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STUDIES ON COLONISATION OF FLY ASH DISPOSAL SITES USING INVASIVE SPECIES AND AROMATIC GRASSES

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Abstract. Fly ash disposal activities by coal based thermal power plants will continue to be a serious issue across the globe due to its hiked generation every year. To obviate the hazardous effects of fly ash disposal sites on the surrounding ecosystems, rapid stabilization of the dumps is essential. This paper conglomerates the past activities, challenges; present scenario of vegetation establishment on these sites as well as future research requirements based on various experimental case studies. An insight has been presented on the usefulness of native, tuft, aromatic grasses which can reduce the length of successive phases in reclamation programmes and also enhance the fertility of the substrate as found from the significantly increased nitrogen content in the present field sites. Metal bioaccumulation studies depicted that by virtue of high biomass production potential of *Saccharum spontaneum* it can also be used as a phytoextractor of toxic metals, thus helping in phytoremediation of the metals in fly ash. Field studies allude the fact that knowledge of phytodiversity of old fly ash deposits is essential for a right choice of species before every reclamation programme. Secondly, application of amendments is conjointly a prerequisite for establishment of plants on fly ash. In a pot scale study it was found that lower rate of amendment application (2–5% farmyard manure and 5–10% topsoil on weight basis) in fly ash improves the growth and biomass of *Cymbopogon citratus*. Extensive root system of the grass was substantiated by high root: shoot biomass which stabilized the surface of the ash. To investigate the possibilities of ground water contamination due to amendments leaching studies were carried out. An initial high concentration of some ions marginally near permissible limit as per Indian drinking water standards was observed but their concentrations were below acceptable limit during harvestable stages. Above studies can contribute significantly in field studies through a properly planned restoration programme.

Keywords: nitrogen, biomass, farmyard manure, *cymbopogon citratus, saccharum spontaneum,* bioaccumulation.

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Introduction

Fly ash is the main industrial waste product generated by coal based thermal power plants. India ranks third across the globe in fly ash production (Ram *et al.* 2008). Fly ash generation is likely to surpass 300 MT by the year 2017 due to very high ash content of the coal, which is about 35–45% (Mathur *et al.* 2003). Year 2012–2013 experienced a standing amount of 63 million tonnes of unutilized ash (37% of the total ash produced) in India which was dumped, encroaching a land area of more than 40 000 Ha (Jain, Gaggar 2013). Fly ash is generally being disposed off in low lying areas, landfills, basins around thermal power plants and in abandoned mine pits (CEA 2012). These dumps have deleterious effects and contaminates nearby aquatic and terrestrial ecosystems. Furthermore in the long run, trace metals in fly ash contaminate ground water and get into living organisms through food chain (Belyaeva, Haynes 2012). Thus there is an urgent need for stabilization of the dumps.

In this context, phytomanagement is the most effective and eco-friendly approach as it stabilizes ash dumps, reduces erosion and incurs gradual restoration of the site. It also reduces gradual leaching of water and solutes into ground water and initiates carbon sequestration. They also

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pave the pathway for future generation of bio-resource (Pandey 2012). This paper conglomerates the past and present status of revegetation of fly ash disposal sites. It also highlights the challenges and future research needs which should be focused on in this aspect. Furthermore an insight has been presented in the usefulness of grasses in stabilization of fly ash dump surfaces. Native hardy and tuft grasses are early colonizers as they can thrive on adverse conditions. With a view of long term management the information collected here will contribute a substantial part on an effective strategy for fly ash dump stabilization.

1. Earlier studies on reclamation of fly ash disposal sites

Vegetation cover development on fly ash disposal sites is difficult at early stages. Fly ash consists of glass-like spherical particles, with a silty loam texture and a natural compaction tendency which inhibits water infiltration as well as restricts root growth to some extent (Haynes 2009). Though, it has high moisture retention capacity, and considerable amounts of plant nutrients (Ca, K, Mg, Cu, Fe, Mn, Mo, Zn, B) in the form of oxides, hydroxides, carbonates and bicarbonates; it lacks microbial activity, and a consistent supply of nitrogen crucial for plant growth (Page *et al.* 1979). Besides, it also contains various toxic metals such as V, Cr, Ni, As, Se, Rb, Sr and Pb which can get its path into higher trophic level through food chain. Various authors have carried out their studies on a number of herb, shrub, grass as well as tree species as enumerated in Table 1. Generally, efficient, stress tolerant, fast growing species which can help in development of a quick cover are recommended. Zolnierz *et al.* (2016) has recently reported the phytodiversity of an abandoned mine filled with fly ash, 11 years after reclamation. Inclusion of native plants in presence of microbial amendments has been reported by many workers (Krzaklewski *et al.* 2012; Babu, Reddy 2011; Hrynkiewiez *et al.* 2009). Few workers have studied the effect of sandy topsoil/farmyard manure/mill mud/compost/biosolids/sewage sludge/vermiculite on ash to support revegetation (Cheung *et al.* 2000). Studies on field practices of revegetation usually involve high rate of fertilizer addition in absence of topsoil. According to agronomic techniques NPK (nitrogen:phosphorus:potassium) fertilizers are generally used in the ratio of 15:15:15 or 19:19:19 to a root tilled depth of 15 cm, (Punshon *et al.* 2002). But high rate fertilizer addition incorporates a great deal of ions and solutes which can erode into the nearby water streams or seep through the ground to contaminate water below in the long run. A cost effective amendment approach is still lacking at the current state to be implemented in the field. Thus, an effort has been made by us in a recent study to grow aromatic grasses as initial colonizers in presence of low rate of amendment application.

Table 1. Plant species used for vegetation establishment on fly ash dumps

Species name	Habitat	Reference
Parthenium hysterophorus	Herb	Dwivedi *et al.* (2008)
Solanum nigrum	Herb	Dwivedi *et al.* (2008)
Limnanthes spp	Herb	Dwivedi *et al.* (2008)
Eclipta alba	Herb	Dwivedi *et al.* (2008)
Typha latifolia	Herb	Maiti and Jaiswal (2008)
Fimbristylis dichotoma	Herb	Maiti and Jaiswal (2008)
Amaranthus defluxes	Herb	Maiti and Jaiswal (2008)
Cassia tora	Herb	Gupta and Sinha (2008)
Chenopodium album	Herb	Gupta and Sinha (2008)
Blumea lacera	Herb	Gupta and Sinha (2008)
Equisetum ramosysma	Grass	Dwivedi *et al.* (2008)
Saccharum munja	Grass	Dwivedi *et al.* (2008)
Saccharum spontaenum	Grass	Maiti and Jaiswal (2008)
Cynodon dactylon	Grass	Maiti and Jaiswal (2008)
Calamagrostis epigejos	Grass	Mitrovic *et al.* (2008)
Festuca rubra	Grass	Mitrovic *et al.* (2008)
Calotropis procera	Shrub	Gupta and Sinha (2008)
Ipomoea Carnea	Shrub	Pandey (2012)
Ricinus Communis	Shrub	Pandey (2013)
Sida cardifolia	Shrub	Gupta and Sinha (2008)
Acacia auriculiformis	Tree	Cheung *et al.* (2000)
Alnus glutinosa	Tree	Jamil *et al.* (2009)
Alnus incana	Tree	Jamil *et al.* (2009)
Cassia seamea	Tree	Juwarkar and Jambulkar (2009)
Jatropha curcas	Tree	Krzaklewski *et al.* (2012)
Leucaena leucocephala	Tree	Cheung *et al.* (2000)
Prosopis juliflora	Tree	Rai *et al.* (2004)

2. Material and method

2.1. Field investigations and sampling

Field surveys were conducted on different aged fly ash disposal sites in and around Jharkhand and West Bengal state of India during dry periods of the year 2015. Approximately, six to seven visibly dominant plant species were selected for sampling. Three replicates for each of the dominant plant species and their rhizospheric fly ash samples (depth = 30 cm) were collected from each site. The replicates for each plant species were chosen on the basis of same age group. All the samples were collected in clean labeled plastic bags and transported to the laboratory for analysis. Encountered plants were identified with the help of related flora. Descriptions of the sites chosen for study are given below.

Study site 1 is located in low lying lands around Tenughat Thermal Power station. It is situated near

Tenughat Dam in the district of Bokaro, Jharkhand India. The total capacity of the plant is 1550 MW and it encroaches an area of 2200 acres which also includes low lying areas for fly ash disposal. Fly ash disposal is generally followed by compaction through heavy machinery and covering with live topsoil acquired from nearby areas. Presence of rich biodiversity in the nearby areas helps in succession of disposal sites with native invasive species in a period of 1 year which generally accelerates after monsoon. Site 2 is located in the abandoned, opencast fly ash filled mines of Damoda located in Dhanbad district of Jharkhand state in India. Fly ash used for filling the mines was taken from nearby Chandrapura thermal power plant of 890 MW capacities located 16 km away from the mines. The process of filling was carried out for 3 years to create a dump of fly ash which is now covered with native and invasive grasses. Study site 3 is another fly ash dump located inside Crescent thermal power plant premises near Asansol, West Bengal India. The thermal power station is of 40 MW and the primary fuel is washery rejects obtained from the same premises. The dump is present in an area of 4–5 hectare of land. The reclamation programme of the dump was commenced with technical steps such as topsoiling to a thickness of about 60 cm, construction of permanent drainage channels along the slopes, garland drain at dump foot ultimately leading to a reservoir. In pit plantation of trees were done along with seeding with native grass legume species. The average annual rainfall of the entire zone is 1200–1300 mm while the temperature varies from 10–40 °C annually. Site 1 and 2 was chosen to account for the natural succession of fly ash disposal sites and identify the dominant plant species. Site 3 was taken as a reference site in contrast to site 1 and 2 wherein a technical restoration programme had been followed. The results of site 1 and 2 were compared to site 3 in this study.

2.2. Experimental design for pot scale study

Fly ash (FA) for the pot scale study was collected from the ash ponds near Chandrapura thermal power plant of Damodar Valley Corporation located at Chandrapura town in Jharkhand state of India. Garden soil (GS) was collected from top 15 cm from the Institute's garden at CSIR-CIMFR, Dhanbad located in Jharkhand state of India. Farmyard manure (FYM) was obtained from a nearby dairy farm. All the samples were air dried for a week, thoroughly mixed and grounded to pass through a 4 mm sieve.

Garden soil and farmyard manure were mixed with fly ash on weight basis, in proportions of 5%, 10% and 2%, 5% respectively. Treatment I was the control with no amendments while treatments IV (FA + 5% GS + 2% FYM), V (FA + 10% GS + 2% FYM), VI (FA + 5% GS + 5% FYM), and VII (FA + 10% GS + 5% FYM) had been prepared with different combinations of garden soil and farmyard manure. The resultant treatments had a pH near 7.00 at initial stage which usually doesn't pose any threat of metal contamination. The pots containing the mixtures were arranged for equilibration under natural light and temperature for 10 weeks. After equilibration period, first leachate (1L) collection was done while second (2L) and third leachates (3L) were collected at intervals of 2 months till final harvest of the plants near after 4 months. Leachate collection from the pots had been done, based on the design of Marseille *et al.* (2000). It was mainly done to investigate the contribution of amendments and vegetation on the amount of ions and metals leaching down which may contaminate the ground water. This was followed by plantation of 2–3 *Cymbopogon citratus* tillers per pot. Regular irrigation of the pots was done five – six times a week with equal amounts of water and recorded. The collected leachate samples were immediately taken to the laboratory for analysis. In an economical point of view *C. citratus* shoots are generally harvested after 3.5–4 months for oil extraction (Maiti, S. K., Maiti, D. 2015; Maiti, Prasad 2016). With this point in view, the plants in this study were harvested at maturity near after 4 months.

2.3. Analysis of samples

The root and shoot parts of the plants were segregated in the laboratory to determine their biomass. Average weight of all the plants from each site was calculated individually. They were repeatedly washed with tap water and deionized water to remove all the adhered fly ash particles followed by drying to a constant weight at 80 °C in oven and finally grinding to a fine powder for heavy metal analysis. Powdered samples of a known weight were reduced to ashes at 450 °C for 45 min and 850 °C for 1 h, followed by dissolution in 25 ml of 6 M HNO_3 and subsequent digestion. The solutions were filtered with Whatman 42 grade filter paper into 50 ml volumetric flasks (Rodriguez *et al.* 2011) followed by metal analysis through atomic absorption spectrophotometer (Thermo Scientific, Germany).

Fly ash samples were air-dried and ground to pass through a 2 mm sieve, for analysis of pH in 1:1 ratio (w/v) with distilled water (Jackson 1973), loss on ignition at 450 °C and 750 °C respectively in a muffle furnace for 1 hour each (Mishra, Das 2010; ASTM D 2974-87). Determination of available nitrogen was done by the method of Subbiah and Asija (1956) while water holding capacity was done through keen's box method (Piper 1942).

The leachate samples were analyzed for pH, EC (electrical conductivity), TH (total hardness), Ca H (calcium hardness), Cl (chloride), TDS (total dissolved solid), total alkalinity (Tot Alk), and SO_4 (sulphate) as per standard methods (APHA, AWWA, WEF 1992; IS-3025 2009).

Sample preparation was done before metal analysis. Approximately, 200 ml samples of each leachate was acidified using concentrated nitric acid and digested on a hot plate at 70 °C to a volume less than 50 ml. The digested and concentrated sample was filtered through Whatman cellulose filters, pore size 0.45 μm using sterile injectors into 50 ml volumetric flasks. The volumes were made up to 50 ml with distilled water. Analysis of each metal was done at respective sensitive wavelength i.e. at 324.7, 279.5, 217.0, 228.8, 213.9, 232.0 and 357.9 nm for Cu, Mn, Pb, Cd, Zn, Ni and Cr respectively. Limits of detection of various metals (Mn, Zn, Cu, Pb, Cd, Cr, and Ni) were in the range of 0.0005 to 0.01 mg L^{-1}. The calculations for metals in leachates were done by dividing the instrument reading for metals by concentration factor. Blanks and different dilution standards were used for calibration and quality assurance. The instrument was recalibrated after analysis of 15 samples. All the glassware used for analysis were acid washed and rinsed with distilled water, dried and kept in a clean dry environment prior to use. All reagents used were of analytical grade (Merck).

2.4. Statistical analysis

Statistical analyses were carried out to interpret the results by using SPSS (version 20.0 for Windows; SPSS Inc. Chicago, USA) and MS Excel 2010. Mean values along with their standard deviation (SD) has been computed and have been shown as error bars in the graphs. Descriptive statistics like one way analysis of variance was used to access the variance between the means of an analyzed parameter between the sampling sites and leachates from the pot study. Difference between individual means was carried out through DMRT (Duncan's multiple range test) model at 95% level of confidence. Hierarchical cluster analysis is performed on dataset of metal concentrations to group similar metal clusters using Eucledian distance and group linkage methods. Relation between general water quality measures and metal associations and their relations to pH have also been performed tested with two-tailed as well as one tailed Pearson correlation to get a matrix of correlations between them.

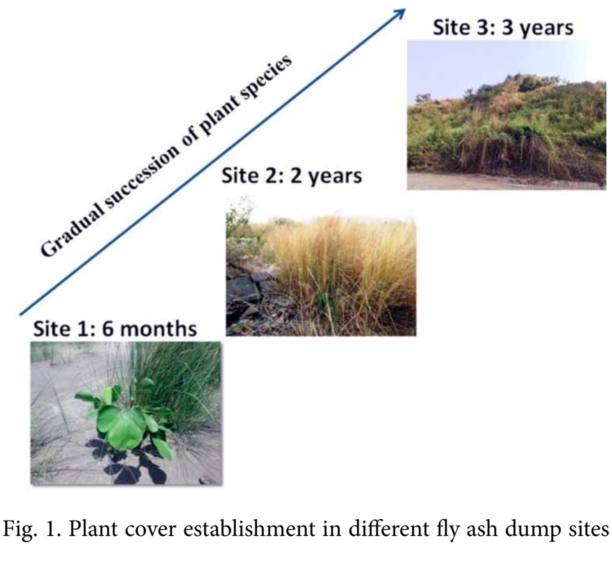


Fig. 1. Plant cover establishment in different fly ash dump sites

3. Result and discussion

3.1. Vegetation succession on fly ash disposal sites

Various field surveys done by us has revealed that natural colonisation of fly ash surfaces depend on the nutrient content of the substrate, efficiency of plant species to grow in adverse conditions and interactions between them (Belyaeva, Haynes 2012). The three field sites chosen by us varied in the age of the vegetation and were of 6 months, 2 years, and 3 years respectively (Fig. 1). Initial colonisation of the sites are dominated by weed herbs such as *Chromolaena odorata, Dysphania ambrosioides, Sida rhombifolia, Tephrosia purpurea* various shrubs and grasses as seen in site 1. At later stages hardy and tuft grasses cover the areas which were observed in site 2. A proper restoration program (such as topsoil blanketing, addition of amendments and seeding with native species) was followed in the 3rd field site (reference site) which showed the presence of more various plant species after 3 years of vegetation. The vegetation cover of more than a meter in site 3 was dominated by *Saccharum spontaneum, Ipomoea* sp., and *Pennisetum pedicellatum*. Presence of few number of tree species were also found on the dump slopes. It was recovered from the site authorities that during initiation of closure activity 2500 number of tree species were planted out of which a very few percent has survived till the present date. The slope length of the present reclaimed dump was 35–40 m with an angle of 55 degrees.

A noticeable fact as found in all the three sites was the dominance of *Saccharum spontaneum* and *Cynodon dactylon*. These types of results were also obtained by various other authors (Dwivedi *et al.* 2008; Pandey *et al.* 2012). These invasive grasses have tolerance to various adverse conditions and shows competitive behaviour towards other species. Narratively, their perennial nature, presence of light persistent seeds and rhizomatous roots imparts the advantage for their invasive nature (Graham *et al.* 2014). On the other hand they also stabilise the fly ash dump surface by holding on to the loose material through their strong roots (Kaith *et al.* 2010). Secondly it was also observed that later stages of reclamation of the dumps lacked an economic end use. A major strategy which can be focussed upon in this context is biomass production at later stages of restoration programmes. Few economically important trees which can be included are pulp and paper tree, biodiesel crops, firewood, timber wood and plywood trees.

3.2. Rhizospheric fly ash characteristics and plant biomass

Figure 2 shows the variation in physicochemical properties of the sites. Site 1 and 3 had near neutral pH and site 2 had an average pH of 5.6 significantly different from other sites may be due to the mixing of moderately acidic minesoil with fly ash. Previous studies on the groups of nearby opencast mines near site 2 also have revealed a mine soil pH value near 4.18–5.35 (Mukhopadhyay *et al.* 2013). Available nitrogen in the sites increased significantly with the age of the vegetation from 39–109 mg kg^{-1}. Approximately 64% of nitrogen increment was observed at the climax of vegetation establishment at site 3. In a study reported by Maiti, S. K., Maiti, D. (2015) a nitrogen level of 34–72 mg kg^{-1} was developed under grass legume vegetation while their reference site (nearby forest area) had approximately 100 mg kg^{-1} of available nitrogen. The presence of dense cover of *S. spontaneum* in site 2 incorporated fine root litter from its extensive root system which may be accountable for the increase in soil nitrogen after 2 years significantly similar to the restored site 3. Analogous to this the average ground cover biomass of the sites also had a significantly increasing trend (135–400 g per plant) with the age of vegetation (Fig. 3). Loss on ignition of the sites varied significantly from 3.7–18%. High value of loss on ignition in site 2 was probably due to mixing with mine soil. The proof of this statement relies on the fact that the loss on ignition value of the original fly ash (also used for pot scale study in this paper) used for filling the mine pit of site 2 is 5.55%. On the other hand the surface rhizospheric samples of site 1 and 2 had water holding capacity of nearly 64% while site 3 had a water holding capacity of 38%. The rhizospheric samples from site 3 were predominantly the topsoil which had been used to blanket the fly ash dump prior to the ecorestoration programme. High water holding capacity of fly ash compared to soil is attributed to the large surface area of the spherically shaped particles of fly ash which increases microporosity (Shaheen *et al.* 2014).

3.3. Metal accumulation in plants

Metal accumulation in the dominant plant species growing on two different aged fly ash dumps have been reported based on their yield in Table 2. The metal content in the plants were multiplied with the biomass data. Similar dominant plant species were chosen from the sites undergoing natural succession (site 1 and 2) to differentiate the metal accumulation under different conditions. *S. sponatneum* has been found to be more efficient and accumulated more amounts of metals than *C. dactylon*

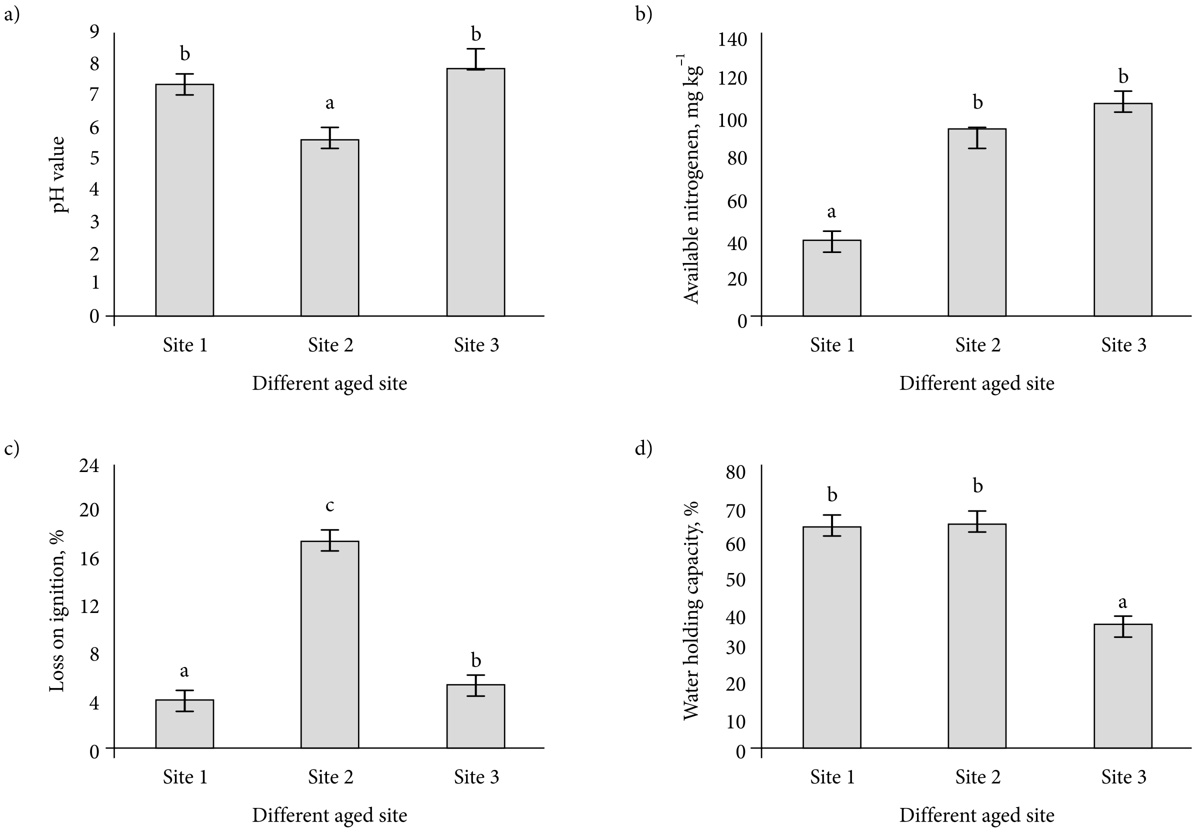


Fig. 2. Physicochemical parameters of rhizospheric samples from different aged fly ash dump sites such as pH (a); available nitrogen (b); loss on ignition (c); water holding capacity (d) for n = 7 replicates. The deviation between the data for each individual parameter for a site has been shown as error bars. Different alphabetical letters above each bar for a graph depict significant differences between the means at $p < 0.05$

due to its greater biomass. Bioaccumulation factor of Cr (4.21–77.27) and Pb (2.20) was found greater than 1 as indicated by bold letters in Table 2. Metal concentration in the plants increased with the age of the vegetation as also obvious from the higher values of metals in *S. spontaneum* from site 2 than in site 1. This is also evident from the data that toxic metals such as Cd, Ni, Pb, and Cr content varied from 0.01 to 0.05 mg/kg, 1.58 to 4.14 mg/kg, 0.30 to 0.58 mg/kg, 32.34 to 48.75 mg/kg in *S. sponatneum* which is approximately 80–90% more in site 2 than site 1. Even though, bioaccumulation factor of Cr in *C. dactylon* from site 1 was found highest (77.27) from site 2 (4.21) which are approximately 18 folds that of the later. Further, *S. spontaneum* also showed a twofold higher bioaccumulation factor for Cr in site 1 than site 2. Metal accumulation in plants also depends on pH, metal concentration in substrate, and differential response of each species to detoxify metals (Gupta *et al.* 2002).

Accumulation of metals in plants varied in the order Cr > Mn ~Zn > Cu ~ Ni > Pb > Cd and Mn ~ Cr > Zn > Ni > Cu > Pb > Cd respectively in site 1 and 2, which varied irrespective of the concentration of metals in fly ash. This was further proved by Figure 4 showing the dendrogram (between groups) obtained using hierarchical cluster analysis with pearson distance. It helps in showing the pattern of metal accumulation in plants from site 1 and 2. Here, Mn and Zn are in the same cluster linked with Cr showing that fly ash is contributing to elevated Cr levels in plants. Cr has also been found to be linked distantly with Ni whereas other metals such as Pb, Cd and Cu have been found in separate groups. Linkage of Cr and Ni are due to their nature of being transitional elements (Das *et al.* 2013). Metal accumulation by yield of Pb and Cd was found to be low in all the cases inspite of unit bioaccumulation factor of Pb in *C. dactylon*. The above results efficiently demonstrate that on virtue of its high biomass production potential *S. spontaneum* can be used for phytoextraction of some metals and subsequently phytoremediate metal contaminated sites.

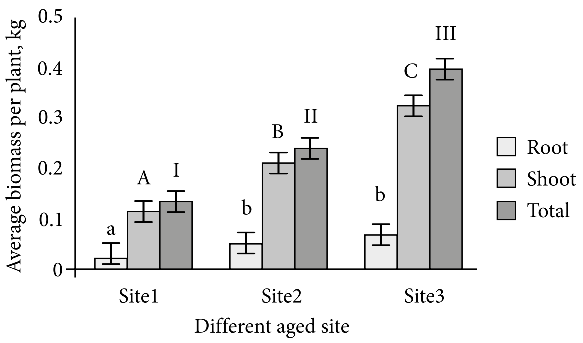


Fig. 3. Average shoot, root and total biomass per plant at different aged fly ash dump sites for $n = 7$ replicates. Different lowercase, uppercase and roman letters above each type of bar represent significant difference between the means for the parameter at $p < 0.05$

3.4. Growth of aromatic grass on amended fly ash with emphasis on leaching studies

In an another study we have found that lower rate of amendment application in fly ash such as 2–5% farmyard manure as well as 5–10% topsoil enhances the growth and biomass of perennial aromatic grass *Cymbopogon citratus*. *C. citratus*, also called lemon grass propagates through old tillers and was chosen for initial plantation in the pots as per literature studies. Maiti, S. K., Maiti, D. (2015) found it to be very promising on waste dumps of a sponge iron plant, in a field study. In this study, the grass grew to a height of more than 50 cm after 45 days of tiller plantation. It has deep fibrous root system which holds the fly ash particles and prevents its erosion (Fig. 7). A single plant produced approximately 30–40 tillers after 3–4 months of growth which usually follows a sigmoid-shaped curve.

Table 2. Metal accumulation in dominant plant species growing on different aged fly ash dump sites (mg kg^{-1}), bioaccumulation factors, and concentration in the rhizospheric fly ash samples (mg kg^{-1})

Parameters	Field site	Plant species	Metal						
			Mn	Cu	Zn	Cd	Cr	Ni	Pb
Accumulation in plants (mg kg^{-1})	1	*Cynodon dactylon*	4.60	0.53	5.35	0.01	12.17	1.04	0.46
	2	*Cynodon dactylon*	9.79	0.64	3.59	0.01	6.46	0.93	0.18
	1	*Saccharum spontaneum*	7.72	3.11	6.44	0.01	32.34	1.58	0.30
	2	*Saccharum spontaneum*	28.30	2.71	13.30	0.05	48.75	4.14	0.58
Bioaccumulation factor	1	*Cynodon dactylon*	0.12	0.29	0.54	0.28	77.27	0.39	2.20
	2	*Cynodon dactylon*	0.44	0.29	0.71	0.34	4.21	0.30	0.37
	1	*Saccharum spontaneum*	0.11	0.47	0.28	0.07	8.99	0.18	1.02
	2	*Saccharum spontaneum*	0.39	0.30	0.52	0.22	2.33	0.24	0.29
Average concentration in rhizosheric FA (mg kg^{-1})	1		255.51	15.69	71.04	0.43	4.93	22.35	1.52
	2		174.65	19.14	49.73	0.38	29.63	32.26	4.18

Commercially, multiple harvesting is generally done after 3.5 months for oil extraction (Akhila 2010). Thus the plants were harvested after 4 months and noticeably the root: shoot biomass ratios were within the range of 0.8–0.9 (Fig. 5). Highest ratio was observed in treatments with combination of amendments (both top soil and farm yard manure). Moreover, destructive harvest of lemon grass at the end of 4 months showed formation of a vigorous root mass in the shape of a basket around the fly ash as shown in Figure 7a.

3.5. Ions and metals in leachates obtained from fly ash treatments

Values obtained from analysis of the leachate samples from fly ash treatments had been compared to the standard drinking water specifications (BIS 10500: 1991). The change in these samples during the growth period of the grass has been represented in Figure 6a–n. Significant differences among the means of the parameters has been shown in Table 5 (supplementary section) to maintain clarity in the corresponding Figure 6a–n. It was observed that garden soil had a significant decreasing effect initially on pH (Fig. 6a) and alkalinity (Fig. 6e) due to its acidic nature. The pH of the control leachate was significantly higher than the other treatments all throughout the growth period may be partially due to high root growth of the grass in them (Maiti, Prasad 2016). Overally pH of 2nd leachate was higher than 1st leachate possibly due to consumption of protons during dissolution of glassy amorphous silicate minerals present in the fly ash (Seoane, Leiros 2001). The combined treatments having both fly ash and garden soil showed the lowest pH (6.97–7.2) in the later stages leachate again. Studies also suggest that grass roots promote weathering of fly ash and act to loosen the fly ash surface by excretion of saccharides (Neuschutz *et al.* 2010). Houben *et al.* (2012) stated that addition of manure increases leachate pH which was also found in our study, while Oste *et al.* (2002) concluded that addition of organic amendments reinforces alkalinity in leachates. Though in our study alkalinity was not alarming and was below the desirable limit. Leaching of ions and metals were observed at a significantly greater level in the first leachates as also supported by positive correlation among cations and anions with electrical conductivity which was primarily due to addition of farmyard manure (Fig. 6b). Electrical conductivity decreased to 275–544 and 197–327 μS cm^{-1} in the 2nd leachate and 3rd leachate respectively. Neuschutz *et al.* (2010) also observed decreasing electrical conductivity in pots with plant growth as they decrease the release of secondary minerals.

Control leachate had the least total hardness (TH) (96–214 mg L^{-1}) and total dissolved solid (TDS) (149–455 mg L^{-1}), chloride (26–320 mg L^{-1}) and sulphate

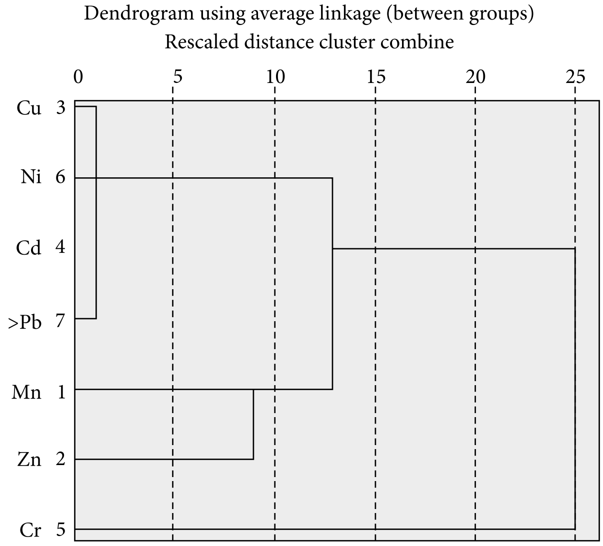


Fig. 4. Hierarchical dendrogram showing clustering of different metals in plants using Pearson correlation as distance and group linkage methods

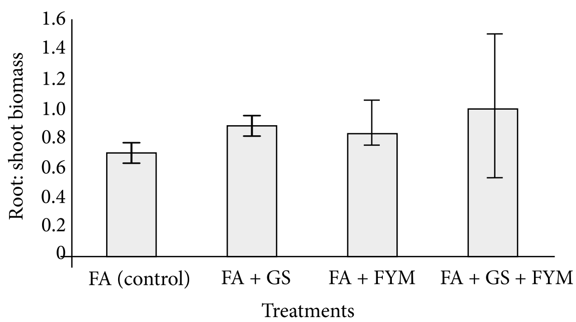
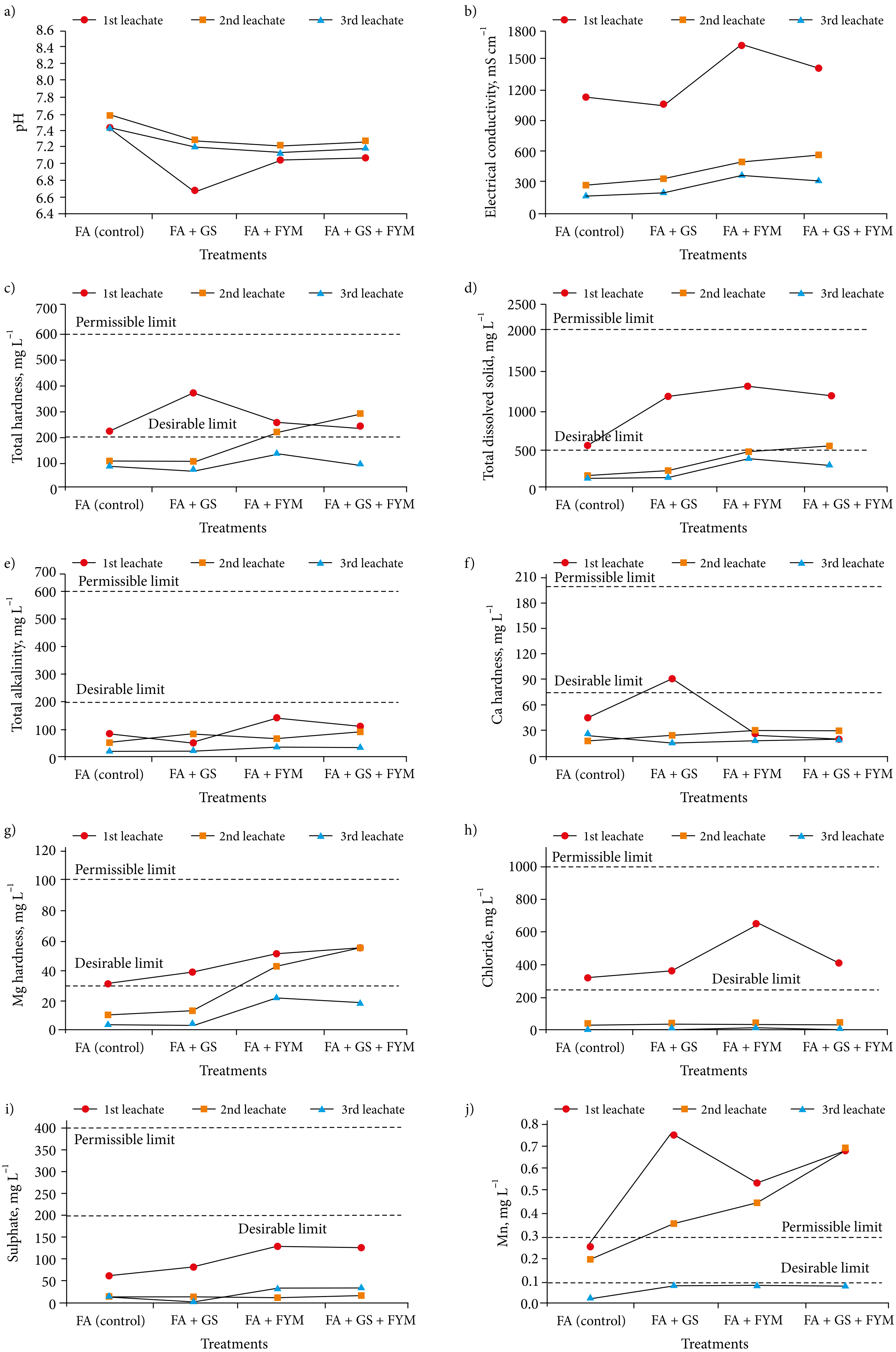


Fig. 5. Root is to shoot biomass ratio of *Cymbopogon citratus* grown of fly ash treatments compared to control having no amendments

(19–59 mg L^{-1}) in all the collection periods while treatment leachates had values marginally below the permissible limit in 1st leachates which went below desirable limit in 3rd leachate (decreased by 80%) (Fig. 6c, d, h, i). On comparison with the control the level of TDS was significantly higher in the treatment leachates and significantly positively correlated to other parameters (Table 3). Leaching of anions from treatments having high level of amendments was mainly due to the presence of high concentration of salts in them also observed by Shimozono *et al.* (2007). Mukhtar *et al.* (2003) in their study used high rate of application of farmyard manure as soil amendments which gave apparently high level of total solids in leachates and therefore they also recommended low rate application of farmyard manure to prevent groundwater contamination.

It is known that Ca is the most largely released cation from fly ash and this depends on its mode of occurrence


a)
1st leachate
2nd leachate
3rd leachate
pH
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
FA (control)
FA + GS
FA + FYM
FA + GS + FYM
Treatments
b)
Electrical conductivity, mS cm^{-1}
1800
1500
1200
900
600
300
0
c)
Total hardness, mg L^{-1}
700
600
500
400
300
200
100
0
Permissible limit
Desirable limit
d)
Total dissolved solid, mg L^{-1}
2500
2000
1500
1000
500
0
e)
Total alkalinity, mg L^{-1}
f)
Ca hardness, mg L^{-1}
210
180
150
120
90
60
30
0
g)
Mg hardness, mg L^{-1}
120
100
80
60
40
20
0
h)
Chloride, mg L^{-1}
1000
800
600
400
200
0
i)
Sulphate, mg L^{-1}
400
350
300
250
200
150
100
50
0
j)
Mn, mg L^{-1}
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

→

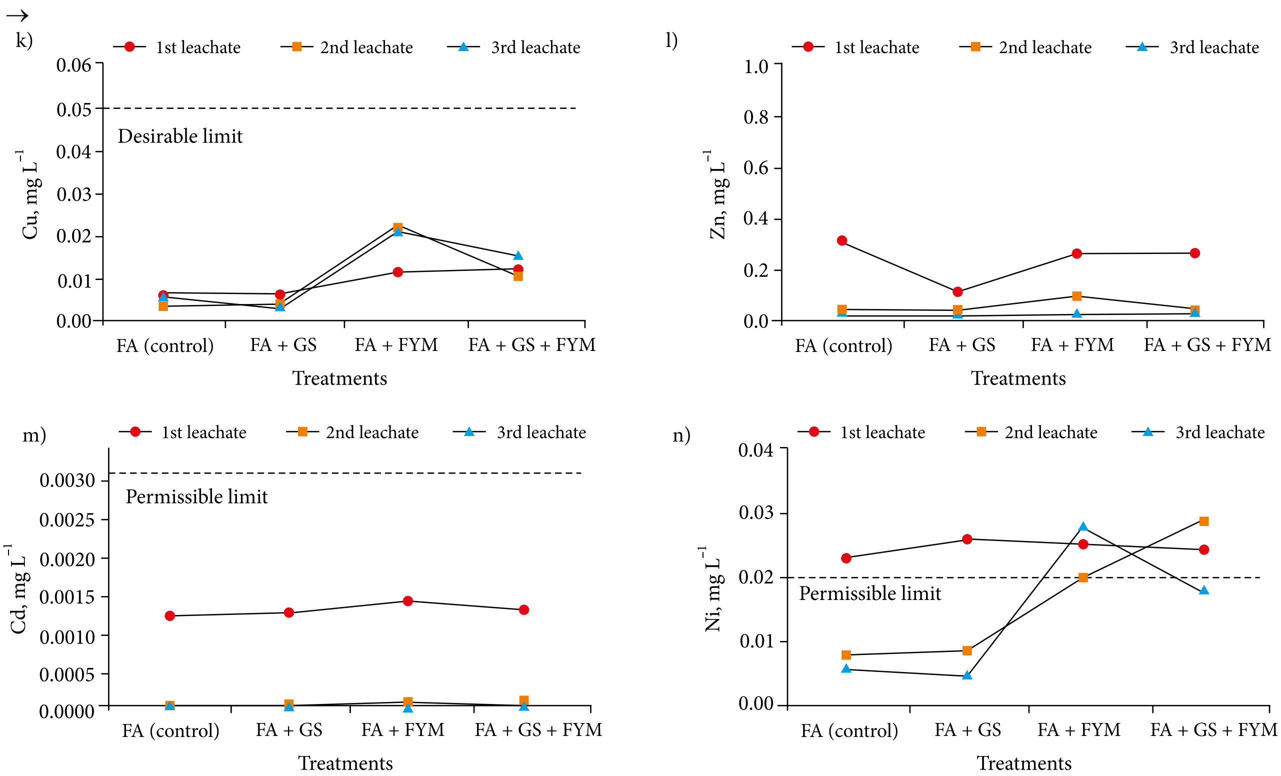


Fig. 6. Characteristics of pot leachates collected at 1st (initial stage), 2nd stage (3rd month), and 3rd stage (4th month or harvest stage) during growth of *Cymbopogon citratus* on amended fly ash; pH (a) electrical conductivity (EC) (b); total hardness (TH) (c), total dissolved solid (TDS) (d) total alkalinity (e), calcium hardness (Ca H) (f), magnesium hardness (Mg H) (g), chloride (h); sulphate (i) Mn (manganese) (j), Cu (copper) (k), zinc (Zn) (l), cadmium (Cd) (m), nickel (Ni) (n)

(Izquierdo, Querol 2012). Unlikely in this study, Ca H in all the leachates had a value marginally below desirable limit but a wider variation in release of Mg was observed (Fig. 6f, g). The pond ash samples collected for the pot study was taken from ash ponds which had already been weathered of the Ca present in it, probably because of being under the influence of water for a long time. Generally, Ca concentration in alkaline FA (like in this study) decreases in a matter of 10 weeks due to precipitation in secondary minerals (Neupane, Donahoe 2013). Ahmad *et al.* (2009) in their study had concluded that addition of farmyard manure increases leaching of Mg when compared to other composts. Release of Mg in this study was also significantly affected by the addition of garden soil and manure and was more pronounced in the combined treatments. Leaching of Mg continued till the 2nd leachate found above desirable limit and subsequently went down after 4 months in the 3rd leachate.

Amidst all the major cations and anions trace metals are most toxic due to their long term persistence (Prasad, Maiti 2016). In this study metals which have been considered are Mn, Cu, Zn, Cd, Ni, Cr, and Pb. Release of these metals in the leachates would finally contaminate the ground water and it was discerned that toxic metals like Pb and Cr were below instrument detection limit throughout the pot study. Further, metal concentration was negatively correlated with leachate pH (Table 4). Cd concentration in 1st leachates (0.0012–0.0013 mg L^{-1}) was also below acceptable limit and subsequently declined below instrument detection limit in 2nd and 3rd leachates (Fig. 6 m). Cd was also not significantly different in the leachates at 1st stage.

Among the metals which act as micronutrients for instance Cu and Zn, leached out in a concentration below acceptable limit (Fig. 6 k, l). Level of Zn in the leachates was not significantly different and was in the range 0.116–0.268 mg l^{-1}, 0.033–0.1 mg L^{-1} and 0.029–0.034 mg L^{-1} in 1st, 2nd and 3rd stage respectively, while the concentration decreased in the successive stages. It was noteworthy that Cu was significantly higher in 2nd (0.022 mg L^{-1}) and 3rd (0.023 mg L^{-1}) leachates from the treatments with only farmyard manure as amendments, while there was no observable decrease in the concentration from initial to final leachate concentration. Mixing of garden soil with farmyard manure complexes or precipitates the metals thus prohibiting their probable release. This may also be due to inherent presence of Cu in organic matter as farmyard manure itself contains high levels of nutrients.

Contrary to this, Mn in the leachates was above acceptable limit in the 1st and 2nd leachates. Though the control leachate (only fly ash) depicted Mn

(0.034–0.246 mg L^{-1}) above acceptable limit which indeed shows the intrinsic property of the fly ash to release loosely bound Mn, added to this the leachates obtained from amended treatments further had significantly higher concentration of Mn (0.087–0.753 mg L^{-1}) above permissible limit. This also exhibited that garden soil and farmyard manure contributed to the Mn release in the samples (Fig. 6j). Even among the amended treatments, pots with only garden soil showed significantly highest Mn leaching in 1^{st} stage. Noticeably in the 3^{rd} leachates Mn was found marginally below the acceptable limit (0.1 mg L^{-1}). Ni concentration also varied arbitrarily in the 3 stages and was significantly above permissible limit in the amended treatments when compared to the control (0.006–0.023 mg L^{-1}). More amount of the metal was observed in those treatments with only garden soil (0.004–0.026 mg L^{-1}) or farmyard manure (0.020–0.027 mg L^{-1}) which shows the presence of Ni in garden soil as well as farmyard manure. In fact, garden soil treatments showed a peak concentration of Ni in 1st leachates which lowered down in later stages whereas farmyard manure treatments gave constant elevated levels of Ni in all the stages. Yet treatments with both the amendments (garden soil and farmyard manure) depicted concentration below permissible level till the end exhibiting some precipitation of Ni. Metal levels in the leachates also showed some significant positive correlations between Mn, Ni; and Cu, Ni likewise observed by Edet and Offong (2002) in their study.

Table 3. Correlation between general parameters analyzed in leachate samples (n = 81)

	EC	TH	TDS	Ca H	Mg H	Cl	SO_4
EC	1						
TH	0.55**	1					
TDS	0.88**	0.61**	1				
Ca H	0.26*	0.79**	0.29**	1			
Mg H	0.64**	0.92**	0.70**	0.49**	1		
Cl	0.93**	0.44**	0.82**	0.26*	0.49**	1	
SO_4	0.89**	0.43**	0.83**	0.07	0.57**	0.85**	1

Notes: EC: electrical conductivity, TH: total hardness, TDS: total dissolved solid, Ca H: calcium hardness, Mg H: magnesium hardness, Cl: chloride, SO4: sulphate.
*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

Table 4. Correlation between metals analyzed in leachate samples (n = 81)

	pH	Mn	Cu	Zn	Cd	Ni
pH	1					
Mn	–0.19	1				
Cu	–0.13	0.05	1			
Zn	–0.19	0.14	–0.09	1		
Cd	–0.38**	0.26*	–0.09	0.61**	1	
Ni	–0.15	0.65**	0.56**	0.13	0.15	1

Notes: *Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed).

a) b)

Fig. 7. Growth of lemon grass after 4 months of plantation (a), massive root growth of lemon grass which stabilizes the fly ash (b)

Moreover, at the time of harvest, leachates (3L) of all the treatments had homogeneous values for all parameters below or marginally around the desirable limit which is not an alarming issue regarding ground water contamination. Fly ash is known to have sufficient quantities of inorganic nutrients which can support plant growth. Therefore addition of lower percentage of easily available NPK supplements in the form of garden soil and farmyard manure can boost the growth of economically valuable aromatic grasses. Further, in previous studies workers have used high rate of amendments for ecorestoration of contaminated sites which can drastically affect the water quality beneath the ground. In this study the treatment with farmyard manure have proved their efficiency by enhancing the growth of *C. citratus* i.e high root: shoot biomass ratio. They can be successfully implemented in the field for revegetation of fly ash dumps without any possibilities of ground water contamination.

Conclusively, the perennial nature of *C. citratus* (Fig. 7b), unpalatability to grazing animals and high commercial end uses makes it an efficient plant species for restoration of fly ash disposal sites.

Conclusions

A reclamation strategy of fly ash disposal sites encompasses discussion on fly ash characteristics, followed by selection of type of amendment and its application rate as well as the plant species. Native and invasive species are an effective choice at initial stages. Apart from increment in fertility of the sites, fly ash surface stabilisation was adequately achieved which was the foremost goal in this context. This was proved from the present status of fly ash dumps in Damoda abandoned mines. Despite of less after care and maintenance species such as *Cynodon dactylon, and Saccharum spontaneum*, were found to colonize the dump creating a thick vegetation mat. Metal bioaccumulation studies proved that on virtue of high biomass potential of *Saccharum spontaneum* than *C. dactylon* it can also be used as phytoextractor of toxic metals and thus phytoremediate the metals in fly ash. Added to this, the pot scale study with amended fly ash showed that *Cymbopogon citratus* efficiently grew in low nutrient conditions and stabilized the fly ash volume through its extensive root system. It is another fruitful choice for revegetation of fly ash disposal sites. Initial leaching studies on the treatments have also supported the effectiveness of the dual amended treatments to be used in the field. The ephemeral effects on leachates due to addition of farm yard manure diminished in a matter of 4 months and acceptably the values were below permissible limit as per drinking water standards. A properly planned reclamation programme can thus be made by incorporating economically useful plant species such as *C. citratus* at later stages. Lastly a regular monitoring schedule is of prime importance in each restoration programme which will help in predicting long term change in fly ash properties due to vegetation and guide the future steps to improve the status of the sites.

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