Determination of Some Heavy Metals Speciation Pattern in *Typha domingensis* Invaded Soil in Bauchi Metropolis, Nigeria

By

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ABSTRACT

The speciation of some heavy metals in Typha domingensis invaded soil along Gombe road, Bauchi were evaluated. Soil samples from the Typha domingensis invaded soil and the control site were collected and analyzed for exchangeable bound metals, carbonate bound metals, manganese bound metals, iron-manganese bound metals, organic/sulphide bound metals and residual bound metals using standard procedures. The results of the Typha domingensis invaded soil were found to be exchangeable bound metals: iron (1.47 ± 0.20 mg/dm^3), zinc (1.45 ± 0.02 mg/dm^3) and lead (0.16 ± 0.04 mg/dm^3), carbonate bound metals: iron (26.10 ± 1.01 mg/dm^3), zinc(2.66 ± 0.17 mg/dm^3) and lead (0.89 ± 0.03 mg/dm^3), manganese bound metals: iron (14.50 ± 0.45 mg/dm^3), zinc(4.03 ± 0.78 mg/dm^3) and lead(1.22 ± 0.06 mg/dm^3), iron-manganese bound metals: iron (120.40 ± 19.15 mg/dm^3), zinc(6.79 ± 1.12 mg/dm^3) and lead (2.16 ± 0.05 mg/ dm^3), organic/sulphide bound metals: iron (5.90 ± 0.50 mg/dm^3), zinc(4.14 ± 0.68 mg/dm^3) and lead (3.58 ± 0.07 mg/dm^3), while residual bound metals: iron (13.10 ± 0.55 mg/dm^3), zinc(6.12 ± 0.17 mg/dm^3) and lead (4.48 ± 0.09 mg/dm^3).The results of the control soil sample (without Typha domingensis) showed the exchangeable bound metals: iron (9.40 ± 1.89 mg/dm^3), zinc (1.71 ± 0.45 mg/dm^3) and lead (0.28 ± 0.05 mg/dm^3), carbonate bound metals: iron (0.70 ± 0.12 mg/dm^3), zinc (2.20 ± 0.71 mg/dm^3) and lead (0.46 ± 0.12 mg/dm^3), manganese bound metals: iron (2.50 ± 0.21 mg/dm^3), zinc (1.90 ± 0.09 mg/dm^3) and lead (1.68 ± 0.04 mg/dm^3), iron-manganese bound metals: iron (221.30 ± 21.12 mg/dm^3), zinc (7.46 ± 0.48 mg/dm^3) and lead (2.75 ± 0.06 mg/dm^3), organic/sulphide bound metals: iron (4.20 ± 0.62 mg/dm^3), zinc (3.70 ± 0.80 mg/dm^3) and lead (3.93 ± 0.04 mg/dm^3) and residual bound metals: iron (30.10 ± 5.80 mg/dm^3), zinc (7.38 ± 0.61 mg/dm^3) and lead (0.53 ± 0.03 mg/dm^3) respectively. Statistical analysis using pooled standard deviation method of computing t indicated significant difference in all the fractions ($p \leq 0.05$). This research work showed that the plant (Typha domingensis) have negative impacts on the soil samples.

Keywords: Speciation, *Typha domingensis*, exchangeable bound metals, carbonate bound metals, manganese bound metals, iron-manganese bound metals, organic/sulphide bound metals, residual bound metals and pooled standard deviation method.

INTRODUCTION

Soil is a heterogeneous mixture of organic and inorganic substances. The binding mechanisms for metals vary with the composition of the soil. The ecological effects of heavy metals in soil are closely related to the distribution of species in the solid and liquid phases of the soil. The presence of heavy metals in soil is of great ecological significance owing to their toxicity at certain concentrations through food chains and non-biodegradability which is responsible for their accumulation in the bio-sphere. Heavy metals like iron, tin, copper, manganese and vanadium occur naturally in the soil and could serve as plant nutrients depending on their concentrations (Opaluwa, 2012).

The levels of heavy metals in the soil have been seriously increased during the last decades due to human activities. Metals like mercury, lead, cadmium, silver, chromium and many others that are indirectly distributed as a result of human activities could be very toxic even at low concentrations. Soil management is the basis of sustainable agricultural production. In the tropical soils, most soil nutrients required by plants especially nitrogen, potassium, phosphorous, calcium and magnesium are often found deficient at the root zones (Kolo *et al.*, 2009).

Since the toxicity of heavy metals is increasingly attracting more attentions, soil organic matter and Fe – Mn oxide have been found to be the most important soil properties and components influencing the biological optics of heavy metals (Calmano *et al.,* 2001). Depending on their origin, trace elements exist in different mineral forms and chemical com-pounds in different combinations with mineral and organic components of the soil and sediments which may vary according to various conditions (Calmano *et al.,* 2001).

Typha domingensis which is the species that is widespread in Bauchi is considered to be among the first wet-land plants to colonize areas of newly exposed wet mud, with its abundant wind dispersed seeds. It survives in the soil for a long period with buried seeds (Albertoni *et al.,* 2005). It also germinates best in sunlight and fluctuating temperatures which is typical of many wetland plants that regenerates on mud lands. It spreads by rhi-zomes, forming large interconnected stands.

Sanders *et al.* (1999) used the ion exchange equilibrium technique to determine complexed forms of Co, Mn and Zn in aqueous extracts of five soils. Olumu *et al.* (1973) found that practically all the soluble iron in some blooded soils was complexed with organic matter, whereas manganese was either not complexed or weakly complexed. Cottenie *et al.* (1982) used the combination of *cation* and *anion* exchange resins to determine the species of selected metals in soluble fractions of a sandy soil. Based on their findings, copper and iron were largely present as stable complexes, manganese being largely present in the free ionic form, while zinc was evenly distributed between the two forms. Due to human and industrial activities, the presence and concentration of heavy metals tend to in-crease in areas where they were not present some years ago. Today, gross symptoms of some heavy metal poisoning are seldom met except in those that are exposed to extreme occupational hazards. This has given reason to seek out ways to remedy the presence of these metals in the soil. The aim of this research work is to determine iron, zinc and lead in *Typha domingensis* invaded soil in Bauchi in the following fractions: Exchangeable bound metals (F1), carbonate bound metals (F2), manganese oxide bound metals (F3), iron-manganese oxide bound metals (F4), organic/sulphide (F5) and residual bound metals (F6) respectively.

MATERIALS AND METHODS

In the preparation of all the solutions that were used in the research work, chemicals of analytical reagent grade purity and distilled water were used throughout the study. All the glass and plastic wares used in the research work were thoroughly washed with detergent solution, followed by 20.00 % (v/v) trioxo-nitrate (V) acid, rinsed with tap water, distilled water and finally with the solution that was used in them. The apparatus were then allowed to dry (Hassan *et al.*, 2017a).

Collection of Samples

Soil samples were collected in polythene bags using auger from *Typha domingensis* invaded soil along Gombe road, Bauchi. Samples were taken randomly round the invaded soil from a depth of 0-30 cm. The control soil samples (without *Typha domingensis*) were also ran-domly taken few metres away from the *Typha domingensis* invaded soil. The samples both from the sampling location and control were brought to the laboratory.

Determination of Metals

The concentrations of iron, zinc and lead prepared as shown in the various sections were determined from the soil extracts using a BUCK SCIENTIFIC Atomic Absorption Spec-trophotometer Model 210 VGP. The Spectro-photometer was calibrated by aspirating standard salt solutions of iron, zinc and lead se-parately at their various wavelengths using acetylene-air mixtures in a ratio of 6:8. Measurements were made after calibration, instrument settings optimized and blue flame obtained. The concentrations of analytes were obtained automatically from the readout on extrapolation of the absorbance of the analytes from the calibration curve by the machine, while maintaining the same condition for both soil samples and the control soil samples.

Sample Pre-treatment

Soil samples(both soil and control samples) were air-dried in the laboratory before being crushed in a ceramic pestle and mortar and sieved in a 2mm screen plastic sieve. The soil samples were stored in plastic bottles and labeled appropriately. The metals were fractionated using the methods of

Elsokkary *et al.* (1980) and Tessier et *al.* (1999). The metal species were classified into six fractions (both soil and control) as indicated in table 1 below:

Table 1: Classification of Metal Species into Six Fractions

Fractions (Soil and Control)	**Symbols**
Exchangeable metals	F1
Carbonate bound metals	F2
Manganese oxide bound metals	F3
Iron-Manganese oxides bound metals	F4
Organic/sulphide bound metals	F5
Residual bound metals	F6

Determination of Exchangeable Metals

A 1.00 g of the soil sample was weighed into a 250cm^3 conical flask and 10.00 cm^3 of 1.00 M sodium acetate solution was added. The pH was adjusted to 8.7 by the addition of acetic acid. The mixture was shaken for 2 hours using Edmund Bahler Swip Mechanical Shaker, filtered into a 100 cm^3 volumetric flask using Whatman Filter Paper Number 1. The filtrate was made up to the mark with water. The metals were determined using Atomic Absorption Spectrophotometer (AAS) and the residue was reserved for further fractionation.

Determination of Carbonate Bound Metals

The residue from the exchangeable metals was leached for 3 hours with sodium acetate solution and the pH adjusted to 5.0 using acetic acid. The leachate was transferred into a 100cm^3 volumetric flask and made up to the mark with water. The leachate was analyzed for metals for metals of interest using AAS and the residue reserved for further analysis.

Determination of Manganese Oxide Bound Metals

The residue from the carbonate bound soil was leached with 10.00 cm^3 of 0.10M hydroxyl-amine hydrochloride and 0.01M nitric acid (adjusted to a pH of 2.0 with acetic acid) after shaking for 3 hours using Edmund Balder Swip Mechanical Shaker. The leachate was quantitatively transferred into a 100cm^3 volumetric flask and made up to the mark with water. The leachate was used to analyze metals of interest using AAS. The residue was reserved for further analysis.

Determination of Iron-Manganese Oxide Bound Metals

The residue from the manganese oxide bound soil was extracted using 10.00 $cm^3$of oxalate buffer of pH 3.0 after shaking for 12 hours at 90°C in a water bath. The extract was filtered into a 100 cm^3 volumetric flask and water added to mark. The extract was also analyzed for the metals of interest using AAS. The residue was again reserved for further analysis.

Determination of Organic Matter-Sulphide Bound Metals

The residue from the iron-manganese oxide bound soil was extracted by shaking with 100.00 $cm^3$of 30.00 % hydrogen peroxide solution. This was adjusted to a pH of 2.0 by the drop-wise addition of nitric acid and heat for 6 hours at 90°C in a water bath. This was re-extracted at room temperature with 10.00 $cm^3$of 1.00 M ammonium acetate solution and the pH still maintained at 2.0. After shaking for three (3) hours, the first extract of the mixture was filtered using Whatman Filter Paper Number 1 into a 100 cm^3 volumetric flask and water added to mark. The extract was analyzed for metals using AAS and the residue reserved for further analysis.

Determination of Residual Metals

The residue from the organic and sulphide bound soil was digested with 10.00

$cm^3$of aqua-regia by heating in a digestion tube at a temperature of 250°C. The clear digest was removed and allowed to cool before transfer-ring quantitatively into a 100 cm^3 volumetric flask. This was then made up to the mark with water and the solution analyzed for the metals of interest.

RESULTS AND DISCUSSION

Results

The results from the sequential extraction carried out on the *Typha domingensis* invaded soil were classified into the following fractions: exchangeable, carbonate bound, manganese oxide bound, iron-manganese bound, organic matter/sulphide and residual fractions are presented in Table 2, while the results of the control soil samples are equally presented in Table 3.

Table 2: Speciation Pattern of Some Heavy Metals (mg/dm^3) in *Typha domingensis* Invaded Soil

Fractions	**Metal Concentrations**		
	Fe	**Zn**	**Pb**
Exchangeable bound metals	1.47 ± 0.20	1.45 ± 0.02	0.16 ± 0.04
Carbonate bound metals	26.10 ± 1.01	2.66 ± 0.17	0.89 ± 0.03
Manganese Oxide bound metals	14.50 ± 0.45	4.03 ± 0.78	1.22 ± 0.06
Iron-manganese bound metals	120.40 ± 19.15	6.79 ± 1.12	2.16 ± 0.05
Organic/sulphide bound metals	5.90 ± 0.50	4.14 ± 0.68	3.58 ± 0.07
Residual bound metals	13.10 ± 0.55	6.12 ± 0.17	4.48 ± 0.09

Values are mean ± standard deviation (n=4)

Table 3: Speciation Pattern of Some Heavy Metals (mg/dm^3) in non-*Typha domingensis* Invaded Soil

Fractions	**Metal Concentrations**		
	Fe	**Zn**	**Pb**
Exchangeable bound metals	9.40 ± 1.89	1.71 ± 0.45	0.28 ± 0.05
Carbonate bound metals	0.70 ± 0.12	2.20 ± 0.71	0.46 ± 0.12
Manganese bound metals	2.50 ± 0.21	1.90 ± 0.09	1.68 ± 0.04
Iron-manganese bound metals	221.30 ± 21.12	7.46 ± 0.48	2.75 ± 0.06
Organic/sulphide bound metals	4.20 ± 0.62	3.70 ± 0.80	3.93 ± 0.04
Residual bound metals	30.10 ± 5.80	7.38 ± 0.61	0.53 ± 0.03

Values are mean ± standard deviation (n=4).

Tables 2 and 3 show the speciation patterns of some selected heavy metals in *Typha domin-gensis* invaded soil and non-*Typha domin-gensis* invaded soil (control) respect-tively. The levels of iron (1.47 ± 0.20 mg/dm^3), zinc (1.45 ± 0.02 mg/dm^3) and lead (0.16 ± 0.04 mg/dm^3) in the exchangeable bound fraction of the *Typha domingensis* invaded soil samples were generally lower than their corresponding control soil sample (without *Typha domingensis)*: iron (9.40 ± 1.89 mg/dm^3), zinc (1.71 ± 0.45 mg/dm^3) and lead (0.28 ± 0.05 mg/dm^3). This may be as a result of the affiliation of the *Typha domingensis* with the exchangeable bo-und fraction and consequently the ability of the exotic plant to phytoremediate the metals in this fraction.

The carbonate bound fraction of the metals in the soil sample investigated (iron: 26.10 ± 1.01, zinc: 2.66 ± 0.17 and lead: 0.89 ± 0.03 mg/dm^3) were generally found to be higher than the control soil samples (iron: 0.70 ± 0.12, zinc: 2.20 ± 0.71 and lead: 0.46 ± 0.12 mg/dm^3) as shown in Tables 2 and 3 respectively. This may be as a result of different buffering capacities associated with the locations (Hassan *et al.*, 2017b). Buffering capacity has been defined as the rate in which some nutrients or elements are converted from a bound to a soluble state (Davidescu and Davidescu, 1982). The values obtained in the *Typha domingensis* invaded soil samples are higher than that of iron (19.76 ± 1.04 mg/dm^3) and zinc (1.87 ± 0.12 mg/dm^3), but in very good agreement to that of lead (0.89 ± 0.08 mg/dm^3) (Uwumaronge *et al.*,2008).

The levels of manganese bound metals in the *Typha domingensis* invaded soil samples as shown in Table 2 revealed that iron and zinc had concentrations of 14.50 ± 0.45 and 4.03 ± 0.78 mg/dm^3 respectively. This implied that these metals were highly distributed in the sampling location as compared to lead (1.22 ± 0.06 mg/dm^3). The concentrations of iron (2.50 ± 0.21 mg/dm^3) and zinc (1.90 ± 0.09 mg/dm^3) in the non-invaded *Typha domingensis* soil samples (control) are lower than the invaded soil samples. This might be as a result of the fact that the location is used as a refuse dump site and the refuse could be responsible for the increased levels of iron and zinc respectively. The level of lead (1.22 ± 0.06 mg/dm^3) in the *Typha domingensis* invaded soil samples were however relatively lower than that observed in the control soil sample.

The concentration of the metals in the iron-manganese bound metals as shown in Table 2 are iron (120.40 ± 19.15 mg/dm^3), zinc (6.79 ± 1.12 mg/dm^3) and lead (2.16 ± 0.05 mg/dm^3) respectively. These values are correspondingly lower than the values of iron (221.30 ± 21.12 mg/dm^3), zinc (7.46 ± 0.48 mg/dm^3) and lead (2.75 ± 0.06 mg/dm^3) respectively (Table 3) found in *Typha domingensis* non-invaded soil samples. The low levels of the metals may be due to the phytoremediation capacity of the noxious plant associated with the iron-manganese bound metals.

The organic matter-sulphide bound fraction of the *Typha domingensis* invaded soil (Table 2) revealed that the levels of iron (5.90 ± 0.50 mg/dm^3) and zinc (4.14 ± 0.68 mg/dm^3) are respectively higher than the corresponding values of iron (4.20 ± 0.62 mg/dm^3) and zinc (3.70 ± 0.80 mg/dm^3) found in non-*Typha domingensis* invaded soil (Table 3). The reason may be due to the non-affiliation of the *Typha domingensis* plant with the organic matter-sulphide bound iron and zinc respectively. The level of lead found in the invaded soil was found to be 3.58 ± 0.07 mg/dm^3, whilst that of the control was 3.93 ± 0.04 mg/dm^3. These values are relatively in close agreement. The values found in this study are also higher than the reported literature values found in refuse dump sites of Awka City, Nigeria: iron, zinc and lead are respectively 3.02 ± 0.32, 1.32 ± 0.12 and 2.01 ± 0.03 mg/dm^3 (Omuka *et al.*, 2009).

The levels of iron (13.10 ± 0.55 mg/dm^3) and zinc (6.12 ± 0.17 mg/dm^3) associated with the residual fraction of the *Typha domingensis* invaded soil are lower than the corresponding and respective values of iron (30.10 ± 5.80 mg/dm^3) and zinc (7.38 ± 0.61 mg/dm^3) in the control soil sample. The low concentration values of these metals (iron and zinc) could be due to phytoremediation ability of the aquatic weed associated with the residual fraction. The level of lead (4.48 ± 0.09 mg/dm^3) in the residual fraction of the soil under test was appreciably higher than the lead (0.53 ± 0.03 mg/dm^3) found in the control site. This could be due to the non-affiliation of the *Typha domingensis* with the lead in the residual fraction.

CONCLUSION

The results of the speciation pattern of some selected heavy metals in *Typha domingensis* invaded soil revealed high levels of most of the metals investigated in the carbonate-bound, manganese-bound and organic-sulphide bound fractions respectively when compared with the control soil sample. The studies further showed low levels of the metals in the exchangeable bound, iron-manganese bound and residual fractions respectively of the sampling location as compared with the control soil sample with only an exception in the residual fraction of lead.

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