

# Supporting Information

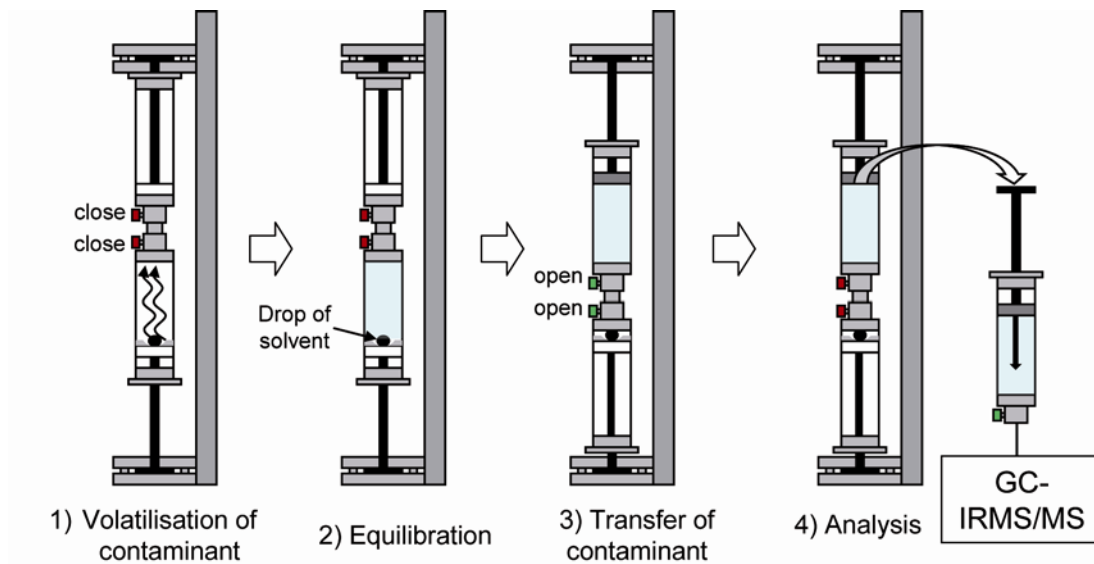
## **Chlorine and carbon isotopes fractionation during volatilization and diffusive transport of trichloroethene in the unsaturated zone**

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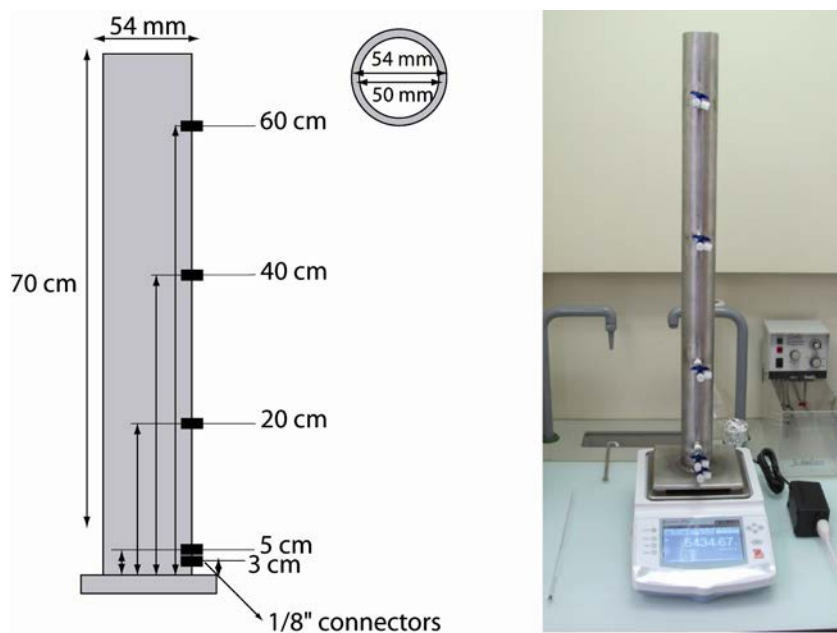
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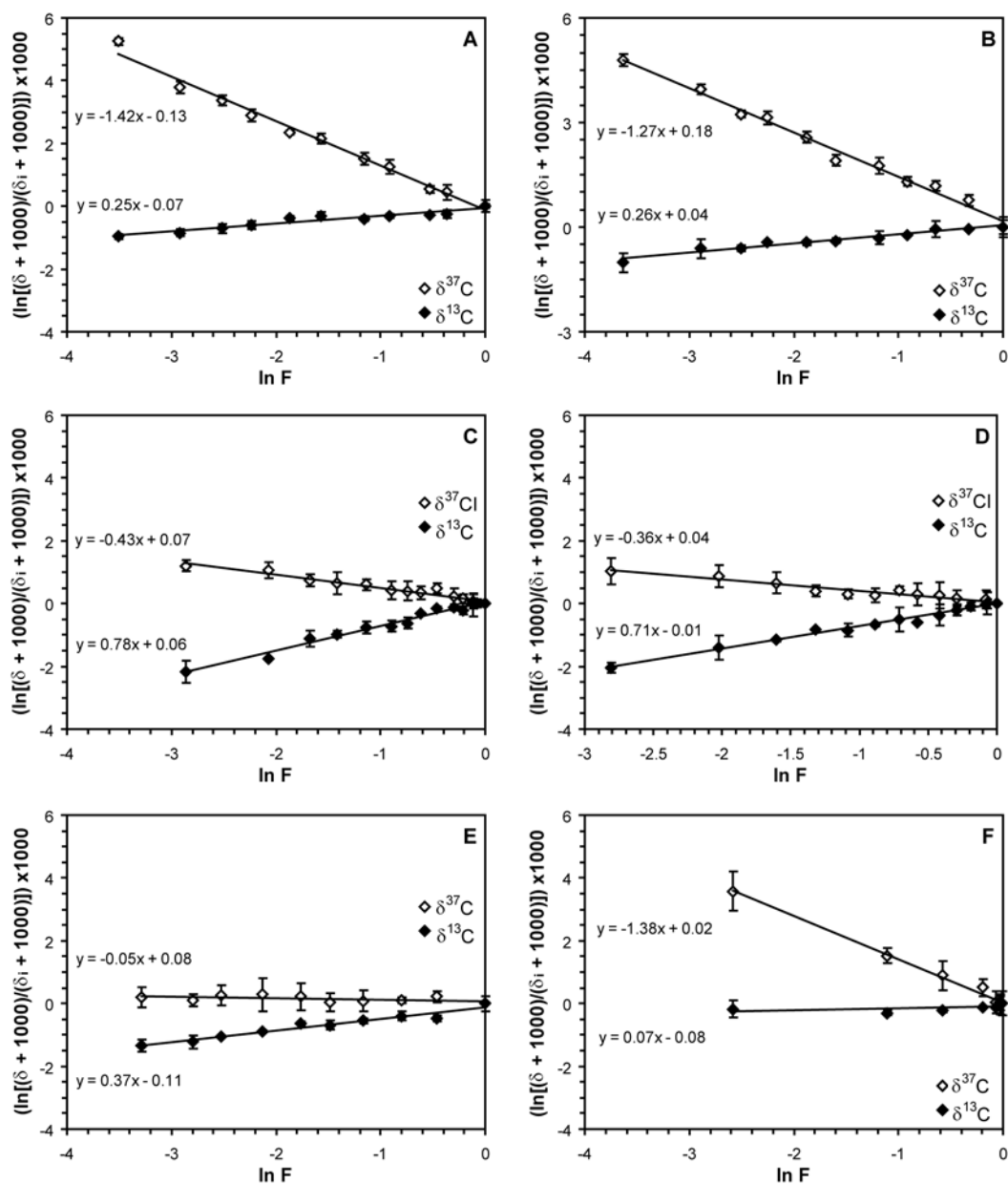
The supporting information consists of 13 pages including 5 figures and 2 tables.



**Figure S1: Setup and procedure for stepwise vaporization experiments.**



**Figure S2: Setup for column experiments.**



**Figure S3: Rayleigh plots for replicate experiments of continuous vaporization (A & B), stepwise vaporization (C & D), air-water partitioning (E) and diffusion-controlled vaporization in a sand-filled column (F). Error bars represent standard deviation.**

# 1. Quantification of isotope fractionation during stepwise experiments

As the Rayleigh relationship can strictly only be applied to continuous processes, equations that describe the isotope evolution during a stepwise partitioning process were derived. The equations were used to quantify the enrichment factor and to evaluate if the data from the stepwise experiments can be approximated by the Rayleigh equation.

For each equilibration step, the isotope ratios in the two phases are related by the following isotope balance question:

$$\delta^{13}C_L^{n+1} = \delta^{13}C_L^n \cdot f_L + \delta^{13}C_g^n \cdot (1 - f_L) \quad (\text{equation S1})$$

with

$$\varepsilon = \delta^{13}C_g^n - \delta^{13}C_L^n \quad (\text{equation S2})$$

with

$\delta^{13}C_L^{n+1}$  isotope ratio in the liquid phase (water or NAPL) before equilibration

$\delta^{13}C_L^n$  isotope ratio in the liquid phase (water or NAPL) after equilibration

$\delta^{13}C_g^n$  isotope ratio in the gas phase after equilibration

$f_L$  fraction of compound in the liquid phase

$\varepsilon$  isotope enrichment factor for equilibrium partitioning

Inserting a rearranged form of equation S2 in equation S1 to substitute  $\delta^{13}C_g^n$  and rearrangement leads to:

$$\Delta\delta^{13}C_L = \delta^{13}C_L^{n+1} - \delta^{13}C_L^n = \varepsilon \cdot (1 - f_L) \quad (\text{equation S3})$$

In case of air-water partitioning,  $f_L$  is constant. Hence the shift in  $\delta^{13}C$  is equal in each step and the shift after n steps is given by:

$$\Delta\delta^{13}C_L^n = n \cdot \Delta\delta^{13}C_L = n \cdot \varepsilon \cdot (1 - f_L) \quad (\text{equation S4})$$

Whereby  $f_L$  can be related to the measured concentration by:

$$f_L = \left( \frac{C_n}{C_0} \right)^{1/n} \quad (\text{equation S5})$$

with

$C_n$  Concentration in aqueous phase after n equilibration steps

$C_0$  Initial concentration in aqueous phase

In case of NAPL-vapor equilibration,  $f_L$  for step n is given by:

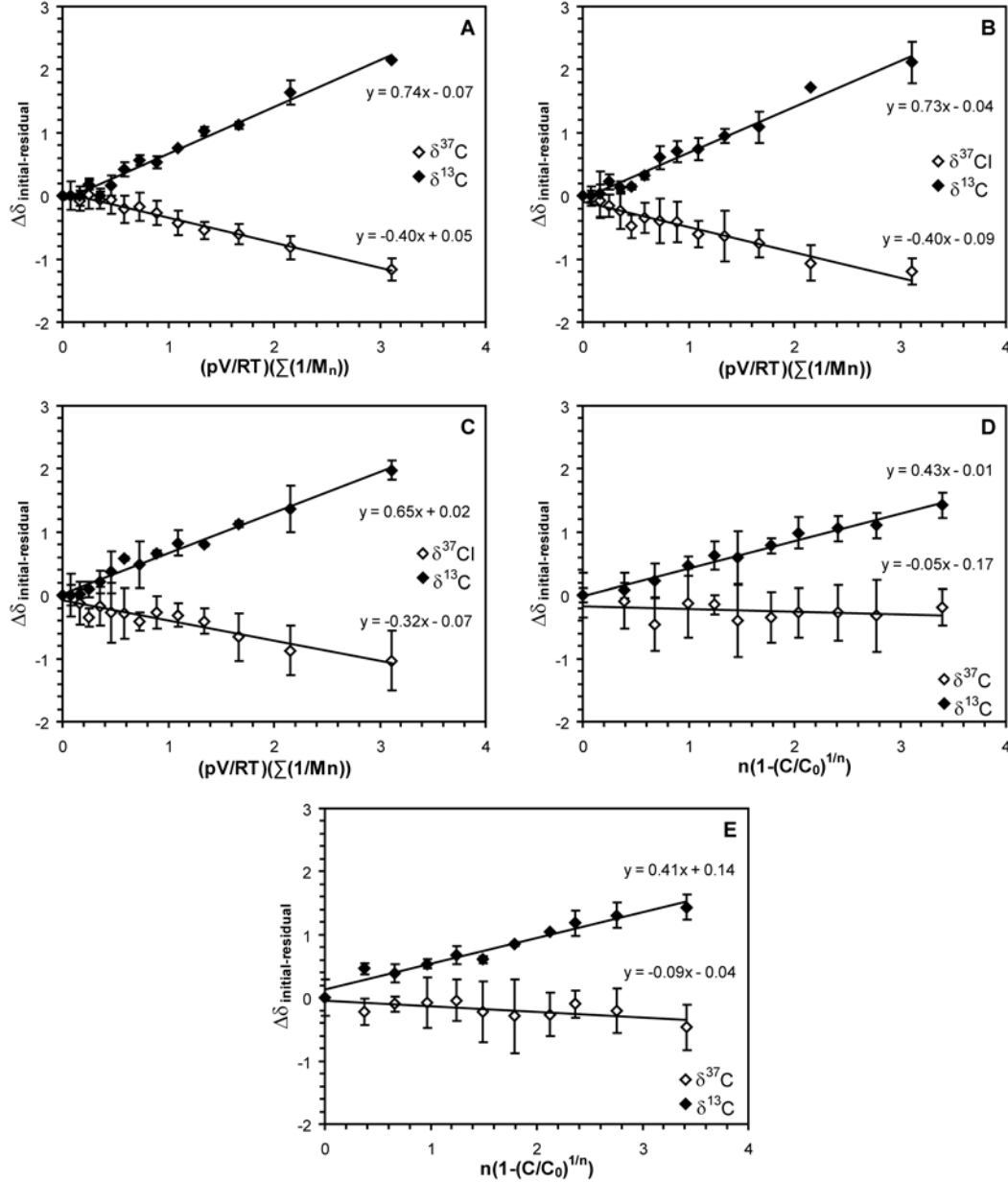
$$(1 - f_L) = \frac{V_g \cdot p / RT}{M_n} \quad (\text{equation S6})$$

with

$M_n$  mass of compound in the NAPL before the n<sup>th</sup> equilibration step.

With each step,  $1-f_L$  increases since  $M_n$  diminishes while all the other parameters remain constant. Hence, the shift in  $\delta^{13}\text{C}$  increases in each step (i.e. is not constant as in case of air-water partitioning). The shift after  $n$  steps is given by:

$$\Delta\delta^{13}\text{C}_L^n = \varepsilon \cdot \frac{p \cdot V}{R \cdot T} \cdot \sum_{n=1}^n \frac{1}{M_n} \quad (\text{equation S7})$$



**Figure S4: Stepwise fractionation plots for stepwise vaporization (A, B and C) and stepwise air-water partitioning (D and E). Error bars represent standard deviation.**

**Table S1 : Enrichment factor ( $\epsilon$ ) values of carbon and chlorine for the stepwise vaporization and air-water partitioning experiments using the stepwise calculation approach. The uncertainty was calculated using the standard error of the slope for all measurements.**

		Expt.1	Expt. 2	Expt. 3	Mean values
Stepwise vaporization	$\epsilon_C$	+0.74‰ ( $\pm 0.02$ ‰)	+0.73‰ ( $\pm 0.03$ ‰)	+0.65‰ ( $\pm 0.03$ ‰)	+0.71‰ ( $\pm 0.03$ ‰)
	$\epsilon_{Cl}$	-0.40‰ ( $\pm 0.02$ ‰)	-0.40‰ ( $\pm 0.02$ ‰)	-0.32‰ ( $\pm 0.03$ ‰)	-0.37‰ ( $\pm 0.02$ ‰)
Air-water partitioning	$\epsilon_C$	+0.43‰ ( $\pm 0.05$ ‰)	+0.41‰ ( $\pm 0.03$ ‰)		+0.42‰ ( $\pm 0.04$ ‰)
	$\epsilon_{Cl}$	-0.05‰ ( $\pm 0.05$ ‰)	-0.09‰ ( $\pm 0.04$ ‰)		-0.07‰ ( $\pm 0.05$ ‰)

**Table S2 : Comparison between the carbon and chlorine enrichment factors ( $\epsilon$ ) of the classical Rayleigh and stepwise approach for the stepwise vaporization and air-water partitioning experiments. The uncertainty was calculated using the standard error of the slope for all measurements.**

		Rayleigh data evaluation	Stepwise data evaluation
Stepwise vaporization	$\epsilon_C$	+0.75‰ ( $\pm 0.04$ ‰)	+0.71‰ ( $\pm 0.03$ ‰)
	$\epsilon_{Cl}$	-0.39‰ ( $\pm 0.03$ ‰)	-0.37‰ ( $\pm 0.02$ ‰)
Air-water partitioning	$\epsilon_C$	+0.38‰ ( $\pm 0.04$ ‰)	+0.42‰ ( $\pm 0.04$ ‰)
	$\epsilon_{Cl}$	-0.06‰ ( $\pm 0.05$ ‰)	-0.07‰ ( $\pm 0.05$ ‰)

For stepwise vaporization (Figure S4A, B&C) and air-water partitioning experiments (Figure S4D&E) the isotopic values plotted vs. the fraction of compound in the liquid phase follow a linear trend. The enrichment factors were calculated using equations S4 to S7 (Table S1). There is no significant difference in the isotope enrichment factors between the two approaches (Table S2). The good agreement between the two approaches is due to the elevated number of equilibration steps used in the experiments. Therefore, data were plotted according to the classical Rayleigh approach in the manuscript.

## 2. Isotope and isotopologue fractionation during vaporization and diffusion

Since the heavy isotope of chlorine is present at a high abundance, several isotopologues of polychlorinated hydrocarbons occur at relevant concentrations. These isotopologues will show different concentration trends during fractionating physico-chemical and reactive processes. However, analytical methods based on GC-qMS and GC-IRMS will usually only measure the abundance of selected fragment and molecular ions. This raises the questions whether isotope ratios and isotope fractionation factors can be quantified from such partial information. For reactive processes, it has been demonstrated that isotope fractionation is proportional to isotopologue fractionation and hence isotope ratios can confidently be derived from fragment and/or molecular ion ratios [1]. However for physico-chemical processes, such a derivation is lacking so far. The main goal of this section is to demonstrate how isotope and isotopologue fractionation are related during diffusion-controlled vaporization as investigated in the column study. To reach this aim, it is first evaluated how isotopologue fractionation during diffusion-controlled vaporization can be expressed in terms of isotopologue fractionation during NAPL-vapor equilibration and diffusion. Then it is evaluated how isotopologue ratios evolve during these processes individually before finally developing relationships that relate isotope to isotopologue fractionation and provide the basis to quantify fractionation factors.

For these derivations, it is assumed that equilibrium conditions are established at the NAPL-vapor interface for all isotopologues and that the vaporization rate is diffusion controlled, in analogy to numerous studies on vaporization of water [2, 3]. This assumption is consistent with field and modeling studies [4] on passive NAPL vaporization in porous media that indicate the establishment of a NAPL-vapor equilibrium in the source zone due to the relatively slow transport of gaseous compounds away from the source zone. The mathematical derivation is carried out for the limiting case where vaporization is sufficiently slow that no isotopologue fractionation occurs in the NAPL phase, an assumption that will be discussed in more detail in section 3 below. Hence kinetic isotopologue fractionation only occurs due to gas phase diffusion.

### Notation

$M_{000}/M_{001}/M_{011}/M_{111}$	Amount of isotopologue with zero/one/two/three $^{37}\text{Cl}$ in NAPL
$X_{000}/X_{001}/X_{011}/X_{111}$	Mole fraction in NAPL of isotopologue with zero/one/two/three $^{37}\text{Cl}$
$P_{000}/P_{001}/P_{011}/P_{111}$	Vapor pressure of isotopologue with zero/one/two/three $^{37}\text{Cl}$
$D_{000}/D_{001}/D_{011}/D_{111}$	Diffusion coefficient of isotopologue with zero/one/two/three $^{37}\text{Cl}$
$C_{000}/C_{001}/C_{011}/C_{111}$	Concentration of isotopologue with zero/one/two/three $^{37}\text{Cl}$ in source
A	Cross-section of column
L	Length of column
$\tau$	Tortuosity
T	Temperature
R	Gas constant

### 2.1 Isotopologue fractionation during diffusion-controlled vaporization

According to Fick's first law, the mass flux of an isotopologue across the 1D column is given by:

$$\frac{dM_{000}}{dt} = -A \cdot \tau \cdot D_{000} \cdot \frac{C_{000}}{L} \quad (\text{equation S8})$$

$$\frac{dM_{001}}{dt} = -A \cdot \tau \cdot D_{001} \cdot \frac{C_{001}}{L} \quad (\text{equation S9})$$

Assuming that a NAPL-vapor equilibrium is established at the source, the gas phase concentration at the source can be expressed using Raoult's law, which leads to:

$$\frac{dM_{000}}{dt} = -A \cdot \tau \cdot D_{000} \cdot \frac{X_{000} \cdot P_{000}}{R \cdot T \cdot L} = -A \cdot \tau \cdot D_{000} \cdot \frac{M_{000} / \sum M_i \cdot P_{000}}{R \cdot T \cdot L} \quad (\text{equation S10})$$

$$\frac{dM_{001}}{dt} = -A \cdot \tau \cdot D_{001} \cdot \frac{X_{001} \cdot P_{001}}{R \cdot T \cdot L} = -A \cdot \tau \cdot D_{001} \cdot \frac{M_{001} / \sum M_i \cdot P_{001}}{R \cdot T \cdot L} \quad (\text{equation S11})$$

Division of S9 by S8 leads to:

$$\frac{dM_{001}}{dM_{000}} = \frac{D_{001} \cdot M_{001} \cdot P_{001}}{D_{000} \cdot M_{000} \cdot P_{000}} \quad (\text{equation S12})$$

Separation of variables leads to:

$$\frac{dM_{001}}{M_{001}} = \frac{dM_{000}}{M_{000}} \cdot \frac{D_{001} \cdot P_{001}}{D_{000} \cdot P_{000}} \quad (\text{equation S13})$$

Integration of equation S13 from t=0 to t=t leads to:

$$\ln \frac{M_{001,t}}{M_{001,0}} = \frac{D_{001} \cdot P_{001}}{D_{000} \cdot P_{000}} \cdot \ln \frac{M_{000,t}}{M_{000,0}} \quad (\text{equation S14})$$

or

$$\frac{M_{001,t}}{M_{001,0}} = \left( \frac{M_{000,t}}{M_{000,0}} \right)^{\alpha_{Eff}^{ITL}} \quad (\text{equation S15})$$

$$\text{with } \alpha_{Eff}^{ITL} = \frac{D_{001} \cdot P_{001}}{D_{000} \cdot P_{000}} = \alpha_{Eqm}^{ITL} \cdot \alpha_{Diff}^{ITL} \quad (\text{equation S16})$$

Division of both sides by  $M_{000,t}/M_{000,0}$  leads to

$$\frac{M_{001,t} / M_{000,t}}{M_{001,0} / M_{000,0}} = \left( \frac{M_{000,t}}{M_{000,0}} \right)^{\alpha_{Eff}^{ITL} - 1} \quad (\text{equation S17})$$

or

$$\frac{R_{000/001,t}}{R_{000/001,0}} = \left( \frac{M_{000,t}}{M_{000,0}} \right)^{\alpha_{Eff}^{ITL} - 1} \quad (\text{equation S18})$$

where

$R_{000/001,t}$  Isotopologue ratio at time t

$R_{000/001,0}$  Initial isotopologue ratio

Analogous equations hold also for other isotopologue ratios. Hence the isotopologue evolution is controlled by a combination on isotopologue fractionation due to NAPL-vapor equilibration and diffusion.

## 2.2. Isotopologue fractionation during NAPL-vapor equilibration and diffusion.

In order to relate isotopologue fractionation to isotope fractionation, it has to be known how ratios between different isotopologue pairs evolve. For vaporization, such relationships can be developed based on the rule of the geometric mean (RGM) for thermodynamic isotope fractionation as developed



by Bigeleisen [5]. The rule basically states that the effect of adding another heavy isotope is additive and independent of how many heavy isotopes are already in the molecule. The RGM has frequently been applied for vapor pressure calculations. Assuming ideal mixing, the vapor pressure of different isotopologues can be related by:

$$P_{XY'_{n-z}Y_z}^n = P_{XY'_{n-z}}^{n-z} \cdot P_{XY_z}^z \quad (\text{equation S19})$$

Where Y' is a light and Y a heavy isotope, n the total number of element Y in the molecule and z the number of heavy isotope of Y in the molecule.

Using TCE as an example

$$P_{001}^3 = P_{000}^2 \cdot P_{111}^1 \quad (\text{equation S20})$$

Dividing by  $P_{000}^3$  leads to

$$\frac{P_{001}^3}{P_{000}^3} = \frac{P_{000}^2 \cdot P_{111}^1}{P_{000}^3} \quad (\text{equation S21})$$

or

$$\left(\frac{P_{001}}{P_{000}}\right)^3 = \frac{P_{111}}{P_{000}} \quad (\text{equation S22})$$

“

Using this rule we can express the vapor pressure of “mixed isotopologues based on the vapor pressure of “pure” isotopologues as follows:

$$P_{001} = P_{000}^{2/3} \cdot P_{111}^{1/3} \quad (\text{equation S23})$$

$$P_{011} = P_{000}^{1/3} \cdot P_{111}^{2/3} \quad (\text{equation S24})$$

Based on these equations we now express vapor pressure ratios of pairs of isotopologues with one heavy isotope difference:

$$\frac{P_{001}}{P_{000}} = \frac{P_{000}^{2/3} \cdot P_{111}^{1/3}}{P_{000}} = \left[\frac{P_{111}}{P_{000}}\right]^{1/3} \quad (\text{equation S25})$$

$$\frac{P_{011}}{P_{001}} = \frac{P_{000}^{1/3} \cdot P_{111}^{2/3}}{P_{000}^{2/3} \cdot P_{111}^{1/3}} = \left[\frac{P_{111}}{P_{000}}\right]^{1/3} \quad (\text{equation S26})$$

$$\frac{P_{111}}{P_{011}} = \frac{P_{111}}{P_{000}^{1/3} \cdot P_{111}^{2/3}} = \left[\frac{P_{111}}{P_{000}}\right]^{1/3} \quad (\text{equation S27})$$

Or

$$\frac{P_{001}}{P_{000}} = \frac{P_{011}}{P_{001}} = \frac{P_{111}}{P_{011}} \quad (\text{equation S28})$$

In other words, if the RGM applies, isotopologue fractionation during NAPL-vapor equilibration is identical for all isotopologue pairs.

For gas phase diffusion, the ratio of diffusion coefficients between two isotopologues is given by:

$$\alpha_{Diff}^{ITL} = \frac{D_{001}}{D_{000}} = \sqrt{\frac{(MW_{001} + MW_{air}) \cdot MW_{000}}{(MW_{000} + MW_{air}) \cdot MW_{001}}} \quad (\text{equation S29})$$

with

$MW_{000/001/011/111}$  is molecular weight of isotopologue with zero/one/two/three heavy isotopes  
 $MW_{air}$  is the molecular weight of air

Since the molecular weight of TCE is high compared to the differences in weight between heavy and light chlorine isotope, the mass ratio of all isotopologue pairs differing by one heavy isotope is similar (i.e. 132/130 is similar to 134/132 to 136/134). As the result, the ratio in diffusion factor is similar in good approximation:

$$\alpha_{Diff}^{ITL} = \frac{D_{001}}{D_{000}} \approx \frac{D_{011}}{D_{001}} \approx \frac{D_{111}}{D_{011}} \quad (\text{equation S30})$$

In other words, also for diffusion, isotopologue fractionation is identical in good approximation for all isotopologue pairs.

### 2.3. Relationship between isotope and isotopologue fractionation during diffusion-controlled vaporization

In the following isotope fractionation is related to isotopologue fractionation for diffusion-controlled vaporization.

Based on equation S29 and S30 above, the effective isotopologue fractionation factor is the same for all isotopologue pairs.

$$\alpha_{Eff}^{ITL} = \frac{D_{001} \cdot P_{001}}{D_{000} \cdot P_{000}} = \frac{D_{011} \cdot P_{011}}{D_{001} \cdot P_{001}} = \frac{D_{111} \cdot P_{111}}{D_{011} \cdot P_{011}} \quad (\text{equation S31})$$

The isotopologue evolution for compounds with zero and one heavy isotopes is given by:

$$\frac{M_{001,t} / M_{000,t}}{M_{001,0} / M_{000,0}} = \left( \frac{M_{000,t}}{M_{000,0}} \right)^{\alpha_{Eff}^{ITL} - 1} \quad (\text{equation S32})$$

For isotopologues with one more heavy isotope each, the following equation is obtained:

$$\frac{M_{011,t} / M_{001,t}}{M_{011,0} / M_{001,0}} = \left( \frac{M_{001,t}}{M_{001,0}} \right)^{\alpha_{Eff}^{ITL} - 1} \quad (\text{equation S33})$$

Inserting equation S15 into equation S33 leads to:

$$\frac{M_{011,t} / M_{001,t}}{M_{011,0} / M_{001,0}} = \left( \frac{M_{000,t}}{M_{000,0}} \right)^{\alpha_{EFF}^{ITL} (\alpha_{Eff}^{ITL} - 1)} \approx \left( \frac{M_{000,t}}{M_{000,0}} \right)^{\alpha_{Eff}^{ITL} - 1} \quad (\text{equation S34})$$

The approximation is associated with only a small error as alpha deviates from one only by a few permille in maximum. Combining equation S33 and S34 leads to:

$$\frac{M_{001,t} / M_{000,t}}{M_{001,0} / M_{000,0}} = \frac{M_{011,t} / M_{001,t}}{M_{011,0} / M_{001,0}} \quad (\text{equation S35})$$

Rearrangement of equation S35 and expressing the isotopologue concentrations at time zero in terms of isotope abundances leads to:

$$\frac{M_{001,t} / M_{000,t}}{M_{011,t} / M_{001,t}} = \frac{M_{001,0} / M_{000,0}}{M_{011,0} / M_{001,0}} = \frac{3 \cdot f_{35}^2 \cdot f_{37} / f_{35}^3}{3 \cdot f_{35} \cdot f_{37}^2 / 3 \cdot f_{35}^2 \cdot f_{37}} = 3 \quad (\text{equation S36})$$

or

$$\frac{M_{001,t}}{M_{000,t}} = 3 \cdot \frac{M_{011,t}}{M_{001,t}} \quad (\text{equation S37})$$

And analogously for isotopologues with one additional heavy isotopes:

$$\frac{M_{011,t} / M_{001,t}}{M_{111,t} / M_{011,t}} = \frac{M_{011,0} / M_{001,0}}{M_{111,0} / M_{011,0}} = \frac{3 \cdot f_{35} \cdot f_{37}^2 / 3 \cdot f_{35}^2 \cdot f_{37}}{f_{37}^3 / 3 \cdot f_{35} \cdot f_{37}^2} = 3 \quad (\text{equation S38})$$

Or

$$\frac{M_{011,t}}{M_{001,t}} = 3 \cdot \frac{M_{111,t}}{M_{011,t}} \quad (\text{equation S39})$$

and inserting equation S39 into S37 leads to:

$$\frac{M_{001,t}}{M_{000,t}} = 9 \cdot \frac{M_{111,t}}{M_{011,t}} \quad (\text{equation S40})$$

Equation S36 and S38 illustrate that also during diffusion-controlled vaporization, isotopologues fractionate proportionally. However, in contrast to a reactive processes the proportionality is only approximate. Experimental data confirm that these relationships indeed apply (Fig. 3 of manuscript).

The isotope ratio can be related to isopologue ratios as follows:

$$\begin{aligned} \frac{{}^{37}\text{Cl}}{{}^{35}\text{Cl}} &= \frac{M_{001,t} + 2 \cdot M_{011,t} + 3 \cdot M_{111,t}}{M_{011,t} + 2 \cdot M_{001,t} + 3 \cdot M_{000,t}} = \frac{M_{001,t} / M_{000,t} + 2 \cdot M_{011,t} / M_{000,t} + 3 \cdot M_{111,t} / M_{000,t}}{M_{011,t} / M_{000,t} + 2 \cdot M_{001,t} / M_{000,t} + 3} \\ &= \frac{M_{001,t} / M_{000,t} + 2 \cdot (M_{011,t} / M_{001,t})(M_{001,t} / M_{000,t}) + 3 \cdot (M_{111,t} / M_{011,t})(M_{011,t} / M_{001,t})(M_{001,t} / M_{000,t})}{(M_{011,t} / M_{001,t})(M_{001,t} / M_{000,t}) + 2 \cdot M_{001,t} / M_{000,t} + 3} \quad (\text{equation S41}) \\ &= \frac{M_{001,t} / M_{000,t} + 2/3 \cdot (M_{001,t} / M_{000,t})^2 + 1/9 \cdot (M_{001,t} / M_{000,t})^3}{1/3 \cdot (M_{001,t} / M_{000,t})^2 + 2 \cdot M_{001,t} / M_{000,t} + 3} \\ &= \frac{1/3 \cdot (M_{001,t} / M_{000,t}) \cdot [3 + 2 \cdot (M_{001,t} / M_{000,t}) + 1/3 \cdot (M_{001,t} / M_{000,t})^2]}{1/3 \cdot (M_{001,t} / M_{000,t})^2 + 2 \cdot M_{001,t} / M_{000,t} + 3} = 1/3 \cdot (M_{001,t} / M_{000,t}) \end{aligned}$$

And by inserting equations S37 and S40 into equation S41:

$$\frac{{}^{37}\text{Cl}}{{}^{35}\text{Cl}} = \frac{1}{3} \cdot \frac{M_{001,t}}{M_{000,t}} = \frac{M_{011,t}}{M_{001,t}} = 3 \cdot \frac{M_{111,t}}{M_{011,t}} \quad (\text{equation S42})$$

Hence also for a diffusion controlled system, the isotope ratio evolves parallel to the isotopologue ratio. It is thus admissible to derive isotope ratios from isotopologue ratios even if not all isotopologues are measured. Furthermore, fractionation factors can be quantified from either isotopologue or isotope ratios and identical values are expected.

### 3. Isotopologue fractionation in the liquid phase

The occurrence of isotopologue fractionation in the liquid phase can be evaluated by the advective-diffusive isotopic model developed by He and Smith [3] adapted to the situation where a NAPL vaporizes through a porous media to a gas phase in which the concentration of the vaporizing compound is close to zero ( $h=0$  in He and Smith model). During slow evaporation, the diffusion of isotopologues in the liquid side boundary layer is sufficiently fast to prevent differences in isotopologue ratios between the surface and the bulk liquid. In contrast, during faster vaporization, light isotopologues become depleted in the surface layer, which leads to a reduction of the effective fractionation factor for vaporization. The speed to vaporization relative to the thickness of the boundary layer can be characterized using a dimensionless number  $N$  according to [3]:

$$N = \frac{u \cdot L_1}{D_L} \quad (\text{equation S43})$$

Where  $u$  is the vaporization rate from an open surface (m/s),  $L_1$  the thickness of the liquid boundary layer (m) and  $D_L$  the diffusion coefficient of the compound in the liquid phase ( $\text{m}^2/\text{s}$ ). The effective fractionation factor is given by [3]:

$$\alpha_{\text{Eff}} = \frac{\alpha_{\text{Eqm}} \cdot \alpha_{\text{Diff}}}{\exp(-N) - \alpha_{\text{Eqm}} \cdot \alpha_{\text{Diff}} \cdot (\exp(-N) - 1)} \quad (\text{equation S44})$$

For  $N \rightarrow -\infty$  (very slow vaporization),  $\alpha_{\text{Eff}}$  approaches  $\alpha_{\text{Eqm}} \alpha_{\text{Diff}}$  corresponding to equation S16 while for the case  $N \rightarrow +\infty$  (very fast vaporization),  $\alpha_{\text{Eff}}$  approaches 1 i.e. no fractionation occurs during vaporization. In Figure S5, it is illustrated how  $\varepsilon_{\text{Eff}}$  varies as a function of  $N$ . As  $N$  increases, the effective chlorine isotope enrichment factor decreases towards 0, while the value for carbon changes very little as it is already close to zero for a small  $N$ .

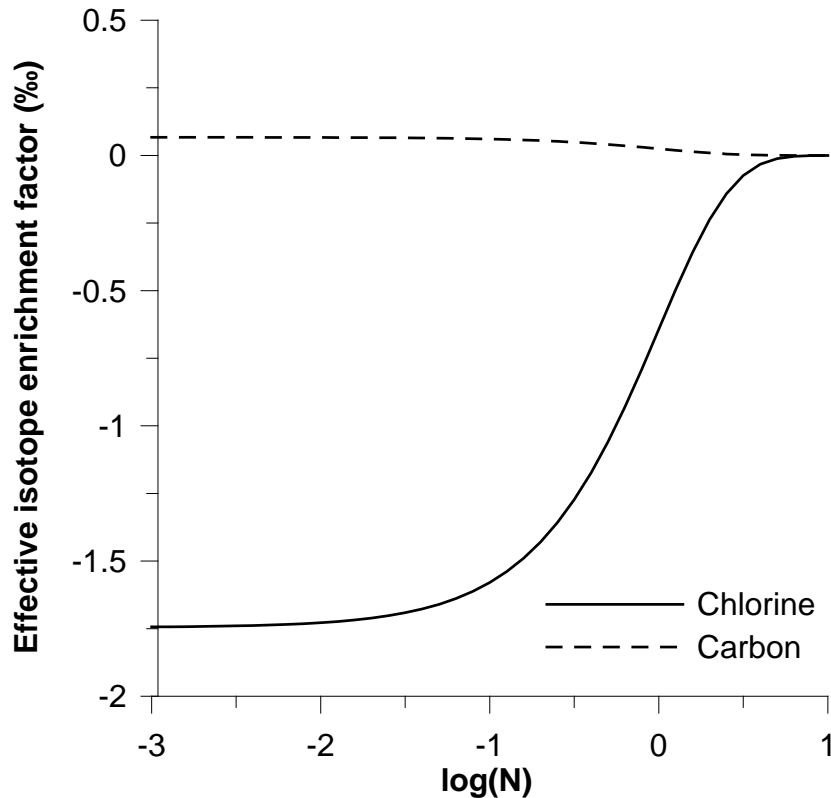


Figure S5. Evolution of the effective isotope enrichment factor as a function of dimensionless parameter  $N$ .

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