BCSIR

Available online at www.banglajol.info

Bangladesh J. Sci. Ind. Res. **44(4)**, 479-484, 2009

BANGLADESH JOURNAL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

E-mail: bjsir07@gmail.com

Amelioration of Heavy Metals from Contaminated Soils of Hazaribagh and Tejgaon Areas from Bangladesh Using Red Mud

A. S. Chamon*, M. N. Mondol and S. M. Ullah

Department of Soil, Water and Environment, University of Dhaka, Dhaka, Bangladesh.

Abstract

Pot experiments with soil from two heavy metals contaminated sites were conducted. The objective of the experiment was to test red mud as an inorganic soil amendment to reduce heavy metal uptake and to alleviate toxicity in tomato (variety- Ratan) and wheat (variety- Agrani) crops. Iron (Fe) oxides contained in red mud, a byproduct of the aluminum industry, reduced soil to plant transfer of zinc (Zn), nickel (Ni), cadmium (Cd), and chromium (Cr). In Hazaribagh soil, tomato fruit yield (dry weight) increased by 72%. Shoot length and biomass production were positively influenced by red mud containing high amounts of Fe_2O_3. Heavy metal uptake into tomato plants was significantly ameliorated in both soil. On Tejgaon soil the effect of red mud on wheat grain yield production was not significantly different but the ameliorative effect of red mud application was clearly observed in the wheat grain samples for Tejgaon soil.

Key words: Red Mud, Wheat, Tomato, Remediation, Heavy metals

Introduction

Bangladesh has at present about 30,000 large and small industrial units. They are discharging their wastes and effluents into the natural ecosystems in most cases without any treatment thus causing environmental pollution especially with heavy metals and organic toxics. These hazardous wastes and effluents are generally discharged in low-lying areas, along road side or in the vicinity of the industrial installations. Trace metal contaminated sites are of growing concern and there is a strong need for remediation of these sites. Remediation aims at protecting humans, animals and the environment from exposure to hazards and interrupting the pathways of pollutants (Tadesse *et al.,* 1994).

Considerable research has been directed towards less expensive remediation *in-situ* technologies that remove metal contaminants from soils. Soil washing methods are based on using extractants to cationic heavy metals from contaminated soil (Ganguly *et al.*, 1998). Unfortunately, field application of soil washing remediation methods is limited to sandy soils with clay and humic content values <15% (Rulkens *et al.*, 1998).

Treatment of soils contaminated by trace metals is classically based on the application of lime and phosphates and the addition of organic matter (Kabata and Pendias, 1992). The addition of lime, however, does not always deliver the aimed effects on the solubility of trace metals (Benninger and Taylor, 1993). Immobilization of Pb and Cd in soil by either synthetic or natural zeolites reduced the Pb, Cd, Cu, and Zn contents of plant tissues (Chlopecka and Adriano, 1996). The hydrous oxides of Al, Fe and Mn are also known to reduce metal mobility in soils through specific sorption processes (Mench *et al.*, 1994).

In soil, heavy metal can be sorbed and immobilized by a large variety of substances, such as the different iron oxides and clay minerals (Tiller *et al.*, 1984). Common inorganic soil components with significant binding ability for the trace metals are iron oxides. Studies have shown that Fe oxides have a binding performance for specific metals (Yong *et al.*, 1992), which becomes important when high levels of several metals are applied to soils. With high concentrations of metals added, the capacity of specific sorption sites (strongly bound metals) could be exceeded and the metal cations would compete with the bulk cations for adsorption sites. Rule and Martin (1999) reported that biosolids treated with Fe-Rich^{TM} (Fe-Rich Trace Metals) sorbed significantly more of all metals with the exception of Pb compared with the untreated biosolids. The proportions of the metals sorbed to the Fe-Rich^{TM} followed the order Pb > Cu > Cd > Zn. Significant reduction in Pb availability was also seen in

* Corresponding author: E-mail: nadiruzzaman_mondol@hotmail.com

some of the compost amended and iron rich amended soil treatments (Brown *et al.*, 1999). Available data on the impact of industrial pollution in Bangladesh especially on soils and crops and the mobility in the human food chain are quite limited. No systematic research work has yet been done on the amelioration of heavy metal uptake into crops from polluted soils. During the course of this research work, oxides of iron (as red mud) were tested as additives in two contaminated soil of Bangladesh, in order to remediate heavy metals from those soil.

Materials and Methods

Pot experiments were conducted with heavy metals contaminated soil (0-15 cm depth) from Tejgaon industrial and Hazaribagh tannery areas. The characteristics of Tejgaon and Hazaribagh soil is given in Table I.

Table I. The characteristics of Tejgaon and Hazaribagh soil

Parameter	Tejgaon soil	Hazaribagh soil
pH	5.67	7.08
%C	8.24	1.02
%N	0.74	0.16
P mg/kg	415	229
K mg/kg	243	213
Mn mg/kg	300	300
Pb mg/kg	136	24.6
Zn mg/kg	685	133
Cr mg/kg	173	11000
Cd mg/kg	2.6	0.08
Cu mg/kg	99.7	115
Ni mg/kg	40.1	21
Hg µg/kg	581	37
Texture	Clay loam	Clay loam

Plastic pots were filled with 8 kg soil. Basal dose of fertilizer was added at low rate (175 kg N/ha, 120 kg P_2O_5/ha and 200 kg K_2O/ha) for tomato (variety-Ratan) (1 plant/pot) and (120 kg N/ha, 60 kg P_2O_5/ha and 100 kg K_2O/ha) for wheat (variety-Agrani) (3 plants/pot) (BARC, 1997) and red mud (collected from the aluminium industry in Mosonmagyarovar, Hungary and analyzed at Seibersdorf, Austria) at a rate of 80 mg/pot was added as remedial measures having 3 replications. Wheat was grown only on Tejgaon soil. There were three control pots (without red mud) for each soil and crop. The composition of red mud used in this experiment is given in Table II. The pots were arranged in a completely randomized design. The plants were irrigated with distilled water whenever required. The crops were harvested at maturity.

Soil samples were digested with $HCl:HNO_3$ (3:1). Plant and tomato fruit samples were digested with a $HNO_3:HClO_4$(5:1) mixture in closed systems (Blum *et al.*, 1996). All elements were determined in the extracts by Atomic Absorption Spectroscopy (AAS), (Model AA-640 IF, Shimadzu Corporation, Japan). The results of the experiment were statistically analyzed and the mean comparisons were made by DMRT (Duncan's Multiple Range Test).

Table II. Chemical composition of red mud from the aluminum industry in Mosonmagyarovar (Hungary)

Red mud	(%)
Al_2O_3	14.7-17.3
Na_2O Total	8.5-9.6
Na_2O Soluble	0.6-0.9
Fe_2O_3	39.0-43.0
SiO_2	12.5-14.0
TiO_2	4.5-5.2
CaO	4.30-5.8

Results and Discussion

Growth and yield parameters

In case of Hazaribagh soil, red mud ameliorated tomato plant growth and yield parameters significantly (Table III). Tomato fruit yield was found to increase by 72%. Shoot length and biomass production were positively influenced by red mud containing high amounts of Fe_2O_3 .

For Tejgaon soil, the tomato fruit fresh weight and shoot length increased by 76% and 23%, respectively. But tomato fruit yield (FW) and shoot length in Hazaribagh soil increased by 75 and 35% respectively (Table III) might be due to the ameliorative effect of red-mud. On Tejgaon soil wheat grain yield production was not significantly different (Table IV).

Table III. Influence of red mud application on tomato yield (g/pot) parameters

Parameters	Hazaribagh soil	Hazaribagh soil+Red mud	Tejgaon soil	Tejgaon soil+red mud
Shoot length (cm)	37 a	50 b	43a	53b
Root length (cm)	29 a	32 a	31 a	33 a
FW-tomato fruit	238a	417 b	237a	419b
FW-Shoot	74a	151 b	76 a	73a
FW-root	14 a	16 a	15 a	17 a
DW-tomato fruit	39 a	67 b	41 a	63 b
DW-Shoot	16 a	35 b	15 a	14 a
DW-root	4 a	5 a	5a	6 a

Mean values within a row with the same letter (s) is not significantly different (P=0.05).

Table IV. Effect of red mud application on wheat yield parameters grown in Tejgaon soil

Parameters	Tejgaon soil	Tejgaon soil+Red mud
Shoot length (cm)	68 a	71 a
FW-Shoot	42 a	46 a
FW-grain	25 a	26 a
DW-Shoot	36 a	41 a
DW-grain	21 a	22 a
1000 grain wt	26 a	30 a

Mineral nutrition and heavy metal

The chemical analysis of tomato shoot and fruit samples clearly reflected the heavy metal toxicity of the tomato plant (Tables V and VII), e.g. heavy metal chlorosis was clearly demonstrated by the very low Fe contents in tomato shoots in unamended soils.

In Hazaribagh soil, red mud amended pot exhibited significantly lower content of N, Mg and slightly lower S content in shoots (Table V) and in fruits significantly lower N, S and Ca content (Tables VII). On the other hand, K and Ca concentration increased in shoot and also K in fruits increased.

In Tejgaon soil the N, P, S and K contents in shoots and K in tomato fruits were increased by red mud amendments but uptake of other micro-nutrient was decreased in shoot and fruits. Similar results were also found in case of wheat (Table VI).

Heavy metal uptake was significantly ameliorated in both soil. Manganese contents in tomato shoots in Hazaribagh

Table V. Influence of red mud application on mineral nutrition of tomato shoot

Rice shoot	Hazaribagh soil	Hazaribagh soil + red mud	Tejgaon soil	Tejgaon soil + red mud
N (%)	2.44 b	2.16 a	2.18 a	2.49 b
P (%)	0.23 b	0.33 c	0.18 a	0.24 b
S (%)	1.80 b	1.59 a	1.62 a	2.33 c
K (%)	0.80 a	1.92 b	1.22 a	2.14 b
Mg (%)	1.19 c	0.82 b	0.92 b	0.58 a
Ca mg/kg	4124 a	4781 ab	5110 b	4296 ab
Fe mg/kg	1.2 a	93.0 b	1.1 a	111 b
Mn mg/kg	151 b	157 b	151 b	82 a
Cu mg/kg	30 b	10 a	18 a	15 a
Zn mg/kg	38.67 a	26.49 a	203.19 c	102.33 b
Ni mg/kg	0.87 b	0.30 a	0.89 a	0.76 a
Pb mg/kg	0.87 b	0.54 b	1.22 c	0.46 a
Cd mg/kg	0.03 a	0.01 a	0.34 b	0.03 a
Cr mg/kg	26.70 c	17.53 b	4.51 a	2.11 a

Mean values within a row with the same latter (s) is not significantly different (P=0.05).

soil were not significantly different though its concentration was above the toxic limit (40-100 mg Mn/kg). In Tejgaon soil, red mud diminished Mn uptake by 46 and 59.7 % in tomato and wheat shoots, respectively. Cu, Zn, Ni and Cd concentrations in wheat shoot was significantly decreased by red mud application (Table IV). The similar ameliorative effect of red mud application was also observed in wheat grain (Table VIII).

Red mud application reduced Cu, Zn, Ni, Pb, Cd and Cr contents in shoot of tomato by, 66.7, 31.5, 65.5, 37.9, 96.7 and 34.3%, respectively, compared with the untreated pots with Hazaribagh soil (Table V). In Tejgaon soil, Cu, Ni and Cr contents in tomato shoot were not significantly different between red mud amended and unamended soils, while 49.6, 62.3 and 91.2% less Zn, Pb and Cd concentrations were observed due to red mud application, respectively (TableV). In Tejgaon soil, the Mn, Cu, Zn, Ni and Cd concentration of wheat shoot decreased significantly for red mud application (TableVI).

The ameliorative effect of red mud application was also clearly observed in the tomato fruit samples for both soils. Zinc, nickel, lead, cadmium and chromium uptake by tomato fruit diminished by 25.03, 21.68, 66.6, 85.7 and 82.52 %, respectively, due to red mud application in Hazaribagh soil (Table VII).

In Tejgaon soil, the fruits of tomato exhibited 76.5, 11.8, 80.14, 92.6, 27.2 and 83.5% lower Cu, Zn, Ni, Pb, Cd and Cr concentrations on red mud treated pots compared to the untreated pots (Table VII).

Table VI. Influence of red mud application on mineral nutrition of wheat shoot

Wheat shoot	Tejgaon soil	Tejgaon soil + red mud
N (%)	1.11 a	1.19 a
S (%)	0.29 a	0.34 a
P (%)	0.09 a	0.10 a
K (%)	2.06 a	2.08 a
Mg (%)	0.74 a	0.78 a
Ca mg/kg	12213 a	14101 a
Mn mg/kg	395 b	159 a
Cu mg/kg	5.51 b	4.36 a
Zn mg/kg	1711.43 b	822.33 a
Ni mg/kg	12.12 b	4.48 a
Pb mg/kg	1.68 a	1.21 a
Cd mg/kg	0.63 b	0.35 a
Cr mg/kg	1.77 a	1.47 a

Mean values within a row with the same latter (s) is not significantly different (P=0.05).

The ameliorative effect of red mud application was also clearly observed in the wheat grain samples for Tejgaon soil. Zinc, nickel, lead, cadmium and chromium uptake by wheat grain diminished by 15.6, 37.2, 8.1, 25.0 and 75.1%, respectively, due to red mud application in Tejgaon soil (Table VIII).

Table VII. Influence of red mud application on mineral nutrition of tomato fruit

Rice grain	Hazaribagh soil	Hazaribagh soil+red mud	Tejgaon soil	Tejgaon soil+red mud
N (%)	1.88 a	1.49 a	1.50 a	1.35 a
P (%)	0.21 a	0.20 a	0.36 b	0.14 a
S (%)	0.89 a	0.32 b	0.62 d	0.50 c
K (%)	0.32 ab	0.37 b	0.28 a	0.36 b
Mg (%)	0.78 a	0.68 a	0.88 a	0.65 a
Ca mg/kg	500.1 b	387.78 a	531.78 b	464.9 ab
Fe mg/kg	186 a	286 a	196 a	216 a
Mn mg/kg	32 a	25 a	91 b	26 a
Cu mg/kg	20 ab	24 ab	34 b	8 a
Zn mg/kg	28.60 b	21.44 a	48 d	42.33 c
Ni mg/kg	0.83 b	0.65 ab	1.41 c	0.28 a
Pb mg/kg	0.27 a	0.09 a	4.35 b	0.32 a
Cd mg/kg	0.07 b	0.01 a	0.11 d	0.08 c
Cr mg/kg	5.33 c	0.93 ab	1.76 b	0.29a

Mean values within a row with the same latter (s) is not significantly different (P=0.05).

Table VIII. Influence of red mud application on mineral nutrition of wheat grain

Wheat grain	Tejgaon soil	Tejgaon soil + Red mud
N (%)	2.58 a	2.72 a
P (%)	0.49 a	0.52 a
S (%)	0.22 a	0.26 b
K (%)	0.43 a	0.54 b
Mg (%)	0.21 a	0.41 b
Ca mg/kg	1221.05 a	1433.66 a
Mn mg/kg	51.33 a	50.76 a
Cu mg/kg	7.49 b	5.71 a
Zn mg/kg	256.09 a	216.09 a
Ni mg/kg	10.44 b	6.55 a
Pb mg/kg	0.61 a	0.56 a
Cd mg/kg	0.08 a	0.06 a
Cr mg/kg	2.77 b	0.69 a

Mean values within a row with the same latter (s) is not significantly different (P=0.05).

Discussion

In case of the Hazaribagh soil, red mud ameliorated plant growth and yield parameters significantly. Wheat grain yield, 1000 grain weight, shoot length and biomass productions were positively influenced as well. Similar trends in increasing yield of rice crops due to red mud application were reported by Chamon *et al.*, (2005). The increase in yield production was probably because of the liming effect of the remnant alkali in the red mud. On the contrary, in Tejgaon soil the effect of red mud on wheat grain yield (FW) production was not significant. But there was an increasing trend of wheat yield production was observed in red mud treated pots. On Tejgaon soil P, K and S contents in tomato fruit were significantly lower on red mud treated pots compared to the control. Also on Hazaribagh soil, significantly lower N and S contents in tomato shoot were observed on red mud treated pots. Because of the sorption mechanism of red mud after application to the respective soils may have caused reductions in some of the macronutrient elements by tomato fruits in our experiments.

In Hazaribagh and Tejgaon soils Mn contents were less in the fruits of tomato and grains of wheat, due to red mud application. Red mud application reduced Cu, Zn, Ni, Pb, Cd and Cr content in shoots of tomato, compared with the untreated pots with Hazaribagh soil. Amorphous Fe oxide is capable of specifically retaining Zn and Cd. This was reported by Friesl *et al.*, (2000).

In Tejgaon soil, Cu, Ni and Cr uptake by tomato shoots were not significantly different between the treatments, while the contents of Zn, Pb and Cd were less due to red mud application. A similar ameliorative effect of red mud application was also clearly observed in the grain samples of rice for both soils (Chamon *et al.*, 2005). Red mud application reduced Cd uptake into *Festuca rubra* (second cut) by 73%, Zn (73%), and Ni (87%) on Weyersdorf (WEY, sandy, acidic) and Cd (42%), Zn (63%) on Untertiefenbach (clayey, neutral) soils, as reported by Friesl *et al.*, (2000). According to Phillip (1998), metal affinity sequence for the red mud followed the general order: Pb^{2+} Cu^{2+}>Zn^{2+}. In our case more or less similar trend was observed (Ni>Cu>Pb>Zn).

Iron and Mn oxides are known to absorb or complex metallic ions. Several studies have been undertaken to determine the influence of these oxides on the extractable concentrations of metals in soils (Brown *et al.*, 1999).

Nuruzzaman *et al.*, (1995) reported values for Cr (1340) in the same site on Hazaribagh tannery area, which was much above the permissible limit (100 mg/kg) (Kloke, 1980), and quite similar to our investigation. The addition of red mud may be suggested as a way to control heavy metal mobility, especially Cr in soil.

Conclusion

The experiment showed that in principle, the taken measures i.e application of red mud and selection of plant species ameliorated plant growth and/or heavy metal toxicity. Applied in small amounts, the ferric oxides, present in red mud led to an increase in biomass production and improved yield for tomato plants and caused significant reductions of soil to plant transfer of Zn, Cu, Ni, Cd and Cr. Heavy metal uptake into tomato plants was significantly ameliorated in both soil. On Tejgaon soil the effect of red mud on wheat grain yield production was not significantly different but the ameliorative effect of red mud application was clearly observed in the wheat grain samples for Tejgaon soil. In summary, it may be stated that selection of plant species and soil amendments caused partly significant reductions of heavy metal accumulation from contaminated soils. Nevertheless, for the optimization of the reduction effects, it is necessary to select and combine the different methods according to site specific and variety/plant specific characteristics.

Acknowledgement

The first author would like to thank the Austrian Research Centre Seibersdorf, Vienna for supporting her successful research in Austria and for providing her with library, laboratory and all other research facilities as and when required.

References

Benninger T. M. and Taylor D. H. (1993). Municipal sludge metal contamination of old-field ecosystems: do liming and tilling affect remediation? *Environ. Toxicol. Chem*. **12:** 1931-1943.

BARC (B. Agri. Res. Co.). (1997). *Fertilizer Recommendation Guide*, Krishi Khamar Sarak, Dhaka, Bangladesh. **41:** 25-48.

Blum W. E. H., Spiegel H. and Wenzel W. W. (1996). BODENZUSTANDSINVENTUR-Konzeption, Durchfuhrung und Bewertung. Bundesministerium fur Land- und Forstwirtschaft.Inst. für Bodenforschung, Univ. Für Bodenkultur, Vienna, 2nd edition: **102**.

Brown S. L., Chaney R. and Berti B. (1999). Field test of amendments to reduce the *in situ* availability of soil lead. In. Proc. 5th Intern. Conf. on the Biogeochemistry of Trace Elements; Wenzel, W.W., Adriano, D.C., Alloway, B., Doner, H.E., Keller, C., Lepp, N.W., Mench, M., Naidu, R., Pierzynski, G.M. Eds.; Vienna, Austria, **1:** 506-507.

Chamon A. S., Gerzabek M. H., Mondol M. N., Ullah S. M., Rahman M. and Blum W. E. H. (2005). Influence of soil amendments on heavy metal accumulation in crops on polluted soils of Bangladesh. *Comm. Soil Sci. and Plant Analysis.* **36:** 907-924.

Chlopecka A. and Adriano D. C. (1996). Mimicked in situ stabilization of metals in a cropped soil: bioavailability and chemical form of zinc. *Environ. Sci. Technol.* **30:** 3294-3303.

Friesl W., Lombim E., Horak and Wenzel W. W. (2000). Use of inorganic soil amendments to reduce Trace elements mobility. In. International Conference on Holistic concept of training for the promotion of sustainable development focused on European Integration for better quality of environment and human life. University of Mining and Metallurgy (AGH), Cracow, Poland. 15-16th Sept. 2000. Aleksandra Wagner and Jan W. Dobrowolski (eds).

Ganguly C., Matsumoto M. R., Rabidean A. J. and Vabenschoten J. E. (1998). Metal ion leaching from contaminated soils: Model calibration and application. *J. Environ. Eng: ASCE.* **124:** 1150-1158.

Kabata-Pendias A. and Pendias H. (1992). Trace metals in soils and plants; CRC Press: Boca Raton, Fl., 1-10.

Kloke A. (1980). Orientierungslaten fur tolerierbare Gesamtgehalte einiger Elemente in Kulturböden. Mitteilungen der VDLUFA. Heft 1-**3:** 9-11.

Mench M., Vangronsveld J., Didier V., Clijsters and H. A. (1994). Mimicked in situ remediation study of metal contaminated soils with emphasis on cadmium and lead. Env. *Poll.* **86:** 279-286.

Nuruzzaman M., Gerzabek M. H. and Ullah S. M. (1995). Studies on heavy metal and microbiological pollution of soils, sediments and water systems in and around Dhaka City; Bericht an die Österr. Akademie der Wissenschaften: Austrian Research Centers Seibersdorf (ÖFZS), Vienna, Austria. I: 5-25.

Phillips I. R.(1998). Use of soil amendments to reduce nitrogen, phosphorus and heavy metal availability. *Journal of Soil contamination*. **7**(2): 191-212.

Rule J. H. and Martin Slacin. (1999). Effect of iron oxides on the bioavailability of trace metals in biosolids. In. Proc. of extended Abstracts. 5th International Conference on the Biogeochemistry of Trace Elements (Wenzel, W.W., Adriano, D.C., Alloway, B., Doner, H.E., Keller, C., Lepp, N.W., Mench, M., Naidu, R., and Pierzynski, G.M. eds) Vienna, Austria. **I:** 282-283.

Rulkens W. H., Tichy R. and Grotenhuis J. T. C. (1998). Remediation of polluted soil and sediment: Perspectives and failures. *Wat, Sci. Tech.* **37**: 27-35.

Tadesse B., Donaldson J. D. and Grimes S. M. (1994). Contaminated and polluted land: A general review of decontamination management and control. *J. Chem. Tech. Biotechnol.* **60:** 227-240.

Tiller K. G., Gerth J. and Brümmer G. (1984). The sorption of Cd, Zn and Ni by soil clay fractions: procedures for partition of bound forms and their interpretation. Geoderma. **34:** 1-16.

Yong R. N., Mohamed A. M. O. and Warkentin B. P. (1992). Principles of contaminant transport in soils. Elsevier Science Publishers B.V., Amsterdam, The Netherlands. 327.

Received : September, 22, 2008;
Accepted : July, 01-, 2009