



## PHYTOEXTRACTION OF FEW METALS FROM FLYASH AMENDED SOIL BY *SCIRPUS LITTORALIS*

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### Abstract

The disposal and treatment of coal fired power plant generated fly ash is a major problem till date. Wetland plants can be used to extract the heavy metals present in the fly ash from aquatic systems like fly ash ponds or constructed wetland systems. For this purpose *Scirpus littoralis*, a wetland plant was chosen to assess its phytoextraction potential of Mn, Ni, Cu, Zn and Pb from the fly ash amended soil under ex-situ conditions. Fly ash from Indraprastha Power Plant of New Delhi was dosed in manure mixed garden soil in 25%, 50% and 100%. Soil without fly ash served as control. The plants were grown for three months in waterlogged condition. Each harvesting was done after one month and growth and metal concentration in roots and shoots were estimated. During these three months metal accumulation and plant growth increased with time. It was found that plant growth and phytoextraction of metals was maximum in 25% fly ash amendment. In this study, total phytoextracted metals by *Scirpus littoralis*, was calculated, as the product of biomass and tissue metal concentration. The concentration of total phytoextracted metal after three months in 25% fly ash dosed plant roots were 6433.96 µg for Mn, 677.43 µg for Ni, 638.3 µg for Cu, 1264.25 µg for Zn, 409.5 µg for Pb. From the study it was concluded that *Scirpus littoralis*, can be used for phytoextraction of fly ash at 25% amendment level as this amendment showed maximum growth and accumulation of metals. However, ANOVA at 0.05 significance level showed that the difference in metal content in the plant parts between the different treatment were not statistically significant.

**Keywords:** Fly ash, *Scirpus littoralis*, Heavy metals, Amendment, Phytoremediation, Accumulation, Phytostabilization, Biomass

### Introduction

Huge amount of fly ash is generated from coal fired power plants. Currently, most fly ashes are disposed off in landfills and surface impoundments like fly ash ponds and dykes, and only about 30% is used in construction, engineering, manufacturing, and agricultural activities (Hassett et al., 2000). Fly ashes are generally highly heterogeneous, consisting of a mixture of glassy particles with various identifiable crystalline phases such as quartz, and various iron oxides. Fly ash also contains metals in significant amounts, including arsenic, barium, beryllium, boron, cadmium, chromium, chromium VI, cobalt, copper, fluorine, lead, manganese, nickel, selenium, strontium, thallium, vanadium, and zinc (Woodbury et al., 1999). Fly ash particles containing metals from ash ponds or mound can contaminate surface water bodies and soil through surface run off. From these contaminated bodies metals can infiltrate or leach out from surface water bodies or surface soil to ground water aquifers. Finer particles can also be carried by wind and transported elsewhere for deposition. Conventional remediation methods such as acid leaching, excavation,

land filling processes are generally ineffective and very costly. Instead phytoremediation is now being widely used for removing heavy metals from both aquatic and terrestrial systems. Aquatic plants, especially wetland plants provide a viable alternative for remediation of metals if proper disposal of the spent plants are employed (Jackson et al., 1994). Moreover phytoremediation is a good option to remediate metals from fly ash because it includes extraction and stabilization of metals from fly ash through uptake by plants and binding the fly ash by their roots (Gupta and Sinha, 2006). These plants have been successfully used for this purpose for a long time as they are good accumulators of metals (Taylor et al, 1983). In addition to this, nowadays, constructed wetlands are used for metal removal as a cheap and environment friendly alternative where aquatic macrophytes are also used as the part of the system as nutrient and metal accumulators from the wastes (Mays and Edwards, 2001; Mahoney et al, 2004; Maine et al, 2007). Heavy metal removal from fly ash can also be done using these constructed wetland systems instead of dumping them in the fly ash ponds. Heavy metal uptake

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potential has been widely studied for different wetland plant species all over the world, such as *Salvinia natans* (Sen and Mondal, 1989; Zayed *et al.*, 1998), *Lemna polyrrhiza* (Sharma and Gaur, 1995), *Ceratophyllum demersum* L., *Spirodela polyrrhiza* (L.) Schleid, *Bacopa monnieri*, *Hygrophiza aristata* (Rai *et al.*, 1995), *Eichornia crassipes* (Vesk *et al.*, 1999, Mehra *et al.*, 2000), *Typha latifolia* and *Phragmites australis* (Ye *et al.*, 2001; Batty *et al.*, 2004), *Paspalum distichum* ( Babcock *et al.*, 1983, Bhattacharya *et al.*, 2009), but there have been few studies on wetland plants for fly ash rich soils.

The present ex-situ study is aimed to evaluate the efficiency to take up Mn, Ni, Cu, Zn, Pb from fly ash by *Scirpus littoralis*, a wetland plant. Different species of *Scirpus* grows worldwide and though are reported as good accumulators of heavy metals by several researchers (Otte *et al.* 1991; Sinicope *et al.* 1992; Kadelec and Knight 1996; De Souza *et al.*, 1999), but the heavy metal uptake potential of *Scirpus littoralis* from fly ash amended soil has not been studied in India except by the same author of this paper. For this purpose, this particular type of wetland plant which is commonly available in Delhi on the flood plains of River Yamuna, was chosen. The origin of the Fly ash used in the present study was Indraprasth power (IPP) station and Rajghat powerhouse (RPH) of New Delhi, India. Ash content of the coal used in these power stations ranges between 38–47%. The ash is collected in electrostatic precipitators which have an efficiency of 99.3% (IPP station), and 99.7% (RPH). There are instances of major dust pollution around the power stations from fly ash dispersal. The main method of disposal of fly ash from the power stations is by mixing with water, the resultant slurry is pumped through pipes to ash disposal ponds. The supernatant from these ponds is discharged into River Yamuna. Field studies have revealed large quantities of fly ash being deposited into the river. Previous studies has been made on the effects of fly ash leachates and run off from the above mentioned ash settling ponds on the river by analyzing river over bank soils and vegetation for their heavy metal contents (Mehra *et al.*, 1998; ). Accumulation of five metals viz. Mn, Ni, Cu, Zn, Pb were studied in the present study as these metals are considered as some of the most leachable and mobile metals under natural conditions (Mehra *et al.*, 2000; Sajwan *et al.*, 2003; Mehra *et al.*, 2004; Jegadeesan *et al.* 2008).

## Material and Methods

Before setting up the experiment plant and fly ash samples were collected. The plant chosen for the experiment viz. *Scirpus littoralis* is of Cyperaceae family and of *Scirpus* Genus. The genus *Scirpus* has a worldwide distribution, being absent only in arctic

regions. They often grow in large colonies in water and are often seen as tall, leafless stems growing in profusion. They are commonly known as bulrush. The sampling is described below. *Scirpus littoralis* is commonly found in Yamuna flood plains of Delhi region.

## Sampling

The plants were collected from Bhalswa Lake, which is a natural freshwater wetland on the northern outskirts of Delhi and visibly an uncontaminated site. It is located in the floodplain of river Yamuna that flow about 8 to 9 km east of the lake in a north-south direction. In the northern end of the lake the area is relatively undisturbed and dominated by *Scirpus littoralis*. Here the plants occur in pure stands. Young plants were used for the present experimental study.

Fly ash was collected from ten different locations from the bank of the fly ash pond behind Pragati Maidan and beside Ring road, Delhi. The fly ash produced from the Indraprasth power station and Rajghat powerhouse are made into slurry with water and then dumped in this fly ash pond. After collection of fly ash samples all the ten samples were homogenized by mixing by quartering and coning method. After homogenizing the fly ash was dosed.

## Experiment design

The study has been done in ex-situ conditions. Four cement tanks measuring 60×60×60 cm were set up in the garden under natural weather conditions. Garden soil was used as uncontaminated soil source. Fresh farmyard manure was mixed with this uncontaminated soil in 1:4 ratios. Then three amendments were done with fly ash as shown below. Ten young plants (about three weeks old) were planted in each of the six tanks. For each amendment total three set of tanks were kept.

Control: 0% by wt. Fly ash +100% by wt. soil-manure mixture

25% FA: 25% by wt. Fly ash + 75% by wt. soil-manure mixture

50% FA: 50% by wt. Fly ash + 50% by wt. soil-manure mixture

100% FA: 100% by wt. Fly ash + 0% by wt. soil-manure mixture

All the tanks were kept waterlogged. The water level was maintained approximately at 5 cm above the soil surface by watering them frequently with distilled water. The plants were grown for a period of three months (September to December, 2008). They were harvested at an interval of one month. Three plants were harvested in each month.

The growth of the plants (shoot length and number of offshoots) was measured at the start of the experiment (during the plantation of species) and during each harvest.

At each harvest, the plants were removed carefully and washed first with tap water followed by double distilled water to remove all soil and organic matter particles from the roots and plant surface. Roots including rhizomes referred as roots and aerial parts (shoots and inflorescence) referred as shoots in the text were separated and kept in oven at 80 °C for 24 h. After drying roots and aerial parts were weighed on digital balance, [Mettler 240]. Then they were grinded and stored for chemical analysis. Metal analysis (Mn, Cu, Zn, Pb, and Ni) of the plant samples were carried out by acid digestion [conc. HNO<sub>3</sub>+conc. HClO<sub>4</sub> (9:4)] (Bhargava et al., 1993) followed by measurement of total metal using AAS (Model No. Philips 9200X). Total N and total P content analysis in fly ash samples were carried out following Anderson and Ingram, (1989) method. Total metal analysis of fly ash samples were digested using tri-acid mixture (9 ml of 70% HNO<sub>3</sub>, 1ml of 60% HClO<sub>4</sub> and 6 ml of 48% HF) (Agemian and Chau 1976).

To manage accuracy and precision all the experiments were carried out in triplicates and the

mean of triplicate analysis was used in all results. Standard stock solutions for all the metals were procured from Merck. These standard stock solutions were further diluted to multilevel standards for all the metals. To minimize the external sources of error, blanks were run simultaneously for all the metal determination. Standard curves for different metals were prepared using different diluted standard solutions and standard curve with regression of 0.99 were only used for calculation of metal concentrations.

Statistics (mean, standard deviation and ANOVA) were estimated in SPSS version 11

## Result and Discussion

### Composition of fly-ash

The total heavy metal contents in fly ash were determined before amendment and their relative abundance was found in the order of Mn > Ni > Zn > Pb > Cu. Fly ash samples had slightly alkaline pH and trace amounts of N and P. The fly ash composition is shown in Table-1.

Table 1. Composition of the fly ash used (Mean ± Standard deviation) (n=3)

Parameters	Concentration
pH	7.43±0.32
Total N (%)	0.10±0.03
Total P (%)	0.18±0.07
Mn (µg)	560.00±13.27
Ni (µg)	155.03±6.23
Cu (µg)	83.51±4.08
Zn (µg)	122.12±8.06
Pb (µg)	99.32±5.11

### Growth of plant

The growth of plant was highest in the control tank both in terms of dry weight of roots and shoots and root shoot length (Table 2 & 3). Among the fly ash amended soils, the plants grown in 25% amendment showed the maximum growth, and lowest growth was observed in plants grown in 100% FA. This might be due to increased stress on plants due to high metal concentration and poor nutrient supply with the higher

amounts of fly ash dose. However, the growth increased with time as shown in different harvest's root shoot biomass and length results in Table 2 and 3. This type of growth retardation with respect to biomass and root-shoot length due to high metal stress is well reported in literatures. (Dirilgen et al. 1994; Lee et al. 1998; Bhattacharya et al. 2006, Bhattacharya et al, 2009).

Table 2: Change in Dry weight of plant roots and shoots through out the study period (average and standard deviation) (g)

	Control	
	Root (g)	Shoot (g)
0 days	0.21±0.02	0.87±0.12
30days	0.75±0.01	2.03±0.12
60days	12.4.0±0.06	14.20±0.05
90days	15.0±0.09	16.10±0.02
25%FA		
0 days	0.25±0.12	0.81±0.02
30days	1.30±0.01	1.90±0.04
60days	9.00±0.02	11.8±0.01
90days	13.0±0.01	12.6±0.06
50% FA		
0 days	0.20±0.05	0.79±0.10

30days	0.54±0.01	1.45±0.01
60days	7.5±0.02	9.10±0.02
90days	8.20±0.10	10.6±0.02
100%FA		
0 days	0.19±0.12	0.84±0.01
0days	0.42±0.04	1.02±0.11
60days	6.9±0.05	8.70±0.01
90days	7.7±0.06	9.6±0.02

Table 3. Changes in Root, shoot length (average and standard deviation) (cm) and number of off shoots (OS) through out the study period

	Control	25%FA	50%FA	100%FA
0day				
Root	6.01±1.05	5.12±0.84	5.15±0.25	6.40±0.12
Shoot	15.31±1.49	16.03±.99	14.48±0.54	15.91±0.02
OS	1.00±0.00	1.00±0.00	1.00±0.00	1.00±0.00
30days				
Root	12.10±2.46	29.50±1.05	33.50±1.82	22.90±2.09
Shoot	50.48±5.61	54.04±4.22	62.30±7.06	42.20±5.06
OS	5.50±0.00	7.50±0.00	4.00±0.00	3.00±0.00
60days				
Root	34.65±3.01	33.50±1.06	39.09±2.34	45.21±1.64
Shoot	78.31±9.16	69.06±7.25	64.73±6.32	76.56±8.03
OS	15.00±0.00	10.50±0.00	5.50±0.00	7.00±0.00
90days				
Root	40.20±2.54	40.01±3.01	40.19±2.16	42.55±1.06
Shoot	90.10±8.09	71.21±6.43	72.25±9.31	81.33±7.66
OS	14.10±0.0	11.50±0.00	6.50±0.00	9.00±0.00

### Metal accumulation

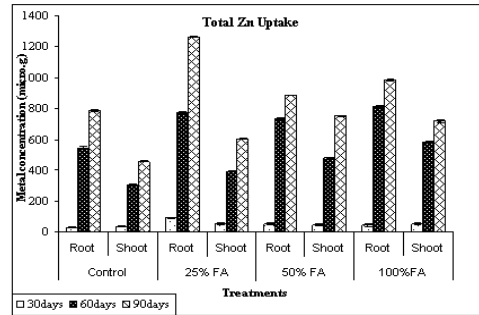
The metal uptake is expressed as the total metal uptake, i.e., the product of biomass (dry wt.) and the tissue concentration of metal (Carucci et al., 2005).

Total metal uptake ( $\mu\text{g}$ ) = biomass (dry wt.)(g) X tissue concentration of different plant part ( $\mu\text{g/g}$ )

This will give a clear picture, how much metal can be scavenged by a plant from the different amendment because for the field applications it is interesting to know the total metal taken up by plant rather than the tissue concentration. The results shows that shoot accumulated less metal than roots (Figure 1. a-e). This may be due to the exclusion strategy adopted by the plant. According to this strategy, the translocation to the more metabolically active and sensitive part, i.e. shoot in this plant is restricted by plant to avoid heavy metal toxicity (Zurayk et al., 2002). However, with time the total metal content increased in both the plant parts. The metal content was more in all the fly ash dosed plants compared to the control plants. Among the fly ash dosed plants highest metal content was observed in the 25% amendment for all the metals. As it was stated above that the biomass produced was highest by these plants at this amendment level, so the total metal content was also high. As the biomass was less in 50FA and 100 FA plants, the total metal content was less despite of the high tissue metal concentration.

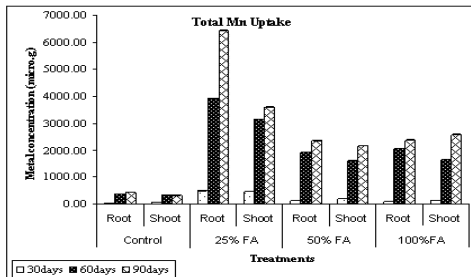
However, ANOVA at 0.05 significance level showed that the difference in metal content in the plant parts between the different treatments were not statistically significant (Table 4) i.e the plants response to different fly ash amendment with respect to metal uptake was not statistically significant. However, all the treated plants showed increase in metal accumulation with time. This is reflected in the figure1. a-e, which shows increase in metal content in plant tissues with each successive harvests. Among the six metals studied, Mn was the most accumulated heavy metal. The concentration of Mn reached upto 6433.96  $\mu\text{g}$  after 90 days of growth in 25% fly ash amended plant roots. Least accumulated metals were Pb, which was in 409.5  $\mu\text{g}$  concentration in the roots of 25% fly ash a dosed plant. The amount of metal scavenged by different parts of *Scirpus littoralis* is in accordance with other reported studies (Mehra et al., 1999; Bhattacharya et al., 2006; Madejon et al. 2006, Chakarabarty et al., 2008; Tiwari et al, 2008). The relative total concentration of accumulated metals in plant roots in all the treated plants was Mn>Zn>Ni>Cu>Pb and in shoot was Mn>Zn> Cu>Ni> Pb. This was not in accordance with the metal abundance order in fly ash which was Mn> Ni > Zn > Pb > Cu. The reason behind this may be the bioavailability of metals. Some metals are more bioavailable in the prevailing soil physico-chemical

conditions and some are less. So plants take metals which are more bioavailable or exchangeable (Chlopecka et al. 1996). As Ni and Pb are usually less bioavailable metals in fly ash they were taken up less despite of their higher concentration in soil (Bhattacharya et al. 2006). Furthermore, the studied metals become available in acidic pH conditions (Forstner, 1991). But for the present study the pH was maintained slightly alkaline, favorable for plant growth (Pendias, 2004), which might result in less metal bioavailability. The rate of translocation of metals from root to shoot also varies with the antagonistic or synergistic effect of other metals and nutrients (Pendias, 2004). So the metal abundance order in shoot differed with that in root.

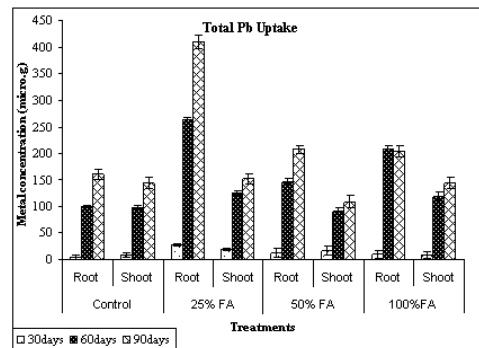


(d)

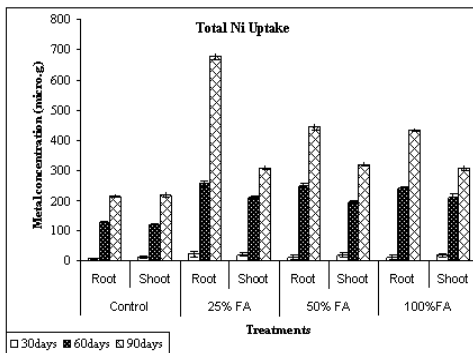
Figure 1. (a-e): Total uptake of metals in roots and shoots in different treatment through out the study period



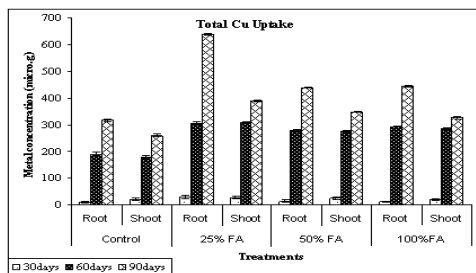
(a)



(e)



(b)



(c)

Table 4: Table for ANOVA

Metals / Treatments	0%FA-25%FA	25%FA-50%FA	50%FA-100%FA
$F_{crit}=7.71, p=0.05$			
Roots			
Mn	3.72	1.35	0.001
Ni	1.01	0.13	0.02
Cu	0.60	0.14	0.0008
Zn	0.39	0.13	0.02
Pb	1.47	0.79	0.04
Shoots			
Mn	4.84	0.90	0.002
Ni	0.39	0.0001	2.76E-05
Cu	0.48	0.03	0.001
Zn	0.18	0.08	0.008
Pb	0.07	0.28	0.13

## Conclusion

From the study it can be concluded that the hazardous part of the fly ash, i.e. metals can be efficiently scavenged by *Scirpus littoralis* in lower amendments, i.e. around 25% amendment with proper harvesting strategy. However at higher amendments the plant can be used as phytostabilizer, so that it can bind and take up the metals by root and hence can reduce the bioavailability of metals. Other studies also reported the phytostabilizing capability of other wetland plants such as *Phragmites australis*, *Typha latifolia*, and *Paspalum distichum* (Shu et al. 2002; Azaizeh et al., 2006; Bhattacharya et al, 2009).

However it is not a good metals accumulator at higher levels of fly ash because the plant produces low biomass at high fly ash level. It can also be used as phytoextractor at higher fly ash levels by increasing the number of plantation thus providing more biomass to accumulate metal. Then proper harvesting strategies must be employed for the metal contaminated plant parts. After harvesting the harvested biomass can be treated by compaction, composting and pyrolysis and final disposal can be done by incineration, ashing or direct disposal in landfill sites (Nowosielska et al, 2004).

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