# Distribution of Arsenic and Trace Metals in the Floodplain Agricultural Soil of Bangladesh

Dewan Ali Ahsan · Tomas Angel DelValls · Julian Blasco

Received: 13 November 2007/Accepted: 14 July 2008/Published online: 12 August 2008 © Springer Science+Business Media, LLC 2008

Abstract Arsenic contaminated groundwater of Bangladesh is one of the largest natural calamities of the world. Soil samples were collected from floodplain agricultural land of Faridpur and Dhamrai regions to estimate the concentration of arsenic and other trace metals (copper, nickel, zinc, chromium, cadmium, lead, selenium, cobalt, mercury, and manganese). Average arsenic in Faridpur soil was recorded more than three times higher than the world limit and nearly five times higher than that of Dhamrai. The average copper, chromium and cobalt both in Faridpur and Dhamrai agricultural soil were also higher than the Dutch and the world standards. Both Fardipur and Dhamrai soil contain low amount of selenium in comparison to world limit  $(0.7 \text{ mg kg}^{-1})$ . A poor correlation between manganese and arsenic was noticed in Faridpur. This may be played a subordinate role in the fixation of arsenic in soil. This study also reveals that the area which has arsenic and trace metal contaminated groundwater may also contain high level of arsenic and trace metals in the agricultural soil due to irrigation with contaminated groundwater.

**Keywords** Bangladesh · Arsenic · Pollution · Agricultural soil

D. A. Ahsan (⊠) · T. A. DelValls UNESCO/UNITWIN/WiCop. Department of Physical-Chemistry. Faculty of Marine and Environmental Sciences, University of Cadiz, Campus Rio San Pedro, 11510 Puerto Real, Cadiz, Spain e-mail: daahsan@yahoo.com

#### J. Blasco

Arsenic is a very toxic metalloid. It has a serious impact on the human health. Several million people are at risk from arsenic (As) contaminated drinking water in India (Chatterjee et al. 1995), Bangladesh (Bhattacharya et al. 2002) and China (Wang et al. 2003). The problem of As contamination groundwater of Bangladesh has been considered as dreadful proportion as nearly 75 million people are now at high risk (Chatterjee et al. 1995). The ground water As concentration is recorded from <2.5 to 846 µg L<sup>-1</sup> in Bangladesh. The survey of Frisbie et al. (2002) revealed unsafe levels of manganese (Mn), lead (Pb), nickel (Ni), and chromium (Cr) in drinking water of Bangladesh. Norra et al. (2005) reported the average concentration of As, zinc (Zn), copper (Cu), lead (Pb), and organic carbon (OC) in rice field (irrigated with As rich groundwater) as 101 mg kg<sup>-1</sup>,  $38.2 \text{ mg kg}^{-1}$ ,  $48.3 \text{ mg kg}^{-1}$ ,  $22.8 \text{ mg kg}^{-1}$ , and 1.4%, respectively in West Bengal, India. The concentrations of Cd, Cu, Pb, and Zn were found in the range of 0.01- $0.12 \text{ mg kg}^{-1}$ ,  $0.10-2.90 \text{ mg kg}^{-1}$ ,  $0.02-0.23 \text{ mg kg}^{-1}$ , and  $0.51-3.35 \text{ mg kg}^{-1}$ , respectively in soil of Lagos, Nigeria (Awofolu 2005). Soil Cd range was recorded from 0.46 to 1.04 mg  $kg^{-1}$  in some parts of China (Dong et al. 2001). Arsenic and trace metal rich ground waters have been using for irrigation in Bangladesh for several decades. So, the top soil of Bangladesh may be at high risk of contamination from arsenic.

The inorganic form of As is toxic to human being. Arsenic and trace metal can inter into the plants from soil and hence in food chain from contaminated soil and may infect human being as well. The terrestrial plants can accumulate a large amount of arsenic (inorganic form) from soils and transfer it to the aboveground biomass (Zhang et al. 2002). On the other hand, marine plants and animals have arsenic detoxification system and for this reason a large amount of arsenic in marine organisms is

Department of Ecology and Coastal Management, Institute of Marine Science of Andalusia (CSIC), Campus Rio San Pedro, 11510 Puerto Real, Cadiz, Spain

found in organic forms, such as arsenosugars in algae, and arsenobetaine and arsenocholine in fish, mollusks, and crustaceans (Francesconi et al. 1994). However, terrestrial plants do not have arsenic detoxification system and this is perhaps the reason why inorganic arsenics are predominant in terrestrial plants (Mattusch et al. 2000). A few studies have been conducted to find out the distribution of As and other trace metals in floodplain agricultural soil of Bangladesh. So, the current study has been taken to get an idea about the magnitude of soil contamination with As, Cu, Pb, Mn, Fe, Zn, Co, Se, Hg, Cd, Cr, and Ni in floodplains agricultural soil of two regions [Faridpur (FD) and Dhamrai (DM)] of Bangladesh.

### **Materials and Methods**

The surface soils samples were collected from floodplain agricultural fields of Faridpur ( $123^{\circ}10'$  to  $23^{\circ}40'$  N and  $89^{\circ}35'$  to  $90^{\circ}10'$  E) and Dhamrai ( $23^{\circ}50'$  to  $24^{\circ}05'$  N and  $90^{\circ}00'$  to  $90^{\circ}20'$  E) during dry season (15-29th December, 2006). Ground water has been using for irrigation in dry season in these areas.

Composite soil samples (about 500 g each for different analysis) were collected at a depth of 0-3 cm level. The area of each sampling field was between 0.5 and 5 ha. Samples were transferred into zip locked polythene bags for analysis with proper labeling. Soils samples were dried in room temperature and sieved with a sieve of <2 mm fraction (ISO/DIS 11464). After that, the samples were transferred into zip locked polythene bags. All the samples were then transferred to University of Cadiz, Spain for chemical analyses.

About 0.5 g dried sample was transferred into HP 500 vessel for total digestion. After that 10 mL of deionised water (milliQ water) was added. A mixture of 5 mL of HNO<sub>3</sub>, 4 mL of HF, and 1 mL of HCL was also added. The vessels were then inserted into a microwave (CEM MARS 5) and heated at 210°C for 20 min at 175 PSI pressure. After cooling the vessels at room temperature, the caps of the vessels were opened slowly and 30 mL of boric acid solution were added in each vessel. Then the samples were again heated at 210°C for 5 min at 175 PSI pressure. After cooling the digested samples were transferred into a volumetric flask and made up to the final volume (50 mL) with deionised water. The samples were then transferred into plastic containers and kept in refrigerator at about 4°C prior to analysis. All reagents were analytical grade or Suprapur quality (Merck, Germany). Milli-Q water (Millipore, Bedford, MA, USA) was used in all experiments. Cleaning of plastics and glassware was carried out by soaking in 14% (v/v) HNO<sub>3</sub> for 24 h and then rinsing with water.

All digested samples were analyzed for As, Hg, Pb, Co, and Se by ICP-MS and Fe, Mn, Cr, Cu, Zn, and Ni by ICP-AES. Cadmium was determined by GF-AAS. Reactive blanks and reference material (CRM 478 BCR) were used to ensure the quality control. The concentration was calculated on a dry weight basis. The organic carbon concentration was determined by using El Rayis (1985) method.

Statistical analyses were performed on a personal computer using Microsoft Excel programme. A probability level of p < 0.05 was considered for statistically significance.

## **Results and Discussion**

The present study showed that in the soil of Faridpur (FD) and Dhamrai (DM) the average As concentration were 33.15 mg kg<sup>-1</sup> and 6.10 mg kg<sup>-1</sup>, respectively (Tables 1 and 2). The positive correlations of As with trace metals (Cu, Pb, Mn, Fe, Zn, Co, Se, Hg, Cd, Cr, and Ni) were found both in Faridpur and Dhamrai. The average As concentration in Faridpur was more than three times higher than the world standard (10 mg kg<sup>-1</sup>) for soil and 100% of the samples exceeded the world's guideline. This value is also much higher than the average As (13.3 mg kg<sup>-1</sup>) of Samta village one of the As rich areas of Bangladesh (Alam et al. 2003).

The ground-water of Faridpur is highly contaminated with As (Frisbie et al. 2002) and the contaminated water has been using for irrigation for long time. The present study indicated that Faridpur soils contained five times more As than Dhamrai soil. This may be occurred due to use of As rich groundwater for irrigation of rice. The mean concentration of Zn was estimated 97.24 mg kg<sup>-1</sup> in soil of Faridpur, whereas Zn concentration was recorded 98.85 mg kg<sup>-1</sup> in soil of Dhamrai (Tables 1 and 2). However, the average Zn was higher than the world standard for Zn (90 mg kg<sup>-1</sup>) and 87% of the samples exceeded that level. Arsenic and Zn correlation (r = 0.0136) was relatively poor in Faridpur soil, whereas that correlation (r = 0.84) was significant in Dhamrai (Tables 3 and 4).

This finding indicates that Zn concentration may effect the As fixation in the soil. The mean concentrations of Zn both in Faridpur and Dhamrai soils were lower than the Dutch standard for Zn (140 mg kg<sup>-1</sup>). This value is also lower than the Zn concentration in soil Nigeria (Awofolu 2005). Zinc is an essential element for human health.

The present study found the average Mn concentrations were 449.68 and 553.75 mg kg<sup>-1</sup> in the soil of Faridpur and Dhamrai, respectively (Tables 1 and 2). Average Mn is lower than the limit of the world standard in both areas. However, the average Mn of these two areas is higher than the Mn (386 mg kg<sup>-1</sup>) in paddy soil of China (Wang et al. 2003).

Table 1 Arsenic and trace metals in soil of Faridpur (FD), Bangladesh with comparison to Dutch and World limit

Metals	Present study (range)	Present study (average)	Dutch standard <sup>a</sup>	World limit	
(mg kg <sup>-1</sup> dry soil)					
As	17.59–65.03	33.15	29	10	
Cu	38.20-63.55	48.42	36	30	
Ni	42.21-61.01	48.85	35	50	
Zn	82.69–117.36	97.24	140	90	
Cr	73.50–108.14	85.95	100	70	
Cd	0.12-0.17	0.153	0.8	0.35	
Pb	24.32-33.95	26.82	85	35	
Se	0.57-1.37	1.04	0.7	7	
Co	14.60-22.09	17.40	9.0	8	
Hg	0.05-0.09	0.081	0.3	_	
Mn	374.09-575.17	449.68	-	1,000	
Fe (mg $g^{-1}$ ) 40.87–56.27		48.37	-	-	

<sup>a</sup> Coskun et al. (2006)

Table 2 Arsenic and trace metals in soil of Dhamrai (DM), Bangladesh with comparison to Dutch and World limit

Metals	Present study (range)	Present study (average)	Dutch standard <sup>a</sup>	World limit	
(mg kg <sup>-1</sup> dry soil)					
As	3.11-8.93	6.10	29	10	
Cu	29.61-33.71	31.84	36	30	
Ni	43.80-47.94	46.09	35	50	
Zn	78.88–125.87	98.85	140	90	
Cr	45.60-84.38	76.08	100	70	
Cd	0.11-0.22	0.155	0.8	0.35	
Pb	23.22–26.61	24.85	85	35	
Se	0.623-1.31	1.01	0.7	7	
Co	15.41–17.26	16.41	9.0	8	
Hg	0.05-0.12	0.78	0.3	_	
Mn	471.09-655.24	553.75	-	1,000	
Fe (mg $g^{-1}$ )	32.70-41.30	37.00	-	-	

<sup>a</sup> Coskun et al. (2006)

Manganese correlated significantly with As (r = 0.86) in Dhamrai soil, whereas that correlation (r = 0.0261) was insignificant in Faridpur soil (Tables 3 and 4). The poor correlation of Mn with As in Faridpur may play a subordinate role in the fixation of As in soil because oxidized Mn phases are well known for their ability to adsorb high amounts of As (Chiu and Hering 2000).Selenium concentrations in Faridpur and Dhamrai soils were 1.04 and 1.01 mg kg<sup>-1</sup>, respectively (Tables 1 and 2) and 100% of samples of the both the areas were under the world standard of Se (7 mg kg<sup>-1</sup>). Selenium and arsenic correlations of FD (r = 0.0420) were very poor and insignificant in comparison to that of DM (r = 0.94) (Tables 3 and 4). The average Se in soil of Faridpur and Dhamrai were also very lesser than the average Se (0.25 mg kg<sup>-1</sup>) of China (Wang et al. 2003). Selenium is an important element of the human body which prevents the cytotoxic effect of As. The average Se contents (0.003  $\mu$ g L<sup>-1</sup>) in Bangladesh groundwater is very low in comparison to WHO limits (0.010  $\mu$ g L<sup>-1</sup>) (Frisbie et al. 2002).This general deficiency of Se both in soil and water can decreases the Se level in human body and hence increases the intensity of arsenic related diseases.

The mean concentrations of Fe in soil of Faridpur and Dhamrai were found 48.37 and 37.00 mg g<sup>-1</sup>, respectively (Tables 1 and 2). A positive insignificant correlation between As and Fe were obtained both in Faridpur (r = 0.36) and Dhamrai (r = 0.39). Norra et al. (2005)

	As	Cu	Ni	Zn	Se	Co	Hg	Cr	Cd	Pb	Mn	Fe
As	1.00											
Cu	0.3140	1.00										
Ni	0.0003	0.1491	1.00									
Zn	0.0136	0.0841	0.839 (S)	1.00								
Se	0.0420	0.0615	0.3133	0.3313	1.00							
Co	0.0043	0.2001	0.9315 (S)	0.7232 (S)	0.3519	1.00						
Hg	0.1409	0.0893	0.3343	0.4474	0.5379 (S)	0.25	1.00					
Cr	0.0078	0.2152	0.9755 (S)	0.7253 (S)	0.2752	0.95 (S)	0.23	1.00				
Cd	0.0453	0.0085	0.4245	0.4242	0.2123	0.27	0.14	0.36	1.00			
Pb	0.0111	0.1389	0.9514 (S)	0.7521 (S)	0.2407	0.86 (S)	0.23	0.93 (S)	0.40	1.00		
Mn	0.0261	0.0473	0.5766 (S)	0.5111 (S)	0.6682 (S)	0.63 (S)	0.17	0.57 (S)	0.29	0.57 (S)	1.0	
Fe	0.3682	0.0048	0.5364 (S)	0.4830	0.2035	0.59 (S)	0.34	0.49 (S)	0.20	0.43	0.15	1.0

Table 3 Correlation coefficient matrix for soil parameters of Faridpur (FD), Bangladesh

S = Significance at 5% level

Table 4 Correlation coefficient matrix for soil parameters of Dhamrai (DM), Bangladesh

	As	Cu	Ni	Zn	Se	Со	Hg	Cr	Cd	Pb	Mn	Fe
As	1.00											
Cu	0.74	1.00										
Ni	0.79 (S)	0.97 (S)	1.00									
Zn	0.84 (S)	0.81 (S)	0.85 (S)	1.00								
Se	0.94 (S)	0.64	0.74	0.84 (S)	1.00							
Co	0.76	0.79 (S)	0.89 (S)	0.91 (S)	0.84 (S)	1.00						
Hg	0.30	0.21	0.28	0.59	0.46	0.57	1.00					
Cr	0.50	0.39	0.54	0.41	0.66	0.65	0.22	1.00				
Cd	0.67	0.80 (S)	0.78 (S)	0.93 (S)	0.63	0.79 (S)	0.56	0.21	1.00			
Pb	0.81 (S)	0.64	0.70	0.95 (S)	0.86 (S)	0.85 (S)	0.72	0.39	0.86 (S)	1.0		
Mn	0.86 (S)	0.88 (S)	0.91 (S)	0.99 (S)	0.83 (S)	0.91 (S)	0.50	0.42	0.93 (S)	0.91 (S)	1.0	
Fe	0.39	0.81 (S)	0.73	0.67	0.32	0.60	0.26	0.11	0.82 (S)	0.5	0.7	1.0

S = Significance at 5% level

reports that Fe- oxides/hydroxides may play a significant role in fixation of As but the present study does not show this tendency. However, soil texture, crystallinity, pH, conductivity and total alkalinity also play significance role in this regard. The average Ni concentrations were 48.85 and 46.09 mg kg<sup>-1</sup> in Faridpur and Dhamrai, respectively (Tables 1 and 2). Nickel concentration (both FD and DM) exceeded the Dutch standard (35 mg kg<sup>-1</sup>) but did not exceed the world limit (50 mg kg<sup>-1</sup>). The average Ni in Faridpur and Dhamrai were lower than Ni (25.5 mg kg<sup>-1</sup>) of paddy soil in China (Wang et al. 2003). Relatively strong positive significant correlations of Ni with As (r = 0.79) were obtained in Dhamrai, whereas the correlation of Ni and As (r = 0.0003) was insignificant in FD (Tables 3 and 4).

Copper concentrations in Faridpur and Dhamrai were 48.42 and 31.84 mg kg<sup>-1</sup>, respectively which exceeded the

world limit for Cu (30 mg kg<sup>-1</sup>) in soil (Tables 1 and 2). These values are also higher than the average Cu concentration (30 mg kg<sup>-1</sup>) of Samta Village, Bangladesh (Alam et al. 2003). However, the average Cu of Faridpur agricultural soil is nearly similar to the Cu concentration  $(48.3 \text{ mg kg}^{-1})$  of rice field soil of neighbouring West Bengal, India (Norra et al. 2005). The correlation coefficient of Cu with As was insignificant (r = 0.3140 and 0.74) both in Faridpur and Dhamrai. On the other hand, the average Cd in Faridpur  $(0.153 \text{ mg kg}^{-1})$  and Dhamrai  $(0.155 \text{ mg kg}^{-1})$  were nearly same and did not exceed the Dutch standard  $(0.8 \text{ mg kg}^{-1})$  and world limit  $(0.35 \text{ mg kg}^{-1})$  as well (Tables 1 and 2). The average Pb  $(26.82 \text{ mg kg}^{-1})$  and Hg  $(0.081 \text{ mg kg}^{-1})$  of Faridpur soil did not exceed the limit of Dutch standard for good soil and world limit as well (Table 1). Lead of Dhamrai floodplain soil did not exceed the Dutch standard and world limit but

Hg (0.78 mg kg<sup>-1</sup>) was found higher than Dutch regulation (Table 2). The average Pb concentration in both Faridpur and Dhamrai did not exceeded the average Pb (28 mg kg<sup>-1</sup>) of Samta village, Bangladesh (Alam et al. 2003). However, Pb in Faridpur and Dhamrai soil is slightly higher than Pb (22.8 mg kg<sup>-1</sup>) in agricultural soil (paddy field) of West Bengal, India (Norra et al. 2005).

The present study also reported that Cr (85.95 mg kg<sup>-1</sup>) concentration in Faridpur soil was higher than the world limit (70 mg kg<sup>-1</sup>) and 100% samples exceeded that limit (Table 1), whereas Cr level in Dhamrai (76.08 mg kg<sup>-1</sup>) was lower than Dutch regulation but higher than the world standard. Average Co was nearly same both Faridpur (17.40 mg kg<sup>-1</sup>) and Dhamrai (16.41 mg kg<sup>-1</sup>). Copper concentration has been exceeded the world limit in both areas as well (Table 2). The concentrations of soil Cr and Co in DM and FD were also higher than the concentration of Cr and Co in rice field of China (Wang et al. 2003).

So, the most important finding of the present study is that the soil of Faridpur contains nearly four times higher As than the world limit and more than five times higher As than the soil of Dhamrai. This study also predicts that the area which has As contaminated ground water may also contain high level of As in the agricultural soil due to irrigation with ground-water. However, further studies are essential to draw the final conclusion in this regard. More studies are also required to determine the concentration of As and trace metals in agricultural soil of other areas of Bangladesh. It is also important to find-out the mechanisms of arsenic and trace metals uptake, translocation and transformation in rice and vegetable plants.

Acknowledgements This work has been funded by UNESCO/ UNITWIN/WiCop under the environmental quality research activities of University of Cádiz.

#### References

Alam MG, Snow ET, Tanaka A (2003) Arsenic and heavy metal contamination of vegetables grown in Samta village, Bangladesh.

Sci Total Environ 308:83–96. doi:10.1016/S0048-9697(02) 00651-4

- Awofolu OR (2005) Survey of trace metals in vegetation, soil and lower animal along some selected major roads in metropolitan city of Lagos. Environ Moni Assess 105:431–447. doi:10.1007/ s10661-005-4440-0
- Bhattacharya P, Jacks G, Frisbie SH, Smith E, Naidu R, Sarkar B et al (2002) Arsenic in the environment, a global perspective. In: Sarkar B (ed) Heavy metals in the environment. Marcel Dekker Inc, New York, pp 147–215
- Chatterjee A, Das D, Mandal B (1995) Arsenic in groundwater of six districts of West Bengal: the biggest arsenic calamity in the world. Part 1. Arsenic species in drinking water and urine of affected people. Analyst 120:640–650. doi:10.1039/an9952000643
- Chiu VQ, Hering JG (2000) Arsenic adsorption and oxidation at manganite surfaces. Method for simultaneous determination of adsorbed and dissolved arsenic species. Environ Sci Technol 34:2029–2034. doi:10.1021/es990788p
- Coskun M, Steinnes E, Viladimirovna F (2006) Heavy metal pollution of surface soil in the Thrace region, Turkey. Environ Moni Assess 119:545–556. doi:10.1007/s10661-005-9042-3
- Dong WQY, Cui Y, Liu X (2001) Instances of soil and crop heavy metal contamination in China. Soil Sedi Contam 10:497–510. doi:10.1080/20015891109392
- El Rayis OA (1985) Re-assessment of the titration method for the determination of organic carbon in recent sediments. Rapp Com Int Mer Medit 29:45–47
- Francesconi KA, Edmonds JS, Morita M (1994) Determination of arsenic and arsenic species in marine environmental samples. In: Nriagu JO (ed) Arsenic in the environment part I: cycling and characterization. Wiley and Sons, Canada, pp 189–219
- Frisbie SH, Ortega R, Maynard DM (2002) The concentrations of arsenic and other toxic elements in Bangladesh's drinking water. Environ Health Perspect 110:1147–1153
- Mattusch J, Wennrich R, Schmidt AC (2000) Determination of arsenic species in water, soils and plants. Fr Esenius J Anal Chem 366:200–203. doi:10.1007/s002160050039
- Norra S, Berner ZA, Agarwala P (2005) Impact of irrigation with As rich groundwater on soil and crops: a geochemical case study in West Bengal Delta Plain, India. Appl Geochem 20:1890–1906. doi:10.1016/j.apgeochem.2005.04.019
- Wang XC, Yan WD, An Z (2003) Status of trace elements in paddy soil and sediment in Taihu lake region. Chemosphere 50:707–10. doi:10.1016/S0045-6535(02)00209-6
- Zhang W, Yong CY, Tub C (2002) Arsenic speciation and distribution in an arsenic hyper accumulating plant. Sci Total Environ 300:167–177. doi:10.1016/S0048-9697(02)00165-1