

Geochemical and microbiological characteristics during in situ chemical oxidation and in situ bioremediation at a diesel contaminated site

Nora B. Sutton^{1}, Mariusz Kalisz², Janusz Krupanek², Jan Marek³, Tim Grotenhuis¹, Hauke Smidt⁴, Jasperien de Weert⁵, Huub H.M. Rijnaarts¹, Pauline van Gaans⁵, Thomas Keijzer⁵*

¹ Environmental Technology, Wageningen University, Bornse Weiland 9, 6708 WG
Wageningen, The Netherlands

² Institute for Ecology of Industrial Areas, Kossutha 6, 40-844 Katowice, Poland

³ POWIZ Sp. z o.o. Przedsiębiorstwo Oczyszczania Wód i Ziemi, Fabryczna 10, 53-609
Wrocław, Poland

⁴ Laboratory of Microbiology, Wageningen University, Dreijenplein 10, 6703 HB, Wageningen,
The Netherlands

⁵ Soil and Groundwater Systems, Deltares, Princetonlaan 6, 3584 CB Utrecht, The Netherlands

Table S1. XRD and TGA mineral data. XRD results are the relative concentration (%) of each component. TGA results give the percent of weight loss upon ignition relative to the dry weight.

		Before treatment	After 1 st injection	Final
Sample Location (as in Table 2 and Figure 1)		C1	P1	P2
Depth (m bgl)		2.5-2.6	2.5-2.6	2.3-2.4
Quartz	SiO ₂	84.0	85.9	78.0
Alkali feldspars	(K,Na)AlSi ₃ O ₈	9.4	8.7	9.2
Plagioclase	(Na,Ca)(Al,Si) ₄ O ₈	2.5	1.3	4.0
Calcite	CaCO ₃	0.4	0.1	0.6
Hematite	Fe ₂ O ₃	n.d. ^δ	n.d. ^δ	0.7
Gypsum	CaSO ₄	n.d. ^δ	0.7	0.4
2:1 Al silicates	(K,Na,Ca,Mg) _x (Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ (OH,F) ₂ •n(H ₂ O)	2.2	0.9	5.3
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	1.1	1.2	1.4
Chlorites	(Mg,Al,Fe) _x Si ₄ O ₁₀ (OH) ₂ (Mg,Al,Fe) _x (OH) ₆ (2<x<3)	n.d. ^δ	n.d. ^δ	0.3
LOI [‡]	(105-1000°C)	2.3	5.4	2.1

^δ not detected

[‡]Loss on Ignition

Table S2. SO₄²⁻ concentrations (mg l⁻¹) in monitoring wells throughout the experimental period.

SO ₄ ²⁻ Day	ROI					Downstream						Upstream			
	C1	C6	C7	C8	C9	C2	C3	C4	C5	C10	T3	C11	T1	T2	T4
-10	4	7	5	4	3	96	97	17	4		175	5	4	27	5
0		1815	2389	2956	3548					19					
1		5681	4618	4116	8099				568			67	13		
2		6826	4648	4224	8272										
3	4236	6981	7049	3824	7290		157		3484	95		58			
6	7873	6302	2519	3480	6528	163	136	471	5123	529	79	319	14	42	13
13	9230	5082	1482	2320	4411	387	299	608	6195	4361	545	319	299		
20	7749	2904	925	2392	3142	467	144	560	5022	4697	104	108		156	
33	117	4573	3499	1017		6972	687	353	176	2835					
45	9809	10214	4826	4267	11614	747	168	809	20719	24269	193	889	122	955	91
51	10581	6901	3571	2848	13561	1226	358	1091	25162	27940	161	1104	67	1182	
65	6005	2333	1192	954	3704	1155	214	816	15074	22740	1033	218	109	2008	50
77	6487	3550	5996	4123	4956	1834	203	462	10018	16234	2330	287	27	1407	
92	4777	1851	1016	803	3073	2346	147	551	8576	14377	82	180	17	1179	1609
112	3854	2433	853	1235	2157	2444			6115	11572					
127	4168	1346	526	614	34640	1218	320	276	4051	7454	56	56	15	1961	2

Table S3. Ca²⁺ concentration (mg l⁻¹) in monitoring wells throughout the experiment.

Ca Day	ROI					Downstream						Upstream			
	C1	C6	C7	C8	C9	C2	C3	C4	C5	C10	T3	C11	T1	T2	T4
-10	252	260	267	273	252	257	241	227	232	270	289	264	268	170	310
0		623	1052	864	754					267					
1		958	1245	1009	693				361			266			
2		801	1108	853	621										
3	821	770	585	702	494		241		966	277		255			
6	925	508	297	405	423	307	242	348	1024	349	259	0	258	185	313
13	435	350	226	234	405	281	262	361	872	892	243	221	240		
20	445	270	229	278	448	358	242	383	665	883	255	267	259	187	
33	418	378	282	317	522	441	271	327	560	776	282	281	257	194	346
42		864	1015	1126	810	426	267	301	634	545		412			
45	632	803	394	454	685	417	277	366	629	573	300	421	266	322	320
51	427	370	226	154	466	463	270	412	481	477	292	415	268	355	0
65	299	173	189	145	353	463	272	402	397	407	262	277	235	463	280
77	270	182	265	208	420	493	298	338	375	360	264	257	259	355	285
92	247	202	193	205	447	535	310	427	365	362	255	268	279	347	23
112	289	291	246		421	528			419	367					
127	377	209	161	173	316	459	377	388	440	353	250	257	243	370	1

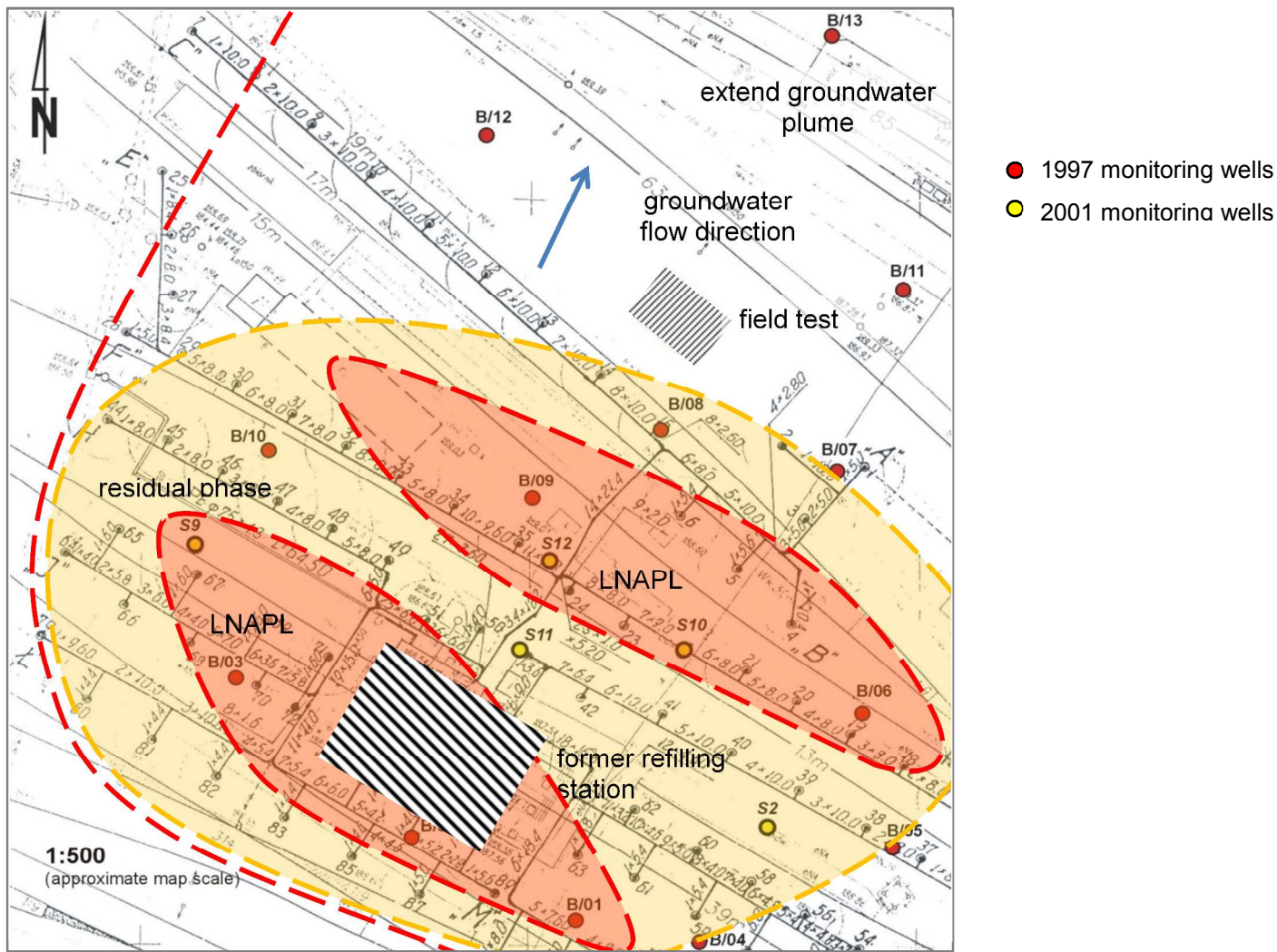
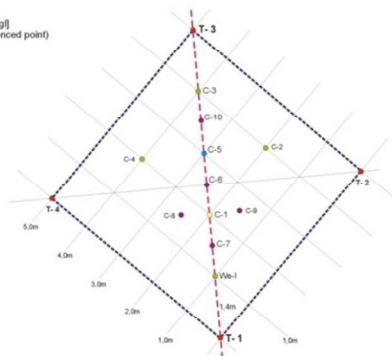
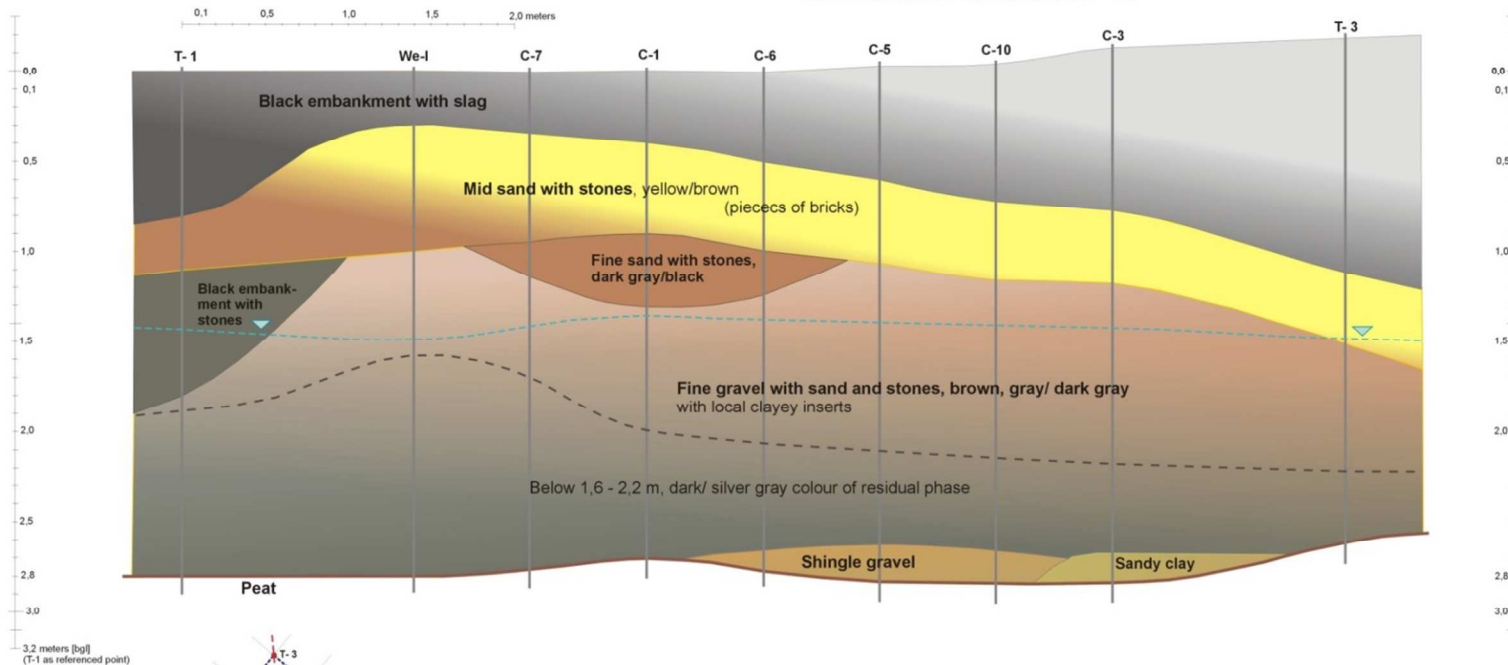


Figure S1. Layout of contaminated railway terrain. Soil surveys conducted in 1997 and 2001 identified two large LNAPL zones under and around the former refilling location. In the area of the refueling station up to 70 cm of pure product is observed. LNAPL spread across the site in north to north-eastern direction with the groundwater flow. A remediation was started in 2003 based on multiple phase vacuum extraction but was aborted shortly afterwards due to clogging of the extraction filters.

Cross-section: direction T1 - T3



--- - cross-section line

T-1 - piesometers drilled 15 IV 2011r

● - piesometers drilled 27-28 VII 2011r

● - controlling piesometer drilled 23 VIII 2011r

● - controlling piesometer drilled 6-7 XII 2011r

□ - test field territorial boundary

--- - groundwater level (28-07-2011)

--- - approximate range of soil saturation by residual phase (based on the field observation during boreholes drilling). No pure product were observed in groundwater.

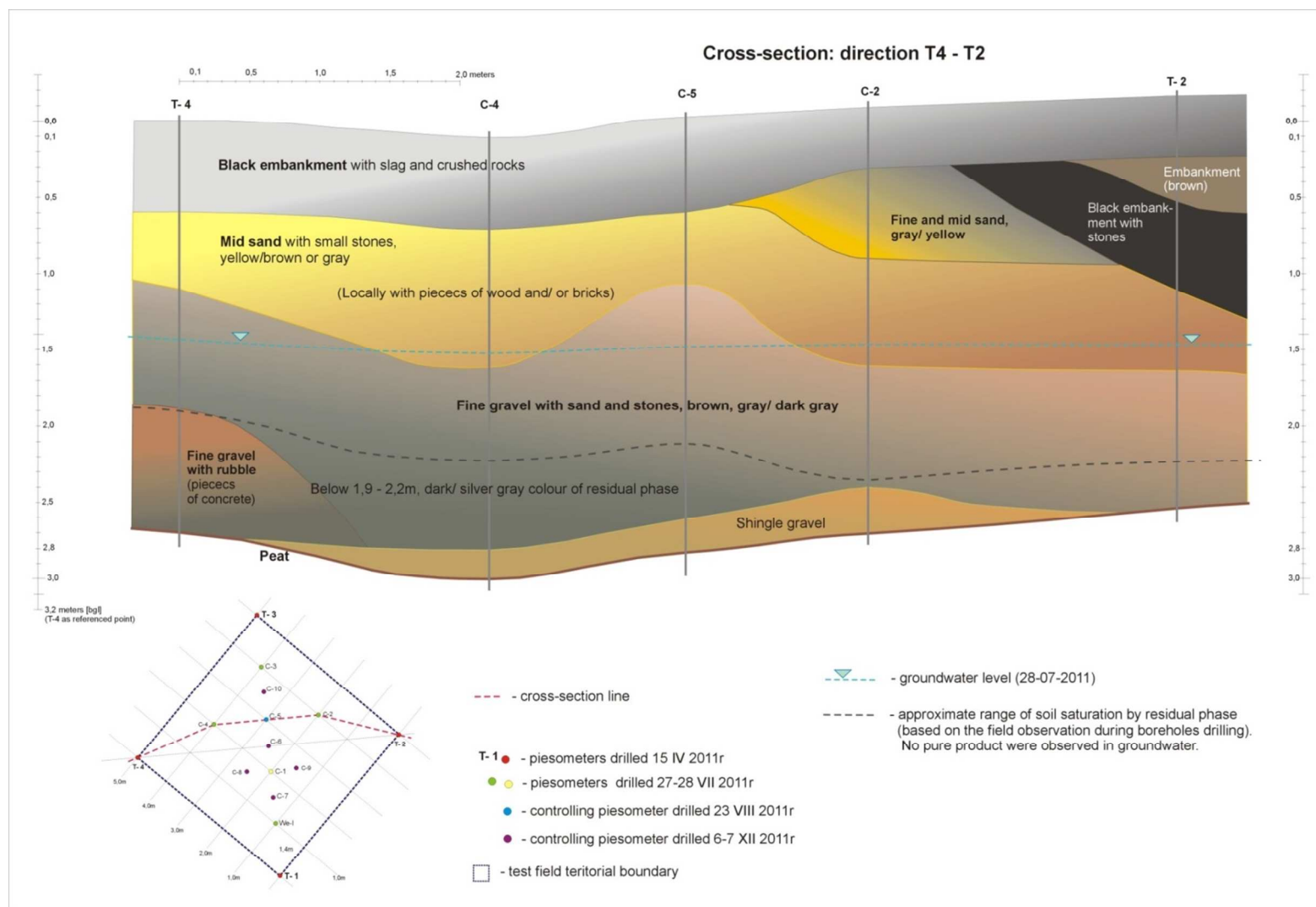


Figure S2. Cross sections of pilot location from T1-T3 (above) and T2-T4 (below).

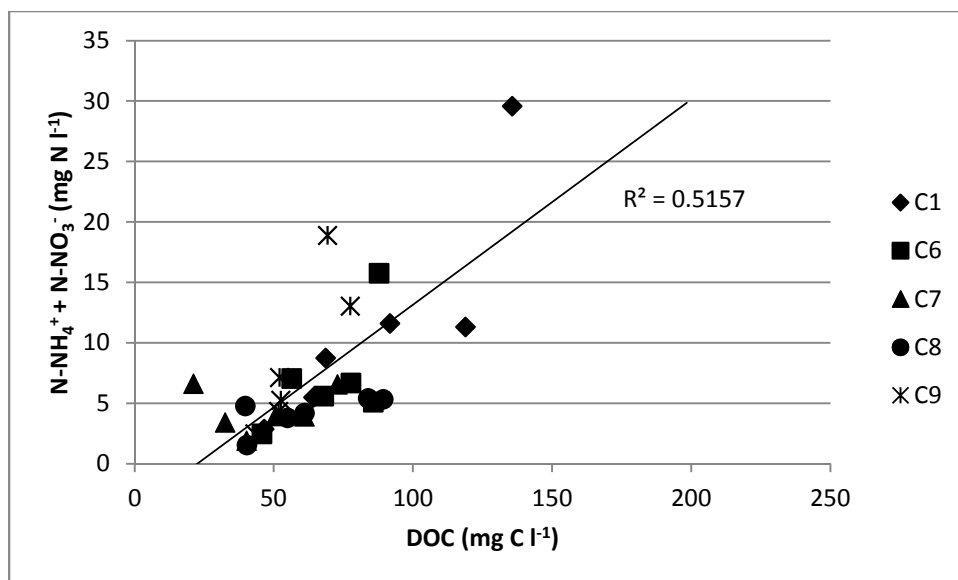


Figure S3. Relationship between DOC and nitrogen species NH₄⁺ and NO₃⁻. Degradation of soil organic matter (SOM) upon oxidation with persulfate releases carbon and nitrogen species into the aqueous phase.

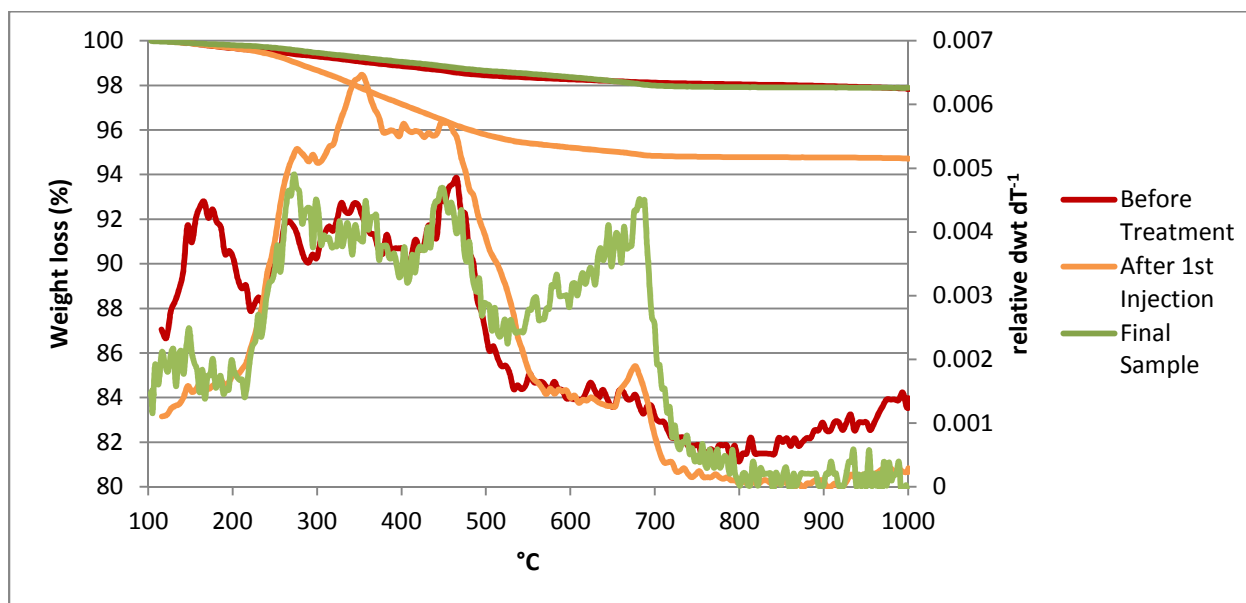


Figure S4. Changes in SOM as measured by TGA analysis. Total weight loss is given on the left axis. On the right axis the derivative of weight loss with respect to temperature relative to the total weight loss is given to allow comparison of the relative contribution of different soil components ⁴.

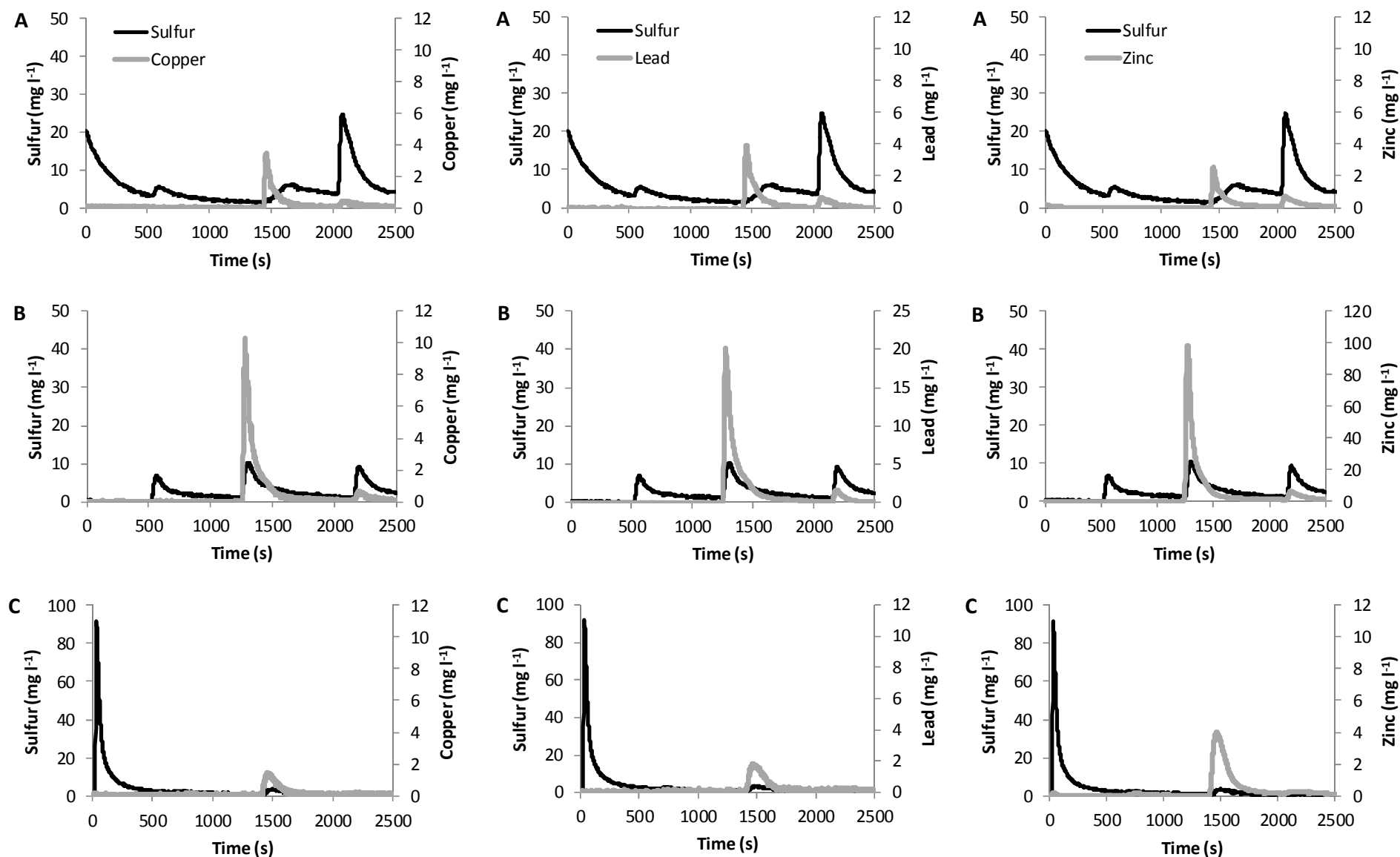


Figure S5. On-line sequential extraction comparison of sulfur and copper (left), lead (middle) and zinc (right) in samples taken prior to injection (A), following the first persulfate application (B) and at the end of the field experiment (C). In the initial sample, metals were associated with more amorphous and mineral phase sulfides, as seen in the simultaneous release of sulfur with the heavy metal. A shift away from concomitant sulfur and metal extraction in (B) and (C) indicates the oxidation of sulfides due to persulfate injection.

1. Claff, S. R.; Sullivan, L. A.; Burton, E. D.; Bush, R. T., A sequential extraction procedure for acid sulfate soils: Partitioning of iron. *Geoderma* **2010**, *155*, (3-4), 224-230.
2. Billon, G.; Ouddane, B.; Laureyns, J.; Boughriet, A., Chemistry of metal sulfides in anoxic sediments. *Phys. Chem. Chem. Phys.* **2001**, *3*, (17), 3586-3592.
3. Huerta-diaz, M. A.; Morse, J. W., A quantitative method for determination of trace-metal concentrations in sedimentary pyrite *Mar. Chem.* **1990**, *29*, (2-3), 119-144.
4. Cuypers, C.; Grotenhuis, T.; Nierop, K. G. J.; Franco, E. M.; de Jager, A.; Rulkens, W., Amorphous and condensed organic matter domains: the effect of persulfate oxidation on the composition of soil/sediment organic matter. *Chemosphere* **2002**, *48*, (9), 919-931.