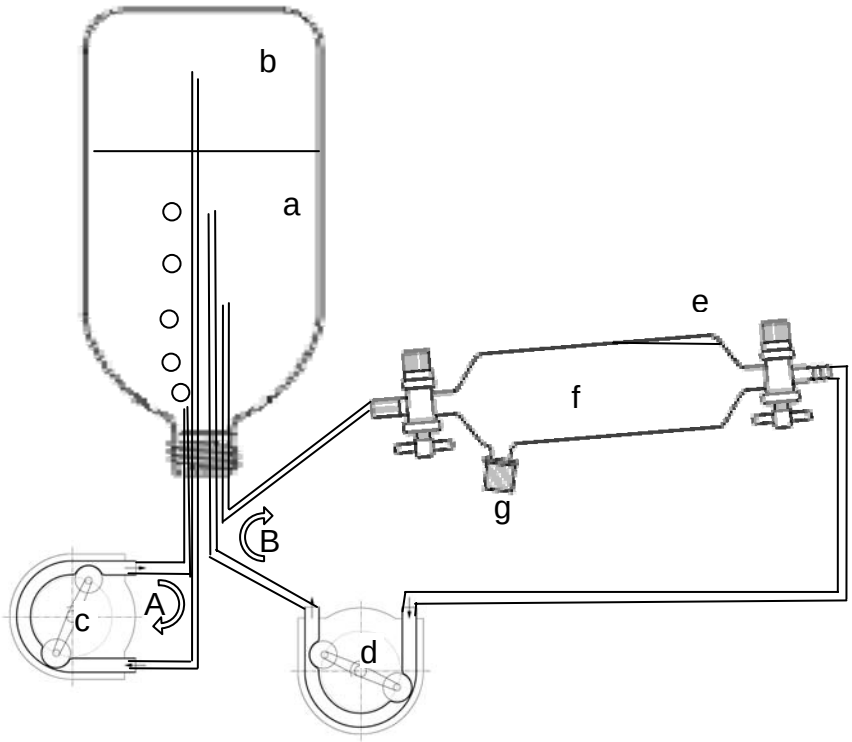

Figure S-1: Laboratory set-up to test bubble stripping

a – 5 L glass bottle, filled with water
b – 1.5 L gas mixture: H_2 in He; filled with simultaneous displacement of water from the bottle
c – peristaltic pump for equilibration loop
d – peristaltic pump for extraction loop
e – 20 mL helium bubble, filled through septum (g)
f – 500 mL gas sampling bulb, see figure 1
g – septum for injection of He (e) and for sampling of gas samples
A – loop A: equilibration of water with hydrogen
B – loop B: extraction loop

The conditions of the bubble stripping of groundwater are simulated with two loops connected to a 5 L bottle filled with water (a) and a headspace (b) with hydrogen in helium (212 ppmV H_2 in He, 1.5 L). The gas circulation with a peristaltic pump (loop A) was done for two hours prior to extraction experiments to ensure stable conditions. The gas sampling bulb (f) was filled with water and the water form the bottle was pumped through the bulb with the second peristaltic pump (loop B). For stripping experiments 20 mL of helium were injected into the bulb through septum (g) (see also fig. 1). Helium subsamples of 1 mL were withdrawn through septum (g) in time intervals of 15 minutes and their hydrogen and methane content was quantified. The maximum run time was 150 min. Levels of hydrogen and methane in these subsamples were compared with those measured in the headspace (b) of the glass bottle after the end of the experiment. It was seen that the concentration of both hydrogen and methane reached 60% of that in the bottle headspace after 50 min during which a total of 30 L of water had passed through bulb (f). Any longer run of the stripping set-up did not increase the contents of hydrogen and methane in the helium bubble (e).

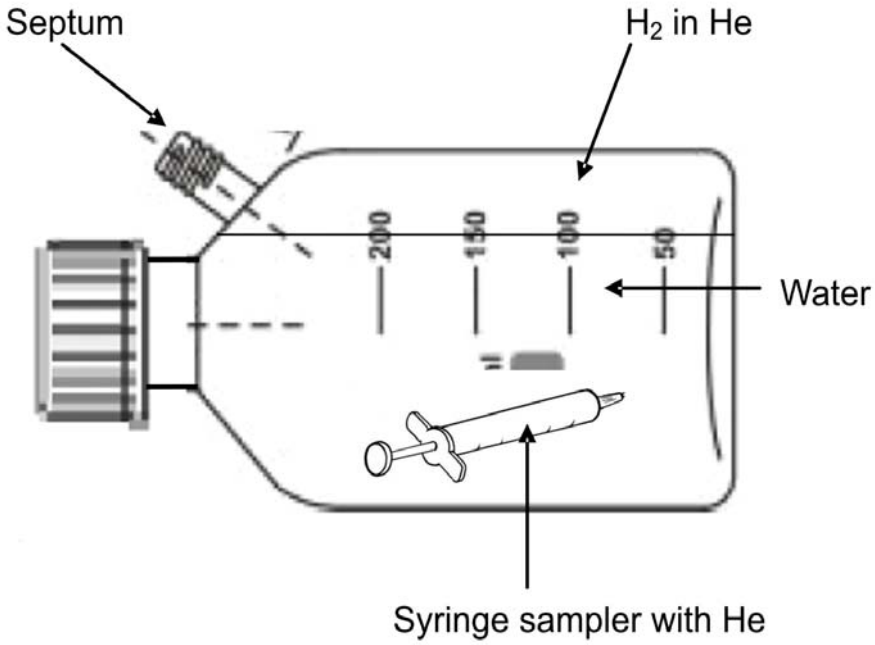

Figure S-2: Laboratory set-up to test syringe samplers

Table S-1: Concentrations of volatile organic contaminants at the sampling points

Sample No. (well)	**Sampling technique**	Methane [a]	Ethene [a]	Vinyl chloride [b]	trans-1.2-Dichloro-ethene [b]	cis-1.2-Dichloro-ethene [b]	Trichloro-ethene [b]	Tetrachloro-ethene [b]
		(μg L^{-1})	(μg L^{-1})	(μg L^{-1})	(μg L^{-1})	(μg L^{-1})	(μg L^{-1})	(μg L^{-1})
Sample 1								
3.6.2009	Active [c]	< 5	0.37 ± 0.10	5.5 ± 0.5	47.3 ± 2.7	38 ± 1.3	4.6 ± 0.3	< 0.1
	Passive [d]	< 5	0.49 ± 0.09	5.8 ± 0.5	47.1 ± 1.6	32 ± 0.8	2.1 ± 0.4	< 0.1
23.6.2009	Active [c]	< 5	0.30 ± 0.1	4.7 ± 0.2	43 ± 8.4	34 ± 3.2	3.2 ± 1.3	< 0.1
	Passive [d]	< 5	0.40 ± 0.04	5.0 ± 0.2	44 ± 3.1	30 ± 3.1	2.2 ± 0.0	< 0.1
Sample 2								
3.6.2009	Active [c]	34.4 ± 8.6	< 0.1	2.93 ± 0.10	132 ± 12.5	1521 ± 66	2873 ± 89	40.1 ± 3.8
	Passive [d]	22.7 ± 7.3	< 0.1	1.75 ± 0.24	186 ± 9.1	1869 ± 64	6083 ± 343	29.5 ± 1.8
22.6.2009	Active [c]	30.0 ± 2.0	< 0.1	2.74 ± 0.10	144 ± 10	1825 ± 200	3532 ± 292	40.4 ± 4.5
	Passive [d]	23.7 ± 0.5	< 0.1	1.89 ± 0.21	213 ± 5	2482 ± 126	5685 ± 214	25.7 ± 1.6
Sample 3								
3.6.2009	Active [c]	8296 ± 313	11.2 ± 1.5	62.4 ± 3.10	1023 ± 25	2136 ± 97	1908 ± 108	< 0.1
	Passive [d]	2811 ± 56	11.5 ± 0.5	41.1 ± 1.23	277 ± 30	1067 ± 50	14 ± 2	< 0.1
22.6.2009	Active [c]	7053 ± 390	9.2 ± 2.1	63 ± 1.2	968 ± 45	1936 ± 96	1710 ± 113	< 0.1
	Passive [d]	2377 ± 16	10.4 ± 1.7	35 ± 0.2	266 ± 27	927 ± 48	25 ± 1	< 0.1
Sample 4								
4.6.2009	Active [c]	< 5	0.33 ± 0.06	6.48 ± 0.40	4.7 ± 0.4	221 ± 12	112 ± 4	< 0.1
	Passive [d]	< 5	0.29 ± 0.05	7.13 ± 0.29	17.9 ± 3.3	396 ± 5.7	513 ± 7.1	< 0.1
23.6.2009	Active [c]	< 5	0.32 ± 0.04	6.18 ± 0.8	5.2 ± 0.3	229 ± 12	99 ± 5	< 0.1
	Passive [d]	< 5	0.21 ± 0.02	5.29 ± 0.1	7.1 ± 0.6	250 ± 17	128 ± 13	< 0.1
Sample 5								
4.6.2009	Active [c]	44.8 ± 13.2	< 0.1 (0.05)	2.19 ± 0.1	18.2 ± 1.2	822 ± 72	388 ± 16.5	< 0.1
	Passive [d]	34.1 ± 2.2	< 0.1 (0.06)	2.68 ± 0.2	19.3 ± 2.3	965 ± 68	503 ± 35	< 0.1
23.6.2009	Active [c]	45.4 ± 10.5	< 0.1 (0.06)	2.35 ± 0.2	17.5 ± 2.2	924 ± 48	340 ± 19	< 0.1
	Passive [d]	36.5 ± 2.7	< 0.1 (0.03)	2.58 ± 0.1	14.4 ± 1.1	947 ± 51	394 ± 8	< 0.1

Methods for determination:
[a] Methane and Ethene according Headspace – GC – FID, [b] VOC headspace – GC – MS according DIN ISO 10301,
[c] active sampling: purge and sample according to DIN 38402-A13, [d] passive sampling with polyethylene diffusion bag (PDB)