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Effects of phosphate on mobility of potentially toxic metals in contaminated soils

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Abstract

Immobilization of potentially toxic metals (PTMs) from contaminated soils using phosphate is one of the remediation measures for controlling leaching of harmful metals in soil into water resources. In this study, sixteen soil samples (4 each) were collected from selected roadsides, farmlands, dumpsites and wetlands for immobilization potential of phosphate on the PTMs at varied pH and phosphate concentrations. PTM concentrations were determined by Atomic Absorption Spectrophotometry and phosphorus concentrations by UV-Visible spectrophotometry. Bioavailable PTMs and bioavailable phosphorus (BAP) were determined before and after immobilization. While the concentrations of total phosphorus in the samples ranged between 8.73 and 204.08 mg kg^{-1} in the order of farmland> dumpsite>roadside> wetland, the concentrations of the PTMs were of the order Zn>Pb>Cr>Cu in roadside soil; Zn>Pb>Cu>Cr in farmland soil; Pb>Cu>Zn>Cr in dumpsites soil and Pb>Zn>Cu>Cr in wetland soil. A decrease in the bioavailable PTM concentration (BAPTM) was observed in all the samples after treatment with dipotassium hydrogen phosphate (K_2HPO_4) at varied concentrations and pH, with Pb being the most immobilized metal. The bioavailable concentrations of Pb and Zn were reduced by more than 80% in all the samples, while the concentrations of bioavailable Cr and Cu were reduced by more than 50% and 70%, respectively. The results showed that immobilization of PTMs using phosphate is an effective strategy for controlling the transfer of harmful metals in contaminated soil into proximate water systems.

Key words: Orthophosphate, Immobilization, remediation, Potentially Toxic Metals

Introduction

Potentially toxic metals (PTMs) such as Cd, Pb, Zn, and Cu are known to be harmful to humans when introduced into their bodies even at low concentrations. Over the years, extensive anthropogenic activities in most urban areas have increased the risk of exposure to PTMs, thereby inducing considerable pressure on the need for safety regulation on the environment and human consumables such as processed foods, especially against the backdrop that these metals are non-biodegradable and toxic above certain threshold concentrations. Once PTMs are absorbed by human, they tend to bio-accumulate in vital organs and tissues (Adekoya *et al.*, 2006; Jannetto and Cowl, 2023) and may induce challenging health complications in the body through disruptions of various biochemical pathways and processes that affect the cardiovascular, circulatory, nervous, and reproductive systems (Jaishankar *et al.*, 2014). The exposure pathways for PTMs into the environment vary from dermal contact with contaminated items, inhalation from air, ingestion of contaminated food and water, leaching from contaminated soil into groundwater and outright mobilization of PTM bearing particulate and organic matter into surface waters (Wuana and Okieimen, 2011; Witkowska *et. al.*, 2012; Masindi and Muedi, 2018).

Soil is a major sink for PTMs released into the environment, and with increasing number of farmlands sited along highways in urban areas such as Lagos, such farmland soils are exposed to PTMs from atmospheric deposition and vehicular activities which may be incorporated into the food chain, and sometimes affect soil quality by altering some of its physico-chemical properties and natural chemistry (Masindi and Muedi, 2018; Rai *et al.*, 2019). Soil mineral, organic matter content (OM) and microbial activities play key roles in determining the speciation, bioavailability and mobility of these metals as the humic and fulvic acids in the soil act as ligands and form complexes with the metals thus limiting their bioavailable (Qu *et al.*, 2019). Insoluble organic matter in roadside soils, originating from exhaust of vehicles, leached asphalt used in road constructions, land use characteristics and other anthropogenic sources have also been reported to influence the concentrations of metals in roadside soils (Guo *et al.*, 2008; Bai *et al.,* 2009; Chen *et al.,* 2010). A study of PTM contamination in roadside soils in Lagos showed that steady industrialization, increasing population and traffic density `contribute to the PTM load in the highway environment with Pb, Zn and Cu contained in the runoffs from these highways (Alo *et al.*, 2007, Abayomi *et al.*, 2011).

Remediation techniques for PTM contaminated matrix depend largely on the chemical and physical properties of the matrix since these influence the mobility and form of the PTMs in the matrix (Lin *et al.*, 2022). Inorganic anions such as CO_3^{2-}, PO_4^{3-}, S^{2-} in a soil matrix also influence the mobilization process by chemical interactions with the PTMs (Caporale and Violante, 2015). Immobilization techniques for remediation of PTM contaminated soils often involve the use of organic and inorganic amendment to alter the chemistry of the soil metals to more geochemically stable phases via sorption, precipitation and complexation processes thereby accelerating the attenuation of the metal's mobility and toxicity in soils (Kumar *et al.*, 2022). Phosphates minerals, microbes, organic composts, clay, cement, and zeolites are common amendments used for contaminants' immobilization in soil by changing the physical characteristics of the contaminated matrix and reducing the mobility of the contaminants (Wuana and Okieimen, 2011).

Immobilization strategy in PTMs polluted soil is aimed to decreasing the bioavailability, bioaccessibility, phytoavailability, and leaching of the metals, thus leading to a reduction in the exchangeable, labile, and water-soluble fractions of the metals in the soil (Palansooriya *et al.*, 2022). The use of phosphate as an immobilizing agent against PTMs in contaminated soil matrixes has been studied for its efficiency (Seshadri *et al.*, 2017). Traina and Laperche (1999) reported that orthophosphate ion forms sparingly soluble solids with several toxic metals including Cd, Zn and Pb with desorption of the metals from their contaminated matrixes leading to the formation of insoluble complexes such as pyromorphites $[Pb_5(PO_4)_3Cl]$ with apatite in situ which resulted in a decrease in the chemical lability and bioavailability of Pb from an initial range of 5 - 100 mg L^{-1} to < 15 μg L^{-1}. Another immobilization strategy for PTMs in soil involved the addition of diammonium phosphate (DAP). Khan and Jones (2008) showed that DAP treatment, when combined with lime or green waste compost was most effective in reducing bioavailability of Pb in copper-mine tailings, while some concentration reduction was observed in Cu, Fe and Zn. Another study on the efficiency of phosphate fertilizers potassium phosphate monobasic (MPP), Calcium superphosphateon (SSP), Calcium phosphate tribasic (TCP) and DAP on Cd showed that immobilization of the metal followed the order: MPP> DAP > SSP > TCP (Yin et al., 2015). Maenpaa *et al.* (2002) also reported that the treatment of soil contaminated by mining activities with KH_2PO_4 and Super Triple Phosphate fertilizer reduced bioavailability of PTMs to earthworm (*Eisenia fetida*). This study aims to investigate the effects of phosphate concentrations on mobility of PTMs in different soil environment with PTM which has implication on the degree of PTM in soluble bioavailable form that could easily be absorbed and accumulated by plants.

Methodology

Sampling

The study was carried out using four different sample pools of roadsides, farmlands, dumpsites and wetlands collected in Lagos. Each sampling pool was made up of four study locations, inclusive of one location of envisaged low PTM contamination (i.e. the Unilag soil environment) (Table 1). Samples were collected within a depth of 0– 30 cm from the soil surface using a plastic spoon. Sixteen (16) soil samples were collected in total i.e. 4 samples from the different georeferenced sample environments for analysis (Fig. 1). The samples were placed in labelled polyethylene bags and kept in a storage bag before been transported to the laboratory where they were air-dried at room temperature. The air-dried samples were passed through a 2-mm mesh stainless steel sieve and stored in well labelled polyethylene bags prior to their analysis (USEPA, 2006; ISO 18400-102, 2017). All sampling materials and containers were soaked in 5% HCl solution, thoroughly rinsed with deionized water and dried before being used. Quality control measures adopted in the laboratory included sample recovery, reagent blank analysis and duplicate sample analysis.

Table 1 Sampled locations and codes

Location	Sample code
Roadside	
Unilag Road	R1
Oshodi	R2
Ojota	R3
Apapa	R4
Farmland	
Unilag	F1
Ojo	F2
Adiyan	F3
Piggery	F4
Dumpsite	
Unilag Dump	D1
Olusosun	D2
Abule-Egba	D3
Isolo	D4
Wetland	
Unilag Lagoon Front	W1
CMS	W2
Oke-Afa	W3
Odo-Iya-alaro	W4

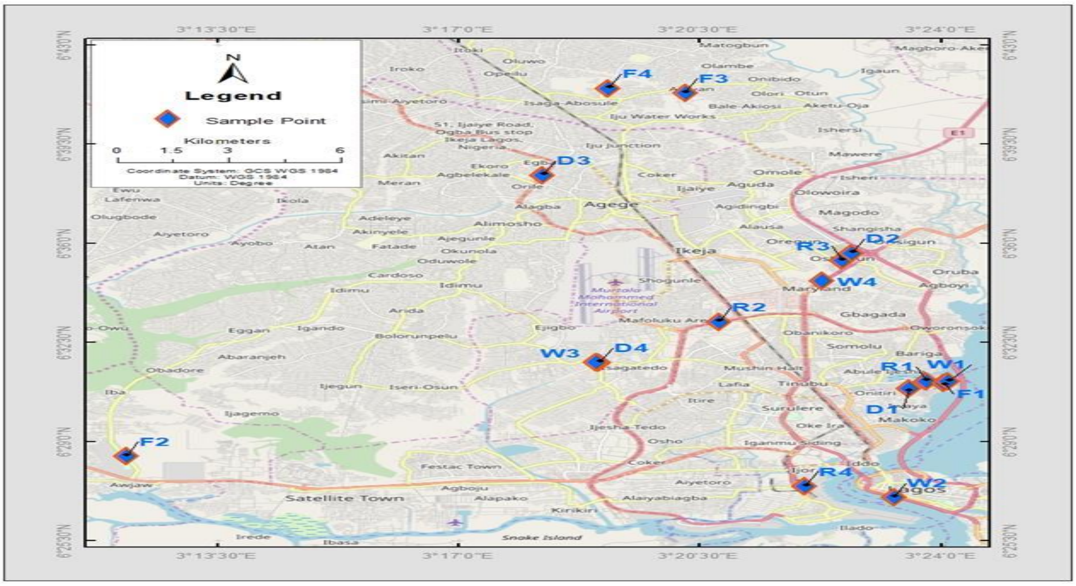

Fig. 1: Geo-referenced Locations of Sampling Locations

Materials and Methods

Soil pH was determined using 1:2 0.01 M calcium chloride solution with a Mettler Toledo pH meter, calibrated with buffers 4, 7 and 9.5. The moisture content (MC) was determined by gravimetry by placing 50 g of the sample in a crucible of known weight and drying to constant weight at 110^{o}C in an oven (Genlab). The sample was allowed to cool in desiccator and MC calculated from the difference in weights of soil before and after drying to constant weight (ASTM D-2216-90). Particle size distribution and sieve analysis were determined using the mechanical and standard hydrometer analysis method by passing soil samples through a set of sieves with progressively increasing diameter size placed on a sieve shaker for 15 min, the mass of soil retained by each of the sieves were determined (Basic Civil Enginnering, 2017). Total organic carbon (TOC) and organic matter (OM) contents were determined using the Walkley-Black wet oxidation method by weighing soil samples between 0.2 and 1 g (depending on the observed organic richness of the sample) into separate conical flasks. A volume of 10 mL standard 0.167 M Potassium dichromate solution and 20 mL of conc. H_2SO_4 were then added in tandem. The mixture was swirled gently and allowed to stand for about 30 mins after which it was diluted with deionized water. Ten millilitres of 85% phosphoric acid and 0.2 g NaF were added with 10 drops of Ferroin indicator just before titrating with standard Fe^{2+} solution to a burgundy end-point. Cation exchange capacity (CEC) of soils was determined using the ammonium acetate method (Poudel, 2020; Gumbara *et al*., 2019).

The bioavailable phosphorus (BAP) was determined by the Olsen P method in which 1 g of soil sample was extracted with 0.5 M $NaHCO_3$ solution at pH 8.5. The mixture of the soil and extractant was placed on a mechanical shaker at 240 rpm for 50 min before being filtered through Whatman filter paper and the phosphate concentration in the extract determined in duplicates by the Murphy and Riley Ascorbic acid – molybdate spectrophotometric method (Oladosu *et al*., 2020). The absorbance of the samples were measured at 880 nm using UV-Visible Spectrophotometer (PG Instruments, T80+). The bioavailable PTM concentration were determined by extracting 1 g of soil sample with 0.5 M HCl solution in a 100 mL Erlenmeyer flask (Peña-Icart, 2014). Total PTMs in soil were determined by digesting 1 g of the sieved soil samples with *aqua regia* (3:1 v/v concentrated HCl : HNO_3) in a kjeldahl flask at 110^{o}C for two hours on a hot plate in a fume cupboard (Melaku et al., 2005; Roje, 2010). The concentrations of the PTMs (Pb, Cr, Cu and Zn) in the digests were determined against standard solutions of the metals prepared as a mixed standard within a concentration range of (0 – 1.0 mg L^{-1}) using the AAS (Perkin Elmer A Analyst 200). Reagent blanks for the extraction and digestion processes were also subjected to the same procedure.

One selected sample from each of the pools (R4, F3, D2 and W4), based on the results of the initial concentrations obtained for the PTMs, was then used for the immobilization study. Dipotassium hydrogen phosphate treatments were evaluated by weighing 2.5 g each of sample into a 100 mL conical flask. Each sample was then spiked with 1.5 mL of K_2HPO_4 solution at concentrations of 0.25 mg L^{-1} PO_4^{3-} / P, 0.50 mg L^{-1} PO_4^{3-} / P and 1.0 mg L^{-1} PO_4^{3-} / P to form slurry and left for 24 hours to allow for adequate contact time for chemical interaction. The 0.5 M HCl extracting solution at variable pH values (6.2, 7.1 and 8.1) was then added to the spiked sample and the mixture shaken on a reciprocating shaker for 30 minutes at 120 rpm. The mixture was allowed to stand for 30 minutes before filtration using Whatman filter paper into clean polyethylene bottles. The bioavailable PTMs concentrations in the filtrates were then determined using AAS. The data obtained was subsequently subjected to statistical analysis.

Results

Physicochemical Properties of the Soil Samples

Results of the physicochemical parameters of the samples are shown in Table 2. The pH values ranged from 5.38 – 7.70 with mean value of 6.98 ± 0.78. While the pH of roadside and dumpsite samples were mostly circum-neutral despite, those of the wetland and farmland soil samples were slightly acidic and may be due to the oxic conditions around these locations, in addition to impacts of effluents released form contiguous industries. Oxic conditions near water-sediment interphase promote the decomposition of organic-based substrate to carbon dioxide which in turn increases the acidity of such environments (Williams, 1992; Maier and Pepper, 2015).

Table 2: Physicochemical Properties of the Selected Soil Samples

Sample	Sample Code	pH	TOC %	OM %	CEC (meq/100g))	MC %	Gravel %	Sand %	Silt %	Clay %
Road Soil	R1	7.70	1.53	1.77	2.52	0.55	0.00	73.4	15.1	11.5
	R2	7.50	1.73	2.29	1.96	0.39	2.00	84.0	12.0	2.0
	R3	7.49	2.50	3.32	2.17	1.41	13.00	67.0	16.0	4.0
	R4	7.66	1.94	2.57	2.95	1.41	25.00	46.0	19.0	10.0
Farmland	F1	6.67	2.99	3.97	5.25	19.23	2.50	54.2	28.6	14.7
	F2	6.72	6.79	9.01	9.47	17.37	4.00	35.3	39.4	21.3
	F3	5.38	6.80	9.03	13.59	15.20	6.00	35.0	20.0	39.0
	F4	7.34	5.48	7.28	7.44	6.20	9.00	69.0	16.0	6.0
Dumpsite	D1	7.23	3.70	4.91	6.44	6.66	7.00	36.0	21.0	36.0
	D2	7.31	3.55	4.71	5.37	8.88	1.00	81.0	16.0	2.0
	D3	7.29	3.45	4.59	4.58	8.58	6.00	35.0	20.0	39.0
	D4	7.13	6.00	7.35	7.68	5.88	9.00	69.0	16.0	6.0
Wetland	W1	6.85	0.34	0.45	2.27	11.46	1.00	94.0	3.20	1.8
	W2	6.72	0.72	0.95	3.11	10.82	2.00	94.0	2.00	2.0
	W3	7.34	4.64	8.00	7.45	23.45	18.00	54.0	18.0	10.0
	W4	5.38	0.50	0.67	2.64	14.48	3.00	90.0	4.00	3.0
Mean		6.98	3.29	4.43	5.31	9.37	6.78	63.6	16.6	13.0
±S.D		±0.70	±2.16	±2.95	±3.25	±6.90	±6.86	±21.3	±9.3	±13.5
Range		5.38-7.70	0.34-6.80	0.45-9.03	1.96-13.59	0.39-23.45	0.00-25.00	35.0- 94.0	2.0-39.4	1.8- 39.0

S.D = Standard Deviation

Total Organic Carbon ranged from 0.34 – 6.80 % with mean of 3.29 ± 2.16% while OM ranged from 0.45% – 9.03% with an overall mean of 4.43 ± 2.95%. The TOC values were lower in the roadside samples but comparatively higher for the farmland followed by dumpsite samples. The lower TOC levels in the roadside is likely due to the fact that exposed roadside soils are likely from dug up soils during road construction or displaced soil from inner streets by vehicular tyres, either ways, these soils tend to have lower TOC and OM concentration (US EPA, 2009). Abayomi *et al.* (2006) had reported similar TOC concentration range in roadside soils of Lagos. The highest was observed in the farmland samples which are due to the rich organic matter composition in the soil of such environment. The lowest MC was observed in the roadside soil pool, R2 (0.39%), while the highest was in the wetland pool, W3 (23.45%). A mean of 9.37 ± 6.90% was obtained across all the sampled locations. All the roadside soil samples had comparatively higher mean sand content, thus indicating the reason for the lower MC as sandy soils generally have low water-holding capacity. The values of the CEC for the samples ranged from 1.96 to 13.59 meq/100 g with a mean of 5.31 ± 3.25 meq/100g. Sample F3 had the highest CEC value, just as it recorded the highest value for OM. The CEC of all the roadside soil samples were also lower in comparison to those of other pools and this may be due to continuous seasonal washing/leaching of roadside soil in paved environment compared to compacted soil environment of the other sample pools (Peters, 2011). The CEC value range of the samples agrees with Rhoades's work (1982) that showed CEC in soils could range from < 3meq/100g, for sandy soils low in OM, to > 25 meq/100g for soils high in certain types of clay or OM.

Concentration of Total PTMs in Soils

The results of the concentration of total PTMs for the sample pools are shown in Fig. 2. The mean range for the pools were Pb 56.88 ± 32.29, Cr 56.59 ± 23.05, Zn 115.76 ± 18.47 and Cu 50.23 ± 24.34 mg kg^{-1} (in roadside soils); Pb 65.93 ± 43.20, Cr 37.39 ± 16.49, Zn 114.56 ± 14.47 and Cu 55.13 ± 7.13 mg kg^{-1}(farmlands); Pb 304.96 ± 316.41, Cr 64.13 ± 65.94, Zn 103.77 ± 18.23 and Cu 181.12 ± 75.94 mg kg^{-1} (dumpsites); and Pb 118.35 ± 99.83, Cr 22.67 ± 24.19, Zn 98.56 ± 27.28 and Cu 33.66 ± 34.39) mg kg^{-1} (wetlands). The order of total metals in the samples were Pb>Zn>Cu>Cr in roadside samples, Zn>Pb>Cr>Cu for farmland samples, Zn>Pb>Cu>Cr for dumpsites samples, Pb>Cu>Zn>Cr and for the wetland samples. In most of the samples, the PTM concentrations were above the WHO permissible limits and USEPA background levels for soil. As an example, Pb concentrations for all the locations, except at F4 and W2, were above the USEPA background levels/permissible limit of 10 mg/kg indicating that the soils were contaminated with Pb. The presence of these metals in the sampled environment could be attributed to various anthropogenic influences including emissions from vehicle sources along a highway environment, discharge of effluent from industries into Lagos wetlands, electronic wastes and other ancillary PTM bearing wastes in waste dumps among others.

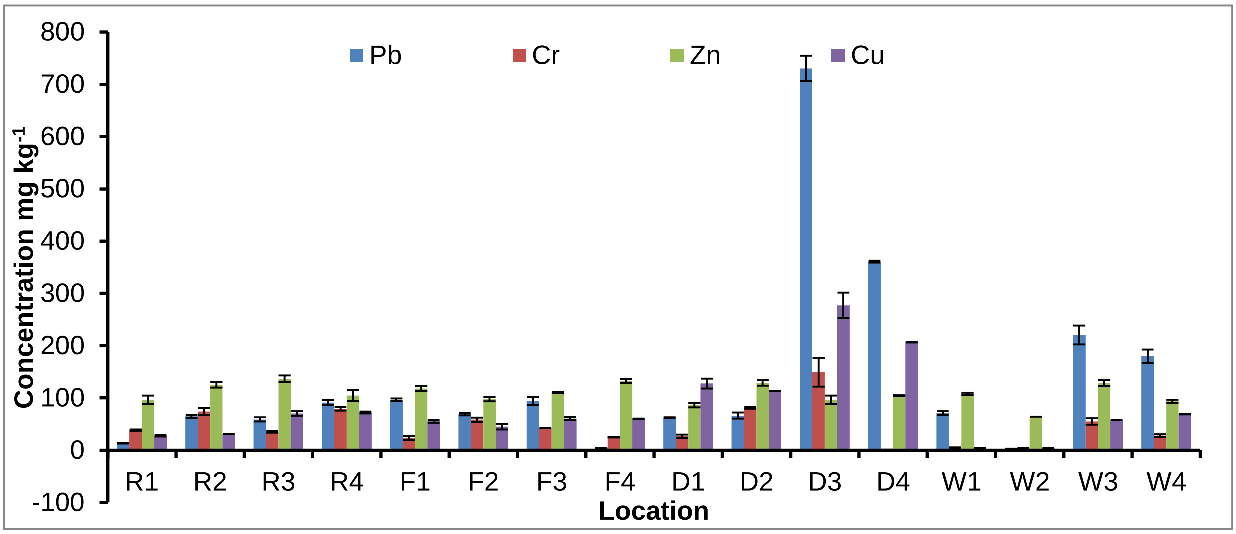

Fig.2: Concentration of Total PTMs in soil samples

Concentration of Bioavailable PTMs (BAPTMs) in Soils

The results obtained for the BAPTMs in the samples showed that the concentration ranges are 0.03 – 242.42 mg kg^{-1} for Pb; BDL – 33.56 mg kg^{-1} for Cr: 7.71 -35.60 mg kg^{-1} for Zn and 32.84 – 50.42 mg kg^{-1} for Cu. Specifically, the BAPTMs in roadside soil had Pb 32.05 ± 34.48, Cr 9.79 ± 8.03, Zn 27.37 ± 4.57 and Cu 6.84 ± 6.06 mg kg^{-1}; farmlands had Pb 7.94 ± 13.97, Cr 12.78 ± 14.62, Zn 27.60 ± 9.83 and Cu 6.15 ± 4.68 mg kg^{-1}; dumpsites had Pb 165.47 ± 196.15, Cr 19.34 ± 13.51, Zn 33.24 ± 1.41 and Cu 102.97 ± 56.09 mg kg^{-1}); and wetlands had Pb 78.54 ± 113.37, Cr 10.08± 13.23, Zn 19.41 ± 12.50 and Cu 15.39 ± 26.31 mg kg^{-1}). Mean concentrations for the entire samples were Pb 71.00 ± 120.01, Cr 12.99 ± 11.96, Zn 26.90 ± 9.00 and Cu 32.84 ± 50.42 mg kg^{-1}.

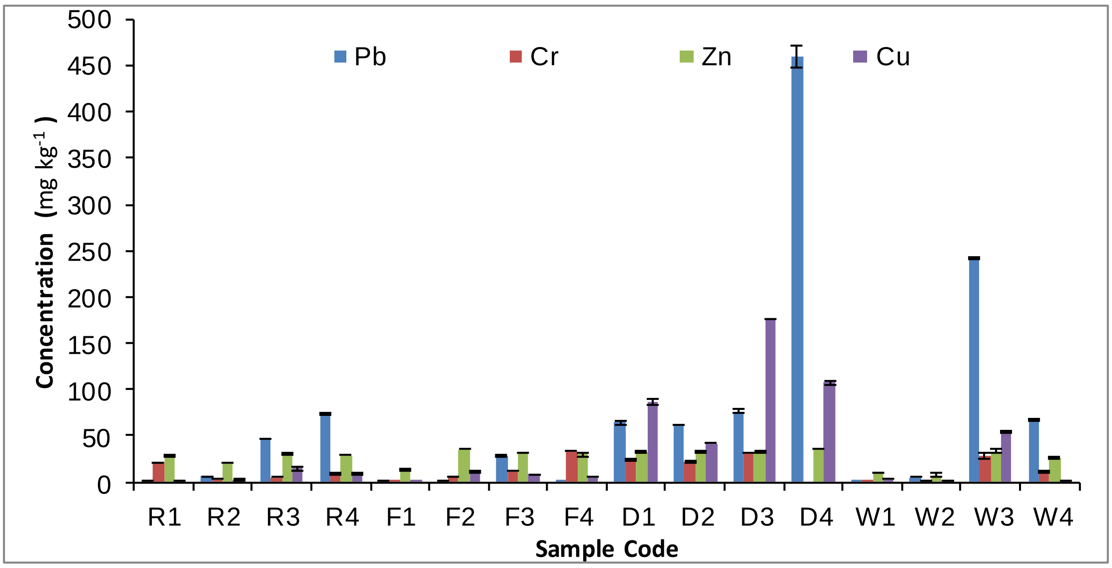

Fig. 2: Concentration of Bioavailable PTMs in soil samples

Total and Bioavailable Phosphorus (BAP)

The results obtained for total phosphorus and BAP are shown in Table 3. The concentration for bioavailable phosphorus ranged from 1.99 – 39.29 mg kg^{-1} with mean 18.86 ± 13.13 mg kg^{-1} while those of total phosphorus ranged from 8.73 – 204.08 mg kg^{-1} with mean of 83.13 ± 63.41 mg kg^{-1}. The farmland and roadside soil samples had comparative higher total P and BAP concentrations which are not unexpected due to the rich organic matter of the two pool of soil samples. The highest and lowest BAP concentrations were obtained in D4 (dumpsite) and R1 (roadside).

Table 3: Results of Total and Bioavailable Phosphorus

Sample	Code	Total P (mg kg^{-1})	BAP (mg kg^{-1})
Roadside	R1	15.96	1.99
	R2	33.03	5.64
	R3	29.03	14.61
	R4	22.13	14.94
Farmland	F1	158.07	14.50
	F2	105.74	12.93
	F3	123.81	21.27
	F4	204.08	19.62
Dumpsite	D1	151.93	17.22

	D2	110.43	37.63
	D3	78.13	34.42
	D4	148.69	39.29
Wetland	W1	8.73	3.10
	W2	13.67	4.32
	W3	103.86	42.49
	W4	22.81	17.71
Mean ± SD		83.13 ± 63.41	18.86 ± 13.13
Range		8.73 - 204.08	1.99 - 39.29

S.D = Standard Deviation,

Correlation of some Physicochemical Parameters with BAPTM, BAP and TP

Pearson's correlation was carried out using IBM SPSS v 20 to study the relationship between BAPTM, TP, BAP, CEC, OM (Table 4). Correlation of BAPTMs before treatment with phosphate using 2- tailed significance at 0.01 level when n=16, Pb had significantly positive correlation with TP ($r = 0.71; p < 0.01$), while Cr had a strongly positive relation with Cu ($r = 1.00; p < 0.01$). This strong relationship between bioavailable Cr and Cu may be suggestive of a common source of pollution. Zn was observed to have a strongly positive relationship with OM ($r = 0.66; p < 0.01$), BAP exhibited strongly positive relationship with CEC ($r = 0.71; p < 0.01$) and OM ($r = 0.76; p < 0.01$). The strong positive relationship between BP with CEC and OM showed that CEC and OM are physicochemical conditions that strongly influence phosphorus availability in soils. However, no relationship was observed between BAP and BAPTM, however total phosphorus showed a strongly positive relationship with Pb at 0.01 level ($r = 0.71; p < 0.01$) and a strongly positive relationship with Zn also at 0.05 level ($r = 0.62; p = 0.01$), while weakly significant relationship occurred between Cr and Cu ($r = 0.504; p < 0.05$)

Table 4: Pearson's Correlation between BAPTM, BAP, Total P, and Physico-chemical Properties of the Soil Samples

		Pb (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	CEC (meq/100g)	OM (%)	TP (mg P/kg)	BP(mg P/kg)
Pb		1							
	p								
Cu		-0.024	1						
	p	0.929							
Zn		0.428	0.530*	1					
	p	0.098	0.035						
Cr		-0.024	1.000**	0.530*	1				
	p	0.929	0.000	0.035					
CEC		0.230	0.205	0.486	0.205	1			
	p	0.391	0.447	0.056	0.447				
OM		0.365	0.320	0.664**	0.320	0.909**	1		
	p	0.165	0.227	0.005	0.227	0.000			
TP		0.705**	0.450	0.621*	0.450	0.439	0.588*	1	
	p	0.002	0.080	0.010	0.080	0.089	0.017		
BP		0.266	0.369	0.391	0.369	0.705**	0.759**	0.512*	1
	p	0.320	0.159	0.135	0.159	0.002	0.001	0.043	

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

Immobilization studies of phosphate on PTMs

The results of the immobilization test using phosphate on the soil samples and subsequent analysis of the BAPTMs are as shown in Table 5. The BAPTMs concentrations after treatment showed a general reduction in the concentration of bioavailable metals in all the soil samples. The bioavailable Pb in sample F3 for all the concentrations of the orthophosphate was below detection limit after treatment, except at a treatment condition of 0.5 M mg L^{-1} PO_4^{3-} and pH of 8.1 which was 0.48 mg kg^{-1}. This was still a significant reduction when compared with its bioavailable mean value of 28.85 ± 0.83 mg kg^{-1} before treatment which resulted in up to 99.83% reduction (Table 6).

The treatment results for the Pb showed that it was completely immobilized after treatment and no more bioavailable to plant. This result is interesting as complete immobilization via precipitation of PTM in farmland soil could be an effective strategy in preventing absorption of PTMs by plant on a contaminated farmland. The level of bioavailable Cr detected in the spiked sample was observed to progressively decrease at a pH of 6.2 and concentration as the phosphate is increased with the Cr level in F3 immobilized by about 72.89 - 95.83%, while at 0.25 mg L^{-1} PO_4^{3-} and pH 7.1, the Cr level was below detection limit (BDL). The level of Zn was reduced by 84.21 – 88.47% (Table 6) while Cu was reduced by over 70.42% at different concentrations and decreased as the pH of the phosphate treatment applied was increased (Table 6). The bioavailability of Pb in D2 after treatment was below detection limit (BDL) at pH 7.1 and phosphate concentration of 0.25 mg L^{-1}. It was observed however, that at varied phosphate concentration and pH conditions the Pb in sample were immobilized by > 90%. These results agree with the work of Traina and Laperche (1999) that application of soluble forms of orthophosphate such as Na_2HPO_4 or KH_2PO_4 or solid-phase phosphates (i.e. apatites) to contaminated soils and sediments induces formation of legacy Pb minerals. The desorption of Pb, which is subsequently adsorbed by hydrous metal oxides, leads to the formation of pyromorphites in situ, thus resulting to a decrease in the chemical lability and bioavailability of the Pb, though without its removal from the contaminated media. The Cr level detected in the treated sample progressively increases with added phosphate concentration and pH. Though there was a significant overall reduction of about 82.49 - 90.99%. Generally, the reduction in levels of Zn (85.06 – 88.87%) and Cu (73.04 – 81.72%) detected at different concentration was observed to decrease as the pH of the orthophosphate was increased.

Immobilization of bioavailable Pb in sample W4 at all the concentrations of the orthophosphate was 91.82 – 98.08%,. The Cr level detected in the treated sample increased sharply as the pH increased from 6.2 to 7.1 and then decreased slightly at pH 8.1 for all concentrations. Overall, there was a reduction of about 56.60 - 93.08% in the bioavailable concentration of Cr in the samples (Table 6). The level of Zn reduced by about 82.09 – 84.95% after treatment with phosphate while that of Cu reduced by over 44.55% (Table 6). Hence, it was observed that at different concentrations and increasing pH of the applied phosphate, the metal concentrations reduced appreciably. The results at W4 which was highly contaminated showed that phosphate-phosphorus amendment was also effective in the immobilization of PTMs at the location.

Table 5: B PTMs (mg kg^{-1}) before and after spiking with orthophosphate

Sample	PO_4^{3-} Treatment Condition	Pb (mg/kg)		Cr (mg/kg)		Zn (mg/kg)		Cu (mg/kg)	
	mg L^{-1} (pH)	Before	After	Before	After	Before	After	Before	After
R4	0.25 (6.2)	73.55	3.70	9.05	3.14	29.32	5.06	8.92	2.16
	0.25 (7.1)		4.43		1.73		3.98		0.64
	0.25 (8.1)		2.87		1.25		4.92		1.66
	0.5 (6.2)		3.59		0.94		3.80		2.31
	0.5 (7.1)		3.94		1.31		4.66		0.55
	0.5 (8.1)		4.15		2.18		3.68		1.50
	1.0 (6.2)		3.28		1.62		4.55		0.12
	1.0 (7.1)		4.19		2.95		4.74		0.51
	1.0 (8.1)		4.53		3.74		4.61		1.50
F3	0.25 (6.2)	28.85	BDL	11.51	2.78	31.92	4.09	7.81	1.50
	0.25 (7.1)		BDL		BDL		4.37		ND
	0.25 (8.1)		BDL		2.26		4.03		1.16
	0.5 (6.2)		BDL		1.80		4.69		2.08
	0.5 (7.1)		BDL		0.48		5.04		1.42
	0.5 (8.1)		0.48		2.28		4.68		1.43
	1.0 (6.2)		BDL		2.36		4.67		2.23
	1.0 (7.1)		BDL		2.95		3.68		2.31
	1.0 (8.1)		BDL		3.12		4.80		1.52
D2	0.25 (6.2)	62.09	2.38	21.80	2.52	32.52	3.90	42.24	8.35
	0.25 (7.1)		BDL		1.90		4.86		7.76
	0.25 (8.1)		3.45		3.37		4.70		7.72
	0.5 (6.2)		3.00		1.90		4.82		11.39
	0.5 (7.1)		3.58		2.35		3.89		10.25
	0.5 (8.1)		4.49		2.84		3.62		8.18
	1.0 (6.2)		3.86		1.84		4.58		8.77
	1.0 (7.1)		4.51		2.63		4.77		9.99
	1.0 (8.1)		5.39		3.69		4.68		7.82
W4	0.25 (6.2)	66.59	2.10	10.99	1.08	26.52	4.23	2.02	1.11
	0.25 (7.1)		2.78		4.38		3.99		0.01
	0.25 (8.1)		3.28		3.37		4.75		0.54
	0.5 (6.2)		1.94		1.52		4.21		0.80
	0.5 (7.1)		1.34		2.29		4.22		ND
	0.5 (8.1)		5.45		4.77		4.40		0.35
	1.0 (6.2)		1.28		0.76		4.02		ND
	1.0 (7.1)		3.64		4.20		4.73		0.22
	1.0 (8.1)		2.45		3.80		4.55		0.77

Table 7 Percentage Immobilization of BAPTMs after Phosphate Treatment

Sample	Conc. of PO_4^{3-} (mg L^{-1})	pH	Pb	Cr	Zn	Cu
R4	0.25	6.2	94.97	65.30	82.74	75.78
		7.1	93.98	80.88	86.43	92.83
		8.1	96.10	86.19	83.22	81.39
	0.5	6.2	95.12	89.61	87.04	74.10
		7.1	94.64	85.52	84.11	93.83
		8.1	94.36	75.91	87.45	83.18
	1.0	6.2	95.54	82.10	84.48	98.65
		7.1	94.30	67.40	83.83	94.28
		8.1	94.30	58.67	84.28	83.18
F3	0.25	6.2	>99.99	75.85	87.19	80.79
		7.1	>99.99	>99.99	86.31	>99.99
		8.1	>99.99	80.36	87.37	85.15
	0.5	6.2	>99.99	84.36	85.31	73.37
		7.1	>99.99	95.83	84.21	81.82
		8.1	98.34	80.19	85.34	81.69
	1.0	6.2	>99.99	79.50	85.37	71.45
		7.1	>99.99	74.37	88.47	70.42
		8.1	>99.99	72.89	84.96	80.54
D2	0.25	6.2	96.17	88.44	88.01	80.23
		7.1	>99.99	91.28	85.06	81.63
		8.1	94.44	84.54	85.55	81.72
	0.5	6.2	95.17	91.28	85.18	73.04
		7.1	94.23	89.22	88.04	75.73
		8.1	92.77	86.97	88.87	80.63
	1.0	6.2	93.78	91.56	85.92	79.24
		7.1	92.74	87.94	85.33	76.35
		8.1	91.32	83.07	85.61	81.49
W4	0.25	6.2	96.85	90.17	84.05	45.05
		7.1	95.83	60.15	84.95	99.50
		8.1	95.07	69.34	82.09	73.27
	0.5	6.2	97.09	86.17	84.13	60.40
		7.1	97.99	79.16	84.09	>99.99
		8.1	91.82	56.60	84.09	82.67
	1.0	6.2	98.08	93.08	84.84	>99.99
		7.1	94.53	61.78	82.16	89.11
		8.1	96.32	65.42	82.84	61.88

A 2-tailed paired sample t-test at 95% confidence limit was conducted for each of the BAPTMs studied. The results for the bioavailable metal concentrations are shown Table 7. For Pb, (M = 55.26, SD= 16.02) t(35) = 20.69, $p < 0.01$. For Cr before and after treatment, (M = 10.94, SD = 5.05), t(35) = 12.99, $p < 0.01$, for Zn before and after treatment, (M = 25.65, SD = 2.41) t(35) = 63.80, $p < 0.01$, for Cu before and after treatment, (M = 12.23, SD = 12.59) t (35) = 5.82, $p < 0.01$. It can be deduced from the result of the t-test that there is a significant difference in the before and after treatment of the soil samples studied and therefore, orthophosphate treatment is effective in treatment of soils against PTMs via immobilization.

Table 7: Results of Paired Sample t-test of the BAPTM in Soil Samples

Paired Test	Samples	Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Pb before - Pb after treatment	55.26778	16.02731	2.67122	49.84492	60.69064	20.690	35	.000
Pair 2	Cr before - Cr after treatment	10.94583	5.05383	0.84230	9.23586	12.65580	12.995	35	.000
Pair 3	Zn before - Zn after treatment	25.65417	2.41237	0.40206	24.83794	26.47040	63.806	35	.000
Pair 4	Cu before - Cu after treatment	12.23000	12.59054	2.09842	7.96997	16.49003	5.828	35	.000

Conclusion

The ability of phosphate as remediation agent for soils contaminated with PTMs was studied and the results showed that the samples while contaminated with PTMs, could be modified such that the levels of BAPTMs in the soil which could be leached to proximate water resources or absorbed by plants could be reduced. Treating the samples with K_2HPO_4 at varied concentrations (0.25, 0.50 and 1.00 mg L^{-1}) and pH (6.2, 7.1 and 8.1), resulted in more than 80% decrease in the bioavailable concentration of the PTMs with marked reduction in the bioavailable Pb concentration i.e. being the most immobilized. The degree of immobilized bioavailable PTMs was in the order of Pb>Zn>Cr>Cu. This study showed that K_2HPO_4 is a cost effective method for chemical immobilization of PTMs in contaminated soil. The fact that phosphate is also a source of soil nutrient for plant makes the method sustainable.

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