

## Aerosols of NW India – A potential Cu source!

Degradation of air quality, particularly in urban areas of developing countries, is one of the most alarming problems of modern civilization. Human activities today release a variety of gases and liquid/solid particles (aerosols) to the atmosphere. The cumulative effect of all these air pollutants on the climate of the earth and on the health of its life system are topics of intensive research. As a part of our research on the geochemistry of dust materials in the northwestern part of India, which witnesses frequent dust storms in summer times<sup>1</sup>, we studied the concentration of certain heavy metals such as Cu, Pb, Cr, V and Ni in three different size fractions, PM<sub>10</sub>, suspended particulate matter (SPM) and dry-deposition dust. We observed abnormally high concentration of Cu in the aerosols and thought it appropriate to report this academically and economically interesting finding. We also speculate on the possible causes and consequences of this finding.

The northwestern part of India, including parts of Gujarat, Rajasthan, Haryana, Punjab and western Uttar Pradesh witnesses regular dust storms just as the rest of India witnesses summer monsoon. A lot of dust material is transported by SW-W summer winds in the Thar desert and adjoining regions. These dust storms apparently deposited silty materials in the downwind direction, for example, on the quartzite ridge in the Delhi area<sup>2</sup>. The deposited Delhi ridge aeolian sediments, as well as the falling dust captured in the present study are geochemically similar to average upper continental crust (UCC<sup>3</sup>; see also ref. 2). In order to geochemically characterize the aerosols in different size fractions along the dominant SW-W wind trajectory, sampling sites were planned along Bikaner in Thar desert, Jhunjhunu, Delhi and east of Delhi at Garhmuktesar located on the bank of Ganga, covering a distance of 600 km from west to east (Figure 1). Although sampling duration was limited in all the sites along the transect because of limitations of infrastructure required for air sampling, the spacing and location of sampling sites, the type of samples collected and the data and their quality all make the findings interesting and worth exploring further in detail.

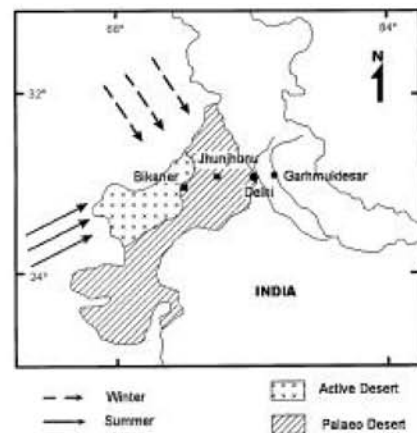
Different size fractions of aerosols were collected using different sampling

techniques. Freely falling dust particles (dry-deposition) were collected in all the stations using plastic trays filled with two layers of glass marble balls kept at a height of 20 m from the ground level. The second type of sample includes the SPM (with a size range of 0.1–100 µm). This size fraction was collected using high volume air samplers, model PEM HVS-1 (Polltech instruments) fitted with EPM 2000 glass micro-fibre filter paper kept at a height of 20 m from the ground level. The airflow was kept at an average rate of 1.2 l/min. Sampling was done simultaneously at all sites for a few days between 19 and 26 May 2000, and 17 and 27 January 2001. Because the filter papers got choked within a period of 24 h or less, we could collect different samples for the same size fraction from a given site and this enabled us to see the variability of aerosol chemistry in a matter of few days. A similar procedure was adopted for the finest size fraction PM<sub>10</sub> (< 10 µm in size) using the high volume air samplers, model PEM HVF-1 (Polltech instruments) kept at the same height at a constant flow rate of 1.2 l/min. At each site we have also collected surface sediments which were used as reference material. The two finer types of aerosols, SPM and PM<sub>10</sub>, collected on glass micro-fibre filter papers were in dry powder form and therefore were easily scraped off the filters. These powders as well as powdered dry-deposition samples and deposited surface sediments (~200 mesh size) were digested in open beakers using a combination of HF + HNO<sub>3</sub> + HClO<sub>4</sub>. These solutions were analysed for copper using a Labtam 8440 ICP-AES at a wavelength of 324.754 nm using international and laboratory internal standards. The precision and accuracy of our analysis were better than 4 and 2% respectively.

At each sampling site and for each season, 5–7 samples of each size fraction were collected as constrained by the sampling process. Minimum and maximum concentrations of Cu during the sampling period at each site for each size fraction are presented in Table 1. The weighted mean concentration for each size fraction is given as average concentration (obtained by the sum of weight fraction of each sample and multiplied by its concentration). Because the number of samples in each fraction is small

and the variation in Cu concentration is large, geometric mean and geometric standard deviation were calculated for PM<sub>10</sub>, SPM and dry deposition (Table 1). In Figure 2, we show the variation in Cu concentration as a function of mean particle size of different size fractions. Summer and winter samples collected from different sites are also distinguished. Cu concentration in deposited sediments as well as the average Cu in the UCC<sup>3</sup> are also shown. We could infer several features from Figure 2. First, the PM<sub>10</sub> size fraction everywhere has the highest Cu concentration relative to the other size fractions. A general decrease in Cu concentration with increasing particle size diameter is observed. Also, samples collected during winter have higher Cu concentration relative to the summer samples. Site dependency of Cu concentration does not appear to be significant, although a small variation is seen from Bikaner to Delhi, particularly in the winter season. Finally, the deposited surface sediments have the lowest concentration of Cu, even lower than that in the average UCC.

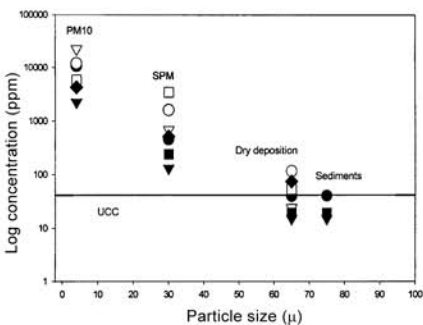
All the aerosol samples, particularly PM<sub>10</sub> and SPM, show significant enrichment of Cu relative to UCC. This suggests a non-crustal source of Cu in the aerosols. This is also supported by the size dependency of Cu concentration in aerosols. It is well known that anthropogenically-generated heavy metals in atmospheric aerosols are commonly enriched in the finest fraction<sup>4</sup>. Crustal



**Figure 1.** Sample locations of the present study. Map also shows the dominant wind trajectory in summer and winter months in the study area.

**Table 1.** Cu concentration (ppm) in the aerosol samples of NW India. (Values in parentheses are in  $\mu\text{g}/\text{m}^3$  of air.)

	Bikaner		Jhunjhunu		Delhi		Garhmuktesar	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
<i>PM<sub>10</sub> (&lt; 10 <math>\mu</math> size aerosols)</i>								
Range (max.–mini.)	1251–4100 (1.653–3.636)		5225–5760 (3.92–5.28)	1216–28000 (.348–7.084)	8437–13000 (2.9–5.33)	5160–28072 (1.37–6.84)	–	–
Average conc.	1862 (3.2831)	22394 (3.784)	5540.5 (4.7271)	15816 (4.0202)	11408 (4.165)	15762 (3.906)	–	4260 (.8008)
Geometric mean	2232 (2.8129)		5486 (4.55)	5835 (1.572)	10655 (3.688)	12035 (3.0661)	–	–
Geometric SD	1586 (.8873)		378 (.959739)	22614 (5.69085)	2298 (1.3196)	17449 (4.1452)	–	–
<i>SPM (0.1–100 <math>\mu</math> size aerosols)</i>								
Range (max.–min.)	53–400 (.3269–1.739)	548–563 (.1304–.1329)	205–276 (.334–.5906)	2511–4725 (.53–.95)	206–677 (.1435–.4536)	1319–1896 (.1424–.491)	–	493–531 (.117–.1348)
Average conc.	105 (.872)	643 (.13115)	250 (.4805)	3741 (.7694)	425 (.31548)	1733 (.3928)	–	513 (.1268)
Geometric mean	130.4 (.7878)	688 (.13165)	238 (.4442)	3445 (.7146)	417 (.2730)	1581 (.2645)	–	511.65 (.1246)
Geometric SD	164 (1.994)	224 (.001752)	50.32 (.18232)	1585 (.30502)	199 (.221688)	410 (.25735)	–	29 (.01229)
<i>Dry deposition samples (mean size between 60 and 80 <math>\mu</math>)</i>								
Range (max.–min.)	11.1–20.3	–	13–26.7	–	34.4–45.4	116	–	–
Geometric mean	15	24	18.6	53	40	–	–	74
Geometric SD	6.58	–	9.85	–	7.78	–	–	–
Reference material (local sediments)	19	–	30	–	35	–	–	–



**Figure 2.** Variation in Cu concentration as a function of particle size of aerosols in NW India. Open and filled symbols represent summer and winter samples. Bikaner:  $\square$ ; Jhunjhunu:  $\nabla$ ; Delhi:  $\circ$ ; Garhmuktesar:  $\diamond$ .

sources in the aerosols/sediments are commonly coarser grained and should have the crustal level concentration of various elements. Surface sediments and samples of dry deposition represent such a crustal component. The observed enrichment of Cu in the finest fraction,  $\text{PM}_{10}$ , is a combined effect of high Cu content in the aerosols of anthropogenic origin and lack of dilution by the crustal component. As the grain size of the aerosols increases, the relative contribution of anthropogenic component decreases. Also, since wind velocity is much reduced on an

average during winter, the dilution effect by coarser crustal component is minimal in the winter season. Greater stability and poorer dispersion of pollutants due to local temperature inversions observed over Indian cities<sup>5</sup> are also responsible for the winter maxima in the Cu concentration of anthropogenic aerosols. Thus the observed concentration of Cu and its variation in different samples point to an anthropogenic source of Cu in aerosols in the northwest part of India.

In the present study, the sampling site Jhunjhunu is located 60 km west of the Cu-mining township of Khetri. However, we did not observe any exceptionally high concentration in Jhunjhunu samples, nor did we observe the lowest concentration in the Bikaner samples, as this site is located in the upwind direction. Therefore, a large part of Cu in these aerosols is likely unrelated to Cu mining or smelting activity. It is tempting to suggest that the major contributor to the Cu in aerosols in this region could be the electric power sector, including power transmission, power consumption and all the materials/appliances associated with this human activity. Surprisingly, we also observe high concentration in Bikaner samples, although a relatively lower value

compared to the other sites. Unfortunately, we do not know what is the relative contribution from local sources and from the cities located in the upwind direction (Karachi in summer time air back trajectory and Islamabad in winter time air back trajectory). Some high concentrations of Cu in SPM samples are reported from Kanpur<sup>6</sup>; however, at Jaipur, Mumbai, Nagpur, Bangalore and Agra<sup>7–9</sup> reported Cu concentrations in SPM samples are lower than the present study. Observed Cu concentration in  $\text{PM}_{10}$  here, on an average, is the highest reported so far in India. High concentrations of Cu ( $\sim 3 \mu\text{g}/\text{m}^3$ ) in  $\text{PM}_{10}$ , similar to those observed here, were reported near a Cu-mining area in Chile<sup>10</sup>; but not so high a value as observed here. This also supports our thinking that the anthropogenic source of Cu in the aerosols of NW India could be dominantly power sector-production, transmission and consumption. On a global scale, Cu takes only the fourth position after Pb, Zn and Ni in terms of atmospheric emission from anthropogenic sources<sup>11</sup>. However, in the present study we observed that Cu is the most abundant among the four trace metals in the aerosols. It is possible that this high level of Cu could be related to

its chemical affinity to organic phases<sup>12</sup> present in large amounts in the atmosphere in this region (the so-called Asian Brown Cloud)<sup>13</sup>, in addition to its anthropogenic emission.

The PM<sub>10</sub> dust samples studied have an average of 6000 and 15,000 ppm Cu concentration in the summer and winter respectively. These values, nearly 1.5% Cu in the aerosols, suggest that they are better than Cu ores in terms of Cu content (any rock containing > 0.5% Cu is a potential Cu ore today). The economics of Cu recovery from the aerosols needs to be understood. Similarly, environmental and health impacts of such high Cu concentration in the air need to be investigated. Although Cu is an essential nutrient required by plants and animals in small amounts, the observed levels of Cu concentration in the respirable fraction of aerosols, i.e. PM<sub>10</sub> could cause gastrointestinal disturbances, including nausea, vomiting, and liver or kidney damage depending on exposure time. We

need to generate sound scientific knowledge about the causes and consequences of heavy-metal concentration in the aerosols at a local, regional and global level for better policy options on development and the environment.

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Received 12 August 2002; revised accepted 7 November 2002

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