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Metal Contamination of Soils and Prospects of Phytoremediation in and Around River Yamuna: A Case Study from North-Central India

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Additional information is available at the end of the chapter

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1. Introduction

The rapid industrialization and intensive agricultural activities over the last few decades have resulted in accumulation of various pollutants in the environment, which are distributed over wide areas by means of air and water. This has caused visible detrimental effects to the ecosystem and consequences to human health. Today, many soils throughout the world have undesirably high concentrations of heavy metals. These include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe), and the platinum group elements. At low or background concentrations, heavy metals are not pollutants. They occur naturally in the environment due to their presence in bedrocks. Some heavy metals such as Zn and Cu are also essential micronutrients for living organisms. Therefore, the term *heavy metal pollution* refers to heavy metal levels that are abnormally high relative to normal background levels. All heavy metals at high concentration have strong toxic effects and are regarded as environmental pollutants.

Some heavy metals (like Fe, Zn, Ca and Mg) have been reported to be of bio-importance to man and their daily medicinal and dietary allowances have been recommended. However, some others (like As, Cd, Pb, and methylated forms of Hg) have been reported to have no known bio-importance in human biochemistry and physiology and consumption even at very low concentrations can be toxic [1]. Even for those that have bio-importance, dietary intakes have to be maintained at regulatory limits, as excesses result in poisoning or toxicity [2]. Although individual metals exhibit specific signs of their toxicity, the following have been reported as general signs associated with Cd, Pb, As, Hg, Zn,

Cu and Al poisoning: gastrointestinal disorders, diarrhoea, stomatitis, tremor, ataxia, paralysis, vomiting and convulsion, depression, and pneumonia when volatile vapours and fumes are inhaled [3]. The nature of effects could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic.

Pb, Zn, Cu, Co, Mn, Fe, Cr and Cd have been found in the streams and rivers of the Americas, Europe, Asia, Africa and Australia [4-9]. In India, presence of heavy metals has been reported in the Brahmaputra [10]; the Kali and Hindon [11]; and more recently, in the Gomti [12]; the Cauvery [13]; and the Ganga [14].

The Yamuna (also Jamuna or Jumna) is the largest tributary of the Ganga in northern India, having the total length of about 1376 km. The source of Yamuna is Yamunotri in the Uttarakhand Himalaya, which is north of Haridwar in the Himalayan mountains. Yamuna river flows through the states of Uttarakhand, Delhi, Haryana and Uttar Pradesh and finally merges with river Ganges at a sacred spot known as Triveni Sangam in Allahabad. A number of prominent cities such as Delhi, Mathura and Agra lie on the bank of river Yamuna. Over 57 million people depend on the Yamuna waters. Just like the Ganges, the Yamuna too is highly venerated in Hinduism and worshipped as goddess Yamuna, throughout its course.

Due to high density population growth, rapid industrialization, today Yamuna is one of the most polluted rivers in the world, especially around New Delhi, where 15 drains discharge waste water into the river. The city dumps ~58% of its waste into it. When the river enters the city, it is already contaminated with 7500 coliform content per 100 ml. when it leaves the city, it carries with a dangerously high coliform content of 24 million per 100 ml. Even the ground water has been affected by leachates that pass down from the dumping sites. According to the Central Pollution Control Board (CPCB), 70% of the pollution in river is from untreated sewage and the remaining 30% is from industrial sources, agricultural run-off, garbage etc. The water quality of Yamuna River falls under the category "E" which makes it fit only for recreation and industrial cooling, completely ruling out the possibility for underwater life. Almost every year mass death of fishes is reported. Biological Oxygen Demand (BOD) load increased by 2.5 times between 1980 and 2005: from 117 tonnes per day in 1980 to 276 in 2005.

Although the government of India has spent nearly \$500 million to clean up the river, the river continues to be polluted with garbage while most sewage treatment facilities are underfunded or malfunctioning. The Ministry of Environment and Forests (MoEF) of the Government of India (GOI) took measures to curb pollution in 12 towns of Haryana, 8 towns of Uttar Pradesh, and Delhi under an action plan (Yamuna Action Plan-YAP) which is being implemented since 1993 [15]. However in 2009, the Union government admitted the failure of the Ganga Action Plan (GAP) and the Yamuna Action Plan (YAP), saying that "rivers Ganga and Yamuna are no cleaner now than two decades ago" despite spending over Rs 1, 700 crore to control pollution [16]. In August 2009, Delhi Jal Board (DJB) initiated its plan for resuscitating a 22 km stretch of the Yamuna in Delhi by constructing interceptor sewers, at the cost of about Rs 1, 800 crore [17].

There are three main sources of pollution in the river, namely household and municipal disposal sites, agricultural run-off, and industrial effluents and run-off. Urban runoff and

agricultural runoff are mainly non-point sources. The major sources of pollution from agriculture are fertilizers containing superabundant nutrients such as nitrogen and phosphorus, and heavy metals such as Cd, Cu, Pb and Zn. Water quality may also be altered by other factors, such as livestock manure, human waste, and atmospheric deposition. Atmospheric pollutants are often the largest source of waterborne metals. It is estimated that 70% of lead in water and over 50% of many of the other trace metals in the Great Lakes (USA) are derived from atmospheric transfer. In general, freshwater ecosystems have low natural background metal levels and therefore tend to be sensitive to even small additions of most trace metals. Heavy metal contamination of soils and water from industrial and traffic sources in urban environments has been studied in North America and Europe [18-22]. Agencies like the World Health Organization (WHO) and the United States Environment Protection Agency (USEPA) have set stringent standards for maximum permissible limits of heavy metals, but there is a paucity of detailed studies on heavy metal pollution and its remediation within industrial zones in developing countries. Yamuna outnumbers any other river in the number of industries on its bank. This is because it passes through many major industrial cities. About 22, 42, and 17 large and medium industrial units in the states of Haryana, Delhi, and Uttar Pradesh have been identified as polluting the river in the action plan area. In addition, the water in this river remains stagnant for almost 9 months in a year aggravating the situation.

According to the Agra District Industrial Centre officials, there were 226 iron foundries and about 340 metal casting units functioning in Agra in the decade of 1990-2000. Before the revised pollution control directives put the Agra diesel generator manufacturing industry off its track, the foundry industry of this town ranked among the country's largest assemblies of metal casting industrial units, generating business of over Rs 6, 000 crores. The ban on coking coal in the blast furnaces utilized by the foundry and metal-casting industry was a serious setback and the number of industrial units reduced drastically. In August 1999, the Supreme Court ordered the closure of 53 iron foundries and 107 other factories in Agra. In September 2010, it again ordered the closure of 212 of the 1, 715 small industries that had failed to disclose their toxic emission levels to the Uttar Pradesh Pollution Control Board (UPPCB). Another 299 were required to install pollution controlling devices, failing which they too would face closure. However, the ground realities are still nowhere near the reduced pollution levels targeted in Yamuna and its adjacent areas whether Agra or elsewhere, after it leaves the Himalayan foothills. The status quo, thus, ultimately leaves much to be desired.

Phytoremediation is an emerging technology that employs the use of green plants for the clean up of contaminated environment. It takes the advantage of the fact that a living plant acts as a solar-driven pump, which can extract and concentrate certain metals from the environment [23]. This remediation method maintains the biological properties and physical structure of the soil. The technique is environmentally friendly, cost-effective, visually unobtrusive, and offers the possibility of bio-recovery of the metals. In the case of heavy metal contamination in soil, phytoremediation techniques are narrowed down to *Phytoextraction*, where plants remove metals from the soil by concentrating them in their harvestable parts [24], and *Phytostabilization*, where plants reduce the mobility and bioavailability of pollutants by immobilization [25].

Phytoremediation is becoming possible because of the successful basic and applied research much of it conducted with the productive interdisciplinary cooperation of plant biologists, soil chemists, microbiologists and environmental engineers. Extensive progress has been made in characterizing and modifying the soil chemistry of the contaminated site to accelerate phytoremediation. The greatest progress in phytoremediation has been made with metals [26, 27]. Phytoremediation leaves the topsoil in usable condition and it is aesthetically pleasing. It requires minimal equipment and less energy inputs as plants do most of the work using solar energy. Thus, it is an eco-friendly process. The plants used can later be harvested, processed and disposed off in an environmentally sound manner. This technology has been receiving attention lately as an innovative, cost-effective alternative to the otherwise tedious and expensive methods in use which are not only a burden on the exchequer but also require efforts on recurring basis.

Phytoremediation employing indigenous species can be an ecologically viable option for sustainable and cost-effective management. Native plants often become adapted to locally elevated levels of metals in soil at contaminated sites, e.g. mines and industrial zones [28-30] and metal toxicity issues do not generally arise. Many native, well adapted plants have been investigated and even used for heavy metal bioindicating and phytoremedial purposes including lemongrass and other wild grasses, vetiver, *Sesbania*, *Avena*, *Crotalaria*, *Crinum asiaticum*, *Typha latifolia* and *Calotropis procera* etc. [31-35, 28]. Native wild species are also important to remediate soils in context of the studied area due to a remark (April, 2006) of the Supreme Court prohibiting the cultivation of plants requiring fertilizers and pesticides along the Yamuna. In the light of this limitation, native wild species are a viable option since these do not require agronomic inputs.

Since the river Yamuna is the life line of Mathura and Agra, the existing pollution level has posed a serious threat not only to the environment but also to the human population. Adjacent areas are highly polluted and are a sink for a variety of chemicals including heavy metals. The present study was undertaken: (i) to get a comprehensive profile of eight metals in water and adjacent soils of the river Yamuna within Mathura, Agra and Bateshwar; (ii) to get a qualitative and quantitative estimate of the species present at test sites through phyto-sociological surveys; and (iii) to inventorize species with potential for phytoremediation present on sites by comparing with those previously reported by the authors as suitable in this context.

2. Case study

Agra (27°10'N, 78°05'E, 169 msl), on the banks of the river Yamuna, is located in Uttar Pradesh in the north central part of India. It is roughly 200 km south-east of the national capital, New Delhi. Bounded by the Thar desert of Rajasthan on its south-east, west and north-west peripheries, it is a semi-arid area. The world renowned Mughal monument, the Taj Mahal is situated here. It is world renowned for its leather industry and marble handicrafts but it also boasts a cast iron and engineering goods industry. Mathura (27.28°N 77.41°E) is located approximately 60 km north of Agra and 145 km south-east of Delhi. According to Hindu

scriptures Mathura is the birthplace of Lord Krishna. It is a fast expanding city with about half a million residents. Mathura oil refinery is one of the biggest oil refineries of Asia. Textile printing, dyeing and silver ornament manufacturing are major industries. Apart from these there are units manufacturing taps, household items, and cotton materials. Bateshwar (26.93°N 78.54°E) is a village on the banks of Yamuna about 120 km downstream from Agra. It is an important spiritual and cultural centre for Hindus.

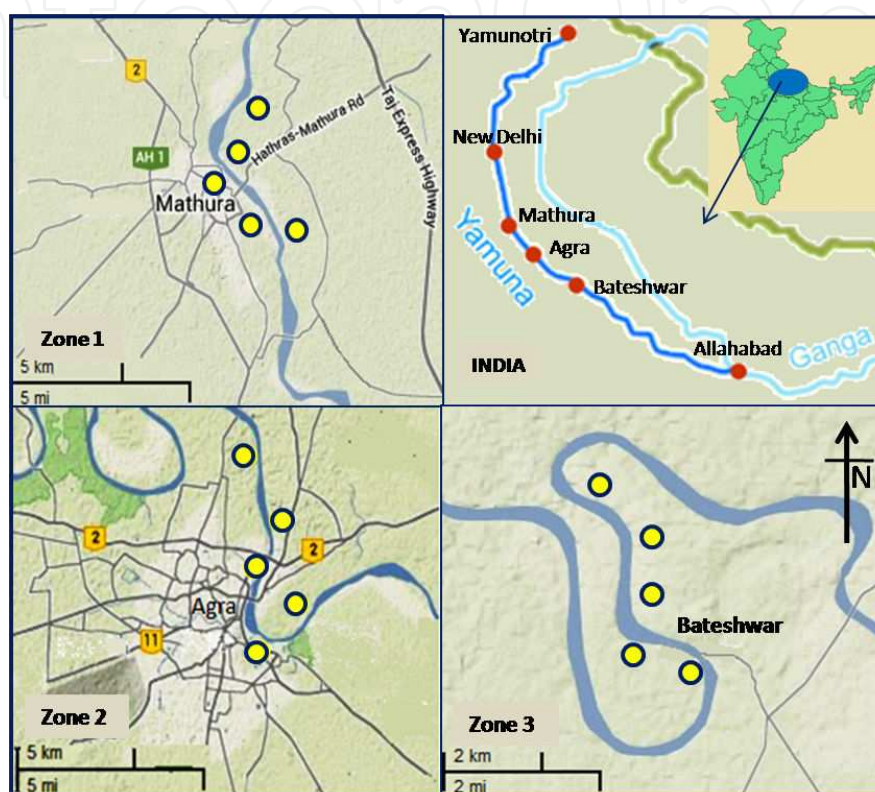


Figure 1. Map of the study area

The study area was divided into three zones (Figure 1); all three along the course of Yamuna and covering two cities viz. Mathura (zone 1) and Agra (zone 2) and a large village i.e. Bateshwar (zone 3). The distance between zones 1 and 2 is 80 km and zones 2 and 3 is 120 km downstream. In all, a total distance of 200 km was covered along the course of river. In each zone, 5 sites were selected ~1 km apart. Five random soil samples were taken from 0-15 cm depth at each site. A total of 75 soil samples (25 from each zone) were analyzed in order to obtain a complete profile. The same number of river water samples was collected from midstream at a depth of about 0.3 m. Soil from the botanical garden of St. John's college, Agra, was utilized as control.

The statistical significance of differences among mean metal content in water and soil was independently determined by one-way analysis of variance (ANOVA) followed by Fisher's LSD test. Pearson's coefficient for correlation of water and soil data was analyzed at a significance level of $P < 0.05$ and $P < 0.01$ with SPSS 16.0 statistics software.

3. Physico-chemical profile

3.1. Water

Physico-chemical properties of the water samples collected from the study zones are mentioned in Table 1. The pH values indicate neutral nature of river water acceptable as per BIS [36] and WHO [37] guidelines. A reading of 6.5 to 7.5 is considered neutral, suitable for general plant growth [38]. Conductance which reflects the status of major ions/inorganic pollution and is a measure of total dissolved solids and ionized species in the water, varies between 434 – 503 $\mu\text{mho/cm}$. Total dissolved solids were highest in zone 2. The hardness of water body is regulated largely by the levels of Ca and Mg salts. Other metals if present such as Fe, Al and Mn may also contribute to hardness. Most parameters were within their respective acceptable limits [36, 37]. Electrical conductivity was low. High COD, BOD and low DO in zones 1 and 2 are due to the discharge of huge amount of the untreated urban and industrial wastewater/effluents indiscriminately. All three zones were faecally contaminated. Bacterial contamination ranged from 19000 – 93000 coliform/100ml; the values are much higher than recommended values of 1coliform/100ml. Most of these coliforms were of faecal type due to gravity discharge of faecal wastes in adjacent areas along the river.

Parameters	Zone 1	Zone 2	Zone 3	Acceptable Limits [36, 37]
pH (1:2.5)	7.31	7.23	7.61	6.5-8.5
Total Dissolved Solids (mg/l)	266	314	245	500
Conductivity ($\mu\text{mho/cm}$)	462	503	434	
N-NO ₃ (mg/l)	3.54	4.37	4.11	10
N-NH ₃ (mg/l)	2.34	2.36	1.63	10
Total hardness (mg/l)	227	223	210	250
Total alkalinity (mg/l)	203	188	209	
Chemical Oxygen Demand (mg/l)	23.5	24.3	11.3	
Chloride (mg/l)	8.5	8	9	250
Fluoride (mg/l)	0.37	0.37	0.32	
Dissolved Oxygen (mg/l)	5.63	-	8.67	>5
Biological Oxygen Demand (mg/l)	9.63	10.7	5.34	
Sodium (mg/l)	6.81	6.62	7.15	
Potassium (mg/l)	0.38	0.4	0.38	
Ca hardness (mg/l)	124	131	115	
Mg hardness (mg/l)	83	96.4	91.6	
Faecal coliforms (MPN/100ml)	86000	93000	19000	
Streptococcus (MPN/100ml)	64000	71000	17000	

Table 1. Physico-chemical profile of water

3.2. Soil

The soil of the study area is characterized by alluvium, which is an admixture of gravel, sand, silt and clay in various proportions deposited during the quaternary period. The area is a part of Indo-Gangetic alluvium of quaternary age and is made up of recent unconsolidated fluvial formations comprising sand, silt, clay and *kankar* with occasional beds of gravel. The topsoil is coarse and angular sand with small clay fraction. The sub-soil is sandy throughout. The stabilized topsoil is reddish brown with sand and clay mixed. The minimum depth of topsoil layer is 60 cm.

Physico-chemical properties of soil samples are given in Table 2. The topsoil in the study area is sandy loam (sand 60-80%, silt 10-24%, clay 8-16%). It has high exchangeable sodium percentage (ESP) values and moderate water retaining capacity. The sub-soil is sandy throughout. Soil pH ranged from neutral to alkaline. Zones 3, 2 and 1 were classified as very low, low and medium in organic matter, respectively.

Zone	pH (1:2.5)	Electrical Conductivity (dS/m) (1:2.5)	Organic Matter (%)	Avail. Phosphate (kg/ha)	Avail. Potash (kg/ha)	Avail. Nitrogen (kg/ha)
1	7.06-7.12	0.46-.50	1.44-1.53	108-115	236-298	53.4-60.8
2	6.24-6.81	0.33-0.38	0.8-1.2	131-140	65-94	50.1-55.2
3	7.43-7.6	0.44-0.47	0.5-0.72	50-65	143-178	75.2-87.8
Control	7.21	0.54	1.68	70.5	393	112.9

Table 2. Physico-chemical profile of soils

The electrical conductivity (EC) of soils ranged from 0.33-0.54 dS/m. Zone 1 and 2 soils fall in very high (>100 kg/ha), soils from zone 3 and control site in the high (50-100 kg/ha) phosphate availability bracket. Soils from zones 1, 3 and control displayed medium (130-330 kg/ha) potash levels while zone 2 was low (<130 kg/ha) in available potash. Nitrogen content in the soil samples ranged from 50.1 – 112.9 kg/ha.

4. Heavy metal profile

4.1. Water

Concentrations of heavy metals in the water samples collected from different location have been summarized in Table 3. It is clearly evident from the table that heavy metals were consistently higher in zone 2 compared to zones 1 and 3. Cr content was markedly higher among the metals in zone 2 followed by zone 1. The concentration of heavy metals in water samples ranged from 0.018 – 0.095 mg Pb l⁻¹, 0.025 – 0.341 mg Cd l⁻¹, 0.47 – 1.76 mg Zn l⁻¹, 0.27

– 1.58 mg Cu l⁻¹, 0.001 – 0.005 mg Co l⁻¹, 0.80 – 9.37 mg Cr l⁻¹ and 0.078 – 0.32 mg Ni l⁻¹. As was not detected in any sample.

Zone		Pb	Cd	Zn	Cu	Co	Cr	Ni
1	Range	0.025-0.041	0.05-0.136	0.7-1.02	0.86-0.98	0.002-0.004	2.87-4.23	0.078-0.12
	Avg.	0.036a	0.088a	0.868a	0.916a	0.003a	3.55a	0.097a
	SD	0.007	0.037	0.128	0.046	0.0005	0.540	0.016
2	Range	0.066-0.095	0.159-0.341	1.37-1.76	1.27-1.58	0.004-0.005	6.42-9.37	0.17-0.32
	Avg.	0.082b	0.243b	1.56b	1.40b	0.005b	7.914b	0.256b
	SD	0.013	0.072	0.166	0.112	0.001	1.138	0.071
3	Range	0.018-0.028	0.025-0.03	0.47-0.61	0.27-0.33	0.001-0.002	0.8-0.97	0.009-0.015
	Avg.	0.023c	0.028c	0.54c	0.3c	0.001c	0.864c	0.01c
	SD	0.004	0.004	0.058	0.042	0.0003	0.066	0.003
F value		*	*	*	*	*	*	*
Permissible limits	WHO [37]	0.01	0.003	5	2	-	-	-
	USEPA [39]	0.015	0.005	5	1.3	-	-	-
World Average		0.004	0.001	0.2	1.4	-	-	-

As content below detection limit.

F value :“*” statistically significant. Different letters in the same column denote significant statistical difference (P≤0.001) in mean metal contents in water samples from different zones

SD- Standard deviation.

WHO – World Health Organization.

USEPA – United States Environment Protection Agency.

Table 3. Heavy metal content of water samples (mg L⁻¹)

All the metals in water samples were positively (P<0.01) correlated with each other (Table 4). In other words, metal concentration trends were identical and increased simultaneously for Pb, Cd, Zn, Cu, Co, Cr, and Ni.

	Cd	Zn	Cu	Co	Cr	Ni
Pb	0.970**	0.985**	0.875**	0.924**	0.960**	0.962**
Cd		0.977**	0.902**	0.944**	0.954**	0.963**
Zn			0.925**	0.953**	0.976**	0.966**
Cu				0.963**	0.940**	0.899**
Co					0.961**	0.930**
Cr						0.947**

** Correlation is significant at the 0.01 level (two-tailed) (two-tailed; n=75)

Table 4. Correlation coefficients: water heavy metal concentrations

Higher concentrations of metals in zone 2 (Figure 2) may be attributed to the discharge of industrial effluents from various sources including untreated sewage, municipal waste and agrochemical runoff from the nearby villages directly into the river. The concentrations of Co and Ni were found to be negligible at all sites. Due to the neutral to alkaline nature of river water, most of the heavy metals have precipitated and settled as carbonates, oxides, and hydroxide bearing sediments and elevated levels indicates higher exposure risks to the benthic biota of the river. Based on the WHO [37] and USEPA [39] drinking water standards (Table 3) the results in the present investigation show that Pb, Cd and Cr at all sites and Ni at most sites far exceeded the prescribed limits. Cu values from zone 2 were above the USEPA [39] threshold. One Way ANOVA and Fisher's LSD test indicate the difference in mean content of each metal among zones was highly significant statistically ($P \leq 0.001$).

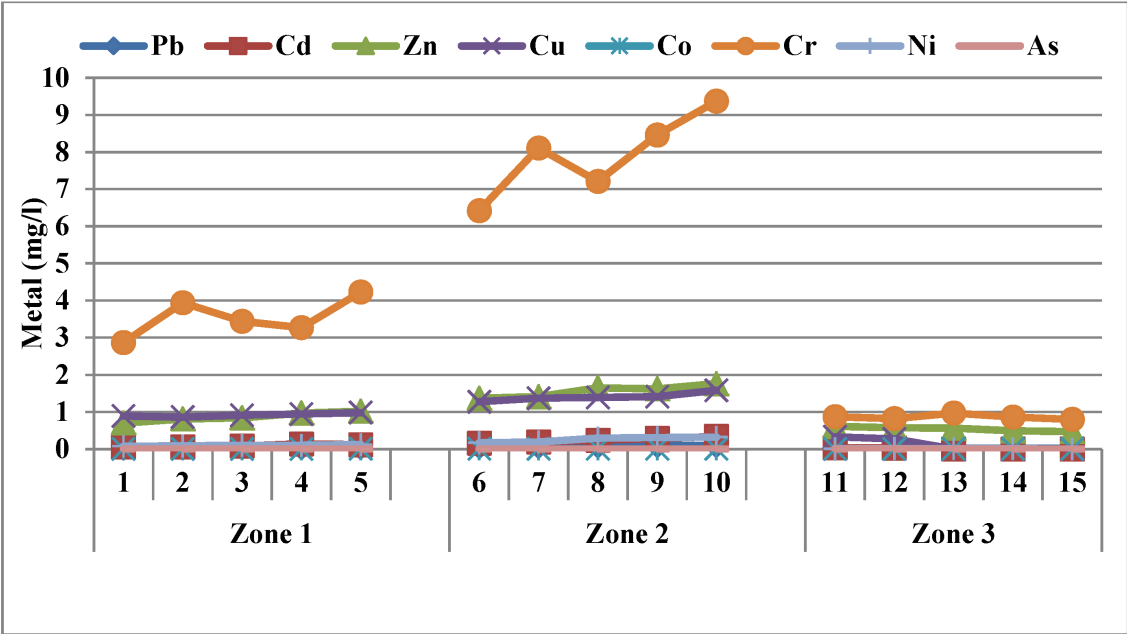


Figure 2. Average heavy metal content in water samples

When compared with the metal profile of the rivers around the world (Table 5) the situation does not seem that desperate here, at least as far as heavy metal contamination is concerned. The picture, however, is quite different when we consider the WHO guidelines for drinking water and World average of trace elements in unpolluted rivers [56, 57], the concentration ranges of Pb and Cd were well above the international guidelines and acceptable concentrations for drinking water (Table 3). When compared to the world average of trace elements for unpolluted rivers, the river was considered polluted by Pb, Cd, Zn and Cu.

Rivers	Pb	Cd	Zn	Cu	Co	Cr	Ni	References
Yamuna river (present study)	0.018-0.095	0.05-0.341	0.47-1.76	0.27-1.58	0.001-0.005	0.8-9.37	0.009-0.32	
Cauvery river, India	13.35	-	47.51	4.57	8.25	1.01	4.53	[13]
Brahmaputra river, India	-	-	916	108	168	222	179	[10]
Ganga river, India	76.36	11.5	332.5	48.39	-	5.36	4.88	[14]
Gomti river, India	3.058	-	63.022	-	-	0.064	0.013	[12]
Challawa river, Nigeria	0.44	-	1.2	0.22	-	0.47	-	[40]
Mghogha river, Morocco	48.25	0.36	299.5	56.7	-	86.4	46.83	[41]
Sava river, Croatia	34	0.5	91	24	-	-	-	[42]
Pasig river, Philippines	70	-	530	-	160	-	21.2	[43]
Rhine river, Netherland	188.2	7.1	684.3	62.5		6.4	33.7	[44]
Zhujiang, China	75.2	-	212	51	17.8	70.6	61.8	[45]
Almendares river, Cuba	93	2.5	262	158	-	90	-	[46]
Montevideo, Uruguay	44-128	1-1.6	174-491	58-135	-	79-253	-	[47]
Ribeira river, Brazil	767102	0.2-5.5	15-5090	60	-		-	[48]
Amazon river, Brazil	83	-	110	37.5	-	65	26.7	[49]
Danube river, Serbia and Montenegro	28.65	3.12	253.74	36.29	-	76.26	70.1	[50]
Msimbazi river, Tanzania	-	0.9	79	14	-	12	8.7	[51]
Brisbane River, Australia	20.1-81.9	1.9	40.8-144.0	31.1-30.2	-	14.2-54.3	-	[52]
Siahroud river, Iran	9.7	0.05	14.9	-	-	1.03	-	[53]
Gediz River, Turkey	1.3	-	2.6	-	1.6	-	4	[54]
Avg. shale value/ world avg.	20	0.3	95	45		90	68	[55]

Table 5. Average heavy metal concentrations of rivers around the world (mg L⁻¹)

4.2. Soil

Concentrations of heavy metals in the soil samples have been summarized in Table 6. Quantitatively the metals were observed in the sequence Pb > Zn > Cr > Ni > Cu > As > Cd > Co (Figure 3), though their thresholds for concern, mobility in soil and toxicity are different so this trend does not necessarily reflect the threat of individual metals. Pb and Zn were found in fairly higher concentrations at all the sampling locations. Generally, an overall linear increasing trend of metal contamination was noted from site 1, before the Yamuna enters the city of Mathura, to site 10 where the river leaves Agra. Thus, maximum values for all metals were observed in the samples pertaining to Agra. In the third zone metal concentrations were

seen to decrease gradually. One-way ANOVA and Fisher's LSD test indicate that mean Pb and Co content was different at all sites ($P \leq 0.001$); while mean Cr, Cd, Cu, Ni, and As in zone 2 differed significantly from zone 1 and 3 ($P \leq 0.001$). The latter did not differ significantly among themselves. Mean Zn content in zone 1 differed significantly from zone 2 and 3 ($P \leq 0.05$). The difference between the latter was not significant statistically.

Zone		Pb	Cd	Zn	Cu	Co	Cr	Ni	As
1	Range	157-230	8.6-20.6	87.3-136	22.4-41.5	1.84-4.8	26.3-53.2	23.1-41.2	14.2-20.4
	Avg.	200a	13.4a	116a	30.5a	3.71a	40.7a	33.6a	17.2a
	SD	29.6	5.36	21.4	8.14	1.25	9.77	6.78	2.97
2	Range	241-285	17.8-25.2	129-222	50.4-64.2	5.91-15.2	76.3-104	57.8-71.3	22.2-28.6
	Avg.	261b	20.3b	173b	57b	9.6b	86.7b	63.5b	25.2b
	SD	16.1	3.13	37.6	5.93	3.80	10.5	5.44	3.10
3	Range	111-136	6.02-14.6	115-167	22.4-30.1	2.91-6.4	14.7-45.6	17.8-32.4	7.9-17.6
	Avg.	125c	10.2a	144b	25.7a	4.95c	28.1a	23.3a	13.8a
	SD	10.4	3.71	21.9	3.43	1.29	11.8	5.57	4.01
Control	Range	13.6-18.4	1.23-1.87	39.6-54.3	12.8-24.3	1.68-2.53	10.2-14.3	7.3-9.7	3.03-5.7
	Avg.	15.6	1.6	47.4	18	2.1	12	8.6	4.2
	SD	1.88	0.25	5.3	4.53	0.31	1.55	1	0.99
	F value	*	*	*	*	*	*	*	*
Suggested thresholds in soil [58]	Industrial	600	22	360	91	-	87	50	12
	Residential	140	10	200	63	-	64	50	12
Suggested thresholds in soil [59]	Background	-	-	140	-	-	100	35	29
	Intervention	-	-	720	-	-	380	210	55
Threshold values [60]	Class I	35	0.2	100	35	-	90	40	15
	Class II	250	0.3	200	50	-	150	60	30
	Class III	500	1.0	500	400	-	300	200	40

F value : '*' statistically significant. Different letters in the same column denote significant statistical difference ($P \leq 0.05$) in mean metal contents in soil samples from different zones.

SD- Standard deviation.

Table 6. Heavy metal content of soil samples (mg kg^{-1})

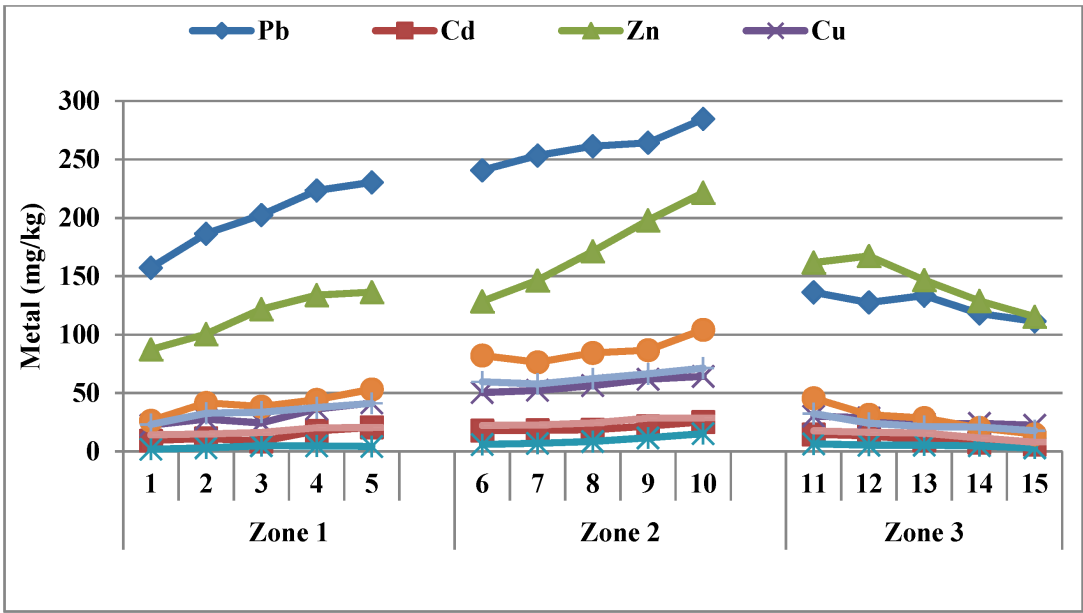


Figure 3. Average heavy metal content in soil samples

All the metals in soils were positively ($P<0.01$) correlated with each other (Table 7). Significant negative correlation was observed between metal concentrations and soil pH ($P<0.01$). The same was observed in the case of Zn and Co with Organic matter. Phosphate is able to increase water-soluble lead forms from contaminated soils by 56.8– 100% [61]. This is clearly shown by the phosphate values (Table 2) obtained for different samples with maximum in zone 2 followed by zone 1 which probably led to higher Pb values in zones 1 and 2 (Table 6). Fertilizers contain from trace to several ppm of Pb, Zn, Cu, Mg [62, 63]. High P_2O_5 -blended fertilizers and the pure phosphates, contain significant concentrations of several elements of potential environmental or agronomic concern [62, 64].

	Cd	Zn	Cu	Co	Cr	Ni	As	OM	pH
Pb	0.821**	0.479**	0.889**	0.629**	0.909**	0.933**	0.894**	0.426**	-0.802**
Cd		0.701**	0.886**	0.724**	0.862**	0.848**	0.906**	0.0876	-0.621**
Zn			0.723**	0.915**	0.689**	0.653**	0.744**	-0.493**	-0.371**
Cu				0.805**	0.966**	0.972**	0.932**	0.0260	-0.773**
Co					0.809**	0.784**	0.806**	-0.304**	-0.529**
Cr						0.991**	0.944**	0.0816	-0.834**
Ni							0.936**	0.138	-0.837**
As								0.106	-0.739**
OM									-0.242*

* Correlation is significant at the 0.05 level (two-tailed; n=75)

** Correlation is significant at the 0.01 level (two-tailed)

Table 7. Correlation coefficients: soil heavy metal concentrations

Agra is the fourth most populated city in Uttar Pradesh, India. With a population of 1.7 million (2011 census) it generates about 700 tonnes of solid wastes every day. It is also a major cause for adding contamination to soil and groundwater. Solid waste is also discharged from 200 hospitals and nursing homes along with 168 foundries, 52 tanneries, 300 shoe industries, 200 petha (a local sweet) manufacturing units, 50 dairies, 56 electroplating units, 15 silver vibrators and 15 galvanizing units. Significantly higher amount of metal pollution in the samples from the city (sites 6-10) is obviously due to untreated domestic/wastewater, sewage and industrial effluent discharged at these sites throughout the year. The increasing contamination as one proceeds downstream mirrors the extent of damage caused to the pedosphere.

Mean concentrations of heavy metals in soils at the sites studied were compared with threshold values of soil suggested by the Canadian Environmental Quality Guidelines [58]. It was observed that As (sites 1-13) and Ni (sites 6-10) crossed their respective industrial thresholds while the other metals (Pb, Zn and Cu) are well within it. Mean concentrations of As at sites 4-10 were approximately twice the thresholds suggested. Cd and Cr levels were above their thresholds only at site 10. However, the situation is drastically different in the perspective of the residential limits where in addition to these, the thresholds are exceeded even by Pb, Cd (10 sites each), Cr (5 sites) and also Zn and Cu at one site.

On comparing metal concentrations with the values suggested for soil remediation by VROM, Netherlands [59], values of Zn (sites 7-13), Ni (sites 4-10) and Cr (site 10) were above the background values but below the intervention level. It is significant to note that in studies similar to the present one, the degree of contamination and the resulting 'hazard indices' for soils may vary when different thresholds, existing in only a few countries, are considered [65]. To increase the reliability of risk estimation due to contaminants, global consensus on such thresholds is urgently needed.

The concentrations of As are usually low, less than 6 ppm, for geological and soil environment [64]. It is estimated that about 60% As in the environment is from anthropogenic sources including As-based pesticides, fertilizers, and wastes from mines, smelter and tannery industries [66]. The relatively high values of As in the samples seem to be directly related to the discharge of domestic and industrial effluent as well as use of phosphate fertilizers, pesticides used in the agricultural activities in the region.

Highly significant positive correlation ($P < 0.01$) was observed between soil and water content of Pb, Cd, Cu, Co, Cr and Ni. The results also indicate that metal concentrations in soil were higher than those in the water. This distribution pattern of heavy metals between the water phase and soil is expected as most heavy metal speciation studies have reported a similar pattern of distribution both in sea water as well as in lakes [67-69].

Several authors have pointed out the need for a better knowledge of urban soils [18, 70]. In the past few years, studies on urban soils in many cities have been carried out around the world. Some examples are Spanish [19, 71] and Italian cities [21, 72]. Other examples for European cities are Aberdeen [73], Athens [74], Oslo [22] and Belgrade [18]. The mean heavy metal contents for all zones are compared in Table 8 to those of some cities around the world. The differences concerning population, living habits, industrial activities, etc., cause significant

differences in the metal contamination profile. Compared to average concentrations in urban soils in the world, the mean concentrations of Pb and Cu are up to 2–4 times higher in some cases but still less than London, Naples and Palermo. In the case of Cd, it is many times higher than Kattedan (India). Zn and Cr contents do not differ much; still they are less than those of Naples and Madrid. Ni content is more than almost all European cities, but less than Kattedan and Firozabad in India. Co values are less than those reported from other industrial regions of India. As content is less than that of Firozabad.

City	Pb	Cd	Zn	Cu	Co	Cr	Ni	As	Reference
London	294	-	183	73	-	-	-	-	[75]
Madrid	161	-	210	72	-	75	14	-	[76]
Rostock	83	-	100	35	-	48	30	-	[77]
Sevilla	161	-	107	64.6	-	42.8	23.5	-	[19]
Belgrade	53.2	-	129.1	29	-	33.2	67.4	-	[18]
Palermo	253	-	151	77	-	39	19.1	-	[72]
Naples	262	-	251	11	-	74	-	-	[21]
Nanjing	107.3	-	162.6	66.1	-	84.7	-	-	[78]
Hong Kong	93.4	-	168	24.8	-	n.a.	-	-	[79]
Kattedan	195-6241	0.08-0.16	130-3191	72-1450	12-36	77-586	63-494	0.10-0.21	[80]
Firozabad	35.5-781	3.64-107	76.4-1247	22.4-300	10.9-63.7	19.1-158	23-218	9.25-204	[29]
Present Study	Zone 1	200	13.4	116	30.4	3.70	40.7	33.6	17.2
	Zone 2	261	20.3	173	57.0	9.60	86.7	63.5	25.2
	Zone 3	125	10.2	144	25.7	4.96	28.1	23.3	13.8

Table 8. Average heavy metal concentrations in urban soils from different cities across the world (mg kg⁻¹)

It is encouraging to note that the mean concentrations of individual metals are below those reported from other industrial hubs within India i.e. Kattedan (Andhra Pradesh) [except Cd and As] and Firozabad (Uttar Pradesh). Kattedan Industrial Development Area (KIDA) is a major industrial area of Andhra Pradesh and houses 400–500 industries, including 150 large scale industries and 300 small-scale industries. Major sources of metals pollution are battery, electrode, oil refining, metal plating, textile, pharmaceutical, chemical paints, rubber, petrochemicals, glass, therapeutics, and Pb extraction facilities [81]. This is also one of the contaminated areas identified by the Central Pollution Control Board (CPCB) in New Delhi, and referred to as an ecological disaster area [81]. Firozabad is the hub of the Indian Glass industry.

5. Assessment of heavy metal contamination in soil

Assessment of soil contamination was performed by the contamination index (P_i) and integrated contamination index (P_c) as expressed by fuzzy functions [82, 29, 28]. Class I criteria [60] could be used as no-polluted threshold; Class II as lowly polluted threshold value; and while Class III as highly polluted threshold value. P_i values ≤ 1 indicate no contamination; $1 \leq P_i \leq 2$

indicates low contamination; $2 \leq P_i \leq 3$ indicates moderate contamination; while $P_i > 3$ indicates high contamination.

Individual elements displayed remarkably different patterns of accumulation in soils. Furthermore, observed differences in the magnitude of accumulation suggest that the relative contribution of the individual elements to total heavy metal contamination varies. Figure 4 shows the proportions of contamination levels (from P_i values) in the soil samples from all the sites studied. Except for 76% samples from zone 2, which showed moderate Pb contamination, the rest exhibited low contamination zone as did all samples from zones 1 and 3. In case of Cd, all samples were in the high contamination zone. For Zn, 24% samples from zone 2 were moderately contaminated while 72%, 76%, and 100% samples from zones 1, 2, and 3, respectively were in the low contamination range. For Cu, 88% samples from zone 2 were moderately contaminated while 36% and 12% samples, from zones 1 and 2, respectively were in the low contamination range. All samples from zone 3 indicated no contamination. Except for zone 2 (20% samples) in the low contamination zone, the remaining samples did not indicate Cr contamination. For Ni, 12% and 72% samples from zones 1 and 2, respectively were moderately contaminated while 16% and 22% samples from, respectively were in the low contamination range. All samples from zone 3 indicated no contamination. In the case of As, 64%, 100%, and 60% samples from zones 1, 2, and 3 were in the low contamination range.

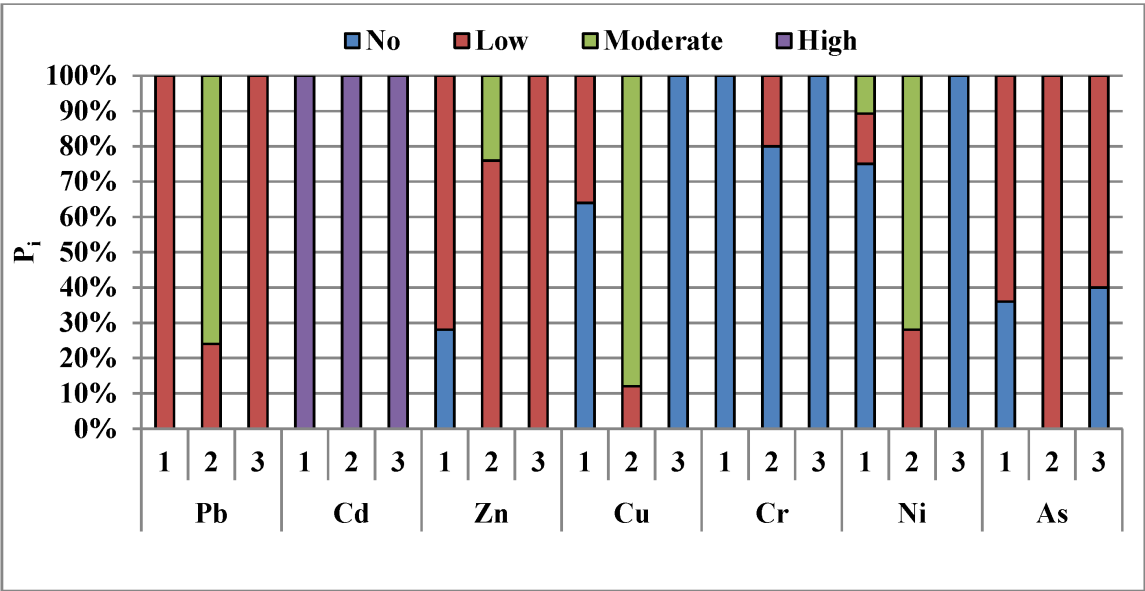


Figure 4. Contamination indices (P_i) of heavy metals in soil samples

Thus, zone 1 was found to be lowly contaminated with Pb, Zn, Cu, Ni and As but highly contaminated with Cd. Zone 2 exhibited low to moderate contamination of Pb, Zn, Cu, Ni; low Cr and As contamination; and high Cd contamination. Zone 3 was lowly polluted with Pb and Zn. As contamination ranged from none to low. No Cu, Cr and Ni contamination was observed. These results agree with the findings regarding metal contamination of soil due to the glass industry at Firozabad, India [29]. Of the nine elements studied, Zn, Cd, and As showed a

greater accumulation in all soils, whereas, accumulation of Ni and Cu was high in limited samples.

Integrated Contamination Indices (P_c) were calculated for all soils to assess the extent of heavy metal contamination at the sites. P_c is defined as the summation of the difference between the contamination index for each metal and 1 (one). It is categorized under the following heads: $P_c \leq 0$ no contamination; $0 \leq P_c \leq 7$ low contamination; $7 \leq P_c \leq 21$ moderate contamination; $P_c > 21$ high contamination. Threshold values for Co could not be obtained hence this metals was excluded in the calculation. A clear ascending trend is visible in the P_c values for all sites (Figure 5). P_c values generally show a moderate to high contamination at studied sites. The P_c indices indicate that 45% sampling locations fall in the moderate contamination while 55% of the samples fall in the high contamination range. All the samples from zone 2 fell under the high contamination category. While in zone 1, 60% samples come under moderate and 40% under high contamination level category. In zone 3, 76% and 24% samples were in the moderate and high contamination range, respectively.

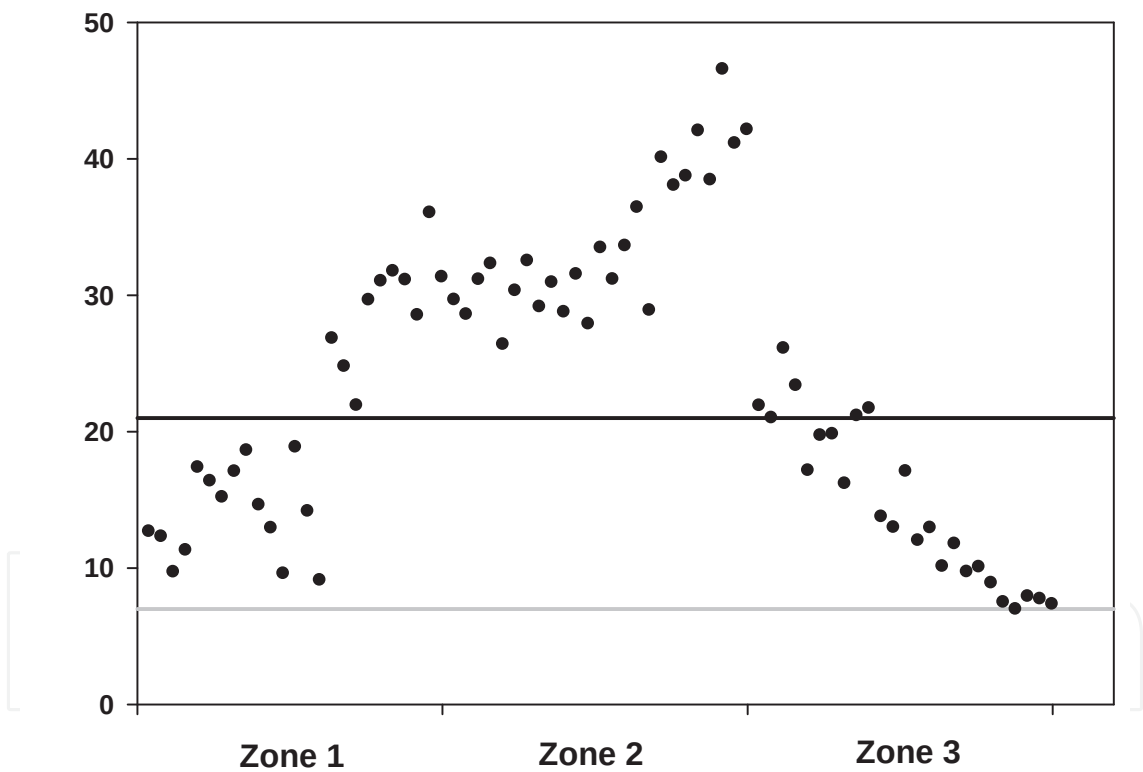


Figure 5. Integrated contamination indices (P_c) of soil samples. Black and gray lines are the upper threshold values of moderate and low contamination, respectively

The effect of the glass industry on urban soil metal characterization was assessed at 25 test sites at Firozabad, India [29]. The area is characterized by little or no monitoring of industrial processes, usage and disposal of hazardous chemicals. A comprehensive profile of Zn, Mn, Co, Cd, Pb, Cr, Ni, Cu and As contamination was obtained. Zn, Cd, and As showed a greater accumulation in all soils, whereas, accumulation of Ni and Cu was high in limited samples.

Integrated contamination indices (P_c) indicate that 60% of the sites were in the high contamination range and 28% were in the moderate contamination range with just 12% sites on the border of the moderate to low contamination range. [83] assessed the impact of both landuse and soil textures on Cd, Zn, Pb and Cu based on samples collected from the major landuse/landcover pattern of Dutch forests and aerable soils drawn from six different sites. Metal content in agricultural and industrial soil is found to be higher than the forest soil.

The fact that no P_c value in the present investigation fell within the low contamination range was not surprising, given the fact that the study was being carried out in an area which has already been contaminated with metals, but moderate to high indices in zone 1 and 2 are alarming because these include heavily populated areas. The local populace is, thus, exposed to wide range of historically well established toxins and even carcinogens. The situation is surely compounded by vehicular pollution at urban sites (1-10). Vehicular emissions are a significant source of many pollutants [21, 84].

6. Phytosociological studies

Plants show differing morpho-physiological responses to soil metal contamination. Most are sensitive to very low concentrations; others have developed tolerance, and a reduced number accumulate metals. The latter capacity has practically opened up the way to phytoextraction. Hyperaccumulation is an unusual occurrence, seen in a narrow range of species which often grow in metal-rich soils. The following thresholds for metal hyperaccumulation in shoots, without evident symptoms of toxicity, have been suggested [85]: 100 mg kg⁻¹ for Cd, 1,000 mg kg⁻¹ for Ni, Cu, Co and Pb, and 10,000 mg kg⁻¹ for Zn and Mn. Known hyperaccumulators are generally minor vegetation components in most European and North American habitats. Currently, more than 400 hyperaccumulator species are known, belonging to 45 different botanical families, among which the most frequent are Brassicaceae and Fabaceae [86].

Lack of information on the agricultural management of hyperaccumulators, together with slow-growing and poor shoot and root growth, increase the difficulties in the practical application of these species in remediation projects [87]. Hence, the potential for any plant species to remediate successfully heavy metal contaminated sites depends on all of the following prerequisite factors: a) the amount of metals that can be accumulated by the candidate plant, b) the growth rate of the plant in question, and c) the planting density [88]. The growth rate of a plant in a chemically contaminated soil is important from the perspective of biomass. Parameters like basal area, canopy, abundance, dominance of species can help obtain a more rounded picture in the case of mixed planting or natural flora at a contaminated site. The rate of metal removal from the soils can be calculated if information on the above mentioned parameters is available. In addition, versatility of the candidate plant to tolerate and at the same time accumulate multiple metal contaminants and/or metal-organic mixtures would be an asset for any phytoremediation system.

The choice of plant species is thus, an important task in any phytoremediation based technique. Decontaminating a site in a reasonable number of harvests requires plants that are both high

yielders of biomass and good metal accumulators by dry weight. It has been demonstrated [89, 90] that, wild native plants may be better phytoremediators for waste lands than the known metal bioaccumulators like *Thlaspi caerulescens* and *Alyssum bertolonii* because the latter are slow growing with shallow root systems and low biomass. Also, the technology for their large-scale cultivation is not fully developed; therefore, their use is rather limited [91].

If soil at contaminated sites, e.g. mines, industrial zones is naturally high in a particular metal, native plants will often become adapted over time to the locally elevated levels [28-30] and metal toxicity issues do not generally arise. Successful establishment and colonization of several pioneer plant species tolerant to Pb/Zn mine spoils has also been demonstrated with tolerant plants including *Phragmites australis*, *Vetiveria zizanioides*, and *Sesbania rostrata* [31, 92]. Many native, well adapted plants have been investigated and even used for heavy metal bioindicating and phytoremedial purposes including lemongrass and other wild grasses, vetiver, *Sesbania*, *Avena*, *Crotalaria*, *Crinum asiaticum*, *Typha latifolia* and *Calotropis procera* etc. [31-35]. Phytoremediation employing indigenous species can be an ecologically viable option for sustainable and cost-effective management.

An important component of any ecosystem is the species it contains. Species also serve as good indicators of the ecological condition of a system [93]. Ecological surveys are necessary for an adequate characterization of a plant community and also to know the diversity and dispersion status of species in the area. Phytosociology aims to characterize and classify plant communities in terms of composition and structure.

At all sampling sites within a zone, ecological indices [relative frequency, relative density, relative dominance and importance value index (IVI)] were estimated, by using a 1m² quadrat. Sampling was done randomly at 10 spots at each site within a zone. The data were compiled and analysed according to some workers [94-96].

Relative density is the proportion of density of a species (plants/unit area) to that of the stand as a whole. The dispersion of species in relation to that of all the species is termed as relative frequency of a species. Relative dominance is the proportion of the basal area of a species to the sum of the basal area of all species present. Basal area refers to area covered by the plant's stem and leaves one inch above the ground surface. The overall picture of ecological importance of a species in relation to the community structure can be obtained by adding the values of the above three parameters [97].

A total of 22 weed species were recorded from the sites (Table 9). Most of the weeds recorded are herbs except *Calotropis procera* and *Datura stramonium* which are shrubby in nature. Two grasses i.e. *P. annua* and *C. dactylon* were observed. The phytosociological parameters obtained from the sites clearly indicate that there are naturally occurring plant species which have the capacity to tolerate the heavy metal content of the soils. The floral composition of the three zones varied qualitatively and quantitatively. Most species were seen to grow vigorously. Relative frequency, relative density, relative dominance and IVI indicate that *Calotropis procera*, *Parthenium hysterophorus*, *Chenopodium murale*, *Croton bonplandianum*, *Rumex dentatus*, *Amaranthus spinosus*, *Datura stramonium* and *Withania somnifera* were the most abundant weeds. All of these species have been reported as potential phytoremediators in earlier studies. It is

important to note that floral diversity decreased with increasing contamination profile of the sites. Maximum species (20) were observed in zone 3, followed by zones 1 and 2.

Zone	Plants	Relative frequency	Relative density	Relative dominance	IVI
1	<i>Amaranthus spinosus</i>	8.42	10.55	0.15	19.12
	<i>Rumex dentatus</i>	6.32	6.00	0.07	12.38
	<i>Calotropis procera</i>	8.42	10.31	0.18	18.92
	<i>Croton bonplandianum</i>	6.32	6.00	0.23	12.54
	<i>Chenopodium murale</i>	6.32	6.24	0.01	12.56
	<i>Datura stramonium</i>	7.37	9.83	0.16	17.37
	<i>Stellaria media</i>	5.26	4.32	0.00	9.58
	<i>Withania somnifera</i>	8.42	9.59	0.13	18.15
	<i>Heliotropium ellipticum</i>	5.26	3.12	0.00	8.38
	<i>Achyranthes aspera</i>	6.32	5.76	0.01	12.08
	<i>Parthenium hysterophorus</i>	7.37	6.95	0.01	14.33
	<i>Amaranthus alba</i>	5.26	4.56	0.01	9.83
	<i>Boerhaavia diffusa</i>	3.16	2.64	0.01	5.80
	<i>Euphorbia hirta</i>	6.32	6.00	0.00	12.31
	<i>Sida longifolia</i>	4.21	4.56	0.00	8.77
	<i>Gnaphalium luteo-album</i>	5.26	3.60	0.02	8.88
2	<i>Parthenium hysterophorus</i>	11.59	16.32	0.22	28.13
	<i>Abutilon indicum</i>	7.25	4.75	0.06	12.06
	<i>Calotropis procera</i>	11.59	15.13	0.20	26.93
	<i>Croton bonplandianum</i>	7.25	8.90	0.14	16.28
	<i>Amaranthus spinosus</i>	4.35	2.08	0.00	6.43
	<i>Rumex dentatus</i>	11.59	13.65	0.15	25.39
	<i>Withania somnifera</i>	8.70	8.61	0.10	17.40
	<i>Cynodon dactylon</i>	7.25	3.56	0.00	10.81
	<i>Chenopodium murale</i>	7.25	9.50	0.11	16.85
	<i>Achyranthes aspera</i>	5.80	4.75	0.02	10.57
	<i>Sida longifolia</i>	7.25	2.97	0.00	10.21
	<i>Gnaphalium luteo-album</i>	5.80	4.15	0.00	9.95
	<i>Boerhaavia diffusa</i>	4.35	5.64	0.00	9.99

Zone	Plants	Relative frequency	Relative density	Relative dominance	IVI
3	<i>Parthenium hysterophorus</i>	7.14	9.65	0.17	16.97
	<i>Abutilon indicum</i>	4.76	3.46	0.01	8.23
	<i>Calotropis procera</i>	7.14	12.57	0.18	19.89
	<i>Croton bonplandianum</i>	5.56	5.65	0.17	11.37
	<i>Cynodon dactylon</i>	4.76	2.91	0.06	7.74
	<i>Chenopodium murale</i>	6.35	12.39	0.14	18.88
	<i>Poa annua</i>	4.76	3.28	0.01	8.05
	<i>Rumex dentatus</i>	3.97	1.64	0.01	5.62
	<i>Barleria diffusa</i>	4.76	4.55	0.00	9.32
	<i>Achyranthes aspera</i>	5.56	4.19	0.01	9.76
	<i>Sida longifolia</i>	4.76	3.64	0.00	8.41
	<i>Withania somnifera</i>	4.76	3.83	0.09	8.68
	<i>Boerahvia diffusa</i>	4.76	2.55	0.00	7.31
	<i>Sida cordifolia</i>	4.76	3.28	0.00	8.04
	<i>Amaranthus spinosus</i>	7.14	8.56	0.10	15.80
	<i>Gnaphalium luteo-album</i>	4.76	3.83	0.03	8.62
	<i>Euphorbia hirta</i>	3.17	3.46	0.00	6.64
	<i>Ageratum conyzoides</i>	3.17	2.37	0.00	5.55
	<i>Datura stramonium</i>	4.76	4.19	0.00	8.95
	<i>Tridex procumbens</i>	3.17	4.01	0.00	7.18

IVI- Importance Value Index

Table 9. Phytosociological parameters of flora at test sites

C. procera has been demonstrated as a potential phytoremediator species. The shrub showed good accumulation of metals and is a potential phytoextractor for As and Zn as well as a promising phytostabiliser for Pb, Cd, Cu and Mn [28, 29, 35]. *C. procera* was observed to have a high degree of sociability i.e. relative frequency, relative density, relative dominance and IVI. *P. hysterophorus* was also important in this context and was most dominant in zone 2. This species has been identified for As phytoextraction along with *A. spinosus*, *C. bonplandianum*, and *D. stramonium* [28]. The latter two have also been indicated for phytoextraction—*C. bonplandianum* for Mn and *D. stramonium* for Mn, Cr, and Cu—together with *R. dentatus* for Pb. Another species with high IVI, *C. murale* has been suggested for Zn, Cd, Pb and Cu phytoextraction [28, 29]. Among the less dominant species, *Tridex procumbens* and *Euphorbia*

hirrta have also been reported as promising tools for phytoextraction of Mn and As, respectively [28]. *E. hirrta* and *D. stramonium* were not found in zone 2.

Poa annua has been identified as a phytostabilizer for Mn, Cd, and As and phytoextractor for Cu and Pb. Cu concentrations up to 742.06 mg kg⁻¹ dry weight have been reported in *P. annua* shoots [28, 29]. *Poa annua* was observed only at sites in zone 1.

Other species found at the sites have also been indicated for further studies following initial field surveys. *Gnaphalium luteo-album* (Mn and As); *Withania somnifera* (Cu); and *Heliotropium ellipticum* (As) have shown promise as phytostabilisers for these metals and metal combinations [28, 29].

7. Discussion

The occurrence as well as concentrations of heavy metals like Pb, Zn, Cu, Co, Mn, Fe, Cr and Cd in streams and rivers all over the world is increasing. In the present case study, heavy metal contamination was consistently higher in city of Agra, which may be attributed to the heavy industrialization combined with agricultural and urban runoff. The situation is made worse by atmospheric deposition, again attributable to industrial and vehicular pollution. In general, freshwater ecosystems have low natural background metal levels and therefore tend to be sensitive to even small additions of most trace metals. The river water far exceeded the limits of metals prescribed by WHO and USEPA for drinking water standards and Pb, Cd, and Cr content at all sites and Ni at most sites exceeded the prescribed limits. In a heavily populated country like India where a sizeable portion of the population is illiterate and resides in slums/poorly planned neighbourhoods without proper sanitation and drainage, day-to-day activities also contribute to the overall pollution load. Provision of suitable alternatives along with proper education and awareness is integral to the minimization of this problem at the source. Apart from taking measures like effluent treatment before it enters the river and subsequent treatment of river water at the most polluted sites, a steady flow of water is to be ensured throughout the year, by way of channelizing the river with canals at crucial points. Such measures can address this problem to a substantial extent. Expenditure of more than US\$ 500 million without much success appears to be an unjustified proposition.

Phytoremediation has been receiving attention lately as an innovative, cost-effective alternative to the otherwise tedious and expensive methods in use, which are not only a burden on the exchequer but also, require efforts on a recurring basis. Lack of information on the agricultural management of hyperaccumulator species, together with their poor biomass and root proliferation, increases the difficulties in their practical application. It has been amply demonstrated that wild native plants may be better phytoremediating tools. These species can be an ecologically viable option for sustainable and cost-effective management especially in scenarios where expertise, technical expertise and/or funding is a limiting factor. Ecological surveys are necessary for adequate characterization of a plant community and subsequent identification of prospective candidates for phytoremedial strategies since metal toxicity issues generally do not arise in plants already established on contaminated soils. Allowing native

species to remediate site is an attractive proposition since these species do not require frequent irrigation, fertilizers, and pesticide treatments, while simultaneously a plant community comparable to that existing in the vicinity can be established. The outcome is, thus site remediation, ecological restoration and addition in aesthetic value. This is also in concurrence with the ruling (2006) of the Hon'ble Supreme Court of India prohibiting cultivation of plants requiring fertilizers and pesticides along the river Yamuna. Using these perennial phytore-medial candidates without any special needs holds much promise in this context. In addition, versatility of the candidate plant to tolerate and at the same time accumulate multiple metal contaminants and/or metal-organic mixtures would be an asset for any phytoremediation strategy.

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References

- [1] Nolan K. Copper Toxicity Syndrome. *Journal of Orthomolecular Psychiatry* 2003;12(4) 270–282.

- [2] Marschner H. Mineral Nutrition of Higher Plants. London: Academic Press Limited; 1995.
- [3] McCluggage D. Heavy Metal Poisoning, NCS Magazine. Columbus, USA: The Bird Hospital; 1991. <http://www.cockatiels.org/articles/Diseases/metals.html>.
- [4] Katz BG, Bricker OP, Kennedy MM. Geochemical mass balance relationships for selected ions in precipitation and stream water, Catoctin Mountains, Maryland. American Journal of Science 1985;285 931–962.
- [5] Houba C, Remade J, Dubois D, Thorez J. Factors affecting the concentrations of cadmium, zinc, copper and lead in the sediments of the Vesdre river. Water Research 1983;17 1281–1286.
- [6] Zhang J, Huang WH. Dissolved trace metals in the Huanghe: The most turbid large river in the world. Water Research 1993;27 1–8.
- [7] Pizarro J, Vila I, Manuel C. Chemical compositions of Chilean rivers. Verth-Int. Ver. Theory of predictive Limnology 1998;26 948–951.
- [8] Alexandrine E, Jean-Marie M, Thevenot DR. Urban runoff impact on particulate metal concentrations in the river Seine. Water, Air, and Soil Pollution 1998;108 83–105.
- [9] Pistelok F, Galas W. Zinc pollution of the Przemsza river and its tributaries. Polish Journal of Environmental Studies 1999;8 47–54.
- [10] Subramanian V, Van't Dack L, Van Grieken R. Chemical composition of river sediments from the Indian sub-continent. Chemical Geology 1985;48 271–279.
- [11] Kumar A, Kaur I, Mathur RP. Water quality and metal enrichment in bed sediment of the river Kali and Hindon, India. Environment and Geochemistry Health 1998;20 53–60.
- [12] Singh VK, Singh KP, Mohan M. Status of heavy metals in water and bed sediments of river Gomti – a tributary of the Ganga river, India. Environmental Monitoring and Assessment 2005;105 43–67.
- [13] Abida B, Ramaiah M, Khan I, Veena K. Heavy Metal Pollution and Chemical Profile of Cauvery River Water. E-Journal of Chemistry 2009;6(1) 47–52.
- [14] Pandey J, Shubhashish K, Pandey R. Heavy metal contamination of Ganga river at Varanasi in relation to atmospheric deposition. Tropical Ecology 2010;51(2) 365–373.
- [15] Daniel Pepper. India's rivers are drowning in pollution. Fortune (magazine); 2007.
- [16] Karthikeyan, A. "Failure of Ganga, Yamuna projects." (http://articles.timesofindia.indiatimes.com/2009-09-04/chennai/28093527_1_cooum-treatment-plants-sewage-treatment). (Assessed 9 september 2009)

- [17] "Inflow to Yamuna to be cleaned up at last" (<http://www.expressindia.com/latest-news/inflow-to-yamuna-to-be-cleaned-up-at-last/509240/>). Indian Express. (Assessed 31 August 2009).
- [18] Crnković D, Ristić M, Antonović D. Distribution of Heavy Metals and Arsenic in Soils of Belgrade (Serbia and Montenegro). *Soil and Sediment Contamination* 2006;15 581–589.
- [19] Madrid L, Diaz-Barrientos E, Madrid F. Metals in urban soils of Sevilla: seasonal changes and relations with other soil components and plant contents. *European Journal of Soil Sciences* 2004;55 209–217.
- [20] Chirenje T, Ma LQ, Reeves M, Szulczewski M. Lead distribution in near surface soils of two Florida cities: Gainesville and Miami. *Geoderma* 2004;119 113–120.
- [21] Imperato M, Adamo P, Naimo D, Arienzo M, Stanzione D, Violante P. Spatial distribution of heavy metals in urban soils of Naples city (Italy). *Environment Pollution* 2003;124 247–256.
- [22] Tjhuus L, Brattli B, Saether OM. A geochemical survey of topsoil in the city of Oslo, Norway. *Environmental Geochemistry and Health* 2002;24 67–94.
- [23] Raskin I, Smith RD, Salt DE. Phytoremediation of metals: using plants to remove pollutants from the environment. *Current Opinion in Biotechnology* 1997;8 221–226.
- [24] Salt DE, Smith RD, Raskin I. Phytoremediation. *Annual Review of Plant Physiology and Plant Molecular Biology* 1998; 49 643–668.
- [25] Vangronsveld J, Cunningham SD. 1998. Introduction to the Concepts. In: Vangronsveld J, Cunningham SD. (ed.) *Metal Contaminated Soils: In situ Inactivation and Phytoremediation*. Georgetown, USA: RG Landes Co.; 1998. p1-15.
- [26] Blaylock MJ, Huang JW. 2000. Phytoextraction of metals. In: Raskin I, Ensley BD (eds.) *Phytoremediation of toxic metals: using plants to clean-up the environment*. New York: John Wiley & Sons Inc; 2000. p53–70.
- [27] Salt DE, Blaylock M, Kumar NPBA, Dushenkov V, Ensley D, Chet I, Raskin I. Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. *Biotechnology* 1995;13 468–474.
- [28] D'Souza R, Varun M, Pratas J, Paul MS. Paul Spatial distribution of heavy metals in soil and flora associated with the glass industry in North Central India: Implications for Phytoremediation. *Soil and Sediment Contamination* 2013;22 1–20.
- [29] Varun M, D'Souza R, Pratas J, Paul MS. Metal contamination of soils and plants associated with the glass industry in North Central India: Prospects of phytoremediation. *Environment Science and Pollution Research* 2012;9(1) 269-281.

- [30] Pratas J, Favas PJC, D'Souza R, Varun M, Paul MS. Phytoremedial assessment of flora tolerant to heavy metals in the contaminated soils of an abandoned Pb mine in Central Portugal. *Chemosphere* 2013;90 2216–2225.
- [31] Yang B, Shu W, Ye Z, Lan C, Wong M. Growth and Metal Accumulation in Vetiver and two *Sebania* species on Lead/Zinc Mine Tailings. *Chemosphere* 2003;52 1593–1600.
- [32] Uraguchi S, Watanabe I, Yoshitomi A, Kiyono M, Kuno K. Characteristics of cadmium accumulation and tolerance in novel Cd-accumulating crops, *Avena strigosa* and *Crotalaria juncea*. *Journal of Experimental Botany* 2006; 57(12) 2955–2965.
- [33] Varun M, D'Souza R, Kumar D, Paul MS. Bioassay as monitoring system for lead phytoremediation through *Crinum asiaticum* L. *Environment Monitoring and Assessment* 2011a; 178(1-4) 373–381.
- [34] Varun M, D'Souza RJ, Pratas J, Paul MS. Evaluation of phytostabilization, a green technology to remove heavy metals from industrial sludge using *Typha latifolia* L. *Biotechnology Bioinformatics and Bioengineering* 2011b; 1(1) 137–145.
- [35] D'Souza R, Varun M, Masih J, Paul MS. Identification of *Calotropis procera* L. as a potential phytoaccumulator of heavy metals from contaminated soils in Urban North Central India. *Journal of Hazardous Material* 2010;184 457–464.
- [36] BIS. Drinking water specification. IS:10500:1991. New Delhi, India: Bureau of Indian Standard; 1991.
- [37] WHO (World Health Organisation). Guidelines for drinking water quality. Vol. 1, recommendations, seconded. World health organization, Geneva; 1993.
- [38] Parkpain P, Sreesai S, Delaune RD. Bioavailability of heavy metals in sewage sludge-amended Thai soils. *Water, Air, and Soil Pollution* 2000;122 163–182.
- [39] USEPA (United States Environmental Protection Agency). Current drinking water standard. <http://www.epa.gov/safewater/mcl.html>. (accessed 2002).
- [40] Azumi, D.S, Bichi, M.H. Industrial pollution and heavy metals profile of Challawa river in kano, Nigeria. *Journal of Applied Sciences and Environmental Sanitation* 2010;5(1) 23–29.
- [41] Rodríguez-Barroso MR, Benhamou M, El Moumni B, El Hatimi I, García-Morales JL. Evaluation of metal contamination in sediments from north of Morocco: geochemical and statistical approaches. *Environmental Monitoring And Assessment* 2009;159(1-4) 169–181.
- [42] Halamić J, Galović I, Šparica M. Heavy Metal (As, Cd, Cu, Hg, Pb and Zn) distribution in topsoil developed on alluvial sediments of the Drava and Sava Rivers in NW Croatia. *Geologia Croatica* 2003;56(2) 215–232.

- [43] Amore RR. Concentration, speciation, provenance and pollution levels of heavy metals in the bottom sediments of the pasig river. M.Sc. Thesis. University of the Philippines, Diliman, Quezon; 2000.
- [44] Middelkoop FI. Heavy metal pollution of the river Rhine and flood plains in The Netherlands, Netherlands. *Journal of Geosciences* 2000;79 411–428.
- [45] Chen HM, Zheng CR. Evaluation of purification ability of suspended substance with log ks for heavy metal in water bodies. *Acta pedologica* 1995;32 86–92.
- [46] Olivares-Rieumont S, de La Rosa D, Lima L, Graham DW, Alessandro KD, Borroto J, Martínez F, Sánchez J. Assessment of heavy metal levels in Almendares River sediments - Havana City, Cuba. *Water Research* 2005;39(16) 3945–3953.
- [47] Muniz P, Danulat E, Yanicelli B, García-Alonso J, Medina G, Bicego MC. Assessment of contamination by heavy metals and petroleum hydrocarbons in sediments of Montevideo harbor, Uruguay. *Environment International* 2004; 29 1019–1028.
- [48] Eysink GGJ, Padua HB, Bertoletti SAEP, Martins MC, Pereira DN, Roberto S. Heavy metals in the Vale do Ribeira and in Iguape-Cananéia CETESB. *Ambiente* 1988;2(1) 6–13. (in Portuguese)
- [49] Siqueira GW. Study of heavy metals levels and other elements in surface sediments at the Santos Estuarine System and Shelf Coastal of the Amazon. PhD thesis. São Paulo University, Instituto Oceanográfico, Brazil; 2003.
- [50] Milenkovic N, Damjanovic M, Ristic M. Study of Heavy Metal Pollution in Sediments from the Iron Gate (Danube River), Serbia and Montenegro. *Polish Journal of Environmental Studies* 2005;14(6) 781–787.
- [51] Akhabuhaya J, Lodenius M. Metal pollution of river msimbazi, Tanzania. *Environment International* 1988;14 511–514.
- [52] Mackey AP, Hodgkinson M, Nardella R. Nutrient levels and heavy metals in mangrove sediments from the Brisbane River, Australia. *Marine Pollution Bulletin* 1992;24(8) 418–420.
- [53] Charkhabi AH, Sakizadeh M, Bayat R. Land use effects on heavy metal pollution of river sediments in Guilan, southwest of the Caspian sea. *Caspian Journal of Environmental Sciences* 2008;6(2) 133–140.
- [54] Kucuksezgin F, Uluturhan E, Batki H. Distribution of heavy metals in water, particulate matter and sediments of Gediz River (Eastern Aegean). *Environmental Monitoring and Assessment* 2008;141 213–225.
- [55] Turekian K, Wedepohl KH. Distribution of the elements in some major units of the earth's crust. *Geological Society of American Bulletin* 1961;72 175–192.
- [56] Meybeck M, Helmer R. The quality of rivers: From pristine stage to global pollution. *Paleogeography, Paleoclimatology, and Paleoecology* 1989;75 283–309.

- [57] Schiller AM, Boyle EA. Variability of dissolved trace metals in the Missisipi river. *Geochimistry and Cosmochim. Acta* 1987;51 3273–327.
- [58] CCME (Canadian environmental quality guidelines). The Canadian Council of Ministers of the Environment; 2003.
- [59] VROM (Dutch Ministry of Housing, Spatial Planning and the Environment) Ministerial circular on target and intervention values for soil remediation. Annex A: target values, soil remediation intervention values and indicative levels for serious contamination, DBO/1999226863, 2004; February 4.
- [60] SEPAC (State Environmental Protection Administration of China). Chinese Environmental Quality Standard for Soils; 1995; (GB15618-1995).
- [61] Skowronski GA, Seide M, Abdel-Rahman MS. Oral bioaccessibility of trivalent and hexavalent chromium in soil by simulated gastric fluid. *Journal of Toxicology and Environmental Health-Part A* 2001;63(5) 351–362.
- [62] Onianwa PC. Monitoring atmospheric metal pollution: a review of the use of mosses as indicators. *Environmental Monitoring and Assessment* 2001;71 13–5.
- [63] Zhang M, He Z, Calvert DV, Stoffella PJ, Jiang X. Surface runoff losses of copper and zinc in sandy soils. *Journal of Environmental Quality* 2003;32 909–915.
- [64] Adriano CD. *Biogeochemistry of Trace Metals*. United States: Lewis publishers; 1992.
- [65] Modis K, Komnitsas K. Optimum sampling density for the prediction of acid mine drainage in an underground sulphide mine. *Mine Water Environment* 2007;26 237–242.
- [66] Loska K, Wiechula D, Barska B, Cebula E, Chojnecka A. Assessment of arsenic enrichment of cultivated soils in Southern Poland. *Polish Journal of Environmental Studies* 2003;12(2) 187–192.
- [67] Maina HM, Barminas JT, Nkafamiya II. Levels and distribution of some heavy metals in soils in the vicinity of ashaka cement factory, gombe state Nigeria. *Journal of Chemical Society of Nigeria* 2009;34 1–5.
- [68] Lone MI, He ZH, Peter J, Stoffella I, Yang X. Phytoremediation of heavy metal polluted soils and water: Progresses and perspectives. *Journal of Zhejiang University Science B* 2008;9(3) 210–220.
- [69] Almå AR, Kweyunga C, Manoko LK. Investigation of trace metal concentrations in soil, sediments and waters in the vicinity of “Geita Gold Mine” and “North Mara Gold Mine” in North West Tanzania (with Barrick Response). IPM-report; 2009.
- [70] Nijkamp P, Rodenburg AC, Wagtendonk JA. Success factors for sustainable urban brownfield development: A comparative study approach to polluted sites. *Ecology Economics* 2002;40 232–252.

- [71] Sánchez-Martin MJ, Garcia-Delgado M, Lorenzo LF, Rodriguez-Cruz MS, Arienzo M. Heavy metals in sewage sludge amended soils determined by sequential extractions as a function of incubation time of soils. *Geoderma* 2007; 142 262–273.
- [72] Manta DS, Angelone M, Bellanca A, Neri R, Sprovieri M. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. *Science of the Total Environment* 2002;300 229–243.
- [73] Paterson E, Sanka M, Clark L. Urban soils as pollutant sinks—a case study from Aberdeen, Scotland. *Applied Geochemistry* 1996;11 129–131.
- [74] Chronopoulos J, Haidouti C, Chronopoulou-Sereli A, Massas I. Variations in plant and soil lead and cadmium content in urban parks in Athens. *Science of the Total Environment* 1997;196 91–98.
- [75] Thornton I. Metal contamination of soil in urban areas. In: Bullock P, Gregory PJ (ed) *Soils in the Urban Environment*. Blackwell. London: Oxford; 1991. p47–75.
- [76] De Miguel E, Jiménez de Grado M, Llamas JF, Martín-Dorado A, Mazadiego LF. The overlooked contribution of compost application to the trace element load in the urban soil of Madrid (Spain). *Science of the Total Environment* 1998;215 113–122.
- [77] Kahle P. Schwermetallstatus Rostocker Gartenböden. *Journal of Plant Nutrition and Soil Science* 2000;163 19–196.
- [78] Li XD, Lee SL, Wong SC, Shi WZ, Thornton I. The study of metal contamination in urban soils of Hong Kong using a GIS-based approach. *Environment Pollution* 2004;129(1) 113–124.
- [79] Lu Y, Gong ZT, Zhang GL, Burghardt W. Concentrations and chemical speciation of Cu, Zn, Pb and Cr of urban soils in Nanjing, China. *Geoderma* 2003;115 101–111.
- [80] Sekhar KC, Chary NS, Kamala CT, Vairamani M, Anjaneyulu Y, Balaram V, Sorlie JE. Risk communications: around the world environmental risk assessment studies of heavy metal contamination in the industrial area of Kattedan, India—A case study. *Human and Ecological Risk Assessment* 2006;12 408–422.
- [81] Prashanthi V, Rao J, Sreenivasa K, Raju A. Soil pollution due to a land disposal of industrial effluents. *Journal of Industrial Pollution* 2001;17 9–18.
- [82] Huang R. *Environmental Pedology*. Beijing: Higher Education Press; 1987.
- [83] Romkens PFAM, Salomons W. Cd, Cu, and Zn solubility in arable and forest soils: consequences of land use changes for metal mobility and risk assessment. *Soil Science* 1998;163(11) 859–871.
- [84] Viard B, Pihan F, Promeyrat S, Pihan JC. Integrated assessment of heavy metal (Pb, Zn, Cd) highway pollution: bioaccumulation in soil, Gramineae and land snails. *Chemosphere* 2004;55 1349–1359.

- [85] Baker AJM, Brooks RR. Terrestrial higher plants which hyperaccumulate metallic elements- a review of their distribution, ecology and phytochemistry. *Biorecovery* 1989;1 81–126.
- [86] Baker AJM, McGrath SP, Reeves RD, Smith JAC. Metal hyperaccumulator plants: a review of the ecology and physiology of a biological resource for phytoremediation of metal-polluted soils. In: Terry N, Bañuelos G. (eds.) *Phytoremediation of Contaminated Soil and Water*. Boca Raton, FL, USA: CRC Press; 2000. p85–108.
- [87] Lasat MM. Phytoextraction of toxic metals: A review of biological mechanisms. *Journal of Environmental Quality* 2002; 31 109–120.
- [88] Saxena PK, Raj SK, Dan T, Perras MR, Vettakkorumakankav NN. Phytoremediation of metal contaminated and polluted soils. In: Prasad MNV, Hagemeyer J. (eds.) *Heavy metal stress in plants – From molecules to ecosystems*. Heidelberg, Berlin, New York: Springer–Verlag; 1999. p305–329.
- [89] Porębska G, Ostrowska A. Heavy metal accumulation in wild plants: implications for phytoremediation. *Polish Journal of Environmental Studies* 1999;8(6) 433–442.
- [90] Saraswat S, Rai JPN. Phytoextraction potential of six plant species grown in multime-tal contaminated soil. *Chemical ecology* 2009;25 1–11.
- [91] Pulford ID, Watson C. Phytoremediation of heavy metal contaminated land by trees –a review. *Environment International* 2003;29(4) 529–540.
- [92] Chiu KK, Ye ZH, Wong MH. Growth of *Vetiveria zizanioides* and *Phragmites aus-tralis* on Pb/Zn and Cu mine tailings amended with manure compost and sewage sludge: a greenhouse study. *Bioresource Technology* 2006; 97 158–170.
- [93] Morgenthal TL, Cilliers SS, Kellner K, Hamburg HV, Michael MD. The vegetation of ash disposal sites at Hendrina Power Station II: Floristic composition. *South African Journal of Botany* 2001;67(4) 520-532.
- [94] Oosting HJ. *The study of Plant Communities*. San Francisco: W.H. Freeman and Co; 1958.
- [95] Phillips EA. *Methods of vegetation study*. New York: Henry Holt & Co. Inc.; 1959.
- [96] Hanson HC, Churchill ED. *The plant community*. New York: Reinhold Publishing Corporation; 1961.
- [97] Curtis JT, McIntosh RP. An upland forest continuum in the prairie forest border re-gion of Wisconsin. *Ecology* 1951; 32 476-496.

