



Effect of Water Soluble Phosphate on Immobilization of Pb^{+2} in Lead Contaminated Soil

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Abstract: There are documented reports that phosphate forms insoluble precipitate with Pb, thereby lowering the concentration of Pb^{+2} in the roots, shoots and leaves of tree species grown in soil amended with phosphate. In this study, the effect of soluble phosphate on immobilization of Pb^{+2} in lead contaminated soil was investigated. Four replicates each of 0 and 5,000mg of lead nitrate were applied alone or in combination with 0, 10, 50 and 250mg of disodium dihydrogen pyrophosphate separately to 3kg soil and mixed thoroughly in plastic pots perforated at the base. The soil samples were watered with tap water for two days. The pH and water soluble phosphate of the soil samples were determined. Water soluble fraction of the soil was extracted with deionized water. Concentrations of Pb^{+2} in soil extracts were determined by Atomic Absorption Spectrometry. The water soluble lead decreased highly significantly ($P < 0.01$) with a corresponding increase in water soluble phosphate and pH due to precipitation of Pb^{+2} from the soil solution.

Keywords: Disodiumdihydrogen pyrophosphate; Water Soluble Lead; Water Soluble Phosphate; Precipitation; Immobilization; pH.

1. Introduction

Soil factors controlling lead availability to plants have been well documented. Perhaps the most important are pH (Cox & Rains, 1972; Arvick & Zimdahl, 1974; Reddy & Patrick, 1977; Harter, 1983), redox potential (Swaine & Mitchell, 1960; Reddy & Patrick, 1977) and organic matter (Gregson & Alloway, 1984; Stevenson, 1986). Some nutrient anions could also control lead solubility and therefore phytoavailability. For example, phosphate formed insoluble precipitate with Pb, thereby lowering the concentration of Pb^{+2} in the roots, shoots and leaves of tree species grown in soil amended with phosphate. This suggests that Pb interacts, at least in part, with phosphate in the soil. MacLarean *et al.* (1969) demonstrated significantly lower Pb concentrations in oat straw and alfalfa tops grown with 500mg/kg added to soil compared with control. This was

particularly effective at higher rates of Pb amendment. Although, there were decreases in the concentrations of Pb extracted with ammonium acetate and calcium chloride, no specific mechanism was proposed by the authors, other than to iterate that lead phosphate compounds are generally insoluble (Rolfe,1973; Nriagu,1974; Lindsay, 1979)

2. Materials and Methods

2.1 The Study Area

The soil sample used for this study was collected from International Institute of Tropical Agriculture (IITA) farm in Wase village, Minjibir Local Government Area of Kano State. **Figures 1 to 3** show the locations of sampling site.

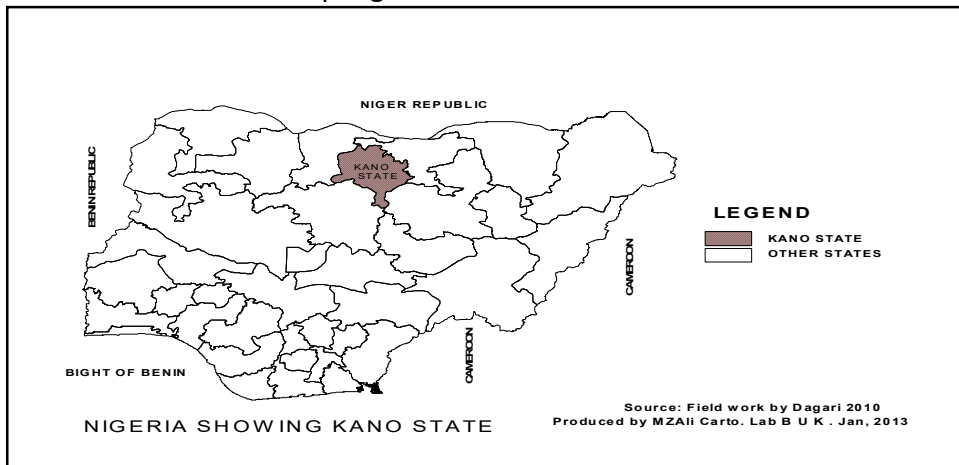


Figure 1: Map of Nigeria Showing Kano State

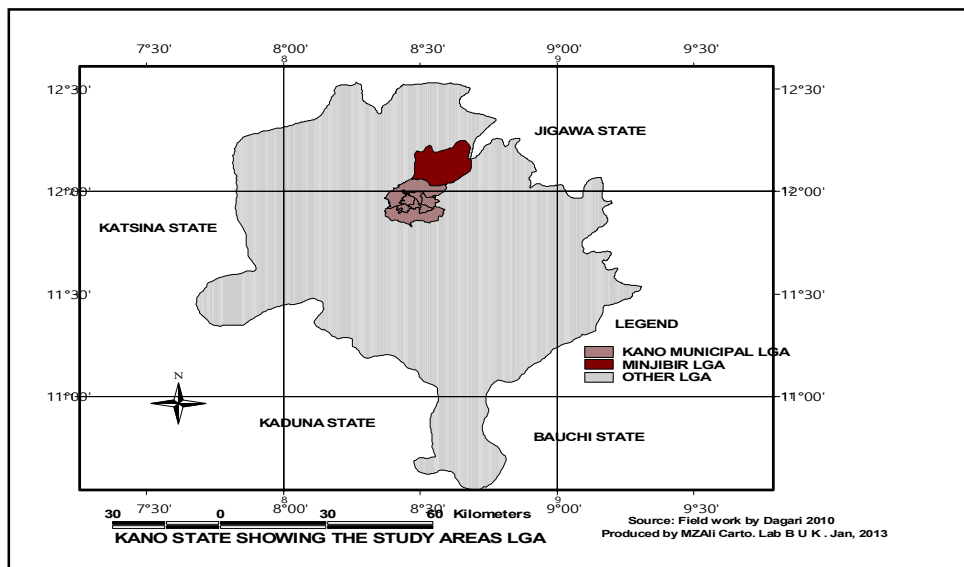


Figure 2: Map of Kano State Showing the Study Local Government Area

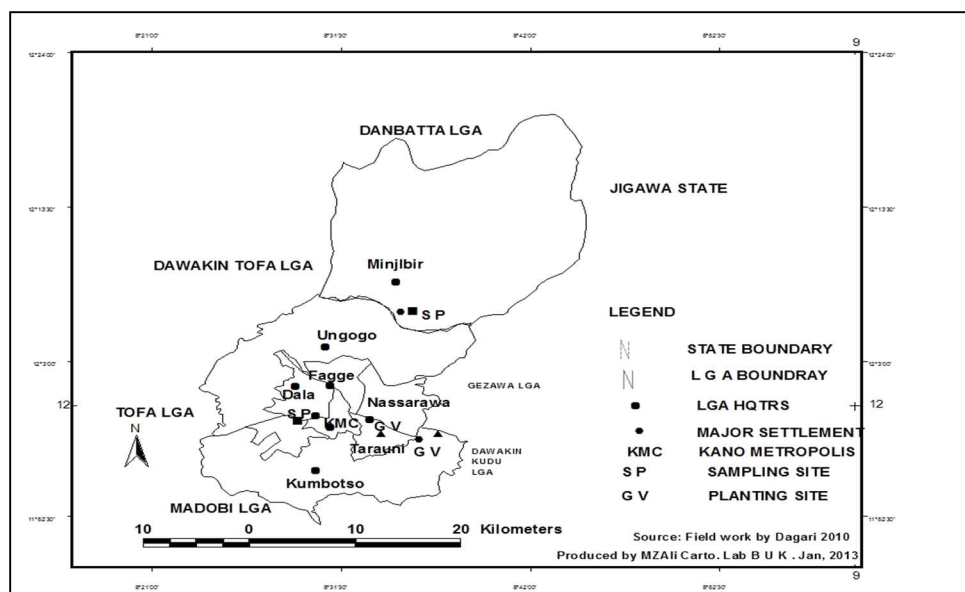


Figure 3: Kano State L.G.A. Map Showing Sampling Site

2.2 Instruments, Apparatus and Reagents

All equipment and instruments used in this research were calibrated before conducting the experiments. All glassware used were thoroughly washed with detergents and tap water and then rinsed with deionized water. Suspected contaminants were cleaned with 10% concentrated nitric acid (HNO_3) and metal surfaces were rinsed with deionized water.

In the preparation of reagents, chemicals of analytical grade purity and distilled water were used. All glassware and plastic containers were washed with detergents.

2.5 Soil Sampling and Pre-Treatment

The soil sample was collected using the method recommended by (Petersen, 1994). 100m^2 of the land was divided into ten equal sized grid cells of 10m^2 . A steel augur was used to dig the soil to a depth of 25cm. Samples collected from all cells were thoroughly air dried, mixed and stored in large plastic bags.

For the purpose of analysis, 1kg of the air-dried soil was taken. After removing the debris, the soil was ground in a wooden mortar and sieved through a 2mm mesh. It was then stored in a labeled plastic container.

2.4 Soil Treatments

Four replicates each of 0 and 5,000mg of lead nitrate were applied alone or in combination with 0, 10, 50 and 250mg disodium dihydrogen pyrophosphate separately to 3kg soil and mixed thoroughly in plastic pots (Wong and Lau, 1985). The soil samples were watered with tap water for two days.

2.5 Soil Analysis

Soil analyses were carried out by standard methods; the pH and conductivity meters were used to measure the pH and electrical conductivity, respectively, in the soil suspension (1:2.5 w/v

dilutions) (IITA, 1982). Organic carbon was determined by Walkley and Black method (Nelson and Sommers, 1996). The hydrometer method was used for the determination of particle size distribution (Gee and Or, 2002). Total nitrogen was determined using the Kjeldahl method (Bradstreet, 1954) and available phosphorus by Bray 1 extraction method (Bray and Kurtz, 1945), exchangeable cation by extraction with 1 N NH₄OAc solution (Page *et al.*, 1982), exchangeable acidity by leaching the soil sample with 1 N KCl solution (Agbenin, 1995), total metal concentration by tri-acid digestion (Stober *et al.*, 1976) and effective cation exchange capacity by summation method.

2.6 Extraction of Water Soluble Lead

The water soluble lead was extracted from a mixture of 10g of pre-treated soil and 100cm³ of deionized water in a 120cm³ of plastic bottle (Stober *et al.*, 1976).

2.7 Atomic Absorption Spectrometric Analysis

The soil extracts were analyzed for lead at 283.5nm using flame atomic absorption Spectrophotometry. Blank determinations were made prior to sample analysis. Concentrations of Pb⁺² in soil extracts were obtained in quadruplicates from calibration curves and expressed as mg/kg (IITA, 1979).

2.8 Statistical Analysis

The data were analyzed in triplets and expressed as mean and standard deviation. The mean of all treatments was subjected to a One-way analysis of variance (ANOVA) using IBM SPSS Statistics 23 software and mean differences were performed using the Tukey test. All graphs were plotted using Microsoft Excel 2013.

2. Results and Discussion

a. Results of Routine Analyses

Table 1: Soil Fertility Parameters

Parameter	Result	RVAS
Texture: Sand (%)	73.8 ± 1.15	
Silt (%)	12.0 ± 0.00	
Clay (%)	14.2 ± 1.15	
Textural class	Sandy loam	Sandy loam
pH	7.08 ± 0.05	6.00–7.80
Organic carbon (%)	0.671 ± 0.09	0.5–0.7
Total nitrogen (%)	0.02 ± 0.00	0.05–0.30
Carbon-nitrogen ratio	34.762 ± 0.04	2.3–10
Total organic matter (%)	1.16 ± 0.12	0.9 –1.2
Cation exchange capacity (cmol/kg soil)	3.44 ± 0.10	2.00–30.00
Exchangeable cations (c mol/kg soil)		
Na	0.15 ± 0.00	0.3 – 2.0

K	0.86 ± 0.01	0.2 – 1.2
Mg	0.11 ± 0.01	0.5 – 8.0
Ca	1.92 ± 0.01	2.0 – 15.0
Exchangeable sodium percentage (%)	4.37 ± 0.11	<15
Electrical conductivity (mS/cm)	0.02 ± 0.01	<4.00
Water soluble phosphate (mg/kg)	2.60 ± 1.00	<10

RVAS: Recommended values for agricultural soil (Landon, 1991)

The soil parameters; pH, total organic matter, cation exchange capacity, exchangeable potassium and calcium, exchangeable sodium percentage, electrical conductivity and water soluble phosphate of the IITA farm soil were within the range of recommended values for agricultural soils. However, the total nitrogen, exchangeable sodium and magnesium were below the recommended values for agricultural purposes (Landon, 1991).

Table 2: Heavy Metal Concentrations (mg/kg) in Soil

Metal	WSF	Total	Alloway (1990)	Landon (1991)	Wild (1996)
Chromium	18.33 ± 10.00	375.00 ± 16.67	5 – 1500	5 – 1500	NA
Manganese	1.26 ± 0.25	11.94 ± 1.08	NA	20 – 10,000	NA
Iron	6.00 ± 2.31	60.00 ± 16.33	2 – 100	NA	NA
Cobalt	0.87 ± 0.16	18.25 ± 0.92	NA	0.05 – 65	NA
Nickel	1.15 ± 0.59	13.76 ± 1.87	2 – 1000	2 – 750	75
Copper	6.62 ± 1.23	15.93 ± 6.17	2 – 250	2 – 250	140
Zinc	18.18 ± 10.50	113.64 ± 26.24	10 – 300	1 – 900	300
Cadmium	0.11 ± 0.02	1.09 ± 0.26	0.01 – 2.4	0.01 – 2.4	3
Lead	3.31 ± 0.74	49.63 ± 3.68	2 – 300	2 – 300	300

NA means value not available

WSF: Water Soluble Fraction **Total:** Total metal concentration

Metal concentrations in the water soluble and exchangeable fractions, as well as total metal concentrations in the soil were compared with Alloway (1990), Landon (1991) and Wild (1996). There was no heavy metal contamination of the soil, since the concentrations of all metals were either less or within the range of these standard values.

b. Effects of Disodium Dihydrogen Pyrophosphate on pH, Water Soluble Lead and Water Soluble Phosphate of Soil Solutions

Among the divalent metals, Pb is usually the least soluble in aerobic soil environments because of its high ability to adsorb to soil particles (Elliot *et al*, 1986), low solubility of several mineral phases (Nriagu 1973; Martínez *et al*, 2004) and limited solubility at high solution pH and high phosphorus activities (Martínez *et al*. 2004; Lindsay 2001).

Table 3: pH, Water Soluble Lead and Water Soluble Phosphate of Soil Solutions

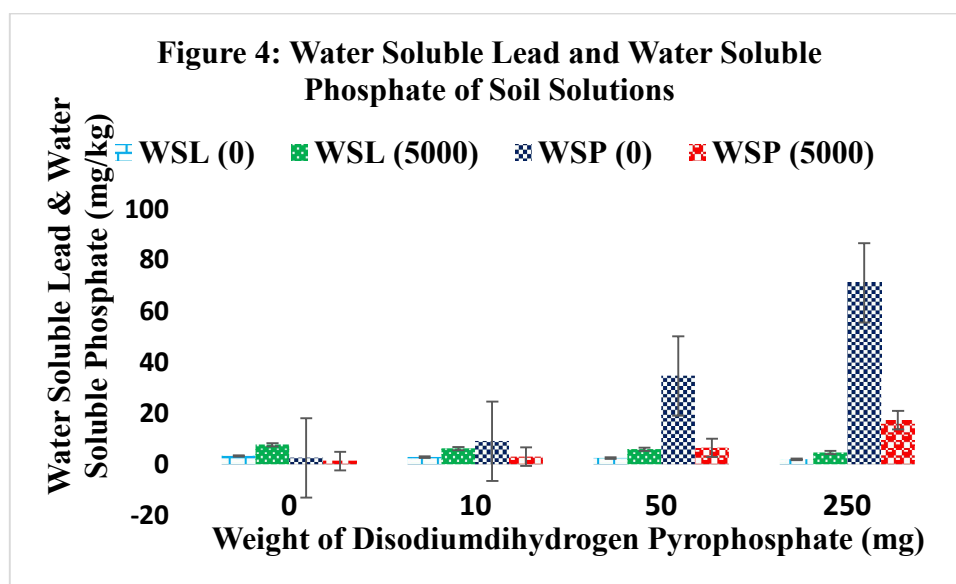
LNT	DSDHP	WSL	pH	WSP
0	0	3.31±0.74	7.08±0.05	2.60±1.00
0	10	2.85±0.96	7.10±0.08	9.11±0.83
0	50	2.46±0.69	7.13±0.05	34.72±0.87
0	250	1.98±0.85	7.15±0.06	71.16±0.00
5000	0	7.72±0.74	7.00±0.00	1.30±0.42
5000	10	6.25±0.06	7.05±0.06	3.04±0.15
5000	50	5.88±0.20	7.10±0.00	6.51±0.67
5000	250	4.68±0.42	7.15±0.06	17.36±0.87

LNT: Lead nitrate (mg in 3kg Soil)

DSDHP: Disodium dihydrogen pyrophosphate (mg in 3kg Soil)

WSL: Water soluble lead **WSP:** Water soluble phosphate

Figure 4 shows the water soluble Pb⁺² and water soluble phosphate of the soil solutions.



The water soluble Pb^{+2} in the control was 3.31mg/kg which decreased highly significantly ($Pr < 0.01$) to 1.98mg/kg when 250mg of disodiumdihydrogen pyrrphosphate (DSDHP) was added to soil, giving a highly significant increase ($Pr < 0.01$) in water soluble phosphate from 2.60 to 71.16mg/kg. When 5000mg of lead nitrate was added to soil, the water soluble Pb^{+2} was 7.72mg/kg which decreased to 4.68 when 250mg of DSDHP was added. The corresponding increase in water soluble phosphate was 1.30 to 17.36mg/kg.

The decrease in water soluble lead with increase in amount of DSDHP was due to precipitation of the heavy metal (MacLean *et al*, 1969; Rolfe, 1973; Zindahl and Forster, 1976; Wong and Lau, 1985).

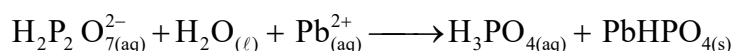
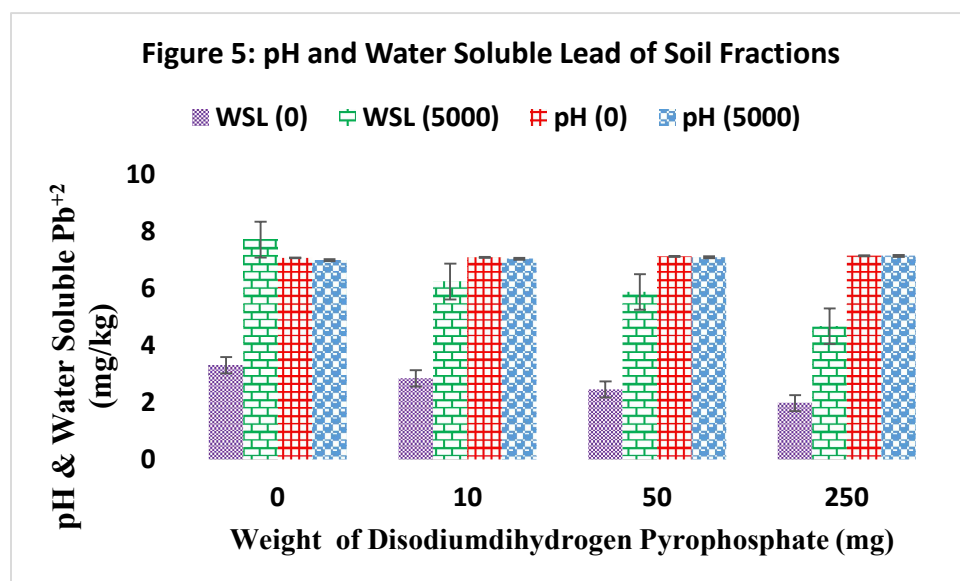


Figure 5 shows the water soluble Pb^{+2} and water soluble phosphate of the soil solutions.



Addition of 0 – 250mg DSDHP to soil amended with 0 and 5000mg of lead nitrate increased the soil pH from 7.08 to 7.15 and 7.00 – 7.15, corresponding to decreases in water soluble Pb^{+2} of 3.31 to 1.98 and 7.72 to 4.68mg/kg respectively. Lagerverff (1971), Zimdahl and Skogerboe (1977) demonstrated that soil pH exerts a significant influence on the solubility of Pb salts. The competition between Pb^{2+} and hydrogen ions for available fixation sites within the soil matrix will govern the Pb availability. Thus, under alkaline conditions most of the Pb salts were insoluble and became unavailable to plants.

4. Conclusion

Disodium dihydrogen pyrophosphate has been found to significantly decrease the concentration of lead by precipitation of Pb^{+2} ion in lead contaminated soil. The use of this chemical substance, though expensive, in reducing extractable Pb^{+2} provides a basis for adopting management practices to lessen the potential hazard of Pb-contaminated soil.

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Authors' Contributions

Dagari M.S.: Conceptualization, design, undertaking the research work, write-up and data analysis

Jimoh W.L.O.: Supervision of the research work; Editing of the write-up

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