

Stabilisation of Groundwater Samples for the Quantification of Organic Trace Pollutants

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Supplemental Information

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1. Transportation of groundwater samples

Groundwater samples taken in the field as described in section 2.1 of the main text were put into an insulated cool box. The groundwater temperature of the sample on site was throughout 12 – 13 °C. The box could accommodate six 1 L amber glass bottles or ten 100 mL amber glass bottles and was equipped with eight thermal packs (size: 8.5 cm x 16.5 cm x 1.7 cm, containing 220 mL cooling liquid) precooled to – 20 °C. The four temperature sensors (type THM 912, Oregon scientific, Portland, USA), were placed between the bottles. The temperature decreases during transport to 4-5 °C.

In the laboratory refrigerator, a temperature of +5 °C was maintained. It is seen that the different sample volume adjusts to this temperature slowly (Fig. S1). Samples were stored up to ten days at 5 °C in connection with investigations on the long term stability. The ambient temperature during transport is insignificant as long as the box is kept tight shut.

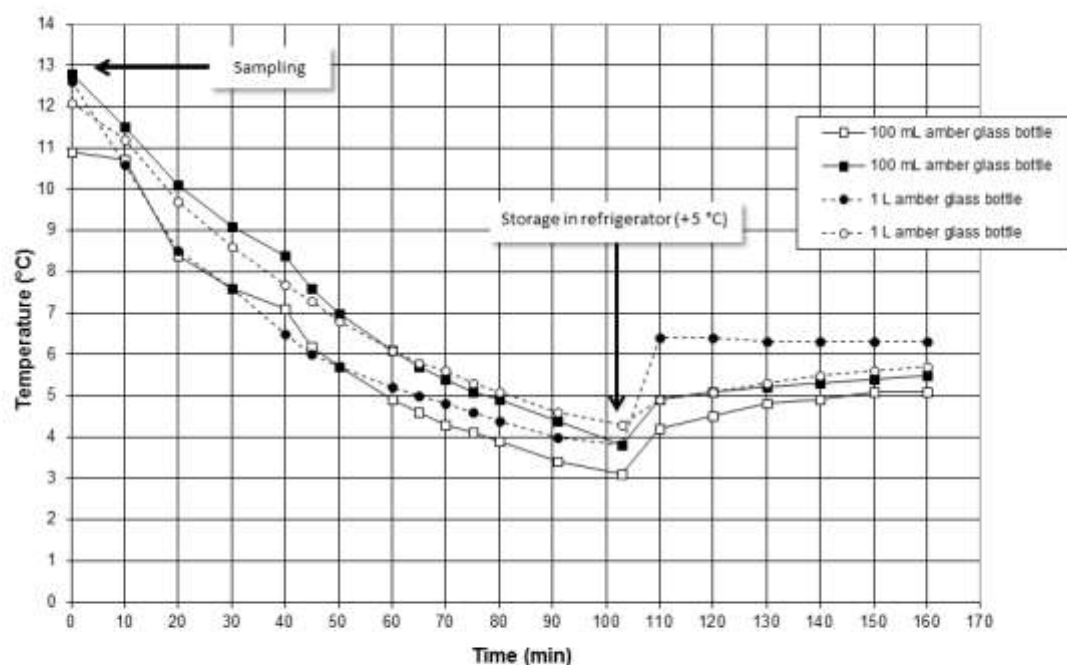


Fig. S1: Temperature monitoring during transportation of groundwater samples

2. Contaminant concentration at the groundwater sampling sites

Table S1: Content of BTEX and naphthalene at the sites I and II, HS-GC/FID (Mean \pm SD, n = 3-5)

	<i>site A(Bio1)</i> ($\mu\text{g/L}$)	<i>site A(Bio2)</i> ($\mu\text{g/L}$)	<i>site A(S2)</i> ($\mu\text{g/L}$)	<i>site B(BR1)</i> ($\mu\text{g/L}$)
Benzene	2,109 \pm 65	3.6 \pm 0.2	20,317 \pm 185	227 \pm 13
Toluene	316 \pm 10	2.3 \pm 0.2	1,513 \pm 32	4,603 \pm 242
Ethyl benzene	169 \pm 6	11.9 \pm 1.2	603 \pm 21	2,702 \pm 147
<i>m/p</i> -Xylene	1,083 \pm 6	388 \pm 40	1,681 \pm 53	2,969 \pm 160
<i>o</i> -Xylene	385 \pm 13	116 \pm 10	549 \pm 16	1,109 \pm 58
Naphthalene	1,227 \pm 31	119 \pm 4	4,753 \pm 182	164 \pm 6
Σ BTEX	4,062	522	24,663	11,610

BTEX and naphthalene are subject to degradation due to the remediation measures. Therefore, the original contaminant concentrations at the time of selection of these sites for the study had been decreased by the time of the systematic investigations (see Fig. 1, 3, S3).

Table S2: Concentration of PAH at sampling site I (HPLC/F, n=2)

PAH congener	<i>S2</i> ($\mu\text{g/L}$)	<i>Bio1</i> ($\mu\text{g/L}$)	<i>Bio2</i> ($\mu\text{g/L}$)
Naphthalene	^a	^a	^a
Acenaphthene	187	171	43
Fluorene	25	23	6.8
Phenanthrene	24	16	3.2
Anthracene	0.82	1.32	1.1
Fluoranthene	0.88	1.90	1.4
Pyrene	0.45	0.20	1.9
Benzo[<i>a</i>]anthracene	0.04	0.28	0.48
Chrysene	0.04	0.24	0.27
Benzo[<i>b</i>]fluoranthene	0.02	0.32	0.41
Benzo[<i>k</i>]fluoranthene	< 0.01	0.08	0.14
Benzo[<i>a</i>]pyrene	0.01	0.23	0.46
Dibenzo[<i>a,h</i>]anthracene	< 0.01	< 0.01	< 0.01
Benzo[<i>ghi</i>]perylene	< 0.01	< 0.01	< 0.01
Indeno[1,2,3- <i>cd</i>]pyrene	< 0.01	< 0.01	< 0.01

^a content determined by GC/FID (table S1).

Table S3: Equivalence of HPLC and headspace GC for the determination of naphthalene in groundwater from sampling site II

	HPLC/FD ($\mu\text{g/L}$)	Headspace-GC/FID ($\mu\text{g/L}$)
No stabilisation	135	138
pH < 2	137	136

Table S4: Concentration of phenols at the sampling site I (GC/MS after acetylation according to DIN 38407-F27:2012, Mean \pm SD, n = 4-9)

Phenolic compound	BIO1 ($\mu\text{g/L}$)	BIO2 ($\mu\text{g/L}$)	S2 ($\mu\text{g/L}$)
Phenol	14.6 \pm 0.79	3.52 \pm 0.17	13.0 \pm 1.36
<i>o</i> -Cresol	11.9 \pm 0.65	0.80 \pm 0.02	24.0 \pm 1.87
<i>m</i> -Cresol	7.27 \pm 0.31	0.21 \pm 0.02	29.1 \pm 3.86
<i>p</i> -Cresol	3.30 \pm 0.12	0.16 \pm 0.02	19.0 \pm 1.61
2,6-Dimethylphenol	162.6 \pm 9.88	7.00 \pm 0.20	178.1 \pm 13.34
3,5-Dimethyl phenol	161.4 \pm 10.70	10.8 \pm 0.30	739.7 \pm 53.6
2,3/2,4-Dimethylphenol	444.1 \pm 13.83	29.8 \pm 1.31	443.1 \pm 44.7
2,5-Dimethylphenol	40.7 \pm 2.63	5.17 \pm 0.18	48.3 \pm 3.11
3,4-Dimethylphenol	63.7 \pm 2.37	4.46 \pm 0.43	99.2 \pm 10.5
2,4,6-Trimethylphenol	153.2 \pm 20.12	45.0 \pm 2.47	147.8 \pm 16.6
2,3,6-Trimethylphenol	303.2 \pm 20.54	37.7 \pm 1.51	130.8 \pm 145.9
2,3,5-Trimethylphenol	60.2 \pm 4.24	8.56 \pm 0.33	58.1 \pm 4.60
3,4,5-Trimethylphenol	5.78 \pm 0.21	0.77 \pm 0.02	4.75 \pm 0.66

Table S5: VOHC concentrations at sampling points on site III in µg/L (headspace-GC/ECD/FID)

VOHC compound			
VC	23.4	22.3	185.1
tDCE	n.d.	n.d.	2.54
cDCE	15.5	50.7	441.8
TCE	0.56	1.65	125.9
PCE	1.21	1.83	16.7

Table S6: VOHC concentrations at sampling points on site IV in µg/L (headspace-GC/ECD/FID)

VOHC compound				
VC	111.6	101.6	59.0	180.5
tDCE	n.d.	n.d.	n.d.	n.d.
cDCE	10.2	10.9	12.2	7.5
TCE	1.20	1.02	1.39	0.56
PCE	n.d.	n.d.	n.d.	n.d.

Table S7: VOHC concentrations at sampling points on site IV in µg/L (headspace-GC/ECD/FID)

	<i>IB5</i>	<i>GWM 35/12 UP</i>	<i>GWM 36/12 UP</i>
	(µg/L)	(µg/L)	(µg/L)
VC	114.7	186.5	145.1
tDCE	n.d.	n.d.	n.d.
cDCE	7.9	5.3	5.0
TCE	4.7	7.0	4.3
PCE	n.d.	n.d.	n.d.

n.d. not detected

Table S8: VOHC content at sampling points at site V in µg/L (headspace-GC/ECD/FID, means ± SD, n=6)

	<i>ISOKOND 27</i>	<i>ISOKOND 31</i>	<i>Brunnen 14</i>
	(µg/L)	(µg/L)	(µg/L)
Methane	2297 ± 85	1374 ± 191	
VC	343 ± 13	199 ± 14	193 ± 4.9
tDCE	249 ± 11	181 ± 9	45.5 ± 13.0
cDCE	1335 ± 48	1133 ± 41	2.3 ± 0.4
TCE	n.d.	n.d.	n.d.
PCE	n.d.	n.d.	n.d.

n.d. not detected

3. Additional figures

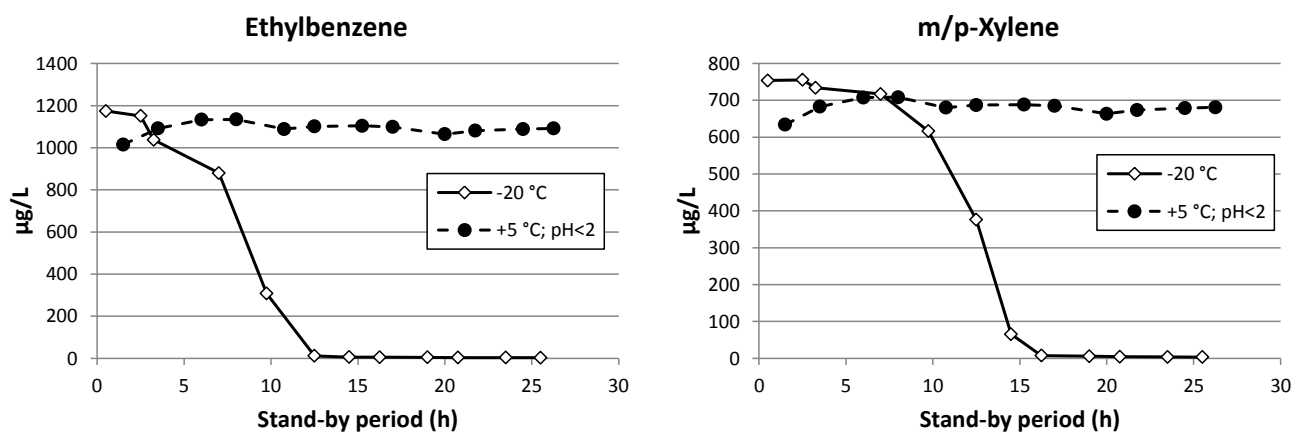


Fig. S2: Stability of ethyl benzene and xylene in groundwater samples from site I (bio1) during stand-by in the autosampler (headspace-GC/MS). Samples were placed at the given Temperatures into the autosampler and reached ultimately +30 °C.

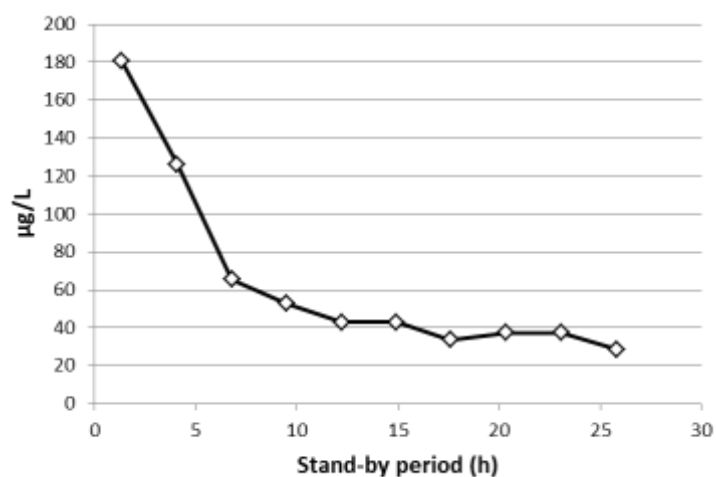


Fig. S3: Degradation of toluene in activated groundwater from site I (bio1) during stand-by period in the autosampler (headspace-GC/FID). The samples were placed at +5 °C into the autosampler and ultimately +30 °C.

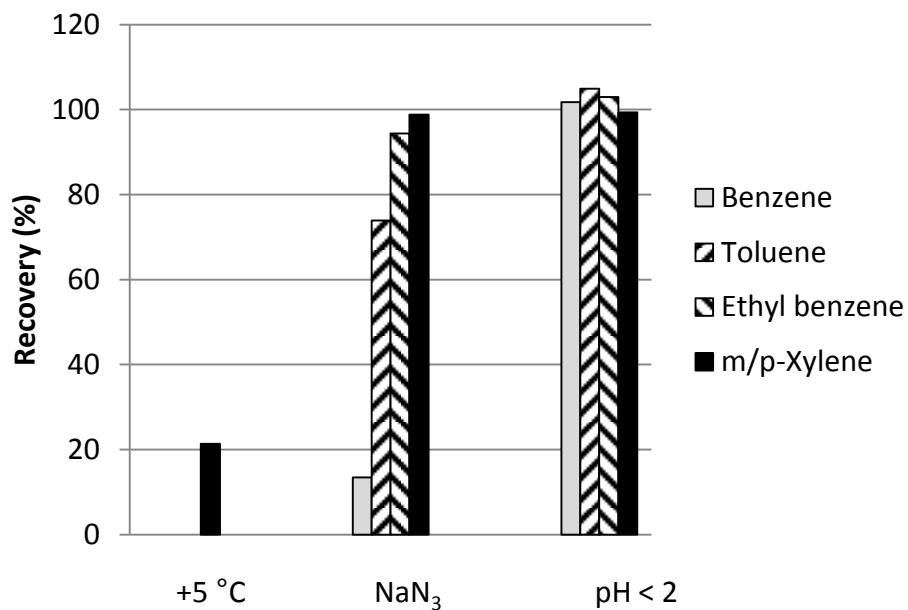


Fig. S4: Recovery of BTEX from activated groundwater (site I, bio2) stored over 7 days compared to the concentration determined directly after sampling (headspace-GC/FID)

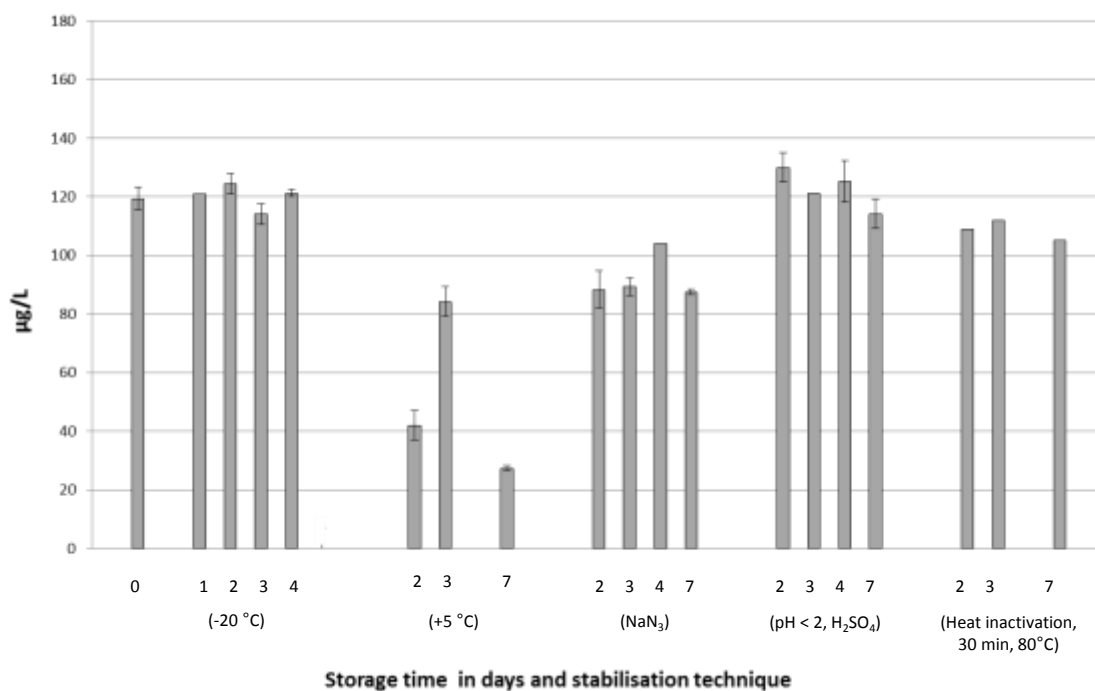


Fig. S5: Stability of naphthalene in biologically activated groundwater sampled at site I, bio2 (headspace-GC/FID)

4. Total petrol hydrocarbons

The groundwater from site 6 displayed obvious degradation of the TPH content between the two sampling dates (Fig. S4). However, groundwater from each sampling revealed no degradation during storage at +5 °C with or without acidification.

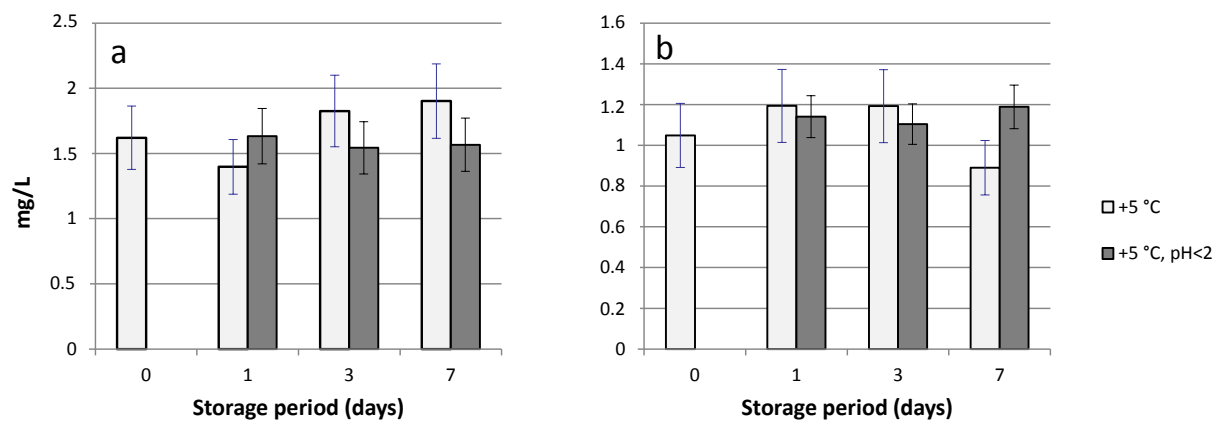


Fig. S6: Total petroleum hydrocarbon content at site VI (**b** sampled four months after **a**)