Volatilization, dissolution and equilibrium isotope effects ($^2$H, $^{13}$C, $^{37}$Cl) of trichloromethane, trichloroethene and methanol dissolved in water

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Abstract

Volatilization is a process that may change the isotopic composition of organic compounds and which needs to be understood if isotopic methods are applied to describe transformation mechanisms in environmental samples. In the current study, isotope fractionation of two nonpolar and one polar compound was investigated during equilibrium partitioning as well as during volatilization from and dissolution in water. For trichloromethane and trichloroethene dissolved in water, volatilization caused considerably smaller ($\delta^{37}$Cl) or negligible ($\delta^2$H) isotope effects than found for pure phase volatilization, confirming previously reported insignificant $\delta^{13}$C fractionation for these compounds volatilizing from water. The data were further used to evaluate two models. The Craig-Gordon model delivered a reasonable estimate of carbon and chlorine isotope fractionation during volatilization of pure organics but it did not provide a reliable prediction of enrichment factors for compounds dissolved in water. A simple exchange model demonstrates that equilibrium isotope effects of compounds dissolved in water may be viewed as the result of the opposed exchange mechanisms volatilization and dissolution. The new isotopic data and the presented exchange model offer more detailed information about the occurrence and magnitude of volatilization isotope effects of environmentally relevant organics dissolved in water, both in open and closed systems.
Introduction

Volatilization isotope effects of organic compounds have been studied widely in the last 70 years and especially so isotope fractionation for equilibrium partitioning between the pure liquid and the gaseous phase.\textsuperscript{1-3} Fractionation at equilibrium conditions is described by the different vapor pressures of isotopologues containing heavy and light isotopes of an element, respectively. These different vapor pressures are caused by different zero point vibrational energies which are additionally influenced by Van der Waals interactions and hydrogen bonding in the liquid phase.\textsuperscript{4-6} Both normal and inverse vapor pressure isotope effects (VPIE) have been reported depending on the investigated isotope and the type of molecular interaction.\textsuperscript{1} For instance, carbon and hydrogen isotopes in non-polar compounds usually show inverse effects; that is, molecules bearing the heavier isotope are enriched in the gas phase. In contrast, carbon and hydrogen isotopes in polar compounds may show normal and inverse effects depending strongly on temperature and position of the element in the molecule.\textsuperscript{2} In methanol, for instance, hydrogen in the methyl group may show inverse isotope effects whereas normal isotope fractionation can be observed in the hydroxyl group which was explained by the role of hydrogen bonding in polar compounds.\textsuperscript{7}

Interest in the study of volatilization isotope effects of organics was re-sparked with the advent of compound-specific isotope analysis about twenty years ago. In the field of contaminant science isotopes have been applied to investigate the fate of pollutants in ground and surface water.\textsuperscript{8} Volatilization and associated fractionation may potentially mask isotope effects which are due to transformation and thereby complicate the quantification of degradation rates. Hence, equilibrium and kinetic volatilization isotope effects were investigated in various studies by simulating closed and open system conditions in laboratory experiments.\textsuperscript{9-16} Most of the available publications, however, reported isotope effects from experiments performed with pure substances which are not necessarily comparable to isotope effects observed in compounds dissolved in water. This fact was demonstrated in a recent paper where nonpolar chemicals, if dissolved in water, did not show measurable carbon isotope effects during open system (kinetic) volatilization even though for pure substances significant isotope effects were determined.\textsuperscript{17}

In previous studies, isotope effects reported for kinetic (or nonequilibrium) volatilization showed different magnitudes than equilibrium isotope effects. Hence it was suggested that fractionation
in organic compounds may be interpreted according to the Craig-Gordon model\textsuperscript{15,16} which was originally developed to explain isotopic enrichment in isolated evaporating water bodies such as lakes and ponds.\textsuperscript{18} This model describes nonequilibrium volatilization isotope effects of hydrogen and oxygen in water as the result of VPIE and diffusive effects with the latter being caused by movement of the molecules through a microns-thick static gas layer above the liquid phase.\textsuperscript{19} This model was previously applied to interpret stable carbon isotope fractionation observed in pure phase volatilization experiments.\textsuperscript{16} For organics dissolved in water, isotope fractionation may be subject to different processes but only very few studies have addressed this volatilization scenario.

Hence, the objective of this work was to provide a better understanding of isotope fractionation in organic compounds occurring during partitioning of these substances between water and air. Experiments were carried out for equilibrium partitioning and the two kinetic effects volatilization (liquid-air transfer) and dissolution (air-liquid transfer). Results for hydrogen, carbon and chlorine isotope measurements in trichloromethane (chloroform, TCM), trichloroethene (TCE) and methanol (only H and C isotopes) were applied to evaluate the validity of the Craig-Gordon model for organics dissolved in water. Furthermore, the results were used to explore the relation of kinetic and equilibrium isotope effects according to a simple exchange model.

**Material and methods**

Trichloromethane (chloroform, TCM), trichloroethene (TCE), and methanol (purity >99.5\% each) were purchased from Fisher Scientific, Fair Lawn, NJ, USA for equilibrium partitioning experiments ($\delta^{13}$C). For all other experiments chemicals were acquired from Carl Roth GmbH & Co KG (TCM >99.9\%), Sigma Aldrich Chemie GmbH, Germany (TCE, >99.5\%), and Th. Geyer GmbH & Co KG, Germany (methanol, > 99.85\%).

**Equilibrium partitioning experiments.** For closed system experiments of pure liquids 5mL of each compound was filled in 10 mL vials, crimp sealed with Teflon coated stoppers (Wheaton) and left for equilibration overnight at 24±1°C. The isotopic composition of hydrogen, carbon and chlorine was determined for both the gas phase and the pure liquid applying previously published
methods (see below). Usually 3-10 analyses were carried out for the liquid phase and headspace respectively.

Stock solutions with a concentration of 100 mg/L (TCM, TCE) and 100 g/L (methanol) were prepared for closed system experiments of compounds dissolved in water. Fifty mL of stock solution were filled in 60 mL serum bottles, crimp sealed and equilibrated overnight. The δ²H, δ¹³C and δ³⁷Cl signatures of the organics in the gas phase were determined by headspace analysis and compared to the isotopic composition of the organic stock which was used to prepare the aqueous solutions.

**Volutilization and dissolution experiments.** In addition to equilibration experiments the processes of volatilization (liquid-air transfer) and dissolution (air-liquid transfer) were investigated. Volatilization of neat compounds and chemicals dissolved in water were carried out according to a previously published protocol.¹⁷ Briefly, three separate samples (ca 5 g in 5 mL beakers) were left for evaporation in a fume hood for pure phase volatilization. Five to seven samples of the remaining liquid phase were taken at different evaporation steps and analyzed for δ²H, δ¹³C, and δ³⁷Cl. For compounds dissolved in water, 6-10 beakers (60 mL) were filled with 50 mL of stock solution each and stirred for 10 to 90 minutes (TCM, TCE) and 5 to 36 hours (methanol). Beakers were sampled at different time points, transferred to 60 mL bottles, crimp-sealed and equilibrated for at least 12 hours. The isotopic composition was measured via headspace analysis. Concentrations for dissolved compounds were determined by using a three-point calibration approach. For pure substances the amount of organic compound remaining after partial volatilization was measured gravimetrically.

For dissolution experiments in water, first 10 mL of compound was filled into a 1L-serum bottle and equilibrated over night at 24°C to create a nearly saturated air-compound gas mixture. Then 250 mL serum bottles were filled with 200 mL of deionized water, crimp sealed, and the air in the headspace was replaced with the air-compound gas mixture. A 60mL gas-tight syringe and an additional needle were used to flush the headspace with the air-compound gas mixture in order to avoid early condensation by keeping the pressure at atmospheric levels. Samples were taken every minute and analyzed for δ²H, δ¹³C and δ³⁷Cl. The liquid was continuously shaken at a slow rate to avoid concentration gradients. Four (methanol) to five (TCM, TCE) separate
experiments were carried out with three (methanol) and five (TCM, TCE) analyses per experiment.

**Stable carbon isotope analysis.** Compound specific stable carbon isotope analysis was carried out by closely following a previously published protocol. Briefly, for headspace analysis, gas samples were injected directly into the GC by using a gastight syringe. After separation on a GSQ column mounted in a Varian 3400, compounds were transformed to CO$_2$ in the connected combustion furnace and transferred to the isotope ratio mass spectrometer (Finigan MAT 252). For dissolution experiments analyses were carried out on a Thermo Finigan MAT 253 connected to an Agilent 7890A. Isotope ratios of the samples and of an external in-house working standard were measured with this procedure. Delta values ($\delta^{13}$C) referenced against V-PDB (Vienna Pee Dee Belemnite) were calculated according to the following equation:

$$\delta^{13}C_{(U}) = \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \quad \text{Equation 1}$$

Where $^iE$ indicates $^{13}$C and R the isotopic ratio $^{13}$C/$^{12}$C. For hydrogen and chlorine $^iE$ denotes $^2$H and $^{37}$Cl and R the isotopic ratios $^2$H/$^1$H and $^{37}$Cl/$^{35}$Cl respectively. Delta values for hydrogen and chlorine are referenced against Vienna Standard Mean Ocean Water (V-SMOW) and Standard Mean Ocean Chloride (SMOC) respectively. The delta values are given in Ur (Urey) according to recent IUPAC recommendations. This unit is interchangeable with the permil scale if given in mUr (milli-Urey): 1 mUr = 0.001 = 1 ‰. Total uncertainty for a single stable carbon isotope analysis is usually better than 0.5 mUr. This error incorporates both the accuracy and the analytical precision of a stable carbon isotope measurement.

**Stable hydrogen isotope analysis.** Stable hydrogen isotope analysis was performed according to the method published by Renpenning et al. After separation on a ZB1 gas chromatographic column mounted in an Agilent 7890A, a chromium reactor is used to convert hydrogen in the analytes to H$_2$. Halogens are converted to CrCl and efficiently trapped at the cold end of the reactor. Hydrogen isotope analysis is carried out using a Thermo Finigan MAT 253. Raw $\delta^2$H values were calculated using equation 1. A two-point calibration approach was applied to adjust raw-$\delta^2$H to the V-SMOW scale by measuring a set of in-house reference compounds (alkanes). The accuracy of this method is usually better than 5 mUr.
Stable chlorine isotope analysis. A universal method for compound specific stable chlorine isotope analysis using gas chromatography coupled with multiple collector inductively coupled plasma mass spectrometry (GC-MC-ICPMS) was recently developed. Samples were measured according to the published protocols.\textsuperscript{24, 25} Compounds were first separated on a ZB1 column mounted in a Thermo Scientific Trace 1310 GC. Transfer into the plasma was accomplished via a heated transferline (250°C) before the organics were ionized in the plasma of a Neptune MC-ICPMS (Thermo Fisher Scientific, Germany). Mass traces for $^{35}$Cl, $^{36}$Ar and $^{37}$Cl were collected by three Faraday cups with the argon-36 being used for peak centering. Three offline-characterized in-house reference compounds were used to correct raw-$\delta^{37}$Cl-values to the SMOC scale applying a two-point calibration approach. The accuracy of this method is usually better than 0.2 mUr. Further details are given in the cited articles.\textsuperscript{24, 25}

Enrichment factors for kinetic and equilibrium conditions. Isotopic enrichment factors ($\varepsilon$) were determined directly for closed system experiments by calculating the difference between the $\delta$-values in the gas phase and in the liquid phase. For open system (kinetic) volatilization and dissolution experiments the Rayleigh equation was applied:\textsuperscript{26}

$$\ln \left( \frac{\delta^i E + 1000}{\delta^i E_0 + 1000} \right) \approx \ln(f) \cdot \varepsilon$$

where $\delta^i E$ is the isotopic signature ($\delta^2$H, $\delta^{13}$C, $\delta^{37}$Cl) of the organic in the liquid after partial evaporation, $\delta^i E_0$ indicates the initial delta value ($\delta^2$H\textsubscript{0}, $\delta^{13}$C\textsubscript{0}, $\delta^{37}$Cl\textsubscript{0}), and $f$ is the fraction of organic remaining in the liquid phase. For dissolution experiments $\delta^i E$ indicates the delta value of the organic in the gas phase after partial dissolution, $\delta^i E_0$ designates the initial delta value and $f$ is the fraction remaining in the gas phase.

Theory

Two film theory and the Craig-Gordon model. The magnitude of kinetic volatilization isotope effects differs from those measured at thermodynamic equilibrium. To explain this discrepancy the so-called Craig-Gordon model was developed to explain isotope fractionation during evaporation of water. This model bases on the two-film theory\textsuperscript{27} which assumes that a viscous diffusive sublayer next to the interface (water vapor in equilibrium with the water) is influencing transfer rates.\textsuperscript{18} Diffusion in this gas layer affects the isotopic composition of the water through partial dissolution of enriched vapor back into the liquid. Hence the CG model considers
volatilization to rather produce a nonequilibrium instead of a purely kinetic isotope effect in water. According to this model, the volatilization isotope effect is the result of two processes: the effect of the different vapor pressures (VPIE) and fractionation due to diffusion through the viscous sublayer. The VPIE can be estimated directly from experiments carried out at equilibrium conditions whereas the maximum diffusive enrichment in the free air compared to this gas layer is usually calculated according to the following equation:  

\[ \varepsilon_{diff}[Ur] = \sqrt{\frac{M_{light}}{M_{heavy}} \frac{M_{heavy} + M_{air}}{M_{light} + M_{air}}} + 1 \]  

Equation 3

where \( M_{light} \) and \( M_{heavy} \) indicate the molecular mass of the light and heavy isotopologues respectively. The mass of air is estimated with 28.8 g/mol. Theoretically, the concentration of the organic in the turbulent layer of the gas phase needs to be considered for the calculation of diffusive isotope effects. If the concentration in the air approaches saturation, diffusion and hence diffusive isotope effects disappear. For that reason, diffusive isotope effects of water are corrected for the humidity of air. In our experiments the concentration of organics in the gas phase was virtually zero and diffusive isotope effects should be maximal. The overall fractionation according to the Craig Gordon model is then simply given by:

\[ \varepsilon_{CGM} = \varepsilon_{equ} + \varepsilon_{diff} \]  

Equation 4

The \( \varepsilon_{CGM} \) is expressed as the isotopic enrichment in air compared to the liquid phase.

**Exchange model.** Isotope effects in nature are the result of kinetic, equilibrium or nonequilibrium fractionation. Kinetic fractionation occurs in open systems due to irreversible (one way) physical or chemical processes; that is, volatilizing organics are withdrawn from the liquid phase without back condensation or dissolution, for example. Equilibrium fractionation observed in closed systems, in principle, causes the isotope effect between two phases at thermodynamic equilibrium. Nonequilibrium fractionation occurs if equilibria between two phases are not fully established due to partial loss of one phase. 

Generally, equilibrium fractionation may be viewed as the result of the two simultaneously occurring opposite kinetic isotope effects, here volatilization and dissolution, when exchange rates are balanced and no net mass transfer occurs. Consequently, the equilibrium fractionation factor \( \alpha_{equ} \), is the quotient of the two kinetic fractionation factors.
\[
\alpha_{equ} = \frac{\alpha_{vol}}{\alpha_{diss}} 
\]

Equation 5

where \(\alpha_{vol}\) is the fractionation factor caused by volatilization/evaporation (liquid-air transfer) and \(\alpha_{diss}\) is the fractionation factor for dissolution in water (air-liquid transfer) or for condensation of the pure liquid respectively. This relationship has been described for chemical equilibria such as gaseous CO\(_2\)/aqueous HCO\(_3^-\) and may also be applied for physical exchange equilibria such as volatilization.\(^{28}\)

For small fractionation factors \(\alpha\), enrichment factors \(\varepsilon\) are related to \(\alpha\) via equation 6:

\[
\varepsilon [Ur] \approx \alpha - 1 
\]

Equation 6

Inserting Equation 4 in Equation 3 and rearranging the expression leads to:

\[
\varepsilon_{equ} = \frac{\varepsilon_{vol} + 1}{\varepsilon_{diss} + 1} - 1 
\]

Equation 7

which can also be written as:

\[
\varepsilon_{equ} = \frac{(\varepsilon_{vol} + 1) - (\varepsilon_{diss} + 1)}{\varepsilon_{diss} + 1} 
\]

Equation 8

Volatilization isotope effects are usually relatively small. Hence, the term \(\varepsilon_{diss} + 1\) yields a value very close to 1 and may be omitted in the denominator. The enrichment factor at equilibrium conditions can thus be estimated from the two kinetic processes with the following expression:

\[
\varepsilon_{equ} \approx \varepsilon_{vol} - \varepsilon_{diss} 
\]

Equation 9

**Results and Discussion**

Experiments for partitioning of organics between air and water and air and the pure phase were carried out under equilibrium and kinetic conditions, the latter including both volatilization and dissolution experiments. Whereas some previous data is available in the literature for natural abundance carbon isotope effects in organics, chlorine and especially hydrogen isotope measurements are very scarce. Certain scenarios such as dissolution in water have not yet been reported at all. Hence this data set offers a unique overview of these fractionation effects and, at the same time, provides possibilities to gain new insights into isotope fractionation associated with these phase changes. Figure 1 shows the Rayleigh plots for all experiments carried out under kinetic conditions. These plots were used to determine enrichment factors for volatilization
(liquid-air transfer, $\varepsilon_{\text{vol}}$) and dissolution (air-liquid transfer, $\varepsilon_{\text{diss}}$). Results of all experiments including enrichment factors for equilibrium partitioning ($\varepsilon_{\text{equ}}$) are summarized in Table 1.

**Equilibrium isotope effects.** Partitioning of organics in closed systems showed both normal and inverse H, C and Cl fractionation effects. For carbon, all three compounds (TCM, TCE and methanol) exhibited inverse isotope effects, that is, the gas phase was enriched in $^{13}$C compared to the liquid phase. For pure phase experiments, the $\varepsilon_{\text{equ}}$ of $\delta^{13}$C were always larger than for compounds dissolved in water. Literature values for pure phase - air equilibration of TCE are slightly smaller (+0.1 to +0.8 mUr)$^9,10$ compared to +1.3±0.1 mUr found in the present study. For TCM and TCE dissolved in water previously published enrichment factors of +1.5 mUr and +0.6 mUr, respectively, are in good agreement with +1.5±0.2 mUr and +0.7±0.1 mUr reported here.$^{13}$ Methanol showed a significant inverse carbon isotope effect of +1.2±0.1 mUr for the pure organic. Two previous studies also reported an inverse but smaller carbon isotope effect with an enrichment factor of +0.3 to +0.5 mUr for distillation of methanol.$^{16,29}$ This smaller isotope effect may be explained with the higher temperature at which distillation is carried out.$^6$ For methanol dissolved in water carbon isotope fractionation was smaller with +0.4±0.2 mUr.

Stable chlorine isotope measurements yielded very small and partially insignificant normal isotope effects of -0.06±0.09 mUr and -0.11±0.05 mUr for pure phase TCM and TCE respectively. These values indicate that organics in the gas phase tended to be depleted in $^{37}$Cl compared to the pure liquid. If dissolved in water, values of -0.24±0.10 mUr and -0.12±0.16 mUr were measured. Even though these values were close to or within analytical uncertainty a consistently normal isotope effect was found in all cases. One previous study reported an $\varepsilon_{\text{equ}}$ of -0.07 mUr for TCE dissolved in water which is in agreement with our findings.$^{14}$

Hydrogen isotope measurements for equilibrium partitioning experiments yielded significant inverse isotope effects for TCM and TCE with +15.6±4.8 mUr and +16.8±3.7 mUr for the pure phase and +7.4±2.7 mUr and +5.2±2.6 mUr for compounds dissolved in water, respectively. For methanol, normal isotope effects of -18.0±6.0 mUr (pure phase) and -24.5±2.3 mUr (dissolved in water) were determined. The $\varepsilon_{\text{equ}}$ of methanol apparently presents an averaged value of all four H-atoms which are subject to either normal or inverse fractionation depending on the position in the molecule.$^2$ The three H-atoms in the methoxy group were shown to undergo inverse fractionation effects, whereas the H-atom in the hydroxyl group shows strong normal isotope
effects due to H-bonding. Hence the normal isotope effect of the H-bonded hydrogen atom seems to dominate the overall $\varepsilon_{\text{equ}}$ in methanol.

**Volatilization isotope effects of compounds dissolved in water and pure organics.** In this study, carbon isotope enrichment factors of volatilization experiments have only been determined for pure phase TCE ($\varepsilon_{\text{vol}} = +0.46 \pm 0.10$ mUr). This $\varepsilon_{\text{vol}}$ is in good agreement with previously published enrichment factors for this compound ranging from +0.24 to +0.35 mUr.\textsuperscript{10, 12, 14, 16} All other pure phase $\varepsilon_{\text{vol}}$ for $\delta^{13}$C were published in our former study together with carbon isotope enrichment factors of compounds dissolved in water\textsuperscript{17} and values are included in Table 1. This former study showed that volatilization of the free product of nonpolar compounds produces significant inverse isotope effects for $\delta^{13}$C but if dissolved in water, isotopic enrichment is negligible. For alcohols, a normal isotope effect of similar magnitude was observed for both, volatilization of the pure phase and for compounds dissolved in water (Table 1). The different isotope effects of nonpolar and polar compounds were explained with the influence of different molecular interactions in the pure phase compared to aqueous solutions.

Chlorine isotope enrichment factors measured in the current study were of similar magnitude for TCM and TCE. Pure phase evaporation generated an $\varepsilon_{\text{vol}}$ of $-1.14 \pm 0.11$ mUr and $-1.01 \pm 0.10$ mUr whereas volatilization from water yielded a smaller $\varepsilon_{\text{vol}}$ of $-0.21 \pm 0.10$ mUr and $-0.34 \pm 0.15$ mUr for TCM and TCE respectively. The enrichment factor of pure phase TCE was determined previously with values ranging from $-1.35$ mUr to $-1.82$ mUr.\textsuperscript{10, 12, 14} Hence all enrichment factors from the current and previous studies indicate that volatilization of pure and dissolved organics produce a significant, but in contrast to carbon, a normal isotope effect.

Hydrogen isotope measurements generated significant inverse $\varepsilon_{\text{vol}}$ of $+13.8\pm1.7$ mUr and $+8.2\pm1.4$ mUr for pure phase evaporation of TCM and TCE, respectively. Only insignificant isotope effects ($\varepsilon_{\text{vol}} < \pm1.6$ mUr) were found for volatilization of these compounds from water. The $\varepsilon_{\text{vol}}$ for pure phase TCE agrees well with the +8.9 mUr reported by Poulson et al.\textsuperscript{10} For methanol, exclusively negligible hydrogen isotope enrichment was found for both volatilization scenarios. This absence of hydrogen isotope fractionation, despite significant normal carbon isotope effects, may be caused by the mentioned competing inverse and normal isotope effects of hydrogen bound in the methoxy group and of hydrogen bound in the hydroxyl group respectively.\textsuperscript{6, 7}
Results from volatilization experiments, in particular, reveal important properties of non-polar compounds. Enrichment factors ($\varepsilon_{\text{vol}}$) measured for all isotopic systems (H, C, and Cl) in TCM and TCE dissolved in water were always smaller than for volatilization of the pure organics. Hydrogen and carbon isotope effects became very small or insignificant if organics evaporated from water whereas $\varepsilon_{\text{vol}}$ for chlorine decreased to about 25-30 % of the magnitude of pure phase enrichment factors. These results corroborate a previous hypothesis about the decrease of isotope fractionation of all elements in a nonpolar molecule dissolved in water if volatilization occurs in an open system. Accordingly, isotope fractionation during volatilization from water is influenced by a rate-determining step during phase transfer which overrides vapor pressure differences of the different isotopologues. Hence these isotope effects may be considered largely negligible for compounds in environmental samples that were subject to partial volatile loss. Similarly, incomplete extraction with pre-concentration methods such as purge and trap should not cause significant isotope fractionation.

**Dissolution of organics in water and associated fractionation.** Isotope effects for the transfer of organic compounds from air to the aqueous phase are not reported in the literature yet. In our experiments, dissolution generated consistently inverse carbon isotope enrichment factors of $-1.3 \pm 0.1$ mUr, $-1.0 \pm 0.1$ mUr and $-5.3 \pm 0.4$ mUr measured in TCM, TCE and methanol respectively. In dissolution experiments, heavier isotopologues are expected to dissolve preferentially according to isotope theory. Correspondingly, a positive $\varepsilon$ describes a normal isotope effect and a negative enrichment factor indicates an inverse effect. Hydrogen isotope effects were either inverse and small/insignificant for TCE and TCM ($-2.8 \pm 2.1$ and $-1.6 \pm 3.0$ mUr) or a normal $\varepsilon_{\text{diss}}$ of $+18.3 \pm 2.1$ mUr was determined for methanol. The $\varepsilon_{\text{diss}}$ for $\delta^{37}$Cl were very small but statistically significant ($p < 0.05$) with $+0.07 \pm 0.03$ mUr and $+0.12 \pm 0.06$ mUr for TCM and TCE, respectively.

Compared to volatilization, dissolution isotope effects often showed a different magnitude and, in some cases, a different type of fractionation. This may be due to the largely absent molecular interactions in the gas phase. Whereas dissolution in water caused a significant carbon isotope effect, no $^{13}$C fractionation was observed for volatilization of TCM and TCE from water. Similarly, a normal $\varepsilon_{\text{vol}}$ turned into an inverse carbon isotope effect during dissolution of methanol. Hydrogen fractionation occurred only during dissolution of methanol but not during volatilization. These examples demonstrate that isotopic changes caused by dissolution may be
very different from those caused by volatilization and therefore the direction of the phase transfer should be considered if, for example, partitioning of an organic contaminant in the environment is investigated with isotopic methods.

**Fractionation according to the Craig Gordon model.** The CG model assumes that two processes contribute to the isotopic enrichment in the liquid phase during volatilization (liquid-air transfer). These processes, diffusive isotope effects $\varepsilon_{\text{diff}}$ and VPIE derived from equilibrium isotope effects $\varepsilon_{\text{equ}}$, sum up to the overall enrichment $\varepsilon_{\text{CGM}}$. Results of these calculated enrichment factors are presented in Table 1 and compared to the measured $\varepsilon_{\text{vol}}$.

Generally, enrichment factors calculated according to the Craig Gordon model ($\varepsilon_{\text{CGM}}$) fit some of the measured $\varepsilon_{\text{vol}}$ whereas in some cases the agreement was rather poor. For pure phase TCE and TCM the deviations of measured and calculated epsilons were within 8 mUr for hydrogen, 0.3 mUr for carbon and 0.56 mUr for chlorine isotopes. These deviations were often outside the limits of analytical uncertainty, but they might be acceptable if only a rough estimate of $\varepsilon_{\text{vol}}$ is needed. In contrast, differences were larger for methanol, namely 23.7 mUr for $\delta^2$H and 2.1 mUr for $\delta^{13}$C. For compounds dissolved in water, TCE and TCM again showed a reasonable agreement for $\delta^2$H and $\delta^{13}$C differing by no more than 6.1 mUr and 0.6 mUr respectively. For $\delta^{37}$Cl, however, the model calculated an even larger $\varepsilon_{\text{CGM}}$ of -1.62 and -1.88 for TCE and TCM, whereas measured $\varepsilon_{\text{vol}}$ were smaller compared to pure phase volatilization experiments (-0.34 and -0.21 mUr). Differences for methanol were as large as 31.7 mUr and 2.4 mUr for hydrogen and carbon respectively. This comparison shows that the CG model does not generally provide a reliable prediction of all volatilization isotope effects in the investigated compounds and especially not for substances dissolved in water.

This partially poor fit of the CG model and our data may be due to the fact that water, for which this model was developed, has very different properties compared to organic compounds. Diffusive isotope effects of water are much larger (about -32 mUr for oxygen and -17 mUr for hydrogen) compared to the relatively small $\varepsilon_{\text{diff}}$ of -0.69 mUr and -0.82 mUr for hydrogen and carbon in TCE and TCM respectively (Table 1). An assumed diffusive isotope effect for hydrogen in TCE and TCM would hence contribute with at most 10% to $\varepsilon_{\text{vol}}$ which is negligible considering the magnitude of hydrogen isotope fractionation during volatilization and the analytical uncertainty of hydrogen isotope measurements. Methanol forms the lightest molecules
of the three compounds and relative mass differences of the isotopologues are larger which also resulted in larger calculated $\epsilon_{\text{diff}}$ of -7.2 mUr for hydrogen and carbon. These higher diffusive isotope effects for CH$_3$OH did, however, not improve the precision of the CG model estimates. In contrast, deviations of measured $\epsilon_{\text{vol}}$ and calculated $\epsilon_{\text{CGM}}$ were even more pronounced causing generally an overestimation of hydrogen and carbon isotope enrichment in the liquid phase. Similarly, the larger diffusive isotope effects for chlorine in TCE (-1.37 mUr) and TCM (-1.64 mUr) caused too enriched $\epsilon_{\text{CGM}}$ values for these compounds dissolved in water.

Altogether, the experimental evidence and calculations presented in this study do not support the Craig Gordon model as a tool to predict volatilization isotope effects of organics dissolved in water. The considered influence of diffusion is very likely overestimated by the model as demonstrated especially for chlorine isotopes. Hence, a more refined view of the fractionating processes within the boundary layer between water and air is needed to better understand any potential influence on volatilization isotope effects.

**Exchange model.** The abundant data collected throughout this study was also used to evaluate the validity of a second model. This exchange model may be used to explain the different magnitudes of kinetic isotope effects if they are compared to fractionation under equilibrium conditions. It was assumed that isotopic equilibria during partitioning may be largely caused by a forward (volatilization) and reverse (dissolution/condensation) process when exchange rates are balanced (Equation 5). This hypothesis was evaluated for compounds dissolved in water for which isotope fractionation data of all three processes was measured. Theoretic $\epsilon_{\text{vol-exch}}$ were calculated according to Equation 8 and results were summarized in Table 1 together with the measured $\epsilon_{\text{vol}}$.

A comparison of calculated and measured enrichment factors overall reveals a good fit of the magnitude and type of volatilization isotope effects. Maximum deviations of theoretic $\epsilon_{\text{vol-exch}}$ and measured $\epsilon_{\text{vol}}$ are within ±6.6 mUr for hydrogen, ±0.5 mUr for carbon and ±0.34 mUr for chlorine isotopes. Enrichment factors $\epsilon_{\text{vol-exch}}$ and $\epsilon_{\text{vol}}$ agree but for one exception ($\delta^2$H for methanol), if analytical errors are taken into account. Hence, it seems conceivable that two enrichment factors may be used to estimate the isotope fractionation caused by the third process. For example, $\epsilon_{\text{vol}}$ and $\epsilon_{\text{equ}}$ can be applied to determine $\epsilon_{\text{diss}}$ which is more difficult to measure in
most cases. This relationship could, however, not be tested for pure phase compounds because the measurement of condensation isotope effects in the pure organic would be very challenging.

Several conclusions may be drawn from the evaluation of the data and the exchange model. It was shown previously that no stable carbon isotope fractionation occurred in non-polar compounds during volatilization from water.\textsuperscript{17} Dissolution, in contrast, caused significant isotope effects. This indicates, according to equation 9, that equilibrium fractionation of non-polar compounds in aqueous solutions may only be attributable to the air-liquid transfer (dissolution). Volatilization does not significantly contribute to $\delta^{13}$C enrichment/depletion in the gas phase whereas dissolution generates the observed isotopic fractionation. Thus, the enrichment factor $\varepsilon_{\text{equ}}$ has a similar absolute value as the $\varepsilon_{\text{diss}}$ obtained from dissolution experiments (Table 1).

A similar phenomenon could be observed for hydrogen in CH$_3$OH dissolved in water. A normal equilibrium isotope effect $\varepsilon_{\text{equ}}$ of $-24.5\pm2.3$ mU was measured while no significant enrichment occurred during volatilization ($\varepsilon_{\text{vol}} = -0.1\pm1.9$ mU) from water. Hence, according to the model, fractionation should occur during dissolution only which is confirmed by the measurements ($\varepsilon_{\text{diss}} = +18.3$ mU).

The larger $\varepsilon_{\text{equ}}$ of $\delta^{13}$C for the free product of TCE, TCM, and other nonpolar compounds may also be explained by this approach provided that air-liquid transfer (condensation) in pure compounds causes a similar isotope effect as for dissolution of organics in water. In that case fractionation would occur during both volatilization and condensation with both processes contributing to the enrichment in the gas phase above the free product. Consequently, a larger equilibrium isotope effect is obtained for $\delta^{13}$C compared to the $\varepsilon_{\text{equ}}$ measured for organics dissolved in water (Table 1).

Overall, experimental results and calculations from this model agree well if analytical uncertainty is considered. Hence this model may be further used in environmental studies to predict isotope effects that occur during partitioning between water and air in open systems. Even though this exchange model is able to deliver these useful insights, it is not able to provide a final explanation if and to which extent the properties of organics, molecular interactions, or additional mechanisms contribute to fractionation during volatilization and dissolution. The good fit of the model and measured data indicates, however, that these additional processes, such as diffusion or any other unknown mechanisms, are probably very small. Still, a deeper
understanding is pending and the mechanisms that influence volatilization isotope effects of organics dissolved in water need to be explained in detail. Despite these missing insights, the presented model may be capable to reveal new information for groundwater contaminants but especially also for atmospheric contaminants such as haloforms and methyl halides for which oceans represent both a large source and sink. Source apportionment based on isotopic measurements needs to consider - or may neglect - these fractionation effects depending on the transfer direction between water and air.

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References


Figures and Tables

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<th>Pure phase volatilization</th>
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<td>Trichloroethene</td>
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<td><img src="image8" alt="Graph" /></td>
<td><img src="image9" alt="Graph" /></td>
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</tbody>
</table>

Figure 1: Rayleigh plots of isotopic signatures ($\delta^2$H, $\delta^{13}$C, $\delta^{37}$Cl) measured during volatilization and dissolution of TCM (chloroform), TCE and methanol dissolved in water and for pure phase volatilization. All experiments were carried out at $23 \pm 2^\circ$C. The slope of the regression line indicates the enrichment factor $\varepsilon$ in Ur. For volatilization of compounds dissolved in water each
data point is the result of a separate experiment whereas for dissolution samples were obtained from 5 (TCE, TCM) and 4 (methanol) individual experiments each including 5 (TCE, TCM) and 3 (methanol) measurements per experiment. Values for the pure phase were obtained from three separate experiments each measured 5-7 times during progressive evaporation. Stable carbon isotope measurements of a previous study were included with a dashed trendline. Corresponding enrichment factors are given in Table 1. Error bars indicate the accuracy for the measurement of δ²H, δ¹³C, and δ³⁷Cl with 5 mUr, 0.5 mUr, and 0.2 mUr respectively. Analytical uncertainty for concentration measurements was usually better than 5% for compounds dissolved in water and better than 0.5% for pure substances.
Table 1: Enrichment factors for volatilization, dissolution, and equilibrium conditions for dissolved and pure organics.

<table>
<thead>
<tr>
<th>Pure phase compounds</th>
<th>Equilibrium</th>
<th>Volatilization</th>
<th>Model calculations</th>
<th>Compounds dissolved in water</th>
<th>Equilibrium</th>
<th>Dissolution</th>
<th>Volatilization</th>
<th>Model calculations</th>
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<tr>
<td></td>
<td>$\varepsilon_{\text{equ meas}}$</td>
<td>error</td>
<td>$n$</td>
<td>$\varepsilon_{\text{vol meas}}$</td>
<td>error</td>
<td>$n$</td>
<td>$\varepsilon_{\text{diff calc}}$</td>
<td>$\varepsilon_{\text{CGM calc}}$</td>
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<tr>
<td>TCE</td>
<td>+16.8</td>
<td>3.7</td>
<td>6</td>
<td>+8.2</td>
<td>1.4</td>
<td>12</td>
<td>-0.69</td>
<td>+16.2</td>
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<tr>
<td>TCM</td>
<td>+15.6</td>
<td>4.8</td>
<td>7</td>
<td>+13.8</td>
<td>1.7</td>
<td>12</td>
<td>-0.82</td>
<td>+14.8</td>
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<tr>
<td>Methanol</td>
<td>-18.0</td>
<td>6.0</td>
<td>6</td>
<td>+1.6</td>
<td>1.9</td>
<td>12</td>
<td>-7.20</td>
<td>-25.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>$\delta^{13}\text{C [mUr]}$</th>
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<tr>
<td>TCE</td>
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</tr>
<tr>
<td>TCM</td>
<td>+2.3</td>
</tr>
<tr>
<td>Methanol</td>
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<table>
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<th>$\delta^{37}\text{Cl [mUr]}$</th>
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<tr>
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<tr>
<td>TCM</td>
<td>-0.06</td>
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</table>

Calculated enrichment factors for liquid-air transfer according to the exchange model ($\varepsilon_{\text{vol-exch}}$) and Craig Gordon model ($\varepsilon_{\text{CGM}}$) are compared to measured values. Errors are given as the standard deviation for equilibrium isotope effects representing the propagated error of measurements in the liquid phase and gas phase respectively. For volatilization and dissolution experiments, the error is reported as the 95% confidence interval. For calculated $\varepsilon_{\text{vol-exch}}$, uncertainty is given as the propagated error from measurements of $\varepsilon_{\text{equ}}$ and $\varepsilon_{\text{diss}}$. Values in italics are those which are not significantly different from 0 for equilibrium experiments or for which no statistically significant regression (p > 0.05) was calculated. Enrichment factors marked with an asterisk * were published in a previous study.\(^{17}\)