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1 **Stable carbon and hydrogen isotope fractionation of volatile organic compounds caused by**
2 **vapor-liquid equilibrium**

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37 **Abstract**

38 Several types of laboratory experiments were conducted to evaluate isotope fractionation caused by
39 phase transfer process for a selection of common environmental contaminants. Carbon and
40 hydrogen isotope fractionation caused by vaporization of non-aqueous phase liquid (NAPL), by
41 volatilization from water and by dissolution into an organic solvent (tetraethylene glycol
42 dimethylether or TGDE) was investigated under closed system experimental setups to isolate the air-
43 liquid partitioning process. A selection of aromatic, aliphatic and chlorinated compounds along with
44 one fuel oxygenate (methyl tert-butyl ether or MTBE) were evaluated to determine isotope the
45 enrichment factor related to respective phase transfer process. During NAPL vaporization, the
46 residual mass of aromatic compounds, aliphatic compounds and MTBE became progressively
47 depleted in heavy carbon and hydrogen isotopes. In contrast, during volatilization from water, the
48 residual mass of aromatic compounds and MTBE dissolved in the water became progressively
49 enriched in heavy hydrogen isotopes, whereas no significant change in carbon isotope was observed,
50 except for MTBE showing a significant depletion. For the air-TGDE partitioning process, most of the
51 aromatic compounds tested led to no significant carbon (except ethylbenzene) or hydrogen (except
52 toluene and *o*-xylene) isotope fractionation. In contrast, significant carbon isotope fractionation was
53 observed for aliphatic and chlorinated compounds and hydrogen isotope fractionation for aliphatic
54 compounds, and are comparable to progressive NAPL vaporization in direction and magnitude. The
55 isotope fractionation factors determined in this study are key for interpreting the change in isotope
56 ratios when assessing the fate of gas-phase VOCs present in the soil air or when gas-phase VOCs are
57 sampled using TGDE as the sink matrix. The results of this study contribute to expand the list of
58 common environmental contaminants that can be assessed by the compound-specific isotope
59 analysis (CSIA) method deployed in the frame of gas-phase studies.

60

61 **Keywords:** Stable isotopes, carbon isotope, hydrogen isotope, VOC volatilization, organic liquid
62 vaporization, isotope fractionation.

63

64 1. Introduction

65 Volatile organic compounds (VOCs) represent an important class of subsurface environmental
66 contaminants, among which chlorinated solvents and petroleum hydrocarbons are commonly
67 encountered. In general, these contaminants have penetrated into the subsurface as non-aqueous
68 phase liquids (NAPL) due to accidental releases above ground or improper storage tank containment
69 in the subsurface. During downward migration through the unsaturated zone, portions of the moving
70 NAPL become immobilized in the soil pores, resulting in a residual saturation ranging from 2 to 20%
71 of the soil pore volume (Boulding, 1995). Due to their high vapor pressure, VOCs are expected to
72 volatilize from the immobilized NAPL and migrate by gas-phase diffusion through the soil porosity,
73 thus forming gas-phase plumes. potentially posing threats to human health if entering buildings (so
74 called vapor intrusion process) (Johnson and Ettinger, 1991; Verginelli et al., 2016) or contaminating
75 sub laying groundwater resources (Grathwohl et al., 2003). Biodegradation and chemical oxidation
76 are naturally occurring attenuation processes limiting gas-phase plume expansion by transforming
77 VOCs into less harmful compounds (see Rivett et al. (2011) for an extensive review of processes).
78 Aerobic biodegradation of VOCs during migration can be expected to readily occur for petroleum
79 hydrocarbons under field conditions (Lahvis et al., 1999; Baker et al., 2000; Christophersen et al.,
80 2005; Davis et al., 2005; Höhener et al., 2006; Molins et al., 2010; Sihota et al., 2016). Aerobic
81 biodegradation of chlorinated compounds in the unsaturated zone may also naturally occur, with
82 biodegradation of *cis*-DCE and VC being commonly reported (Kirtland et al., 2003; Patterson et al.,
83 2013; Kurt et al., 2014). The literature remains scarce regarding aerobic biodegradation of TCE. While
84 shown to occur in aqueous media (Barth et al., 2002; Chu et al., 2004; Clingenpeel et al., 2012),
85 occurrence during gas-phase transport in unsaturated soil remains to be demonstrated. Similarly,
86 chemical oxidation of TCE under oxic conditions was shown to occur in aqueous media (Pham et al.,
87 2008; Schaefer et al., 2018), but occurrence during gas-phase transport in unsaturated soil also
88 remains to be validated. Finally, anoxic environments favorable to anaerobic biodegradation can also

89 be developed at sites where the oxygen is consumed at higher rates than supplying rates (Molins et
90 al., 2010), which was also shown to contribute limiting petroleum hydrocarbon plume expenditure.
91

92 Natural source zone depletion (NSZD) by physical and reactive processes has been presented as a
93 viable site management strategy (Johnson et al., 2013). Relying on natural attenuation processes as a
94 site management strategy is acceptable when one can scientifically document the occurrence and
95 contribution of attenuation processes along with quantification of contaminant mass reduction rates,
96 while posing no risk to nearby population or natural resources. Quantification of mass reduction
97 rates associated with a source zone located in the unsaturated zone is generally carried out by
98 evaluating concentration changes for each targeted VOC in the soil gas over time (Cozzarelli et al.,
99 2001; Lundegard and Johnson, 2006). However, understanding the VOC mass-transfer dynamics of a
100 multiple-component NAPL is critical to accurately assess fate and contaminant transport, and yet
101 represents a challenge to predict (Wang et al., 2003; Broholm et al., 2005; McColl et al., 2008). In
102 addition, while VOC concentrations are dependent on many environmental factors (for instance
103 seasonal temperature variation, recharge water or groundwater level fluctuation), representative
104 concentrations over space and time remain a limiting factor in quantifying accurate NSZD rates
105 (Ponsin et al., 2015; Sihota et al., 2016). When remediation actions on the source are required, some
106 engineered systems will take advantage of the high vapor pressure of the contaminants to accelerate
107 source mass reduction. Soil vapor extraction (SVE) systems were shown to be an effective method for
108 removing VOCs from the unsaturated zone, and thus became a common technology deployed by
109 remediation engineers. Over prolonged treatment duration, the treatment efficiency tends to
110 decrease indicated by reduced mass-removal rates and concentration tailings. This efficiency loss is
111 caused by different physical, chemical, and biological factors influencing contaminant transport
112 (McColl et al., 2008), from which emerges the question whether or not the treatment efficiency
113 reached its limitations and should thus be ended. To confidently determine proper NSZD rates in the
114 unsaturated zones or to appropriately evaluate the efficiency of remediation systems applied to

115 unsaturated zones, field practitioners therefore need assessment tools that are suitable for gas-
116 phase investigations.

117

118 Compound-Specific Isotope Analysis (CSIA) is a process-specific assessment tool increasingly used in
119 gas-phase studies. CSIA was shown to be an appropriate assessment tool to evaluate NSZD in the
120 unsaturated zone (Bouchard et al., 2008b; Höhener et al., 2008; Bouchard et al., 2011), to assess for
121 vapor intrusion (McHugh et al., 2011; Jeannotat and Hunkeler, 2013; Beckley et al., 2016) and to
122 evaluate the performance of remediation systems (Bouchard et al., 2017a; Bouchard et al., 2018b;
123 Zamane et al., 2020). Basically, the CSIA method aims at tracking the isotope ratio evolution of an
124 element ($^{13}\text{C}/^{12}\text{C}$, $^2\text{H}/^1\text{H}$, $^{37}\text{Cl}/^{35}\text{Cl}$) for selected VOC with time (and/or distance) to demonstrate VOC
125 biodegradation (Aelion et al., 2010) or to identify the dominant attenuation process (Kuder et al.,
126 2009; Bouchard et al., 2018a). The impact of biodegradation on the isotopic composition of VOC is
127 well understood and leads to an accumulation of heavy isotopes (i.e. isotope enrichment) in the
128 remaining pool of VOCs due to slower reaction kinetics of molecules including a heavy isotope.
129 However, it was shown that some physical attenuation processes, which had been neglected when
130 applying CSIA for VOCs in saturated soil conditions (i.e. groundwater), must be considered in
131 unsaturated soil conditions as causing significant isotope fractionation. For instance, vaporization of
132 organic liquid, air-water partitioning and gaseous diffusion are physical processes known to change
133 the isotopic composition of gas-phase VOCs (Bouchard et al., 2008b; Kuder et al., 2009). These
134 processes are hence expected to impact the isotopic signature of the VOCs during the course of
135 passive vaporization (such as during natural source zone depletion) or during an active engineered
136 remediation treatment. The direction (i.e. enrichment or depletion in heavy isotopes) and the
137 magnitude of the isotope fractionation is, however, dependent on the conditions under which the
138 processes are occurring. For equilibrium conditions in a closed system (i.e. static conditions), an
139 isotope fractionation is expected due to different vapor pressure properties for isotopically different
140 molecules (and called isotopologues) (Van Hook, 2006; Wolfsberg et al., 2010). In contrast, for non-

141 equilibrium conditions in an open system (i.e. dynamic conditions), isotope fractionation due to
142 kinetic processes such as gaseous and aqueous diffusion is occurring, and the observed isotopic
143 change reflecting the processes interplay (vapor pressure and diffusion) is explained by the Craig-
144 Gordon model (Kuder et al., 2009; Jeannotat and Hunkeler, 2012; Julien et al., 2015b; Kopinke and
145 Georgi, 2017). Currently, the direction and the magnitude of the isotope fractionation caused by
146 vaporization and air-water partitioning process (under equilibrium conditions) are known for only
147 few VOCs and elements, which limits the number of VOCs that can be assessed on field sites.

148

149 Lastly, application of CSIA in gas-phase studies is still largely limited due to lack of appropriate
150 sampling devices specific to isotope measurements. A simple and robust solvent-based method
151 specifically developed to facilitate isotope measurement on collected gas-phase VOCs has been
152 recently documented as an alternative sampling method (Bouchard et al., submitted). The method
153 uses tetraethylene glycol dimethylether (TGDE) as a liquid sink matrix to accumulate the gaseous
154 VOCs. TGDE was selected among other potential solvents due to its lower vapor pressure property,
155 increased affinity with polar and apolar compounds, and lastly due to absence of interference with
156 the analytes during the analytical measurements (Bouchard et al., 2017b). During the sampling
157 process, dissolution of gas-phase VOC into TGDE is controlled by the air-solvent partitioning process.
158 This air-solvent partitioning process potentially leads to an isotope fractionation during the sampling
159 process, which warrants further evaluations.

160

161 This study has two objectives, both focusing on isotope fractionation caused by phase transfer
162 processes. First, carbon and hydrogen isotope fractionation factors related to vaporization from
163 organic liquid and air-water partitioning under equilibrium conditions were determined for a
164 selection of aromatic, aliphatic and fuel oxygenate compounds. A large subset of hydrocarbons was
165 tested to evaluate the isotope fractionation variability related to different molecular structure, and in
166 view to expand the CSIA application in soil gas studies to additional common contaminants observed

167 at contaminated sites. Second, with the aim to support the development of the solvent-based
168 sampling method specific to CSIA, carbon and hydrogen isotope fractionation related to air-TGDE
169 partitioning was evaluated for a selection of aromatic, aliphatic, fuel oxygenate and chlorinated
170 compounds. An isotope-specific analytical simulation was subsequently conducted reproducing the
171 progressive accumulation of VOCs into TGDE during a sampling event. The analytical simulation was
172 performed with the purpose of gaining comprehensive insights on the isotope fractionation caused
173 by air-TGDE partitioning process during transient and steady state conditions.

174

175 **2. Material & methods**

176 **2.1. Laboratory experiments**

177 **2.1.1. Stepwise NAPL vaporization in closed system**

178 Multi stepwise NAPL vaporization experiments were carried out as previously performed for
179 chlorinated ethenes by Jeannotat and Hunkeler (2012) to quantify carbon and hydrogen isotope
180 fractionation factor for benzene (B), toluene (T), *o*-xylene (*o*-X), cyclopentane, *n*-octane, 2,2,4-
181 trimethylpentane (isooctane) and methyl tert-butyl ether (MTBE) (99% purity, various suppliers). The
182 experimental setup consisted of two 5 mL air-tight syringes (Hamilton – model 1005 RN SYR for screw
183 RN nut end tip) connected using a custom-designed screwing metal connector and maintained in
184 vertical position during the experiment. A small 25 μ L metal receptacle was welded on the lower
185 syringe plunger to contain the NAPL. Once spiked in the receptacle, the NAPL was allowed to
186 equilibrate (20 minutes) with a fixed volume of air inside the lower syringe only by keeping the lock
187 closed. The selected air volume was the smaller, the higher the VOC vapor pressure. The lock was
188 reopened, and the headspace of the lower syringe was then transferred into the upper syringe. Once
189 the syringes disconnected, clean air was reintroduced in the lower syringe whereas isotope analysis
190 for the gas-phase compound contained in the upper syringe was performed. The VOC mass removed
191 per step was related to the syringe volume and the vapor pressure of the compound at the
192 experimental temperature (25°C). The mass removal evolution was tracked by using the total

193 integrated peak area obtained during each isotopic analysis (see further explanation in
194 Supplementary material). Repeated equilibration and dispense steps were performed until >95% of
195 the NAPL mass was depleted, except for MTBE (>88%). Each compound was individually tested. For
196 each VOC, carbon and hydrogen isotopes were evaluated separately respectively in duplicate and in
197 triplicate experiments.

198

199 **2.1.2. Stepwise air-water partitioning in closed system**

200 Multi stepwise air-water partitioning experiments were carried out as previously performed for
201 chlorinated ethenes by Jeannotat and Hunkeler (2012) to quantify carbon and hydrogen isotope
202 fractionation factor for BTO-X and MBTE. An aqueous solution of 10 mg/L was separately prepared
203 for each VOC in a 250 mL glass vial. Ten (10) mL of the solution was introduced into a 25 mL gas-tight
204 glass syringe with the plunger fully extended to the 25 mL mark, hence leaving 15 mL of headspace.
205 The syringe was closed and was slightly shaken (200 rpm) for at least 20 minutes to reach the air-
206 water equilibrium. The headspace was dispensed in a fume hood and followed by the introduction of
207 15 mL of ambient air in the syringe. The equilibration-dispense step was repeated until a defined
208 mass proportion was removed based on Henry's law (at room temperature). The relative VOC mass
209 decrease over time was validated by concentration analysis carried out on each aqueous sample.
210 One experimental series involved six (6) independently produced water samples with increasing
211 number of equilibration steps. Three series were conducted for each compound (individually tested),
212 except for MTBE (2 series). Isotope analyses were performed on the water samples in duplicates.

213

214 **2.1.3. Air-TGDE partitioning in closed system**

215 Single step air-TGDE partitioning experiments were carried out to quantify carbon and hydrogen
216 isotope fractionation factor for a selection of aromatic compounds (BTO-X, ethylbenzene (E) and *m,p*-
217 xylene (*m,p*-X)), aliphatic compounds (cyclopentane, *n*-hexane and *n*-octane) and one fuel oxygenate
218 compound (MTBE). In addition, a selection of chlorinated compounds including perchloroethene

219 (PCE), trichloroethene (TCE), 1,1,2-trichloroethane (1,1,2-TCA), *cis* 1,2-dichloroethene (*cis*-DCE) and
220 1,2-dichloroethane (1,2-DCA) were evaluated to quantify carbon isotope fractionation factor. TGDE
221 was obtained from Sigma-Aldrich (>99% purity) whereas the chlorinated compounds were obtained
222 from various suppliers (all > 99 %). One (1) mL of TGDE was pipetted into a 20 mL glass vial. A defined
223 volume of one pure compound was pipetted into the vial containing TGDE and then closed with
224 teflon-lined septa using screw caps. The volumes were chosen according to the air-tetraglyme
225 partitioning constant to produce about equal concentrations of each element C or H in the
226 headspace. Additional vials without TGDE and reduced NAPL volume were prepared to measure the
227 isotope ratio of the neat material (Table 1), again adjusting the amount of C and H to about equal
228 vapor concentrations. These concentrations produced peaks within the IRMS linear range calibration,
229 with amplitudes equal to reference gas peaks. For each VOC, a set of 5 vials with and without TGDE
230 was prepared and left to equilibrate for 24 hours at 30°C. Carbon and hydrogen isotopes were
231 evaluated in separate experiments.

232

233 **Table 1: Volume of NAPL added per 20 mL vial containing TGDE (1 000 μL) or without TGDE, for**
 234 **each VOC tested.**

Compound	With TGDE (μL)		Without TGDE (μL)	
	For ^{13}C analysis	For ^2H analysis	For ^{13}C analysis	For ^2H analysis
Benzene	20	158	0.5	0.5
Toluene	34	269	0.5	0.5
Ethylbenzene	115	462	1	1
<i>m,p</i> -xylene	230	230	0.5	0.5
<i>o</i> -xylene	115	400	0.5	2
cyclopentane	4	7	0.7	1
<i>n</i> -hexane	5	7	0.6	1
<i>n</i> -octane	40	8	0.6	1
MTBE	230	--	0.5	--
PCE	80	--	1.2	--
TCE	101	--	1.4	--
1,1,2-TCA	695	--	1.4	--
<i>cis</i> -DCE	150	--	1	--
1,2-DCA	180	--	1	--

235

236

237 2.2. Analytical methods and data treatment

238 . The methods for concentration and for carbon and hydrogen isotope analysis are described in the
 239 Supplementary Material.

240

241 For all cases, isotope ratios are reported in the delta (δ) notation (Coplen, 2011):

242

$$243 \delta = \left(\frac{R}{R_{std}} - 1 \right) \quad \text{eq. 1}$$

244 where R and R_{std} are the isotope ratio of the sample and the international reference standard,
 245 respectively (VPDB for carbon and SMOW for hydrogen). The δ value obtained was then multiplied
 246 by 1000 to conveniently express it in units of per mil (‰).

247

248 For single step equilibrium conditions, the isotope fractionation caused by phase partitioning
 249 (between the gas and liquid) was quantified using:

250
$$\alpha = \frac{(1000 + \delta_{gas})}{(1000 + \delta_{liquid})}$$
 eq. 2

251 Where α is the isotope fractionation factor, and where δ_{gas} and δ_{liquid} are the isotope values for the
252 VOC in gas phase and in the liquid phase, respectively. For convenience, the isotope fractionation
253 factor is further transformed into an isotope enrichment factor (ϵ) using:

254
$$\epsilon = (\alpha - 1) * 1000$$
 eq. 3

255 An ANOVA test was carried out to evaluate difference between δ_{gas} and δ_{liquid} measurements, and the
256 standard deviation reported for ϵ is the sum of the two standard deviations of the mean for each
257 sample.

258 For multi stepwise equilibrium conditions, the general equation to quantify the isotope fractionation
259 factor for NAPL-vapor equilibration and air-water partitioning was developed in Jeannotat and
260 Hunkeler (2012):

261
$$\Delta\delta_{liquid} = \epsilon(1 - f_{liquid})$$
 eq. 4

262

263 Where $\Delta\delta_{liquid}$ is the isotopic shift measured in the liquid, and f_{liquid} is the fraction of the VOC in
264 the liquid. Since the latter expression was shown to provide equivalent results to the Rayleigh
265 approach, the air-NAPL ($\epsilon_{air-NAPL}$) and the air-water ($\epsilon_{air-water}$) enrichment factor for each compound
266 was quantified using the Rayleigh equation:

267
$$\ln [(\delta + 1000)/(\delta_i + 1000)] = \frac{\epsilon}{1000} \ln f$$
 eq. 5

268 Where δ_i is the initial isotopic composition of the compound, δ is the isotopic composition of the
269 compound at the remaining fraction f .

270 For each compound, ϵ (for C and H) was determined by plotting $\ln [(\delta + 1000)/(\delta_i + 1000)] * 1000$ as function of $\ln f$, where ϵ is the slope of the linear regression. A slope was determined for
271 each replicate and also by regrouping triplicate experiments as a whole to report the bulk slope. The
272 slope was not forced through the origin, as suggested by Scott et al. (2004). A Student-T test for
273 regression method (to validate a slope different than zero) and a 95% confidence interval (for slope
274 uncertainty) were calculated using the Statistics module from Grapher-Golden software®.

276 Finally, the relationship $\Lambda = H \cdot \epsilon_{\text{air-NAPL}} / C \cdot \epsilon_{\text{air-NAPL}}$ was applied to report Λ values as $H \cdot \epsilon_{\text{air-NAPL}}$ and $C \cdot \epsilon_{\text{air-NAPL}}$
277 Λ were determined in separate experiments. The Λ values contribute to enlarge the dataset used
278 in the frame of 2D-CSIA approach to assess the dominant contaminant mass removal process during
279 remediation treatment (Bouchard et al., 2018a).

280 **2.3. Isotope modeling**

281 A simple analytical simulation was performed describing the increasing VOC concentration into a
282 solvent when an air stream loaded with gaseous VOCs is forced through. The analytical simulation
283 incorporates isotope fractionation during dissolution process to investigate for potential isotope
284 fractionation effect. The mathematical solution applied was previously described in Huybrechts et al.
285 (2001):

$$286 \quad C_L = \frac{C_g}{K} \left(1 - e^{\left(-\frac{KF}{V}\right)t} \right) \quad \text{eq. 6}$$

287 Where C_L is the VOC concentration in the liquid at time t , C_g is the VOC concentration in the gas
288 phase, K is the air-solvent partitioning constant for the VOC, F is the air flow rate passing through the
289 solvent and V is the total volume of air injected. At infinite time (leading to VOC concentration
290 equilibrium between gas and solvent), equation 6 simplifies to:

$$291 \quad C_L = \frac{C_g}{K} \quad \text{eq. 7}$$

292 To evaluate the isotope composition evolution of TCE used as the modeled compound, TCE
293 molecules including a ^{13}C (^{13}C -TCE) or without (^{12}C -TCE) were distinguished (forming 2 isotopologues)

294 and modeled as two different contaminants. Different initial concentrations and air-solvent
 295 partitioning coefficients were attributed to each isotopologue, which were determined as follow:

296 *initial concentrations:* For a given initial TCE concentration (C_{TCE}) in the gas stream and isotopic
 297 composition ($\delta^{13}C$), initial concentrations for ^{13}C -TCE ($C_{^{13}C-TCE}$) and ^{12}C -TCE ($C_{^{12}C-TCE}$) were determined
 298 using:

$$299 \quad C_{^{13}C-TCE} = \frac{C_{TCE}}{1 + \frac{\delta^{13}C + 1000}{1000} / R_{std}} \quad \text{eq. 8}$$

$$300 \quad C_{^{12}C-TCE} = \frac{C_{TCE}}{1 + \frac{\delta^{13}C + 1000}{1000} * R_{std}} \quad \text{eq. 9}$$

301 *air-solvent partitioning constants:* To account for isotope fractionation during dissolution, the air-
 302 TGDE isotope fractionation factor ($\alpha_{air-TGDE}$) for TCE determined in this study was used. The literature
 303 air-TGDE partitioning constant (K) was attributed to ^{12}C -TCE (K_L) and the K value for ^{13}C -TCE (K_H) was
 304 determined by:

$$305 \quad \alpha_{air-solvent} = \frac{K_H}{K_L} \quad \text{eq. 10}$$

306 The two isotopologues were independently treated to evaluate their respective accumulation in the
 307 solvent during a simulated sampling event. For given periodicities, the simulated quantities of the two
 308 isotopologues were combined to calculate the $\delta^{13}C$. See Bouchard et al. (2011) for further
 309 explanation on the isotopic modeling approach.

310 Finally, a second simulation was performed to reproduce the isotope change measured during a
 311 multi step air-water equilibrium experiment. The equation 4 was expanded to include the number of
 312 equilibrium steps (n) as follow:

$$313 \quad \Delta\delta_{liquid}^n = n\varepsilon(1 - f_{liquid}) \quad \text{eq. 11}$$

314 with

315 $f_{liquid} = \left(\frac{C_n}{C_0}\right)^{1/n}$ eq.12

316 where C_n and C_0 are respectively the concentration in aqueous phase after n equilibration steps and
317 Initial concentration in aqueous phase.

318

319 **3. Results**

320 **3.1. NAPL vaporization**

321 During stepwise NAPL vaporization of VOCs conducted in closed systems, the residual VOC mass
322 became progressively depleted in heavy carbon and hydrogen isotopes for all tested VOCs (Figure 1
323 and 2). The depletion trends indicate that molecules with heavy isotopes are more volatile than
324 those with light isotopes only. For carbon, the magnitude of isotope fractionation is small, but was
325 consistently reproduced over triplicate experiments. The carbon enrichment factors ($C-\epsilon_{air-NAPL}$)
326 obtained for the bulk slope of the triplicates range between 0.14 ± 0.04 ‰ (cyclopentane) and $0.38 \pm$
327 0.05 ‰ (MTBE) (Table 2). The enrichment factors for aromatic compounds are within the same range
328 as aliphatic compounds, whereas the oxygenate compound (MTBE) provided a larger factor. For
329 hydrogen, the isotope enrichment factors ($H-\epsilon_{air-NAPL}$) determined were at least an order of
330 magnitude larger than for carbon, and ranged between 2 ± 1 ‰ (MTBE) and 12 ± 2 ‰ (*n*-octane)
331 (Table 3). The hydrogen enrichment factors for aromatic compounds are smaller than for aliphatic
332 compounds, whereas the oxygenate compound (MTBE) provided a significantly smaller factor
333 compared to the two other groups. The variation of enrichment factors (C and H) among all tested
334 VOCs is best visualized when plotting $H-\epsilon_{air-NAPL}$ values as function of $C-\epsilon_{air-NAPL}$, where the resulting Λ
335 values ($H-\epsilon_{air-NAPL} / C-\epsilon_{air-NAPL}$) allowed dissociating the 3 main compounds groups (Figure 3). The fuel
336 oxygenate (MTBE) provided the lowest Λ value ($\Lambda=5$), whereas the aliphatic compounds (*n*-octane,
337 cyclopentane and isooctane) provided the largest values (Λ ranging from 35 to 59), and with the
338 aromatic compounds (BTo-X) positioning in between (Λ ranging from 20 to 26).

339 **Table 2:** Carbon enrichment factors ($C-\epsilon_{\text{air-NAPL}}$) related to stepwise NAPL vaporization and air-water
 340 partitioning process in closed system experimental setups (measured in the current study) and
 341 related to gas-phase diffusion and biodegradation (literature data) for selected aromatic, aliphatic,
 342 oxygenate and chlorinated compounds.

Compound	Air-NAPL partitioning	Air-water partitioning	Gas-phase diffusion*	Aerobic biodegradation**
	ϵ (‰)			
Benzene	0.18 ± 0.03	n.s. to 0.09 ± 0.05	-1.71	-0.5 to -3.65
Toluene	0.22 ± 0.04	n.s. to 0.17 ± 0.09	-1.28	n.d. to -3.3
Ethylbenzene	--	--	-1.00	-0.4 to -0.6 ^a
<i>m,p</i> -Xylene	--	--	-1.00	-0.6 to -1.7 (<i>m-X</i>)
<i>o</i> -xylene	0.24 ± 0.04	n.s.	-1.00	--
<i>n</i> -octane	0.21 ± 0.03	--	-0.88	-0.7 to -1.1
cyclopentane	0.14 ± 0.04	--	-2.05	--
isooctane	0.17 ± 0.02	--	-0.88	--
MTBE	0.38 ± 0.05	0.22 ± 0.06	-1.42	-1.5 to -2.4
PCE	--	--	-0.45	--
TCE	--	--	-0.69	-11.6 \pm 4.1 ^b to -18.2 ^c
1,1,2-TCA	--	--	-0.66	--

343 n.s.= not significant. * calculated as described in Aelion et al. (2010), using 28,8 g/mol for air mass. **
 344 In Aelion et al. (2010), if not specified. ^aDorer et al. (2014), ^bClingenpeel et al. (2012), ^cBarth et al.
 345 (2002).

346

347 **Table 3:** Hydrogen enrichment factors ($H-\epsilon_{\text{air-NAPL}}$) related to stepwise NAPL vaporization and air-
 348 water partitioning process in closed system experimental setups (measured in the current study) and
 349 related to gas-phase diffusion and biodegradation (literature data) for selected aromatic, aliphatic,
 350 oxygenate and chlorinated compounds.

Compound	Air-NAPL partitioning	Air-water partitioning	Gas-phase diffusion*	Aerobic biodegradation**
	ϵ (‰)			
Benzene	4 ± 1	-5 ± 1	-1.71	-11 to -17
Toluene	6 ± 1	-5 ± 2	-1.28	-8.6 to -159
Ethylbenzene	--	--	-1.00	+4 to -28 ^a
<i>m,p</i> -Xylene	--	--	-1.00	--
<i>o</i> -xylene	6 ± 1	-9 ± 4	-1.00	--
<i>n</i> -octane	12 ± 2	--	-0.88	--
cyclopentane	9 ± 2	--	-2.05	--
isooctane	6 ± 1	--	-0.88	--
MTBE	2 ± 1	-9 ± 3	-1.42	-29 to -66
PCE	--	--	-0.45	--
TCE	--	--	-0.69	--
1,1,2-TCA	--	--	-0.66	--

351 * calculated as described in Aelion et al. (2010), using 28,8 g/mol for air mass. ** In Aelion et al.
 352 (2010), if not specified. ^aDorer et al. (2014).

353

354 3.2. Air-water partitioning

355 During stepwise air-water partitioning of MTBE in closed systems, the remaining MTBE in the water
 356 became progressively depleted in heavy carbon isotopes, indicating that MTBE molecules with a
 357 heavy carbon isotope are more volatile than those including light carbon isotopes only (Figure 4).
 358 Significant change occurred for MTBE in both duplicate experiments, from which a carbon
 359 enrichment factor ($C-\epsilon_{\text{air-water}}$) of $0.22 \pm 0.06\text{‰}$ was calculated based on the bulk slope of the two
 360 repetitions (Table 2). For benzene and toluene (with mass removed proportion > 97%), only one
 361 repetition of each VOC showed a significant depletion trend (respectively $C-\epsilon_{\text{air-water}}$ of $0.09 \pm 0.05\text{‰}$
 362 and $0.17 \pm 0.09\text{‰}$), whereas the other two repetitions and the bulk slope of the three repetitions

363 indicated no significant change (Figure 4). Finally, no significant carbon isotope enrichment was
364 observed for *o*-xylene in all three repetitions, for a mass removed proportion >97% (Figure 4). For
365 hydrogen, in contrast, the residual VOC in water became progressively enriched in heavy hydrogen
366 isotopes for every repetition of all four tested compounds (Figure 5), hence indicating that molecules
367 with a heavy hydrogen isotope are less volatile than those with light hydrogen isotopes only. The
368 bulk slope for BTo-X compounds respectively provided hydrogen enrichment factors ($H-\epsilon_{\text{air-water}}$) of -5
369 $\pm 1\text{‰}$, $-5 \pm 2\text{‰}$ and $-9 \pm 4\text{‰}$, whereas the oxygenate MTBE compound provided $H-\epsilon_{\text{air-water}} = -9 \pm 3\text{‰}$
370 (Table 3).

371

372 **3.3. Air-TGDE partitioning**

373 *Petroleum hydrocarbons:* During single step air-TGDE partitioning in closed systems, the carbon
374 isotope composition of gas phase aliphatic compounds (cyclopentane, *n*-hexane and *n*-octane)
375 became enriched in heavy carbon isotopes, indicating that molecules with a heavy carbon isotope
376 are less soluble in TGDE than molecules with light isotopes only (inverse isotope effect). The carbon
377 enrichment factors ($C-\epsilon_{\text{air-TGDE}}$) determined for the three aliphatic compounds tested were uniform
378 and averaged $0.4 \pm 0.2 \text{‰}$ (Table 4). For the aromatic compounds, in contrast, no significant isotopic
379 change compared to the initial NAPL composition was measured for benzene, toluene, *m,p*-xylene
380 and *o*-xylene (Table 4), with the exception of ethylbenzene. The isotopic composition of gas phase
381 ethylbenzene became depleted in heavy carbon isotopes, indicating a normal isotope effect ($C-\epsilon_{\text{air-}}$
382 $\text{TGDE} = -0.6 \pm 0.2\text{‰}$). For hydrogen, the isotope composition measured for benzene and ethylbenzene
383 in the gas-phase showed no significant change compared to the initial NAPL value, whereas the
384 isotope composition of gas-phase toluene ($H-\epsilon_{\text{air-TGDE}} = 6 \pm 4 \text{‰}$) and *o*-xylene ($H-\epsilon_{\text{air-TGDE}} = 28 \pm 2 \text{‰}$)
385 became enriched in heavy hydrogen isotopes (Table 4). Accordingly, molecules with a heavy
386 hydrogen isotope are less soluble in TGDE than those with light isotopes only (inverse isotope effect).
387 For the aliphatic compounds, no significant isotope composition change was observed for *n*-hexane

388 and *n*-octane, whereas the isotope composition of gas phase cyclopentane ($H-\epsilon_{\text{air-TGDE}} = 6 \pm 1 \text{ ‰}$)
389 became enriched in heavy hydrogen isotopes (Table 4).

390

391 *Chlorinated compounds:* gas-phase composition of all five chlorinated compounds tested (PCE, TCE,
392 1,1,2-TCA, *cis*-DCE and 1,2-DCA) became enriched in heavy carbon isotopes, indicating that molecules
393 with a heavy carbon isotope are less soluble in TGDE than molecules with light isotopes only (inverse
394 isotope effect) (Table 4). The $C-\epsilon_{\text{air-TGDE}}$ determined for the chlorinated compounds ranged from $0.3 \pm$
395 0.2 ‰ (*cis*-DCE) to $1.1 \pm 0.3 \text{ ‰}$ (1,1,2-TCA) (Table 4), which are generally larger than those
396 determined for petroleum hydrocarbons.

397

398 **Table 4:** C and H enrichment factors ($\epsilon_{\text{air-TGDE}}$) related to air-TGDE partitioning process for selected
 399 aromatic, aliphatic, oxygenate and chlorinated compounds.

Compound	Carbon						Hydrogen				
	$\delta^{13}\text{C}$ (‰)				ϵ (‰)		$\delta^2\text{H}$ (‰)				ϵ (‰)
	pure	std	with TGDE	std	Thiswork	literature	pure	std	with TGDE	std	Thiswork
Benzene	-24.3	0.2	-24.1	0.1	<i>0.2 ± 0.2</i>	n.s. ^a	-52	1	-50	2	<i>2 ± 3</i>
Toluene	-26.4	0.2	-26.3	0.1	<i>0.1 ± 0.3</i>		-28	2	-22	2	<i>6 ± 4</i>
Ethylbenzene	-27.0	0.1	-27.6	0.1	<i>-0.6 ± 0.2</i>		-13	2	-9	2	<i>4 ± 4</i>
<i>m,p</i> -Xylene	-25.1	0.2	-25.2	0.1	<i>-0.1 ± 0.3</i>		-49	1	-47	1	<i>2 ± 2</i>
<i>o</i> -xylene	-29.2	0.1	-29.1	0.1	<i>0.1 ± 0.2</i>		-138	1	-114	1	<i>24 ± 2</i>
<i>n</i> -octane	-49.6	0.1	-49.3	0.1	<i>0.3 ± 0.2</i>		-213	3	-212	2	<i>1 ± 6</i>
<i>n</i> -hexane	-27.0	0.2	-26.6	0.1	<i>0.4 ± 0.2</i>		-101	2	-99	1	<i>2 ± 3</i>
cyclopentane	-22.6	0.1	-22.2	0.1	<i>0.4 ± 0.2</i>		-22	1	-16	1	<i>6 ± 2</i>
MTBE	-27.3	0.1	-27.7	0.1	<i>0.4 ± 0.2</i>		--	--	--	--	--
PCE	-26.5	0.1	-26.1	0.10	<i>0.4 ± 0.2</i>		--	--	--	--	--
TCE	-25.8	0.1	-24.8	0.1	<i>1.0 ± 0.2</i>	0.7 ^a	--	--	--	--	--
1,1,2-TCA	-33.6	0.2	-32.5	0.1	<i>1.1 ± 0.3</i>		--	--	--	--	--
<i>cis</i> -DCE	-22.9	0.1	-22.6	0.1	<i>0.3 ± 0.2</i>		--	--	--	--	--
1,2-DCA	-28.0	0.1	-27.1	0.1	<i>0.9 ± 0.2</i>		--	--	--	--	--

400 n.s.= not significant. ^aBouchard et al. (2017b). Italic font indicates no significant change.

401

402 4. Discussion

403 4.1. Phase transfer isotope effect

404 The distribution of isotopologues between the gas phase and liquid phase upon equilibrium in closed
 405 systems is controlled by quantum mechanics, which accounts for the free energy involved for
 406 molecule translation, rotation and vibration in the system. The energy difference between the two
 407 isotopologues results in a vapor pressure isotope effect (VPIE) (Bigeleisen, 2006). The chemical
 408 environment provided by each phase will impact the energy distribution involved in the system. The
 409 chemical environment in the gas phase is governed by the intramolecular (vibrational) forces, while
 410 the chemical environment in the liquid phase is governed by the intermolecular forces (rotation and
 411 translation) and the intramolecular forces (Bigeleisen, 2006). Therefore, the different chemical
 412 environment provided by the NAPL compared to water is expected to influence the direction (inverse

413 or normal isotope effect) and the magnitude of the isotope fractionation. For partitioning systems
414 where the solute is dissolved into water, the isotope effect related to a different solubility property
415 (i.e. the Henry constant) of each isotopologue can be evaluated using the same theoretical
416 considerations (i.e. translation, rotation and vibration energy) as for the NAPL system described
417 above (Jancso, 2002). The discussion below will first treat results involving NAPL vaporization, and will
418 be followed by results obtained when VOC is a solute in water.

419

420 **4.1.1. Isotope fractionation during stepwise NAPL vaporization**

421 The results of all experiments evaluating NAPL vaporization for a selection of petroleum
422 hydrocarbons and one fuel oxygenate consistently underlined a higher volatility for molecules with a
423 heavy isotope (either a ^{13}C or ^2H), hence producing an inverse isotope fractionation effect. This
424 inverse direction of the isotope fractionation observed for hydrocarbons was expected as previously
425 discussed by Van Hook (2006) and reflects the interaction of intramolecular and intermolecular
426 molecular forces in the NAPL. An inverse isotope effect is generated when the effect of
427 intramolecular forces associated with vaporization becomes larger than the effect of intermolecular
428 forces in the NAPL. For hydrocarbons, the reduction of the vibrational frequencies of molecules in
429 the NAPL relatively to the air-phase due to interactions among the molecules creates this inverse
430 isotope effect (Jancso and Van Hook, 1974). The reduced vibrational frequencies for hydrocarbons
431 was empirically rationalized by Bartell and Roskos (1966) to be caused by longer C–H bonds compared
432 to C–D bonds, which leads to a preferential retention of light isotopes in the NAPL. However, this
433 empirical molar vapor isotope effect (MVIE) does not consider the temperature effect, and only
434 applies to liquids near the melting point (Van Hook, 2006). Furthermore, theoretical calculations
435 performed by Lacks (1995) underlined the necessity to consider additional intermolecular effects
436 (intermolecular separations) to more accurately foresee MVIE.

437 The magnitude of $\epsilon_{\text{air-NAPL}}$ values determined in this study compare well to the very few values
438 available in the literature determined using similar closed system experimental setups. For carbon,
439 similar depletion magnitudes of heavy isotopes in the NAPL caused by vaporization were observed
440 for benzene and for toluene (Table S-1 in Supplementary Material). For hydrogen, larger $\text{H-}\epsilon_{\text{air-NAPL}}$
441 were expected compared to carbon as the isotope effects in general depend on the masses of the
442 isotopic atoms involved and the force constants bonding 2 atoms in the molecule (Van Hook, 2006).
443 The $\text{H-}\epsilon_{\text{air-NAPL}}$ determined for benzene and toluene in this current study are also in good agreement
444 with older literature (Table S-2 in Supplementary Material). It should be noted that studies
445 conducted with open system experimental setups (i.e. non-equilibrium conditions such as
446 progressive NAPL vaporization from an open beaker in a fume hood) give enrichment factors that
447 cannot be compared to our values due to additional isotope effects brought by diffusion (Kuder et
448 al., 2009; Jeannotat and Hunkeler, 2012; Julien et al., 2015a). The impact of open system
449 experimental setups on isotope fractionation is discussed further in section 4.1.3. Table S-1 and S-2 in
450 Supplementary Material summarize $\epsilon_{\text{air-NAPL}}$ values determined for C and H, respectively, for studies
451 conducted using open system experimental setups.

452 The results of the current study for closed systems revealed smaller carbon isotope fractionation for
453 petroleum hydrocarbons (carbon atoms number ranging from 5 to 8) compared to fuel oxygenate (5
454 carbon atoms) (Table 2) and also compared to chlorinated compounds (2 carbon atoms) (Table S-1).
455 It must be considered that the $\text{C-}\epsilon_{\text{air-NAPL}}$ values reported are “bulk” isotope effect, contrasting with
456 the concept of specific reactive position as considered for kinetic isotope fractionation during
457 biodegradation (Elsner et al., 2005). For thermodynamic isotope fractionation at equilibrium
458 conditions, the molecular structure and the positioning of the heavy isotope were shown to be of
459 importance (Van Hook, 2006). While all positions are considered reactive, the positioning of the
460 heavy isotope at the terminal position of a molecule is expected to lead to larger isotope
461 fractionation (Bigeleisen and Ishida, 1973). This terminal-position specific impact for carbon was
462 addressed for heptane by Julien et al. (2015a), but the difference in isotope fractionation compared

463 to the other position was very small. The latter study additionally showed minor position-specific
464 isotope fractionation for toluene. For hydrogen, isotope fractionation of monodeuterated benzene
465 (C_6H_5D) was shown to be equivalent to 1/6 of the isotope fractionation of perdeuterated benzene
466 (C_6D_6) (Jakli et al., 1978), thus also suggesting no significant reactive position for hydrogen as well for
467 petroleum hydrocarbons. Our results agree with this lack of reactive-position isotope fractionation,
468 showing no clear trend between isotope enrichment factors obtained for petroleum hydrocarbons
469 and increasing number of C or H atoms (Table 2). Therefore, the larger $C-\epsilon_{air-NAPL}$ values for MTBE and
470 TCE are more likely related to the presence of the oxygen or chlorine atoms in the molecule,
471 respectively, impacting more significantly the vibrational frequencies of molecules in the NAPL phase
472 compared to petroleum hydrocarbons. Furthermore, the molecular structure and H-saturation
473 extent of petroleum hydrocarbon seems to be a distinctive aspect for $H-\epsilon_{air-NAPL}$ values, as discernible
474 on Figure 3 where Λ values distinguish the aromatic compounds from aliphatic and fuel oxygenate
475 compounds. Distinction is mainly due to the various magnitudes of $H-\epsilon_{air-NAPL}$ values. While the
476 molecular structure impacts differently the motion (rotation and translation) of molecules in the
477 NAPL phase, hydrogen bonds and different polarization potential of molecules also contribute to the
478 isotope fractionation (Lacks, 1995; Wade, 1999). In our case, the electrical configuration of aliphatic
479 compounds (involving H-saturation) suggests a stronger polarization impact on the $H-\epsilon_{air-NAPL}$ values
480 compared to aromatic rings (involving π electrons) and MTBE. This polarization impact trend on the
481 $H-\epsilon_{air-NAPL}$ values for the three different groups respect the polarizability potential expressed by each
482 group, with aliphatics having the least polarizability potential and MTBE having the largest (Reichardt
483 and Welton, 2010). However, this polarizability potential impact trend is not respected when
484 considering chlorinated solvents. A $H-\epsilon_{air-NAPL}$ value for TCE larger than for petroleum hydrocarbons
485 was reported in the literature (Table S-2) while the polarizability potential would predict a smaller
486 value, hence suggesting additional chemical interactions contributing to isotope fractionation for
487 chlorinated solvents.

488

489 **4.1.2. Isotope fractionation caused by stepwise air-water partitioning**

490 The air-water partitioning experiments conducted in this study indicated that the partitioning of BTo-
491 X compounds between the air and water (polar protic solvent) does not create significant carbon
492 isotope fractionation (not significant in 2 out of 3 experiments). Our results for toluene agree with the
493 published work investigating this process using a closed system experimental setup (Table S-1). This
494 absence of a systematic carbon isotope fractionation for BTo-X is contrasting with the systematic, yet
495 small, observed carbon isotope fractionation caused by NAPL vaporization (Table 2). While for MTBE
496 the air-water partitioning process created a significant inverse carbon isotope fractionation ($C-\epsilon_{\text{air-water}}$
497 = 0.22 ± 0.06 ‰), the latter process also created a smaller isotope fractionation compared to air-NAPL
498 vaporization ($C-\epsilon_{\text{air-NAPL}}$ = 0.38 ± 0.05 ‰), which is in agreement with MTBE values reported by
499 previous works using similar experimental setups (Table S-1). Based on different isotope
500 fractionation magnitude obtained for the two liquids, the intermolecular forces applied by the water
501 on aromatic compounds and MBTE seem to generate a smaller difference in free energy between
502 heavy and light isotopes than the NAPL phase, which is leading to smaller isotope fractionation. This
503 trend for larger carbon isotope fractionation caused by air-NAPL vaporization compared to air-water
504 partitioning was also observed for TCE by Jeannotat and Hunkeler (2012) and Horst and Lacrampe-
505 Couloume (2020) (Table S-1). The reported $C-\epsilon_{\text{air-water}}$ values for TCE are larger compared to BTo-X and
506 MTBE determined herein. In this case, the presence of chlorine atoms in the molecules and the
507 different molecular structure of chlorinated compounds compared to aromatic compounds are likely
508 impacting differently the intermolecular forces with water. As mentioned above, values derived from
509 open system experimental setups cannot be compared to our values but are summarized in Table S1
510 and S-2 respectively for carbon and hydrogen.

511 For hydrogen, the normal isotope fractionation observed during air-water partitioning is contrasting
512 with the inverse hydrogen isotope fractionation observed for air-NAPL vaporization, as predicted
513 when changing the chemical environment from a nonpolar to a hydrogen bonded liquid (Wolfsberg
514 et al., 2010). In this case, the motion forces (rotation and translation) exerted by water molecules

515 surrounding BTX and MTBE compounds outweigh the vibrational forces, generating higher volatility
516 for molecules including a heavy hydrogen isotope in the molecular structure. The motion forces seem
517 more impactful for *o*-xylene and MTBE compared to benzene and toluene, generating a smaller $H-\epsilon_{\text{air-}}$
518 water value for the latter two compounds (Table 3). For MBTE, the polar nature of the compound likely
519 initiating stronger interactions with water molecules would explain the larger $H-\epsilon_{\text{air-water}}$ value
520 compared to benzene and toluene. However, the forces leading to larger $H-\epsilon_{\text{air-water}}$ value for *o*-xylene
521 compared to benzene and toluene requires more detailed investigations. In addition, the normal
522 isotope fractionation for TCE ($H-\epsilon_{\text{air-water}} = 5.2 \pm 2.6 \text{ ‰}$) and for trichloromethane recently reported by
523 Horst and Lacrampe-Couloume (2020) and contrasting with the inverse isotope fractionation
524 obtained herein for aromatic compounds and MTBE would also require more detailed investigations.

525 **4.1.3. Significance for gas-phase VOC assessments**

526 Extending the application of CSIA to soil gas studies will significantly improve assessment strategies
527 relying on VOC concentration measurements such as NSZD monitoring or remediation treatments
528 like SVE or air-sparging systems. The enrichment factors determined in this study during volatilization
529 of common subsurface contaminants contributes to increase the number of VOC candidates for CSIA-
530 based assessments. However, ϵ values for CSIA data interpretation should be cautiously selected.
531 Whilst our study focused on closed system experiment setups (i.e. equilibrium conditions) to
532 determine isotope fractionation strictly related with the phase partitioning process, several other
533 studies have reported values determined using open system experiment setups (i.e. non-equilibrium
534 conditions). In the latter case, the gas-phase volume above the liquid is constantly renewed at an
535 experiment-specific rate, hence involving additional physical isotope fractionation process such as
536 gas-phase diffusion. Table S-1 and S-2 (in Supplementary Material) compiles respectively carbon and
537 hydrogen isotope fractionation factors determined using open system experiment setups for VOC
538 volatilization from NAPL or water. One can note a wider ϵ value range for open system experimental
539 setups, even observing opposite fractionation direction in the case for carbon, thus confirming the
540 contribution of one or several other isotope fractionation processes. For a porous system with very

541 slow air renewal rate, one can assume quasi-equilibrium conditions to control the isotope
542 fractionation evolution in the soil air immediately surrounding the residual NAPL. In contrast, non-
543 equilibrium conditions would control the isotope fractionation evolution during forced air flow
544 circulation applied by specific remediation treatment systems. Therefore, the interplay of physical
545 processes (i.e. phase transfer and diffusion) must be properly considered to correctly interpret CSIA
546 field data. For instance, during NSZD of trapped NAPL in the unsaturated zone, NAPL vaporization
547 leads to VOC mass input into soil gas and pore water. With small $C-\epsilon_{\text{air-NAPL}}$ and insignificant $C-\epsilon_{\text{air-water}}$
548 determined for BTX, progressive NAPL vaporization will not create significant change in isotope
549 composition of gas-phase VOCs over time as long as the gas-phase VOC concentration in soil air
550 remains in equilibrium with the NAPL (i.e. steady state condition) (Bouchard et al., 2008a; Bouchard
551 et al., 2011). This can also be assumed although the occurrence of biodegradation as the kinetic rate
552 of VOC mass input at the NAPL fringe may overwhelm the biodegradation rate, hence masking the
553 isotopic effect of the latter as commonly observed for groundwater assessments within source zone
554 areas. However, once the VOC mass in the NAPL has significantly decreased and equilibrium
555 conditions can no longer be maintained, hence initiating a transient state condition, gas-phase
556 diffusion process will lead isotope composition towards enriched values. For all petroleum
557 hydrocarbons tested herein, the larger carbon isotope fractionation related to gas-phase diffusion
558 (Table 2) will dominate over air-NAPL partitioning. This evolution from constant to gradually enriched
559 isotope composition appears to be a more reliable metric than concentration analysis to support
560 source vanishing. Given the small and narrow range of $C-\epsilon_{\text{air-NAPL}}$ values determined for petroleum
561 hydrocarbons herein, similar enrichment trends can be expected for other petroleum hydrocarbons
562 such as ethylbenzene and trimethylbenzene, hence allowing additional compounds to be assessed.
563 For hydrogen, with inverse $H-\epsilon_{\text{air-NAPL}}$ and normal $H-\epsilon_{\text{air-water}}$ values determined for BTX (Table 3), the
564 interplay between air-NAPL, air-water and gas-phase diffusion during steady and transient state
565 conditions should be further investigated to confidently predict the direction and the magnitude of
566 the isotope change.

567 For remediation techniques focusing on physical mass removal process such as SVE systems, the air-
568 liquid isotope effects can be exploited to monitor the progress and the limitations of the treatment.
569 Contrasting with NSZD, the isotope composition in this case will evolve as for an open system (i.e.
570 non-equilibrium conditions). During non-equilibrium conditions, not only that the diffusive isotope
571 effect is additive to air-liquid isotope effect, but a number of studies have previously described that
572 the expression of the diffusive isotope effect is impacted by the air volume renewal rate (Bouchard et
573 al., 2008a; Bouchard et al., 2008b; Höhener et al., 2008; Kuder et al., 2009; Julien et al., 2015b;
574 Bouchard et al., 2017a; Zamane et al., 2020). In cases where biodegradation occurs during the VOC
575 transit through the unsaturated soil (as for petroleum hydrocarbons), this third process will also need
576 to be considered to appropriately interpret isotopic trends. Due to those many uncertainties, the
577 mass removal process is best characterized with the use of two elements (i.e. dual-isotope
578 assessment) (Kuder et al., 2009; Bouchard et al., 2017a). To appreciate the additive isotope effects
579 on VOCs studied herein, enrichment factors related to gas-phase diffusion and biodegradation under
580 aerobic conditions are reported in Table 2 and 3, respectively for carbon and hydrogen. For carbon,
581 the diffusion effect will systematically mask both the air-NAPL and air-water partitioning effects for
582 every petroleum hydrocarbon tested, leading to carbon isotope enrichment (as biodegradation
583 does). For hydrogen in contrast, the air-NAPL partitioning is the only process leading to significant
584 hydrogen isotope depletion. Thorough combined interpretation of the carbon and hydrogen isotope
585 evolution pattern over time will therefore indicate the controlling mass-removal process.

586 **4.2. TGDE and isotope fractionation**

587 **4.2.1. Isotope fractionation caused by air-TGDE partitioning**

588 Despite a single equilibration step, $C-\epsilon_{\text{air-TGDE}}$ values determined for air-TGDE partitioning (Table 4) can
589 be directly compared to ϵ values derived by multistep equilibration experiments based on equation
590 4. Accordingly, the lack of significant carbon isotope fractionation observed for benzene, toluene and
591 both xylenes during air-TGDE partitioning is akin to inconsistent carbon isotope fractionation
592 observed for the same compounds during air-water partitioning and also to the lack of significant

593 carbon isotope fractionation previously reported for benzene during similar testing with TGDE
594 (Bouchard et al., 2017b). These non-significant carbon isotope fractionations observed for BTX
595 compounds during air-TGDE partitioning underline minor impact for phase transfer process, and
596 where the prevailing partitioning forces would be more comparable to water than neat compounds.
597 The significant fractionation obtained for ethylbenzene, in contradiction to the other 4 aromatic
598 compounds tested, are counter intuitive. Additional evaluations are needed to understand this
599 distinctive behavior. In contrast to aromatic compounds, the phase transfer process involving
600 aliphatic and chlorinated compounds generated significant isotope fractionation. The global set of
601 chlorinated compounds showed isotope fractionation generally of larger magnitude, with chlorinated
602 ethane compounds more likely to generate larger fractionation compared to chlorinated ethene
603 compounds (Table 4). The lack of available works assessing isotope fractionation of aliphatic and
604 chlorinated compounds during air-water and air-NAPL partitioning, however, limits the comparison
605 with air-TGDE. For PCE, the $C-\epsilon_{\text{air-TGDE}}$ value determined ($0.4 \pm 0.2 \text{ ‰}$) is in the range of the $C-\epsilon_{\text{air-water}}$
606 value reported by Jeannotat and Hunkeler (2013) ($0.46 \pm 0.04 \text{ ‰}$), although no air-NAPL partitioning
607 values for PCE are available for comparison. For TCE, the $C-\epsilon_{\text{air-TGDE}}$ values determined ($1.0 \pm 0.2 \text{ ‰}$)
608 and previously reported (0.7 ‰) (Bouchard et al., 2017b) are in the range of reported $C-\epsilon_{\text{air-NAPL}}$ values
609 (ranging from 0.4 to 1.0 ‰), and slightly larger than the reported $C-\epsilon_{\text{air-water}}$ range values (0.4 to 0.7
610 ‰) (Table S-1 in Supplementary Material). The result comparison for different compounds outlines
611 some partitioning specificities. Overall, this polar aprotic solvent with multiple ether oxygen atom
612 functional groups generates inverse carbon isotope effect as for water and NAPL, with magnitude of
613 isotope fractionation being larger for chlorinated compounds compared to aromatic and aliphatic
614 compounds. Once more, the degree of H saturation of the molecules and the presence of chlorine
615 atoms in chlorinated compounds seem to be responsible for the various isotope fractionation
616 magnitudes observed for those three different types of compounds.

617

618 For hydrogen, no clear molecular structural trend can be outlined when comparing compounds
619 expressing no isotope fractionation (benzene, ethylbenzene, *m,p*-xylene, *n*-hexane and *n*-octane)
620 with those undergoing isotope fractionation (toluene, *o*-xylene and cyclopentane) during air-TGDE
621 partitioning. Nonetheless, the inverse isotope fractionation observed for aromatic and aliphatic
622 compounds during air-TGDE partitioning, when significant, is analogous to air-NAPL vaporization, and
623 is contrasting with the normal isotope fractionation observed for air-water partitioning. The
624 magnitude of $H-\epsilon_{\text{air-TGDE}}$ values determined for toluene and cyclopentane are relatively in the same
625 range or lower than for NAPL vaporization, hence suggesting that the vibrational forces outweighing
626 the motion forces in TGDE are similar to the air-NAPL system, and that functional groups of TGDE act
627 on those compounds differently than do water molecules. In this regard, influence of different
628 functional groups causing isotope fractionation was recently investigated using benzene and toluene
629 as tested compounds (Imfeld et al., 2014). The latter study demonstrated the occurrence of isotope
630 fractionation for specific functional groups represented by a subset of different organic solvents. For
631 instance, 1-octanol (hydroxyl functional group with hydrogen-bridging interaction) led to significant
632 inverse carbon and hydrogen isotope fractionation for benzene. However, as their experimental
633 setup involved solute partitioning into two liquids (solvent and water), the additional hydrophobic
634 factor impacting the isotope fractionation impedes direct ϵ comparison with our study. Finally, the
635 larger $H-\epsilon_{\text{air-TGDE}}$ value determined for *o*-xylene compared to the other aromatic compounds is
636 prominent. Additional evaluations are needed to understand this distinctive behavior.

637

638 **4.2.2. TGDE and gas-phase VOC sampling**

639 *Gas-phase sampling process:* an innovative solvent-based method has been recently developed to
640 perform CSIA on VOCs collected in the gas-phase (Bouchard et al., 2015). The sampling method
641 consists in pulling the ambient air through a solvent via an adapted sampling device, hence relying on
642 the VOC affinity with the solvent to accumulate (by dissolution) during the sampling process. To
643 evaluate TCE dissolution efficiency and the potential for isotope fractionation during the process, a

644 gas-phase sampling event was mimicked at the laboratory scale (see Bouchard et al. (2017b) for
 645 further experimental details). While the measured dissolved TCE concentrations in TGDE over time
 646 followed the theoretical expectation (equation 6), no $\delta^{13}\text{C}$ evolution simulation was attempted to
 647 reproduce the measured isotope values. The equation 6 and $C\text{-}\epsilon_{\text{air-TGDE}}$ were used herein to scrutinize
 648 the potential carbon isotope fractionation caused during the sampling process and to reproduce the
 649 isotope values measured over the 3 mimicked gas-phase sampling events. The calculations made use
 650 of two TCE isotopologues ($^{13}\text{C-TCE}$ and $^{12}\text{C-TCE}$) as described in section 2.4. Both $C\text{-}\epsilon_{\text{air-TGDE}}$ values
 651 available (0.7 ‰ and 1.0 ‰) were sequentially implemented to evaluate the sensitivity of the
 652 parameter. Table 5 summarizes the values used for $^{13}\text{C-TCE}$ and $^{12}\text{C-TCE}$ isotopologues for the
 653 calculations, as well as the fixed parameters.

654 **Table 5:** Initial gas phase concentration (C_g) and air-TGDE partitioning coefficient (K) specific to $^{13}\text{C-}$
 655 TCE and $^{12}\text{C-TCE}$ isotopologues, TCE initial isotopic composition ($\delta^{13}\text{C}$), air flow rate (F) and volume of
 656 solvent (V) used for the analytical simulation.

Parameter	Simulation 1		Simulation 2		Simulation 3	
	$^{12}\text{C-TCE}$	$^{13}\text{C-TCE}$	$^{12}\text{C-TCE}$	$^{13}\text{C-TCE}$	$^{12}\text{C-TCE}$	$^{13}\text{C-TCE}$
C_g (ug/m ³)	20.7736	0.2264	78.1484	0.8516	165.1999	1.8001
K (unitless) with $\epsilon_{\text{air-TGDE}} = 0.7\text{‰}$	0.0003400 ^a	0.0003402	0.0003400 ^a	0.0003402	0.0003400 ^a	0.0003402
K (unitless) with $\epsilon_{\text{air-TGDE}} = 1.0\text{‰}$	0.0003400 ^a	0.0003403	0.0003400 ^a	0.0003403	0.0003400 ^a	0.0003403
F (mL/minute)	800		200		100	
V (mL)	35		35		35	
Initial $\delta^{13}\text{C}$ (‰)	-30.3		-30.3		-30.3	

657 ^a(Bouchard et al., 2017b)

658 The simulated dissolved concentration and $\delta^{13}\text{C}$ results obtained for three different gas-phase TCE
 659 concentrations (21, 79 and 167 $\mu\text{g}/\text{m}^3$) over a sampling duration of $t = 50\text{h}$ are presented on Figure 6.
 660 The simulated concentrations indicate a non-linear TCE increase in TGDE during the sampling
 661 process. The steady state is reached (i.e. saturation condition) within 10h for the smallest gas-phase
 662 concentration (figure 6a, 21 $\mu\text{g}/\text{m}^3$), while a quasi-steady state is reached around $t = 50\text{h}$ for gas-
 663 phase concentration of 79 $\mu\text{g}/\text{m}^3$ (figure 6b), and a transient state is still observed at $t=50\text{h}$ for the
 664 gas-phase concentration of 167 $\mu\text{g}/\text{m}^3$ (Figure 6c). Note that the difference in concentration
 665 evolution is due to different sampling flow rates used (Table 5), and not the gas-phase concentration.

666 During the sampling event, the isotopic composition of dissolved TCE evolved from -30.30 ‰
667 (equivalent to the gas-phase TCE composition) to a maximum depleted value of -30.98 ‰ (using C - $\epsilon_{\text{air-TGDE}} = 0.7$ ‰) and -31.25 ‰ (using C - $\epsilon_{\text{air-TGDE}} = 1.0$ ‰) when saturation conditions are reached
668 (Figure 6A). At early sampling phase, the higher solubility of ^{12}C -TCE is not yet apparent, hence the
669 dissolved TCE isotope composition was reflecting the gaseous TCE isotope composition. With time,
670 the higher solubility of ^{12}C -TCE eventually disrupts the initial ^{13}C -TCE / ^{12}C -TCE mass proportion,
671 which leads to a gradual depleting isotope trend. The shift of 0.68 ‰ and 0.95 ‰ observed at
672 saturation conditions compared to the source signal (Figure 6A) is respectively equivalent to the C -
673 $\epsilon_{\text{air-TGDE}}$ of 0.7‰ and 1.0 ‰ experimentally determined (Table 4). Moreover, this slight isotopic
674 depletion trend provided by the analytical solution was able to reproduce the measured laboratory
675 values, validating the impact of different solubility coefficient for the two distinct TCE isotopologues.
676 While laboratory results for gas-phase TCE at 21 $\mu\text{g}/\text{m}^3$ (Figure 6A) and 167 $\mu\text{g}/\text{m}^3$ (Figure 6C) are
677 mostly contained within the variation expressed by the two different C - $\epsilon_{\text{air-TGDE}}$ values, the laboratory
678 results for gas-phase TCE at 79 $\mu\text{g}/\text{m}^3$ (Figure 6B) showed good fit only at later time (quasi-steady
679 state). This can perhaps be related to a gas leak in the system delivering less TCE than expected.
680

681

682 According to these isotopic simulations, sampling gas phase VOCs using TGDE (or any other solvent)
683 will create an isotopic shift that can be predicted by the $\epsilon_{\text{air-TGDE}}$ value. Based on $\epsilon_{\text{air-TGDE}}$ values
684 reported in Table 4 for the tested VOCs, no significant carbon isotope shift is expected for BTX,
685 aliphatic compounds (*n*-octane, *n*-hexane, cyclopentane), MTBE, PCE and *cis*-DCE, no significant
686 hydrogen isotope shift is expected for B, E, *m,p*-X, *n*-hexane and *n*-octane, and lastly no significant
687 chlorine isotopic shift for TCE, as respective $\epsilon_{\text{air-TGDE}}$ value is either not detectable or within the
688 common analytical uncertainty of 0.5 ‰ (for C and Cl) and 5 ‰ (for H). However, carbon isotope
689 measurements for ethylbenzene, TCE, 1,1,2-TCA and 1,2-DCA, and hydrogen isotope measurement
690 for toluene, *o*-xylene and cyclopentane will request an adjustment for sampling conducted until the

691 saturation condition is reached. In this case, the equivalence of the $\epsilon_{\text{air-TGDE}}$ value has to be added to
 692 provide a more positive final $\delta^{13}\text{C}$ composition (or more negative in the case of ethylbenzene).

693 *Post sampling event:* An additional simulation was further carried out to evaluate the impact of
 694 repeated headspace volume exchange potentially occurring during sample handling and storage on
 695 the isotope composition of the dissolved VOCs. This evaluation made use of equation 11 to calculate
 696 the related hydrogen isotopic shift caused by multi equilibrium steps using either TGDE or water as
 697 solvent. Between each equilibrium step, a complete headspace renewal with fresh air was
 698 considered. For the evaluation purpose, toluene was the modeled compounds as results of the air-
 699 water and air-TGDE partitioning experiments performed in the laboratory led to significant hydrogen
 700 isotope fractionation. In addition, the dataset collected during the air-water partitioning experiment
 701 can be used as reference to validate the calculations. Table 6 summarizes the parameters and
 702 coefficients used for those two air-liquid partitioning evaluations.

703 **Table 6:** Parameters used to calculate the hydrogen isotope shift expected for toluene caused by
 704 multistep air-water or air-TGDE partitioning process (equilibrium conditions).

Parameter	Coefficient	Unit
$\text{H-}\epsilon_{\text{air-TGDE}}$	6*	‰
$\text{H-}\epsilon_{\text{air-water}}$	-5**	‰
C_0	1	$\mu\text{g/L}$
Air-water partitioning (Henry coefficient, at 25 °C)	0.244 ^a	unitless
Air-TGDE partitioning (K , at 25 °C)	0.000344 ^b	unitless
Vial volume	40	mL
Liquid volume	35	mL

705 *This study. ** Value obtained for replicate 2, Figure 5. ^aMackay et al. (2006). ^bHuybrechts et al. (2001)

706 Changes in hydrogen isotope composition of dissolved toluene caused by 12 equilibrium steps with
 707 water or TGDE are shown on Figure 7. For the air-water partitioning simulation, the equation
 708 reproduced well the isotopic trend observed with the laboratory experiment, to ultimately predict a
 709 significant hydrogen shift of 11.8 ‰ after 12 equilibration steps. For the air-TGDE partitioning
 710 simulation, a shift of 0.03 ‰ can be expected for the hydrogen isotope composition of dissolved
 711 toluene dissolved after proceeding to 12 equilibration steps. Compared to a common uncertainty

712 error of 5 ‰ for hydrogen analysis, this shift remains not significant. This negligible isotopic impact is
713 explained by the strong affinity of toluene with TGDE, providing a very small air-TGDE partitioning
714 coefficient (Table 6). Upon equilibrium, a mass fraction of 99.97% of toluene is expected to be in
715 TGDE, thus leaving a small 0.03% mass fraction in the gas-phase. This very small mass fraction of
716 gaseous toluene lost by each equilibrium step is not sufficient to significantly impact the isotope
717 signature of toluene dissolved in TGDE, although several multiple equilibrium steps are carried out.
718 This is in agreement with Bouchard et al. (2015) reporting no significant change in the carbon isotope
719 composition of TCE after 12 months of storage in methanol. Therefore, although carbon and
720 hydrogen isotope fractionation have been observed for diverse VOCs during the air-TGDE
721 partitioning process, no further impacts on the isotopic signature of dissolved VOCs is expected once
722 the sampling process is ended. This can be assumed for every compound with similar low range of
723 air-TGDE partitioning coefficients than toluene.

724 **5. Conclusion**

726 Several types of laboratory experiments were conducted in the present study to evaluate isotope
727 fractionation caused by phase transfer process for a selection of common environmental
728 contaminants, with the general objective being to contribute in expanding the use of CSIA as an
729 assessment tool for gas-phase studies. For this purpose, the occurrence of isotope fractionation
730 related to NAPL vaporization and VOC volatilization from different liquids (water or TGDE) was
731 investigated through closed system experimental setups. In contrast to open system, conducting
732 stepwise VOC mass removal from a closed system setup insures the isolation of the partitioning
733 process from other potential physical process. A selection of aromatic, aliphatic, fuel oxygenate and
734 chlorinated compounds was evaluated for carbon and hydrogen isotope fractionation. NAPL
735 vaporization consistently indicated a preferential volatility for molecules including a heavy isotope,
736 either ^{13}C or ^2H isotope, for all tested VOCs. The magnitude of the carbon isotope enrichment was
737 small and relatively uniform among the selected petroleum hydrocarbons, and globally smaller
738 compared to chlorinated compounds. The magnitude of the hydrogen isotope enrichment was more

739 substantial and distinctive among petroleum hydrocarbons, but still globally smaller compared to
740 chlorinated compounds. The carbon and hydrogen isotope fractionation pattern, evaluated through
741 the Λ value, was found to differ between aromatic, aliphatic and fuel oxygenate compounds.
742 Furthermore, during VOC volatilization from the water, the partitioning process led to no significant
743 carbon isotope fractionation for aromatic compounds. These observations for aromatic compounds
744 contrast with significant fractionation observed for MTBE and the reported isotope fractionation for
745 chlorinated compounds (PCE and TCE), underlying for the latter three compounds a higher volatility
746 for molecules including a heavy carbon isotope. In contrast, for hydrogen, volatilization of BTX
747 compounds from water consistently created a normal isotope fractionation, translating into a
748 preferential solubility for molecules including the heavy hydrogen isotope. The numerous isotope
749 enrichment factors derived in this study relative to NAPL vaporization and air-water partitioning
750 process provide the possibility to expand the application of CSIA to a broader range of common
751 environmental contaminants in view to assess their fate in the unsaturated zone, either passively
752 attenuating (for instance, to document a natural source zone depletion in the unsaturated zone) or
753 actively removed (for instance, to assess the performance of a remediation treatment). The second
754 goal of this study was also achieved by quantifying carbon and hydrogen isotope enrichment factors
755 related to air-TGDE partitioning for a subset of VOCs. For carbon, most of the aromatic compounds
756 tested led to no significant isotope fractionation (except ethylbenzene), whereas MTBE, aliphatic and
757 chlorinated compounds led to significant enrichment, underlying potential for higher volatility of
758 molecules including a heavy isotope similarly to progressive NAPL vaporization. The carbon isotope
759 composition of chlorinated compounds was found to be more affected than petroleum hydrocarbons
760 by air-TGDE partitioning. For hydrogen, selected aromatic and aliphatic compounds showed no
761 significant enrichment, except for toluene, *o*-xylene and cyclopentane, which showed significant
762 enrichment. When significant, both isotopes underlined the potential for higher volatility of
763 molecules including a heavy isotope similarly to progressive NAPL vaporization. The impact of isotope
764 fractionation related to air-TGDE partitioning during a sampling event using TGDE as a sink matrix to

765 collect gas-phase VOCs was further addressed by means of analytical simulations. The simulation
766 results indicated an isotopic shift equivalent to the enrichment factors, once the VOC concentration
767 equilibrium between the air and TGDE is reached. Therefore, the need for an isotopic correction post
768 sampling event only applies to VOCs having an enrichment factor larger than the GC-IRMS analytical
769 uncertainty. The quantification of enrichment factors by the current investigations and the
770 knowledge gained through analytical simulations support the field application of the solvent-based
771 sampling method specific to CSIA. Although a broad range of common environmental contaminants
772 were evaluated for carbon and hydrogen isotopes, potential for chlorine isotope fractionation
773 remains to be evaluated for chlorinated compounds.

774 **Supplementary Material: Description of analytical techniques, Tables S1+S2,**

775 **Is available.**

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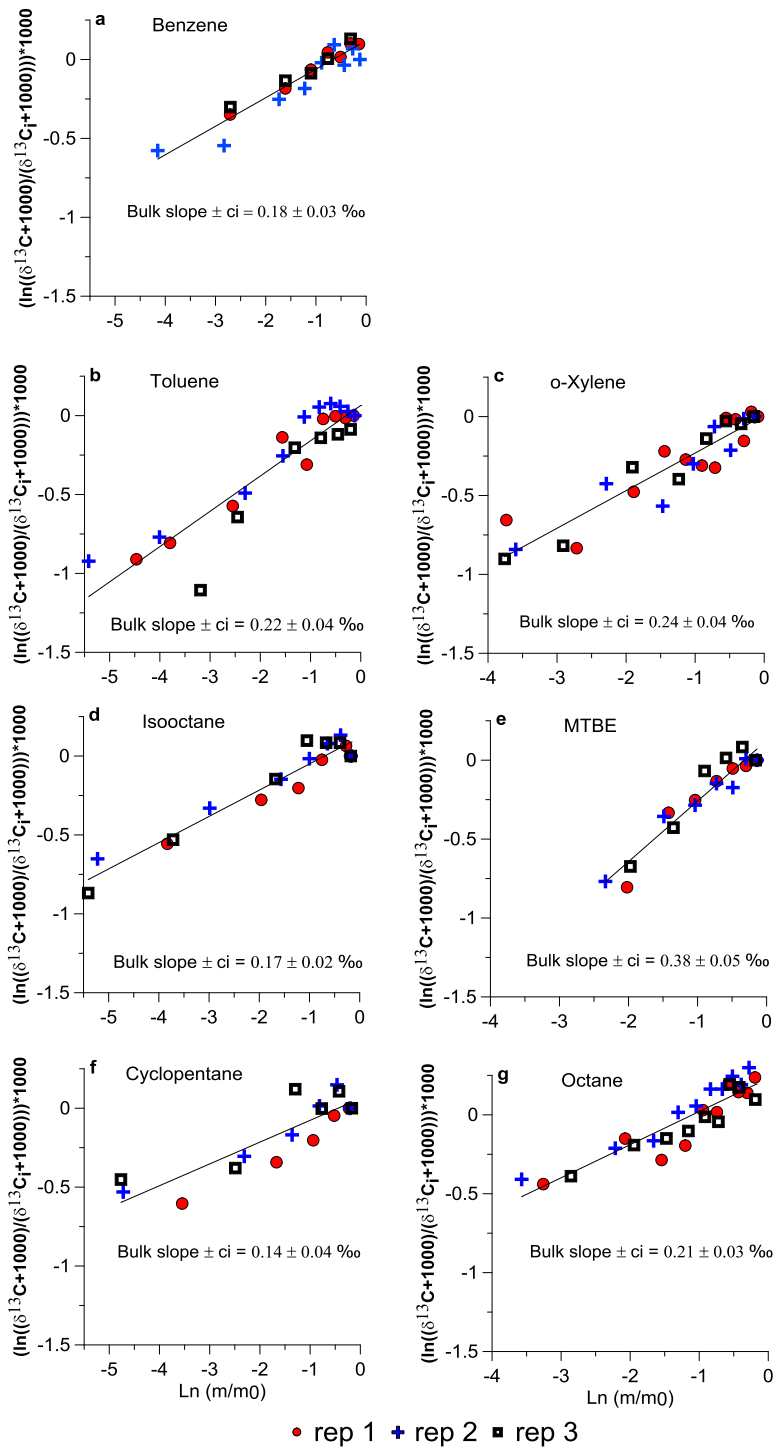
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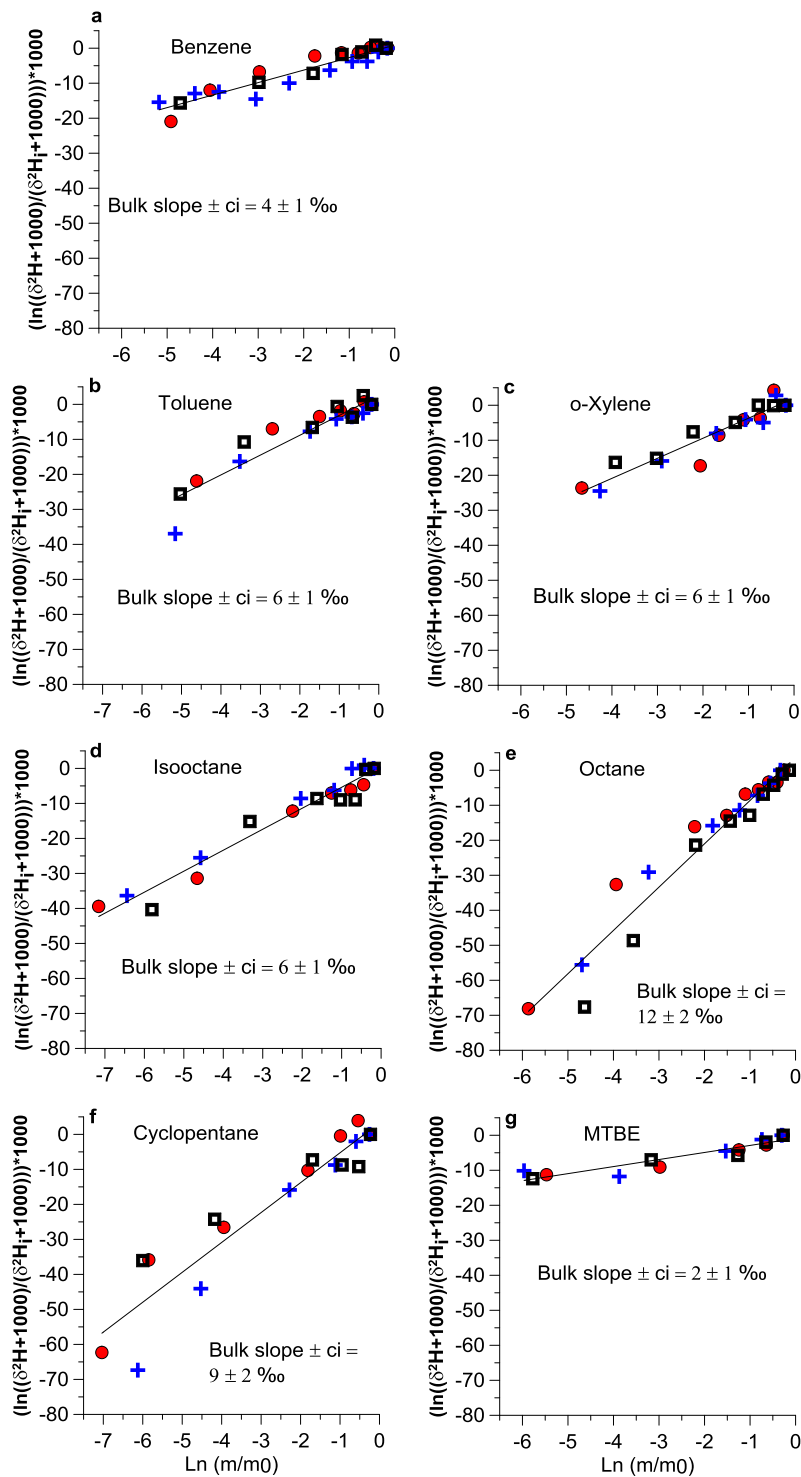
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970 **Figure 1:** Carbon isotope fractionation during stepwise air-NAPL vaporization for selected
 971 compounds. The change in carbon isotope ratio is plotted as function of the remaining mass (m/m0)
 972 in the Ln scale. The bulk slope and the 95% confidence interval (ci) were determined using all plotted
 973 data (triplicate experiments). NAPL designates the neat liquid of each compound.

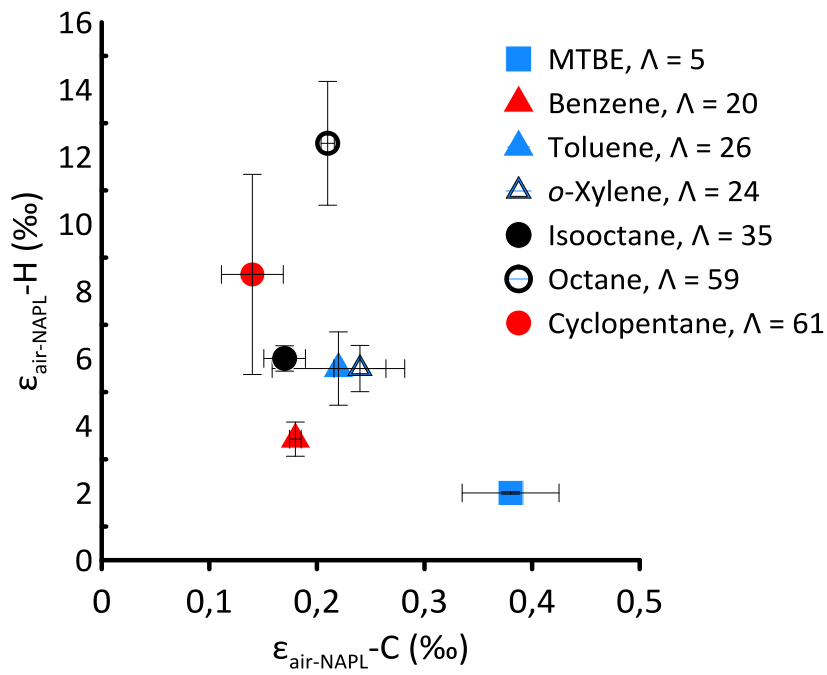
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● rep 1 + rep 2 ■ rep 3

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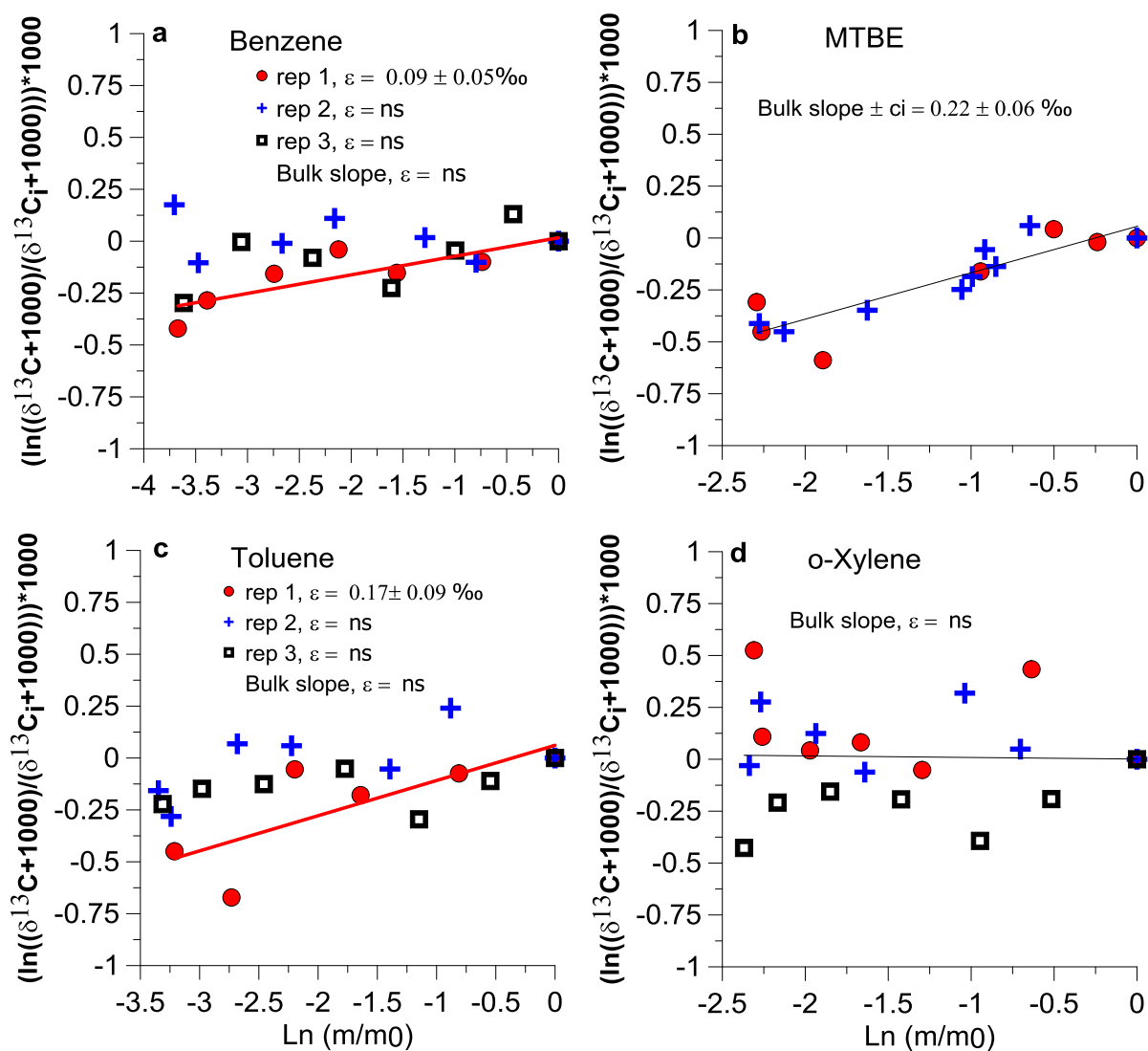
976 **Figure 2:** Hydrogen isotope fractionation during stepwise air-NAPL vaporization for selected
 977 compounds. The change in hydrogen isotope ratio is plotted as function of the remaining mass
 978 (m/m₀) in the Ln scale. The bulk slope and the 95% confidence interval (ci) were determined using all
 979 plotted data (triplicate experiments). NAPL designates the neat liquid of each compound.



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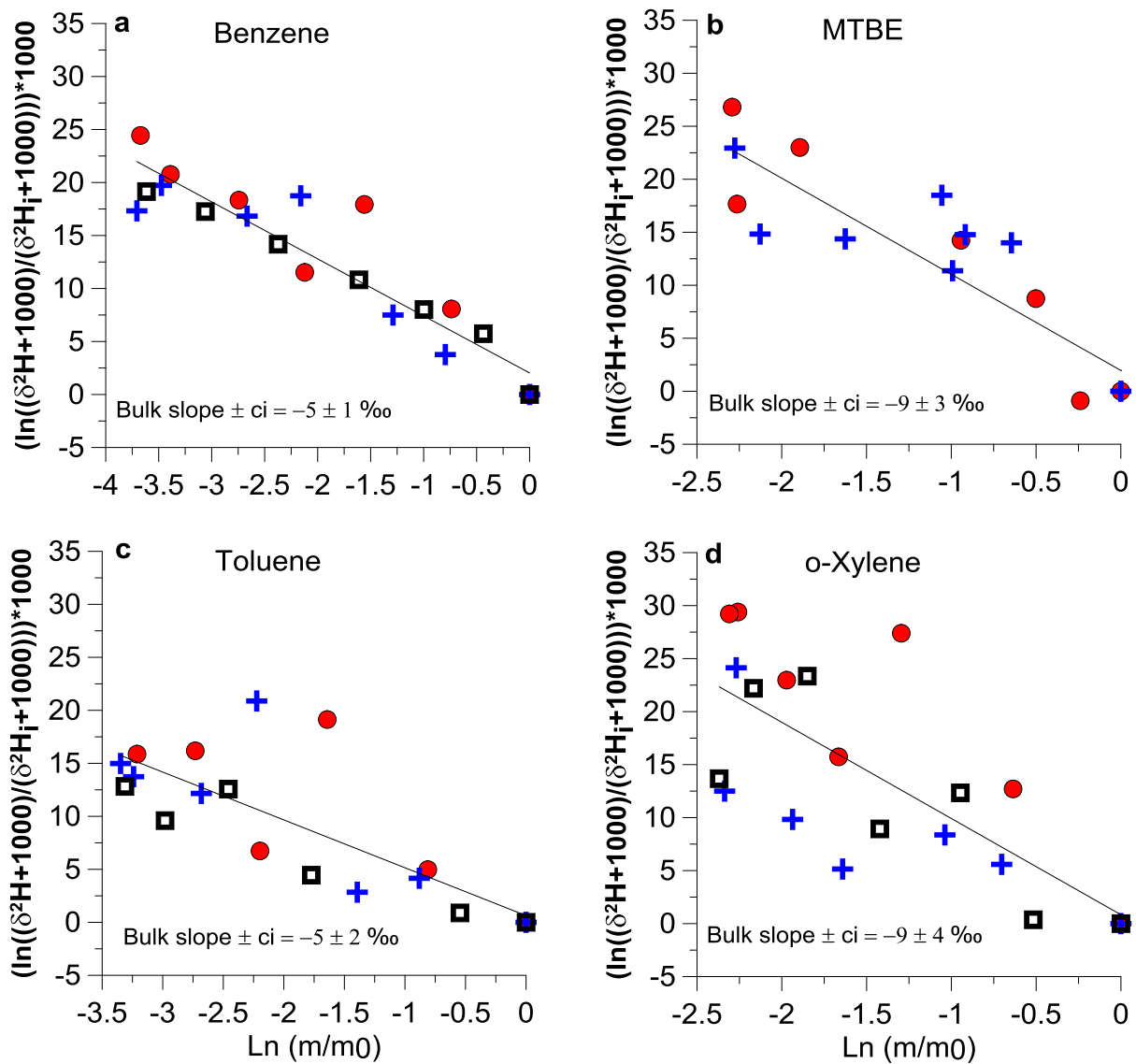
981 **Figure 3:** Plot of $H\text{-}\epsilon_{\text{air-NAPL}}$ as function of $C\text{-}\epsilon_{\text{air-NAPL}}$ measured for monoaromatic (BTo-X) aliphatic (*n*-
 982 octane, isooctane and cyclopentane) and fuel oxygenate (MTBE) compounds caused by air-NAPL
 983 vaporization. The Λ values reported represent $H\text{-}\epsilon / C\text{-}\epsilon$ ratios.

984



986

987 **Figure 4:** Carbon isotope fractionation during stepwise air-water partitioning for selected
 988 compounds. The change in carbon isotope ratio is plotted as function of the remaining mass (m/m0)
 989 in the Ln scale. The bulk slope (black line) and the 95 % confidence interval (ci) were determined
 990 using all plotted data (triplicate experiments), except for MTBE (duplicate experiments). Replicate-
 991 specific slope is represented by a red line. ns: not significant.



● rep 1 + rep 2 □ rep 3

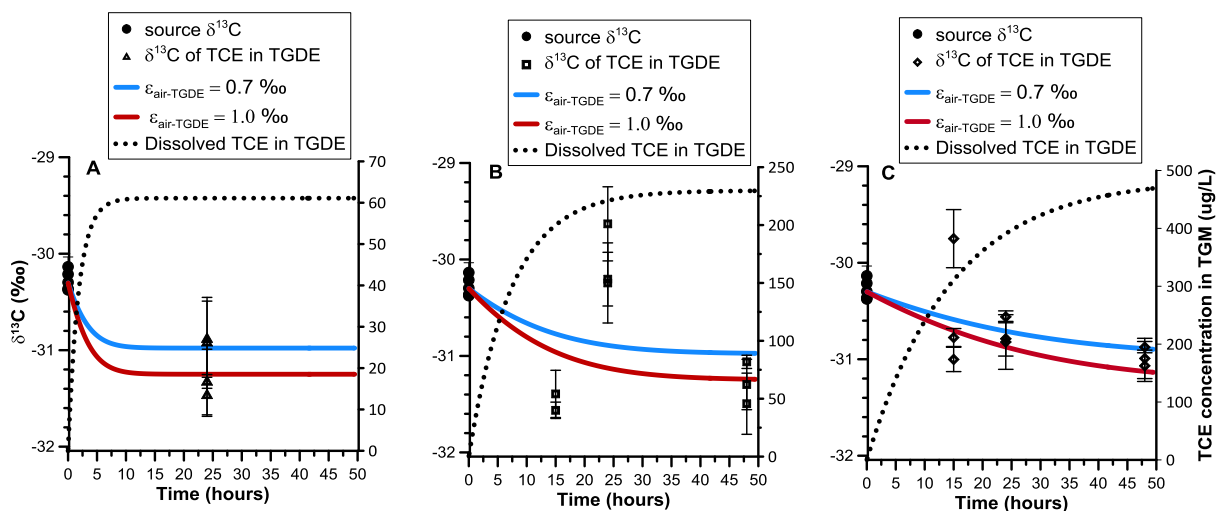
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993 **Figure 5:** Hydrogen isotope fractionation during stepwise air-water partitioning for selected
 994 compounds. The change in hydrogen isotope ratio is plotted as function of the remaining mass
 995 (m/m0) in the Ln scale. The bulk slope and the 95 % confidence interval (ci) were determined using
 996 all plotted data (triplicate experiments), except for MTBE (duplicate experiments).

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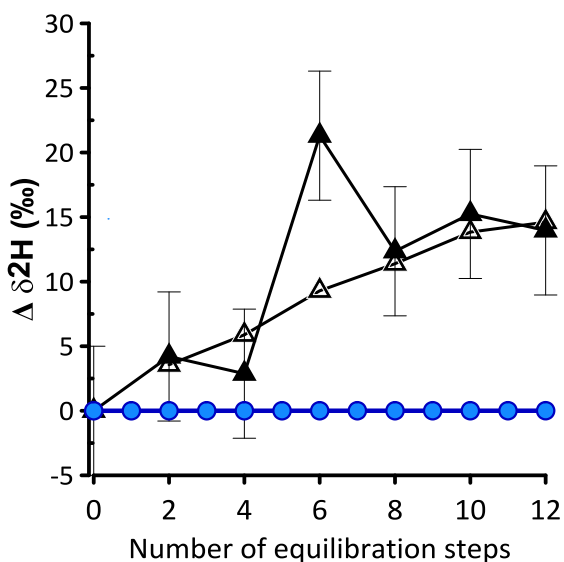
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1000 Figure 6: Evolution of concentrations (black line) and $\delta^{13}\text{C}$ composition (blue and red lines,
 1001 considering different isotope enrichment factors $\epsilon_{\text{air-TGDE}}$ for TCE dissolved in TGDE during 3
 1002 simulated gas-phase sampling events using TCE gas-phase concentration of $21 \mu\text{g}/\text{m}^3$ (A), $79 \mu\text{g}/\text{m}^3$
 1003 (B), and $167 \mu\text{g}/\text{m}^3$ (C), and respective gas flow rate of 800, 400 and 200 mL/minute. Laboratory data
 1004 from Bouchard et al. (2017b)
 1005
 1006

1007

- Air-tetraglyme stepwise isotope fractionation for toluene: theoretical
- △ Air-water stepwise isotope fractionation for toluene: theoretical
- ▲ Air-water stepwise isotope fractionation for toluene: experimental



1008
 1009 Figure 7: $\delta^2\text{H}$ composition for remaining toluene in the liquid after 12 mass removal steps from a
 1010 closed system caused by air-water partitioning (triangles) and by air-TGDE partitioning (circles).
 1011