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Isotope fractionation ($^2H/^1H$, $^{13}C/^{12}C$, $^{37}Cl/^{35}Cl$) in trichloromethane and trichloroethene caused by partitioning between gas phase and water

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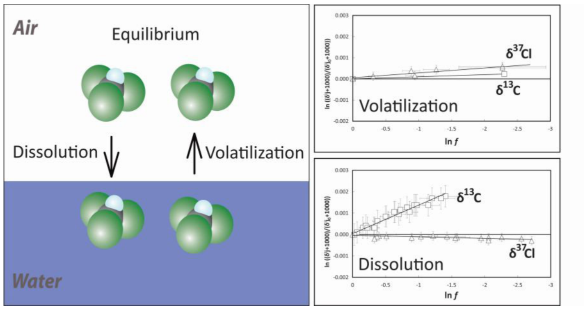
Table of Contents



This article scrutinizes volatilization isotope effects of chlorinated organic compounds by taking into account all measurable stable isotopes of present elements and the three main kinetic and equilibrium partitioning scenarios.

Abstract

Transfer of organic compounds between aqueous and gaseous phases may change the isotopic composition which complicates the isotopic characterization of sources and transformation mechanisms in environmental samples. Studies investigating kinetic phase transfer of compounds dissolved in water (volatilization) are scarce, even though it presents an environmentally very relevant phase transfer scenario. In the current study, the occurrence of kinetic isotope fractionation ($^{2}H/^{1}H$, $^{13}C/^{12}C$, $^{37}Cl/^{35}Cl$) was investigated for two volatile organic compounds (trichloroethene, TCE and trichloromethane, TCM) during volatilization from water and gas-phase dissolution in water. In addition, experiments were also carried out at equilibrium conditions. The results indicated that volatilization of trichloromethane and trichloroethene from water, in contrast to pure phase evaporation, only caused small (chlorine) or negligible (hydrogen, carbon) isotope fractionation whereas for dissolution in water significant carbon isotope effects were found. At equilibrium conditions, hydrogen and carbon isotopes showed significant differences between dissolved and gaseous phase whereas small to insignificant differences were measured for chlorine isotopes. The results confirm the hypothesis that isotope effects during volatilization of organics from water are caused by transport inhibition in the aqueous phase. The consideration of gas-phase diffusion and vapor pressure isotope effects (Craig-Gordon model) could not reproduce the measured isotopic data. Overall, this study provides an overview of the most common kinetic and equilibrium partitioning scenarios and reports associated isotope effects. As such it illustrates under which environmental conditions isotopic signatures of chlorinated volatile organics may change, or remain constant, during transfer between surface waters and air.

1 Introduction

Chlorinated organic compounds are both naturally occurring as well as human-made chemicals.[1, 2] Many of these compounds are toxic, persistent, and have adverse effects on flora, fauna, and human health.[3] Stable isotope analysis has become a routinely used tool to more precisely identify the sources of these compounds and to characterize transformation and degradation pathways.[4] The interpretation of the results from isotopic measurements may, however, be complicated by additional processes such as adsorption, diffusion, or phase transfer (evaporation, volatilization). Even though those processes do not break any bonds and leave the molecules unchanged, they are able to cause changes in the isotopic composition of these organic compounds. As a consequence, isotopic fingerprints for the sources of chemicals may be changed or the quantification of degradation rates in contaminated aquifers may be over- or underestimated, for example.[4]

Phase transfer processes and associated isotope fractionation in organic compounds have been studied widely in the last 70 years, and especially isotope fractionation for equilibrium partitioning between the pure phase and the gaseous phase of chemicals.[5-8] With the advent of compound-specific isotope analysis about twenty years ago interest arose in the study of kinetic evaporation (pure phase – air transfer) and associated isotope fractionation of organic compounds.[9-12] The environmentally very relevant transfer of dissolved organic compounds from water to air (kinetic volatilization), however, has largely remained understudied and was only reported by few publications.[13-15]

The processes causing fractionation during volatilization of organics from water are at debate. The classic theory suggests that isotope fractionation during equilibrium partitioning between the pure phase and gas phase is caused by small differences in the vapor pressure of the different isotopologues.[5] Isotopologues are molecules that differ in their isotopic composition at least at one position.[16] Diffusive isotope effects are often assumed in addition to vapor pressure isotope effects (VPIE) during non-equilibrium/ kinetic conditions, that is, when the gaseous organic is continuously removed.[13, 14, 17] The existence of diffusive isotope effects was rationalized with diffusive transport models such as the Two-Film theory.[18] Furthermore, the so-called Craig-Gordon model (CG model) was adopted for organics to describe isotope effects during phase transfer.[13, 17] Originally, this model was developed to interpret isotope fractionation during evaporation of water considering both VPIE and diffusive isotope effects.[19] The mentioned models do, however, not consistently reproduce all data reported for organic compounds in the literature. A recent study demonstrated that only insignificant carbon isotope fractionation occurs during passive volatilization of TCE and other chlorinated organics from water.[15] It was suggested that fractionation, or the lack thereof, might be attributed mainly to molecular interactions and/or transport limitations in the aqueous phase. Another study applied a different experimental volatilization approach. The authors reported significant carbon and also chlorine isotope fractionation for TCE dissolved in water and results were interpreted according to the Craig-Gordon Model considering both VPIE and diffusive effects.[14] Other authors proposed that isotope fractionation during volatilization is dominated by diffusion with contributions from VPIE being negligible.[20] This discrepancy between few publications shows that isotope fractionation due to phase transfer processes of dissolved organics are currently still not well understood.

Hence, the objective of this work was to carry out a systematic study of phase transfer processes and associated isotope fractionation for organic compounds including both kinetic and equilibrium partitioning between water and air. For this purpose, two nonpolar volatile chlorinated organic compounds were chosen: trichloromethane and trichloroethene. Nonpolar compounds are, according to definition,[21] not able to form permanent hydrogen bonds. This definition includes apolar compounds such as hexane but also monopolar compounds such as trichloromethane.[21] Both TCE and TCM represent important pollutants in the environment[22] and results from this study might also be representative for similar volatile halogenated contaminants possessing similar physicochemical properties. To investigate phase transfer processes as detailed as possible, experiments were carried out for all conceivable scenarios including equilibrium partitioning of dissolved compounds and continuous kinetic volatilization of dissolved compounds from open water surfaces. For the first time, to our knowledge, we report isotopic enrichment factors for dissolution of gaseous organic compounds in water. For all these scenarios we measured the isotope fractionation for stable hydrogen, carbon and chlorine isotopes. The results were used to scrutinize currently common models for the interpretation of isotope fractionation and the corresponding processes in organic compounds volatilizing from open water surfaces.

2 Material and Methods

Trichloromethane and trichloroethene (purity >99.5 % each) were purchased from Fisher Scientific, Fair Lawn, NJ, USA for carbon isotope analyses of equilibrium partitioning experiments. For all other experiments chemicals were acquired from Carl Roth GmbH & Co KG (TCM >99.9 %) and Sigma Aldrich Chemie GmbH, Germany (TCE, >99.5 %).

2.1 Volatilization, dissolution, and evaporation experiments.

Experiments for open system volatilization of chemicals dissolved in water and evaporation of pure phase compounds were carried out according to a previously published protocol.[15] For volatilization (water-air transfer of dissolved organics) two different scenarios were investigated: (a) volatilization under dynamic conditions and (b) volatilization under static conditions (see ESI 1 for experimental setup). For (a), 6 - 10 beakers (60 mL) were filled with 50 mL of stock solution (100 mg L^{-1}) each and stirred 10 to 90 minutes for TCM and TCE respectively. A constant turbulent movement of both, the water and the air above the water was present throughout the whole experiment. For the static setup (b), 8 open septum bottles (120 mL) were filled with 50 mL of stock solution and left completely still over the entire experiment which, in this case, lasted for up to 8 hours. After defined volatilization times, the aqueous solution from beakers (a) and open septum bottles (b) was transferred to 60 mL septum bottles by using a 60 mL plastic syringe to slowly extract the water from the beakers and the 120 mL open septum bottles. There was no significant loss (< 3%) of TCE and TCM associated with this transfer procedure. The 60 mL bottles were then crimp-sealed and equilibrated for at least 12 hours thus providing an equal treatment to all bottles which maintains the relative quantitative and isotopic differences between the individual samples of each experiment. Concentrations for dissolved compounds were determined before isotopic analysis by using the peak areas of calibration standards (4-point calibration) and samples which were recorded by the IRMS. Details of the quantification procedure are provided in the electronic supplementary information (ESI 2).

For kinetic dissolution experiments of gas phase chemicals in water, first 10 mL of compound was filled into a 1 L custom-made septum bottle, crimp-sealed, and equilibrated over night at 23 ± 1ºC to create a nearly saturated air – organic compound gas mixture. Then 250 mL septum bottles were filled with 200 mL of deionized water, crimp sealed, and the air in the headspace was replaced with the air-organic gas mixture. This replacement was performed using a 60 mL gas-tight syringe and an additional needle. The headspace was flushed with the air-organic gas mixture using the second needle as an outlet thus avoiding early condensation by keeping the pressure at atmospheric levels. During dissolution experiments, samples of headspace gas were taken approximately every minute and analyzed for δ^{2}H, δ^{13}C and δ^{37}Cl. The aqueous phase was continuously shaken at a slow rate to avoid concentration differences within one phase. Equilibrium conditions were not reached throughout all experiments. Five separate experiments were carried out with five analyses per experiment. It can be assumed that glass walls of the bottles or the stoppers did not cause adsorptive isotope effects and hence did not disturb the measurements (ESI 3).

Evaporation experiments of pure phase compounds were carried out to provide a full set of enrichment factors also for this process. In these experiments three separate samples (usually 5 g ± 0.2 g in 5 mL beakers) were left for evaporation in a fume hood for passive pure phase volatilization. The remaining aqueous phase was sampled 5 to 7 times at different evaporation steps and analyzed for δ^{2}H, δ^{13}C, and δ^{37}Cl. The amount of organic compound remaining after partial evaporation (*f)* was measured gravimetrically (ESI 2).

2.2 Equilibrium partitioning experiments.

For compounds dissolved in water, stock solutions with a concentration of 100 mg L^{-1} were prepared. Fifty mL of stock solution were filled in 60 mL septum bottles, crimp sealed and equilibrated overnight. The δ^{2}H, δ^{13}C and δ^{37}Cl signatures of the organic compounds in the gas phase of the closed and equilibrated bottles were determined by headspace analysis and compared to the isotopic composition of the organic stock (pure phase) which was used to prepare the aqueous solutions. Calculations based on Henry's constant (see ESI 4) had shown that in our experiments 97.3 % of TCM and 93.3 % of TCE, remained in the aqueous phase and only negligible amounts partitioned into the headspace. No significant isotopic difference may be observed between the pure phase (organic stock) and the dissolved chemical at equilibrium. Thus, equilibrium isotope effects could be determined by simply comparing isotopic values of headspace gas and the pure phase which was used to prepare the aqueous stock solutions.

For experiments studying the pure phase of organic substances at equilibrium conditions, 5 mL of each compound was filled in 10 mL vials, crimp sealed with PTFE-coated stoppers (Wheaton®) and left for equilibration overnight at 23 ± 1ºC. The isotopic composition of hydrogen, carbon and chlorine was determined for both the gas phase and the pure liquid phase. For gas phase analyses, aliquots of the headspace were collected with a gas tight syringe with pressure lock (VICI precision sampling) and injected into the injector (split mode) of the GC. Extracted volumes were replaced by air to keep pressure balance in the bottles. Liquid phases were vaporized and diluted in He. In these conditions, liquids could be analyzed in a similar way as headspace gases to avoid overly high split ratios and this procedure was previously evaluated for conservation of the isotopic composition.[23, 24] After each injection into the GC, syringes were flushed 5 times with air to remove remaining organic compounds and to avoid memory effects. Usually 6–10 analyses were carried out for the liquid phase and headspace, respectively.

2.3 Stable isotope analysis of carbon, hydrogen and chlorine.

Compound specific stable isotope analyses for carbon, hydrogen, and chlorine were carried out according to the procedures and methods published in previous articles.[23-27] The details are provided in the electronic supplementary information (ESI 5). Isotopic ratios measured by these various methods are given in delta notation[28]:

Equation 1

where ^{i}E indicates ^{13}C, ^{2}H, and ^{37}Cl, and R the isotopic ratios $^{13}C/^{12}C$, $^{2}H/^{1}H$, and $^{37}Cl/^{35}Cl$, for carbon, hydrogen, and chlorine, respectively. Delta values express the relative difference of the sample ratio versus a standard that represents an international agreement scale: V-PDB (Vienna Pee Dee Belemnite) for carbon, V-SMOW (Standard Mean Ocean Water) for hydrogen, and SMOC (Standard Mean Ocean Chloride) for chlorine. The delta values are given in Ur (urey) according to recent IUPAC recommendations.[29] This unit is interchangeable with the permil scale if given in mUr (milli-urey): 1 mUr = 0.001 = 1 ‰.[30] Total uncertainty of the analytical procedures, including accuracy, reproducibility, linearity, and scale normalization are usually better than 5 mUr (hydrogen),[23] 0.5 mUr (carbon),[31] 0.2 mUr (chlorine).[24]

2.4 Enrichment factors for kinetic and equilibrium conditions.

For kinetic volatilization and dissolution experiments the Rayleigh equation was applied to determine isotopic enrichment factors:[32]

Equation 2

where $\delta^{i}E$ is the isotopic signature ($\delta^{2}H$, $\delta^{13}C$, $\delta^{37}Cl$) of the organic compound in the aqueous phase after partial volatilization, $\delta^{i}E_0$ indicates the initial delta value ($\delta^{2}H_0$, $\delta^{13}C_0$, $\delta^{37}Cl_0$), f is the fraction of organic compound remaining in the aqueous phase, and ε indicates the isotopic enrichment factors ε_H, ε_C, and ε_{Cl} in Ur. For dissolution experiments, $\delta^{i}E$ indicates the delta value of the organic substance in the gas phase after partial dissolution, $\delta^{i}E_0$ designates the initial delta value and f the fraction remaining in the gas phase. Enrichment factors at equilibrium express the isotopic difference between the pure organic phase and the organic in the gas phase (εequ_{pure}) or the dissolved organic phase and the organic in the gas phase (εequ_{wat}). A negative ε indicates a depletion of the heavy isotopes in the organic compound in the gaseous phase compared to the pure liquid or aqueous phase organic. Kinetic enrichment factors express the isotopic enrichment for pure phase–air transfer (evaporation, εevap), dissolved phase–air transfer (volatilization, εvol) and air–dissolved phase transfer (dissolution, εdiss). All volatilization and dissolution experiments were carried out with water as solvent. For evaporation and volatilization, negative enrichment factors indicate normal isotope fractionation and hence an enrichment of the heavier isotope in the remaining pure liquid or aqueous phase because heavier isotopologues possess higher boiling points due to lower zero-point vibrational energies.[33] For dissolution, in contrast, the substrate reservoir is situated in the gas phase. Preferential dissolution of heavier isotopologues into the aqueous phase causes depletion in the gaseous reservoir and thus positive enrichment factors indicate a normal isotope effect.

For experiments at equilibrium conditions isotopic enrichment factors (ε) were determined directly by calculating the difference between the measured δ-values in the gas phase and in the liquid phase.

2.5 Two-film theory and Craig-Gordon model.

Previous studies interpreted phase transfer isotope effects of organic compounds according to the Craig-Gordon model and the underlying two-film theory.[13, 14, 17] Generally, mass transfer of organic compounds from a liquid phase to the gas phase may be viewed as the movement of molecules through a boundary layer; the liquid-gas interface.[21] It is assumed that transport through this boundary layer is significantly slower than in adjacent layers creating a bottleneck for the liquid-gas transfer of organic molecules. Various models and theories were developed to describe the exchange of organic compounds between the liquid phase (pure phase organic or organic dissolved in water) and air, such as the two-film theory, surface renewal model, or boundary layer model.[21] The two-film theory, first proposed by Whitman,[18] assumes that the air-water interface consists of two static layers, one situated on the air side of the interface and the other one on the water side. The movement of organic molecules is controlled by one of these films depending on the air-water partition coefficient and transfer velocities in water and air. Based on this two-film theory, the Craig-Gordon model was developed to describe isotope fractionation during evaporation of water. It assumes an air-side limitation of transfer rates of water and incorporates diffusive isotope effects caused by the movement of water molecules through this static gas layer.[19] Furthermore, the isotope effect caused by the different vapor pressures (VPIE) of different isotopologues is taken into account. Consequently, isotope effects caused by evaporation of water are the result of two processes: the effect of the different vapor pressures and fractionation due to diffusion through the static gas layer. The VPIE can be estimated directly from experiments carried out at equilibrium conditions (ε-equ$_{\text{pure}}$ for evaporation and ε-equ$_{\text{wat}}$ for volatilization) whereas the maximum diffusive enrichment (ε-diff) in the stagnant gas layer compared to the free air is usually calculated according to the following equation:[34]

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^{-1}. Theoretically, the concentration of the organic substance 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 or, if strong winds prevail in the studied environments, for partial rupture of the diffusive layer.[34] In our evaporation and volatilization experiments the concentration of organic compounds in the gas phase was virtually zero and diffusive isotope effects should be maximal. The overall fractionation during evaporation according to the Craig Gordon model is then simply given by:

Equation 4.1

and for volatilization:

Equation 4.2

The calculated enrichment factors εvol_{CG} and $\varepsilon evap_{CG}$ are expressed as the isotopic enrichment of gaseous organic compounds in the free air compared to the dissolved phase in water.

3 Results and Discussion

The objective of this study was to elucidate the occurrence, or the absence, of the processes (diffusion and VPIE) that influence isotope fractionation during phase transfer. Subsequently, we first present the isotopic results for the three possible phase transfer scenarios for compounds dissolved in water (volatilization, dissolution, equilibrium partitioning). Enrichment factors for equilibrium partitioning and evaporation of pure phase compounds are also provided in Table 1 for comparison. The data is then used to evaluate the validity of the currently used hypotheses for the occurrence of volatilization isotope effects.

3.1 Volatilization isotope effects.

Isotope fractionation during water-air transfer of TCM and TCE was investigated for two different scenarios: (a) dynamic conditions and (b) static conditions (experimental setup shown in ESI 1). The experimental setup for dynamic conditions was adopted from a previous study.[15] These dynamic experiments (a) simulate a constant movement of the water surface by stirring the organic-water solution. Thus, these experiments may provide insights into volatilization isotope effects of organics from open water bodies such as ponds and lakes that possess moving water surfaces due to wave formation, for example, and which undergo turbulent mixing at least in the upper layers. Experiments were carried out in a fume hood, thereby simulating a constant exchange of the air above the aqueous phase. Static experiments (b) were carried out to investigate whether completely static conditions and a near-static air column above the aqueous phase would generate different enrichment factors which would hint toward an increasing influence of diffusion and associated isotope effects.

Stable carbon isotopic enrichment factors for dynamic volatilization (a) of compounds dissolved in water ($\varepsilon_C vol_d$) were published in our previous article using a similar experimental approach as in the current study[15] (Table 1). This former study demonstrated that carbon isotope fractionation was negligible for continuous dynamic volatilization of hydrophobic compounds such as chlorofluorocarbons, TCE, and TCM when dissolved in water. For stable chlorine isotopes, volatilization of TCM and TCE from water yielded $\varepsilon_{Cl} vol_d$ of 0.21 ± 0.10 mUr and 0.34 ± 0.15 mUr, respectively. Hydrogen isotopes showed exclusively insignificant isotope effects ($\varepsilon_H vol < \pm 2$ mUr) for volatilization of both compounds from water.

Volatilization under static conditions (b) generated enrichment factors for carbon and chlorine isotopes which were indistinguishable from those obtained for the dynamic experiment. Rayleigh plots are provided in the supplementary information (ESI 6). For carbon, insignificant enrichment factors ($\varepsilon_C vol_s$) of 0.0 ± 0.3 mUr and -0.1 ± 0.3 mUr were measured for TCM and TCE respectively. For chlorine, $\varepsilon_{Cl} vol_s$ of 0.29 ± 0.19 mUr and 0.17 ± 0.15 mUr were obtained for TCM and TCE respectively. Enrichment factors for hydrogen isotopes could not be determined for this experiment but it is conceivable that $\varepsilon_H vol_s$ for the static experiment is similarly insignificant as $\varepsilon_H vol_d$ determined in the dynamic experiment. The comparable enrichment factors obtained from both the dynamic and the static experiment clearly shows that gas phase diffusion, even though a likely process in the static air column, does not influence the isotopic composition in the aqueous phase. These findings are also in agreement with boundary layer models because transport of TCM and TCE should be limited by the water-side film[21] and isotopic enrichment factors usually reflect the rate limiting process or reaction (see also discussion below).[35]

Evaporation experiments of pure TCM and TCE were also carried out during this study. The carbon isotope enrichment factor determined for evaporation of TCE yielded a value of $\varepsilon_C$evap = +0.46 ± 0.10 mUr. This $\varepsilon_C$evap is in good agreement with previously published enrichment factors for this compound ranging from +0.24 to +0.35 mUr.[9, 10, 14, 17] The $\varepsilon_C$evap for TCM was published in our former study and is given in Table 1 ($\varepsilon_C$evap = +1.20 ± 0.10 mUr).[15] Chlorine isotope measurements for pure phase evaporation of TCM and TCE yielded ε_{Cl}evap of 1.14 ± 0.11 mUr and 1.01 ± 0.10 mUr, respectively. The enrichment factor of pure phase evaporation of TCE was determined previously with values ranging from 1.35 mUr to 1.82 mUr.[9, 10, 14] All enrichment factors from the current and previous studies indicate that evaporation of pure phase compounds produces a significant, but in contrast to carbon, a normal chlorine isotope effect. For hydrogen isotopes, pure phase evaporation of TCM and TCE generated significant inverse enrichment factors ($\varepsilon_H$evap) of +14 ± 2 mUr for TCM and +8 ± 1 mUr for TCE. The $\varepsilon_H$evap for pure phase TCE agrees well with the +9 mUr reported by Poulson et al.[10]

These comparisons of the results from evaporation of pure organics and volatilization of dissolved organics reveal important properties of these compounds. Enrichment factors (εvol) measured for the isotopes of all elements (H, C, and Cl) in TCM and TCE were always smaller than enrichment factors obtained for evaporation of the pure phase (εevap, Table 1). Hydrogen

($\varepsilon_H$vol) and carbon isotope effects ($\varepsilon_C$vol) became very small or insignificant if dissolved compounds volatilized from water whereas ε_{Cl}vol for chlorine decreased to about 25-30 % of the magnitude of the pure phase ε_{Cl}evap. These results may corroborate the previous hypothesis that isotope fractionation during volatilization of volatile nonpolar compounds from water is inhibited due to the rate limitation of the slow mass transfer in the water.[15] These results may also be in line with the assumption that diffusion in the liquid boundary layer could be responsible for the measured fractionation but results from dissolution experiments do not support this hypothesis (see discussion below). Overall, our measurements demonstrate that volatilization isotope effects may be considered largely negligible for these chemicals in environmental surface water samples if they were subject to volatile loss. This fact was previously shown for stable carbon isotopes[15] but the current study also demonstrates this fact for hydrogen and chlorine isotopes. Similarly, incomplete extraction with pre-concentration methods such as purge and trap should also not cause significant H and Cl isotope fractionation as previously already shown for stable carbon isotopes.[25, 36]

3.2 Dissolution of gas phase organic compounds in water.

Isotope effects for the kinetic transfer of organic compounds from air to the aqueous phase are, to our knowledge, not reported in the literature yet. Dissolution is the reversal of volatilization and thus it may provide additional insights into phase change processes and validity of models. In our experiments, dissolution generated consistently inverse carbon isotope fractionation ($\varepsilon_C$diss) of 1.3 ± 0.1 mUr and 1.0 ± 0.1 mUr measured in TCM and TCE, respectively. In dissolution experiments, heavier isotopologues should dissolve faster due to lower zero-point vibrational energies and resulting lower volatility.[33] Taking into account the direction of the transfer (air–dissolved phase), a positive ε-diss describes a normal isotope effect. The dissolved compound in the water should become more enriched in heavy isotopes compared to the gas phase. Such depletion of the substrate reservoir leading to positive enrichment factors was also reported for rainout effects of pure water in the atmosphere, for example. Correspondingly, a negative enrichment factor indicates an inverse effect for transfer from air to the dissolved phase during which the gas phase becomes more enriched in heavy isotopes. Hydrogen isotope effects for dissolution were inverse (enrichment in the gas phase) and small/insignificant for both TCE and TCM (ε_{H}diss = 3 ± 2 mUr and 2 ± 3 mUr). The ε_{Cl}diss for δ^{37}Cl of TCM and TCE were very small but Rayleigh plots showed statistically significant regressions (95 % confidence interval, $p < 0.05$) with $+0.07 \pm 0.03$ mUr and $+0.12 \pm 0.06$ mUr for TCM and TCE, respectively. Enrichment factors indicate normal isotope effects, that is, the molecules containing the heavier chlorine dissolve faster and the gas phase becomes more depleted.

These measured enrichment factors demonstrate that for hydrogen and chlorine isotopes gas phase dissolution caused similarly small fractionation effects as during volatilization. Stable carbon isotopes, however, showed significant inverse fractionation (enrichment of the gas phase) during dissolution, in contrast to the insignificant fractionation observed during volatilization. These different isotope effects might be explained with the absence of molecular interactions (van der Waals) in the gas phase due to the much larger distances between molecules.[21] During volatilization from water, however, isotope fractionation may be suppressed by mass transfer limitations due to stronger molecular interactions in the aqueous phase as hypothesized previously.[15] Overall, these results demonstrate that isotope fractionation patterns caused by gas phase dissolution may be different from the opposite phase transfer volatilization. Consequently, the direction of the kinetic phase transfer (waterair or airwater) should be considered if the fate of an organic contaminant in the environment is investigated with isotopic methods.

3.3 Equilibrium isotope effects of compounds dissolved in water and in pure substances.

Equilibration of compounds dissolved in water with air yielded inverse carbon isotope enrichment factors ($\varepsilon_C equ_{wat}$) of +1.4 ± 0.2 mUr and +0.7 ± 0.1 mUr for TCM and TCE which is in accordance with previously published enrichment factors of +1.5 mUr and +0.4 to +0.6 mUr, respectively.[14, 37] Stable chlorine isotope measurements revealed normal $\varepsilon_{Cl} equ_{wat}$ of 0.24 ± 0.10 mUr for TCM and 0.12 ± 0.16 mUr TCE. One previous study reported an $\varepsilon_{Cl} equ_{wat}$ of 0.07 mUr for TCE which is in good agreement with our findings.[14] Even though $\varepsilon_{Cl} equ_{wat}$ values were close to or within analytical uncertainty, a consistently normal chlorine isotope effect was found in all cases. Stable hydrogen isotope analysis of TCM and TCE revealed small inverse $\varepsilon_H equ_{wat}$ of +7 ± 3 mUr and +5 ± 3 mUr, respectively.

Equilibrium partitioning of organics between pure substances and air generated overall larger fractionation effects than for dissolved compounds. For carbon, $\varepsilon_C equ_{pure}$ of +1.0 ± 0.3 mUr for TCE and +2.2 ± 0.4 mUr for TCM were obtained. Literature values were available for pure phaseair equilibration of TCE which were slightly smaller (+0.1 to +0.8 mUr)[14, 38] compared to +1.0 ± 0.3 mUr found in the present study. Stable chlorine isotope measurements yielded very small and partially insignificant normal $\varepsilon_{Cl} equ_{pure}$ of 0.06 ± 0.09 mUr and 0.11 ± 0.05 mUr for pure phase equilibration of TCM and TCE with air, respectively. Previously reported $\varepsilon_{Cl} equ_{pure}$ agree for TCM (0.1 mUr)[39] but differ slightly for TCE (0.39 mUr)[14] which may be attributed to the different experimental method to determine these equilibrium isotope effects (stepwise equilibration for TCE). Hydrogen isotope measurements for pure phase–air equilibrium partitioning has not been reported in the literature. Our experiments indicated significant inverse isotope effects ($\varepsilon_H equ_{pure}$) for TCM and TCE with +16 ± 5 mUr and +17 ± 4 mUr.

In general, equilibrium isotope effects of hydrogen and carbon measured for the pure and dissolved organic phases of TCE and TCM were always larger than evaporation and volatilization isotope effects. For chlorine, in contrast, evaporation isotope effects were larger than for pure phase equilibrium. Compounds dissolved in water showed comparably small chlorine isotope fractionation under equilibrium and kinetic conditions.

3.4 Evaluation of current hypotheses for volatilization isotope effects of organics from water

The data collected throughout this study was used to test current hypotheses for the occurrence of isotope effects during continuous volatilization of organics dissolved in water. Current hypotheses assume that isotope effects are caused, according to common transport models, either by diffusion alone[20] (I) or a combination of diffusion and VPIE[14] (II, CG model, see section 2.5 for details). A third hypothesis assumed transport limitations or molecular interactions in the water being responsible for observed volatilization isotope effects (III).[15]

For TCE and TCM dissolved in water, the stagnant water layer controls transfer according to common classifications of organic substances[21] and diffusion in water may potentially dominate transfer velocities (I). Wanner and Hunkeler[40] reported diffusive fractionation factors of $\alpha_{131/130} = 0.99978$ and $\alpha_{132/130} = 0.99963$ for TCE isotopologues in water. These fractionation factors correspond to $\varepsilon_C$diff and $\varepsilon_H$diff of 0.22 mUr (Equation 6) and ε_{Cl}diff of 0.37 mUr and agree within analytical uncertainty with the $\varepsilon_C$vol and ε_{Cl}vol measured for TCE in the present study (Table 1). For the opposite air-water transfer (dissolution), however, measured enrichment factors for the three elements do not agree with the occurrence of diffusive isotope effects. Here, $\varepsilon_C$diss of 1.3 ± 0.1 mUr and 1.0 ± 0.1 mUr were obtained for stable carbon isotopes in TCM and TCE but only insignificant fractionation was observed for hydrogen and chlorine in the same molecules. The two-film theory assumes a water-side limitation for TCE and TCM based on the physical properties (e.g. diffusivity) of these two compounds. If diffusion was the sole or dominating fractionating process, measured enrichment factors for dissolution would be similarly small (or insignificant) as those observed in volatilization experiments. Hence, our experiments indicate that diffusion may not be the main fractionating process during water-air and also not during air-water transfer of these compounds.

The Craig-Gordon model (II) not only considers diffusion in the stagnant gas layer, but it also includes vapor pressure isotope effects (VPIE) to account for the slightly different tendencies of heavy and light isotopologues to evaporate. Stable carbon isotope fractionation for evaporation of pure substances calculated by the CG model (ε_{C}-evap$_{CG}$) agree reasonably well with measured ε_{C}-evap but larger variations occur for hydrogen (ε_{H}-evap) in TCE and chlorine (ε_{Cl}-evap) in TCM (Table 1). Previous studies investigating stable carbon isotope fractionation during evaporation of pure organics also achieved a satisfying fit of measured and calculated data.[17] The measurement of all three isotopes, however, reveals that not all elements can be satisfactorily described by the Craig-Gordon model.

Similar discrepancies are observed, if the CG model is used to calculate volatilization isotope effects of compounds dissolved in water. Here, calculated enrichment factors for chlorine (ε_{Cl}-evap$_{CG}$) deviate by 1.28 mUr (TCE) and 1.67 mUr (TCM) from measured ε_{Cl}vol even though carbon and hydrogen isotope enrichment factors from the CG model are in satisfactory agreement with measured ε_{H}vol and ε_{C}vol. The likely reason for the discrepancy might be the overestimated diffusive isotope effects derived from equation 3 for gas phase diffusion. Due to the physical properties of TCE and TCM, transport should be controlled by the water-side film of the boundary layer[21] and hence the assumption of gas-phase diffusion in the CG model is misleading.

Generally, diffusion of organics in the gas phase may only influence the isotopic composition of organics in the aqueous phase, if organics dissolve back into the aqueous phase. This dissolution is possible only if, to some extent, equilibrium is reached between gas phase and aqueous phase. However, if compounds volatilize rapidly, equilibration of the gas-side boundary layer with the organics in the aqueous phase is quite unlikely. Without equilibration, dissolution of gas phase organics is rather negligible. This means that even if diffusive fractionation occurred in the gas phase, it would not have changed the isotopic composition in the aqueous phase. Such scenarios are conceivable only for pure water or less volatile organic compounds (pure or dissolved) where liquid-gas exchange rates are slow enough to allow for a partial equilibration between gas phase and liquid. Thus, a backward dissolution into the liquid phase may occur and, given enough time, homogeneous mixing of the liquid reservoir is possible. Hence the CG model, in its current form, may only be applicable for water or less volatile organic compounds that evaporate/volatilize on a slower rate than the tested compounds.

Another hypothesis proposed that insignificant carbon isotope enrichment factors during volatilization are simply the result of transport limitations and/or molecular interactions in the aqueous phase.[15] In this current study also hydrogen and chlorine isotope fractionation was largely insignificant or small which would be consistent with the presence of a rate-limiting non-fractionating transfer in the aqueous phase. Such limitation should, however, not occur in the gas-phase during dissolution experiments and this fact is also reflected in the data. Here, stable carbon isotope measurements showed a significant inverse isotope effect which can be rationalized with dissolution of the lighter isotopologues. Hydrogen and chlorine isotope effects for TCE and TCM dissolved in water were not only small for dissolution experiments but also for volatilization and under equilibrium conditions. Hence, H and Cl isotopes seem to generally show only small fractionation for phase transfer between gas phase and water. For stable carbon isotopes, transfer limitations during volatilization and vapor pressure differences during dissolution are conceivably the drivers of isotope fractionation, or the lack thereof.

4 Conclusion

In this study we provide experimental evidence that isotope fractionation for the three elements in TCM and TCE is insignificant (H, C) or small (Cl) during continuous volatilization of chlorinated organics from water. The results seem to confirm a previous hypothesis that fractionation of these volatile, nonpolar compounds is suppressed due to transport limitations in the aqueous phase. It is conceivable that this absence of fractionation may be generally observed for other important volatile halogenated compounds such as chlorinated ethenes, haloforms, and methyl halides.

Results from volatilization experiments might also be indicative for a diffusive isotope effect in the liquid boundary layer but dissolution experiments did not confirm this hypothesis. Measured results were not in agreement with enrichment factors calculated by the Craig Gordon model because both, diffusion in air and the effect of the different vapor pressures, would have caused significantly larger isotope fractionation which was not observed. Consequently, the CG model and the underlying processes should not be generally assumed for continuous volatilization of nonpolar chlorinated organics from surface water.

Our results may also have important implications for environmental studies of volatile halogenated compounds which are pollutants in groundwater[3, 4] and the atmosphere.[2] For groundwater pollutants additional work will be necessary to fully understand the influence of phase transfer on the isotopic composition in the saturated zone of the aquifer. Recent studies indicated that gas phase diffusion in the porous sediments of the unsaturated zone might cause more complicated volatilization scenarios (movement through small pore spaces of various sizes, presence of pore water, etc).[14, 41] For atmospheric pollutants such as haloforms, methyl halides and (hydro-) chlorofluorocarbons the current study has direct implications. Isotopic methods are increasingly used to apportion sources and to quantify degradation of these substances. In this context, phase transfer isotope effects only need to be considered for certain scenarios. The current study demonstrates that volatilization isotope effects are largely negligible when organics are emitted from water to the atmosphere; for instance, for compounds produced by algae, such as methyl halides and haloforms. In contrast, for dissolution of these chemicals from the atmosphere in surface waters, or when equilibrium conditions are established, fractionation might occur for the isotopes of some elements and this fact needs to be considered in environmental studies where air-water transfer of organics is involved.

Conflict of interest

There are no conflicts of interest to declare

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Figures and Tables

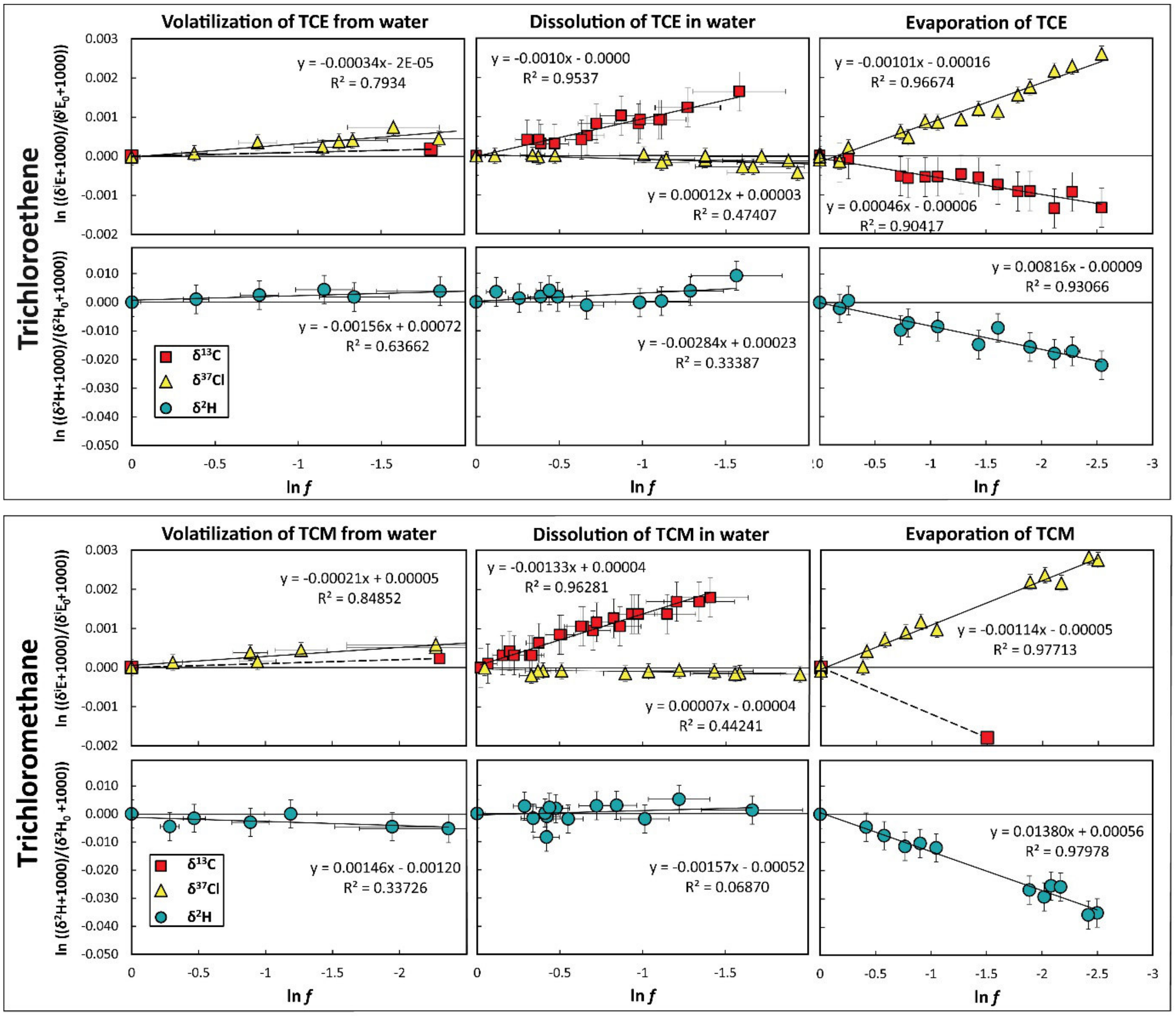

Figure 1: Rayleigh plots of isotopic signatures (δ^2H, δ^{13}C, δ^{37}Cl) measured during volatilization (dynamic experiment), dissolution, and evaporation of TCM and TCE. The regression lines were not forced through the origin according to recommendations by Scott et al.[42] All experiments were carried out at 23 ± 1ºC. The slope of the regression line indicates the enrichment factor ε in Ur. For volatilization of compounds dissolved in water each data point is the result of a separate sacrificial sample. For dissolution, data points were obtained from 5 individual experiments each including 5 measurements per experiment. Values for evaporation of 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 and a single marker and corresponding enrichment factors are included in Table 1 along with the data of the present study[15]. Error bars indicate the total uncertainty, including accuracy, reproducibility, linearity, and scale normalization, for a measurement of δ^{2}H, δ^{13}C, and δ^{37}Cl which amount to 5 mUr, 0.5 mUr, and 0.2 mUr respectively[23, 24, 31]. Analytical uncertainty for concentration measurements was usually better than 5 % for compounds dissolved in water and better than 0.5 % for pure phase compounds.

Table 1: Enrichment factors for evaporation, volatilization (dynamic experiment), dissolution, and equilibrium partitioning of pure and dissolved compounds. Calculated enrichment factors for volatilization according to the CG model (εvol_{CG}) are compared to measured enrichment factors (εvol_d). Enrichment factors for static volatilization (εvol_s) were indistinguishable from the dynamic experiment and are not shown. Calculated enrichment factors are further given for evaporation according to the CG model ($\varepsilon evap_{CG}$) including also εdiff for gas-phase diffusion. Errors are given as the standard deviation for equilibrium isotope effects representing the propagated error of isotopic measurements of the liquid phase and gas phase, respectively. For evaporation, volatilization, and dissolution experiments, the error is reported as the 95% confidence interval of the regression. 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 and were determined with similar experimental setups and procedures.[15]

Pure phase compounds								Compounds dissolved in water									
Equilibrium			Evaporation			Model calculations		Dissolution						Volatilization			Model calculations
ε-equ$_{pure}$ meas	error	n	ε-evap meas	error	n	ε-diff calc	ε-evap$_{CG}$ calc	ε-equ$_{wat}$ meas	error	n	ε-diss meas	error	n	ε-vol$_d$ meas	error	n	ε-vol$_{CG}$ calc
Hydrogen [mUr]																	

TCE	+16.8	3.7	6	+8.2	1.4	12	-0.69	+16.2	+5.2	2.6	8	-2.8	2.3	10	-1.6	1.4	6	+4.5
TCM	+15.6	4.8	7	+13.8	1.7	12	-0.82	+14.8	+7.4	2.7	5	*-1.6*	*3.0*	*14*	*+1.5*	*2.4*	*7*	+6.6
Carbon [mUr]																		
TCE	+1.0	0.3	9	+0.5	0.1	15	-0.69	+0.3	+0.7	0.1	9	-1.0	0.1	16	*+0.1***	*0.2*	*8*	±0.0
TCM	+2.2	0.4	10	+1.2*	0.1	12	-0.82	+1.4	+1.4	0.2	9	-1.3	0.1	23	+0.1*	0.1	7	+0.6
Chlorine [mUr]																		
TCE	-0.11	0.05	6	-1.01	0.10	15	-1.37	-1.43	*-0.12*	*0.16*	6	+0.12	0.06	15	-0.34	0.15	8	-1.62
TCM	*-0.06*	*0.09*	*7*	-1.14	0.11	12	-1.64	-1.70	-0.24	0.10	7	+0.07	0.03	17	-0.21	0.10	7	-1.88