Int. J. Environ. Sci. Technol.
DOI 10.1007/s13762-013-0350-9

ORIGINAL PAPER

Heavy metals concentration in soils under rainfed agro-ecosystems and their relationship with soil properties and management practices

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Received: 11 April 2012 / Revised: 18 March 2013 / Accepted: 26 May 2013

Abstract Heavy metals are governed by parent material of soils and influenced by the soil physicochemical properties and soil and crop management practices. This paper evaluates total heavy metal concentrations in rainfed soils under diverse management practices of tropical India. Vertisols (clayey soils with high shrink/swell capacity) had the highest concentrations of heavy metals. However, chromium (Cr) content was above the threshold value in Aridisol [calcium carbonate ($CaCO_3$)]-containing soils of the arid environments with subsurface horizon development. Concentration increased at lower depths (>30 cm). Basaltic soils showed higher concentrations of nickel (Ni), copper (Cu) and manganese (Mn). Cadmium (Cd), cobalt (Co), Cu and Mn concentrations were higher in soils cultivated to cotton, whereas Cr concentration was above the threshold level of 110 mg kg^{-1} in food crop cultivated soils. As the specific soil surface is closely related to clay content and clay type, soil's ability to retain heavy metals is more closely tied to the specific surface than to the soil cation exchange capacity. Higher positive correlations were found between heavy metal concentrations and clay content [Cd($r = 0.85$; $p \leq 0.01$); Co ($r = 0.88$; $p \leq 0.05$); Ni ($r = 0.87$; $p \leq 0.01$); Co ($r = 0.81$; $p \leq 0.05$); Zn ($r = 0.49$; $p \leq 0.01$); Cr ($r = 0.80$; $p \leq 0.05$); Mn ($r = 0.79$; $p \leq 0.01$)]. The amounts of nitrogen–phosphorus–potassium applied showed a positive correlation with Co and Ni ($r = 0.62$; $p \leq 0.05$). As several soils used for growing food crops are high in Ni, Cr and Mn, the flow of these metals in soil–plant–livestock/human chain needs further attention.

Keywords Fertilization practices · Parent material · Tropical climate · Vertisols · Inceptisols · Alfisols · Aridisols

Introduction

The increased flux of metallic substances in the environment during the recent past can be attributed to large increase in heavy metal concentrations in soils. The contamination of agricultural soils and crops by heavy metals is of concern due to their potential effects on human health and the sustainability of food production systems in contaminated areas (Zarcinas et al. 2004). The presence of heavy metals is of special concern because they are highly persistent and pose potential danger to human and animal health. Ingestion of vegetables grown in soils contaminated with heavy metals poses a possible risk to human health (Intawongse and Dean 2006). The main route of exposure to these toxic heavy metals is through food (Liu et al. 2006).

Rainfed agriculture in India extends over 80 m ha with nearly 57 % net cultivated area, contributing 44 % of the country's food production and supports 40 % of the

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Published online: 03 July 2013

country's human population. Agriculture in rainfed areas is uncertain because of its full dependence on rain, and generally, the soils are degraded and low in fertility. Alfisols, Vertisols, Aridisols and Inceptisols are major soil orders, which occur predominantly in rainfed regions of India. Soil pollution in agricultural areas surrounding big cities is a major environmental problem (Taghipour et al. 2013). The urban and dense cities of India with significant industrial waste generation have been found to have heavy metal contaminated soils.

Govil et al. (2001) carried out geochemical study in and around the Patancheru industrial development area of Andhra Pradesh, just north of Hyderabad city, to determine the extent of chemical pollution in the soil. Their data revealed significant contamination, showing two to three times higher levels of toxic elements than normal. Heavy metals like chromium (Cr), vanadium (V), iron (Fe), arsenic (As), cadmium (Cd), selenium (Se), barium (Ba), zinc (Zn), strontium (Sr), molybdenum (Mo) and copper (Cu) were found to be present above the normal concentrations in the soil. Krishna and Govil (2004) collected soil samples from the Pali industrial area in the western state of Rajasthan. Their data revealed that the soil in the study area was significantly contaminated with high concentrations of heavy elements like lead (Pb), Cr, Cu, Zn and Sr. Krishna and Govil (2007) also made a similar study in the soils of industrial area of Surat city in Gujarat state. Their data revealed that the soil in the study area was significantly contaminated with high concentrations of heavy elements like Ba, Cu, Cr, Co, Ni, Sr, V and Zn.

The dumping of discarded industrial waste materials leads to the contamination of soils and eventually of surface and ground waters and plants (Larison et al. 2000). In addition, activities such as mining and smelting are some of the causes of heavy metals. The concentrations of metals such as Cu and Zn in the environment including in soil and water resources are directly associated with mining and smelting of Cu and Zn metal ores (Cao et al. 2009). Coal fly ash (FA) incorporation in the soil modifies its physicochemical, biological and nutritional quality. However, higher rates of FA applications result in heavy metal pollution (Pandey and Singh 2010). Coal fly ash is an anthropogenic source of As, and in the recent years, the occurrence of As contamination cases of agricultural soils, groundwater and humans in India has caused great concern, and hence, there is an urgent need for mitigation of the problem (Pandey et al. 2011).

With accumulation of heavy metals in the soil, beyond its holding capacity makes them available to growing plants, leading to the contamination of food, which potentially could be a health hazard (Muchuweti et al. 2006). A survey along the Musi River in Hyderabad city, India, revealed the transfer of metal ions from wastewater to cow's milk through the use of para grass as fodder, produced by irrigating with wastewater containing these metals (Qadir et al. 2008). Prolonged consumption of unsafe concentrations of heavy metals through foodstuffs may lead to the chronic accumulation of heavy metals in the kidney and liver of humans, causing disruption of numerous biochemical processes, and potentially leading to cardiovascular, nervous, kidney and bone diseases (Jarup 2003).

Not all heavy metals in soils are the result of human activity. Heavy metals in soils may be inherited from the parent materials or added through use of organic and chemical fertilizers and pesticides. Weathering and pedogenic processes (clay migration, gley formation, podzolization, etc.) determine the quality of phases formed in soils, and thus, they also affect the distribution and behavior of heavy metals in soils (Palumbo et al. 2000). Most of the soils studied originated from basaltic alluvium, calcareous alluvium and granite-gneiss parent materials. Metal concentrations and mineralogical composition of alluvial soils underlain by quaternary sediments are directly related to the parent materials from which the soil is derived (Siddiqui and Khattak 2012). Fertilizers used as carriers of macro and micronutrients and other amendments used in agriculture also contribute to heavy metal additions to the surface soil. In general, the fertilizers carrying N, P and K are lower in heavy metals as compared to the fertilizers used to supply Zn, although it should be noted that Zn is added in smaller amounts than are the N, P and K fertilizers. A study by Atafar et al. (2010) has shown that most Zn fertilizer brands have a low Zn and a relatively high Cd content as a result a low quality for use in agriculture. On the other hand, high levels of Zn and Cd impurities exist in trace element fertilizers. Metals of concern in fertilizers and amendments include As, Cd, Pb and to a lesser extent Ni and Zn. The main source of fertilizer-derived heavy metals in soils is phosphatic fertilizers, manufactured from the phosphate rocks that contain various metals as minor constituents in the ores. Phosphate fertilizers are among the sources of heavy metal inputs to the agricultural systems (Ramadan and Al-Ashkar 2007). The nutrient application is mainly done as DAP (diammonium phosphate). Association of DAP application with heavy metal contamination of soils in New Zealand and Australia has been reported (Bolan et al. 2003).

As most of the studies on heavy metals were carried out in industrial areas of India, it was considered necessary to study the agricultural soils of different soil orders of India in order to assess the distribution of heavy metals in these soils. The study sites have been selected to cover diverse production systems where fertilizer application rates varied to a greater extent. These are representative sites for all 8 major rainfed production systems. All major soil types of rainfed agro-ecological region in India with different parent material were selected. The temperature and rainfall varied widely among these locations. The purpose of this study, therefore, was to evaluate the concentrations of heavy metals in rainfed agricultural soils of the tropical and subtropical regions of India, in relation to parent material on which soils developed, soil properties and fertilizer management practices followed, and to examine whether any of these rainfed soils are high in heavy metals which would have hazardous implications in soil–plant–livestock/human food chain, as most researchers have described the potential risks of transferring heavy metals into the human bodies through edible plants grown on contaminated soils (Dumat et al. 2006; Notten et al. 2005). The study was conducted at the Central Research Institute for Dryland Agriculture (CRIDA), Hyderabad, India, during 2008–2010.

Materials and methods

Study area and soil sampling

Representative soil samples were collected from 21 major sites representing a wide range of climatic conditions; these sites have been under long-term cultivation of various dryland crops under All India co-ordinated Research Project in Dryland Agriculture (AICRPDA), and the sites capture the range in various soil types (Fig. 1). Representative soil profile samples from 8 diverse rainfed production systems: rice (*Oryza sativa*), groundnut (*Arachis hypogaea*), soybean (*Glycine max*), cotton (*Gossypium spp.*), winter (Rabi) sorghum (*Sorghum bicolor*), pearl millet (*Pennisetum glaucum*), finger millet (*Eleusine coracana*) and maize (*Zea mays*) were collected. Soil profiles represented soil types considering the variables: production systems, soil taxonomy and fertility status. Soil samples were collected from different depths after harvest of the respective crops, and they were analyzed for selected soil physical, chemicals and biological variables. Composite soil samples from 7 depths (0–0.15, 0.15–0.30, 0.30–0.45, 0.45–0.60, 0.60–0.75, 0.75–0.90, 0.90–1.05 m) $\times$ 3 replicates were taken with the help of soil auger after the harvest of the crop. As the annual and perennial, cereal and legume food crops or vegetables are covered, the soil sampling was done to a depth of up to 1 m. At each location, sampling was done based on 8–10 dug out pits, and finally, a composite sample was made for each depth. The samples were ground and passed through 2-mm sieve and homogenized. The sample was air-dried and stored in plastic bottles for chemical analysis. Details of locations, climate, soil type and rainfall and the physico-chemical properties of soil profiles are given in Tables 1 and 2 (Srinivasarao et al. 2009). The twenty-one sites covered agro-ecological regions from semiarid, arid and sub-humid climate, soils of Vertisols, Vertic sub-groups, Alfisols, Inceptisols and Aridisols. Rainfall at these sites ranges from 412 to 1,378 mm (Tables 1, 2).

Soil analysis

Soil organic carbon (SOC) content was determined by the modified Walkley–Black wet digestion method. Organic carbon in 1 g of 0.2-mm sieved soil was oxidized with a mixture of 10 ml of potassium dichromate ($K_2Cr_2O_7$) and 20 ml of concentrated sulfuric acid (H_2SO_4). After 30 min, the contents were diluted with 200 ml of distilled water and were mixed with 10 ml of orthophosphoric acid and 1 ml of diphenylamine indicator. The unused $K_2Cr_2O_7$ is back titrated with 0.5 N ferrous ammonium sulfate ($FeSO_4$. $(NH_4)_2$ SO_4. $6H_2O$) (Walkley and Black 1934). Piper's (1942) rapid titration method was used to determine $CaCO_3$ (Jackson 1973). Total heavy metal concentrations in soil samples were determined using the reverse aqua regia method as described in Page et al. (1982). Samples were digested with a hot acid solution of nitric acid and Hg-free hydrochloric acid to extract total metals. The mean value of heavy metal concentrations for all the depths, i.e., 0.5–1.05 m, was considered as profile mean. Bulk density of each horizon was determined by weight by volume using the core method (Grossman and Reinsch 2002). Clay content of all the soil types was determined according to the hydrometer method (Bouyoucos 1962). By leaching the soil with neutral normal ammonium acetate solution, cation exchange capacity (CEC) was determined as described by Jackson (1973).

Statistical analysis

Soil parameters were statistically analyzed following the procedure described by Gomez and Gomez (1984) using Microsoft Excel and SPSS packages (Version 11.0, SPSS, Chicago, IL). The simple correlation and regression analysis were done among variables, i.e., correlation coefficients and regression equations (r and R^2 values) were used to evaluate the relationships between the soil physico-chemical properties (pH, EC, SOC, CEC, CC) and with the profile mean concentrations of heavy metals at 95 % probability level.

Results and discussion

Soil properties

The heavy metal concentrations were correlated with soil properties like pH, EC, SOC, CEC, clay content and total fertilizer consumption. There was wide variation in pH and EC among soil samples collected from 21 sites.

Fig. 1 Map of India showing sites studied (Source Srinivasarao et al. 2009)

Cationic metals are more soluble at lower pH levels, so increasing pH make them less available to plants and therefore, low probability of their getting incorporated in plant tissue (USDA 2000). The pH of a soil controls to a great degree the availability of heavy metals to plants. The ranks of hydration of heavy metals along with their ionic radius are the factors influencing bonding with soil particles (Dobrzanski et al. 1994). The pH of soils among the studied sites varied, with the highest average pH recorded in soils from Agra and Bellary (8.7) and the lowest one in soils from Bangalore (5.8). The high pH of soils in Agra and Bellary had an impact on reducing the total heavy metal concentrations as compared to soils at other sites studied sites, whereas soil samples from Bangalore with low pH showed comparatively higher heavy metal concentrations in the soil. These results could be explained by the fact that increasing soil pH leads to a rapid increase in net negative surface charge causing reduced affinity for metal ions. The effect of <6 pH in increasing metal ion activities in soil can be attributed to the decrease in pH-dependent surface charge on oxides Fe, Al and Mn, chelation by organics of metal hydroxide (Adriano et al. 2002).

Studies by Golia et al. (2008) have shown that low soil pH may induce metals to be soluble and have ion exchange comparable to high soil pH. Studies by (Shivhare and Sharma 2012) demonstrated that the pH of soil affects the solubility and mobility of Ni and other heavy metals. The soil samples from the 21 sites were generally low in organic carbon (SOC, <0.5 %), except for the site at Indore where the average SOC was 0.61, and soil fertility in general was low due to low organic matter. Correlation studies of SOC with heavy metals showed significant correlation with Zn, with r value of (0.47, $p \leq 0.05$) and non-significance with other heavy metals (Table 5). The soil EC was not related to heavy metal concentrations (Table 5).

From our study, it is evident that heavy metal concentrations in the soils are not directly influenced by pH, EC and SOC; however, these parameters are involved in the

Table 1 Details of location, climate, soil type, rainfall and production systems

Order/location/state	Production system	Climate/agro-ecological sub region	Soil type	Mean annual rainfall (mm)	Length of growing period (days)
Inceptisols					
1. Varanasi Uttar Pradesh[a]	Rice	Sub-humid (9.2)	Alluvial-deep Inceptisols	1,080	150–180
2. Faizabad Uttar Pradesh	Rice	Sub-humid (9.2)	Alluvial-deep Inceptisols	1,057	150–180
3. Agra Uttar Pradesh	Pearl millet	Semiarid (4.1)	Alluvial-deep Inceptisols	665	90–120
4. Ballowal Saunkri Punjab	Maize	Semiarid (9.1)	Alluvial-deep Inceptisols	1,000	120–150
5. Rakh Dhiansar Jammu & Kashmir	Maize	Semiarid (14.2)	Alluvial-deep Inceptisols	1,180	150–210
6. Jhansi Uttar Pradesh	Rabi Sorghum	Semiarid (4.4)	Alluvial-deep Inceptisols	1,017	120
Alfisols/oxisols					
7. Phulbani Orissa	Rice	Sub-humid (12.1)	Red/yellow deep Alfisols	1,378	180–210
8. Ranchi Jharkhand	Rice	Sub-humid (12.3)	Red-shallow Alfisols	1,299	150–180
9. Anantapur Andhra Pradesh	Groundnut	Arid (3.0)	Red-shallow Alfisols	590	90–120
10. Bangalore Karnataka	Finger millet	Semiarid (8.2)	Red-deep Alfisols	926	120–150
Vertisols/Vertic group					
11. Rajkot Gujarat	Groundnut	Arid (2.4)	Black-deep Vertisols	615	60–90
12. Indore Madhya Pradesh	Soybean	Semiarid (5.1)	Black-deep Vertisols	944	120
13. Rewa Madhya Pradesh	Soybean	Sub-humid (10.3)	Black-medium deep Vertisols	590	150
14. Akola Maharashtra	Cotton	Semiarid (6.3)	Black-medium deep Vertic/Vertisols	825	120–150
15. Kovilpatti Tamil Nadu	Cotton	Semiarid (8.1)	Black-deep Vertisols	743	120
16. Bellary Karnataka	Rabi Sorghum	Semiarid (3.0)	Black-deep Vertisols	500	90–120
17. Bijapur Karnataka	Rabi Sorghum	Semiarid (3.0)	Black-medium deep Vertisols	680	90–120
18. Solapur Maharashtra	Rabi Sorghum	Semiarid (6.1)	Black-medium deep Vertic/Vertisols	723	90–120
19. Arjia Rajasthan	Maize	Semiarid (4.2)	Black-shallow deep Vertisols	656	90–120
Aridisols					
20. Hisar Haryana	Pearl millet	Arid (2.3)	Alluvial-deep Aridisols	412	60–90
21. Sardarkrushinagar Gujarat	Pearl millet	Arid (2.3)	Desert-deep Aridisols	550	60–90

d dry, *m* moist

[a] State

adsorption/immobilization of heavy metals (Dube et al. 2001). The results of our study are in agreement with correlation studies carried out in Egypt and Greece (Shaheen 2009) and Ghana (Eze et al. 2010) on soil parameters such as pH, and SOC, which showed no significant relationships with heavy metal distribution. The

Table 2 Physicochemical properties of soil profiles under diverse rainfed crop production systems of India

Order/production system location/state	pH (1:2)	EC (dS m^{-1})	$CaCO_3$ (%)	SOC (%)	Particle size (%)			CEC Cmol (p^+) kg^{-1}
					Sand	Silt	Clay	
Inceptisols								
1. Varanasi (rice)	6.3–7.9[b]	0.06–0.27	4.3–6.8	0.1–0.37	35.2–54.2	12–20	27.8–46.8	9–59
Uttar Pradesh[a]	(7.2)[c]	(0.13)	(6.03)	(0.21)	(39.2)	(17.7)	(42.2)	(29.3)
	{±0.36}[d]	{±0.006}	{±0.30}	{±0.01}	{±1.96}	{±0.88}	{±2.11}	{±1.46}
2. Faizabad (rice)	7.5–8.3	0.10–0.61	0.46–1.88	0.08–0.52	26.1–32.1	28.0–38.0	29.9–43.9	21.7–29.3
Uttar Pradesh	(8.1)	(0.29)	(1.10)	(0.18)	(28.5)	(32.0)	(39.3)	(25.9)
	{±0.40}	{±0.014}	{±0.05}	{±0.01}	{±1.42}	{±1.60}	{±1.96}	{±1.29}
3. Agra (pearl millet)	8.1–9.2	0.34–1.08	0.5–2.1	0.12–0.36	41.8–52.1	14.0–20.0	33.9–39.9	19.4–27.2
Uttar Pradesh	(8.7)	(0.68)	(1.6)	(0.19)	(45.5)	(17.4)	(37.0)	(25.1)
	{±0.43}	{±0.034}	{±0.08}	{±0.01}	{±2.27}	{±0.87}	{±1.85}	{±1.25}
4. Ballowal Saunkri (maize)	7.2–8.4	0.10–0.21	3.11–4.84	0.20–0.52	65.0–84.1	13.0–17.0	15.9–17.9	8.20–10.0
Punjab	(7.8)	(0.13)	(3.94)	(0.36)	(72.1)	(14.2)	(16.8)	(9.5)
	{±0.39}	{±0.006}	{±0.19}	{±0.01}	{±3.60}	{±0.21}	{±0.84}	{±0.47}
5. Rakh Dhiansar (maize)	6.7—7.6	0.03–0.11	2.20–2.85	0.32–0.56	77.1–82.1	5.0–8.0	11.9–18.1	5.25–7.28
Jammu and Kashmir	(7.2)	(0.04)	(2.43)	(0.38)	(79.5)	(7.14)	(14.0)	(6.3)
	{±0.36}	{±0.002}	{±0.12}	{±0.01}	{±3.97}	{±0.36}	{±0.70}	{±0.31}
6. Jhansi (rabi sorghum)	7.2–7.5	0.16–0.33	6.9–8.9	0.34—0.40	36.2–50.2	14.0–16.0	35.8–46.8	25.5–33.7
Uttar Pradesh	(7.3)	(0.22)	(7.5)	(0.38)	(39.5)	(15.7)	(45.2)	(30.3)
	{±0.36}	{±0.011}	{±0.37}	{±0.01}	{±1.97}	{±0.78}	{±2.26}	{±1.51}
Alfisols/Oxisols								
7. Phulbani (rice)	5.2–6.5	0.02–0.07	0.11–0.62	0.06–0.24	46.6–66.6	10.0–14.0	19.4–43.4	8.6–15.6
Orissa	(6.0)	(0.02)	(0.38)	(0.12)	(55.4)	(11.1)	(33.4)	(13.2)
	{±0.30}	{±0.001}	{±0.01}	{±0.006}	{±2.77}	{±0.55}	{±1.67}	{±0.66}
8. Ranchi (rice)	6.1–7.6	0.04–0.05	0.30–1.76	0.13–0.62	35.4–61.4	17.0–20.0	20.6–46.6	18.9–31.7
Jharkhand	(6.9)	(0.05)	(1.09)	(0.28)	(43.5)	(18.4)	(38.0)	(28.8)
	{±0.34}	{±0.002}	{±0.05}	{±0.01}	{±2.17}	{±0.92}	{±1.90}	{±1.44}
9. Anantapur (groundnut)	6.5–6.9	0.03–0.13	0.98–4.90	0.16–0.19	55.6–69.6	6.0–12.0	24.6–37.3	10.8–13.7
Andhra Pradesh	(6.8)	(0.09)	(3.19)	(0.17)	(60.5)	(9.1)	(30.3)	(13.0)
	{±0.34}	{±0.004}	{±0.15}	{±0.008}	{±3.02}	{±0.45}	{±1.51}	{±0.65}
10. Bangalore (finger millet)	5.5–6.2	0.05–0.08	0.20–1.48	0.12–0.22	51.1–75.0	1.0–4.0	24.9–44.9	7.7–15.9
Karnataka	(5.8)	(0.07)	(0.93)	(0.16)	(57.5)	(3.3)	(39.2)	(11.7)
	{±0.29}	{±0.003}	{±0.04}	{±0.008}	{±2.87}	{±0.16}	{±1.96}	{±0.58}
Vertisols/Vertic group								
11. Rajkot (groundnut)	7.8–8.5	0.08–0.12	5.82–12.96	0.10–0.52	19.3–33.5	10.0–14.0 (12.1)	56.5–66.7	21.1–34.7
Gujarat	(8.1)	(0.10)	(8.45)	(0.38)	(26.5)	{±0.60}	(61.3)	(28.5)
	{±0.40}	{±0.005}	{±0.42}	{±0.01}	{±1.32}		{±3.06}	{±1.42}
12. Indore (soybean)	7.8–8.0	0.19–0.39	4.30–4.91	0.57–0.68	2.9–12.0	24.0–32.5	60.0–66.2	51.0–55.8
Madhya Pradesh	(7.9)	(0.24)	(4.64)	(0.61)	(7.5)	(30.1)	(62.6)	(53.5)
	{±0.39}	{±0.012}	{±0.23}	{±0.03}	{±0.37}	{±1.50}	{±3.13}	{±2.67}
13. Rewa (soybean)	7.3–7.6	0.05–0.18	0.57–1.06 (0.78)	0.11–0.23	26.7–29.6	22.8–24.0	47.4–49.4	20.8–22.1
Madhya Pradesh	(7.4)	(0.10)	{±0.03}	(0.17)	(28.0)	(23.2)	(48.7)	(21.4)
	{±0.36}	{±0.005}		{±0.008}	{±1.40}	{±1.16}	{±2.43}	{±1.07}
14. Akola (cotton)	8.2–8.5	0.11–0.14	18.1–20.3	0.12–0.25	18.1–20.8	16.0–20.0	60.2–65.9	59.3–61.4
Maharashtra	(8.3)	(0.13)	(19.0)	(0.18)	(18.8)	(19.1)	(62.2)	(60.4)
	{±0.41}	{±0.012}	{±0.95}	{±0.009}	{±0.94}	{±0.95}	{±3.11}	{±3.02}

Table 2 continued

Order/production system location/state	pH (1:2)	EC (dS m^{-1})	$CaCO_3$ (%)	SOC (%)	Particle size (%)			CEC Cmol (p^+) kg^{-1}
					Sand	Silt	Clay	
15. Kovilpatti (cotton)	7.9–8.1	0.26–2.60	9.70–12.5	0.26–0.45	28.0–32.1	5.0–6.0	61.9–66.0	52.2–55.4
Tamil Nadu	(8.0)	(0.80)	(11.25)	(0.36)	(29.8)	(5.8)	(64.4)	(53.6)
	{±0.40}	{±0.005}	{±0.56}	{±0.01}	{±1.49}	{±0.29}	{±3.22}	{±2.68}
16. Bellary (rabi Sorghum)	8.2–8.9	0.21–0.72	14.5–17.9	0.18–0.30	15.9–23.5	10.0–16.0	61.5–70.1	27.4–30.0
Karnataka	(8.7)	(0.33)	(15.8)	(0.22)	(20.4)	(13.1)	(66.4)	(29.2)
	{±0.43}	{±0.006}	{±0.79}	{±0.01}	{±1.02}	{±0.65}	{±3.32}	{±1.46}
17. Bijapur (rabi sorghum)	8.5–8.8	0.24–2.85	18.5–20.9	0.14–0.37	7.3–32.4	12.0–26.0	55.6–66.7	29.4–37.7
Karnataka	(8.6)	(1.40)	(19.9)	(0.27)	(20.40)	(17.7)	(61.9)	(33.9)
	{±0.43}	{±0.040}	{±0.99}	{±0.01}	{±1.02}	{±0.88}	{±3.09}	{±1.69}
18. Solapur (rabi sorghum)	8.0–8.2	0.08–0.15	3.7–6.2	0.30–0.31	10.4–13.3	12.0–14.0	74.5–75.6	36.7–41.5
Maharashtra	(8.1)	(0.12)	(5.37)	(0.30)	(11.5)	(13.6)	(74.8)	(39.5)
	{±0.40}	{±0.016}	{±0.26}	{±0.01}	{±0.57}	{±0.68}	{±3.74}	{±1.97}
19. Arjia (maize)	8.1–8.6	0.12–0.18	2.15–4.70	0.14–0.47	50.9–78.9	8.0–16.0	13.1–33.1	10.0–27.4
Rajasthan	(8.3)	(0.14)	(3.37)	(0.24)	**(63.6)**	**(13.1)**	(23.2)	(18.7)
	{±0.41}	{±0.070}	{±0.16}	{±0.01}	{±3.18}	{±0.65}	{±1.16}	{±0.93}
Aridisols								
20. Hisar (pearl millet)	7.1–7.9	0.25–3.60	0.5–1.2	0.11–0.19	42.1–66.1	14.0–24.0	19.9–33.9	12.7–22.8
Haryana	(7.4)	(1.79)	(0.91)	(0.15)	(55.9)	(17.5)	(26.6)	(18.2)
	{±0.37}	{±0.006}	{±0.04}	{±0.007}	{±2.79}	{±0.87}	{±1.33}	{±0.91}
21 Sardarkrushinagar (pearl millet)	7.9–8.2	0.03–0.06	0.24–1.34	0.16–1.06	82.2–85.8	4.0–5.0	10.2–12.8	7.3–9.3
	(8.0)	(0.04)	(1.09)	(0.43)	(84.1)	(4.1)	(11.7)	(8.3)
Gujarat	{±0.40}	{±0.007}	{±0.05}	{±0.02}	{±4.20}	{±0.20}	{±0.58}	{±0.41}

[a] Location

[b] Profile range

[c] Profile mean

[d] Values in parentheses indicate standard error (SE)

Table 3 Range and threshold concentrations of heavy metals for various sources

Metals	Range of heavy metals in soils (mg kg^{-1})	Agricultural soils (mg kg^{-1})	Drinking water mg L^{-1} (WHO)	Irrigation water (FAO)
		Threshold values (maximum permissible limit)		
Cd	0.01–100.00	20	0.003	0.01
Co	5–60	42	0.05	0.05
Ni	5–500	50	0.02	0.2
Cu	2–100	63	1–2	0.2
Zn	10–300	200	3.0	2.0
Cr	1–1,000	110	0.05	0.1
Mn	20–3,000	600	0.1–0.5	0.2

Sources (Pendias and Pendias 2001; Murthy 2008; WHO; FAO)

lack of relationships between heavy metals and SOC has also been reported by others (Hernandez et al. 2003).

Heavy metal concentration

The concentration of heavy metals (Cd, Co, Ni, Cu, Zn, Cr and Mn) in soils varied from 1.0 to 967 mg kg^{-1} and, the values for majority of metals were within the critical limit for Indian soils (Table 3). The concentration of Cd was low compared to other heavy metals and ranged from 1.0 to 5.1 mg kg^{-1}. The concentration of Co ranged from 5.8 to 37.8 mg kg^{-1}, Cr ranged between 57.0 and 199.1 mg kg^{-1}, Ni ranged between 18.1 and 84.6 mg kg^{-1}, Cu between 7.4 and 94.6 mg kg^{-1}, Mn between 196.8 and 967.3 mg kg^{-1} and Zn ranged between 19.1 and 65.0 mg kg^{-1} in the soil samples. Krishna and Govil (2007) also reported higher

Table 4 Concentrations of heavy metals in soils of the studied sites developed on three types of parent materials

Heavy metals in soil	Basaltic (Black soils) mg kg^{-1}	Calcareous (Alluvial) mg kg^{-1}	Granite-gneiss (Red soils) mg kg^{-1}
Cd	4.35–5.11[a] (4.68)[b] {±0.23}[c]	1.93–2.71 (2.35) {±0.12}	2.08–3.46 (2.81) {±0.14}
Co	24.01–37.88 (30.54) {±1.52}	8.94–11.78 (9.93) {±0.49}	7.08–15.49 (12.04) {±0.60}
Ni	47.69–84.60 (60.92) {±3.04}	21.86–29.12 (24.85) {±1.24}	18.82–32.51 (23.62) {±1.18}
Cu	51.56–94.65 (77.69) {±3.88}	8.82–15.66 (12.28) {±0.61}	7.80–16.97 (11.84) {±0.59}
Zn	55.71–92.85 (68.99) {±3.44}	35.66–46.64 (42.26) {±2.11}	20.35–43.06 (32.51) {±1.62}
Cr	66.56–97.06 (79.11) {±3.95}	112.73–156.13 (128.13) {±6.40}	99.64–141.97 (123.47) {±6.17}
Mn	691.50–967.30 (851.69) {±42.58}	246.31–416.65 (338.47) {±16.92}	396.88–577.52 (486.19) {±24.30}

[a] Profile range

[b] Profile mean

[c] Values in parentheses indicate standard error (SE)

Table 5 Correlation of different heavy metals, pH, EC, soil organic carbon (SOC), cation exchange capacity (CEC), clay content (CC) and total fertilizer consumption (TFC) of the soils of the studied sites

	pH	EC	SOC	CEC	CC	TFC	Cd	Co	Ni	Cu	Zn	Cr	Mn
pH	1.00												
EC	0.24	1.00											
SOC	0.24	0.10	1.00										
CEC	0.41	0.17	0.39	1.00									
CC	0.33	0.1	0.28	0.81	1.00								
TFC	0.1	0.1	0.003	0.14	0.10	1.00							
Cd	0.21	0.04	0.28	0.76*	0.85*	0.40	1.00						
Co	0.09	0.09	0.27	0.71*	0.88*	0.49*	0.91*	1.00					
Ni	0.11	0.07	0.13	0.69*	0.87*	0.62*	0.81*	0.85*	1.00				
Cu	0.29	2lE-	0.34	0.72*	0.81*	0.62*	0.81*	0.95*	0.83*	1.00			
Zn	0.42*	06	0.47*	0.31	0.49*	0.27	0.79*	0.71*	0.63*	0.68*	1.00		
Cr	0.2	0.07	0.32	0.72*	0.80*	0.32	–	–	–	–	–	1.00	
Mn	0.45	0.12	0.05	0.65*	0.79*	0.3	0.66*	0.61*	0.46*	0.54*	0.62*	–	1.00

*Indicates correlation is significant at the 0.05 level

concentrations of Cu (137.7 mg kg^{-1}) and Ni (139 mg kg^{-1}) in the soil samples collected from Surat, western India. But these soils were adjacent to industrial areas.

From our study, it is evident that soil samples collected from the 21 sites under rainfed production systems of India vary widely in heavy metal concentrations. Total Zn was below critical limit in Arjia, and Mn was below critical limit in Rakh Dhiansar, Anantapur and Arjia sites. Concentrations of Ni, Cr and Mn in the soil samples are above the critical limits (Table 4). The greater content of these heavy metals reflects the diversity of parent material and also supports the contention that Indian soils are derived from contrasting parent materials. There might be another possibility that greater content of Cr is related to the diverse geological source deposits by the surrounding geology and bedrock geology. Manganese is normally present in large quantities in soils, and it is commonly associated with silicate clays. Correlation studies have shown that among the heavy metals, a significant negative correlation was observed between Cr with rest of the studied heavy metals, and a significant positive correlation was observed among the other heavy metals (Table 5). These correlation studies therefore help in understanding the chemistry of heavy metals in Indian soils and their association among them.

Heavy metals and parent material

Geographical variation of heavy metals in Indian soils is to a large extent determined by the nature of the parent material. Heavy metals concentration is related to several factors in non-contaminated soils. Among those factors are biogeochemical cycling, parent material, particle-size distribution, soil age, mineralogy, organic matter content and drainage (Lavado et al. 1998). The heavy metal concentration in soils is strongly influenced by the parent materials in which they form. The background concentration of heavy metals in soils depends on the geological characteristics of soils and also, normal agricultural practices generally cause accumulation of these elements (Atafar et al. 2010). Basaltic alluvium, basaltic bedrock, alluvium of metamorphic rocks and granite-gneiss, calcareous alluviums are some of the common parent materials found at the sites studied.

The concentrations of heavy metals in the soils of the studied sites developed from different parent materials showed significant variation (Table 4). Sandy soils from granite rocks generally contain lower concentrations of heavy metals than clay soils derived from mafic rocks (Ross 1994). The range of heavy metal concentrations (mg kg^{-1}) in igneous and sedimentary rocks as classified by Cannon et al. (1978) are given in Table 6. From our study, higher Cu content was found in basaltic rocks. The abundance of Cu in basaltic rocks is greater than for granitic rocks, and the concentration is very low in carbonate rocks. Gabbro and basalt rocks have the highest Cu contents, and granodiorite and granite the lowest. Studies by Niemyska-Lukaszuk et al. (1998) have shown that heavy metal concentrations in particular Zn, Cu, Pb and Cd concentrations are primarily determined by their chemical properties conditioned by parent rock and further showed that the abundance of Cu in igneous rocks is partly controlled by the process of differentiating during crystallization. It is known that heavy metals present as impurities in phosphate rocks (PRs) are transferred from fertilizers during processing.

The bedrock is the primary source of chemical elements in soil. In general, the concentration of Cr and Ni in granitic igneous rocks ranges from 2 to 90 mg kg^{-1} for Cr and 2–20 mg kg^{-1} for Ni (Krishna et al. 2011). From our study, the soils originating from granite-gneiss showed Cr and Ni ranges of the same order (Table 4). The main reason for heavy metals in soils of granite-gneiss could be attributed to erosion of granite rather than anthropogenic sources (Baltrenaite and Butkus 2004). Studies by Olaniya et al. (1998) showed that a major part of heavy metals is taken up by crops from the soil via roots. Heavy metal transportation from the soil to the roots largely depends on the type and genetic features of soil forming rocks, granulometric soil composition, amount of organic matter, pH of the soil, sorption capacity, amount of $CaCO_3$, anthropogenic load, and other chemical and physical properties of the soil.

Profile distribution

The distribution of heavy metals in soils is widely influenced by soil physicochemical properties. Figures 2–5 give an overview of soil type, parent material, rainfall and production systems influencing heavy metals concentrations in soils. From our study, it is evident that with increase in rainfall, heavy metal concentration increased up to 1,000 mm rainfall, beyond that it decreased (Fig. 4). Metals accumulated in the moderate rainfall zones, as the solubility of heavy metals could be affected in less and heavy rainfall zones. CEC and clay content greatly influence the distribution of heavy metals in soils. The pH value and the percentage of clay content determine the solubility of metals in the soil and their availability for uptake by plants (Golia et al. 2008). Heavy metals content usually decreases from clay to coarse silt due to relatively high surface area of clay minerals and weak pH dependence of CEC (Modaihsh et al. 2004). From our study, it is evident that there is an obvious relationship between clay content and the amount of heavy metals in soils. Clay content varied widely among the studied soils. Soil samples from Solapur had the highest clay content among all of the studied sites, followed by Bellary, Kovilpatti, Akola, Bijapur and Rajkot. All the other studied sites have less than 50 % clay content.

The type and amount of clay, along with organic matter, are the principal factors determining the CEC, which increases with clay content, particularly when it contains a high proportion of 2:1 lattice-type minerals (Aydinalp and Marinova 2003). Correlation analyses of clay content with

Table 6 Range of heavy metal concentrations (mg kg^{-1}) in igneous and sedimentary rocks

Heavy metals in soil	Basaltic (Black soils) mg kg^{-1}	Calcareous (Alluvial) mg kg^{-1}	Granite-gneiss (Red soils) mg kg^{-1}
Cd	0.006–0.6	0.0–11.0	0.003–0.18
Co	24–90	5–25	1–15
Ni	45–410	20–250	2–20
Cu	30–160	18–120	4–30
Zn	48–240	18–180	5–140
Cr	40–600	30–590	2–90

Source (Cannon et al. 1978)

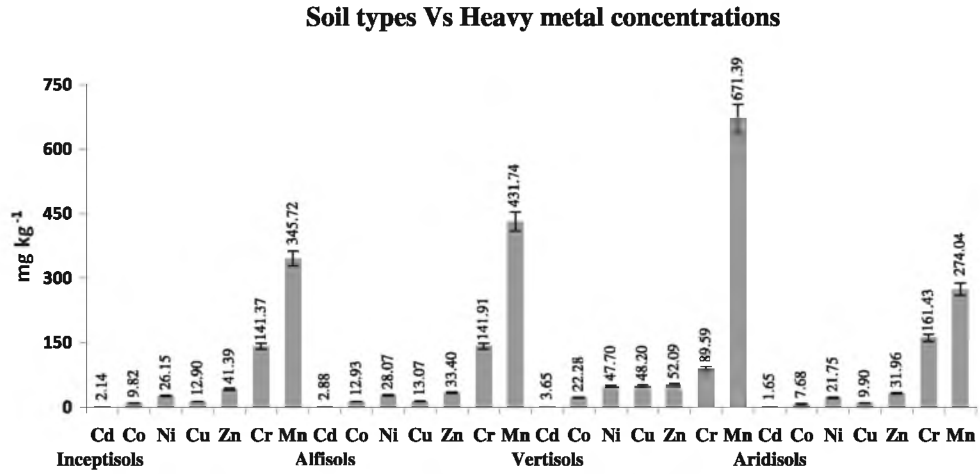

Fig. 2 Relationships between soil types and heavy metal concentrations. (±Standard error is indicated)

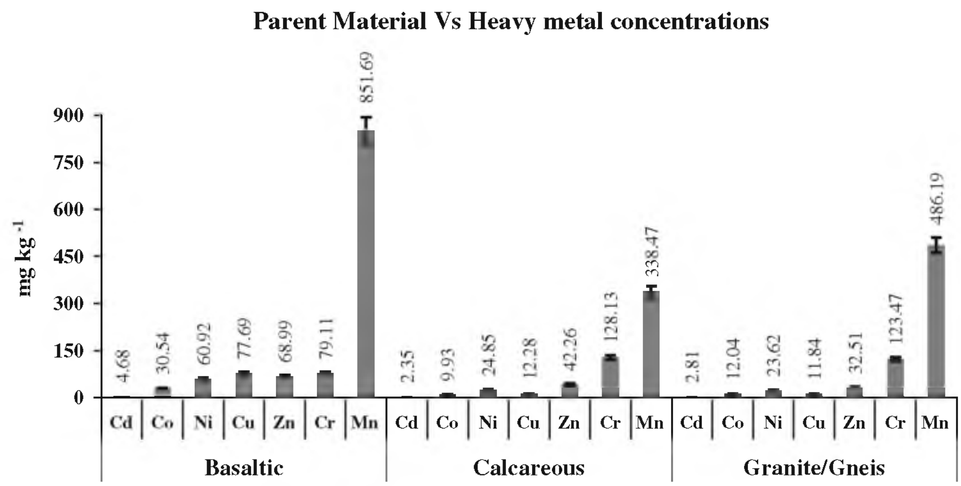

Fig. 3 Parent material versus heavy metal concentration. (±Standard error is indicated)

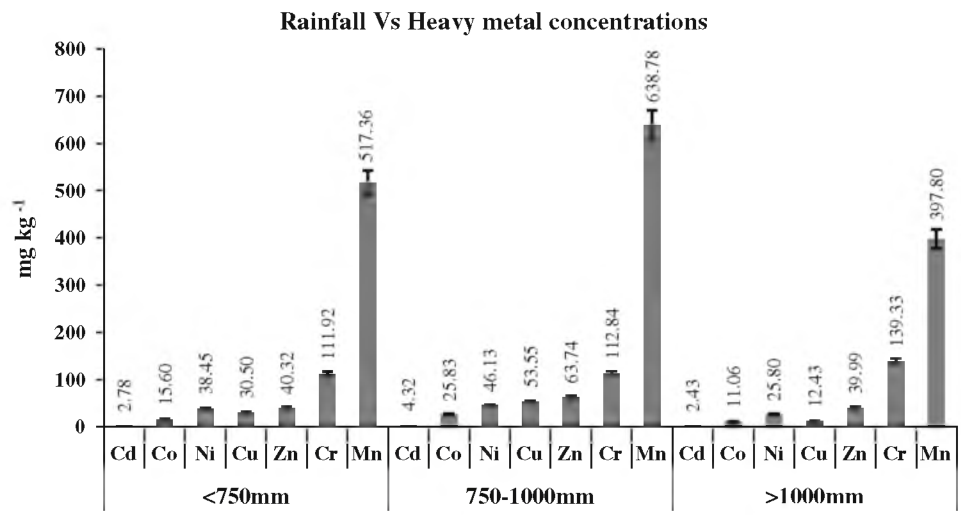

Fig. 4 Association of mean annual rainfall and heavy metal concentrations. (±Standard error is indicated)

metal concentrations across the sites revealed significant correlation for all the metals analyzed. Large variation in heavy metal concentrations in soils on different parent materials could be accounted for by the clay mineralogy of soils, characterized by pedogenic processes. The variation in heavy metal concentrations in soils in relation to parent material is associated with the clay content (Sipos and Nemeth 2001). From our study, the clay content in parent

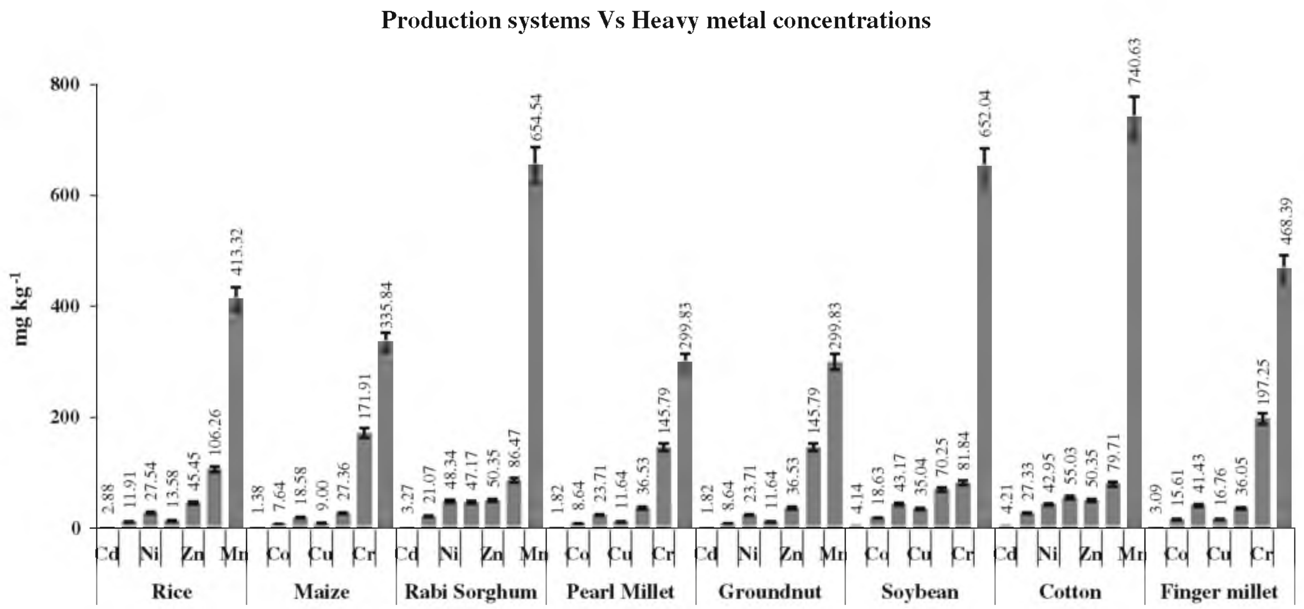

Fig. 5 Relationships of crop production systems with heavy metal concentrations. (±Standard error is indicated)

materials followed the hierarchy: basaltic > calcareous > granite-gneiss. Soils of basaltic alluvium parent material had the highest concentration of heavy metals, as its clay content was higher than that in calcareous and granite-gneiss parent materials. Correlation studies showed a significant positive correlation (Table 5) with r values of (0.84, $p \leq 0.05$) for Cd, (0.88, $p \leq 0.05$) for Co, (0.81, $p \leq 0.05$) for Cu, (0.86, $p \leq 0.05$) for Ni, (0.49, $p \leq 0.05$) for Zn, (0.80, $p \leq 0.05$) for Cr and (0.79, $p \leq 0.05$) for Mn. These results are in accord with those reported by Eze et al. (2010) who showed that among all the major soil properties examined in Accra Plains, Ghana, only soil clay content was significantly correlated with Cu and Zn concentrations ($r = 0.57$, $p \leq 0.05$). Studies by Aydinalp and Marinova (2003) showed that expandable clays have much greater CEC than the non-expanding types and, therefore, have a greater capacity for immobilizing metal ions. From our study, relationship between heavy metals and CEC showed moderate positive correlation with r values of (0.76, $p \leq 0.05$ for Cd; 0.71, $p \leq 0.05$ for Co; 0.72, $p \leq 0.05$ for Cu; 0.69, $p \leq 0.05$ for Ni; 0.31, $p \leq 0.05$ for Zn; 0.72, $p \leq 0.05$ for Cr and 0.65, $p \leq 0.05$ for Mn) (Table 5).

Vertical distribution

Depth-wise profile sampling showed a big variation in the heavy metal concentrations for all the studied metals. The increase in the concentrations of heavy metals at lower depths can be associated with parent material. In our study, basaltic soils at lower depth had higher concentration of heavy metals. These results are in accord with studies by Serelis et al. (2010), whereby higher Co and Ni contamination in the lower depth (10–25 cm) indicated that they are derived from the parent material, while higher concentrations for Cd, Zn and Pb in the upper depth (0–10 cm) probably are due to anthropogenic sources. Leaching also plays a role in depth-wise vertical distribution of heavy metals, which is affected by weathering and excessive rainfall.

Effects of fertilizer usage

Studies by Lukowski and Wiater (2009) have shown that concentrations of Cu and Ni mobile forms in the soil have been significantly influenced by the addition of mineral fertilizers. Concentrations of heavy metals in NPK and $ZnSO_4$ fertilizers vary widely, and long-term simultaneous application of fertilizer and manure on the commercial farm show higher metal accumulation in the soil and plants than those of cooperative farms (Parkpian et al. 2003). Recommendations emanating from the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT) and other international organizations for the application of $ZnSO_4$, gypsum and borax/Agribor depending upon the soil test values have increased the use of these chemical fertilizers more frequently than required. Addition of $ZnSO_4$ as a fertility amendment in our studied sites showed a strong correlation with zinc (r value = 0.96, $p \leq 0.01$) (Fig. 6). The higher concentration of Zn in the soil may also be ascribed to the use of Zn in fertilizers and metal-based pesticides. These results do suggest that NPK fertilizers along with $ZnSO_4$ might have an influence on the heavy metal occurrence in soils. These results are in accord

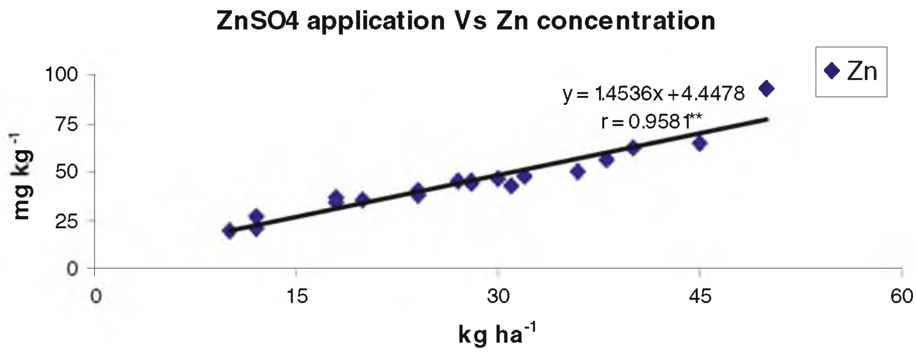

Fig. 6 Relationship between heavy metal concentrations and total $ZnSO_4$ consumption (kg ha^{-1}). *Double asterisks* indicate significance at ($p \leq 0.01$)

with studied by Zahra et al. (2010) who demonstrated that high concentration of Zn, Ni and Cu present in the soils are highly correlated with the application of composite fertilizer, triple super phosphate and zinc sulfate fertilizer.

Heavy metals can also accumulate in the soil due to application of liquid and solid manure (or their derivatives, compost or sludge) or inorganic fertilizers (Huang and Jin 2008). A previous study on heavy metal contents in phosphatic fertilizers (DAP) revealed the following order: Co (11.8) < Cd (33.2) < Ni (72.1) < Cr (249.3) mg kg^{-1} (Modaihsh et al. 2004). In general, DAP (diammonium phosphate) fertilizers contain 10 mg kg^{-1} Cd; 71 mg kg^{-1} Cr; 19 mg kg^{-1} Ni; 1.6 mg kg^{-1} Mn; 170 mg kg^{-1} Zn, and these metals may contribute toward heavy metal deposition in soils over time (Battelle 1999). From our study, it is evident that heavy metal concentrations in soils at Akola and Solapur are higher than in soils from the other sites studied. The application of DAP can be considered as one of the factors contributing to heavy metal accumulation in soils as Maharashtra is one of the states, which has a high DAP application rate of the order of 537,000 tons during 2011 rainy season (*kharif*) (Chandar et al. 2010). A study was conducted in Montana, USA, to assess metal concentrations following twenty years of DAP application. Results revealed that fertilized soils had significantly higher metal concentrations compared to non-fertilized soils both under irrigated and non-irrigated conditions (Jones et al. 2002).

From our study, moderate positive correlations of total fertilizer consumption (NPK) with heavy metal concentration in soils (Table 5) were obtained for Cu, Ni, Co, Cd with r values of (0.62, $p \leq 0.05$ for Cu; 0.62, $p \leq 0.05$ for Ni; 0.49, $p \leq 0.05$ for Co; 0.40, $p \leq 0.05$ for Cd), and very low positive correlations were obtained for Cr, Mn, Zn with r values of (0.32, $p \leq 0.05$ for Cr, 0.30, $p \leq 0.05$ for Mn, 0.27, $p \leq 0.05$ for Zn). Cd concentration in Akola soils was 5.11 (mg kg^{-1}) and therefore might be liable to accumulation in plants as Cd is relatively mobile in soil system for uptake by plants than other heavy metals (Prokop et al. 2003). Studies in North China showed higher incidence of Cd concentration in plant tissue, which was attributed to over usage of manure in particular phosphate fertilizers (Ju et al. 2007).

From our study, it can be concluded that Ni, Cr and Mn are the heavy metals which are above the maximum permissible limit in the tropical soils of India. These findings are in conjunction with the findings of Purohit et al. (2001), whereby Ni and Cr exceeded the critical threshold value in the Doon valley soils of outer Himalayas, India. In other tropical parts of the world such as the Accra Plains of Ghana, these three heavy metals are the dominant ones in soil, but well within the maximum permissible limits. The other important finding is the high clay content of soils associated with basaltic alluvium parent material has the highest heavy metal concentrations among the sites studied.

Conclusion

This study contributes to the understanding of the content, distribution, controlling factors and potential sources of heavy metals in tropical soils. The heavy metal concentrations in soils of basaltic parent material origin were comparatively higher than that in soils originating from the calcareous and granite-gneiss parent material types. In the sites studied, Ni, Cr and Mn concentrations exceeded the maximum allowable limits in soils set by WHO and FAO. As the concentrations of these three metals are above the threshold limits, there might be direct linkage to the food chain through plant uptake. Cd, Co, Cu and Zn concentrations in the studied sites were within the maximum allowable limit. Clay content of soils as influenced by parent materials plays a vital role in controlling heavy metal influx. Heavy fertilizer application particularly DAP and $ZnSO_4$ is associated with heavy metal concentration in soil, and therefore, in-disproportionate DAP application should not be promoted particularly in growing commercial crops like cotton, maize, high-value vegetables and fruits. All the studied soils are agricultural soils. It is not necessary that these soils will contain higher heavy metals than critical limit. Industrial pollution is not the source of heavy metals, but excessive use of fertilizers or parent materials can contribute toward higher accumulation of heavy metals in soils. As of yet, it is not above danger level; however, in the future, it may have serious consequences if farming practices are not properly managed.

Acknowledgments The authors are thankful to the in charges of All India Coordinated Research Project on Dryland Agriculture (AICRPDA) centers, and other staff for helping with profile-based soil sampling.

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