

Effects of Wastewater Discharge on Heavy Metals Pollution in Fadama Soils in Kano City, Nigeria

S. A. MASHI¹ AND M. M. ALHASSAN

Department of Geography, University of Abuja, PMB 117 Abuja, NIGERIA

Objective To present the results of a research project on 6 heavy metals (Cd, Cu, Zn, Pb, Hg, and Cr) at 30 Fadama fields scattered around Kano. **Methods** Following a reconnaissance conducted, 30 representative Fadama lands being irrigated with wastewater were selected from zones of the city under residential, industrial, commercial, and mixed but largely residential landuses. Five additional Fadama lands not being irrigated with wastewater were selected to serve as control. Using grid sampling procedure, soil samples were selected from 0-15 cm and 20-30 cm depths and analyzed for the above listed heavy metals using atomic absorption spectrophotometry. T-test was used to compare the mean values of the metals for the Fadama lands under different landuse zones with those of the control. **Results** Analyses of the soil data collected showed that the metals were concentrated in higher amounts in the lower (20-30 cm) than the upper (0-15 cm) depths, which was an indication of downward movement of the metals in profile of the soils. In the two soil depths, Zn was generally the most abundant, followed by Cr, then Pb, Cu, and Cd while Hg was the least. The Fadama soils in areas of mixed landuses with industrial as the dominant ones maintained the highest concentrations of the various metals. **Conclusions** These results indicate clearly that the Fadama soils are significantly polluted by industrial and household wastewater and that there is a particular threat from Cr and Pb pollution. There is also evidence that the metals are accumulating at lower layers of the soil profile, suggesting that not only plants and soil, but even water bodies could be under the threat of heavy metal pollution in the area.

Key words: Fadama; Wastewater; Heavy Metals; Soil Pollution; Kano City

INTRODUCTION

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb). They are natural components of the Earth's crust and cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams,

lakes, rivers, and groundwater.

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

Cadmium derives its toxicological properties from its chemical similarity to zinc, an essential micronutrient for plants, animals, and humans. Cadmium is biopersistent and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted. In humans, long-term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer. Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. The average daily intake for humans is estimated as 0.15 µg from air and 1 µg from water.

¹Correspondence should be addressed to S. A. MASHI, Tel: 234-080-3606-6564. 234-080-2508-7064. E-mail: sanimashi2000@yahoo.com

Biographical note of the first author: Dr. S. A. MASHI, associate professor, majoring in environmental applications of remote sensing and GIS, and the impact of human activities on environmental quality.

Smoking a packet of 20 cigarettes can lead to the inhalation of around 2-4 μg of cadmium, but levels may vary widely^[1].

Cadmium is produced as an inevitable by-product of zinc (or occasionally lead) refining, since these metals occur naturally within the raw ore. However, once collected the cadmium is relatively easy to recycle. The most significant use of cadmium is in nickel/cadmium batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance and high tolerance to physical and electrical stress. Cadmium coatings provide good corrosion resistance, particularly in high stress environments such as marine and aerospace applications where high safety or reliability is required; the coating is preferentially corroded if damaged. Other uses of cadmium are as pigments, stabilisers for PVC, in alloys and electronic compounds. Cadmium is also present as an impurity in several products, including phosphate fertilisers, detergents and refined petroleum products. In the general among the non-smoking population, the major exposure pathway is through food, via the addition of cadmium to agricultural soil from various sources (atmospheric deposition and fertiliser application) and uptake by food and fodder crops. Additional exposure to humans arises through cadmium in ambient air and drinking water.

Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage to circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of the metal.

Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth.

In humans, exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure^[2]. Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system. At intermediate concentrations, however, there is persuasive evidence that lead can have small, subtle, subclinical effects, particularly on neuropsychological developments in children. Some studies suggest that

there may be a loss of up to 2 IQ points for a rise in blood lead levels from 10 to 20 $\mu\text{g}/\text{dL}$ in young children^[3]. Although most people receive the bulk of their lead intake from food, in specific populations other sources may be more important, such as water in areas with lead piping and plumbosolvent water, air near point of source emissions, soil, dust, paint flakes in old houses or contaminated land. Lead in the air contributes to lead levels in food through deposition of dust and rain containing the metal, on crops and the soil.

Lead in the environment arises from both natural and anthropogenic sources. Exposure can occur through drinking water, food, air, soil, and dust from old paint containing lead. In the general non-smoking adult population, the major exposure pathway is from food and water. Food, air, water, and dust/soil are the major potential exposure pathways for infants and young children. For infants up to 4 or 5 months of age, air, milk formulae, and water are the significant sources. The metal is among the most recycled non-ferrous metals and its secondary production has therefore grown steadily in spite of declining lead prices. Its physical and chemical properties are applied in the manufacturing, construction and chemical industries. It is easily shaped and is malleable and ductile. There are eight broad categories of use: batteries, petrol additives, rolled and extruded products, alloys, pigments and compounds, cable sheathing, shot and ammunition.

Mercury is a toxic substance which has no known function in human biochemistry or physiology and does not occur naturally in living organisms. Inorganic mercury poisoning is associated with tremors, gingivitis and/or minor psychological changes, together with spontaneous abortion and congenital malformation. Methylmercury causes damage to the brain and the central nervous system, while foetal and postnatal exposure have given rise to abortion, congenital malformation and development changes in young children^[4].

Mercury is a global pollutant with complex and unusual chemical and physical properties. The major natural source of mercury is the degassing of the Earth's crust, emissions from volcanoes and evaporation from natural bodies of water. World-wide mining of the metal leads to indirect discharges into the atmosphere from where it can fall out onto soils and plants. The usage of mercury is widespread in industrial processes and in various products (e.g. batteries, lamps, and thermometers). It is also widely used in dentistry as an amalgam for fillings and by the pharmaceutical industry. Concern over mercury in the environment arises from the extremely toxic forms in which mercury can occur. Natural biological processes can cause methylated forms of mercury to

form, which bioaccumulate over a million-fold and concentrate in living organisms, especially fish. The monomethylmercury and dimethylmercury forms of mercury are highly toxic, causing neurotoxicological disorders. The main pathway for mercury to humans is through the food chain and not by inhalation.

Small amounts of nickel are needed by the human body to produce red blood cells. However in excessive amounts, it can become mildly toxic. Short-term overexposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation. Nickel can accumulate in aquatic life, but its presence is not magnified along food chains.

Selenium is needed by humans and other animals in small amounts, but can cause damage to the nervous system, fatigue, and irritability in larger amounts. Selenium accumulates in living tissue, causing high selenium content in fish and other organisms, and greater health problems in humans over a lifetime of overexposure. These health problems include hair and fingernail loss, damage to kidney and liver tissue, circulatory tissue, and more severe damage to the nervous system.

Kano City is the largest city in northern Nigeria. It is located in a special geographical position where many favorable conditions for economic development converge. The area of the City is about 2 000 km² and the population over 2 million. It has the highest rate of development in industry and handicrafts in northern Nigeria. Among the varieties of industries in the City are those of metallurgical, pharmaceutical manufacture, pain making, batteries producing, textile making, tanneries, ceramics, lamps making, petrochemical products producing, fertiliser and agro-chemicals making, PVC pipes making, paper and rubber making among others. Most of the industries have been operating since early 1960s with many having outdated equipments and without effective wastewater treatment systems. Beside, the City has one of the largest markets for imported goods in the Country. In fact, there is virtually no single commodity in the international market that one cannot buy from Kano. The inhabitants can therefore be said to be leaving in a city where they have access to potential heavy metal polluting goods and services. There are thus many sources by which industrial and domestic activities can release heavy metals to the City's environment.

There is a good network of drainage lines (man-made canals and naturally occurring rivers) that collect water being discharged (i.e. wastewater) away from the various industries, houses and other built-up areas. Because of the high demand for crops (especially vegetables) by the City's teeming

population, this wastewater is being used directly to cultivate the fertile alluvial, seasonally flooded soils that lie on river banks (called Fadama in local Hausa language of the area). This no doubt has a potentially serious polluting effect on soil and agricultural produce from those Fadama lands. There is thus the need for monitoring to be carried out from time to time on the levels of heavy metals (especially Cd, Cu, Zn, Pb, Hg, and Cr) in Fadama soils of the area. The need for this monitoring constitutes the problem of research interest that this paper sought to address. The objective of this paper therefore was to examine the levels of Cd, Cu, Zn, Pb, Hg, and Cr in Fadama soils in Kano City.

MATERIALS AND METHODS

Selection of Suitable Sites

A reconnaissance survey was first carried out to have an overview of the spatial distribution of all the Fadama lands in and around the city that depend on the city's waste water. Following this survey, 30 representative Fadama lands were chosen to serve as the sampling points from where soil samples were to be drawn. Five lands were chosen from areas of the city under residential, industrial, commercial, mixed but largely residential landuses, respectively, from which the main ones were found in the city. Five other Fadama lands not being irrigated with waste water in the city were also chosen to serve as the control.

Soil Sampling

The Fadama lands in the area vary in sizes, between about 28 m² and 45 m². For the purpose of soil sampling, quadrants of 5 m by 5 m each were demarcated on every selected land and in every quadrant 25 equal-sized grid squares were again demarcated. At mid-point of every grid-square, soil samples were collected from 0-15 cm and 20-30 cm depths (giving a total of 25 samples per sampling depth for every land). Sampling at these pre-determined depths was deliberately conducted because most of the crops growing on the soils (mainly vegetables) had about 30 cm as their maximum rooting depth. Sampling at these uniform depths also helped to ensure uniformity in sampling across all the selected lands.

Soil Analyses

The collected soil samples were oven-dried at 105 °C in order to obtain constant weights. The dried samples were then crushed and sieved through a 2 mm sieve to remove gravel fractions. One g

sub-samples was taken into crucibles to which few drops of distilled water were added to prevent sputtering. DTPA (diethylenetriamine pentaacetic acid) extraction method^[5] was then used to extract the metals from the samples because it has widely been used as an extractant to indicate the bioavailability of numerous heavy metals in soils^[6-8]. The concentrations of various heavy metals in the extractants were determined by atomic absorption spectrophotometry.

Statistical Analysis

Mean and coefficient of variation values for every metal were computed for each of the six selected areas of varying types and levels of human activities (residential, industrial, commercial, mixed but largely residential landuses, and control) for the two sampling depths (0-15 cm and 20-30 cm). Students' *t*-test was then used to test for significant difference in mean values of each metal between the soils of the control and each of those of the Fadama areas under varying levels of human activities.

RESULTS

Tables 1 and 2 give respectively the mean and coefficient of variation percentage values for the various heavy metals for each of the six selected landuse types in the City. It is clear from the two tables that the metals were concentrated in higher amounts in the lower (20-30 cm) than in the upper (0-15 cm) depths, which was an indication of downward movement of the metals in profile of the

soils. This downward movement was a reflection of the ease with which water penetrated the depth in the extensive network of large cracks characterising alluvial Fadama soils (mainly Vertisols) in northern Nigeria. The comparatively lower topsoil values of the various metals could also be an indication of higher rates of their immobilisation by crops in the layer, since most of those growing in the area had a shallow (mostly not more than 20 cm) rooting depth.

A close look at the two tables indicated that in the two soil depths, Zn was generally the most abundant, followed by Cr, then Pb, Cu, and Cd while Hg was the least concentrated metal in the soil samples. The elevated levels of Zn, Cr, Pb, Cu, and Cd in the soils above that of Hg were a reflection of comparatively lower numbers of industries utilising Hg in production processes in the area.

The Fadama soils in areas of mixed landuses (industrial, residential, commercial, Institutional *etc.*) with industrial as the dominant ones maintained the highest concentrations of the various metals. This was followed by those of industrial areas, then residential areas of mixed landuses as the dominant ones, while the soils of commercial areas maintained the least concentrations of the metals, indicating that heavy metal pollution of Fadama soils in the area was not restricted to industrial activities alone but that activities in residential areas (such as domestic usage of products containing heavy metals) also contributed significantly towards the problem. In a number of studies, the contributions of domestic activities alongside that of industrial activities towards heavy metal pollution in agricultural soils have been well documented^[8-10].

TABLE 1

Concentrations of Some Heavy Metals in Fadama Soils in Kano City, Nigeria (0-15 cm Depth)

Sampling Area Category	Statistical Parameter	Concentrations of the Various Metals (mg/kg)					
		Cd	Cu	Zn	Pb	Hg	Cr
Residential	Mean	7.9 ^a	25.4 ^b	125.3 ^b	62.4	0.09 ^a	132.5 ^b
	CV%	34.2	22.3	15.6	30.6	31.0	15.6
Industrial	Mean	10.3 ^b	25.7 ^b	132.6 ^b	112.0 ^b	0.21 ^b	175.6 ^b
	CV%	23.4	32.1	23.6	20.3	40.5	32.5
Commercial	Mean	5.6	15.4 ^a	120.3 ^b	45.0 ^a	0.08 ^a	92.0 ^b
	CV%	14.6	12.5	26.0	26.4	11.0	45.6
Mixed, But Largely Residential	Mean	8.5 ^a	29.3 ^b	144.0 ^b	85.2	0.20 ^b	156.3 ^b
	CV%	24.6	12.7	33.5	21.4	7.0	32.6
Mixed, But Largely Industrial	Mean	19.2 ^a	36.7 ^b	153.6 ^b	121.6 ^a	0.13 ^b	195.2 ^b
	CV%	17.2	32.7	25.0	13.7	10.6	42.5
Control	Mean	2.2	5.6	45.2	72.4	0.02	32.6
	CV%	6.7	12.5	14.2	20.2	7.7	7.5

Note. The mean value for every sampling area category is for 125 soil samples (i.e. 25 samples for the selected five Fadama lands. ^aDenotes the mean values of the various metals that are statistically different from those of the control, at 0.05 probability level. ^bDenotes the mean values of the various metals that are statistically different from those of the control, at 0.001 probability level.

TABLE 2

Concentrations of Some Heavy Metals In Fadama Soils in Kano City, Nigeria (20-30 cm Depth)

Sampling Area Category	Statistical Parameter	Concentrations of the Various Metals (mg/kg)					
		Cd	Cu	Zn	Pb	Hg	Cr
Residential	Mean	9.5 ^b	32.5 ^b	169.2 ^b	53.7	0.49 ^b	166.0 ^b
	CV%	24.2	21.1	10.3	23.4	27.0	15.6
Industrial	Mean	15.0 ^b	45.2 ^b	180.4 ^b	153.6 ^b	0.31 ^b	194.3 ^b
	CV%						
Commercial	Mean	14.2	12.1	25.4	20.5	21.4	15.6
	CV%	9.2 ^b	22.5 ^b	152.0 ^b	67.8	0.07 ^a	96.5 ^b
Mixed, But Largely Residential	Mean	4.2	9.1	13.6	18.4	19.0	15.6
	CV%	12.4 ^b	35.9 ^b	170.5 ^b	72.6 ^a	0.25 ^b	172.6 ^b
Mixed, But Largely Industrial	Mean	24.2	17.1	15.6	13.5	21.0	15.6
	CV%	36.3 ^b	45.6 ^b	142.6 ^b	175.2 ^b	0.15 ^b	182.5 ^b
Control	Mean	16.2	22.1	12.3	28.0	31.0	15.6
	CV%	1.9	3.1	22.7	40.7	0.01	21.2

Note. The mean value for every sampling area category is for 125 soil samples (i.e. 25 samples for the selected five Fadama lands. ^aDenotes the mean values of the various metals that are statistically different from those of the control, at 0.05 probability level. ^bDenotes the mean values of the various metals that are statistically different from those of the control, at 0.001 probability level.

All the areas of various human activities in general maintained significantly higher levels of all the metals than in the background soil samples (i.e. the control) in the two depths, indicating that use of wastewater from the various areas of varying type and level of human activities in the city could result in significantly elevate of the levels of the studied metals in Fadama soils in the area. This is consistent with observations of several others^[11-13].

The various metals in the background soil samples (the control) exhibited a low spatial variability (6.7%-20.2% in the 0-15 cm layer, and 6.1%-10.2% in the 20-30 cm layer), while in the Fadama soils involving the use of wastewater the variability were much higher (7.0%- 40.5% in the 0-15 cm layer, and 9.1%-28% in the 20-30 cm layer), indicating that continuous applications of wastewater to irrigate the Fadama soils in the area could result in increased spatial variability in concentrations of the metals.

DISCUSSION

In managed agricultural soils, it is generally assumed that heavy metals are immobile^[17]. However, in an agricultural ecosystem, some factors that enhance the mobility of such metals can result in plant uptake or leaching to groundwater. Such factors include texture, pH and competing cations in soil solution^[18]. Dowdy and Volok^[19] and Smith^[20] have shown that where waste disposal is made on sandy, acidic, low organic matter soils receiving high

rainfall or irrigation water, the movement of heavy metals into lower soil layers tends to be high. On the other hand, Kuo *et al.*^[21] observed that Cd retention is greater in fine textured soils with high CEC than in coarse-textured soils with lower CEC while McBride^[17] noted that heavy metal mobility is most closely associated with metal-organic complexation and soil pH. The soils of the area are typical alfisols (aqualfs) fine textured with high clay content and CEC. Use of organic manure by the farmers cultivating the soils brings about some improvement in organic carbon contents of the soils. It is thus expected that the heavy metals studied here exhibit high mobility in the soils.

Use of effluents for raising crops is a common practice in peri-urban areas of many developing cities. Accumulation of heavy metals on lands receiving such effluents is however of much scientific significance and health concerns^[22]. Under natural conditions, bioavailable forms of heavy metals in soils of such lands are expected to concentrate in higher amounts in the topsoil because the factors that promote such bioavailability (such as pH and organic matter) are typically concentrated in higher amounts there^[14-15]. With continuous applications of wastewater to excessively drained soils in hot climatic regions, like those of the study area, downward movement of the metals in a soil profile could be expected^[11]. As this downward movement of the metals continues, it is possible that ground water sources could be polluted as well. In Vadodara district of India, Maliwal *et al.*^[23] have observed significant positive correlations between organic

carbon content and DTPA extractable Fe, Mn, Cd, and Co contents of soils of different profiles irrigated with mix industrial effluent water, and that the metals progressively move to lower soil layers, a process which they attribute to cheluvation.

In semi-arid tropical soils, it has been well established that clay particles migrate to lower from upper soil horizons, in a process called eluviation. This process leads to accumulation of the particle in sub-surface horizons leading to formation of a layer massively impregnated with clay particles called argillic horizon^[24]. Since clay is an important colloid promoting retention of metallic elements in soils, it is expected that such an argillic horizon can promote retention of the heavy metals migrating to the lower soil layers in the study area from where they can be lost to underground water sources in solution. This can consequently serve as an important source of groundwater pollution in the area.

Compared with the other heavy metals studied, Zn has the least toxicity effects and is in fact a metal essentially required in minute amounts. It however has a tendency of being phytotoxic. Thus the observation made here that the metal has the highest accumulating tendency in the soils should be of much concern here. Likewise, the mean concentrations of the other metals (Cd, Cu, Pb, and Cr) in the soil samples analyzed, which range between 5.6 and 195.2 mg/kg) are on a high side for environmental safety standards. In fact there are no known lower limits of Pb and Cd for tolerance by human body systems. Hg, the most unwanted heavy metal has mean concentrations that are all below 0.5 mg/kg in the soils which is no doubt a good development at least for safety reasons. The most notable usage of Hg is in lamp and batteries making, in which there are very few industries specialising in the study area. This may account for the comparatively lower concentration of the metal in the soil samples analysed, compared with the other metals. Comparatively, in almost all the industries in the city, there is widespread usage of petrochemicals and fuel additives especially in power generation and lubrications of machineries. Beside, there is equally widespread use of domestic appliances and equipments that are principally produced from alloys of Cr, Cu, Zn, Cd, and Pb. Hg is regarded as the most unwanted heavy metal^[12] and thus the fact that it is concentrated in comparatively lower amounts in the soils compared to the other five metals is no doubt a good development here.

The use of wastewater in irrigating the soils has clearly raised the background level of the metals in soils of the area, as well as their spatial variability in the soils. This no doubt is a further confirmation of the fact that wastewater use in agriculture, especially

in areas where there are little of no wastewater treatment facilities, brings about elevated levels of heavy metals in the irrigated soils^[25]. It is of particular concern here that in the study area, the elevations are as in most cases high as about 200%, suggesting that high financial investments are needed where recovery programmes are decided to reclaim the soils. The increase in spatial variability of the metals is also of much concern here because as a soil becomes more spatially variable, farmers are faced with difficulties of deciding on which management measure is to uniformly be applied. In Indonesia for instance, it was observed that farmlands dotted with bare spots are those where acid sterile subsoil are exposed by bull dozers during tillage operations, with such spots deliberately being left uncultivated^[26].

The heavy metal concentration in the topsoil could be attributed to the effect of soil-forming processes, as well as agricultural and human activities (such as irrigation with wastewater containing heavy metals). The comparatively lower topsoil values of the various metals, as observed in the study area, could also be an indication of higher rates of their immobilisation by crops in the layer, since most of those growing in the area have shallow (mostly not more than 20 cm) rooting depth. On the other hand, the observed higher subsoil content of the studied metals could be a reflection of the ease with which water penetrates the depth in the extensive network of large cracks that characterise alluvial Fadama soils (mainly Vertisols) in northern Nigeria. However, the time of application of wastewater on the soil (such as dry or rainy season) can particularly have a significant contributory effect on the higher extent of accumulation of heavy metals in the subsoil horizon, because the metals in a soil are present in the solid phase and in solution, as free ions, or adsorbed to soil colloidal particles and the proportions of each of these could vary with time in a soil.

Adsorption, defined as the accumulation of a substance or material at an interface between the solid surface and the bathing solution, is identified as the most important chemical process controlling the behavior and bioavailability of metals in soils^[27-28]. Surface charge, pH and the concentration of ions, as well as of its accompanying anions, can affect electrostatic adsorption of metals, while organic matter, Fe and Al hydrous oxides, and clay content are recognized as the most significant soil properties influencing sorption reactions^[29-30]. Additionally, soil pH, cation exchange capacity (CEC) and redox potential can also regulate the mobility of metals in soils^[31]. All these factors vary with time in a soil. pH which fluctuates easily with time in a soil is, for instance, very important for most heavy metals, since metal availability is relatively low when pH is around

6.5 to 7. With the exception of Mo, Se, and As, the mobility of trace elements is reduced with increasing soil pH because of the precipitation as insoluble hydroxides, carbonates, and organic complexes. At high pHs, ion hydrolysis (MOH^+) is favored, and the energy barrier that must be overcome when these ions approach the surface of soil particles is decreased^[32]. Thus, surface and subsurface samples of the same soil can exhibit different capacities of adsorbing heavy metals at different times since the adsorption behavior depends on the combination of the soil properties and the way they affect each specific element^[32].

The presence of competitive cations, which also varies with time, can affect metal adsorption in soils. For instance, Ca^{2+} competes effectively with cationic heavy metals for adsorption sites, and this competition seems to be greater for Zn and Cd than for Cu and Pb^[33]. This occurs because Zn and Cd are basically retained in the soil by exchange reactions, while Cu and Pb form inner-sphere complexes with organic matter and Fe, Al, and Mn oxides.

Another time-dependent factor that can influence variation in heavy metal content overtime in surface and subsurface soil layers is the presence of inorganic and organic ligands in the soil solution. Soil redox potential, which also varies with time, can also influence the solubility of heavy metals in soils. In conditions where oxidation reactions are involved, the solubility of heavy metals increases with decreasing pH. But, in reducing conditions, the solubility of Zn, Cu, Cd, and Pb is higher in alkaline pHs, as a result of formation of stable soluble organomineral complexes. On the other hand, if pH ranges between 4 and 6, the solubility of these metals would be lower because of formation of insoluble sulfides or insoluble organomineral complexes^[33].

CONCLUSION

Fadama lands relying on wastewater in Kano City are significantly polluted by the wastewater high in contents of several heavy metals, especially Zn and Cr. Concentrations of the two metals in the Fadama soils under wastewater application are in general above 100 mg/kg while in the background samples they are generally below 50 mg/kg. The fact that the levels of all the studied metals have significantly been elevated in the Fadama soils should be of much concern because most of the studied metals have no known threshold levels for human intakes. Moreover, as Fadama agriculture progresses in the area, the elevation might reach catastrophic levels. To mitigate this problem, it is recommended that (1) the industries should be compelled to improve their wastewater

treatment processes to make them free of heavy metals, (2) legislations against pollution of streams in the area should be made more strict and (3) efforts should be made to provide alternative, cleaner water for Fadama irrigation in the area. Finally, it should be noted that increases in the concentration of the studied metals in the soils are expected to cause higher levels of the metals in various growing crops and ground water in the area. Further research is thus required in the area to ascertain the extent to which the crops are so polluted by the metals.

REFERENCES

1. WORLD BANK (1999). Pollution Prevention and Abatement Handbook. World Bank, Washington D. C.
2. Mashi S A, Yaro S A, Galadanci K M (2005). Lead accumulation in surface soils and components of *Balenites aegyptica* specie in a Katsina urban area, Nigeria. *Biomed Environ Sci* **18**, 15-20.
3. AECLP (Alliance to End Childhood Lead Poisoning) (1994). The Global Dimension of Lead Poisoning. EAELP, Washington D.C.
4. Singh B R, Steinnes E (1994). Soil and Water Contamination by Heavy Metals. Lewis Publishers, Boca Raton. pp 233-271.
5. Hanlon E A, Schaffer B, Ozore Hampton M, *et al.* (1996). Ammonium bicarbonate-DTPD extraction of elements from waste-amended calcareous soil. *Commun Soil Sc Plant Anal* **27**, 2321-2335.
6. Chlopecka A (1996). Assessment of forms of Cd, Zn, and Pb in contaminated calcareous and gleyed soils in southwest Poland. *Sci Total Environ* **188**, 253-262.
7. Gallardo-Lara F, Azcon M, Quesada J L, *et al.* (1999). Phytoavailability and extractability of copper and zinc in calcareous soil amended with composted urban wastes. *J Environ Sci Health. Part B – Pest, Food Contamin Agric Wastes* **34**, 1049-1064.
8. Brun L A, Mailet J, Hessinger P, *et al.* (2001). Evaluation of copper availability to plants in copper contaminated vineyards soils. *Environ Pollu* **111**, 293-302.
9. Korentajer A (1991). A review of the agricultural use of sewage sludge: benefits and potential hazards. *Water South Africa* **17**, 189-196.
10. Berti W R, Jacobs L W (1998). Distribution of trace elements in soil from repeated sewage sludge applications. *J Environ Qual* **27**, 1280-1286.
11. McBride M B, Richards B K, Steenhuist T, *et al.* (1999). Long-term leaching of trace elements in a heavily sludge amended silty clay loam soil. *Soil Sci* **164**: 613-623.
12. McBride M B (1994). Environmental Chemistry of Soils. Oxford University Press, Inc, New York.
13. Keller C A, Kayser A, Schulin R (2001). Heavy-metal uptake by agricultural crops from sewage-sludge treated soils of the upper Swiss Rhine valley and the effect of time. In: Environmental Restoration of Metals-Contaminated Soil (I K Iskander, Ed.), pp. 53-71. Lewis Publishers, Washington D. C.
14. Alloway B J (1995). Soil processes and the behaviour of heavy metals. In Heavy Metals in Soils (B J Alloway, Ed.), pp 11-37. 2nd Edition. Chapman and Hall, London.
15. Tsadilas C D (2000). Soil pH influence on cadmium uptake by tobacco in high cadmium exposure. *J Plant Nutr* **23**, 1167-1178.
16. Chang, A C, Hae-Nam H, Page A L (1997). Cadmium uptake for Swiss chard grown on composted sewage treated fields: plateau or time bomb? *J Environ Qual* **26**, 11-19.
17. McBride M B (1995). Toxic metal accumulation from

- agricultural use of sewage sludge: Are USEPA regulations protective? *J Environ Qual* **24**, 5-18.
18. Udom B E, Mbagwu J S C, Adesodun J K, *et al.* (2004). Distributions of zinc, copper, cadmium and lead in a tropical ultisol after long-term disposal of sewage sludge. *Environ Internl* **30**, 467-470.
 19. Dowdr R H, Volk V V (1984). Movement of heavy metals in soils. In: *Chelate Mobility and Reactivity in Soil Systems* (D W Nelson, D E Elrick D E, K Tanji, Eds.). Soil Science Society of America Publication, Madison WI, pp 229-240.
 20. Smith S R (1991). Effects of sewage sludge application on soil microbial processes and soil fertility. *Adv Soil Sci* **16**, 191-212.
 21. Kou S, Jellium E J, Baker A S (1985). Effects of soil type, liming and sludge application on Zinc and Cadmium availability to Swisschare. *Soil Sci* **12**, 350-359.
 22. Nriagu J O (1992). Global metal pollution. *Environ* **32**, 7-11.
 23. Maliwal G L, Patel K P, Patel K C, *et al.* (2004). Distribution of heavy metals in soils irrigated with mixed industrial effluents and their relationship with soil properties. *Ecol Environ Conserv* **10**(3), 323-328.
 24. Sanchez P A (1976). *Properties and Management of Soils in the Tropics*, Wiley, New York.
 25. Asok K, Yadav B R, Singh S K, *et al.* (1998). Effect of mixed industrial effluent on properties of ground water and irrigated soils. *Indian J Soil Sci* **46**, 427-429.
 26. McCants C B (1985). Variability piece by piece. *Tropical Soils, Trainee Technical Report 1981-1984*. No. 2, pp 55.
 27. Alloway B J (1990). *Heavy Metals in Soils*. New York: Wiley, 1990. 339p.
 28. Sparks D L (1995). *Environmental Soil Chemistry*. Academic Press, San Diego. 267p.
 29. Barry G A, Chudek P J, Best E K, *et al.* (1995). Estimating sludge application rates to land based on heavy metal and phosphorus sorption characteristics of soil. *Water Res* **29**, 2031-2034.
 30. Bolan N S, Duraisamy V P (2003). Role of inorganic and organic soil amendments on immobilisation and phytoavailability of heavy metals: a review involving specific case studies. *Austr J Soil Res* **41**, 533-555.
 31. Lombi E, Gerzabek M H (1998). Determination of mobile heavy metal fraction in soil: result of a plot experiment with sewage sludge. *Commun Soil Sci Plant Anal* **29**, 2545-2556.
 32. Yu T R, Sun H Y, Zhang H (1997). Specific adsorption of cations. In: *Chemistry of Variable Charge Soils*: (T R Yu, Ed.). Oxford University Press, New York. pp 140-174.
 33. Kiekens L (1983). Behavior of heavy metals in soils. In: *Utilization of Sewage Sludge on Land: Rates of Application and Long-term Effects of Metals* (S Berglund, R D Davis, P L Hermite, Eds.). D Reidel Publishing, Dordrecht. pp 121-135.

(Received January 2, 2006 Accepted August 15, 2006)