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# Multistep partitioning causes significant stable carbon and hydrogen isotope effects during volatilization of toluene and propan-2-ol from unsaturated sandy aquifer sediment

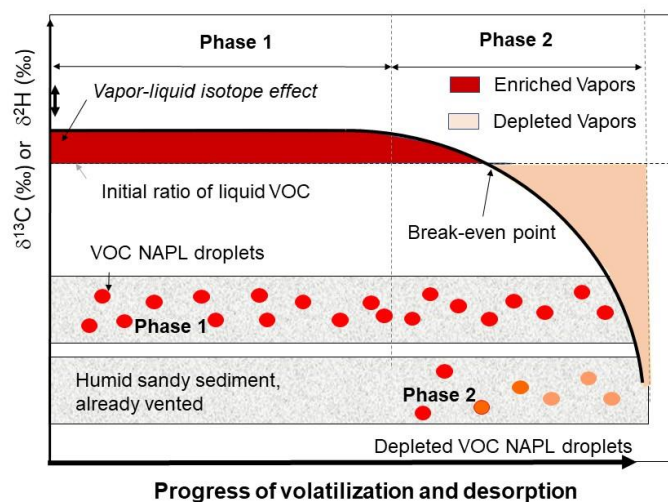
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*Graphical abstract*



## Highlights

Compound-specific stable isotope analysis is used for monitoring of soil venting

Volatilization of toluene and propan-2-ol were studied with C and H isotopes

Column experiments with aquifer sediment yielded large isotope effects (IE)

A numerical model based on multistep vapor-liquid partitioning reproduces these IE

The isotope shifts found here are larger than shifts created by equilibrium processes

**Abstract**

This study aimed at investigating whether stable isotopes can be used to monitor the progress of volatile organic compounds (VOCs) volatilization from contaminated sediment during venting. Batches of a dry aquifer sediment were packed into stainless steel HPLC columns, humidified with distilled water and later contaminated by either liquid toluene or propan-2-ol. The VOCs were then volatilized by a stream of gas at room temperature, and the concentrations and stable isotope ratios of gaseous VOCs were recorded by isotope-ratio mass spectrometry. During early stages of volatilization of toluene, the isotope ratios  $\Delta\delta^{13}\text{C}$  shifted to more negative values by about -3 to -5 ‰ and the  $\Delta\delta^2\text{H}$  by more than -40 ‰, while the concentration remained at or near initial saturated vapor concentration. Depletion of the isotope ratios in the gas was explained by the vapor-liquid fractionation process, which is amplified by successive self-partitioning steps of gaseous VOC into remaining liquid VOC. For propan-2-ol the carbon isotope shift was negative like for toluene, whereas the H shift was positive. Hydrogen bonding in the liquid propan-2-ol phase causes a normal vapor-liquid H isotope effect which was described already in classical literature. The isotope shifts in the present experiments are larger than previously reported shifts due to phase-change processes and reach the magnitude of shifts usually observed in kinetic isotope fractionation.

**Keywords**

Carbon-13, Deuterium, Partitioning, Soil venting, Remediation

37

38

## 39        **1. Introduction**

40 Spills of volatile organic compounds (VOCs) such as e.g. petroleum products or solvents to soils  
41 are a frequent environmental problem that needs corrective actions. In situ soil venting or  
42 bioventing is a widespread technique to treat sites with contaminations in the unsaturated zone  
43 (Aelion and Kirtland, 2000; Ostendorf and Kampbell, 1990; Rathfelder et al., 1995). In order to  
44 better predict its feasibility, the understanding of rates controlling volatilization and desorption are  
45 needed. Numerous investigations have already contributed to a better understanding of these  
46 mechanisms (Allen-King et al., 2002; Balseiro-Romero et al., 2018; Brusturean et al., 2007; Delle  
47 Site, 2001). Grathwohl and Reinhard (1993) performed pioneering work on the volatilization and  
48 desorption of trichloroethene from aquifer sediments and found that diffusion at the grain scale  
49 exhibits a rate-limiting control for the desorption process at late stages of remediation.

50 Compound-specific isotope analysis (CSIA) is a now established tool for monitoring of  
51 remediation progress (Thullner et al., 2012; Vogt et al., 2016). In VOCs from petroleum, stable  
52 carbon and hydrogen isotopes can be used to assess the progress of isotope-fractionating reactions.  
53 Applications were reported for tracking processes which lead to significant isotope fractionation.  
54 These are bond-breaking processes on one hand (Elsner, 2010) and gas-phase diffusion-controlled  
55 processes on the other hand (Bouchard et al., 2008; Höhener et al., 2008). Both processes are  
56 subject to kinetic isotope effects, remove preferentially the light isotopes and lead to isotopic  
57 enrichment of the remaining pollutant (normal isotope effect, IE). Besides these two kinetic  
58 fractionation effects, equilibrium-based phase-transfer processes like sorption, desorption and  
59 partitioning (neat liquid – air or water-air) were reported to create negligible (Schuth et al., 2003;  
60 Slater et al., 2000) or only small fractionations for both, C and H (Imfeld et al., 2014; Kopinke et  
61 al., 2005) (see Tables S4+S5). For toluene, the largest phase-transfer isotope shifts so far observed

62 caused by multistep sorption to various sorbents were +1.4 ‰ for  $^{13}\text{C}$  and +12 ‰ for  $^2\text{H}$  (Imfeld et  
63 al., 2014). These isotope shifts were qualified as “insignificant” compared to shifts by bond-  
64 breaking reactions or by gas-phase diffusion (Imfeld et al., 2014). For both isotopes, the IE was  
65 inverse meaning that the heavy isotopologue adsorbed less strongly than the light isotopologue.  
66 Such an inverse behavior of apolar compounds is well known, especially for deuterated  
67 compounds, and can lead to chromatographic separation of fully deuterated hydrocarbons on gas  
68 chromatographic columns, with first elution of the heavy compounds (Höhener and Yu, 2012;  
69 Morasch et al., 2001). It should be noted here that passive volatilization of apolar COVs includes  
70 diffusive fractionation in a stagnant boundary layer which can overcome the inverse vapor-liquid  
71 effect to result in an overall normal effect (Julien et al., 2015).

72 The objective of our work was to use CSIA in order to get a better insight into the process  
73 significance of forced volatilization of VOCs from unsaturated aquifer sediments. To this end, the  
74 fractionation of isotopes occurring during volatilization were quantified in column experiments  
75 and compared to previously known fractionations for biodegradation, diffusion and phase-change  
76 processes. Toluene was chosen as a typical apolar pollutant, and for comparison, the polar solvent  
77 propan-2-ol was added. For both compounds vapor-liquid isotope effects for C and H are known  
78 (Table S5).

## 79 **2. Material and methods**

80 Toluene and propan-2-ol (both >99.8 purity) were purchased from Sigma-Aldrich. The aquifer  
81 sediment was from an uncontaminated quarry in the Crau aquifer plain (Ponsin et al., 2015). The  
82 fraction > 2 mm was removed by dry sieving and the material was then sieved wet on a mesh of  
83 0.124 mm rinsed with distilled water and dried at 110°C. Its characteristics are given in the table  
84 S3. A stainless steel HPLC column of 25 cm length and 4.6 mm internal diameter was emptied and

85 filled with 6.6 grams of dry aquifer sediment, using small packs of glass wool at both ends to retain  
86 the sand in between.

### 87 **2.1 Contamination procedure**

88 A volume of 360  $\mu\text{L}$  of distilled water was pipetted into the column which was then closed with  
89 two plugs and incubated overnight at 80°C in order to distribute water vapor uniformly. After  
90 cooling to room temperature, a known volume of liquid VOC (Table S1) was inserted on the top  
91 of the column, which was closed again by plugs and heated to 80°C during 18 h. After cooling to  
92 25°C, condensing the VOCs as liquid phase, the column was weighted. Then the column was filled  
93 homogeneously with humid aquifer sediment containing liquid toluene drops and toluene in vapor,  
94 aqueous phase and adsorbed to sediment. The volumetric fluid contents were 0.108 for toluene,  
95 0.087 for water and 0.234 for air for the experiment shown in Figure 1. Thereafter volatilization  
96 was studied recording stable carbon isotope ratios. When no more VOC vapors left the column, the  
97 column was disconnected, vented, then re-humified and re-contaminated with VOC in identical  
98 manner. Volatilization was then again studied recording hydrogen isotopes ratios in the GC-IRMS.  
99 Similar experiments were performed with other HPLC columns of the same dimensions but without  
100 adding water in order to avoid microbial degradation. The columns were closed by plugs, and the  
101 VOC could sorb onto the sediments for variable periods of 30 minutes to up to 10 days at room  
102 temperature.

### 103 **2.2 Volatilization experiments**

104 The HPLC columns were connected in horizontal position to polyether-etherketone (PEEK) tubing  
105 and volatilization was performed with a stream of Helium gas (different flow rates were tested  
106 from 3 to 12  $\text{mL min}^{-1}$ , corresponding to 0.5 to 2  $\text{mL cm}^{-2} \text{min}^{-1}$ ). Volatilization by air was avoided  
107 since it could promote biodegradation. Four experiments were also performed with  $\text{N}_2$  gas in order

108 to test a gas more similar to air. The gas flow rates were controlled via the entry pressures which  
109 ranged from 1.5 to 2 atm. The first volumes of the gas stream were discarded if liquid VOC  
110 emerged. The gas stream was then led through a 6 mL headspace autosampler vial in a rack of an  
111 autosampler (Triplus, Thermo-Fisher Scientific) heated to 60°C. The flow rate of the gas was  
112 monitored at the vent tube using a soap flow meter. Automated injections from this vial flushed  
113 continuously by the vented VOCs were performed with a gas-tight syringe into a GC-C-IRMS  
114 system composed of the Trace GC connected via Isolink II interface to a Delta V Advantage Isotope  
115 Ratio Mass Spectrometer (all from Thermo Fisher Scientific). The experimental scheme and the  
116 running conditions are given in the SI, Figs. S1+2 and Tab. S2. VOC concentrations were recorded  
117 using the amplitude of mass 44 of CO<sub>2</sub> in IRMS in combustion mode or the amplitude of mass 2  
118 of H<sub>2</sub> in pyrolysis mode.

119 The measured delta δ<sup>13</sup>C or δ<sup>2</sup>H (‰) were calculated following eq. (1):

$$120 \quad \delta \text{ (‰)} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \cdot 1000 \quad (1)$$

121 With  $R_{\text{sample}}$  being the ratio of the sample and  $R_{\text{standard}}$  the abundance ratios of the international  
122 standards (VPDB, 0.0112372 or VSMOW, 1.5575E-4). Values were corrected using two  
123 secondary lab standards, toluene and benzene, running on GC-C-IRMS which were themselves  
124 compared to primary standards (VSMOW, NBS-22 from IAEA, and urea from Thermo  
125 Scientific) by EA-IRMS. The linearity and uncertainty of the measured isotope ratios were  
126 checked by additional injections of toluene from vials with different vapor concentrations and are  
127 shown in Fig. S3 which shows also the analytical errors of the δ values (± 0.5 ‰ for <sup>13</sup>C and (±  
128 5.0 ‰ for <sup>2</sup>H) The pore volumes of the sand-filled chromatographic columns were determined  
129 from subtracting sediment volume from total column volume after each experiment, and the gas  
130 flow rates were transformed to number of pore volumes (PVs) flushed during each run. The

131 results from one experiment were also displayed as isotope ratios as a function of mass loss,  
132 using the Rayleigh plot approach (eq. 2). If data plotted with equation 2 fall on a straight line, the  
133 slope is equivalent to the enrichment factor  $\epsilon$ .

$$134 \quad 1000 * \ln \left( \frac{\delta + 1000}{\delta_0 + 1000} \right) = \epsilon \ln \left( \frac{M}{M_0} \right) \quad (\text{eq. 2})$$

135

## 136 **2.3 Modelling**

137 A numerical model was created in order to investigate whether a multistep vapor-liquid IE is a  
138 plausible cause of our observations. The column was schematically represented as a sequence of  
139 stirred non-aqueous liquid solutions (NAPLs) containing light and heavy toluene isotopologues  
140 which partition into a gas stream. The two isotopologues were handled as two different  
141 compounds, and the theoretical vapor pressure was attributed to light isotopologues whereas the  
142 vapor pressure for the heavy isotopologues was derived using an IE from the literature.

143 The model parameters are given in the table S6. The model is based on PHREEQC (USGS, 2002)  
144 and its code is presented in the SI.

## 145 **3. Results**

### 146 **3.1 Volatilization of toluene**

147 A total of 31 volatilization experiments were done, and the conditions which were tested, and the  
148 rationales for choosing each condition were given in Table S1. The first experiment shown here is  
149 one for a sediment contaminated with 0.39 g of liquid toluene for a duration of 18 hours (Figure  
150 1). The evolution of the vapor concentration, expressed as amplitude 44, and the isotope ratio  $\delta^{13}\text{C}$ ,  
151 can be described as happening in four distinct phases. In phase 1, during the first 1100 PVs, both  
152 amplitude and  $\delta^{13}\text{C}$  did not change significantly. In phase 2, lasting about 300 PVs, the amplitude  
153 stayed constant, whereas  $\delta^{13}\text{C}$  values decreased from the initial -26,9 ‰ to -28.7 ‰. Then, in a



154 third phase, lasting about 500 PVs, the amplitude dropped quickly from more than 2500 to less  
155 than 200 mV, while  $\delta^{13}\text{C}$  values increased back to the initial values. During the last phase 4, the  
156 amplitude 44 sank to less than 50 mV, while  $\delta^{13}\text{C}$  could not be measured anymore.

157 The isotope data of figure 1A are also shown as a plot in function of mass loss using equation 2  
158 (Fig S4). No straight line could be established in that plot, as in phase 1 mass is lost without any  
159 marked change in isotope ratios, and in phase two isotope ratios are changing without much mass  
160 loss.

161 The evolution of stable hydrogen isotope ratios in the experiment repeating the conditions shown  
162 in Figure 1A is shown in Figure 1B. The amplitude 2 stayed near the initial value of 8000 mV until  
163 1370 eluted PVs and dropped then sharply to less than 200 mV. The  $\delta^2\text{H}$  values stayed unchanged  
164 until about 750 eluted PVs and then decreased gradually from -35 ‰ to -71 ‰ at 1370 PVs and  
165 were not measurable thereafter. The experiment observed with IRMS set to hydrogen mode showed  
166 thus almost the same behavior as for carbon in phases 1 and 2, with the exception that the magnitude  
167 of isotope shift was larger in the hydrogen experiment. Phases 3 and 4 could not be assessed due  
168 to the lack of isotope data after the too large drop in amplitude (Fig. 1B).

169 In order to understand the causes of these behaviors, a total of > 40 other experiments were  
170 performed. The factors which were varied were 1) increasing time of sorption (only performed in  
171 dry sediments in order to avoid biodegradation); 2) decreasing mass of VOC; 3) variation of gas  
172 flow rate; and 4) use of  $\text{N}_2$  instead of He. Increasing the contact time of toluene to sediment to up  
173 to 10 days was showing an equal behavior during all phases. Also, replacement of the flushing gas  
174 He by  $\text{N}_2$  led to equal results both for C and H (data not shown). However, it was found that the  
175 initial mass of toluene had a significant effect on the start of the drop of amplitude. This could best  
176 be visualized by experiments with column (Figure 2 and Fig. S4).

177

178 In Figure 2, a proportionality between VOC mass and number of PVs is evident in the drops of the  
179 amplitudes. The increase of the flow rate from 6 to 12 mL min<sup>-1</sup> retarded the drop of the amplitude  
180 slightly. The magnitude of the drop of the isotope ratio, in contrast, was not found to give a  
181 systematic trend with initial mass. It was found to depend on whether the timing of the last data  
182 point was close to the drop of the amplitude.

### 183 **3.2 Volatilization of propan-2-ol**

184 In order to study the evolution of stable isotope ratios in another more polar VOC, propan-2-ol was  
185 selected. Figure 3 shows the evolution of  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  in propan-2-ol (~0.3 g) during  
186 volatilization/desorption with He for a contamination of dry sediment aged for 12 hours.

187 The evolution of  $\delta^{13}\text{C}$  in propan-2-ol (Fig. 3A) was like that of toluene (Fig. 1), with an isotope  
188 shift of -3 ‰. In contrast, the  $\delta^2\text{H}$  showed a shift to more positive values in the final stage of phase  
189 2, with a rise of approximately +20 ‰.

### 190 **3.3 Modelling**

191 In order to better understand the influence of VOC mass and other factors on the volatilization  
192 behavior, a numerical model was created. Results from the model for carbon isotopes in toluene  
193 are shown in Figure 4. A base case scenario assumed that the modeled column contained 0.26 g of  
194 liquid toluene, distributed in 20 cells. Additional model runs were performed for other toluene  
195 masses (Fig. 4A), for other numbers of cells forming the column (Fig. 4B), for other dispersivities  
196 (Fig. 4C) and for variations in the vapor-liquid IE (Fig. 4D). As shown in Fig. 4, the variation of  
197 VOC mass had the largest influence on the modeled isotope ratios, followed by the variation of the  
198 vapor-liquid IE. The number of cells and the dispersivity had little or insignificant influence on the  
199 results.

200

201 **4. Discussion**202 **4.1 Toluene**

203 These experiments reveal significant isotope shifts of C and H during volatilization of toluene  
204 from unsaturated sandy aquifer sediment. The shifts for both C and H occur in phase 2 of venting,  
205 during which the vapor concentration was near saturation. A shift back to initial isotope ratios  
206 occurred later for  $\delta^{13}\text{C}$  but could not be observed for  $\delta^2\text{H}$  because the sensitivity of the IRMS is  
207 lower for  $^2\text{H}$  than for  $^{13}\text{C}$ . This shift back to initial  $\delta^{13}\text{C}$  was accompanied by a large drop of  
208 vapor concentrations. Before the drop, vapors were supposed to be generated from liquid VOC,  
209 while after it they were supposed to be generated by desorption from sediment or by  
210 volatilization from water.

211 The isotope shifts for C and H were larger than shifts observed for the volatilization of neat  
212 compounds in beakers (summarized in Tables S4 and S5 in SI). The discussion of the results will  
213 focus mainly on IEs observed during phases 1 and 2 of the experiments with respect to vapor-liquid  
214 partitioning, because data for phases 3 and 4 are only available for carbon. During phases 1+2,  
215 liquid toluene was present in the column and the vapor concentration at the outlet was at or near  
216 saturation point. All known vapor-liquid IEs for both studied VOCs are listed in tables S4+S5. The  
217 equilibrium vapor-liquid IEs for toluene was reported as being +0.2 ‰ for  $^{13}\text{C}$ . (Harrington et al.,  
218 1999) Similar values of +0.3 ‰ and +0.4 ‰ were obtained for low-pressure evaporation at room  
219 temperature and for distillation at 110°C, respectively (Julien et al., 2017). For ring-  
220 monodeuterated toluene a value of +7.0 ‰ was reported (Kiss et al., 1972). Both heavy  
221 isotopologues  $^{13}\text{C}$  and  $^2\text{H}$  are more volatile than their lighter counterparts because of the lower  
222 molar volume of the liquid phase causing more collisions in the liquid which creates a higher vapor

223 pressure (Bartell and Roskos, 1966). A preferential volatilization of heavier toluene is thus  
224 occurring during volatilization from the liquid phase into the column gas phase. The gas flow in  
225 the column is dominated by advection and no diffusion should control the phase-transfer. This is  
226 different from volatilization from an open beaker in a fume hood where a stagnant diffusive gas  
227 boundary layer between the liquid phase and the turbulent air is present which causes an additional  
228 diffusive IE, as discussed in detail in previous works. (Julien et al., 2017; Kuder et al., 2009).  
229 Without stagnant boundary layer, it can be postulated that the vapor is at any point in the column  
230 enriched compared to the liquid VOC, and that the difference corresponds to the vapor-liquid IE.  
231 While both light and heavy toluene volatilize and move through the column, the light toluene has  
232 a larger tendency to partition back into the liquid phase along the column. Initially, the loss of  
233 liquid phase is high at the column inlet, and low or zero near the column outlet. As volatilization  
234 proceeds during phase 1, the liquid phase volatilizes and disappears progressively along the  
235 column, and the remaining liquid phase near the column outlet gets gradually depleted by the back-  
236 partitioning of light isotopologues. The number of pore volumes which form phase 1 for a given  
237 constant flow rate depends intuitively on the VOC liquid mass since the saturated vapor  
238 concentration at the outlet is invariant. Phase two starts when this isotopically depleted liquid phase  
239 starts to volatilize, and it ends when the column does not contain any depleted liquid toluene  
240 anymore. This point is easily identified because the vapor concentration drops drastically.  
241 For carbon, the isotope ratios then returned to near initial values in phase 3 during elution of  
242 toluene desorbed from sediment (Fig. 1A). The drop of vapor concentrations during phase 3 and  
243 4 followed a trend described by (Grathwohl and Reinhard, 1993) as a desorption rate governed  
244 by intra-particle diffusion and sorption. For short desorption times, the decrease in concentration  
245 or flux follow both a linear slope on a diagram  $\log C/C_0$  or  $\log$  flux versus PVs (Grathwohl and

246 Reinhard, 1993). Our vapor data converge to such a linear slope at the end of phase 4 in the  
247 experiment (Fig. 1).

248 The evolution of the isotope ratio during phases 1+2 is not related to the mass loss in the column  
249 by a Rayleigh-type evolution (Fig. S4) since during phase 1 mass is lost without any marked  
250 change in isotope ratio. Therefore, no Rayleigh-type concept can be applied to quantify  
251 enrichment factors.

## 252 **4.2 Propan-2-ol**

253 This compound is more polar but with a slightly higher volatility than toluene, with a vapor  
254 pressure of 5.8 kPa compared to the one of toluene of 3.8 kPa (Broholm et al., 2005) As an  
255 alcohol, hydrogen bonds interfere in its liquid. Therefore, the vapor-liquid IE for H is normal and  
256 not inverse like for toluene (Tab. S5). In contrast, for carbon the IE is inverse (Julien et al., 2017).  
257 Our experiments (Figure 3) yielded a clear opposite IE between C and H, which confirmed that  
258 the vapor-liquid IE is the main cause for the isotope shifts in the column experiments. Classical  
259 data on vapor pressure IE of different propan-2-ols having deuterium at different positions of the  
260 molecule are available (Tab. S5) but do not allow to estimate the magnitude of the deuterium IE  
261 at natural abundance ratios. For example, when deuterium was bound to O, a huge normal IE was  
262 observed whereas when D was bound to a C the IE was smaller but remained normal.

## 263 **4.3 Modelling**

264 The results of the model developed for this study (Fig. S5) show the same type of behavior like  
265 that observed in the experiments for the phases 1+2 of forced volatilization. The mass of VOC  
266 influences the number of pore volumes that need to be vented but does not influence the isotope  
267 shift. This agrees with observations in Fig. 2. In contrast, the magnitude of the vapor-liquid IE  
268 directly influences the magnitude of isotope shift. In our experiments, the experimental shifts for  
269 carbon were higher than the one modeled with a vapor-liquid IE of +0.2 permille in the base case

270 scenario. This suggests that the true vapor-liquid IE is maybe somewhat higher than 0.2 permille.  
271 However, increasing the number of stirred model compartments (cells) increases its maximum  
272 isotope shift also slightly at the end of phase 2, while it retards the onset of the isotope shift. As  
273 depicted in the graphical abstract, an excess of heavy isotopologues is eluted during phase 1,  
274 whereas an excess of light isotopologues follows in phase 2. At its end, when liquid VOCs is  
275 gone, the isotope balance is closed. A break-even point separates the two regimes depicted in  
276 blue and orange in the graphical abstract. The position of this point depends on the number of  
277 stirred solutions chosen in the model. The way of packing the columns affects this number.  
278 Figure 1B shows, however, that the variation of isotope shifts is not strongly affected by this  
279 number. No sorption or intra-particle diffusion was incorporated in the model. Therefore phases  
280 3+4 were not represented. This will be the objective of future studies. At the beginning of phase  
281 3, when desorption starts, it is plausible that the isotope ratio shifts back to near the initial ratio  
282 (Fig. 1) since both light and heavy isotopologues underwent almost equal sorption. Entering  
283 phase 4 of the experiment, intra-particle diffusion and desorption might change isotope ratios  
284 progressively and this needs to be analyzed with a better resolution.

#### 285 **4.4 Environmental implications**

286 Soil venting and bioventing of petroleum products targets mainly monoaromatic hydrocarbons  
287 like toluene and benzene. In the following, the results of our study on toluene are compared to all  
288 other IEs potentially occurring during soil bioventing which were reviewed in a recent  
289 publication (Bouchard et al., 2018) (Fig. 5).

290

291 As shows Figure 5, biodegradation causes isotope enrichment for both isotopes in the remaining  
292 toluene, whereas volatilization from water causes enrichment only in hydrogen. Volatilization of  
293 NAPL was known to cause depletion in H isotopes, and either depletion or enrichment in carbon

294 isotopes. This depends whether diffusion is involved: volatilization from a buried NAPL in soil  
295 was known to cause C enrichment by diffusion (Bouchard et al., 2008a+b) whereas volatilization  
296 of a NAPL exposed to windy air can lead to depletion in C isotopes when the diffusive boundary  
297 layer is absent. Our results showed all in depletion of both isotopes and lie in the same area of the  
298 graph like the NAPL volatilization in turbulent air, but the overall shifts of our results are larger  
299 due to multistep volatilization and back-partitioning.

## 300 **5. Conclusions**

301 In conclusion, this study finds isotope shifts for carbon and hydrogen exceeding previously  
302 known shifts for equilibrium-based phase-transfer processes of the investigated VOCs. The shifts  
303 are in the order of magnitude of shifts created by kinetic isotope effects. The findings give new  
304 insights in the monitoring of the remediation of soils contaminated by VOCs by means of venting  
305 or bioventing. More work is needed for extending the experimental scale to 3 dimensions, and for  
306 the study of late stages of forced volatilization.

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311

312

313 **ASSOCIATED CONTENT**

314 **Supplementary Information**

315 Scheme and picture of laboratory setup, characterization of the aquifer sediment, details on  
316 linearity of IRMS, isotope effects for phase changes of toluene and propane-2-ol, additional data  
317 for hydrogen isotope experiments and PHREEQC model for volatilization. This material is  
318 available free of charge on the Journal web site.

319



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402 **Figure Captions**

403

404 **Figure 1:** *A) Evolution of concentration (expressed as amplitude, circles) and of carbon isotope*  
405 *ratio (squares) during volatilization of toluene from unsaturated humid sandy aquifer sediment. B)*  
406 *Evolution of the hydrogen isotope ratios and vapor concentrations expressed as amplitudes of mass*  
407 *2 during desorption of toluene from sandy aquifer sediment.*

408 **Figure 2:** *Vapor concentration expressed as amplitude mass 44 (A) and carbon stable isotope*  
409 *change (B) during volatilization/desorption of toluene from unsaturated sandy sediment with*  
410 *distinct initial masses of toluene. Flow rates varied from 6 to 12 mL min<sup>-1</sup>.*

411 **Figure 3:** *Evolution of concentration expressed as amplitude, and of Carbon (A) and Hydrogen*  
412 *(B) isotope during volatilization/desorption of propan-2-ol from unsaturated sandy aquifer*  
413 *sediment.*

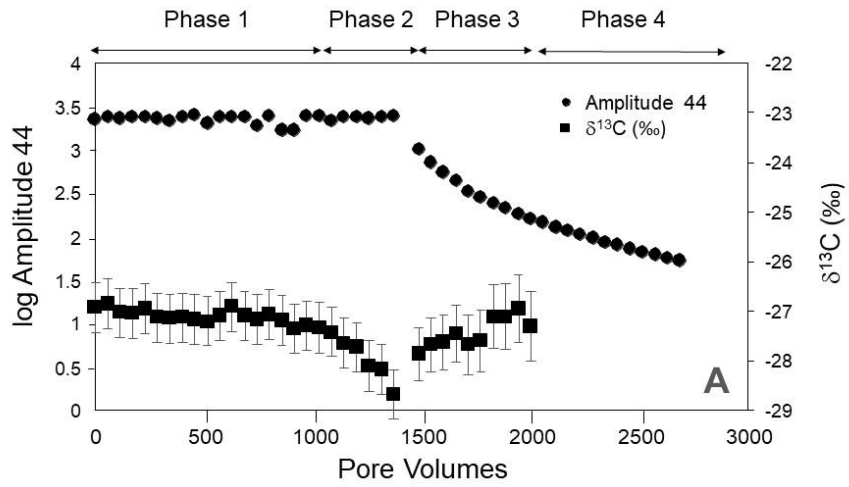
414 **Figure 4:** *Results for <sup>13</sup>C of the numerical model, with variation of 4 model parameters: A) toluene*  
415 *mass B) number of stirred cells forming the columns C) dispersivity, and D) vapor-liquid isotope*  
416 *effect VPIE. See Tab. S5 for other parameters. The vapor concentration at the column end is always*  
417 *at saturation and drops to zero after the last data point.*

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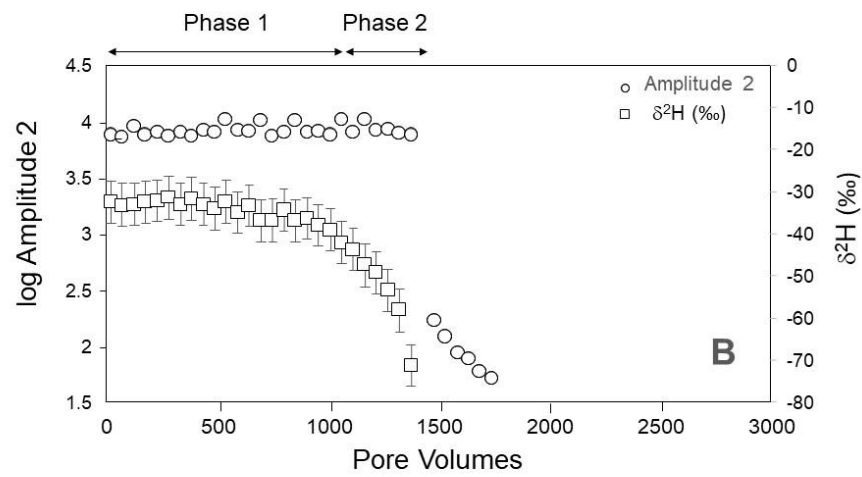
419 **Figure 5:** *Magnitude of isotope shifts observed in this work for toluene compared to isotope shifts*  
420 *by other processes as reviewed in (Bouchard et al., 2018).*

421

422 Figure 1:

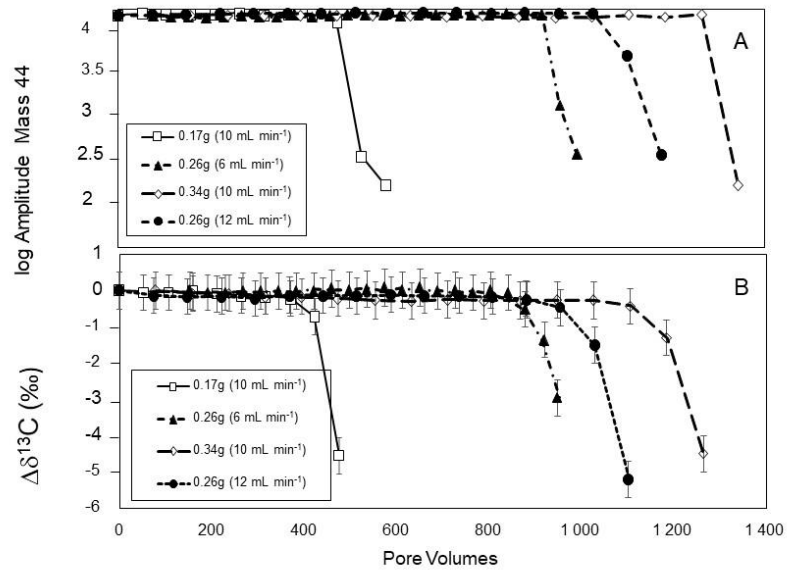


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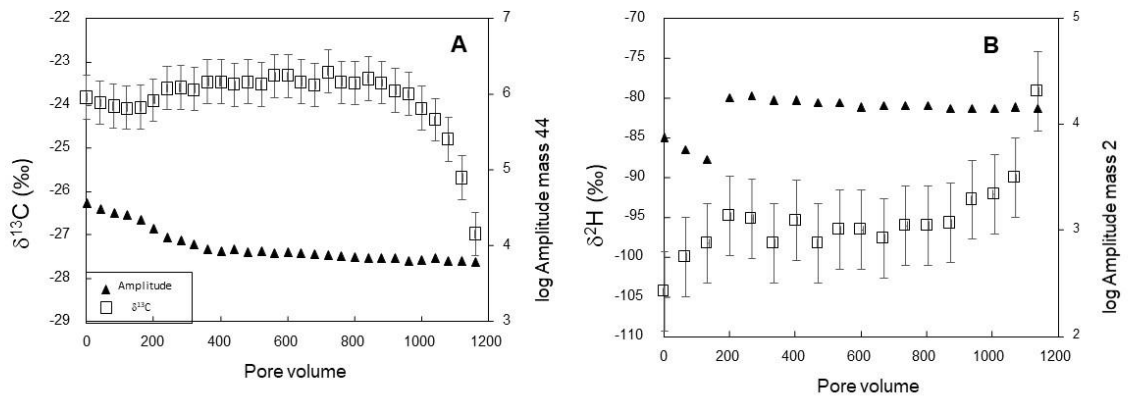
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425 Figure 2:



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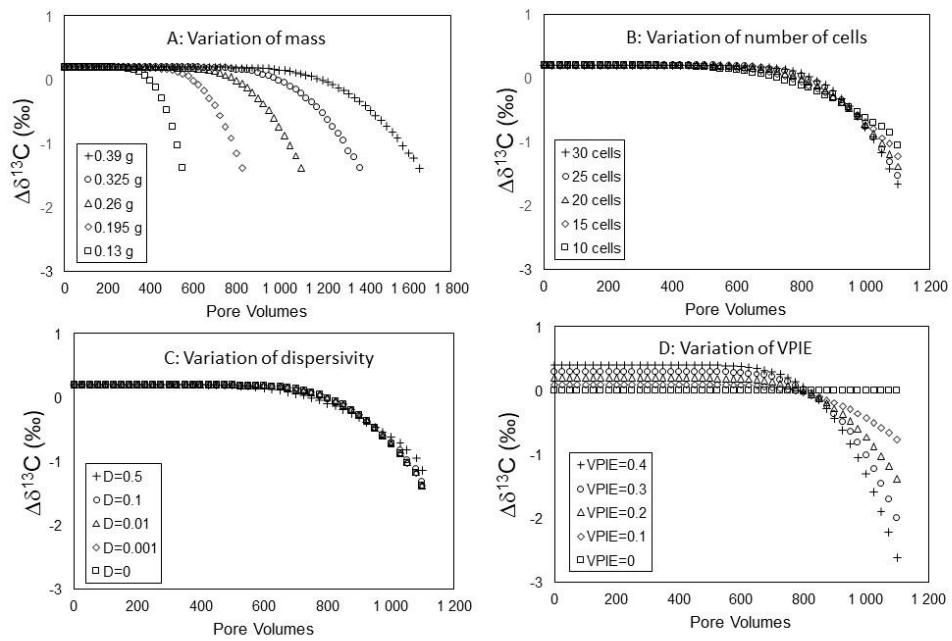
427 Figure 3:



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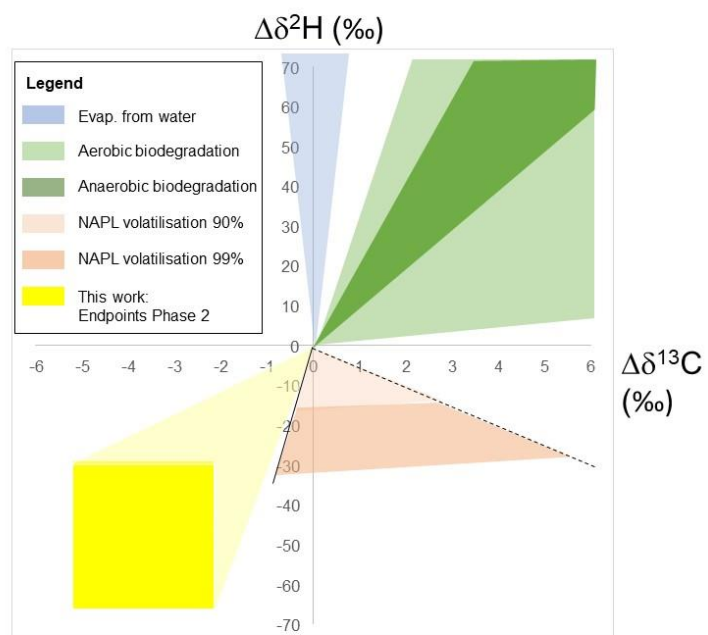
429 Figure 4:



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432 Figure 5:



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