Water Air Soil Pollut (2007) 178:373–384
DOI 10.1007/s11270-006-9205-z

Heavy Metal Content of Suspended Particulate Matter at World's Largest Ship-Breaking Yard, Alang-Sosiya, India

Shaik Basha · Premsingh Mansingh Gaur · Ravikumar Bhagwan Thorat · Rohitkumar Harikrishna Trivedi · Sandip Kumar Mukhopadhyay · Nisha Anand · Shalin Hemantbhai Desai · Kalpana Haresh Mody · Bhavnath Jha

Received: 20 December 2005 / Accepted: 12 June 2006 / Published online: 22 July 2006

Abstract This study vividly presents results from a seasonal particulate matter measurement campaign conducted at world's largest ship-breaking yard i.e., Alang-Sosiya (Gujarat, India) at six locations and a reference station at Gopnath which is 30 km south of this ship-breaking yard. The collected suspended particulate matter (SPM) 24-h samples were critically analyzed for heavy metals (Pb, Cd, Co, Ni, Cr, Mn, Fe, Cu, Zn). The average concentration of SPM within the ship-breaking yard during the investigation was 287.5 ± 20.4 μg m^{-3} and at reference station it was 111.13 ± 5.81 μg m^{-3}. These values are found to be in excess of the permitted national standards. The levels of heavy metals at Alang-Sosiya are very high as compared to US EPA and WHO guidelines. The mean concentrations of all metals are in the order: Fe >>Zn >Cu > Mn > Cd >Pb > Co >Ni >Cr. The results on enrichment factors (EF) suggest that most of the metals in the ship-breaking yard exhibit EF values of near or above 100 which must have been comprehensively affected by ship-breaking activities. Metal data was used to evaluate the role of spatial factors on their distribution characteristics. Thereafter, factor analysis was carried out to identify the main components liable for the variance of the data set.

Keywords Alang-Sosiya · enrichment factor · factor analysis Gopnath · suspended particulate matter

1 Introduction

Accumulation of trace metals in suspended particulate matter is of seminal concern to all of us as they adversely affect human health and ecosystem when present in excess concentration. The nature of airborne suspended particulate matter (SPM) and its impact on earth's environmental system are gauged by an interplay of various factors and processes that can exert controls on their formation, transformation, and transport (Fang, Zheng, Wang, Chim, & Kot, 1999). Frequently, anthropogenic emissions cause the levels of metals in suspended particles above natural background levels (Pitts & Finlayson-Pitts, 2000). The environmental behavior of SPM-bound metals, being subsidiary to the fate of SPM, is more intricate owing to the implicit differences in their chemical properties. There are various types of sources emitting these metals into the atmosphere, e.g., fossil fuel combustion, vehicular traffic, electroplating and metal alloy industries.

The incidence of environmental pollution induced by metallic components has been investigated in several urban localities of the world (Harrison &

S. Basha (✉) · P. M. Gaur · R. B. Thorat ·
R. H. Trivedi · S. K. Mukhopadhyay · N. Anand ·
S. H. Desai · K. H. Mody · B. Jha
Marine Algae and Marine Environment Department,
Central Salt and Marine Chemicals Research Institute,
GB marg, Bhavnagar, Gujarat 364002, India
e-mail: sbasha@csmcri.org

Sturges, 1996; Fidalgo, Mateos, & Garmendia, 1988; Van Borm, Adams, & Maenhaut, 1989; Lioy, Zelenka, Cheng, Reiss, & Wilson, 1989; Voutsa & Samara, 1996). When the results of those previous studies were compared on a parallel basis, the status of metal pollution among different sites was found to be quite different with wide variations in their concentration levels. Enormous research on heavy metals in particulate matter has also been carried out in India (Chakraborti, Van Vaeck, & Van Espen, 1984; Kulshrestha, Saxena, Kumar, Kumar, & Srivastava, 1994; Kulshrestha, Rao, Azhaguvel, & Kulshrestha, 2004; Balachandran, Meena, & Khillare, 2000; Tripathi et al., 2004). All these studies were confined to residential and industrial areas in cities. Alang-Sosiya Ship-breaking Yard is especially selected for this study, as this area has become the focal point for criticism of environmentalists in recent years (Aage, 2001; Derek, 2004). Long-term exposure to particulate metals may affect the lungs of children and adults alike and may reduce life expectancy by a few months. In spite of risks to the human population, no studies have been carried so far out to assess the metal levels in particulate matter.

The Alang-Sosiya ship-breaking yard established in 1982 is world's largest ship-breaking zone on the NW of Gulf of Cambay, India, with an annual turnover of US$1.3 billions (Gujarat Maritime Board, Alang, personal discussions [2003]). The average highest tide recorded at this site is around 13 m, which is second in the world's parameter. It has a moderate sloping with a hard and firm rocky bottom, which facilitates the incoming ships right up to the scrapping yard afloat with minimum investment and risk factors. The yard stretches to about 14 km along the north-south encompassing a total area of approximately 67 km^2 with a bifurcating small creek. The southern part is designated as Alang while the other is known as Sosiya. These two put together has earned the popular name Alang-Sosiya ship scrapping yard. Here, there are ship-breaking activity in 112 plots in Alang and 80 plots in Sosiya, each having a length of 50–240 m and a width of 30–120 m. Presently, about 40,000 people are getting their livelihood per annum from this ship-breaking yard (Gujarat Maritime Board, Alang, personal discussions [2003]). The statistical data till October 2003 reveal that about 3,677 ships mainly cargo vessels, oil tankers, passenger liners and warships having about 26–27 million MT light dead tonnage (LDT) were broken at the yard (Gujarat Maritime Board, Alang, personal discussions [2003]). The ship-breakers on an average dismantle a ship of about 10,000–13,000 tons in a day or two.

The deleterious impact of the ship-breaking process on the environment has received global publicity. The ship-breaking activity over here creates pollution of land, sea and air. At present, the technology used in the ship-breaking process is relatively simple and labour-intensive. The ship is stripped entirely and then cut into fragments using oxygen torches. Cranes are used for loading and unloading of heavy machinery and for dragging the ship further up the shore. The process itself as well as from fires that burn non-recyclable waste materials produces toxic fumes. Torch cutting generates fumes, smoke and particulates having toxic effects. Each plot uses on an average 250 to 300 oxygen cylinders and 35 to 40 LPG cylinders per day.

Metals of concern associated with the ship-breaking industry are noxious heavy metals such as lead and cadmium. These are biologically inessential metals that can injure human health and/or ecological systems. Other metals in the breaking industry are iron, manganese, nickel, chromium, copper and zinc. These can be found in many products on board of a vessel in varying quantities. An investigation at four ship-breaking operations in Canada has proved that widespread excessive exposure of humans to this condition could be perilous and even fatal. Air sampling results for lead shows the level is above recommended standards at all locations. It has been reported that the ship scrapping yard workers in Taiwan showed that the workers' involvement with steel cutting activity have caused higher lead values in their blood and urine than the dock workers (Aage, 2001).

In this scenario, this study intends to assess, for the first time, the air quality of Alang-Sosiya Ship-breaking yard and also at Gopnath, which is chosen as a reference station for the suspended particulate matter and its heavy metal content. The temporal variations are analyzed to evaluate the behavior of these metal components. Enrichment factors are considered to evaluate the strength of crustal and non-crustal sources and statistical methods based on principle component analysis are used for ascertaining and distinguishing the pollution sources and their contribution.

2 Materials and Methods

2.1 Site description

The ship-breaking yard at Alang-Sosia lies in a semi-arid, drought prone, coastal zone of saline soils. The region has an average annual rainfall of 55.8 cm during the monsoon season (June to August) and the mean highest and lowest temperatures are 34.2 and 21.9 °C, respectively (Derek, 2004). Six ambient air quality monitoring stations (S1– S6) at a distance of about 2 km each and covering the entire Alang-Sosiya ship-breaking yard and a reference station at Gopnath (Sc), which is 30 km south of the Alang-Sosiya, were selected for collection of suspended particulate matter (SPM) samples (Figures 1 and 2). All the sampling stations at Alang-Sosia are mainly affected by ship-breaking activities and consequent moderate vehicular traffic. The reference station, Gopnath was selected as a background site due to absence of major primary sources affecting particle concentrations as well as far from any settlement zones or industrial facilities. There are residential areas located ≈2 km south west of reference site.

2.2 Sampling and analysis

Samples were collected on glass fiber filters with High-Volume sampler (Envirotech-APM 415), operated at constant flow rate ($1.2\,\mathrm{m^3 min^{-1}}$) and programmed to collect 24 h samples. Quality audits of flow rates were found within specifications. The high volume samplers at all the stations were kept at a height of 3 – 5 m. SPM samples were collected using Whatman glass fiber filters with a total sample area of 25.4 × $20.3\,\mathrm{cm^2}$ (0.1 mm pore-size and 99.9% collection efficiency). The SPM mass was determined by gravimetric analysis on glass fiber filters stabilized and weighed before and after sampling. The air volume pulled through each filter was 1,728 $\mathrm{m^3}$ (U.S. Environmental Protection Agency, 1999). Although sampling was conducted initially simultaneously (on a routine basis), this principle was not observed on certain occasions perhaps due to bad weather condition or to mechanical failure. Resultantly, the total number of measurements differed slightly between three seasons. Overall, 21, 20 and 25 samples during pre-monsoon, post monsoon and winter seasons, respectively, were collected. A summary of the sampling information (sampling date and meteorological conditions) is provided in Table I.

Cleaned glass fiber filters were transported to the field in containers without exposure to ambient air. After sampling, the filters were placed back into their containers and brought to the laboratory and stored in the dark before they were analyzed. Glass fiber filters were rinsed with dilute nitric acid and milli pore water, wrapped loosely with aluminum foil, and dried in an oven at 105 °C for several hours. Then they were allowed to cool to room temperature in desiccators

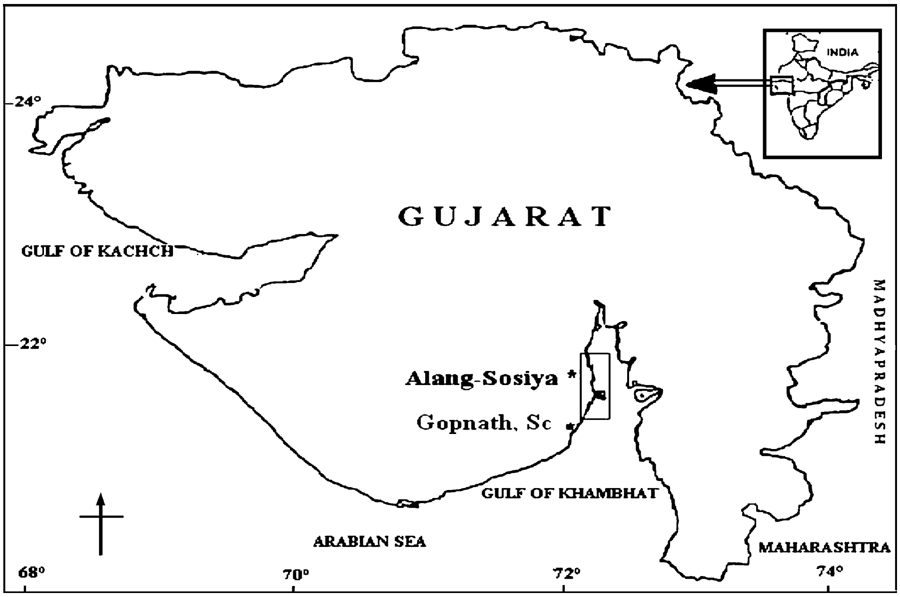

Figure 1 Location map of Alang-Sosiya and Gopnath (reference station).

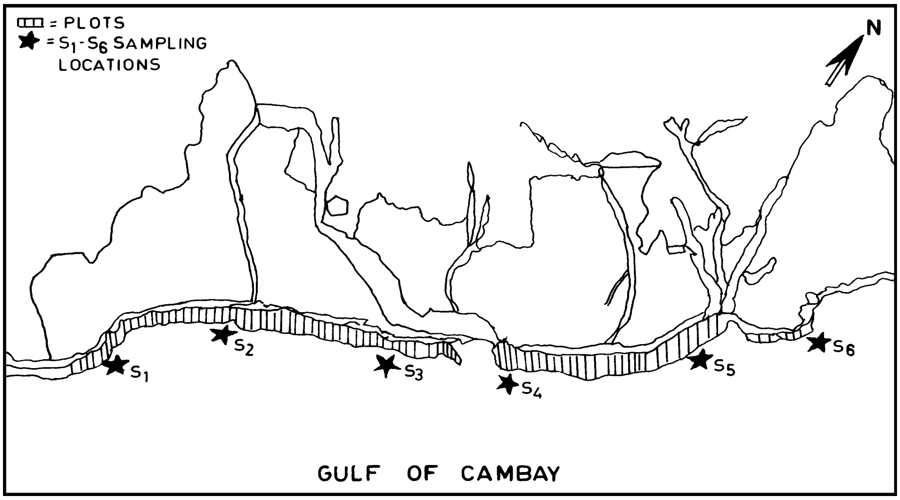

Figure 2 Sampling stations in Alang-Sosiya ship-breaking yard.

(Odabasi, Sofuoglu, Vardar, Tasdemir, & Holsen, 1999; Bozlaker, 2002; Bagiroz, 2002). Filter samples, cut in to several pieces, were filled in polyethylene bottles containing 125 ml of 20% nitric acid solution. The polyethylene bottles were put into a water shaker for 24 h at 60 °C and 270 rpm. The solution was then transferred from the bottle to a clean 250-ml Teflon beaker and the bottle was rinsed with milli pore water three times. Thereafter, the Teflon beaker was placed on a hot plate at a temperature of about 150 °C to evaporate the nitric acid solution to l5 ml. An additional 20 ml of Supra-pure grade nitric acid was added to the beaker, and hot acid extraction continued until 15 ml solution had vanished. The extracted solution was filtered through an ash less filter. The filtrates were stored in clean 100-ml HDPE bottles in the dark until they were analyzed (Yi, Holsen, & Noll, 1997). Unused filters from the same batch were extracted in the same way to determine the blank values. Samples were analyzed using flame atomic absorption spectrophotometer (Shimadzu AA-680) and predefined quality control standard solutions were used (U.S. Environmental Protection Agency, 2001). Detection limits of the chemical analysis for Zn, Fe, Pb, Mn, Cd, Ni, Cr, Co and Cu were 0.01, 0.2, 0.1, 0.1, 1.0, 0.1, 0.1, 0.1 and 0.2 μg m^{-3}, respectively. The metal content of blank filters was observed to be below detection limits. Background contamination of the trace elements as routinely monitored using operational blanks (unexposed filters) were simultaneously processed with field samples. Each measurement was replicated thrice, and the difference between the three measurements was found less than 5%. Recovery efficiencies were checked by spiking a known amount of trace metals onto the unused filters before extraction. The recovery efficiency for AAS ranged from 93 to 96%.

3 Results and Discussion

3.1 The evidence of concentrations of airborne trace metals in all study sites

A statistical finding of the metal and suspended particulate matter measurement data obtained from seven monitoring sites during the study period are presented in Tables I, II and III. The mean concentrations of all metals within the Alang-Sosiya ship-breaking yard, derived by using the values of each individual site, during all seasons are computed as: Fe (31.02), Zn (3.97), Cu (2.56), Mn (2.04), Cd (1.66), Pb (0.50), Co (0.41), Ni (0.30) and Cr (0.24 μg m^{-3}) whereas at reference station, Gopnath, the concentrations were 0.76, 0.15, ND, 0.13, 0.16, 0.13, ND, 0.08, ND, respectively. The mean concentrations of all metals were hence found to vary two orders of magnitude at the ship-breaking yard. If the magnitude of the mean concentrations is ranked among all metals investigated at Alang-Sosiya, it can be sequenced as: Fe >>Zn >Cu > Mn > Cd >Pb > Co >Ni >Cr. If this type of comparison is extended to each individual study site, the magnitude of metal concentration data can be divided into four different classes in the sequence: (1) Fe; (2) Zn, Cu, and Mn; (3) Cd, Pb, and Co; and (4) Ni and Cr. It is amply evident that in all cases Fe

Table I Summary of sampling information and meteorological parameters (meteorological parameters except wind direction were averaged over the duration of sampling)

Parameters	Monitoring Stations						
	S1	S2	S3	S4	S5	S6	Gopnath (Sc)
Pre-monsoon season							
Sampling dates	12/05/2004 to 14/05/2004	12/05/2004 to 13/05/2004, 15/05/2004	12/05/2004 to 14/05/2004	16/05/2004 to 17/05/2004, 19/05/2004	16/05/2004 to 18/05/2004	16/05/2004 to 17/05/2004, 19/05/2004	20/05/2004 to 22/05/2004
Wind speed (km h^{-1})	3.5 ± 1.2	3.4 ± 1.1	3.5 ± 1.2	4.2 ± 1.6	4.1 ± 1.7	4.2 ± 1.7	5.6 ± 0.9
Prevailing wind direction	SSW	SW	SSW	NW	NNW	NW	SE
Air temperature (°C)	34.5 ± 0.4	34.7 ± 0.3	34.5 ± 0.4	36.2 ± 0.3	36.5± 0.2	36.2 ± 0.3	36.0 ± 0.4
Relative humidity (%)	63.5 ± 3.4	62.4 ± 3.2	63.5 ± 3.4	67.3 ± 4.5	66.4 ± 3.2	67.3 ± 4.5	61.4 ± 4.8
Post-monsoon season							
Sampling dates	21/09/2004 to 23/09/2004,	21/09/2004 to 23/04/2004,	22/09/2004 to 23/09/2004	24/09/2004 to 25/09/2004, 27/09/2004	24/09/2004 to 26/09/2004	24/09/2004 to 25/09/2004, 27/09/2004	28/09/2004 to 30/09/2004
Wind speed (m s^{-1})	5.5 ± 1.8	5.5 ± 1.8	5.9 ± 1.6	5.2 ± 1.5	5.0 ± 1.6	5.2 ± 1.5	4.9 ± 1.1
Wind direction	SE	SE	SSE	NNE	NE	NNE	S
Air temperature (°C)	31.5 ± 0.3	31.5 ± 0.3	31.6 ± 0.3	31.7 ± 0.2	31.5± 0.4	31.7 ± 0.2	30.9 ± 0.4
Relative humidity (%)	60.5 ± 2.4	60.5 ± 2.4	59.5 ± 3.0	57.2 ± 4.9	56.4 ± 3.2	57.2 ± 4.9	57.6 ± 3.6
Winter season							
Sampling dates	21/01/2005 to 22/01/2005, 24/01/2005	21/01/2005 to 23/01/2005, 25/01/2005	21/01/2005 to 22/01/2005, 24/01/2005	25/01/2005 to 27/01/2005, 29/01/2005	25/01/2005 to 28/01/2005	26/01/2005 to 28/01/2005, 30/01/2005	29/01/2005 to 31/01/2005
Wind speed (m s^{-1})	2.2 ± 1.0	2.2 ± 1.1	2.2 ± 1.0	2.9 ± 1.2	3.1 ± 1.4	3.2 ± 1.4	4.3 ± 0.8
Wind direction	WSW	SW	WSW	NNW	WNW	NW	SE
Air temperature (°C)	22.4 ± 0.4	22.9 ± 0.3	22.4 ± 0.4	22.2 ± 0.3	23.5 ± 0.2	23.9 ± 0.3	20.8 ± 0.3
Relative humidity (%)	35.5 ± 2.4	32.4 ± 1.2	35.5 ± 2.4	31.3 ± 1.4	30.4 ± 1.2	32.3 ± 1.5	31.2 ± 1.8

Table II Concentrations of particulate heavy metals and particulate matter at ship-breaking yard, Alang-Sosiya (S1–S6) and a reference station at Gopnath (Sc), during pre monsoon season (May'04)

	Monitoring Stations						
	S1	S2	S3	S4	S5	S6	Gopnath (Sc)
Cd	2.95 ± 0.35	3.70 ± 0.42	1.30 ± 0.14	0.57 ± 0.03	ND	0.22 ± 0.03	ND
Co	ND	0.37 ± 0.03	0.15 ± 0.07	ND	0.7 ± 0.14	0.32 ± 0.03	ND
Cr	0.27 ± 0.04	0.15 ± 0.01	0.15 ± 0.007	0.11 ± 0.01	0.355 ± 0.13	0.25 ± 0.05	ND
Cu	3.87 ± 0.36	4.28 ± 0.90	4.32 ± 0.27	3.60 ± 0.42	1.670 ± 0.34	1.35 ± 0.18	0.18 ± 0.11
Fe	21.46 ± 3.51	41.88 ± 3.42	38.30 ± 2.62	20.78 ± 2.17	32.51 ± 1.54	33.95 ± 2.05	0.54 ± 0.18
Mn	1.25 ± 0.57	1.64 ± 0.52	1.57 ± 0.16	2.240 ± 0.24	2.23 ± 0.16	2.09 ± 0.21	0.15 ± 0.07
Ni	0.55 ± 0.07	ND	0.25 ± 0.03	0.65 ± 0.07	ND	0.15 ± 0.03	ND
Pb	0.10 ± 0.00	ND	0.44 ± 0.21	0.48 ± 0.02	0.800 ± 0.42	1.10 ± 0.14	ND
Zn	3.30 ± 0.424	4.40 ± 1.556	4.30 ± 0.57	4.30 ± 0.42	5.20 ± 0.99	3.70 ± 0.71	0.29 ± 0.09
SPM	216.0 ± 7.64	261.0 ± 6.65	406.15 ± 8.98	203.70 ± 3.43	255.45 ± 9.73	241.90 ± 4.81	121.55 ± 4.31

All the values are in microgram per cubic meter.

ND Non-detectable, *SPM* suspended particulate matter.

and Cr maintain the maximum and minimum concentration values, respectively. However, the patterns of relative ordering are not that simple for other metals. For example in the second category (Zn, Cu, and Mn), their relative ordering changes somewhat: The highest value of these three is found most frequently from Zn (13 times), and the next one with Cu (five times). In the third category, the dominance of Ni over Cr is more evident (15 times). This shows that the relative ordering between different metals tends to be maintained to a certain extent among all study sites. The results of this analysis in fact appear to be quite analogous to those seen previously except for Mn and Pb (e.g., Chakraborti et al., 1984).

The average concentration of SPM within the ship-breaking yard during three seasons was 287.5 μg m^{-3}, which was about 2.5 times higher as compared to reference station, Gopnath (111.1 μg m^{-3}). These values were found to be exceeding the accepted national standards (150 for industrial area and 100 for residential area for 24 h) for SPM as specified by Central Pollution Control Board of India (Central Pollution Control Board, 1994). The high values of both SPM and trace metal concentrations with wind

Table III Concentrations of particulate heavy metals and particulate matter at ship-breaking yard, Alang-Sosiya (S1–S6) and a reference station at Gopnath (Sc), during post monsoon season (Sep'04)

	Monitoring Stations						
	S1	S2	S3	S4	S5	S6	Gopnath (Sc)
Cd	2.20 ± 0.29	3.55 ± 0.49	1.90 ± 0.28	1.65 ± 0.35	1.35 ± 0.35	1.11 ± 0.14	ND
Co	0.95 ± 0.21	ND	0.50 ± 0.07	0.15 ± 0.07	1.400 ± 0.141	0.35 ± 0.07	ND
Cr	0.32 ± 0.02	0.29 ± 0.02	0.11 ± 0.007	0.21 ± 0.14	0.12 ± 0.01	0.31 ± 0.01	ND
Cu	3.75 ± 0.49	3.60 ± 0.42	1.40 ± 0.28	2.10 ± 0.42	1.30 ± 0.14	1.60 ± 0.35	0.17 ± 0.01
Fe	30.60 ± 3.03	35.02 ± 2.51	30.81 ± 2.64	31.78 ± 2.31	29.88 ± 0.37	28.35 ± 4.88	0.68 ± 0.23
Mn	1.40 ± 0.61	1.73 ± 0.70	1.98 ± 0.2	2.75 ± 0.28	2.20 ± 0.31	1.94 ± 0.41	0.19 ± 0.03
Ni	0.42 ± 0.57	0.15 ± 0.07	0.45 ± 0.07	0.15 ± 0.14	0.15 ± 0.49	0.10 ± 0.07	ND
Pb	0.35 ± 0.21	0.12 ± 0.07	0.15 ± 0.14	0.75 ± 0.35	0.65 ± 0.35	1.05 ± 0.21	0.25 ± 0.07
Zn	3.70 ± 1.13	2.60 ± 0.85	4.05 ± 0.78	2.15 ± 0.49	5.60 ± 0.57	3.40 ± 0.28	0.17 ± 0.05
SPM	269.40 ± 7.35	322.75 ± 14.35	254.95 ± 13.93	298.35 ± 5.87	285.15 ± 13.22	392.95 ± 12.23	101.55 ± 5.73

All the values are in microgram per cubic meter.

ND Non-detectable, *SPM* suspended particulate matter.

speed at reference site, Gopnath can be ascribed to greater re-suspension of soil particles during the windy periods and also the contribution of aerosols from the ship-breaking yard.

In Table IV, the magnitude of our heavy metals measurement data during the study period is compared to air quality standards of regulatory agencies and those reported previously from other study sites in India and Pakistan with a view to indirectly diagnose the relative level of pollution in our study area. Axiomatically, the levels of heavy metals at Alang-Sosiya are very high in comparison with US EPA and WHO standards except Cr, which was 4.5 time less than the WHO standards. Cd mean concentration was 262 and 334 times higher than the US EPA and WHO standards, respectively. Fe, Mn, Zn, Cu, Ni and Pb levels were also found to be higher than the average value obtained for USA and European cities (Lantzy & Mackenzie, 1979). The mean Fe concentration is comparable to Kolkatta (Chakraborti et al., 1984) whereas it was 10 and three times higher than the Mumbai (Sharma & Patil, 1992) and Lahore (Smith et al., 1996), respectively. It is amazing to note that Pb levels are 13 and eight times lower than the Kolkatta and Lahore, respectively. This may be due to the prohibition of leaded gasoline in vehicles which tends to render the use of lead as tracer of vehicular emissions obsolete in India. Cu levels are higher than the reported values for not only Kolkatta, Mumbai and Lahore, but also many industrial areas such as Chicago (Sweet, Vermette, & Landsberg, 1993) and Tito Scalo, Italia (Ragosta, Caggiano, D'emilio, & Macchiato, 2002). Mn mean concentrations are about 5, 4.7 and 5.8 times higher than Mumbai, Kolkatta and Lahore, respectively. Zn levels are about seven times lower than Lahore while 19 and 1.3 times higher than Mumbai and Kolkatta, respectively.

This data accentuates that the concentrations of airborne metals in this industrial area are very high, representing a potential hazard to the local population. Even for the metals found in lower concentrations, the values are still excessive than the unit risk concentrations. For example, WHO nickel unit risk for lung cancer is 0.38 ng m^{-3} (WHO Air Quality Guidelines for Europe, 2000) and the European guideline (European Commission (EC) Position Paper, 2000) is 2.6–4 ng m^{-3} while the average value in ship-breaking yard is 306 ng m^{-3}. Presently, the study on particle size distribution of aerosols at this ship-breaking yard is underway. Epidemiological and laboratory studies have established a strong association between health effects and particle size (Dockery et al., 1993; Heyder et al., 1996; Peters, Dockery, Heinrich, & Wichmann, 1997; Li et al., 2003). Ferin, Oberd orster, Soderholm, and Gelein (1991) reported that for the same amount of particulate matter in the lung, toxicity seems to increase as the particle size decreases. Similar results were obtained by Li et al. (2002, 2003) who demonstrated that smaller particles caused a greater degree of response in epithelial cells from human airways exposed to particles of different sizes. In view of this, it is desirable to develop a future

Table IV Concentrations of particulate heavy metals and particulate matter at ship-breaking yard, Alang-Sosiya (S1–S6) and a reference station at Gopnath (Sc), during winter season (Jan'05)

	Monitoring Stations						
	S1	S2	S3	S4	S5	S6	Gopnath (Sc)
Cd	1.98 ± 0.46	2.55 ± 0.32	1.63 ± 0.14	1.28 ± 0.29	1.14 ± 0.35	0.95 ± 0.21	ND
Co	0.55 ± 0.64	0.15 ± 0.35	0.35 ± 0.07	0.52 ± 0.25	0.25 ± 0.21	0.75 ± 0.21	ND
Cr	0.23 ± 0.03	0.42 ± 0.01	0.26 ± 0.07	0.38 ± 0.04	0.135 ± 0.007	0.35 ± 0.01	ND
Cu	3.80 ± 0.42	2.85 ± 0.78	2.05 ± 0.35	2.25 ± 0.64	0.85 ± 0.21	1.47 ± 0.14	0.15 ± 0.07
Fe	26.27 ± 0.94	32.88 ± 2.37	32.44 ± 4.52	26.95 ± 3.54	35.06 ± 0.76	29.42 ± 1.14	1.06 ± 0.06
Mn	1.62 ± 0.61	1.86 ± 0.70	2.15 ± 0.20	2.55 ± 0.28	3.75 ± 0.31	1.85 ± 0.41	0.06 ± 0.19
Ni	0.35 ± 0.21	0.41 ± 0.21	0.51 ± 0.14	0.35 ± 0.35	0.42 ± 0.35	0.45 ± 0.21	0.25 ± 0.21
Pb	0.24 ± 0.21	0.35 ± 0.07	0.21 ± 0.21	0.80 ± 0.29	0.44 ± 0.28	1.13 ± 0.29	0.15 ± 0.07
Zn	5.12 ± 0.85	2.95 ± 0.35	4.15 ± 0.35	2.90 ± 0.57	6.15 ± 0.35	3.60 ± 0.28	ND
SPM	220.50 ± 6.93	312.90 ± 16.55	297.40 ± 18.10	266.00 ± 13.15	319.10 ± 10.89	352.65 ± 8.41	110.30 ± 1.98

All the values are in microgram per cubic meter.

ND Non-detectable, *SPM* suspended particulate matter.

study in the ship-breaking yard with elaborate information about size distribution of SPM and its trace metal concentrations, in relation to epidemiology.

3.2 Sources

Trace metals in particulate matter are derived from assorted sources including the Earth's crust, the oceans, volcanic activities, the biosphere, and a number of anthropogenic processes (i.e., fossil fuel burning, waste incineration, various industrial activities including ship-breaking). The degree to which trace elements are enriched, or depleted, relative to a specific source can be evaluated using enrichment factors (EFcrust) (Chester, Nimmo, & Preston, 1999). We computed enrichment factors (EF) relative to the Fe concentration using the following equation considering average values for three seasons:

$$\mathrm{EF}_{\mathrm{crust}} = (\mathrm{Tr}/\mathrm{Fe})_{\mathrm{air}}/(\mathrm{Tr}/\mathrm{Fe})_{\mathrm{crust}}.$$

For this computation, we used the data set of Taylor and McLennan (Taylor & McLennan, 1985) as reference concentrations for the earth's crustal composition. By convention, an arbitrary average $\mathrm{EF}_{\mathrm{crust}}$ value of <10 was taken as an indication that a trace metal in an aerosol has a significant crustal source, and these are termed as non-enriched elements (NEEs). Conversely, an EFcrust value of >10 is considered to indicate that a significant proportion of an element has a non-crustal source, and these are referred to the anomalously enriched elements (AEEs). The results shown in Figure 3 suggest the possibility that a number of metals in our study site, which exhibit EF values of near or above 100 (i.e., Co, Ni, Cu, and Mn), must have been significantly affected by ship-breaking activities. Such contribution from anthropogenic sources can also be expected to a certain degree from other metals (e.g., Pb or Zn); however it is also likely to be salient for Cr because it had an EF of 23.8. As already confirmed by simple comparison of absolute metal contents among different studies, the results of our EF computation display good agreement with those of highly to moderately polluted urban environments, at least in a relative sense. For instance, on the basis of the measurements made in four different urban locations of La Plata city, Argentina, Bilos, Colombo, Skorupka, and Rodriguez (2001) found that their study area was enriched in Pb, Cd, and Cu, while other metals (e.g., Mn, Cr, and Ni) were low enough to be compatible with those controlled mainly by natural sources.

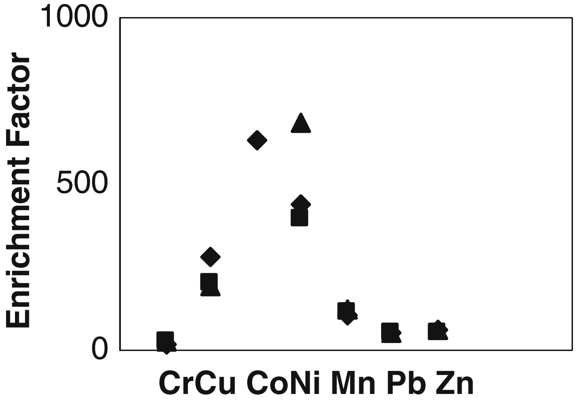

Figure 3 Enrichment factor values using the metal concentrations of Alang-Sosiya sampling during three seasons pre-monsoon (♦), post-monsoon (■), winter (▲).

3.3 Spatial variations and relationships between spatial and temporal factors on metal distributions

In view of the above, our measurements were made from several locations during three seasons from the ship-breaking yard using our metal data to evaluate the role of spatial factors on metal distribution characteristics. As the simplest means to assess its importance, we first compared the absolute magnitude of our measurement data between different sites within the ship-breaking yard. To arbitrarily set the status of metal pollution among all study sites, they were ranked for each metal in terms of its absolute concentration. When such ranks for each metal were combined for all study sites, excluding reference station, the level of pollution could be distinguished among different study sites such as: S2 > S3 ~ S5 > S6 > S1 > S4. The highest concentrations of each metal were seen most frequently at stations S1 and S5 (three out of nine metals), and the lowest values in S1 site (three out of nine metals). The results of this analysis propose that the strengths of source processes and the related pollutant emissions may differ rather systematically among all study sites, notwithstanding their general similarity in being within the ship-breaking yard.

To make a meticulous inspection of the bond between spatial and temporal factors, seasonal distribution patterns of each metal were compared among different study sites (Figure 4). The results of this seasonal comparison and of EF computation indicate that the springtime peak of particle-bound metal concentrations should be the dominant pattern for many metals at all study sites, within the ship-breaking yard. As such, Cu, Fe and Zn exhibited their peak concentrations in pre-monsoon season and

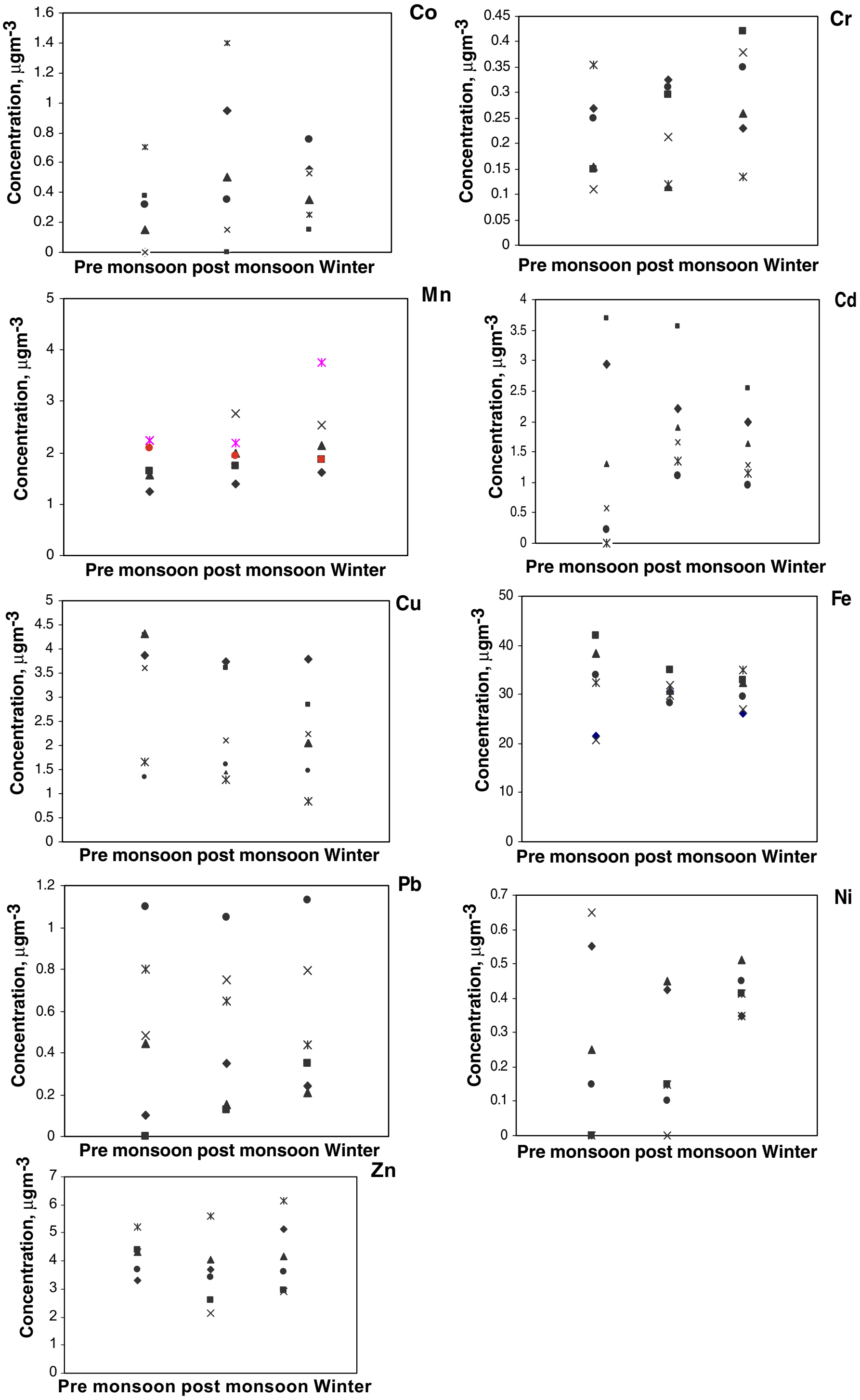

Figure 4 Comparison of seasonal distribution patterns of each metal. For each metal, comparison is made between different sites within ship-breaking yard: *S1* (♦), *S2* (■), *S3* (▲), *S4* (x), *S5* (*), *S6* (•).

Table V Comparison of Alang-Sosiya mean metal concentration with standards of regulatory agencies (US EPA, WHO) and other studies in India and Pakistan

Metals	US[a] EPA ($\mu g\ m^{-3}$)	WHO[b] ($\mu g\ m^{-3}$)	Alang -Sosiya ($\mu g\ m^{-3}$)	Mumbai (India) ($\mu g\ m^{-3}$)	Kolkatta (India) ($\mu g\ m^{-3}$)	Lahore (Pakistan) ($\mu g\ m^{-3}$)
Cd	0.00637	0.005	1.669	0.04	nm	0.04
Cr	0.10	1.10	0.246	0.04	0.11	0.11
Cu	ND	ND	2.56	0.29	1.12	0.42
Co	ND	ND	0.414	nm	nm	nm
Fe	ND	ND	31.02	2.95	26.4	9.93
Ni	0.00024	0.00038	0.306	0.04	nm	0.08
Mn	0.50	0.15	2.04	0.4	0.43	0.35
Pb	1.50	0.50	0.509	0.55	6.63	3.92
Zn	ND	ND	3.97	0.21	3.04	27.65

Sampling Locations: Ship-breaking yard, Alang-Sosiya (this study), Bhandup-Thane, Mumbai, India (24), Park Street, Kolkatta, India (8), University of Engineering and Technology, Lahore (25).

ND Non-detectable, *nm* not measured.

[a] Air quality standards (EPA – Environmental Protection Agency, USA, ATSDR, 2002 (39)).

[b] WHO – World Health Organization (28).

Cd and Co showed during post monsoon season. The results of this comparison evidently indicate the occurrence of coinciding seasonal patterns from sites of different environmental conditions. This observation of spatio-temporal distribution patterns for each individual metal hence suggests that spatial factors can be incorporated with temporal factors to control metal distribution patterns and the extent of such incorporation cannot vary dramatically between metals.

3.4 Statistical analysis

In order to reinforce the main pollutant sources in the ship-breaking yard, statistical analyses using Software SPSS were applied as they constitute one of the most useful methods to treat data in order to identify the main sources affecting ambient concentrations (Hopke, 2000; Henry, Lewis, Hopke, & Williamson, 1984). PCA applying a Varimax rotated component matrix was performed to the nine heavy metals studied, considering mean values for three seasons, in order to know the sources contributing to explain the fraction of the SPM analyzed (Tables V and VI). Three factors accounted for 97.5% of the accumulative variance in Ship-breaking yard. The highest percentage of variance (80.8%) was explained by a component with high loadings on Cd, Cu, Cr and Co associated with ship-breaking activities. Actually, ship-breaking yard, established in 1982, has scrapped 167 ships on an average with 1.20 million MT LDT per year (till 2003). In general, the steel content of a ship varies from 90 to 95%. The second component accounting for 11.5% of the accumulative variance was related to Mn, Ni, Pb and Zn. It was also associated with ship-breaking activities as well as ever increasing vehicular traffic. The fumes generated during cutting operations and vehicular movements (carrying material) have contributed to higher metal loadings in the ambient air

Table VI Principal component analysis after Varimax rotation for heavy metals in particulate matter, during three seasons (only factor loading values greater than 0.6 are shown)

Rotated Component Matrix			
	Component		
	1	2	3
Cd	0.854		
Cr	0.829		
Cu	0.885		
Co	0.831		
Fe			0.872
Ni		0.908	
Mn		0.924	
Pb		0.796	
Zn		0.760	
Percent of variance explained	80.82	11.46	5.24
	Ship-breaking	Ship-breaking + traffic	Crustal

in this yard. The third component causing 5.2% of the accumulative variance was related to Fe, crustal element indicating that soil dust and wind resuspension were responsible for this.

4 Conclusions

Our study on SPM bound metal concentrations from Alang-Sosiya ship-breaking yard vehemently suggest that their levels in this industrial area were very high, representing a prospective risk to the local population. The results on enrichment factor and statistical analysis suggest the possibility that a number of metals must have been affected significantly by ship-breaking activities. The results on seasonal distribution indicate that the springtime peak of particle-bound metal concentrations should be the dominant pattern for many metals in the ship-breaking yard. Each individual metal has unique properties to exhibit its own spatial and/or temporal distribution characteristics. To further comprehend the control mechanism of spatial factors on different metals, we need to focus more efforts in the future which will reveal the nexus between source/sink processes and the metal chemistry in air.

Acknowledgment The authors express their sincere thanks to Dr P.K. Ghosh, Director of this institute for his constant encouragement during this study and anonymous reviewer for valuable comments.

References

Aage, B. A. (2001). *Worker safety in the ship-breaking industries* (pp. 30–31). Geneva: International Labour Office.

Bagiroz, O. (2002). *Sulfate dry deposition in Izmi*. MS thesis, Graduate School of Natural and Applied Sciences. Izmir, Turkey: Dokuz Eylul University.

Balachandran, S., Meena, B. R., & Khillare, P. S. (2000). Particle size distribution and its elemental composition in the ambient air of Delhi. *Environment International, 26*, 49–54.

Bilos, C., Colombo, J. C., Skorupka, C. N., & Rodriguez, P. M. J. (2001). Sources, distribution and variability of airborne trace metals in La Plata City area, Argentina. *Environmental Pollution, 111*, 149–158.

Bozlaker, A. (2002). *Trace metals in airborne particles and their dry deposition in Izmir*. MS thesis, Graduate School of Natural And Applied Sciences. Izmir, Turkey: Dokuz Eylul University.

Central Pollution Control Board (1994). National ambient air quality standards.

Chakraborti, D., Van Vaeck, L.,Van Espen, P. (1984). Calcutta pollutants. Part 2. Polynuclear aromatic hydrocarbons and some metal concentrations on air particulates during winter. *International Journal of Analytical Chemistry, 88* (32), 109–120.

Chester, R., Nimmo, M., & Preston, M. R. (1999). The trace metal chemistry of atmospheric dry deposition samples collected at Cap Ferrat: A coastal site in the western Mediterranean. *Marine Chemistry, 68*, 15–30.

Derek, E. (2004). *Impacts and challenges of a large coastal industry Alang-Sosiya ship-breaking yard Gujarat, India. UNESCO report on environment and development in coastal regions and in small islands* (pp. 16–17). France: UNESCO.

Dockery, D. W., Pope, C. A., Xu, X., Spengler, J. D., Ware, J. H., Ferris, B. G. et al. (1993). Mortality risks of air pollution: A prospective cohort study New England. *Journal of Medicine, 329*, 1753–1759.

European Commission (EC) Position Paper (2000). Ambient air pollution by As, Cd and Ni compounds. Working group on As, Cd and Ni compounds, DG Environ. 361.

Fang, M., Zheng, M., Wang, F., Chim, K. S., & Kot, S. C. (1999). The long-range transport of aerosols from northern China to Hong Kong — A multi-technique study. *Atmospheric Environment, 33*, 1803–1817.

Ferin, J., Oberd orster, G., Soderholm, S. C., & Gelein, R. (1991). Pulmonary tissue access of ultrafine particles. *Journal of Aerosol Medicine, 4*, 57–68.

Fidalgo, M. R., Mateos, J., & Garmendia, J. (1988). The origin of some of the elements contained in the aerosols of Salamanca (Spain). *Atmospheric Environment, 22*, 1495–1498.

Harrison, R. M., & Sturges, T. W. (1996). The measurement and interpretation of Br/Pb ratios in airborne particles. *Atmospheric Environment, 17*, 311–328.

Henry, R. C., Lewis, C. W., Hopke, P. K., & Williamson, H. J. (1984). Review of receptor model fundamentals. *Atmospheric Environment, 18*, 1507–1515.

Heyder, J., Brand, P., Heinrich, J., Peters, A., Scheuh, G., Tuch, T. et al. (1996). *Size distribution of ambient particles and its relevance to human health*. Presented at the second colloquium on particulate air pollution and health, Park City, Utah, 1–3 May, 1996.

Hopke, P. K. (2000). *Workbook on data analysis*. Prepared for participants in the UNDP/RCA/IAEA, subproject on air pollution and its trends, RAS/97/030/A/01/18, IAEA, Vienna, Austria.

Kulshrestha, U. C., Rao, N. T., Azhaguvel, S., & Kulshrestha, M. J. (2004). Emissions and accumulation of metals in the atmosphere due to crackers and sparkles during Diwali festival in India. *Atmospheric Environment, 38*, 4421– 4425.

Kulshrestha, U. C., Saxena, A., Kumar, N., Kumar, K. M., & Srivastava, S. S. (1994). Measurement of heavy metals in the ambient air of Agra. *Indian Journal of Environmental Protection*, 685–687.

Lantzy, R. J., & Mackenzie, F. T. (1979). Atmospheric trace metals: Global cycles and assessment of man's impact. *Geochimica Et Cosmochimica Acta, 43*, 511–525.

Li, N., Kim, S., Wang, M., Froines, J., Sioutas, C., & Nel, E. (2002). Use of a stratified oxidative stress model to study the biological effects of ambient concentrated and diesel exhaust particulate matter. *Inhalation Toxicology, 14*, 459–486.

Li, N., Sioutas, C., Cho, A., Schmitz, D., Misra, C., Sempf, J. et al. (2003). Ultrafine particulate pollutants induce oxidative stress and mitochondrial damage. *Environmental Health Perspectives, 111*, 455–460.

Lioy, P. J., Zelenka, M. P., Cheng, M. D., Reiss, N. M., & Wilson, W. E. (1989). The effect of sampling duration on the ability to resolve source types using factor analysis. *Atmospheric Environment, 23*, 239–254.

Odabasi, M., Sofuoglu, A., Vardar, N., Tasdemir, Y., & Holsen, T. M. (1999). Measurement of dry deposition and air–water exchange of polyaromatic hydrocarbons with the water surface sampler. *Environmental Science and Technology, 33*, 426–434.

Peters, A., Dockery, D. W., Heinrich, J., & Wichmann, H. E. (1997). Short-term effects of particulate air pollution on respiratory morbidity in asthmatic children. *European Respiratory Journal, 10*, 872–879.

Pitts Jr., J. N., & Finlayson-Pitts, B. J. (2000). *Chemistry of the upper and lower atmosphere: Theory, experiments and applications*. Florida, New York: Academic.

Ragosta, M., Caggiano, R., D'emilio, M., & Macchiato, M. (2002). Source origin and parameters influencing levels of heavy metals in TSP, in an industrial background area of southern Italy. *Atmospheric Environment, 36*, 3071–3087.

Sharma, V. K., & Patil, R. S. (1992). Chemical composition and source identification of Bombay aerosol. *Environmental Technology, 13*, 1043–1052.

Smith, D. J. T., Harrison, M., Luhana, L., Casimiro, A. P., Castro, I. M., Tariq, M. N. et al. (1996). Concentrations of particulate airborne polycyclic aromatic hydrocarbons and metals collected in Lahore, Pakistan. *Atmospheric Environment, 30*, 4031–4040.

Sweet, C. W., Vermette, S. J., & Landsberg, S. (1993). Sources of toxic trace elements in a urban air in Illinois. *Environmental Science and Technology, 27*, 2502–2510.

Taylor, S. R., & McLennan, S. M. (1985). *The continental crust: Its composition and evolution* (p. 312). Cambridge, Massachusetts: Blackwell Science.

Tripathi, R. M., Kumar, A. V., Manikandan, S. T., Bhalke, S., Mahadevan, T. N., & Puranik, V. D. (2004). Vertical distribution of atmospheric trace metals and their sources at Mumbai, India. *Atmospheric Environment, 38*, 135–146.

U.S. Environmental Protection Agency (1999). *Air quality criteria for particulate matter, Vol. 1.* Washington, District of Columbia: U.S. EPA Office of Research and Development. EPA/600/P-65/001aF.

U.S. Environmental Protection Agency (2001). *Air quality criteria for particulate matter, Vol. 1.* Washington, District of Columbia: U.S. EPA Office of Research and Development. EPA/600/P-65/001aF.

Van Borm, W. A., Adams, F. C., & Maenhaut, W. (1989). Characterization of individual particles in the Antwerp aerosol. *Atmospheric Environment, 23*, 1139–1151.

Voutsa, D., & Samara, C. (1996). Trace elements in vegetables grown in an industrial area in relation to soil and air particulate matter. *Environmental Pollution, 94*, 325–335.

WHO Air Quality Guidelines for Europe (2000). *WHO regional publications Eur Ser No. 91*. Copenhagen, Denmark: Regional office for Europe.

Yi, S. M., Holsen, T. M., & Noll, K. E. (1997). Comparison of dry deposition predicted from models and measured with a water surface sampler. *Environmental Science and Technology, 31*, 272–278.