Electronic Supplementary Information for

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

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Content:

ESI 1: Experimental setup for dynamic and static volatilization

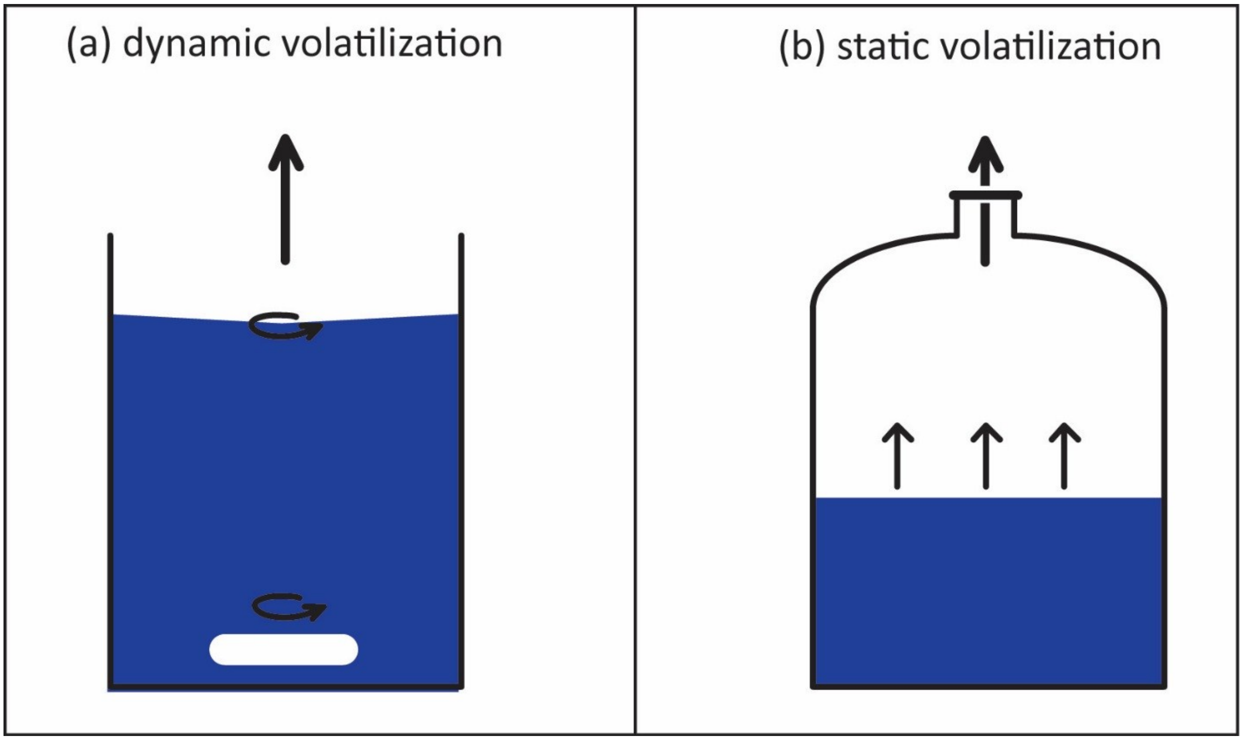

Figure ESI 1: Illustration of the experimental setups used to investigate volatilization isotope effects of compounds dissolved in water. (a) illustrates the dynamic experiment which was constantly stirred and where a slight air draft above the liquid constantly removed volatilized gases. (b) illustrates the static experiment where the liquid was not stirred, and where the gas phase should not have undergone turbulent mixing.

(Note: The figures are not drawn to scale, the beaker in (a) is enlarged compared to the septum bottle)

ESI 2: Quantification of *f* in the different experiments

The quantification of *f*; that is, the fraction of compound remaining after partial loss, was determined in two different ways: (a) by determining directly the mass of the pure liquid in evaporation experiments and (b) by generating a calibration curve with 4 standards of known relative concentrations for volatilization of compounds dissolved in water.

For evaporation of pure liquid compounds, *f* was determined by weighing the vials after each evaporation step (a). The mass of the full vials (subtracting the mass of the empty vial) was set to *f* =1.0 and the fraction of all subsequent values was determined relative to this starting mass. After each evaporation step, 5µL of the pure compound remaining was injected into a glass bottle (flushed with helium and crimp-sealed with a gray Wheaton® stopper, see ESI 3). One bottle was prepared for each isotopic measurement. Three replicate experiments were carried out. All *f* -values were corrected for the removal of the pure liquid compound due to sampling.

Quantification for volatilization experiments was carried out by creating a calibration curve using 4 standards (b). The standards corresponded to *f* =1, *f* =0.5, *f* =0.25 and *f* =0.05 of the initial concentrations and were prepared from the same stock solutions as the samples. Before isotope analyses of the samples started, aliquots of the headspace of each standard were injected three times into the GC-C-IRMS and a calibration curve was created from the recorded areas of the chromatographic signals (peaks). Figure ESI 2 exemplarily illustrates a calibration curve created for quantification of volatilization of TCE from water. This calibration curve was used to determine concentrations of the samples after partial volatile loss. For dissolution experiments, *f* was determined in a similar way as for volatilization experiments by using known dilutions of the corresponding compounds dissolved in water and injecting aliquots of the headspace to create calibration curves for each compound.

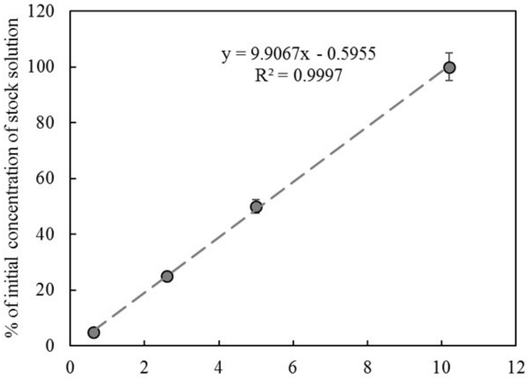

Figure ESI 2: Calibration curve for TCE dissolved in water. The value of 100% corresponds to *f* =1 (starting concentration of 100 mg L^{-1}). Error bars indicate the standard deviation of three replicate measurements which was usually smaller than 5%.

ESI 3: Conservation of the isotopic composition of pure liquids during vaporization in glass bottles

In order to facilitate the analysis of organic chemicals, pure substances were often analyzed as a vaporized organic-He gas mixture. This technique avoids dilution of organics in solvents or the overly high split ratios which are necessary to obtain isotopic signatures from pure substances. This technique of vaporizing pure organics in glass bottles has been tested in previous studies for a wide array of organic compounds and especially for chlorinated substances such as TCE and TCM. Specifically, substances were first characterized with reference methods for their hydrogen and chlorine isotopic composition using Elemental Analyzer IRMS[1] and Dual Inlet IRMS[2] respectively. The same substances were then analyzed as pure substances and also as organics vaporized in glass bottles for their hydrogen[3] and chlorine isotopic composition.[4] The isotopic values obtained from these three techniques were identical within analytical uncertainty and hence it can be assumed that no significant fractionation has occurred in our experiments due to adsorption on the glass walls or the gray Wheaton® stoppers, leakage or other effects.

ESI 4: Evaluating carbon isotope effects in dissolved TCE and TCM due to partial loss to the gas phase at equilibrium.

Isotope effects for equilibrium partitioning of TCM and TCE in aqueous solutions were determined by comparing $\delta^{13}C$ values measured for gaseous compounds to those measured for pure TCM and TCE. In this experiment we assumed that (a) the dissolved phase was isotopically indistinguishable from the pure compound used to prepare the stock solutions and (b) that, in our specific setup, partitioning of some compound into the headspace did not significantly change the isotopic composition of the remaining dissolved organics. Assumption (a) was investigated and confirmed by previous studies using purge & trap methods to extract organics from the aqueous phase.[5, 6] The isotopic composition of the extracted compounds such as TCM, TCE, and chlorofluorocarbons was indistinguishable from the pure compounds used to prepare the solutions.

To investigate (b) the dimensionless Henry constants (0.17 for TCM and 0.43 for TCE)[7] were used to calculate the amount of compound partitioning from 50 mL solution into the 10 mL headspace in a closed system. A starting concentration of 100 mg/L corresponds to 42 µmol of TCM and 38 µmol of TCE in 50 mL of water. Assuming the dimensionless Henry constants, the amount of compound partitioning into the 10 mL headspace of the bottles at 25°C is 1.2 µmol for TCM and 2.7 µmol for TCE. Consequently, only 2.7 % of TCM and 6.7 % of TCE partitioned into the headspace. This small loss to the headspace leaves the isotopic composition of the dissolved compound (97.3 % for TCM and 93.3 % TCE) basically unchanged. This can be illustrated by assuming the equilibrium enrichment factors for carbon (+1.5 mUr for TCM and +0.6 mUr for TCE) published by Hunkeler and Aravena.[8] The partitioning of 2.7 % of TCM and 6.7 % of TCE into the gas phase would only cause a change of -0.04 mUr (both compounds) in the dissolved compounds compared to the pure liquids. This small change is considerably smaller than the precision of repeated measurements (0.1 - 0.2 mUr) for equilibrium isotope effects (carbon) of compounds dissolved in water and hence can be neglected in our specific case. The extent of isotope fractionation is illustrated in Figure ESI 4 for TCM.

The calculations above demonstrate further that mass transfer isotope effects due to extraction of headspace gas with the syringe should be negligible. For stable carbon isotope analysis of TCE and TCM, for instance, 100 µL of headspace gas was extracted for each analysis. A maximum amount of 6 analyses was carried out per bottle. Hence a total amount of 0.16 % of TCM and 0.4

% of TCE were extracted corresponding to a change of the isotopic composition of dissolved TCM and TCE of 0.002 mUr.

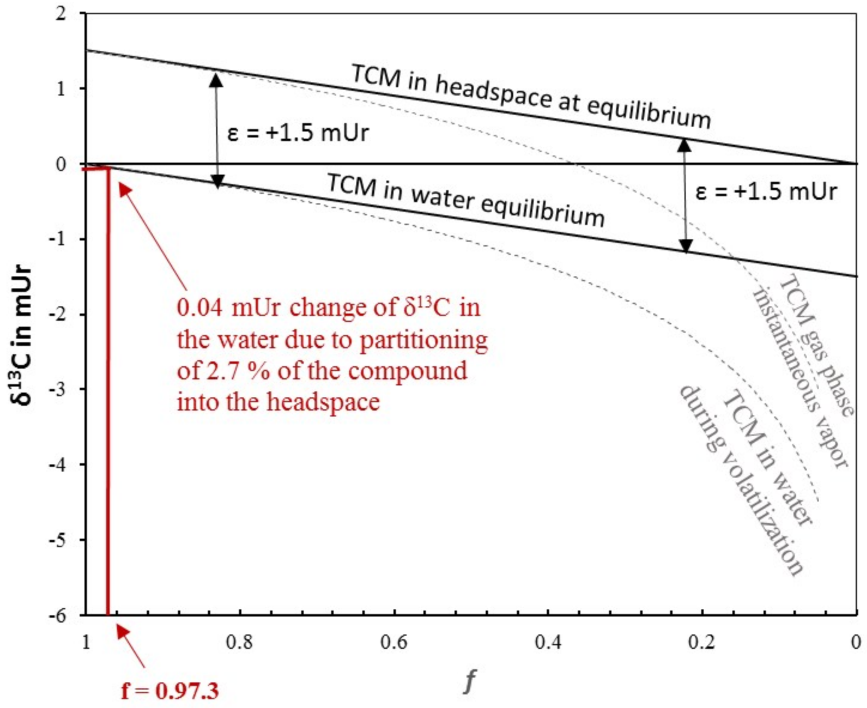

Figure ESI 4: Illustration of the extent of isotope effects due to partitioning into headspace in equilibration experiments. Straight black lines illustrate the isotopic composition of dissolved phase and gas phase depending on the distribution of TCM between water and air assuming an ε-equ$_{wat}$ of +1.5 mUr. The carbon isotope composition of TCM in water changes by at most 0.04 mUr due to partitioning of 2.7% of the substrate into the headspace. This change is negligible given the analytical precision in our experiments. The gray lines illustrate the evolution of the isotopic composition of TCE dissolved in water and in the gas phases if headspace gas is continuously (or in small increments) removed (e.g. by extracting small volumes with a syringe)

ESI 5: Compound specific stable carbon, hydrogen, and chlorine isotope analyses

Stable carbon isotope analysis. Compound specific stable carbon isotope analysis for equilibrium partitioning experiments was carried out by closely following a previously published protocol.[6] Briefly, for headspace analysis, gas samples were injected directly into the GC by using a gastight syringe (VICI Precision Sampling). After separation on a G-SQ plot column (Agilent J&W GC columns, 60 m x 0.32 mm, isothermal temperature of 140°C, flow 1.6 mL/min) mounted in a Varian 3400 GC, compounds were transformed to CO_2 in the connected combustion furnace and transferred to the isotope ratio mass spectrometer (Finnigan MAT 252). For volatilization and dissolution experiments, analyses were carried out using an Agilent 7890A GC, equipped with a ZB1 column (Phenomenex, 60m, 0.32 mm ID, 1µm film, continuous flow 2 mL/min), coupled via an IsoLink and ConfloIV to a Thermo Finnigan MAT 253. Scale consistency was checked with several in-house reference compounds. Scale correction via a two-point calibration (see below) was usually not necessary for $\delta^{13}C$. Delta values ($\delta^{13}C$) referenced against V-PDB (Vienna Pee Dee Belemnite) were calculated according to the following equation:

$$\delta^{i}E\ (Ur) = \frac{(R)sample}{(R)standard} - 1 \qquad \text{Equation 1}$$

Where ^{i}E indicates ^{13}C and R the isotopic ratio $^{13}C/^{12}C$. The delta values are given in Ur (urey) according to recent IUPAC recommendations.[9] This unit is interchangeable with the permil scale if given in mUr (milli-urey): 1 mUr = 0.001 = 1 ‰. In contrast to the dimensionless expression per mil, urey (Ur) is a SI unit and hence common SI prefixes such as milli- and micro- can be used. Urey provides the possibility to express isotope ratios of different magnitudes with one unit and avoids terms such as ppm and permeg.[9, 10] 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.[11]

Stable hydrogen isotope analysis. Stable hydrogen isotope analysis was performed according to the method published by Renpenning et al.[3] Separation of pure phase compounds was carried out at isothermal temperature (140°C) on a ZB-1 column (Phenomenex, 60m, 0.32 mm ID, 1µm film, continuous flow 1.2 mL/min) mounted in an Agilent 7890A GC. For compounds dissolved in water a PoraBond Q gas chromatographic column (Agilent J&W GC columns, 50 m x 0.32 mm ID, 5 µm film thickness, continuous flow 1.2 mL/min) was operated at isothermal temperature

(180°C) for TCE and TCM. A chromium reactor was used to convert hydrogen in all three analytes to H_2. Halogens were converted to $CrCl_3$ and efficiently trapped at the cold end of the reactor. Hydrogen isotope analysis was carried out using a Thermo Finnigan MAT 253. Raw δ^2H values were calculated using Equation 1. Here, ^iE indicates ^2H and R the isotopic ratio $^2H/^1H$. A two-point calibration approach was applied to adjust raw - δ^2H 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 was recently developed to carry out compound specific stable chlorine isotope analysis using gas chromatography coupled with multiple collector inductively coupled plasma mass spectrometry (GC-MC-ICPMS). Samples were measured according to the published protocols.[4, 12] After injection with a gas tight syringe, compounds were first separated on a ZB1 column (Phenomenex, 60m, 0.32 mm ID, 1 μm film, continuous flow 2 mL/min) 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. Raw-$\delta^{37}Cl$ values were calculated by using Equation 1. For chlorine, ^iE indicates ^{37}Cl and R the $^{37}Cl/^{35}Cl$ ratio. 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.[4, 12]

ESI 6: Rayleigh plots for the static volatilization experiment

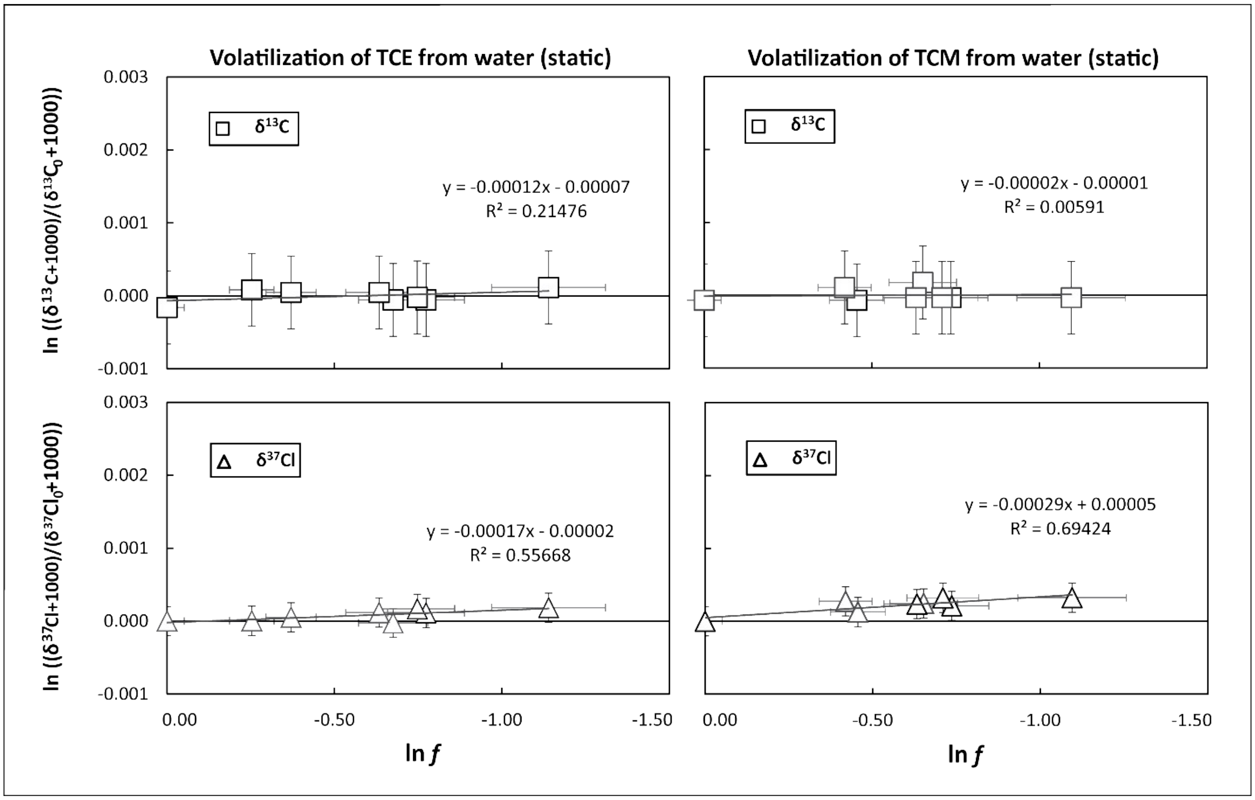

Figure ESI 6: The figure shows Rayleigh plots obtained for kinetic volatilization of the static experiment (see ESI 1, b). The slope of the regression line indicates the magnitude of the enrichment factor in Ur. Enrichment factors correspond to insignificant fractionation for stable carbon isotopes and to -0.17 mUr and -0.29 mUr for TCE and TCM, respectively. These enrichment factors are indistinguishable from those obtained for dynamic volatilization (see main manuscript)

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