

Greenpeace Research Laboratories Analytical Results 2016-01

Metals concentrations for ambient airborne particulates (PM_{2.5}) collected close to the DangJin coal fired power station in the Republic of Korea.

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1. Introduction

Four samples of airborne PM_{2.5} particulates that had been collected on cellulose acetate filters using an active personal particulate monitor were received at the Greenpeace Research Laboratories from Greenpeace Korea on 23rd December 2015. According to documentation supplied, all samples were collected between 14th and 16th December 2015 from a location 4.5 km south-southeast of the DangJin coal fired power station in The Republic of Korea.

The samples were collected from ambient air during two time periods, the first for a period of approximately 12 hours and the second of approximately 14 hours. On each occasion, two samples were collected using two separate devices located adjacent to each other. Details provided by Greenpeace Korea for the samples received are shown in Table 1, including GPS coordinates for the sampling location.

Each sample was analysed quantitatively for the presence of a range of metals within the particulate fraction bound to the filter.

Sample code	Area	Location	Coordinates	Start date	Start time	Sampling time (hrs)	Sampling volume (m ³)
SK15001	Godae-Meon, Dangjinsi, Chuncheongnam -do, S.Korea City	roof of the 1 story Kyoro-Ri Townhall building	37° 1'8.24"N 126°31'27.80"E	14.12.15	14.09	12.00	1.094
SK15002				14.12.15	14.09	11.75	1.072
SK15003				15.12.15	14.33	13.30	1.213
SK15004				15.12.15	14.33	13.78	1.257

Table 1: details of samples collected from a location in The Republic of Korea at different times

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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 Metrical MCE membrane disc filter, 0.8 µm pore size, 37 mm diameter), using a flow rate of 1.52 litres/minute combined with the appropriate inlet cyclone for PM_{2.5} airborne particulates.

Following each 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 within the PM_{2.5} particulate fraction bound to the filter was determined by acid digestion of the filters followed by analysis using inductively coupled plasma – mass spectrometry (ICP-MS). The concentrations of metals per unit of filtered air (ng/m³) 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_{2.5} 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 metals in air within PM_{2.5} particulates) and Table 4 (concentrations of metals in PM_{2.5} particulates). In some cases, concentrations in samples analysed 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.

The data show acceptable agreement between the two instruments for concentrations of PM_{2.5} particulates. The concentrations of PM_{2.5} differed from the average value of the two readings by 15% and by 22% for the first and second set of measurements, respectively. Similarly, the concentrations of each metal in particulates collected by the two instrument were in good agreement for both time periods.

The average PM_{2.5} concentrations for the first time period (78.20 µg/m³ and 91.14 µg/m³) were 2-3 times higher than those for the second period (27.37 µg/m³ and 34.03 µg/m³). This was reflected in the concentration of metals per volume of air. Where detected, concentrations of individual metals differed by approximately the same ratio between the two time periods, with higher concentrations obtained for filters from the first period.

Relevant regulatory limits and guideline values, where set, are presented in Table 3. The average PM_{2.5} concentrations for the first set of readings (SK15001 & SK15002) were higher than the 24 hour average limit of 50 µg/m³ set by the South Korean Government Ministry of Environment (MOE 2011), the highest being 1.8 times the limit. Furthermore, for all samples, the average PM_{2.5} concentrations were higher than the more stringent 24 hour mean guideline value of 25 µg/m³ set by the World Health Organisation (WHO). The values for the first time period were 3.1-3.6 times the WHO guideline value, while the values for the second time period were 1.1-1.4 times this guideline value (WHO 2005).

Sample code	SK15001	SK15002	SK15003	SK15004
Start date	14.12.15	14.12.15	15.12.15	15.12.15
Sampling period (hr)	12.00	11.75	13.30	13.78
PM _{2.5} average (µg/m ³)	78.20	91.14	27.37	34.03
Metal (ng/m ³)				
Antimony	3	4	<2	<2
Arsenic	4	7	2	2
Barium	<20	<20	<20	<20
Beryllium	<0.5	<0.5	<0.5	<0.5
Cadmium	1	1	<0.8	<0.8
Chromium	<200	<200	<200	<200
Cobalt	<0.5	<0.5	<0.5	<0.5
Copper	<30	<30	<30	<30
Gallium	<0.5	<0.5	<0.5	<0.5
Iron	230	260	400	<200
Lead	<30	<30	<30	<30
Manganese	24	26	8	6
Mercury	<5	<5	<5	<5
Molybdenum	1	1	<0.8	<0.8
Nickel	<5	<5	<5	<5
Selenium	<1	<1	<1	<1
Strontium	<10	<10	<10	<10
Vanadium	2.7	2.8	<0.8	<0.8
Zinc	<90	<90	<90	<90

Table 2. Average concentration of PM_{2.5} particulates (µg/m³) within air over the sampling period, and average concentrations of metals in air (ng/m³) within the PM_{2.5} particulates collected during that period.

Most metals were not present at detectable concentrations. This was predominantly due to the concentrations of PM_{2.5} during the sampling periods being somewhat lower than for previous investigations and the relatively short time period over which the particulates were collected (11.75-13.78 hours), which resulted in lower quantities of PM_{2.5} particulates collected on each filter.

None of the samples contained any metal at a concentration in air higher than the guideline values for annual average metal concentrations in the air set by the WHO (see Table 3; WHO 2000, 2005). In addition, none of the samples revealed particulate-bound concentrations of lead exceeding the annual average limit for lead set by the South Korean Government Ministry of Environment (MOE 2011).

It must be noted that both The Republic of Korea limit and the WHO guideline values for concentrations of certain metals 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 time periods of approximately 12-14 hours, but the guideline values do provide a useful guide for comparison nonetheless.

	The Republic of Korea annual (24 hour) time weighted average ^(a)	WHO Guidelines annual (24 hour) mean ^(b)
PM _{2.5} (µg/m ³)	25 (50)	10 (25)
Metal concentration limit (ng/m³)		
Arsenic	-	
Cadmium	-	5
Lead	500	500
Manganese	-	150
Mercury	-	1000

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

Metal concentrations by mass in PM_{2.5} particulates are presented in Table 4. These data give information about the average composition of the PM_{2.5} particulates for each sample. For the metals present at detectable concentrations, the average composition of the PM_{2.5} particulates were similar for all four samples, with the exception of the somewhat higher iron concentration in SK15003 (15 ng/µg PM_{2.5}), though not in the other sample collected during the same time period (SK15004). The reason for the higher iron concentration in the PM_{2.5} particulates in this one sample (SK15003) is not clear.

Sample code	SK15001	SK15002	SK15003	SK15004
Start date	14.12.15	14.12.15	15.12.15	15.12.15
Sampling period (hr)	12.00	11.75	13.30	13.78
PM _{2.5} average (µg/m ³)	78.20	91.14	27.37	34.03
Metal (ng/µg PM_{2.5})				
Antimony	0.04	0.04	<0.06	<0.05
Arsenic	0.05	0.07	0.06	0.07
Barium	<0.2	<0.2	<0.6	<0.5
Beryllium	<0.006	<0.005	<0.02	<0.01
Cadmium	0.01	0.01	<0.03	<0.02
Chromium	<2	<2	<6	<5
Cobalt	<0.006	<0.005	<0.02	<0.01
Copper	<0.4	<0.4	<1	<0.8
Gallium	<0.006	<0.005	<0.02	<0.01
Iron	2.9	2.8	15	<5
Lead	<0.4	<0.3	<0.9	<0.7
Manganese	0.31	0.28	0.29	0.18
Mercury	<0.05	<0.05	<0.2	<0.1
Molybdenum	0.01	0.01	<0.03	<0.02
Nickel	<0.006	<0.005	<0.02	<0.01
Selenium	<0.01	<0.01	<0.03	<0.02

Strontium	<0.1	<0.1	<0.3	<0.2
Vanadium	0.035	0.031	<0.03	<0.02
Zinc	<1	<1	<3	<2

Table 4. Average concentration of PM_{2.5} particulates (µg/m³) within air over the sampling period, and average concentrations of metals within the particulates collected during that period (ng/µg PM_{2.5}).

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 Korea.

4. References

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 metals 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; 0.5, 5, 50 µg/l respectively). Analysis employed in-line addition of an internal standard mix at 1000 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 certified reference material (CRM) sample was prepared in an identical manner; 2584, Trace Elements in Indoor Dust, certified by the National Institute of Standards and Technology (NIST).

Calibration of the ICP-MS was validated by the use of quality control standards at 800 µg/l and 80 µg/l (40 µg/l and 4 µg/l for mercury) prepared in an identical manner but from different reagent stocks to the instrument calibration standards.