Bull. Environ. Contam. Toxicol. (2004) 73:756–761

DOI: 10.1007/s00128-004-0490-1

Bulletin of Environmental Contamination and Toxicology

Essential Heavy Metals in Environmental Samples from Western India

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Received: 7 November 2003/Accepted: 13 July 2004

Human beings are exposed to large amount of toxic metals and their oxides during various occupational situations. They are also environmentally exposed to these metals through food, water and air with small doses. The toxic effects of certain metals in different animal system are well documented. However, reports of toxicity due to metal exposure in human are scanty with the exception of lead and mercury. Metals are not biodegradable, have long biological half-lives and have the potential for accumulation in the different body organs leading to unwanted side effects. In recent years, it is realized that heavy metals also have a role in the environmental pollution. Thus there is a need to have the base line environmental data on each metal so that total pollutants can be judged in the environment. In this paper we are presenting the chromium, copper, zinc and manganese concentrations in the environmental samples of western India, as there is scanty data on environmental concentration of these metals from this part of the world. However, data on environmental concentration of these metals are available from other parts of the world. Chang (2003) reported that in China, the geological background level of heavy metals was low, but with the activity of humans; water, air and plants are polluted in some cases and even affect human health through the food chain.

Heavy metals are incorporated into the body through food ingestion and inhalation. Chromium, zinc, copper, and manganese are the essential metals required for various physiological functions. However, higher exposure to these may be toxic to the human. Chromium is a naturally occurring element found in rocks, animals, plants, and soil and in volcanic dust and gases. In human and animals chromium trivalent is an essential nutrient that plays an important role in glucose, fat and protein metabolism by potentiating the action of insulin suggested by Anderson et al. (1981). Chrome ore mining and chrome – based industries also release chromium into the environment. Human beings may be exposed to high doses of chromium during certain occupational and environmental situations. Industrial workers exposed to high doses of chromium compounds may develop asthma, nasal perforation and respiratory diseases. Exposure to hexavalent chromium (Cr VI) reported to cause pulmonary carcinoma, dermatitis, hepatotoxicity, nephrotoxicity and gastrotoxicity in human and laboratory animals (WHO 1988). Manganese is widely distributed in the nature in various forms. Excessive exposure via inhalation has been shown to affect the lungs, and cause pneumonia, bronchitis, and irreversible brain disease to some extent similar to Parkinson's disease. Zinc is also one of the essential nutrients in humans and animals that is necessary for the function of a large metalloenzymes. Zinc deficiency

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has been associated with adverse effects in humans and animals, however, over exposures to zinc also have been associated with toxic effects. (ATSDR 1994). Copper is an essential trace element and required for various biological process. Deficiency or excess may lead to various clinical manifestations. Keeping in view of the scanty environmental data on these metals, the present study was undertaken with the view to find out the base line concentration on these metals from western India.

MATERIALS AND METHODS

The air samples were collected randomly from urban and rural area of three western states of India i.e. Maharastra, Gujarat and Rajasthan using high volume air sampler. Looking at the industrial development of the country, Maharashtra and Gujarat have attained considerable degree of industrial growth. From Maharashtra, the samples were collected from Mumbai and Pune (urban) and New Bombay (rural), Pimpri and in Gujarat; samples were collected from Baroda, Kandala, Mehsana, Rajkot and nearby rural villages-Baroda (Rural), Narayan Sarovar, Modhera and Ribda, while samples from Rajasthan were collected from Udaipur, Jaipur and Kota and from rural area Eklinji, Amer and Sawai Madhopur. The water samples from tube wells as well as tap water were also collected from the same urban and rural area. The numbers of samples collected from different area are shown in Table 2-5.

The air samples were collected using Whatman's EPA 2000 glass micro-fibre filter paper (size 8"x 10") by high volume sampler (Model APM Envirotech, India). The sample device was set up at the height of 5 ft. at the breathing zone from ground level. The sampler was run for 24 hours at a rate of about 1 cubic meter/min with 30 minutes rest after every 5 hours. For the collection of water samples, metal free plastic bottles of 500 ml capacity were used. The samples were brought to the laboratory for the determination of concentration of chromium, copper, zinc and manganese. Water samples were concentrated five times by heating. The concentration of chromium, copper, zinc, and manganese was measured in water and air using Atomic Absorption Spectrophotometer (Perkin Elmer, USA). For quality control, standard stock solutions were prepared for each metal. The Standard Reference Materials (SRMS) supplied for air by Bhabha Atomic Research Centre (BARC), Bombay, India were also analyzed, which show a good agreement with the reference value provided by BARC and values obtained in our laboratory (Table 1).

Table 1. Analysis of fortified air samples supplied by BARC, Bombay.

No.	Element	Lab Values (μg)	BARC Values (μg)
1	Manganese	17.10	20.50
2	Chromium	8.05	7.50
3	Copper	25.30	20.20
4	Zinc	106.40	99.00

RESULTS AND DISCUSSION

The mean level of manganese in the air of rural places studied of Maharashtra, Gujarat and Rajasthan was 0.390, 0.166 and 0.149($\mu g/m^3$) respectively. These values were lower than the concentration observed in urban area except Maharashtra where slightly higher concentration was noticed in rural area. Whereas the manganese concentration was higher in the water as compared to air of the rural area (Table-2). Overall, mean concentration of this metal in urban air was higher while it was lower in water as compared to rural area.

Table 2. Manganese levels in ambient air and water in urban and rural centers of Maharashtra, Gujarat and Rajasthan States.

State	Center	Ambient Air (μg/m^3)			Water (μg/ml)		
		No.	Mean	S.D.	No.	Mean	S.D.
Maharashtra	Urban	48	0.332	0.189	50	0.046	0.074
	Rural	36	0.390	0.420	31	0.196	0.029
Gujarat	Urban	97	0.238	0.146	88	0.051	0.025
	Rural	60	0.166	0.101	62	0.115	0.180
Rajasthan	Urban	73	0.230	0.210	74	0.023	0.105
	Rural	37	0.149	0.105	37	0.041	0.066
Mean for western India*	Urban	218	0.56	0.179	212	0.040	0.073
	Rural	133	0.222	0.235	130	0.113	0.130

* *Mean value of Maharashtra, Gujarat and Rajasthan*

The mean level of chromium concentration in the air of rural as well as urban center of Maharashtra was higher with respect to mean concentration of Gujarat and Rajasthan. The level was higher in the urban air of all the three states as compared to rural area of the respective states. The mean concentration of this metal was higher in water samples of urban area of Gujarat than Maharashtra and Rajasthan (Table-3) Further, mean level of chromium of these three states higher in urban air and water with respect to rural mean of the rural area.

Table 3. Chromium levels in Ambient Air and Water in Urban and Rural Centers of Maharashtra, Gujarat and Rajasthan States.

State	Centre	Ambient Air (μg/m^3)			Water (μg/ml)		
		No.	Mean	S.D.	No.	Mean	S.D.
Maharashtra	Urban	48	0.089	0.077	50	0.016	0.088
	Rural	36	0.055	0.034	31	0.062	0.145
Gujarat	Urban	95	0.052	0.069	81	0.095	0.278
	Rural	50	0.049	0.055	54	0.016	0.014
Rajasthan	Urban	65	0.018	0.013	61	0.026	0.058
	Rural	34	0.016	0.008	34	0.004	0.003
Mean for western India*	Urban	208	0.051	0.022	192	0.053	0.189
	Rural	120	0.041	0.040	119	0.025	0.074

* *Mean value of Maharashtra, Gujarat and Rajasthan*

The mean level of copper in the air of urban places of Maharashtra, Gujarat was higher as compared to rural area. However the level was slightly higher in the rural area of Rajasthan than urban area of Rajasthan. Further, copper concentration was slightly higher in water of rural area as compared to the water of urban area in all the three states (Table-4)

Table 4. Copper levels in ambient air and water in urban and rural centers of Maharashtra, Gujarat and Rajasthan states.

State	Centre	Ambient Air (μg/m³)			Water (μg/ml)		
		No.	Mean	S.D.	No.	Mean	S.D.
Maharashtra	Urban	48	2.002	1.27	50	0.017	0.032
	Rural	36	0.862	0.66	31	0.018	0.036
Gujarat	Urban	94	2.203	4.31	85	0.016	0.018
	Rural	60	1.486	1.06	62	0.031	0.041
Rajasthan	Urban	72	1.018	0.89	74	0.016	0.018
	Rural	37	1.200	1.62	38	0.019	0.016
Mean for western India*	Urban	214	1.750	2.969	209	0.016	0.022
	Rural	133	1.237	1.182	131	0.024	0.034

** Mean value of Maharashtra, Gujarat and Rajasthan*

The mean level of zinc in the air of urban and rural areas was 0.841μg/m³, 0.527μg/m³, 0.515μg/m³ and 0.596μg/m³, 0.397μg/m³, 0.185μg/m³ of Maharastra, Gujarat and Rajasthan respectively (Table-5). The concentration in the rural area was lower than urban area. Further, concentration of zinc in water shows different pattern. The concentration of Zn in water was higher in urban area of Maharashtra as compare to rural area but it was reverse in case of Gujarat and Rajasthan where the level was higher in rural areas. Further, mean level of zinc in air of all three states is higher in urban than to rural while in case of water it is about the same (Table-5).

Table 5. Zinc levels in ambient air and water in urban and rural centers of Maharashtra, Gujarat and Rajasthan states.

State	Centre	Ambient Air (μg/m³)			Water (μg/ml)		
		No.	Mean	S.D.	No.	Mean	S.D.
Maharashtra	Urban	48	0.841	0.423	50	0.176	0.218
	Rural	36	0.596	0.206	31	0.126	0.134
Gujarat	Urban	83	0.527	0.575	85	0.076	0.105
	Rural	49	0.397	0.490	62	0.094	0.141
Rajasthan	Urban	70	0.515	1.011	75	0.063	0.075
	Rural	37	0.185	0.101	38	0.089	0.112
Mean for western India*	Urban	201	0.598	0.732	210	0.095	0.133
	Rural	122	0.391	0.335	131	0.100	0.132

**Mean value of Maharashtra, Gujarat and Rajasthan*

Manganese, chromium, zinc and copper concentrations were higher in the air urban area as compared to rural area in part of this world except copper which was higher in the air of the rural areas of Rajasthan. This is an agreement with various available studies, which suggests higher level in the urban areas. Earlier, a survey of public drinking water supplies in 100 large United States cities reported 97% contained <100 μg/L of manganese (Durfor and Becker, 1964). Later another survey of 969 systems reported 91% contained <50 μg/L, with a mean concentration of 22 μg/L (U.S. DHEW 1970). Several other studies reported similar manganese concentrations, with mean values ranging from 4 to 32 μg/L (EPA,1984; NAS 1980a; WHO,1981). In the present study, the lowest concentration of 0.023 μg/ml in urban water of Rajasthan and highest concentration of 0.196 μg/ml in rural water in Maharashtra was observed.

Chromium concentrations ranging from 0.002 to 0.2 μg/m^3 in air for twenty-two American cities have been reported by Taber and Warren (1958). While concentrations ranging from 0.017 to 0.087 ug/m^3 have been reported for Osaka, Japan (US-EPA, 1978). The chromium concentration was observed higher in the urban air as well as in water except Maharashtra as compared to rural area in the present study. Banerjee (2003) analysed the street dust samples from three different localities like industrial, heavy traffic and rural in Delhi area, India. He observed remarkably high level of Cr, Ni and Cu in the industrial area, while Pb and Cd did not show any discernible variations between the three localities. The highest chromium level i.e. 0.089 μg/m^3 and 0.062 μg/ml was observed in the urban air and rural water of Maharashtra respectively, which is an industrialized state as compared to 0.018 μg/m^3 in urban air and 0.004 μg/ml in rural water of Rajasthan, India. The average concentrations of Chromium in drinking water for urban centers were observed as 0.016 μg/ml, 0.095μg/ml and 0.026 μg/ml for Maharashtra, Gujarat and Rajasthan respectively, whereas mean Chromium level of 0.027 μg/ml in the water of rural areas of Western India was observed (Maharashtra, Gujarat and Rajasthan). Fishbein (1984) reported atmospheric total chromium concentration in the United States is typically ≤10 μg/m^3 in rural areas and 10–30 μg/m^3 in urban areas. The chromium concentrations in U.S. drinking water typically range from 0.4 to 8.0 μg/L, with a mean value of 1.8 μg/L observed by Greathouse and Craun (1978).

The copper concentration was in the range of 0.86 to 1.48 μg/m^3 in the air of rural area while the range was 1.018 μg/m^3 to 2.203 μg/m^3 in urban area of western India. According to the EPA's National Air Surveillance Network report for the years 1977, 1978, and 1979, median copper concentrations were 133, 138, and 96 ng/m^3, respectively, for urban samples and 120, 179, and 76 ng/m^3 for non-urban samples (Evans et al. 1984). Davies and Bennett (1985) reported average atmospheric copper concentrations of 5- 50 ng/m^3 in rural areas and 20-200 ng/m^3 in urban locations. The concentrations in rural areas are considerably lower than those reported in the EPA survey. Data from many urban locations in the United States over the last l0-15 years show concentrations of copper associated with particulate matter ranging from 3-5140 ng/m^3 (Schroeder et al. 1987). Remote and rural areas have concentrations of 0.029 - 12 and 3-280 ng/m^3, respectively. The levels reported by Schroeder et al. (1987) are consistent with those obtained in a study of airborne trace elements in national parks by the Davidson et al. (1985).

Zinc has been detected in air, surface water, groundwater, and soil; the frequency of detection and the concentrations are greatest near source areas (e.g., hazardous waste sites and industrial areas such as lead smelters) ATSDR, (1994). In a survey by the National Air Surveillance Network, the mean concentration of zinc in the air in the United States in 1977-1979 was 0.02-0.16 μg/m^3 for urban air compared to 0.01-0.05 μg/m^3 for rural air. The concentrations of zinc in the air of remote areas range from <0.003 to 0.027 μg/m^3. The mean concentrations of zinc in ambient water and drinking water range from 0.02 to 0.05 mg/L and from 0.01 to 0.1 mg/L, respectively. ATSDR, (1994). In the present study also Copper concentration was higher in the air of urban area of western India with respect to rural area of the region.

In conclusion the concentration of all the four heavy essential metals estimated in the air of urban area was higher as compared to rural area except Copper in Rajasthan and manganese in Maharashtra. Further, constant monitoring of these heavy metals are needed due to rapid industrialization of India as well as rapid industrial growth and increasing uses of various products, which might have these metals. Thus there is a need for periodical monitoring of pollutants in the environment to assess the pollution due to heavy metals.

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