

SUPPLEMENTARY MATERIAL

Table S1. Detected volatile organic compounds (VOCs) and concentrations, measured by the Purge-and-Trap-gas chromatography-mass spectrometer (PT-GC-MS) equipment of the chlorinated-solvent-polluted aquifer, in Besòs groundwater (GW). Transport blank (TB), field blank (FB), and monitoring well (MW). Limits of detection (LOD) and quantification (LOQ) of VOCs analysed by PT-GC-MS and headspace solid-phase microextraction gas chromatography electron capture detector (SPME-GC-ECD). All values are expressed in µg/L.

#	Compound	PT-GC-MS						PT-GC-MS		SPME-GC-ECD	
		TB	FB	Well	MW_2	MW_6	MW_14	LOD	LOQ	LOD	LOQ
1	Dichlorodifluoromethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.026	0.088	-	-
2	Chloromethane	<LOD	<LOD	<LOD	<LOD	1.354	<LOD	0.053	0.177	-	-
3	Vinyl chloride	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.038	0.125	-	-
4	Bromomethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.174	0.580	-	-
5	Chloroethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.261	0.870	-	-
6	Trichlorofluoromethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.046	0.155	-	-
7	1,1-dichloroethylene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.044	0.148	-	-
8	Methylene chloride	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.911	6.371	-	-
9	Trans-1,2-dichloroethylene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.055	0.182	-	-
10	1,1-dichloroethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.015	0.049	-	-
11	2,2-dichloropropane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.006	0.021	-	-
12	Cis-1,2-dichloroethylene	<LOD	<LOD	<LOD	<LOD	0.450	0.844	0.012	0.041	0.039	0.130
13	Bromochloromethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.011	0.038	-	-
14	Chloroform	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	0.090	0.300	-	-
15	1,1,1-trichloroethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.006	0.020	-	-
16	Carbon tetrachloride	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.017	0.057	-	-
17	1,1-dichloropropylene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.021	0.069	-	-
18	Benzene	<LOD	<LOD	<LOD	<LOD	0.665	<LOD	0.011	0.036	-	-
19	1,2-dichloroethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.030	0.099	-	-
20	Trichloroethylene	<LOD	<LOD	<LOD	<LOD	2.864	7.808	0.020	0.065	0.003	0.010
21	1,2-dichloropropane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.015	0.049	-	-
22	Dibromomethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.007	0.022	-	-
23	Bromodichloromethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.004	0.012	-	-
24	Cis-1,3-dichloropropylene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.007	0.023	-	-
25	Toluene	<LOD	<LOD	<LOD	<LOD	1.959	0.202	0.059	0.196	-	-
26	Trans-1,3-dichloropropylene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.008	0.027	-	-
27	1,1,2-trichloroethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.006	0.019	-	-
28	Tetrachloroethylene	<LOD	<LOD	<LOD	<LOD	0.283	6.332	0.046	0.153	0.024	0.080
29	1,3-dichloropropane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.003	0.009	-	-
30	Dibromochloromethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.023	0.076	-	-
31	1,2-dibromoethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.011	0.035	-	-
32	Chlorobenzene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.006	0.021	-	-
33	1,1,1,2-tetrachloroethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.002	0.005	-	-
34	Ethylbenzene	<LOD	<LOD	<LOD	<LOD	0.874	<LOD	0.004	0.014	-	-

35	M-xylene/p-xylene	<LOD	<LOD	<LOD	<LOD	0.669	<LOD	0.004	0.012	-	-
36	O-xylene	<LOD	<LOD	<LOD	<LOD	1.483	<LOD	0.003	0.010	-	-
37	Styrene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.003	0.008	-	-
38	Bromoform	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.024	0.081	-	-
39	Isopropylbenzene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.003	0.009	-	-
40	Bromobenzene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.004	0.012	-	-
41	1,1,2,2-tetrachloroethane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.004	0.014	-	-
42	1,2,3-trichloropropane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.003	0.009	-	-
43	N-propylbenzene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.005	0.018	-	-
44	2-chlorotoluene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.004	0.012	-	-
45	1,3,5-trimethylbenzene	<LOD	<LOD	<LOD	<LOD	0.312	<LOD	0.004	0.015	-	-
46	4-chlorotoluene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.005	0.018	-	-
47	Tert-butylbenzene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.003	0.011	-	-
48	1,2,4-trimethylbenzene	<LOD	<LOD	<LOD	<LOD	0.601	<LOD	0.004	0.013	-	-
49	Sec-butylbenzene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.006	0.021	-	-
50	1,3-dichlorobenzene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.006	0.021	-	-
51	4-isopropyltoluene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.006	0.020	-	-
52	1,4-dichlorobenzene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.007	0.024	-	-
53	N-butylbenzene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.011	0.038	-	-
54	1,2-dichlorobenzene	<LOD	<LOD	<LOD	0.275	<LOD	<LOD	0.003	0.010	-	-
55	1,2-dibromo-3-chloropropane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.049	0.164	-	-
56	1,2,4-trichlorobenzene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.013	0.042	-	-
57	Hexachlorobutadiene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.035	0.115	-	-
58	Naphthalene	<LOD	<LOD	<LOD	<LOD	0.257	<LOD	0.011	0.037	-	-
59	1,2,3-trichlorobenzene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.014	0.047	-	-

Table S2. Physico-chemical characterization of the chlorinated-solvent-polluted aquifer in the GW. All values are expressed in mg/L.

Samples	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Br ⁻	Cl ⁻	PO ₄ ³⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
TB	<0.5	<0.3	<0.1	<0.1	<0.1	<0.3	<0.1	<0.5	<0.4	-
FB	<0.5	<0.3	<0.1	<0.1	<0.1	<0.3	<0.1	<0.5	<0.4	-
Well	44	2	19	11	<0.1	72	<0.1	0.6	5.1	71
MW-2	104	20	14	139	<0.2	212	<0.2	0.8	109	209
MW-6	5820	521	41	244	<20	24600	<20	216	81	-
MW-14	1990	175	12	186	<2.0	5410	<2.0	259	128	-

Table S3. GW metals' occurrence in the chlorinated-solvent-polluted aquifer. All values are expressed in µg/L.

Samples	Cd	Co	Pb	Zn	Fe	Ni	V	Cu	Ba	Mn	As
TB	<0.5	<0.5	<2.5	<25	<25	<2.5	<0.25	<2.5	<1	<1	<0.5
FB	<0.5	<0.5	<2.5	<25	<25	<2.5	<0.25	<2.5	<1	<1	<0.5
Well	<1	2	<5	1970	<50	<5	<0.5	<5	432	3510	<1

MW-2	<1	5	<5	110	360	8	<0.5	<5	550	4420	7
MW-6	302	990	83	3091000	1842000	6930	<5	3050	1830	116000	<10
MW-14	42	226	24	267000	3950	782	<5	170	498	34400	<10

Table S4. Concentration ($\mu\text{g/L}$) of chlorinated solvents in unspiked and spiked ($10 \mu\text{g/L}$) real GW samples at 0 and 5 h of incubation time, detected by SPME-GC-ECD, and their removal rates (%). No removal (N.R.) quantified since DCE was undetected in unspiked GW at 0 or 5 h.

	Concentration ($\mu\text{g/L}$)				Removal (%)	
	Spiked GW 0h	Spiked GW 5h	Unspiked GW 0h	Unspiked GW 5h	Spiked GW 5h	Unspiked GW 5h
DCE	3.6 ± 0.3	1.8 ± 0.5	< LOD	< LOD	49.9 ± 3.5	N.R.
TCE	14.7 ± 0.3	< LOD	5.2 ± 1	0.3 ± 0.1	99.8 ± 0.2	93.9 ± 6.4
PCE	12.7 ± 0.9	5.3 ± 0.2	5.9 ± 0.9	1.6 ± 0.3	58.3 ± 1.3	72.9 ± 6.3

Table S5. Log Octanol-Water Partition Coefficient ($\text{Log } K_{\text{ow}}$) of studied compounds.

Compounds	$\text{Log } K_{\text{ow}}$	Ref
Cis-1,2-dichloroethylene	1.86	[30]
Tetrachloroethylene	3.40	[30]
Trichloroethylene	2.29	[30]

Table S6. Literature review of chemical reagents and their reported removal yield with chlorinated solvents. Persulfate (PS), nano zero-valent iron (nZVI), cis-1,2-dichloroethylene (DCE), trichloroethylene (TCE), and tetrachloroethylene (PCE).

Treatment	Monitored molecules	Reported removal	Type of experiment	pH	Temperature	Type of water	Reference
PS	TCE	< 30% removal.	Batch experiments in 40 mL septum sealed vials, duration: 16 h.	Final pH 6.2	20 °C	Synthetic water spiked with 50 or 375 mg/L TCE and a molar ratio of TCE: PS of 1:20.	[34]
Fe(VI)	TCE	Maximum removal with ultrapure water at pH 7: 97%. Maximum removal with real water at pH 7 (containing dissolved organic carbon): 42%.	Batch experiments with 10 mL containing solution in 20 mL septum sealed vials, duration: 30 min.	Initial pH 3, 5, 7, 9 or 11	Not reported	Ultrapure water or real GW spiked with 0.1-10 mg/L of TCE and with Fe(VI) at 50 mg/L.	[8]
nZVI	TCE, PCE and DCE	Removal generally >80% for each of these molecules depending on the pilot test and on the type of employed nZVI.	Full-scale experiments.	Real conditions	Real conditions	Unspiked real water.	[22]
PS+Fe(II)	TCE	Nearly 100% removal.	Batch experiments in 60 mL glass reactors, duration: 1 h.	Final pH around 3	20 °C	Synthetic water spiked with 60 mg/L TCE and a molar ratio of PS:Chelate:Fe(II):TCE molar ratio of 20:2:10:1.	[33]
	PCE	Complete removal.	Batch experiments in 250 mL glass reactors, duration: 30 min.	Initial pH of 3	20 °C	Synthetic water spiked with 0.015 mmol/L PCE and a molar ratio of PS:Fe(II):Hydroxylamine:PCE molar ratio of 30:4:20:1.	[43]
PS+nZVI	TCE	> 95% removal.	Batch experiments in 40 mL septum sealed vials, duration: 16 h.	Final pH 2.6	20 °C	Synthetic water spiked with 50 or 375 mg/L TCE and a molar ratio of TCE: PS: nZVI of 1:20:150.	[34]
PS + S-nZVI	DCE, TCE and PCE	93 – 133 %	Batch experiments in 70 mL glass reactors, duration: 0.9 - 300 h	Not reported	Not reported	S-nZVI (Fe content: 81.6 %; S/Fe molar ratio: 99.95:0.05) concentration: 1.36 – 33.9 mmol/g	[26]
	TCE	97-99 % removal	Batch experiments in 250 mL glass reactors, duration: 60 min	3, 5, 7, 9, 11	Not reported	Synthetic groundwater with PS: 4 mM; S-nZVI: 250 mg/L TCE: 1.5 mM	[35]

Table S7. Human health (hazard quotient (HQ), cancer risk (CR)) and environmental (risk quotient (RQ)) risk assessment parameters obtained necessary for calculations. * According to the Agency for Toxic Substances and Disease Registry, there is inadequate information to assess the carcinogenic potential of cis-1,2-dichloroethylene (DCE).

			DCE	TCE	PCE
Human health	Non-cancer risk	RfD	2.0E-03	5.0E-04	6.0E-03
	Cancer risk	CSF	*	4.6E-02	2.1E-03
Environmental		PNEC Fw	6.8	10.0	10.0