

Supplementary Material

Site Characteristics

The Dan River Steam Station is a 276 MW coal fired power generation facility that was under operation from 1949 to 2012¹. The Dan River Steam Station is located to the southeast of Eden, North Carolina on the northern bank of the Dan River. Coal combustion residues (CCR) from the power plant are stored on-site in an unlined coal ash basin, in a dry ash basin, or in a dredged ash basin (Fig. 1). The coal ash spill of February 2nd, 2014 began when a stormwater pipe that ran under the primary cell of the coal ash basin gave way and began spilling the contents of the ash basin into the Dan River.

Sample Collection

Water was collected from two Dan River Steam Station inflows to the Dan River. The first was an active discharge just upstream of the primary ash basin (0.5 km upstream; Inflow A in Fig. 1). This discharge receives water from several sources, one identified as being non-contact cooling water (Outfall 009)² and one is a 36" stormwater pipe that drains a depression that is adjacent to the primary ash basin and an access road. The valley that feeds this 36" stormwater discharge pipe has in the past received seep water from the primary ash basin^{3, 4}, from another 36" stormwater pipe, and from "yard drains"³. The resulting effluent then cascades down rip-rap into the Dan River leaving a bright orange deposit. The second inflow was from a stream that runs along the earthen dam of the secondary ash basin and into the Dan River (0.5 km downstream of the spill; Inflow B). This stream was expected to potentially have high concentrations of CCR associated metals given high groundwater concentrations in wells in its vicinity⁵. At the time of sampling, the one permitted discharge from the ash basins to the Dan River (Outfall 002) had no flow, and so it was not sampled.

Statistics. To examine whether there were differences in metal concentration in individual size fractions (*i.e.*, bulk water, < 0.45 μ m, <1 kDa) in water collected from Inflow A, for each metal we carried out a one-way analysis of variance (ANOVA) test. To look for concentration

differences between each of the surface water samples, we conducted one-way ANOVAs for each metal between all five surface water sites and the two inflows, and used Tukey-HSD post hoc tests to examine where those differences existed. Due to lack of normality, data in the second comparison were log transformed prior to analysis. Concentrations below the limit of detection were censored by taking values from a uniform distribution between zero and the limit of detection (LOD). All analyses were performed in JMP Pro 11 (SAS Institute, Inc., Cary, NC, USA).

Materials and Methods

Filtration of water samples.

Concentration factor (cf) was chosen to be 25 for the following reasons: (1) according to previous studies, a cf of minimum 10 was found necessary for the reliable determination of the colloidal pool for trace elements in the surface water⁶ and high cf values give more representative colloidal fraction data⁷; (2) The total recoveries of elements are 74.1-108.6 %, which indicates that the CFUF separation based on a cf of 25 is validated.

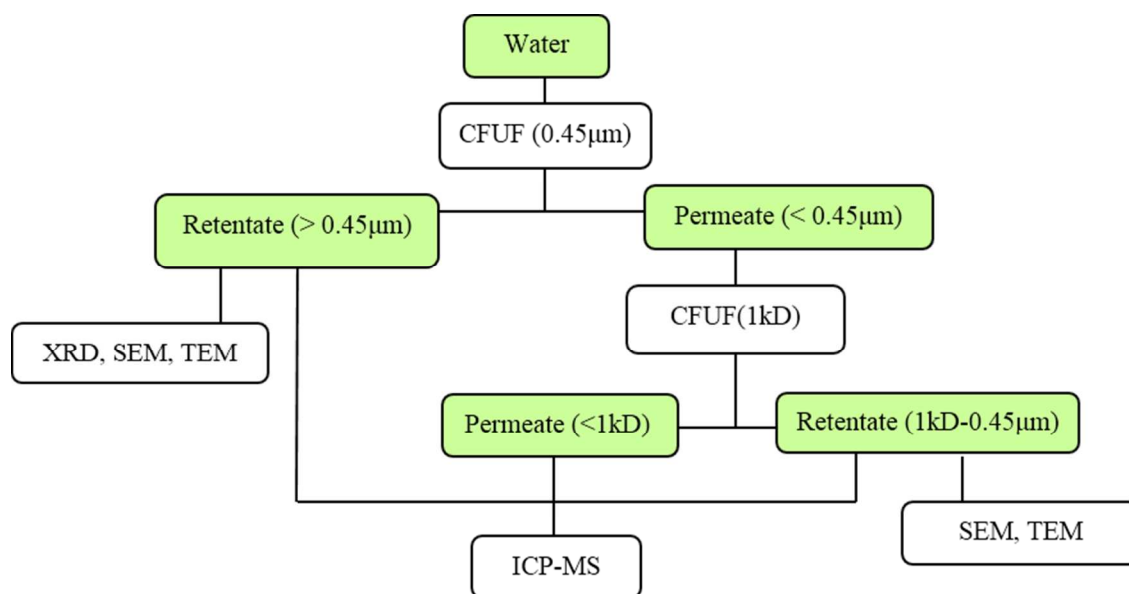


Fig. S1 Water sample processing flow chart.

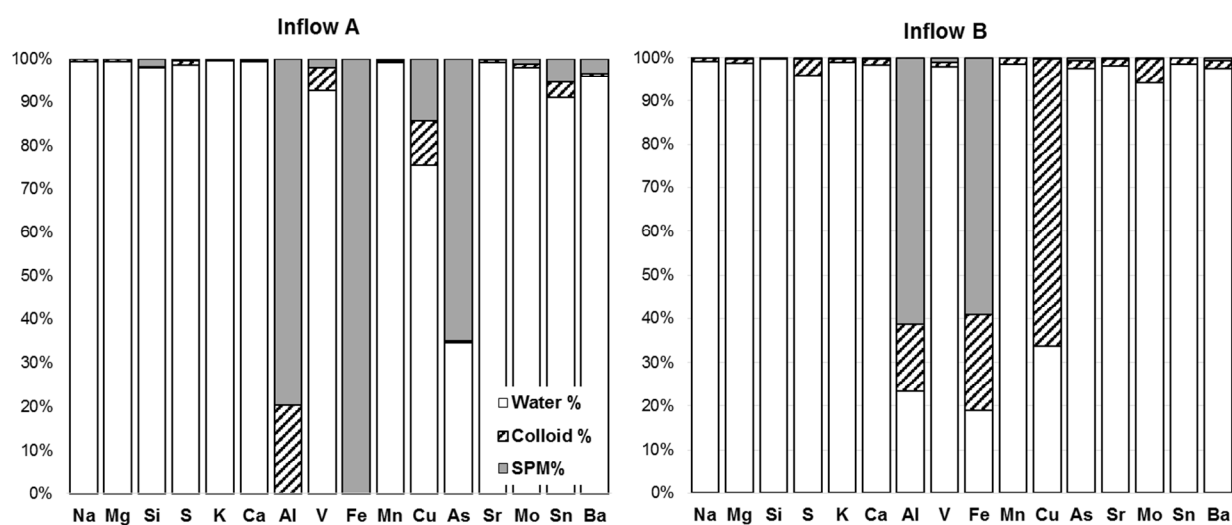


Fig. S2 Contribution of each fraction to the total elements in bulk inflow water samples
The mass balance of elements was calculated by including the SPM, colloidal and dissolved phases.

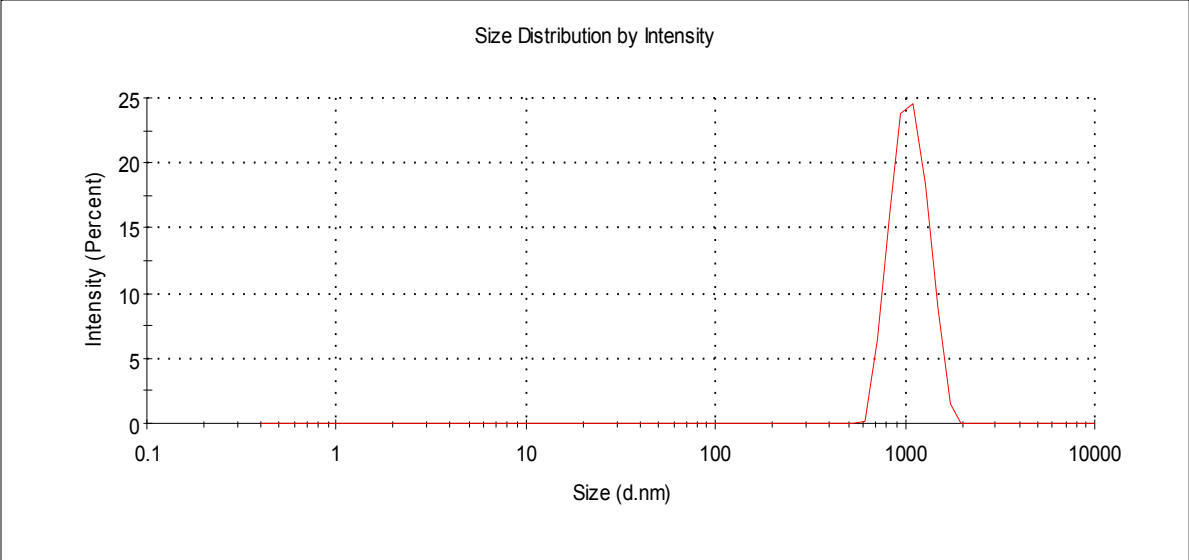
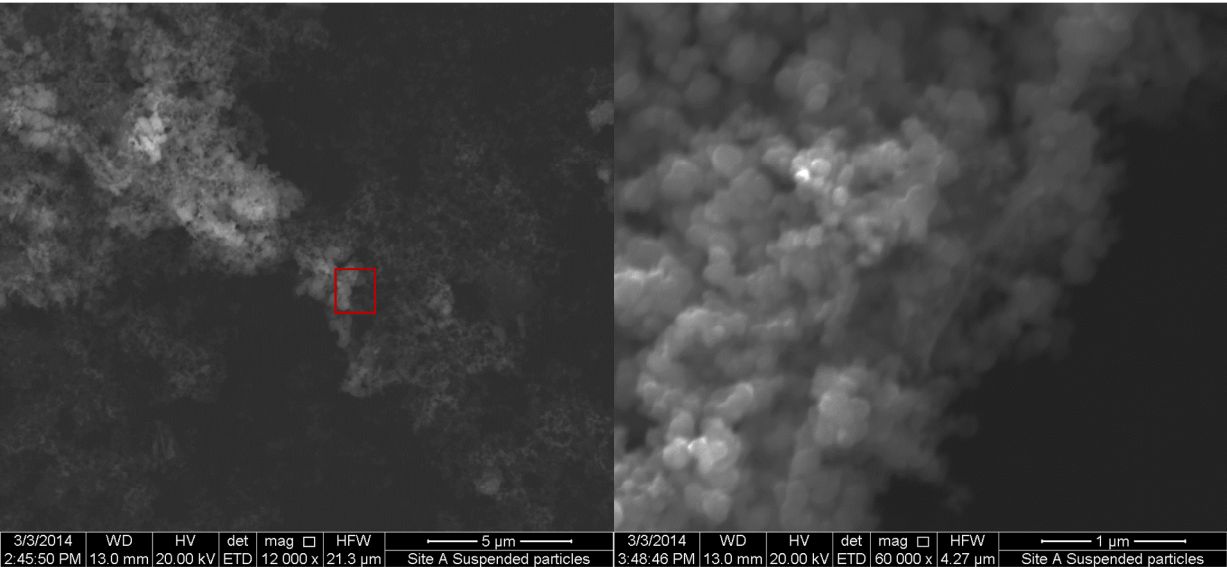


Fig. S3 Size distribution of SPM in Inflow A with an average size of 1641 nm



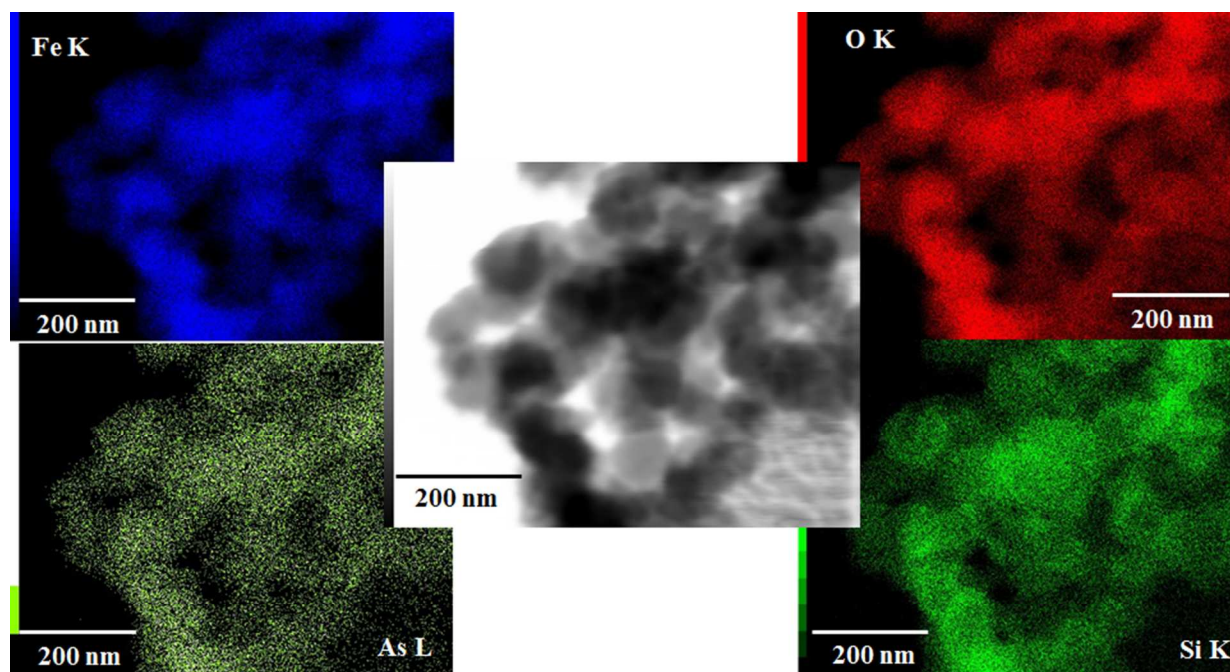


Fig. S4 SEM (top) and Scanning TEM images (bottom) of $>0.45 \mu\text{m}$ fraction in Inflow A. SEM images show the ubiquitous occurrence of ferrihydrite in the >0.45 fraction.

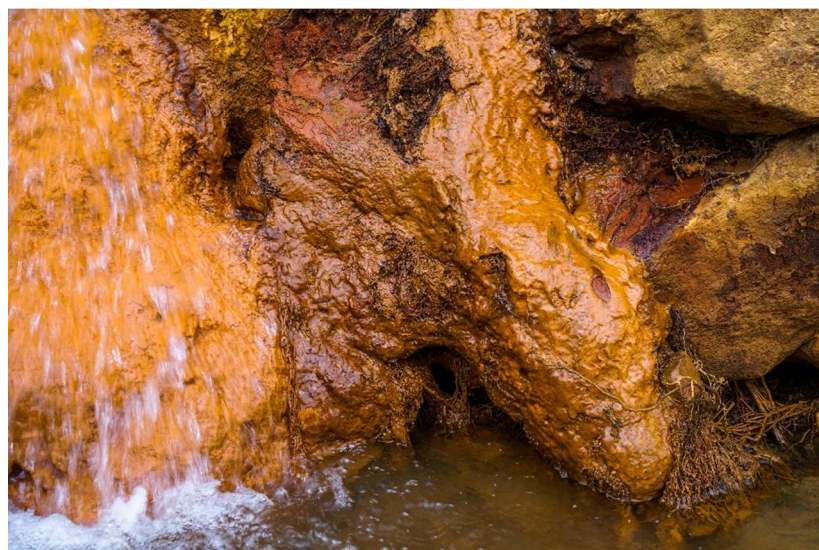


Fig. S5 Deposition of ferrihydrite on the riprap leading to the stream from Inflow A

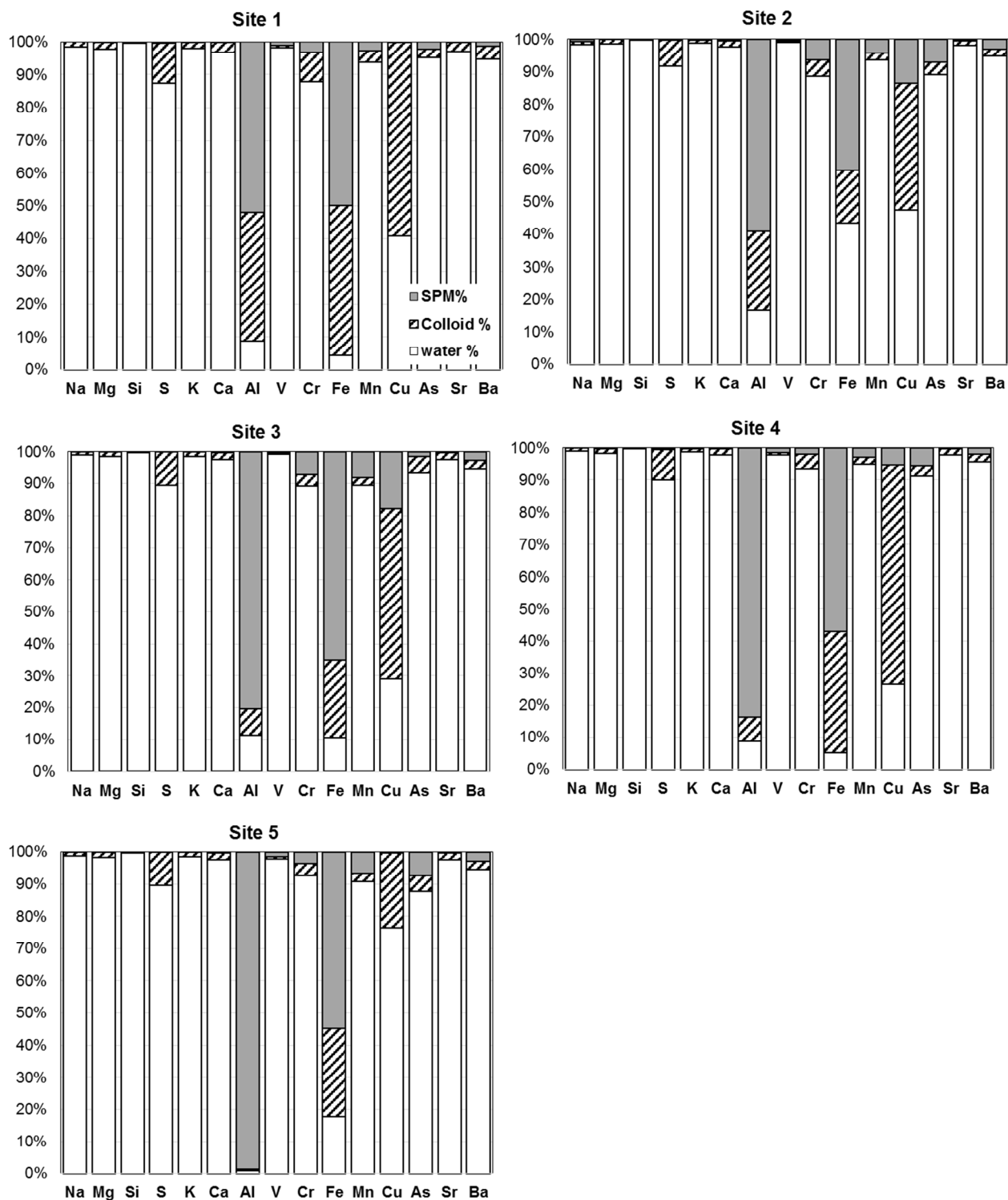


Fig. S6 Phase distribution pattern of major and trace elements in river water samples

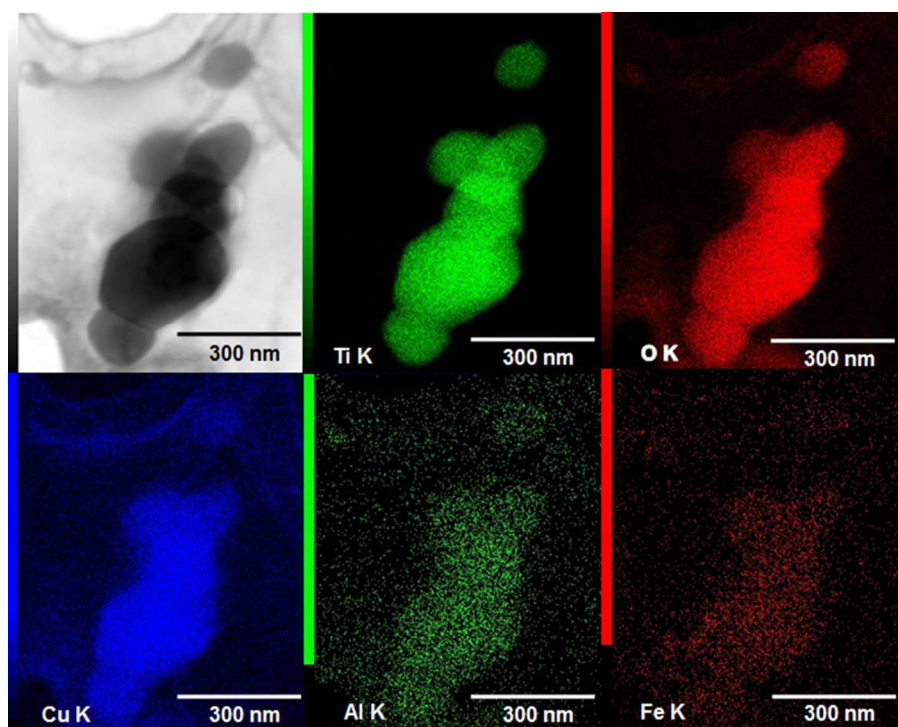
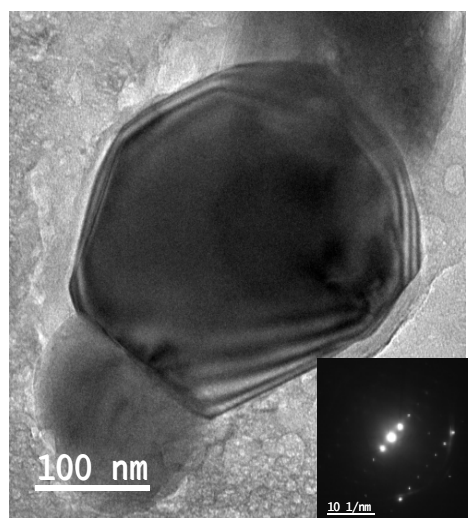


Fig. S7 TiO_2 associated with Cu, Al and Fe in the colloidal fraction investigated by TEM, SAED and STEM

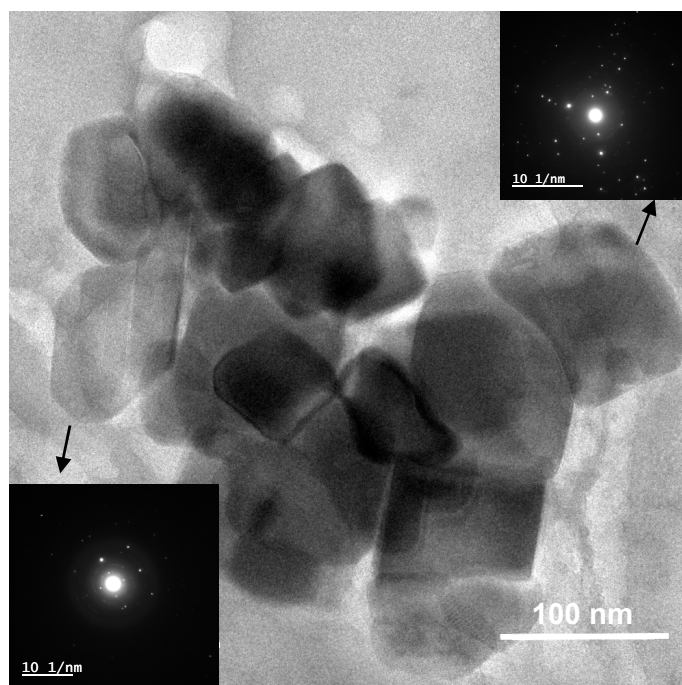


Fig. S8 TEM and SAED images of goethite (left, more euhedral) and hematite (right, more rounded) in 1kD – 0.45 μ m fraction at Site 2.



Fig. S9 Downstream river sediments with gray and black color

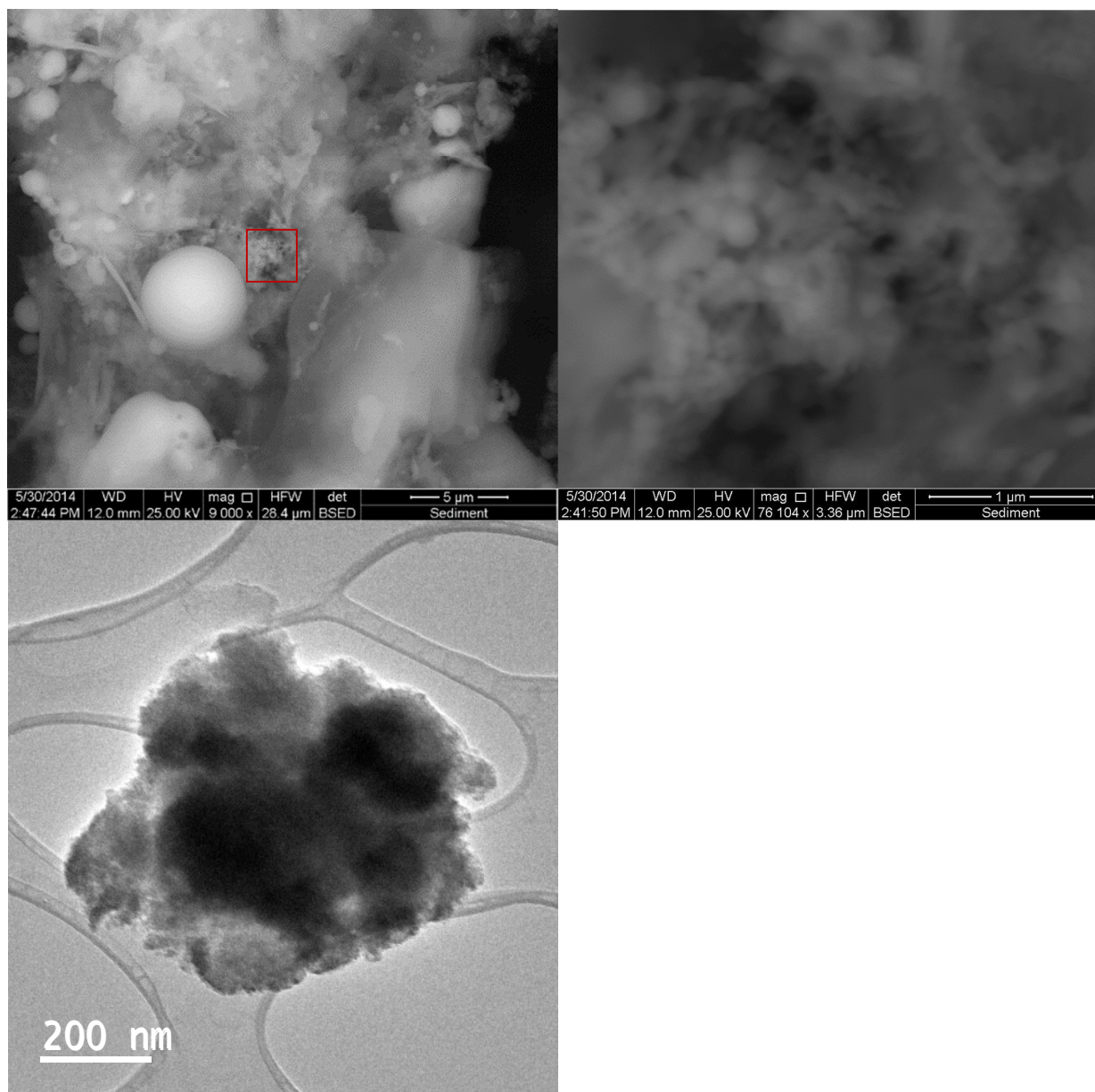


Fig. S10 SEM (top) and TEM (bottom) images of a sediment sample 2 km downstream of the spill site. SEM images show the abundance of fly ash in the sediment sample (the upper right image is at much higher magnification and shows the occurrence of ferrihydrite aggregates)

Table S1 Average concentrations of major (mg/L) and trace elements (µg/L) in <0.45 µm water

	Na	Mg	Si	S	K	Ca	Al	Ti	V	Cr	Fe
	mg/L						µg/L				
Inflow A	17.2±0.7	10.8±0.1	6.6±0.2	132±5.3	7±0.2	57.5±1.2	0.6±0.03	0.4±0.05	6±0.6	0.3±0.05	DL
Inflow B	8.7±0.4	3±0.2	5.5±0.3	11.5±0.3	1.4±0.06	9.7±0.6	0.9±0.1	0.6±0.01	11.2±0.9	0.3±0.07	8.5±0.3
Site 1	3.2±0.2	1.9±0.1	5.9±0.3	3.2±0.04	1.1±0.05	5.9±0.1	4±0.05	0.5±0.06	12.2±0.8	0.3±0.07	29.9±0.19
Site 2	4.1±0.2	2.1±0.2	6.3±0.2	3.5±0.2	1.2±0.05	5.9±0.3	6.2±0.4	1.1±0.08	10.8±0.8	0.4±0.06	83.2±4.5
Site 3	4.3±0.2	2.1±0.2	6.2±0.3	3.5±0.08	1.2±0.06	5.7±0.2	1.3±0.1	0.5±0.09	11.8±0.97	0.4±0.08	23.2±1.8
Site 4	3.4±0.2	2±0.2	6±0.3	3.2±0.2	1.1±0.05	5.7±0.2	1.3±0.09	0.4±0.001	11.7±1	0.4±0.07	15.3±1.2
Site 5	3.7±0.2	2±0.2	5.9±0.2	3.3±0.3	1.2±0.06	5.7±0.2	1.4±0.2	0.5±0.09	12.3±0.4	0.4±0.05	17.6±1.1
LOD	0.02	0.0004	0.001	0.03	0.005	0.01	0.48	0.3	0.23	0.1	0.79

Mn	Co	Ni	Cu	Zn	As	Sr	Mo	Sn	Ba
µg/L									
780.7±12.8	0.6±0.05	2.5±0.2	0.3±0.01	1.4±0.2	30.9±0.7	1502.3±12.1	36.8±1.8	0.9±0.01	56.3±1
94±2.9	0.1±0.006	0.4±0.008	1±0.06	DL	10.7±0.4	132.4±0.4	2±0.05	2.7±0.2	16.4±0.05
14.2±0.2	0.1±0.004	0.2±0.004	2.2±0.1	1.2±0.2	0.9±0.1	44.2±0.6	DL	DL	17.8±0.7
12.5±0.06	DL	0.3±0.006	0.4±0.02	3.5±0.09	1.2±0.04	45.5±1.1	1.2±0.02	2.5±0.05	18±0.6
12.1±0.2	0.1±0.008	0.2±0.01	0.5±0.01	0.7±0.03	0.8±0.07	44±0.7	DL	2.6±0.4	18±0.5
11.1±0.2	DL	0.2±0.01	0.4±0.03	DL	0.7±0.08	42.3±0.8	DL	2.5±0.4	17±0.5
8.9±0.1	DL	0.2±0.02	1.6±0.05	DL	0.7±0.07	43±0.7	DL	2.3±0.3	17.9±0.6
0.05	0.04	0.1	0.19	0.38	0.07	0.24	0.72	0.24	0.92

Table S2: Comparison of major and trace elements in Inflows and surface water; values are mean \pm the standard error of the mean. Data were log transformed for normality, then tested by a two sample t-test with unequal variance.

Element	Units	Inflows		Surface water		p	
Na	mg/L	12.3	\pm 0.96	3.7	\pm 0.105	0.008	*
Mg		5.6	\pm 1.22	2.0	\pm 0.063	0.070	
Si		6.0	\pm 0.19	6.1	\pm 0.046	0.821	
S		38.9	\pm 7.50	3.3	\pm 0.056	0.040	*
K		3.1	\pm 1.28	1.2	\pm 0.113	0.130	
Ca		23.6	\pm 3.84	5.8	\pm 0.034	0.071	
Al	μ g/L	0.7	\pm 0.29	2.2	\pm 0.626	0.001	*
Ti		0.5	\pm 0.08	0.6	\pm 0.111	0.572	
V		8.2	\pm 0.70	11.7	\pm 0.109	0.141	
Cr		0.3	\pm 0.02	0.4	\pm 0.016	0.050	*
Fe		1.2	\pm 9.17	27.4	\pm 1.663	0.069	
Mn		270.9	\pm 29.6	11.6	\pm 0.245	0.014	*
Co		0.2	\pm 0.10	0.0	\pm 0.003	0.009	*
Ni		1.0	\pm 24.2	0.2	\pm 0.007	0.069	
Cu		0.5	\pm 0.27	0.7	\pm 0.614	0.418	
Zn		0.3	\pm 0.29	0.7	\pm 0.614	0.530	
As		18.1	\pm 1.92	0.9	\pm 0.343	0.002	*
Sr		446.0	\pm 51.3	43.8	\pm 0.108	0.045	*
Mo		8.5	\pm 3.36	0.5	\pm 0.136	0.043	*
Sn		1.6	\pm 1.12	1.1	\pm 9.67	0.581	
Ba		30.4	\pm 3.17	17.7	\pm 0.068	0.227	

* denotes comparisons that were different at $p < 0.05$.

Table S3 Trace metal concentrations ($\mu\text{g/g}$) in river sediments

location	Mg	Al	V	Cr	Fe	Mn	Co	Ni	Cu	Zn	As	Sr	Mo	Sn	Ba
Site 2 (within the sediment curtain)	1159	5286	23.6	11.9	10885	172	5.2	10.4	22.6	23.2	23.2	62.1	1.2	4.2	223
Site 2 (outside of the sediment curtain)	662	4078	23.3	14.6	16154	133	4.9	15.3	29.1	24.2	29.2	52.1	1.2	2.1	364
Downstream 0.5 km	721	4087	22.7	9.1	6158	85.5	4.1	6.9	23.0	15.5	28.9	64.7	0.9	3.8	369
Downstream 1.1 km	891	4231	20.8	9.1	7530	99.3	4.4	7.2	17.4	17.2	18.4	64.6	0.6	2.1	348
Downstream 2 km	1256	6106	31.9	13.4	8285	127	6.9	11.0	30.4	30.4	22.8	69.5	0.7	1.1	299

References:

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