Greenpeace Research Laboratories Analytical Results 2015-09

Metals concentrations for ambient airborne particulates ($PM_{2.5}$ or PM_{total}) collected at various locations in Delhi, India.

December 2015

1. Introduction

Ten samples of airborne particulates that had been collected on cellulose acetate filters using an active personal particulate monitor were received at the Greenpeace Research Laboratories from Greenpeace India on 16th November 2015. In the case of 9 of the samples, the sampling device had been configured to collect $PM_{2.5}$ airborne particulates, while in the remaining sample it was configured to collect total particulates (PM_{total}). According to documentation supplied, all samples were collected between 16th October 2015 and 10th November 2015, from locations in Delhi, India.

Seven of the samples were collected from ambient air over periods of approximately 24 hours, with three samples being collected in a similar way but over shorter time periods. Details provided by Greenpeace India for the samples received are provided in Table 1, including GPS coordinates for each sampling location.

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

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Sample code	Area	location	Coordinates	Start date	Start time	Sampling time (hrs)	Sampling volume (m^3)
IN15001	Chandni chowk	Red fort to India gate (car free day)	28°39'22.27" N 77°14'27.60" E	21.10.2015	07:38:01	4.10	0.374
IN15002 (a)	SafdarJung enclave	Greenpeace Guest House	28°33'46.54" N 77°11'29.71" E	17.10.2015	17:41:24	13.44	2.418
IN15003	West kidwai nagar	Dilli Haat	28°34'23.74" N 77°12'23.16" E	18.10.2015	09:33:48	7.47	0.681
IN15005	Dhaula kuan	Army Public School	28°36'00.49" N 77°10'05.41" E	28.10.2015	09:09:22	23.33	2.128
IN15006	Yusuf sarai	BMDAV School	28°33'35.36" N 77°12'24.83" E	29.10.2015	12:32:43	25.59	2.334
IN15007	Paschim vihar	Shah International School	28°39'52.07" N 77°04'59.58" E	03.11.2015	10:12:43	21.78	1.987
IN15008	Tagore garden	Holy Child School	28°39'02.25" N 77°06'52.34" E	04.11.2015	10:27:59	21.66	1.975
IN15009	Meera bagh	St. Marks Senior Secondary School	28°37'12.01" N 77°04'42.74" E	06.11.2015	10:06:06	20.84	1.901
IN15010	Pusp vihar, saket	Andra Education Society	28°31'50.89" N 77°13'27.39" E	09.11.2015	11:12:29	23.95	2.184
IN15011	Meera bagh	St. Marks Senior Secondary School (Empty Class Room)	28°37'12.01" N 77°04'42.74" E	16.10.2015	13:10:27	24.49	2.234

Table 1: details of samples collected from various locations in Delhi, India. (a) filter for total particulates (PM_{total})

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 either 1.52 litres/minute combined with the appropriate inlet cyclone for $PM_{2.5}$ airborne particulates, or 3.00 litres/minute for total particulates (PM_{total}).

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 within the $PM_{2.5}$ or 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 metals 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 and peak $PM_{2.5}$ or 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, with relevant regulatory limits and guideline values, where set, presented in Table 3.

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. In addition to the data presented in Table 2, all samples were also analysed semi-quantitatively for palladium, platinum and tungsten, though these three elements were not present at detectable concentrations in any of the samples.

The National Ambient Air Quality Standards for India set limits on both an annual basis (time weighted average with a minimum of 104 measurements of 24 hours) and on a daily basis (time weighted average for 24 hours, which must be met 98% of the time and must not exceed the limit on two consecutive days). This regulation sets limits for $PM_{2.5}$ particulates in ambient air, and also for three of the analytes quantified in this study (arsenic, lead and nickel), as shown in Table 2.

The average $PM_{2.5}$ concentrations in all but one sample were higher than the 24 hour time weighted average limit value of 60 $\mu g/m^3$ set by the Indian Government, being between 1.8 to 10.5 times the limit, the exception being IN15005 (Army Public School). All samples were higher than the 24 hour mean guideline value of 25 $\mu g/m^3$ set by the World Health Organisation (WHO), being between 4.3 and 25.2 times that limit. See Table 3 for details.

Note that limits and guideline values for concentrations of certain metals in the air, set either by the Indian Government or the WHO, are given as an annual average concentration values, based on a series of 24 hour measurements made through the year, though in the case of lead a one-off 24 hour time weighted average limit of 1000 $\mu g/m^3$ is also set by the Indian Government (See Table 3). Concentration limits set on an annual average basis clearly cannot be applied in a regulatory sense to these samples, which were single samples collected over time periods up to approximately 24 hour, but the limits do provide a useful guide for comparison nonetheless.

Six samples contained one or more metal at a concentration higher than the respective limit and/or guideline value for annual average metal concentrations in the air set either by the Indian Government or the WHO.

Of these, one sample had all but one metal (mercury) at a concentration higher than one or other limit/guideline value. This sample (IN15001) was collected at 'Red Fort to India Gate' on car free day (21st October). For this sample, the concentrations of these metals were higher than annual average limit/guideline value (between 1.3 and 3.5 times the limit) for arsenic, lead, manganese and nickel, and were 13.8 times the limit value for cadmium, with the lead concentration being 1.5 times the 24 hour time weighted average limit for India. This sample also contained a number of other metals at concentrations notably higher than in the remaining samples, with concentrations more than five times the respective median values for all $PM_{2.5}$ samples, including antimony, barium, chromium, copper, iron, molybdenum, strontium, vanadium and zinc.

Two other samples (IN15010 and IN15009) contained three or more metals at concentrations above the limit / guideline value. Sample IN15010, collected at the Andra Education Society, contained

concentrations of arsenic and lead at between 1.5-1.7 times the limit / guideline value, with the concentration of cadmium being over 60 times the WHO guideline value. This sample also had notably high concentrations of antimony, barium, copper and strontium, each at more than five times the respective median values for all $PM_{2.5}$ samples.

Sample IN15009, collected at the St. Marks Senior Secondary School, had concentrations of arsenic, cadmium, lead and nickel at between 1.1 to 1.9 times the annual limits / guideline values.

In addition, sample IN15008, collected at the Holy Child School, had a concentration of arsenic at just over the Indian annual limit, and that of cadmium at 3 times the WHO annual guideline value.

Sample IN15007, collected at Shah International School, had a cadmium concentration 14 times the annual WHO annual guideline value. IN15007 also had a copper concentration more than five times the median value for all $PM_{2.5}$ samples. In addition, sample IN15002, collected at the Greenpeace Guest House, had a nickel concentration at 1.7 times the Indian annual limit.

Two samples were collected from St. Marks Senior Secondary School, Meera bagh. The first sample was collected from an empty class room on the 16-17th October (IN15011). The second sample was collected on the 6-7th November (IN15009). As noted above, for sample IN15009 concentrations of arsenic, cadmium, lead and nickel were between 1.1 to 1.9 times their respective annual limits/guideline values set either by the Indian Government or the WHO, while this was not the case for any of these in sample IN15011. However, the average $PM_{2.5}$ concentration for IN15009 (629.98 $\mu g/m^3$) was just over 5 times the average $PM_{2.5}$ concentration for IN15011 (119.38 $\mu g/m^3$). Similarly the concentrations of arsenic, lead and nickel were approximately 4 to 5 times higher in IN15009 compared to IN15011, with the concentration of cadmium being approximately 2 times higher in IN15009 compared to IN15011. These results suggest that the higher metals concentrations observed on the 6-7th November (IN15009) compared to the 16-17th October (IN15011) were primarily due to the higher loading of $PM_{2.5}$ in the atmosphere during the sampling period, with the possible exception of cadmium, for which the difference in concentrations between the two sampling periods differed by a smaller extent.

The two samples with a number of metals at notably higher concentrations compared to the median values (IN15001 and IN15010) were also the samples with the two highest values of average $PM_{2.5}$ concentrations amongst all $PM_{2.5}$ samples, suggesting that the higher concentration of particulates was an important factor contributing to the airborne metal concentrations determined for these samples.

Sample code	IN15001	IN15002 [a]	IN15003	IN15005	IN15006	IN15007	IN15008	IN15009	IN15010	IN15011	$PM_{2.5}$ Median (b)
Date	21.10	17.10	18.10	28.10	29.10	03.11	04.11	06.11	09.11	16.10	-
Sampling period (hr)	4.1	13.44	7.47	23.33	25.59	21.78	21.66	20.84	23.95	24.49	-
Particulate type	$PM_{2.5}$	PM_{total}	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	-
$PM_{2.5}$ or PM_{total} ($\mu g/m^3$) av.	428.62	343.06	192.38	48.37	141.9	419.29	329.49	629.98	365.81	119.38	329.49
Metal (ng/m^3)											
Antimony	75	27	3	2	3	15	9	11	46	4	4
Arsenic	**21**	2.6	3.1	<0.5	0.7	4.2	**6.1**	**7.4**	**10**	1.7	4.3
Barium	164	58	26	8	11	134	58	74	845	12	26
Beryllium	<1	<0.2	<0.7	<0.2	<0.2	<0.3	<0.3	<0.3	<0.2	<0.2	<0.2
Cadmium	**69**	3.6	4.8	0.8	8.2	**70**	**15**	**9.4**	**306**	4.8	8.2
Chromium	1200	131	520	156	180	168	194	149	143	187	180
Cobalt	<3	2	<1	<0.5	<0.4	<0.5	<0.5	<0.5	<0.5	<0.4	<0.5
Copper	195	43	33	15	22	260	85	35	325	16	33
Gallium	2.3	0.5	<0.7	<0.2	<0.2	0.7	<0.3	<0.3	1.3	<0.2	1.0
Iron	4500	2270	1470	380	479	649	591	509	1880	335	509
Lead	**1500**	136	245	36	97	406	142	**676**	**731**	131	222
Manganese	**190**	54	44	7	14	34	26	23	61	17	23
Mercury	<10	<2	<7	<2	<2	<3	<3	<3	<2	<2	<2
Molybdenum	8.8	1.4	<1	<0.5	<0.4	0.8	1.0	<0.5	4.1	<0.4	1.0
Nickel	**68**	33	**26**	6.1	9.0	12	12	**21**	13	5.4	12
Selenium	<30	<4	<10	<5	<4	<5	<5	<5	<5	<4	<5
Strontium	41	19	12	2.2	4.2	13	4.9	8.8	64	2.6	4.9
Vanadium	120	29	13	1.4	4.7	10	13	4.2	17	6.3	6.3
Zinc	1830	370	423	47	110	573	351	337	649	180	337

Table 2. Average concentration of $PM_{2.5}/PM_{Total}$ particulates ($\mu g/m^3$) within air during over the sampling period, and average concentrations metals (ng/m^3) in the $PM_{2.5}/PM_{Total}$ particulates collected during that period. (a) values for sample IN15002 are for PM_{total}, not $PM_{2.5}$. Metal values higher than the annual limits/guideline values set either by the Indian Government or the WHO are presented in red (see Table 3). Median values are for $PM_{2.5}$ samples, and does not include IN15002

	India Annual (24 hour) time weighted average [a]	WHO Guidelines Annual (24 hour) Mean [b]
$PM_{2.5}$ ($\mu g/m^3$)	40 (60)	10 (25)
Metal concentration limit (ng/m^3)		
Arsenic	6	
Cadmium		5
Lead	500 (1000)	500
Manganese		150
Mercury		1000
Nickel	20	

Table 3. Regulatory limits and guideline values set by the Government of India and the World Health Organisation (WHO). (a) National Ambient Air Quality Standards for India (CPCB 2009); (b) WHO air quality guidelines (WHO 2000, 2005)

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 India.

4. References

CPCB (2009) National Ambient Air Quality Standards, Central Pollution Control Board (CPCB), Ministry of Environment & Forests, Government of India.
http://cpcb.nic.in/National_Ambient_Air_Quality_Standards.php

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, four 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.