Greenpeace Research Laboratories Analytical Results 2017-06

Metal/metalloid concentrations for ambient airborne particulates (PM_{total}) collected in the vicinity of the DangJin coal fired power station in the Republic of Korea.

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1. Introduction

Two samples of airborne PM_{total} particulates that had been collected on cellulose acetate filters using an active personal particulate monitor were received at the Greenpeace Research Laboratories from Greenpeace East Asia (Korea) on 15th May 2017. According to documentation supplied, the samples were collected between 16th and 25th January 2017 from locations in the vicinity of the DangJin coal fired power plant (CFPP) in The Republic of Korea.

The samples were collected from ambient air at two separate locations using two identical air sampling devices operating at a flow rate of 3 litres per minute. Both sampling periods were started at approximately the same time, though due to a technical fault with one device, the samples were then collected over different total time periods (just over 8 days at one location and a little under 2 days at the second location). Details provided by Greenpeace East Asia (Korea) for the samples received are shown in Table 1, including GPS coordinates for the sampling locations.

Each sample was analysed quantitatively for the presence of a range of metals and metalloids within the particulate fraction bound to the filter, and used to calculate average concentrations in the air passing through the filters during the investigation period, correcting for the differences in total air volumes sampled at the two locations.

Sample code	Area	Location	Coord-inates	Start date	Start time	Sampling time (hrs)	Sampling volume (m^3)
KR17001	Dangjinsi, Chuncheongnam-do, S.Korea City	roof of 4 story building, Eupnea-dong 211. 21.36 km from Dangjin CFPP	36°53' 36.99"N 126°37' 40.92"E	16.01.17	13:57	199	35.9
KR17002		roof of 2 story building, 960 Sambong-ri, Seokmun-myeon. 5.85km from Dangjin CFPP	37° 0' 48.65"N 126°32' 20.64"E	16.01.17	14:23	45.5	8.18

Table 1: details of samples collected from locations in the vicinity of the DangJin CFPP in The Republic of Korea

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2. Materials and methods

Samples were collected using an active personal particulate monitor (MIE pDR-1500) fitted with a cellulose acetate filter (Pall GN-4 Metricel MCE membrane disc filter, 0.8 μm pore size, 37 mm diameter), using a flow rate of 3.00 litres/minute combined with the appropriate inlet for PM_{total} airborne particulates. Following the collection period, the filter was removed from the monitor using clean plastic tweezers and transferred to a petri dish which was immediately sealed, and in which the filter was stored during transport to the analytical laboratory.

The mass of each metal/metalloid within the PM_{total} particulate fraction bound to the filter was determined by acid digestion of the filter followed by analysis using inductively coupled plasma – mass spectrometry (ICP-MS). The concentrations of metal/metalloids per unit of filtered air (ng/m^3) were calculated using the air filtering flow rate and total collection time in order to calculate the total volume of air that had passed through each filter. In addition, the average PM_{total} concentrations during the sampling period are given, as determined by the particulate monitor.

3. Results and Discussion

The results for the samples are reported in Table 2 (concentrations of particulate bound metal/metalloids in air) and Table 4 (concentrations of metal/metalloids in PM_{total} particulates). In some cases, concentrations were below limits of detection for the analytical method employed and these are shown in the results tables as '<xx', where xx is the method detection limit for the individual analyte for that sample.

In the case of sample KR17002, the filter showed little or no visual colouration that would be expected over to the sampling period with the average PM_{total} concentration during that period. The reason for this is not clear, but does suggest some form of malfunction during the sample collection for KR17002.

The average PM_{total} concentrations for the monitoring site closest to the CFPP (KR17002) was 44.6 μg/m^3, while that for the monitoring station located further from the CFPP and over a longer time period (KR17001) was 92.8 μg/m^3. No relevant regulatory limits or guideline values are set for PM_{total} concentrations, in Korea or elsewhere, as limit values tend to focus on those particulate fractions that are recognised as more inherently harmful to health (normally PM_{10} or $PM_{2.5}$).

Although some guideline values are applicable for concentrations of certain metals and metalloids in air, such as those for annual average metal/metalloid concentrations in the air set by the WHO (see Table 3; WHO 2000, 2005) and the particulate-bound concentrations of lead set by the South Korean Government Ministry of Environment (MOE 2011), average concentrations in air for both samples KR17001 and 2 were far below any of these guidelines.

It must be noted, in any case, that both The Republic of Korea limit and the WHO guideline values for concentrations of certain metal/metalloids in the air, as set out in Table 3, are given as annual average concentrations. Concentration limits set on an annual average basis cannot be directly compared with data from these samples, which were collected over shorter time periods, though they do provide a useful guide for comparison nonetheless.

Sample code	KR17001	KR17002
Start date	16.01.17	16.01.17
Sampling period (hr)	199	45.5
PM_{total} average (µg/m^3)	44.6	92.8
Metal/metalloid (ng/m^3)		
Aluminium	120	<20
Antimony	1.7	<0.05
Arsenic	1.2	<0.1
Barium	4.32	2.7
Beryllium	<0.01	<0.02
Cadmium	0.56	<0.05
Chromium	<0.1	9.3
Cobalt	<0.03	<0.1
Copper	3	<2
Iron	170	33
Lead	7.1	0.5
Manganese	5.6	0.6
Mercury	<0.03	<0.1
Molybdenum	0.37	0.07
Nickel	2.8	0.8
Selenium	0.2	<0.5
Strontium	1.2	0.7
Titanium	9.5	<1
Vanadium	0.9	<0.2
Zinc	17	<10

Table 2. Average concentration of PM_{total} particulates (µg/m^3) within air over the sampling period, and average concentrations of metal/metalloids in air (ng/m^3) within the PM_{total} particulates collected during that period.

For both samples, the air concentrations (ng metal/m^3) were generally lower than for 4 samples collected in nearby locations and using identical equipment in 2015 (GRL 2016). Where detected, metal/metalloid concentrations for KR17002 (ng/m3) were lower than those for KR17001, as may be expected from the lack of any visible colouration of the filter in the former case. As noted above, the reason for this anomaly is not known, but could relate to technical problems with the air sampling device in this case..

Metal/metalloid concentrations calculated by mass of PM_{total} particulate material (ng metal/ug PM_{total}) are presented in Table 4. These data give information about the average composition of the PM_{total} particulates for each sample. The values for KR17001 are reasonably similar to, though generally slightly lower than, those for 4 samples collected from the same area in 2015 (GRL 2016), though it must be kept in mind that those previously reported concentrations were for metals exclusively on the $PM_{2.5}$ particulate fraction, which typically contains higher metal/metalloid concentrations than the PM_{total} fraction (Duan *et al*. 2012).

Metal/metalloid concentration limit (ng/m^3)		
	The Republic of Korea Annual time weighted average [(a)]	WHO Guidelines Annual mean [(b)]
Cadmium	-	5
Lead	500	500
Manganese	-	150
Mercury	-	1000

Table 3. Regulatory limits and guideline values set by the Government of The Republic of Korea and the World Health Organisation (WHO). (a) The Republic of Korean air quality standards and air pollution level, based on PM_{10} derived concentrations (MOE 2011); (b) WHO air quality guidelines (WHO 2000, 2005)

The values (ng metal/ug PM_{total}) for KR17002 are notably lower than for KR17001, indicating that the material collected on that filter (KR17002) is of a somewhat different composition to that of the other sample (KR17001), especially for metals such as iron, lead and manganese which are usually reasonably prevalent in outdoor PM samples. These results suggest that material on the filter for KR17002 is not predominantly ambient air PM_{total} particulates, which is consistent with the visual appearance of the filter.

Sample code	KR17001	KR17002
Start date	16.01.17	16.01.17
Sampling period (hr)	199	45.5
PM_{total} average (µg/m^3)	44.6	92.8
Metal/metalloid (ng/µg PM_{total})		
Aluminium	1.2	<0.5
Antimony	0.018	<0.001
Arsenic	0.013	<0.003
Barium	0.035	0.061
Beryllium	<0.0001	<0.0005
Cadmium	0.0051	<0.001
Chromium	<0.001	0.21
Cobalt	<0.0003	<0.003
Copper	0.03	<0.05
Iron	1.7	0.7
Lead	0.074	0.01
Manganese	0.06	0.01
Mercury	<0.0003	<0.003
Molybdenum	0.004	0.001
Nickel	0.02	0.02
Selenium	<0.001	<0.01
Strontium	0.007	0.01
Titanium	0.1	<0.03
Vanadium	0.009	<0.005
Zinc	0.15	<0.3

Table 4. Average concentration of PM_{total} particulates (µg/m^3) within air over the sampling period, and average concentrations of metal/metalloids within the particulates collected during that period (ng/µg PM_{total})

For more information please contact: Kevin Brigden or David Santillo

Disclaimer: Description of samples and sampling sites are purely according to information supplied with the samples by Greenpeace East Asia (Korea).

4. References

Duan, J., Tan, J., Wang, S., Hao, J., Chai, F. (2012) Size distributions and sources of elements in particulate matter at curbside, urban and rural sites in Beijing. Journal of Environmental Sciences, 24(1): 87–94

GRL (2016) Metals concentrations for ambient airborne particulates (PM2.5) collected close to the DangJin coal fired power station in the Republic of Korea. Greenpeace Research Laboratories (GRL) Analytical Results 2016-01, January 2016: 6 pp. http://www.greenpeace.to/greenpeace/wp-content/uploads/2016/06/Analytical-Results-Korea-PM-metals-AR-01-2016-FINAL-for-publication.pdf

MOE (2011) Air Quality Standards and Air Pollution Level, Ministry of Environment (MOE), Republic of Korea Government. http://eng.me.go.kr/eng/web/index.do?menuId=253

WHO (2000) World Health Organisation (WHO) Air quality guidelines for Europe, 2nd Edition. www.euro.who.int/__data/assets/pdf_file/0005/74732/E71922.pdf

WHO (2005) World Health Organisation (WHO) Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide, Global update 2005. http://www.who.int/phe/health_topics/outdoorair/outdoorair_aqg/en/

Appendix 1: Details of methodologies

For each sample, the filter was transferred into a digestion vessel, to which was added 1 ml concentrated nitric acid. The samples were digested using microwave-assisted digestion with a CEM MARS Xpress system with a temperature ramp to 180°C over 20 minutes followed by holding at 180°C for a further 20 minutes. Following cooling to room temperature the digest was filtered and made up to 10 ml with deionised water. In all cases no material from the filter remained after the digestion process. To determine the concentrations of metal/metalloids in the filter material, three unused but otherwise identical filters were separately digested in an identical manner to that used for the sample filters.

Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent 7900 Spectrometer utilizing a collision cell with helium as the collision gas to minimize polyatomic interferences. Multi-element standards, matrix matched to the samples, were used for instrument calibration (at concentrations of 1, 10, 100 and 1000 μg/l respectively, other than for mercury; 1, 2, 5 μg/l respectively). Analysis employed in-line addition of an internal standard mix at 500 μg/l (Scandium, Germanium, Yttrium, Indium and Terbium).

Quality control

With the batch of samples, the digestion procedure employed a blank digest sample (1 ml nitric acid). To check the method efficiency, a reference material (CRM) sample was prepared in an identical manner; LGC6180 Pulverised Fuel Ash, assessed by LGC, UK.

Calibration of the ICP-MS was validated by the use of quality control standards at 800 μg/l and 80 μg/l (4 μg/l for mercury) prepared in an identical manner but from different reagent stocks to the instrument calibration standards.