

Distribution of Heavy Metals in Rice Plant Cultivated in Industrial Effluent Receiving Soil

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Abstract

Heavy metals can have a serious impact if released into the environment even in trace quantities (Lin *et al.*, 2005). These can enter into the food chain from aquatic and agricultural ecosystems and threaten human health indirectly (Lin *et al.*, 2004). Dhalai Beel produces rice with DEPZ (Dhaka Export Processing Zone) effluent fed water. A field experiment was carried out to investigate the uptake of heavy metals by paddy crop using Thermal Neutron Activation Analysis (TNAA). Rice plants were divided into root, stem, leaf, husk and unpolished rice grain. The distribution of heavy metals in the different parts was investigated. The order of average contents of metals in rice was Zn > Rb > Se > Sc > Cr > Cs. The concentrations were Se 1.92–7.78 ppm, Cr BDL (Below Detection Limit) - 0.74 ppm, Sc 0.01–0.04 ppm, Rb 2.25–16.1 ppm, Fe–BDL, Zn 62.7–102.5 ppm and Co–BDL. Highest TF (Transfer Factor) value is obtained for Fe which is 0.24 and the lowest TF value is for Sc which is 0.02. The concentrations are within acceptable limits.

Keywords: heavy metal; industrial pollution; industrial effluent; neutron activation analysis; rice

1. Introduction

The discharge of effluents from industry into agricultural compartments has become a growing environmental problem. Long term land application of effluent water (EW) may cause excessive accumulation of heavy metals such as Cr, Ni, Cd in soil and toxicity in plants (Hamid Reza Rahmani *et al.*, 2007). Heavy metals like Fe, Cu, Zn, Ni and other trace elements are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders (Hamid Reza Rahmani *et al.*, 2007). Rice (*Oryza Sativa*) is a plant of the grass family, which provides the bulk of the human diet throughout Asia. It is the staple food of Bangladesh and the world's third largest crop, which has significant uses of human nutrition (Songül Karaaslan AKSU *et al.*, 2004). Heavy metals can enter into this food chain from aquatic and agricultural ecosystems and threaten human health (Zozoli *et al.*, 2006). People, especially those who take rice as main food for daily energy are exposed to significant amount of heavy metals via rice (Watanabe *et al.*, 1996).

DEPZ industrial effluents enter the adjacent water body (Dhalai Beel) through an inland waterway. During the rainy season, the EW directly flows over the agricultural field. Local farmers frequently use water from this Beel for irrigation purposes. A study (Rezaur *et al.*, 2008) shows that the deposition of some heavy metals are elevated in water, sediment and agricultural

soil of this area. The aim of the present study is to assess the uptake of heavy metals by paddy crop and their transformation from soil to paddy using neutron activation analysis technique.

2. Experimental

2.1. Study area

Dhalai Beel (a natural low land cum lake), Dhamsona, Savar, Dhaka is located at 23°57'16" N and 90°15'48" E to 23°56'22" N and 90°14'38" E. DEPZ is situated at the east bank of this Beel contains 96 enterprises (72 garments and related, 3 footwear, 4 plastic etc). Effluents from DEPZ are discharged almost untreated into the adjacent Dhalai Beel which is the only natural resource of irrigation water to the nearby agricultural land. Besides this, during the rainy season, the land is overflowed and the EW is directly discharged into the land. The paddy crops produced in this land were chosen for the present study.

2.2. Samples

Paddy crops and surface soil were collected in polyethylene bags on the 2nd week of May 2008 from three representative locations (total number of samples, n=9, from each location three samples were taken, then a representative one was made by mixing up these three) of the study area. Paddy crop samples were thoroughly

washed to remove all adhered soil particles. Roots, stems, leaves, husk and rice were separated by cutting using teflon scissor then washed using deionized water. Roots, stems, leaf and husk were cut into small pieces. The dried soil and rice samples were ground without any chemical treatment using agate mortar to make powder and ensure homogeneity (Agate mortar is made of natural agate with highly polished surfaces, excellent for preparing laboratory samples and high purity powders. Because of the ability to control the grinding, and also to virtually eliminate contamination from the mortar and pestle set itself, agate is the preferred material and is used in laboratories). All the items were again dried in an oven at 70°C until they got constant weight. All the samples were weighed using a microbalance. Samples (~100 mg powder for each sample) and standards (about 50 mg of each of IAEA Certified Reference Materials Soil-7, SL-1 and NIST Standard Reference Material Coal fly ash 1633b) were doubly packed separately using clean polyethylene and heat sealed. The samples and standards were stacked into an irradiation vial. The IRMM Al-0.1%Au flux monitors were inserted to determine neutron flux gradients at the bottom, middle and top of the stack of samples.

2.3. Reactor Irradiation and gamma spectrometry

The samples and reference standards were irradiated simultaneously at the Dry Central Thimble (DCT) facility of 3 MW TRIGA MARK-II research reactor at the Atomic Energy Research Establishment, Savar, Dhaka, Bangladesh for 40 minutes at a thermal neutron flux of 1.52×10^{13} n/cm²/s at a power level of 500kW. The High Purity Germanium (HPGe; Canberra 25% relative efficiency and 1.85 keV resolution of ⁶⁰Co) detector coupled with a personal computer based multiport-II spectrometry system and genie 2000 acquisition software were used for measurement of the γ ray activities of the irradiated samples and standards. The dead time was kept below 10% by adjusting the source to detector distance (SDD). The counting was performed after 3 weeks from the end of irradiation. The peak analysis was performed manually.

2.4. Calculation of element concentration and transfer factor

The comparative method is used to determine the concentrations of heavy metals in the investigated samples. Following is the equation of this method:

$$W_{sample} = \frac{A_{sample} (e^{\lambda T})_{sample}}{A_{std} (e^{\lambda T})_{std}} \times W_{std}$$

Transfer Factor (TF) was calculated for each metal according to the formula $TF = Ps(\mu\text{g/g}) / St(\mu\text{g/g})$, where, Ps is the plant metal content originating from the soil and St is the total metal content in the soil (Lokeshwari et al., 2006).

2.5. Accuracy of the analysis and detection limit

Quality control test was performed by measuring concentration levels in standard / certified reference materials. Deviation was less than or around 10% of the certified values. 3σ criteria are used for calculating the detection limit. The calculated detection limits for this experiment are 1.25 $\mu\text{g/g}$ for Cr, 0.08 $\mu\text{g/g}$ for Co, 0.89 $\mu\text{g/g}$ for Cs, 0.01 $\mu\text{g/g}$ for Sc, 80.3 $\mu\text{g/g}$ for Fe, 6.85 $\mu\text{g/g}$ for Zn, 2.83 $\mu\text{g/g}$ for Rb and 1.11 $\mu\text{g/g}$ for Se.

3. Results and Discussion

The paddy crop samples were analyzed for concentrations of heavy metals present in rice, husk, leaf, stem, root and surface soil. Table 1 summarizes the concentrations of eight heavy metals identified in this experiment namely Cr, Co, Cs, Sc, Fe, Zn, Rb and Se. According to Kabata-Pendias and Pendias (1992) the recommended safe limit of Cr uptake concentration for paddy was 30 mgCr/kg, whereas Kitagishi and Yamane (1981) reported that tolerable limit of upper part of paddy crops was 35 mgCr/kg in Japan (Battacharia et al., 2005). In the present study, the Cr concentrations at the upper part of the paddy crops are 0.74–3.91 mg/kg. The concentration of some essential trace heavy elements in Nigerian rice were found as follows: 0.18–0.98 ppm Cr, 27–307 ppm Fe, 0.13–0.24 ppm Co, 12.4–17.8 ppm Zn (JIMBA et al., 1990), whereas in the present study the concentrations are 0.74–3.91 ppm Cr, below Detection Limit for Fe, and Co, 62.7–102.5 ppm Zn. The concentration of heavy metals in some rice samples from Vietnam were as follows: Se 0.04–0.07 ppm, Cr 2.13–8.65 ppm, Sc 0.02–0.06 ppm, Rb 0.84–2.71 ppm, Fe 26.3–96.1 ppm, Zn 10.6–27.4 ppm and Co 0.02–0.15 ppm (Van Tran et al., 1988). In the present study these were: Se 1.92–7.78 ppm, Cr BDL–0.74 ppm, Sc 0.01–0.04 ppm, Rb 2.25–16.1 ppm, Fe–BDL, Zn 62.7–102.5ppm and Co–BDL. From Fig. 1, it is seen that, the descending order of the average contents of metals in rice was Zn > Rb > Se > Sc > Cr > Cs, in husk Fe > Zn > Rb > Se > Cr > Cs > Co > Sc, in leaf Fe > Zn > Se > Rb > Cr > Co > Cs > Sc, in stem Zn > Fe > Rb > Se > Cr > Co > Cs > Sc, in root Fe > Zn > Cr > Se > Rb > Co > Sc > Cs and in the surface soil it was Fe > Zn > Cr > Rb > Se > Co > Sc > Cs. The major metal constitutes of the samples is iron except at the rice part

Table1. Concentrations of heavy elements

Location No.	Co (µg/g)	Cr (µg/g)	Cs (µg/g)	Fe (µg/g)	Rb (µg/g)	Sc (µg/g)	Se (µg/g)	Zn (µg/g)
<i>Concentrations of elements in unpolished rice grain</i>								
1	BDL	0.74 ± 0.09	0.11 ± 0.02	BDL	6.44 ± 0.78	0.01 ± 0.00	2.55 ± 0.14	98.3 ± 4.93
2	BDL	BDL	BDL	BDL	2.25 ± 0.34	0.01 ± 0.00	7.78 ± 0.35	62.7 ± 3.43
3	BDL	BDL	BDL	BDL	16.1 ± 1.83	0.04 ± 0.00	1.92 ± 0.12	102.5 ± 5.27
<i>Concentrations of elements in husk</i>								
1	0.11 ± 0.01	BDL	0.15 ± 0.02	114.1 ± 8.31	7.42 ± 0.85	0.02 ± 0.00	4.27 ± 0.19	56.3 ± 3.01
2	BDL	2.59 ± 0.26	0.19 ± 0.03	178.1 ± 11.6	9.33 ± 1.09	0.03 ± 0.00	7.75 ± 0.34	73.6 ± 3.83
3	BDL	2.19 ± 0.23	0.17 ± 0.03	161.5 ± 11.9	20.6 ± 2.27	0.028 ± 0.00	2.36 ± 0.13	92.4 ± 4.7
<i>Concentrations of elements in leaf</i>								
1	0.25 ± 0.03	2.77 ± 0.28	0.19 ± 0.03	311.7 ± 17.1	7.35 ± 0.92	0.09 ± 0.00	5.42 ± 0.25	73.5 ± 3.93
2	0.59 ± 0.06	3.51 ± 0.35	0.36 ± 0.05	746.1 ± 30.0	BDL	0.21 ± 0.01	11.8 ± 0.51	150.3 ± 7.23
3	0.56 ± 0.05	2.76 ± 0.27	0.44 ± 0.06	555.7 ± 24.3	22.9 ± 2.48	0.19 ± 0.01	35.8 ± 1.48	104.7 ± 5.33
<i>Concentrations of elements in stem</i>								
1	0.26 ± 0.03	3.42 ± 0.33	0.25 ± 0.04	BDL	13.3 ± 1.51	0.03 ± 0.00	4.09 ± 0.19	89.3 ± 4.50
2	0.24 ± 0.03	3.91 ± 0.39	BDL	255.1 ± 16.3	26.9 ± 2.9	0.05 ± 0.00	14.4 ± 0.6	170.9 ± 8.18
3	0.20 ± 0.02	2.95 ± 0.29	0.32 ± 0.04	115.1 ± 8.92	45.4 ± 4.74	0.02 ± 0.00	2.37 ± 0.12	292.9 ± 13.1
<i>Concentrations of elements in paddy root</i>								
1	2.01 ± 0.17	299.9 ± 2.72	0.80 ± 0.11	6758.9 ± 173.0	16.9 ± 1.93	0.86 ± 0.06	7.80 ± 0.36	391.9 ± 17.6
2	4.3 ± 0.35	40.9 ± 3.7	0.59 ± 0.08	31840.6 ± 738.2	14.7 ± 1.6	1.47 ± 0.09	59.1 ± 2.4	846.8 ± 36.5
3	2.57 ± 0.22	11.1 ± 1.07	0.67 ± 0.09	10831.9 ± 280.7	BDL	0.52 ± 0.04	8.93 ± 0.43	217.6 ± 10.9
<i>Concentrations of elements in surf ± 15.4ace soil</i>								
1	11.74 ± 0.94	171.5	6.09 ± 0.78	33034 ± 764	99.6 ± 10.2	9.18 ± 0.62	3.27 ± 0.16	864.2 ± 37.1
2	12.3 ± 0.99	142.6 ± 12.8	5.58 ± 0.72	28117.1 ± 655.1	58.0 ± 6.07	8.39 ± 0.56	23.5 ± 0.98	1356.9 ± 57.9
3	10.0 ± 0.80	143.5 ± 12.9	4.68 ± 0.60	29644.9 ± 686.5	82.4 ± 8.53	8.04 ± 0.54	30.4 ± 1.25	680.7 ± 29.3

BDL – Below Detection Limit

+/- – means the uncertainties in data. The uncertainties due to counting statistics were determined. Some typical values established by the NAA group of INST, Savar, Dhaka was used to calculate the uncertainties from other sources.

of paddy crop. The rice samples do not contain Fe or Co in detectable amounts.

All the studied heavy metals except Rb are present in high concentrations in the roots of the paddy crops compared to other parts of the plant. The descending order of Fe concentration in paddy crop was root > leaf > husk > stem, for Zn the concentration order is root > stem > leaf > rice > husk, for Co the concentration order is root > leaf > stem > husk, for Sc the concentration order is root > leaf > stem > husk > rice, for Cs the concentration order is root > leaf > stem > husk > rice, for Rb the concentration order is stem > husk > root > leaf > rice, for Cr the concentration order is root > stem > leaf > husk > rice and for Se the concentration order is root > stem > leaf > rice > husk.

The uptake mechanism of heavy metals includes both adsorption (from soil) and absorption (from water) and takes place through roots (Lokeshwari *et al.*, 2006). Fig 2(a) shows an analogy between amount of metal uptake by paddy crop and average concentration of metals in the soil (Rezaur *et al.*, 2008) of the study area. It is seen that Fe is the prime metal of soil as well as paddy crop. The order of metal in soil is Fe > Zn > Cr > Rb > Se > Sc > Co > Cs, the order of metal in paddy crop is different: Fe > Zn > Rb > Se > Cr > Co > Cs > Sc. Fig 2(b) shows the transfer factors (TF) of different heavy metals from soil to paddy crop, which is one of the key components of human and animal exposure to metals through the food chain (Lokeshwari *et al.*, 2006). Highest TF value is obtained for Fe which is 0.24 and the lowest TF value is for Sc which is 0.02.

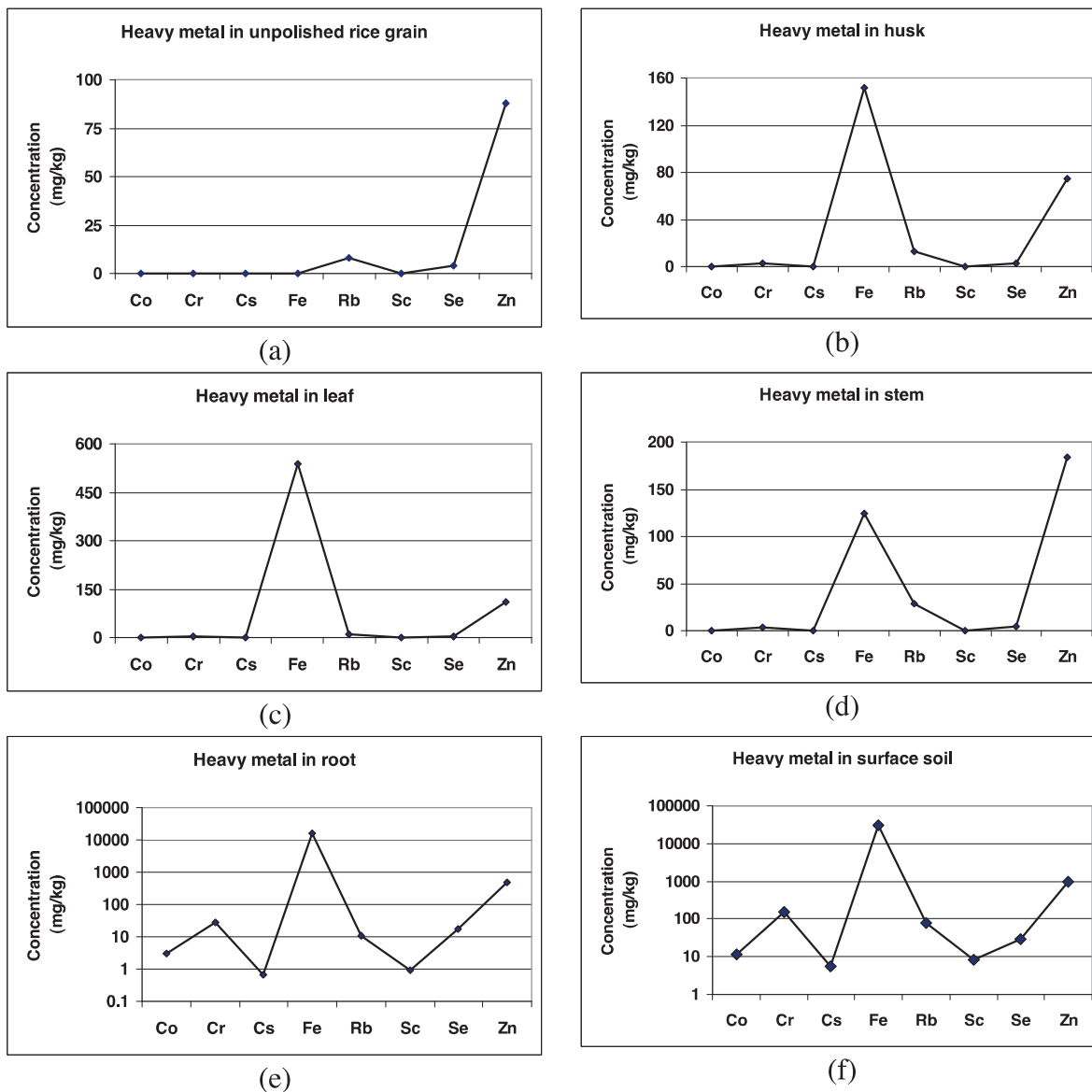


Figure 1. Distribution of heavy metals in (a) rice, (b) husk, (c) leaf, (d) stem, (e) root and (f) surface soil

4. Conclusion

The concentration of metals in paddy crop will provide baseline data and there is a need for intensive research in this field. Soil, plant and irrigation water quality monitoring, together with the prevention of metals entering the plant, is a prerequisite in order to prevent potential health hazards of irrigation with EW fed water.

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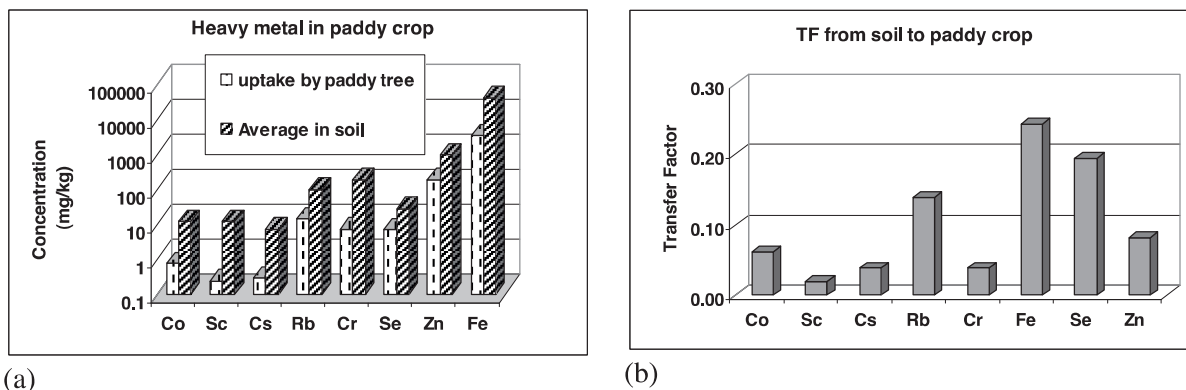


Figure 2. Total concentrations of heavy metals (a) and Transfer Factor (TF) of heavy metal (b)

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