

Greenpeace Research Laboratories Analytical Results 2015-03

Analysis of soil, sediment and ash samples collected from an area impacted by a large spill of coal fly ash slurry from the CEO-Oltenia coal power plant in Turceni, Gorj, Romania

5th May 2015

Introduction

A total of 20 samples consisting of soil, ash, sediment or surface water were received from Greenpeace Romania for analysis at the Greenpeace Research Laboratories in 2 separate batches; the first batch was collected on 17th July 2014 and the second on 19th March 2015.

The samples were collected from an area on the outskirts of the town of Turceni, in the vicinity of the CEO-Oltenia coal power plant in Turceni, Gorj, Romania. Prior to the collection of the first batch of samples, a large spill of ash slurry had occurred from an area where ash from the coal power plant was being stored. The spill left large quantities of ash within a channel leading to the Jiu River and on land bordering the channel, including within residential areas. The second batch of samples was collected from the same area following work to remediate parts, though not all, of the affected land.

Details of the samples received are provided in Table 1a, together with GPS coordinates for the sample collection locations in Table 1b.

All samples were analysed quantitatively for the presence of a range of metals and metalloids.

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Sample	Location	Sample type	Description
1st batch, 17-07-2014			
RO14001	Residential area near CEO-Oltenia coal power plant impacted by ash spill	ash/soil	Collected from an area where the ash spill covered the soil
RO14002		ash/soil	Collected from an area where the ash spill covered the soil
RO14003		ash/soil	Collected from an area where the ash spill covered the soil
RO14004		soil	Collected from an area where ash did not impact the soil
RO14005		soil	Collected from an area where ash did not impact the soil
RO14006	ash disposal area	ash	Collected from ash slurry discharge pipe
RO14007	discharge channel	sediment	Collected from channel flowing from ash storage area to the Jiu River
RO14008	discharge channel	surface water	Collected from channel flowing from ash storage area to the Jiu River
2nd batch, 19-03-2015			
RO15001	Residential area near CEO-Oltenia coal power plant impacted by ash spill	soil	Collected from an area where ash did not impact the soil
RO15002		soil	Collected from an area where ash did not impact the soil
RO15003		soil	Collected from an area where ash did not impact the soil
RO15004		Remediated soil	Collected from an area where the ash spill covered the soil, after soil remediation work
RO15005		Remediated soil	Collected from an area where the ash spill covered the soil, after soil remediation work
RO15006		Remediated soil	Collected from an area where the ash spill covered the soil, after soil remediation work
RO15007		ash/soil	Collected from an area where the ash spill covered the soil which has not undergone remediation
RO15008		ash/soil	Collected from an area where the ash spill covered the soil which has not undergone remediation
RO15009		ash/soil	Collected from an area where the ash spill covered the soil which has not undergone remediation
RO15010		discharge channel; upper section	sediment
RO15011	separate channel	sediment	Collected from a nearby separate channel which was not impacted by the coal ash spill or any related discharges
RO15012	discharge channel; lower section	sediment	Collected from channel flowing from ash storage area to the Jiu River

Table 1a. Details of samples received and analysed at the Greenpeace Research Laboratories

Sample code	N			E		
	degree (°)	minutes (')	seconds (")	degree (°)	minutes (')	seconds (")
RO14001	44	39	5.7	23	24	29.31
RO14002	44	39	3.61	23	24	32.99
RO14003	44	39	9.5	23	24	22.48
RO14004	44	39	8.15	23	24	20.52
RO14005	44	39	8.15	23	24	20.52
RO14006	44	39	36.6	23	21	37.94
RO14007	44	39	33.72	23	22	23.67
RO14008	44	39	33.72	23	22	23.67
RO15001	44	39	157	23	24	301
RO15002	44	39	135	23	24	323
RO15003	44	39	149	23	24	325
RO15004	44	39	202	23	24	362
RO15005	44	39	171	23	24	401
RO15006	44	39	148	23	24	375
RO15007	44	39	164	23	24	382
RO15008	44	39	179	23	24	340
RO15009	44	39	215	23	24	354
RO15010	44	39	559	23	22	386
RO15011	44	39	604	23	22	899
RO15012	44	38	900	23	24	679

Table 1b. GPS coordinated of sample collection locations

Materials and methods

Heavy metal concentrations were determined for all samples by ICP atomic emission spectrometry (AES) following acid digestion and using appropriate certified reference materials in addition to intra-laboratory standards. For the water sample, both the total concentrations in the whole (unfiltered) sample and the concentrations of dissolved forms in a filtered sample were determined separately.

Results and Discussion

The results for the two batches of samples are presented in Table 2, with average values for key metal/metalloids in Table 3. These data are also presented in graphical form in Figures 1 and 2. Where the concentration was below the limits of detection for the analytical methods employed in this study the results are presented as '<xx' where xx is the method detection limit for the individual metal or metalloid.

3.1 Batch 1 (17-07-2014)

The samples of ash/soil (RO14001-03) and the sediment sample (RO14007) had higher concentrations of arsenic and copper, and to a lesser extent vanadium, compared to the two samples of soil not impacted by the ash (RO14004-05). In contrast, concentrations of lead and manganese were somewhat lower in the ash/soil (RO14001-03) and sediment sample (RO14007) compared to the soil samples (RO14004-05).

These differences were reflected in the concentrations for the ash sample (RO14006), which had higher concentrations of arsenic and copper, and to a lesser extent vanadium, compared to the soil samples (RO14004-05), as well as somewhat lower concentrations of lead and manganese.

A similar pattern was found for pH values; higher values (more alkaline) were found for samples of ash (RO14006; pH 8.33), sediment (RO14007; pH 8.66) and ash/soil (RO14001-03; pH 7.86-8.89) compared to soil not impacted by the ash (RO14004-05; pH 6.54-6.58).

Concentrations in the ash sample (RO14006) were generally low compared to typical concentration ranges reported for coal fly ash (EPRI 2009), though the composition of coal fly ash can vary depending on the type of coal being burned as well as other factors, including burning conditions.

Arsenic and manganese were also detected in the water sample (RO14008), though at concentrations not unusual for uncontaminated surface waters.

Sample code	Batch 1 (17-07-2014)									Batch 2 (19-03-2015)												
	RO14001	RO14002	RO14003	RO14004	RO14005	RO14006	RO14007	RO14008		RO15001	RO15002	RO15003	RO15004	RO15005	RO15006	RO15007	RO15008	RO15009	RO15010	RO15011	RO15012	
	type	A/S	A/S	A/S	S	S	A	Sed	SW		S	S	S	RS	RS	RS	A/S	A/S	A/S	Sed	Sed	Sed
	(mg/kg dw)							(µg/l)		(mg/kg dw)												
pH	7.86	8.89	8.84	6.58	6.54	8.33	8.66	-	-	6.68	6.65	6.35	8.20	7.88	7.85	8.09	7.84	8.35	8.72	8.05	8.62	
Antimony	<10	<10	<10	<10	<10	<10	<10	<100	<100	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Arsenic	43	34	30	8	7	20	52	19	19	7	8	7	24	16	16	28	49	34	44	6	41	
Cadmium	1	2	2	1	1	1	2	<5	<5	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chromium	53	69	64	59	65	66	59	<10	<10	64	62	69	72	69	53	53	50	71	64	43	69	
Cobalt	13	16	16	15	17	14	14	<20	<20	17	18	17	15	15	13	12	13	16	15	12	16	
Copper	45	58	54	24	26	53	46	<10	<10	18	19	20	37	31	29	35	40	52	45	21	51	
Lead	6	8	7	15	16	7	7	<50	<50	18	18	16	17	16	15	5	9	9	9	16	10	
Manganese	217	274	256	499	579	209	325	64	70	747	807	595	452	514	529	280	323	320	348	482	377	
Mercury	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<2	<2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Molybdenum	4	<4	4	<4	<4	4	<4	<30	<30	<2	<2	<2	2	3	3	4	5	5	4	<2	5	
Nickel	59	73	69	51	56	68	64	<20	<20	38	40	46	61	56	45	51	56	68	64	34	69	
Selenium	<40	<40	<40	<40	<40	<40	<40	<10	<10	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	
Vanadium	131	89	84	51	55	78	75	<20	<20	63	64	64	75	71	57	86	88	90	85	41	86	
Zinc	54	70	66	75	82	53	55	<5	6	64	65	70	100	94	90	44	62	68	66	69	77	

Table 2. pH values and concentrations of metals and metalloids in samples of ash (A), ash/soil (A/S), remediated soil (RS), soil not impacted by ash spill (S) and channel sediment (Sed) (mg/kg dry weight), and in filtered (filt.) and whole (wh.) surface water sample (SW) (µg/l).

	Batch 1		Batch 2		
	RO14001-03	RO14004-05	RO15001-03	RO15004-06	RO15007-09
	A/S	S	S	RS	A/S
pH	8.53 (0.6)	6.56 (0.03)	6.56 (0.2)	7.98 (0.2)	8.09 (0.3)
Arsenic	36 (7)	8 (0.5)	7 (0.3)	19 (5)	37 (11)
Copper	52 (7)	25 (1)	19 (1)	32 (4)	42 (8)
Molybdenum	4 (-)	<4 (-)	<2 (-)	3 (0.3)	5 (0.7)
Vanadium	101 (26)	53 (3)	64 (0.5)	67 (9)	88 (2)
Lead	7 (1)	15 (0.7)	17 (1)	16 (0.8)	8 (2)
Manganese	249 (29)	539 (57)	716 (109)	498 (41)	308 (24)
Zinc	63 (9)	78 (5)	66 (4)	94 (5)	58 (13)

Table 3. Average pH values and concentrations of key metals/metalloids, with standard deviations given in brackets, for samples of ash (A), ash/soil (A/S), remediated soil (RS) and soil not impacted by ash spill (S) (mg/kg dry weight)

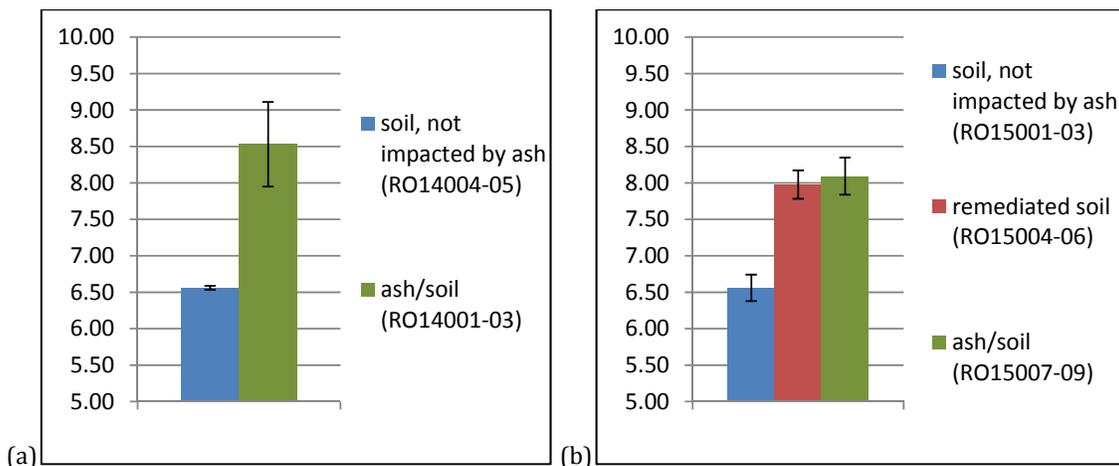


Figure 1. Average pH values, with bars indicating standard deviations, for samples of ash/soil (A/S), soil not impacted by ash spill (S) and remediated soil (RS) for samples from (a) Batch 1 and (b) Batch 2

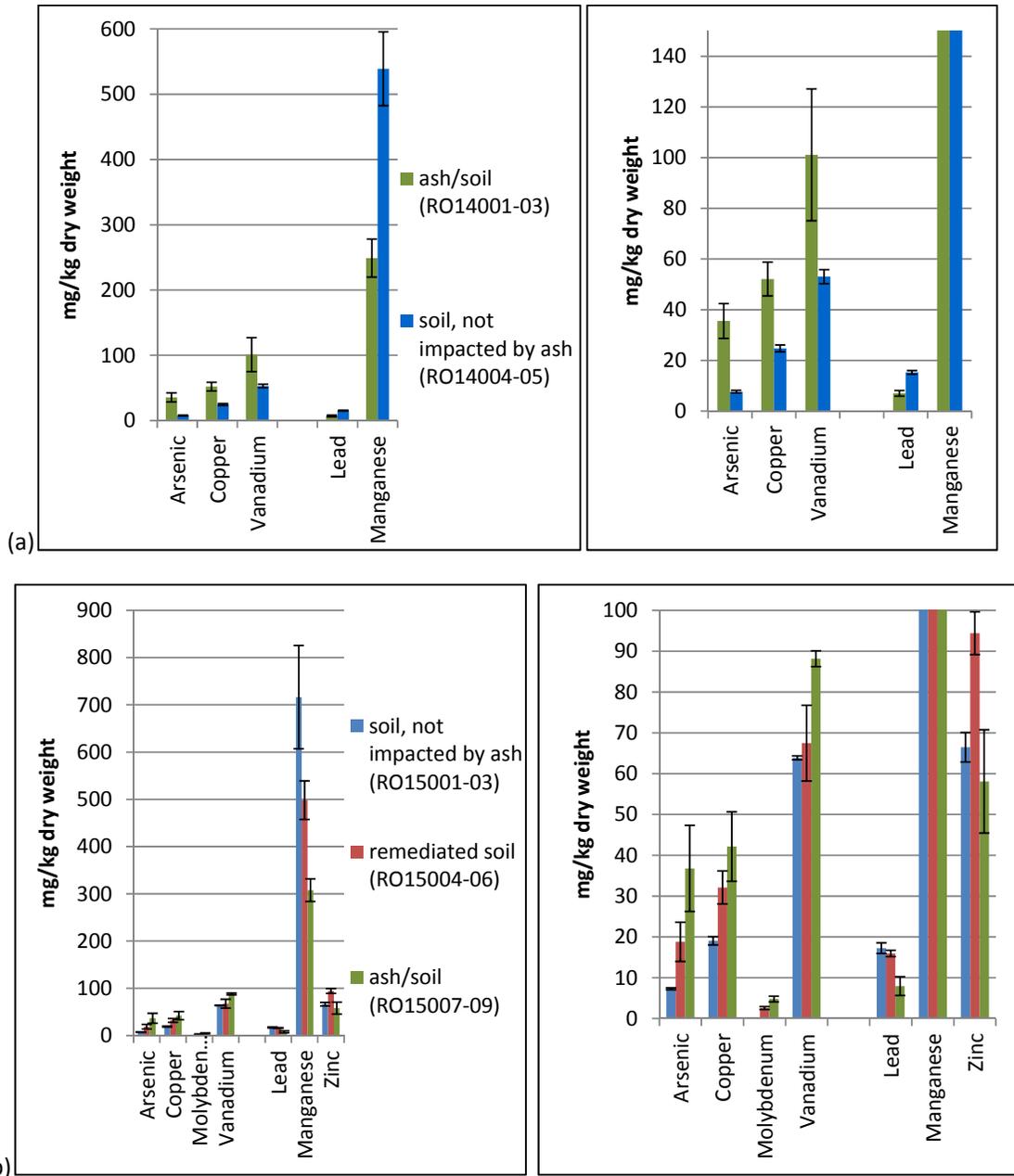


Figure 2. Average concentrations of key metals/metalloids, with bars indicating standard deviations, for samples of ash/soil (A/S), soil not impacted by ash spill (S) and remediated soil (RS) for samples from (a) Batch 1 and (b) Batch 2

3.2 Batch 2 (19-03-2015)

For the second batch of samples, the pH values and concentrations of metals/metalloids for different types of samples were very similar to the equivalent samples from the first batch, including soil not impacted by ash (RO15001-03), ash/soil samples (RO15007-09) and sediment from the channel flowing from ash storage area to the Jiu River (RO15010 & RO15012).

As for the first batch, the samples of ash/soil (RO15007-09) and the sediment samples (RO15010 & RO15012) had higher pH values and higher concentrations of arsenic and copper compared to the samples of soil not impacted by the ash (RO15001-03). There was also difference in the concentrations of vanadium between ash/soil samples and uncontaminated soil, though to a lesser extent compared to the first batch of samples. In addition, molybdenum concentrations were higher in samples of ash/soil and channel sediment compared to unimpacted soil for the second Batch.

Concentrations of lead and manganese were lower in the samples of ash/soil and of sediment compared to the samples of soil not impacted by the ash, as was the case for the first batch.

Comparing the data for the remediated soil samples (RO15004-05) with those of unimpacted soil (RO15001-03), the pH values were higher for remediated soils, being very similar to those for ash/soil samples. Similarly, concentrations of arsenic, copper and molybdenum were higher in the remediated soil samples compared to unimpacted soil samples, though to a lesser extent than for the ash/soil samples. As for ash/soil samples, concentrations of manganese in the remediated soil samples were lower than for unimpacted soil samples, though a similar pattern was not seen for lead.

Comparing sediment from the channel flowing from ash storage area to the Jiu River (RO15010 & RO15012) to sediment from a nearby separate channel which was not impacted by the coal ash spill or any related discharges (RO15011), there were higher concentrations of arsenic, copper, molybdenum and vanadium, and lower concentrations of lead and manganese. The pH values of samples from the impacted channel were slightly higher than that for the unimpacted channel, though all sediment samples were alkaline (pH>7). These data show a similar pattern to that found between samples of ash/soil and of remediated soil with samples of soil not impacted by the ash.

3.2 Statistic significance of observed differences

Measures of the statistic significance of comparisons noted above between different types of samples were made using t-test for each of the two batches (Table 4). It should be noted that the statistic power of these comparisons is low due to the relatively small number of replicates for each set of samples, especially for the first batch of samples in which there were only two samples of unimpacted soil.

In most cases, reported differences were found to be significant using the t-test analysis at the 0.05 level, with some at the more significant 0.01 level. Notable exceptions were the difference between concentrations of some elements in remediated soils samples (RO15004-06) and unimpacted soil samples (RO15001-03) from the 2nd batch; lead, vanadium and to a lesser extent arsenic and manganese. However, the lack of statistically significant differences in these cases may be due to the relatively low number of replicates, especially for arsenic and manganese.

	Batch 1	Batch 2	
Set 1	Ash/soil (RO14001-03)	Remediated soil (RO15004-06)	Ash/soil (RO15007-09)
Set 2	Unimpacted soil (RO14004-05)	Unimpacted soil (RO15001-03)	Unimpacted soil (RO15001-03)
pH	0.027 (*)	0.001 (**)	0.002 (**)
Arsenic	0.019 (*)	0.053	0.040 (*)
Copper	0.015 (*)	0.025 (*)	0.041 (*)
Lead	0.002 (**)	0.223	0.008 (**)
Manganese	0.053	0.060	0.019 (*)
Molybdenum	-	0.016 (*)	0.011 (*)
Vanadium	0.083	0.569	0.001 (**)

Table 4. Statistical significance of differences between sets of samples using t-test (2 tail, non-equal variance), noting significant differences at a 0.05 level (*) and at a 0.01 level (**). For samples with non-detect values, the t-test was calculated using 0.5 times the detection limit.

For more information please contact:

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References

EPRI (2009) Coal Ash: Characteristics, Management, and Environmental Issues. Electric Power Research Institute (EPRI). Report 1019022, September 2009, 12pp.
<http://www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000000001019022>

Appendix 1: Details of methodologies

Preparation

Water sample: To obtain total metal concentrations, a representative portion of the whole water sample was acidified by the addition of concentrated nitric acid to give a final concentration of 10% v/v. Separately, a portion of the whole sample was filtered through a 0.45 micron filter and then acidified in the same way to enable determination of dissolved metal concentrations. 50 ml of each acidified sample was digested firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180°C over 15 minutes followed by holding at 180°C for a further 15 minutes. Cooled digests were filtered and made up to 50 ml with deionised water.

Soil, sediment and ash samples: A representative portion of each sample was air dried to constant weight, homogenised, sieved through a 2mm mesh and then ground to a powder using a pestle and mortar. Approximately 0.5 g of the dried and ground sample was digested with 2 ml concentrated hydrochloric acid and 8 ml concentrated nitric acid, firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180°C over 15 minutes followed by holding at 180°C for a further 15 minutes. Following cooling, the digest was filtered and made up to 50ml with deionised water.

Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian MPX Simultaneous Spectrometer. Multi-element standards at concentrations of 0.5, 1.0, 2.5 and 5.0 mg/l respectively, and matrix matched to the samples, were used for instrument calibration. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed. Analysis of the mercury and arsenic content in the samples was carried out separately using cold vapour generation ICP-AES. Through reaction of the sample with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar), ionic mercury was reduced to elemental mercury, Hg (0), and ionic arsenic was converted to arsenic hydride (AsH₃). The elemental mercury and arsenic hydride vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared; One with Hg at 10 µg/l and As at 50 µg/l, and a second with Hg at 20 µg/l and As at 100 µg/l, both matrix matched to the samples.

Quality control

Three samples (two soil samples and one ash/soil sample) were prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample (10% v/v nitric acid in deionised water). To check the method efficiency, three certified reference material (CRM) samples were prepared in an identical manner; GBW07311, stream sediment certified by the China National Analysis Centre for Iron and Steel, Beijing, China; LGC6187, leachable metals in river sediment certified by the Laboratory of the Government Chemist, UK; and LGC6180, Pulverised Fuel Ash certified by the Laboratory of the Government Chemist, UK.

One water sample was prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample (10% v/v nitric acid in deionised water), and two mixed metal quality control solution of 0.4 mg/l and 4 mg/l, other than mercury at 0.2 mg/l and 0.8 mg/l. All control samples were prepared in an identical manor to the samples.

Calibration of the ICP-AES was validated by the use of quality control standards at 4 mg/l and 0.4 mg/l prepared in an identical manner but from different reagent stocks to the instrument calibration standards. For cold vapour generation mercury and arsenic analysis, the calibration was validated using a quality control standards with mercury (16 µg/l) and arsenic (80 µg/l), prepared internally from different reagent stock.

pH

To determine the pH of each soil, sediment or ash sample, 10 ml deionised water was added to a 10 g portion of air dried homogenised sample, the slurry was mixed well and allowed to stand to 10 minutes. The pH of the slurry was determined using a Hanna Instruments HI98129 pH meter calibrated using pH 4.01, pH 7.01 and pH 10.01 Hanna buffer solutions. The pH meter and electrode was rinsed with deionised water between samples.

Further details of the methods employed can be provided on request.