or low-pressure evaporation is still visible after passive evaporation. An interesting outcome of these experiments is that toluene that undergoes passive or air flux-induced volatilization in the environment would change its \(^{13}\)C/\(^{12}\)C ratio at the C-1 and C-5, whereas the other
positions would remain approximately the same as the bulk ratio. This could be exploited in the identification of sources of unknown toluene emitters that have undergone volatilization after release to the environment.

In our study, equation 1 and position-specific isotope analysis explained the evaporation behavior perfectly for 5 compounds (toluene, heptane, ethanol, propanol and trichloroethene). For all these compounds, the air-film boundary limits the overall evaporation rate. In contrast, we found for MTBE, bromoethane and acetone a different behavior, suggesting that for these compounds the liquid film may limit the overall evaporation.

![Fig.1. Position-specific isotope effects in toluene after different modes of volatilization: PE: passive evaporation; AFE: air-flux evaporation; LPE: low-pressure evaporation; DE: distillation. The uncertainty for $\varepsilon$ is calculated to be +/- 0.2‰](image)

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**References**