

# Effects of Addition of Lead Nitrate on Available Lead in Soil

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**Abstract**: The available form of heavy metals in soil consists of water soluble and exchangeable fractions in equilibrium. The water soluble fraction is readily available for plant uptake. The exchangeable fraction is potentially available, and goes into solution to replace depleted water soluble fraction. In this study, four replicates each of 0, 1000 to 10,000mg of lead nitrate were added 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. Two cowpea seeds per pot were planted. Watering was continued until the plants were harvested. The water soluble and exchangeable  $Pb^{+2}$  before planting and after harvest were extracted with deionized water and 1M ammonium oxalate respectively. Concentrations of  $Pb^{+2}$  in these fractions were determined by Atomic Absorption Spectrometry. In the range 0 to 10,000 mg  $Pb(NO_3)_2$ , the water soluble  $Pb^{+2}$  before planting and after harvest increase in exchangeable  $Pb^{+2}$  before planting and 2.94 to 4.04mg/kg respectively. Similarly, the increase in exchangeable  $Pb^{+2}$  before planting of  $Pb^{+2}$  before planting and Agricultural Organization (36 - 250mg/kg). Concentrations of  $Pb^{+2}$  determined were insignificant compared to the total amount of Pb added to the soil, a result consistent with the findings of Marten and Hammond (1966) that soils contaminated with Pb released only a small amount to plants. The pH values in the various fractions were found to significantly (Pr < 0.05) decrease.

Keywords: Water Soluble; Exchangeable; Lead nitrate; Deionized water; Ammonium oxalate.

#### 1. Introduction

In spite of regulatory measures adopted in many countries, which include a ban on leaded paints, water pipes and gasoline, Pb continued to be No.1 global environmental threat to children (Chaney and Ryan, 1994).

Many rural children in Europe died in the 1980s due to the leaching of Pb particles from leaded water pipes. Studies conducted in the United States of America in 1989 revealed that lead can slow development in children and make them less intelligent. In 1992, the US centre for disease control issued urgent warning alerting doctors that Pb concentration above 0.10ppm could be harmful to children (Newsweek, 1992). Over 400 children in Zamfara state, Nigeria died of lead poisoning due to illegal mining (Weekly Trust, 2011a). The return of the mining activities is threatening the lives of thousands of children (Weekly Trust, 2011b).

Figure 1 below shows the various sources of environmental Pb contamination.



As these Pb sources are indispensable for modern human life, soil contamination with Pb is not likely to decrease in the near future (Jarüp, 2003). Uncontaminated soils contain Pb in the range 2 to 200mg kg<sup>-1</sup> (Lindsay, 1979). A soil is generally considered contaminated with Pb when its total Pb concentration exceeds 300mg kg<sup>-1</sup> (EPA, 1993), and remediation is required when total Pb concentration is above 400mg kg<sup>-1</sup> (OSWER, 1994). A national survey in the U.K. indicated that total Pb concentration in garden soils ranged from 13 to 14,000mg kg<sup>-1</sup> (Cotter-Howells and Thornton, 1991).

A soil sample, obtained from a former battery-cracking site in Florida United States, had Pb concentrations up to 135,000 $\mu$ gg–1 (Trnovsky *et al*, 1987). Soil obtained from long-term polluted sites via industrial and urban sources from Britain, France, Norway and Japan contained Pb concentrations of 187 to 47,187mg kg<sup>-1</sup>. As a result of such widespread Pb contamination in soils, considerable attention and resources are being focused on remediating Pb contaminated soils (Alloway and Morgan, 1985).

## 2. Materials and Methods

## 2.1 The Study Area

The soil sample and cowpea seeds (*Vigna unguiculata*) used for this study were collected from International Institute of Tropical Agriculture (IITA) farm in Wase village, Minjibir Local Government Area of Kano State. Figures **2 to 4** show the locations of sampling and planting sites.



Figure 2: Map of Nigeria Showing Kano State



Figure 3: Map of Kano State Showing the Study Local Government Area



Figure 4: Kano State L.G.A. Map Showing Sampling and Planting Sites

# 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<sub>3</sub>) and metal surfaces rinsed with deionized water. The digestion tubes were soaked with 1% (w/v) potassium dichromate in 98% (v/v) H<sub>2</sub>SO<sub>4</sub>.

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

# a. 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 preliminary studies, 1kg of the air-dried sol 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.

# b. Soil Treatments and Planting of Cowpea Seeds

Four replicates each of 0, 2000 to 10,000mg of lead nitrate were added separately to 3kg soil and mixed thoroughly in plastic pots perforated at the base (Wong and Lau, 1985). The soil samples were watered with tap water for two days. Two cowpea seeds per pot were planted. Watering was continued until the plants were harvested

#### c. Measurement of Soil pH

Soil pH before planting and after harvest was measured in a calibrated Labtech digital pH meter using a suspension of 10g of pre-treated soil and 25cm<sup>3</sup> of deionized water was added (IITA, 1979).

## 2.6 Extraction of Water Soluble and Exchangeable Lead

The water soluble lead was extracted from a mixture of 10g of pre-treated soil and 100cm<sup>3</sup> of deionized water in a 120cm<sup>3</sup> of plastic bottle.

The exchangeable fraction was extracted by adding  $100 \text{cm}^3$  of 1M ammonium oxalate to the residue of the water soluble fraction (Stober *et al*, 1976).

## 2.7Atomic 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 quadruplicates 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.

## 3. Results and Discussion

Soils are a rich ecosystem, consisting of both living and non-living matter with varying levels of interaction between them. It is also a critical component due to its ability to accumulate pollutants produced by natural and anthropogenic activities from agriculture, industry, mining, vehicular movement etc. Different processes interact together to aid the movement of heavy metals in soil, and this includes processes of biological, chemical and physical nature (Violante *et al.*,2008). These polluted soils serve as the source of dispersal of heavy metals in the environment and may enter the food chain and food web (Gholizadeh *et al.*, 2015).

The biggest problem of heavy metals is that, they are persistent and non-degradable. Their presence in soil is stable and long-term (Lizárraga-Mendiola *et al.*, 2009), and these pose risks to public health and the environment (Zhu *et al.*, 2019).

Recently, some attention has been given to the potential hazard of lead from automobile exhausts and other sources as a contaminant of soils and plants. Warren and Delavault (1962) reported that plants subjected to atmospheric pollution or grown in soils high in lead may contain 10 times the normal amounts (0.1-1.0 ppm). Mitchell and Reith (1966) found that pasture herbage during the active period of growth contained only 0.3-1.5 ppm lead. By late winter or early spring, however, the amounts advanced to 30-40 ppm.

Normally, soils contain only small amounts of lead. For example, surface samples of 10 cultivated soils in Eastern Canada contained 6 -14 ppm lead. Amounts considerably higher than these may occur in surface horizons of some soils (Wright *et al.*1955).

There is evidence that soils contaminated with lead may release only a small portion of it to plants. Marten and Hammond (1966) found only 2.5 ppm lead in the first crop of bromegrass grown in a contaminated sandy loam soil containing 680 ppm. They cited the work of Kloke and Riebartsch,

who concluded that grass absorbed considerable lead into the roots but that only limited quantities; were translocated to the above-ground parts.

The study of heavy metal contamination of soils had been reported by several authors (Stober *et al*, 1976; Garcia et al, 1990; David *et al*, 2003; Fatima, 2015; Maryam, 2015; Yang *et al*, 2018; Jadwiga *et al*, 2018; Zhangjun *et al*, 2019). The investigation involved either;

- Sampling from a contaminated site (Yang *et al*, 2018; Zhangjun *et al*, 2019) or
- Amendment of the soil sample with calculated weights of the heavy metals (Stober *et al*, 1976; Garcia et al, 1990; David *et al*, 2003; Fatima, 2015; Maryam, 2015; Jadwiga *et al*, 2018).

The various forms of heavy metals in soil include (i) water- soluble, (ii) exchangeable, (iii) linked to organic substances (iv) occluded or co-precipitated with oxides, carbonates and phosphates, or other secondary minerals and (v) ions in the crystalline lattices of the primary minerals (Emmerich et al., 1982; Lake et al., 1984; He et al., 1992; Iwegbue et al., 2007).

The significance of sequential extraction of metals in soil is to determine and compare the

concentrations of metals in soil with threshold values for plant and animal growth. In this work, soil sample collected from the International Institute of Tropical Agriculture (IITA) farm in Wase, Minjibir Local Government Area of Kano State was treated with deionised water and 1M ammonium oxalate respectively, as recommended by Stober *et al* (1976) to extract water soluble and exchangeable fractions.

#### 3.1 Water Soluble and Exchangeable Lead

The water soluble fraction is the most available form for plant nutrition. It is the most biologically active soil fraction, with high potential of contamination of food chain, surface water, groundwater and high toxicity for plant growth (Leita and De Nobili, 1991; He *et al*, 1992). The exchangeable is in equilibrium with the water soluble fraction, and is potentially available to replenish the water soluble fraction when depleted by plants (Landon, 1991).

Results of the mean concentrations of  $Pb^{+2}$  in water soluble and exchangeable fractions are presented in Table 1.

Concentration (mg/kg)							
LNT	WSLBP	ELBP	WSLAH	ELAH			
0	3.31±0.74	6.99±1.41	2.94±1.70	6.25±1.41			
1000	3.68±0.85	11.95±5.51	3.31±2.21	10.48±5.32			
2000	4.77±0.74	15.63±4.63	3.31±0.74	14.70±12.01			
3000	6.25±1.30	29.41±12.01	5.88±2.21	25.74±7.35			
4000	6.99±0.74	36.76±8.49	6.25±1.41	33.09±7.35			
5000	7.72±0.74	44.12±12.01	$5.88 \pm 2.08$	40.44±7.35			
6000	8.09±0.85	51.47±14.71	4.78±0.74	48.71±27.41			
7000	8.82±1.70	$58.82 \pm 0.00$	5.51±0.74	54.23±34.14			

Table 1: Mear	n Concentrations (m	g/kg) of Pb <sup>+2</sup> i	n Water Soluble a	and Exchangeable
Fractions				

8000	9.56±0.85	66.18±25.47	6.25±0.74	60.66±9.25
9000	$10.29 \pm 0.00$	69.85±7.35	$5.88 \pm 0.00$	64.34±27.76
10000	$10.48 \pm 5.32$	73.53±0.00	4.04±2.21	69.85±7.35

LNT: Lead nitrate (mg in 3kg Soil), WSLAH: Water soluble lead after harvest ELAH: Exchangeable lead after harvest **WSLBP**: Water soluble lead before planting **ELBP**: Exchangeable lead before planting

The mean concentrations of  $Pb^{+2}$  in water soluble and exchangeable fractions are shown in **Figure 5** 



Concentrations of Pb<sup>+2</sup> in the soil fractions increased in the order; water soluble after harvest < water soluble before planting < exchangeable after harvest < exchangeable before planting. The water soluble Pb<sup>+2</sup> before planting and after harvest was found to increase significantly (Pr < 0.05). The water soluble  $Pb^{+2}$  before planting increased from a control value of 3.31mg/kg to on addition of 3.68±0.85, 4.77±0.74,.....10.48±5.32 mg/kg on addition of 1000, soluble Pb<sup>+2</sup> after harvest from a control value of 2.94mg/kg were  $3.31\pm2.21$ ,  $3.31\pm0.74$ , ......4.04±2.21 mg/kg on addition of 1000, 2000, .....10,000mg lead nitrate to soil respectively. Similarly, the increases in exchangeable lead before planting and after harvest from control values of 6.99 and 6.25mg/kg were 11.95±5.51, 15.63±4.63, .......73.53±0.00mg/kg and nitrate to soil respectively. Results of water soluble and exchangeable Pb<sup>+2</sup> in this study are below the recommended values of the World Health Organization (40 -250mg/kg) and Food and Agricultural Organization (36 - 250 mg/kg). The increase in water soluble and exchangeable Pb<sup>+2</sup> in this study was insignificant compared to the total amount of Pb added to the soil, a result consistent with the findings of Marten and Hammond (1966) that soils contaminated with Pb released only a small amount to plants.

#### 3.3 pH of Soil Fractions

The pH of a solution is the negative logarithm of its hydrogen ion concentration. The pH ranges normally found in soils varies from 3 to 9. The USDA (2010) classification of soil pH is given in 2;

Table 2: USDA (2010) Classification of Son pit						
S/N	Description	pH Range	S/N	Description	pH Range	
1	Ultra acidic	< 3.5	7	Neutral	6.6 -7.3	
2	Extremely acidic	3.5 - 4.4	8	Slightly alkaline	7.4 - 7.8	
3	Very strongly acidic	4.5 - 5.0	9	Moderately alkaline	7.9 -8.4	
4	Strongly acidic	5.1 -5.5	10	Strongly alkaline	8.5 -9.0	
5	Moderately acidic	5.6 -6.0	11	Very strongly alkaline	>9.0	
6	Slightly acidic	6.1 -6.5				

Table 2: USDA	(2010)	<b>Classification</b>	of Soil	рH
				P

Soil pH is considered a master variable in soils as it controls many chemical processes that take place. It specifically affects <u>plant nutrient</u> availability by controlling the chemical forms of the nutrient (Sparks, 2003). Results of mean pH values of soil solutions are presented in Table 3.

LNT (mg)	pHBP	рНАН	LNT (mg)	pHBP	рНАН
0	$7.08 \pm 0.05$	$7.53 \pm 0.05$	6000	$7.03 \pm 0.05$	7.43±0.10
1000	$7.03 \pm 0.05$	$7.50 \pm 0.00$	7000	$7.03 \pm 0.05$	$7.40{\pm}0.08$
2000	$7.03 \pm 0.05$	$7.50{\pm}0.00$	8000	7.03±0.10	$7.38 \pm 0.10$
3000	$7.00 \pm 0.00$	$7.45 \pm 0.06$	9000	7.03±0.10	$7.38 \pm 0.05$
4000	$7.00 \pm 0.08$	$7.45 \pm 0.06$	10000	$7.05 \pm 0.06$	$7.38 \pm 0.05$
5000	$7.00 \pm 0.00$	7.45±0.10			

Table 3: Mean pH Values of Soil Solutions

LNT: Lead nitrate (mg in 3kg of Soil), pHBP: pH of soil solution before planting pHAH: pH of soil solution after harvest

The mean pH values of soil solutions are shown in Figure 6



There was a general slight increase in pH of the soil solution from the values before planting and after harvest. On addition of 1000, 2000, .....10,000mg lead nitrate to soil, the pH of the soil solution before planting and after harvest fluctuated from a control values of  $7.08\pm0.05$  and  $7.53\pm0.05$  to  $7.05\pm0.06$  and  $7.38\pm0.05$  respectively. Marten and Hammond (1966) reported increase in solubility of soil Pb with decrease in soil pH. The pH values are in the neutral (6.6 – 7.3) and slightly alkaline (7.4 – 7.8) ranges of the USDA (2010) classification of pH values. **4. Conclusion** 

The mean concentrations of Pb<sup>+2</sup> in the water soluble and exchangeable soil fractions before planting and after harvest were below the values recommended by the World Health Organization (40 - 250 mg/kg) and Food and Agricultural Organization (36 - 250 mg/kg). The pH values of the soil solutions were in the neutral (6.6 - 7.3) and slightly alkaline (7.4 - 7.8) ranges of the USDA (2010) classification of pH values.

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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

Kanada, Y.B: Assisted in editing and formatting the manuscript

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