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## Supplementary Information

### Compound specific stable carbon isotope analysis of aromatic organic contaminants in water using gas chromatograph coupled to mid-infrared laser spectroscopy

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38 • **Text S2.** Description of carbon CSIA using GC-IRMS.

39 • **Text S3.** Qualitative analysis of drilling fluid using GC-MS.

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45 ■ **Table:**

46 Table S1. The  $\delta^{13}\text{C}$  values determined for the target compounds by headspace injection

<b>Compounds</b>	<b>Conc. (<math>\mu\text{g/L}</math>)</b>	<b><math>\delta^{13}\text{C}</math> (‰)</b>	<b>STDV (1<math>\sigma</math>, n=5)</b>
<b>benzene</b>	800	-28.07	0.48
	1000	-28.48	0.18
	2000	-25.41	0.42
	4000	-24.38	0.20
	5000	-24.70	0.22
<b>toluene</b>	800	-28.20	0.46
	1000	-28.48	0.18
	2000	-28.02	0.20
	4000	-28.28	0.27
	5000	-28.45	0.18
<b>ethylbenzene</b>	800	-28.76	0.27
	1000	-28.94	0.25
	2000	-28.83	0.20
	4000	-29.04	0.25
	5000	-29.17	0.07
<b>1,2,4-trimethylbenzene</b>	800	-28.15	0.38
	1000	-29.04	0.28
	2000	-29.26	0.20
	4000	-29.48	0.12
	5000	-29.51	0.13

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62 Table S2. The  $\delta^{13}\text{C}$  values determined for the target compounds by SPME injection

Compounds	Conc. ( $\mu\text{g/L}$ )	$\delta^{13}\text{C}$ (‰)	STDV ( $1\sigma$ , n=5)
<b>benzene</b>	<b>100</b>	-28.33	0.45
	<b>200</b>	-26.31	0.73
	<b>300</b>	-25.85	0.33
	<b>500</b>	-25.71	0.40
	<b>800</b>	-25.74	0.45
<b>toluene</b>	<b>100</b>	-30.09	1.64
	<b>200</b>	-28.98	0.43
	<b>300</b>	-28.64	0.17
	<b>500</b>	-28.90	0.17
	<b>800</b>	-28.87	0.15
<b>ethylbenzene</b>	<b>100</b>	-31.28	1.71
	<b>200</b>	-29.03	0.29
	<b>300</b>	-29.07	0.09
	<b>500</b>	-29.18	0.26
	<b>800</b>	-29.22	0.08
<b>1,2,4-trimethylbenzene</b>	<b>100</b>	-28.14	0.89
	<b>200</b>	-29.41	0.22
	<b>300</b>	-29.33	0.15
	<b>500</b>	-29.67	0.22
	<b>800</b>	-29.63	0.12

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73 Table S3. The calculated on-column mass of the analytes and carbon.

<b>Compounds</b>	<b>Conc. (µg/L)</b>	<b>Injected Amount* (nmol)</b>	<b>Injected Carbon (nmol)</b>
<b>benzene</b>	<b>800</b>	13.62	81.72
	<b>1000</b>	17.03	102.18
	<b>2000</b>	34.05	204.3
	<b>4000</b>	68.12	408.72
	<b>5000</b>	85.15	510.9
<b>toluene</b>	<b>800</b>	13.39	93.73
	<b>1000</b>	16.74	117.18
	<b>2000</b>	33.48	234.36
	<b>4000</b>	66.96	468.72
	<b>5000</b>	83.7	585.9
<b>ethylbenzene</b>	<b>800</b>	19.98	159.84
	<b>1000</b>	24.98	199.84
	<b>2000</b>	49.96	399.68
	<b>4000</b>	99.92	799.36
	<b>5000</b>	124.9	999.2
<b>1.2.4-trimethylbenzene</b>	<b>800</b>	10.1	90.9
	<b>1000</b>	12.63	113.67
	<b>2000</b>	25.26	227.34
	<b>4000</b>	50.52	454.68
	<b>5000</b>	63.15	568.35

74      \*: The compounds Henry's constants are adopted from Staudinger et al. (2001)<sup>1</sup>.

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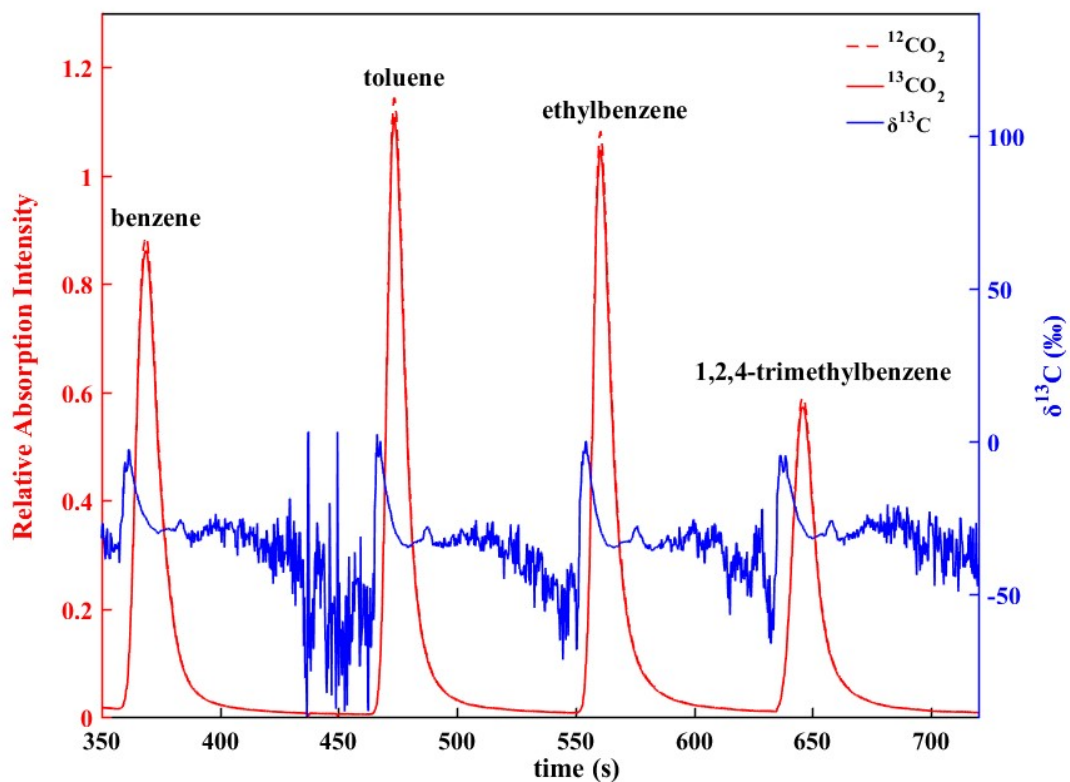
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81    ■ **Figure:**

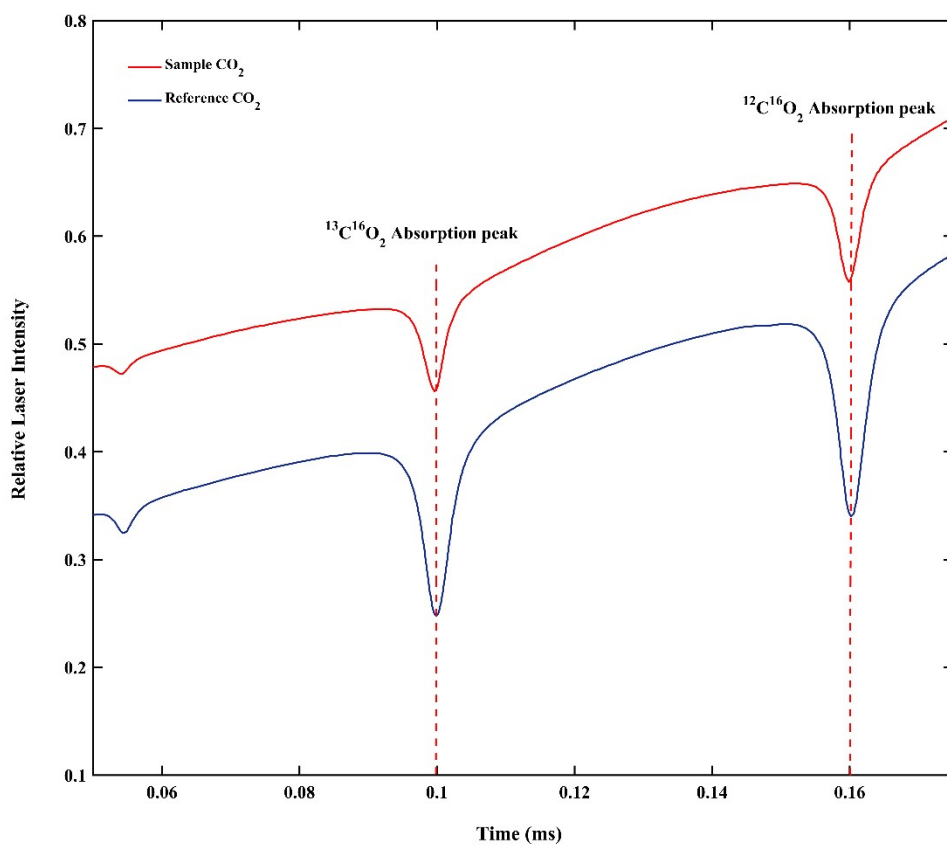
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84 **Figure S1.** Chromatograph of compound-specific  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  signals obtained from mixture of  
 85 benzene, toluene ethylbenzene and 1,2,4-trimethylbenzene in headspace sample. The dark solid line  
 86 shows the compound-specific  $\delta^{13}\text{C}$  values over time.

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89 **Figure S2.** On-line CO<sub>2</sub> isotopologue signal obtained by MCT detector. Y-axis represents relative laser  
 90 intensity. X-axis represents the time since laser is emitted from QCL. Red and blue line records the  
 91 signals from sample CO<sub>2</sub> and reference CO<sub>2</sub>, respectively.

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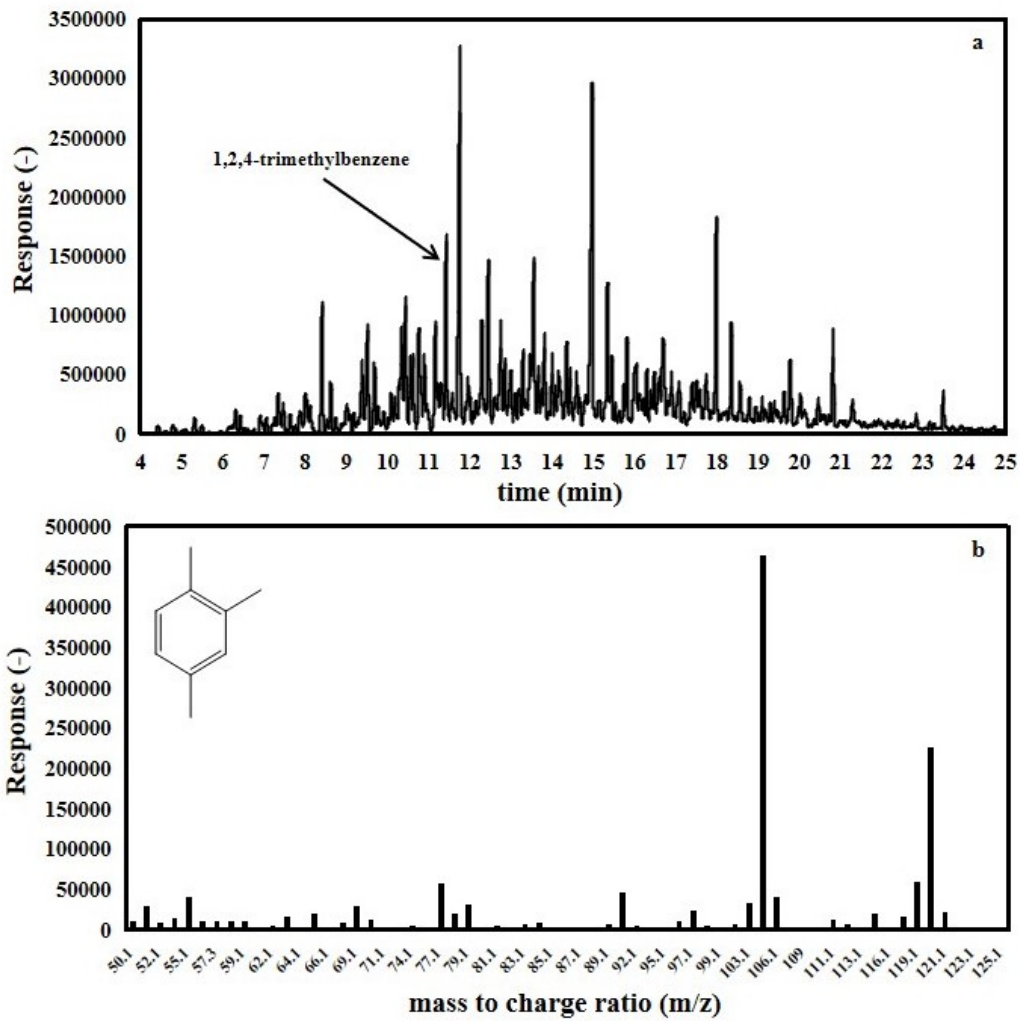
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110 **Figure S3.** Chromatogram of drilling fluid and mass spectra of 1,2,4-trimethylbenzene appearing at  
 111 10.9min from GC-MS in SCAN mode.

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123 ■ **Text:**

124 **Carbon CSIA using GC-IRIS.** To prepare the standard samples, the stock solution  
125 containing target compounds were spiked into a headspace glass vial (10 ml) containing  
126 5ml Millipore water, and sealed immediately using aluminum screw caps with Teflon  
127 coated septa (CNW, China). The standard solutions containing target compounds were  
128 prepared at different aqueous concentration, which are 100 $\mu$ g/L 200 $\mu$ g/L, 300 $\mu$ g/L,  
129 500 $\mu$ g/L, 800 $\mu$ g/L, 1000 $\mu$ g/L, 2000 $\mu$ g/L, 4000 $\mu$ g/L, and 5000 $\mu$ g/L, respectively. Five  
130 sample replicates at each concentration were prepared to calculate mean values as well  
131 as for statistical analysis. The GC was operated at a flow rate of 4ml/min, and the GC  
132 oven temperature was programmed as follow: 40 °C for 3 min, increase to 200°C by 15  
133 °C/min and hold for 2min. The GC inlet was operated in splitless mode. The combustion  
134 temperature was set at 850°C for a complete combustion of the target compounds. The  
135 headspace samples at 800 $\mu$ g/L, 1000 $\mu$ g/L, 2000 $\mu$ g/L, 4000 $\mu$ g/L and 5000 $\mu$ g/L, were  
136 measured by static headspace gas injection (1ml gas sample). By using a temperature  
137 programmable heater, the headspace samples are incubated for 30 min at 70°C before  
138 injection. Aqueous headspace samples were prepared at lower aqueous concentrations,  
139 including 100 $\mu$ g/L, 200 $\mu$ g/L, 300 $\mu$ g/L, 500 $\mu$ g/L and 800 $\mu$ g/L, for SPME injection.  
140 Specifically, the SPME injection unit contains a temperature programmable incubator  
141 and a SPME syringe. Carboxen/polydimethylsiloxane (CAR/PDMS) fibers  
142 (SUPELCO, USA) were used for extraction. Four target compounds were extracted for  
143 30min at 40°C simultaneously, and then the fiber of the SPME syringe was manually

144 inserted into the inlet (at 250°C) of GC for 2min for desorption and injection. The four  
145 target compounds were sequentially separated by GC, indicated by the four peaks  
146 appearing at different retention time (see Fig.S4). The compound-specific  $\delta^{13}\text{C}$  values  
147 were obtained by the laser isotope analyzer.

148 **Carbon CSIA using GC-IRMS.**  $\delta^{13}\text{C}$  values of the aqueous headspace samples  
149 containing benzene, toluene, ethylbenzene and 1,2,4-trimethylbenzene at 500  $\mu\text{g/L}$   
150 were analyzed by using GC-IRMS via SPME injection. The GC-IRMS includes a  
151 Agilent 6890 GC (Agilent, U.S.A.) equipped with capillary column (PoraPLOT Q,  
152 25m, 0.32mm i.d., Thermofisher, USA) and split/splitless injector, a combustion  
153 interface filled with CuO operated at 880°C and an isotope ratio mass spectrometer  
154 (IsoPrime100, Elementar, UK). The SPME setup includes a syringe holder and a  
155 carboxen/polydimethylsiloxane (CAR/PDMS) fiber (SUPELCO, USA). The fiber was  
156 inserted into headspace of sample to extract target compounds at 40°C for 30min, and  
157 then the fiber was inserted into inlets of GC at 250°C for 2min for desorption and  
158 injection.  $^{13}\text{C}/^{12}\text{C}$  isotopic ratios are reported as  $\delta^{13}\text{C}$  values by referencing to the VPDB  
159 standard (see Eq 1). A software, IonVantage, was utilized for data extraction and  
160 processing.

161 **Scanning organic compounds in drilling fluid using GC-MS.** Compounds in drilling  
162 fluid were separated and identified using GC (Agilent, 7890A, USA)-MPS (Gerstel,  
163 Germany)-MS (Agilent, 5795C, USA) by headspace sample injection (see Fig. S3). The  
164 GC was equipped with capillary column (DB-5, 30m, 0.25mm i.d., Agilent, USA). The

165 headspace samples were incubated for 30 min at 70°C before injection. The GC was  
166 operated at a flow rate of 1ml/min, and the GC oven temperature was programmed as  
167 follow: 40 °C for 3 min, increase to 250°C by 5 °C/min and hold for 5min. MS was  
168 operated under scan mode. Target compounds of 1,2,4-trimethylbenzene was identified  
169 by NIST database as well as confirmed by injecting 1,2,4-trimethylbenzene standards.

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171 ■ **REFERENCES**

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