ANALYSIS OF WASTEWATER SLUDGES FOR SOME METALS AND THEIR APPLICATION IN SMALL SCALE FARMING

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D E C L A R A T I O N

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any other University or Institution. Information derived from the published or unpublished work of others has been acknowledged in the text.

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D E D I C A T I O N

Dedicated in memory of my late mother, Lolo Adaji Anodere, and my wife and children for their patience and endurance during my absence.

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A B S T R A C T

In carrying out this analytical study, a total of eighteen samples of sewage sludges from Kaduna and Zaria were analysed for the following metals: sodium, potassium, magnesium, calcium, lead, zinc, copper, iron, manganese, cadmium, nickel, chromium and cobalt.

Nitric acid digestion method, was used to bring the metals in organic matrices into solution.

Atomic absorption spectrophotometric and flame photometric techniques were used to determine the amounts of the metal ions in the wastewater sludges. Flame photometric technique was used in potassium and sodium determination while atomic absorption spectrophotometric technique was used for determination of other metals.

Calibration curves were obtained for all the metals using the appropriate working range standard solutions and amounts of the metals in the samples determined with the aid of the standard curves.

Withe the exception of the macro-nutrients (calcium, magnesium, potassium, iron, and sodium) whose amounts in the wastewater sludges were relatively high, those of the micronutrients or heavy metals were very low compared to the maximum amount allowed in any sewage sludge,

Experimental values were also compared with some suggested standards for sludge application on farmland.

ANALYSIS OF WASTEWATER SLUDGES FOR SOME METALS AND THEIR APPLICATION IN SMALL SCALE FARMING

CHAPTER ONE

I N T R O D U C T I O N

1.1 DESCRIPTION OF WASTEWATER SLUDGES

Sludge in general term is a mixture of plant and animal organic materials, oils, greases and metals obtained from wastewaters. The sludge itself is a semi-solid which is usually odiferous, unmanageable and dangerous[1]. It is dangerous and unmanageable in the sense that it might contain some toxic substances such as heavy metals.

Apart from this unsavoury language used to describe sludge, sludge has its good attributes for it contains substantial nutrients (macro and micro nutrients) and organics which are considered to be replenishable natural resource for plant food as well as for soil amendment.

1.2 TYPES OF SLUDGE

In wastewater treatment plant different types of sludges are obtained depending on the stages of treatment of the wastewater.

The first sludge extract from treatment plant and the wastewater sludge before treatment are collectively known

as "raw sludge". The raw sludge is the semi-solid obtained by decantation of most of the supernatant liquid when the wastewater is allowed to settle down or sediment.

The second extract after the secondary stage of wastewater treatment is known as "activated sludge"(2). This sludge is different from the first because of the removal of the BOD (biochemical Oxygen demand.) This removal helps in stablizing the sludge.

1.3 SOURCES OF WASTEWATER SLUDGES.

The main sources of watewater sludges are the domestic wastewater sludges, industrial wastewater sludges, municipal wastewater sludges and wastewater sludges from storm run off(3).

1.3.1 DOMESTIC WASTEWATER SLUDGES

This type of sludge is obtained from water closet: washing and bathing obtained from wasbasins, showers and bath; and a range of miscellaneous operations in the home which include food and drink operations, washing household utensils, clothes and cars.

The wastewater sludges obtained from the water closet is highly offensive to sight and smell because of faeces,

urine and paper, which it contains. The sludge obtained from preparati n of food and drinks as well as from washing of household utensil consists mainly of soap, detergent, food particles, silt, soluble and colloidal materials. This wastewater sludge is less offensive than the first.

1.3.2. INDUSTRIAL WASTEWATER SLUDGES

Industrial wastewater sludges include sludges from food and drink manufacturing industies as well as those from chemical and metallurgical industries. Sludges from food and drink industries produce degradable wastes of high pollutional load while those from chemical and metallurgical industries are more likely to contain toxic materials(3)

1.3.3. MUNICIPAL WASTEWATER SLUDGES

Municipal wastewater sludge is a mixture of both domestic and industrial wastewater sludges and as such may contain a higher pollutional load than eith r the domestic or industrial wastewater sludges.

1.4 EFFECT OF WASTEWATER SLUDGE ON SEED GERMINATION(4)

Elizabeth wollan, R.D. Davis and Salley Jenner(4) observed in their pot trial experiments that germination

periods of barely and ryegrass were prolonged or delayed owing to application of sewage sludge. The lag period was dose-dependent increasing in proportion to the amount of sludge added. This effect was also induced by heavy metals (CU,Ni, and Zn) in aqueous solution but only by concentrati n much higher than those in sludge, considering that most of the total metal load in sludge is in insoluble or unavailable forms. Further experiments showed that the delay in the germination period was more closely related to the organic matter content of sludge-soild mixtures on which the seeds were planted than on the concentration of the metals.

This is so because of the intense microbial activity of the freshly applied sludge leading to reduction of supply of Oxygen (which is neccessary for seed germination) and production of volatile inhibitors such as ethylene and ammonia(4).

1.5 DESPOSAL OF WASTEWATER SLUDGES

Many countries, especially the advanced ones, apply sewage sludge on farmlands as one of the ways of disposing the sludge. This way of disposal causes a great concern to the farmer because of the possibility of the wastewater

sludge affecting the fertility of the soild when sludge contains high level of toxicants. To avoid this ugly situation many countries have proposed different standards and sometimes legislation to regulate the application or desposal of wastewater sludge, especially, on farmlands.

1.5.1 FACTORS GOVERNING THE APPLICATION RATE OF WATERWASTE SLUDGE ON FARMLAND

The maximum application rates of sludge for a given agricultural land depend on a number of vfactors. Such factors include the type of soil the farm is composed of, potential for water contamination; weather; potential for odour production and method of application. Other important factors are the sludge characteristics which include its, concentration of pathogenic organisms, heavey metals, nutrient and other toxins(6).

Although the above factors are needed to incorporate a fair and enforceable land application standards, the standards adopted for land application of wastewater sludges at the moment are calculated on the bais of heavy metals or nitrogen because of the ease with which toxins (heavy metals) and nitrates are seeped into the ground. The lower of the

values obtained either from heavy metals consideration or nitrogen consideration is used as the standard for the application of that wastewater on farmland.

As my project is on determination of metals in wastewater sludge, application of sludge on land is based on standards derived from metal consideration.

1.6 STANDARDS FOR APPLICATION OF WASTEWATER SLUDGES ON FARMLAND

There are no Universally accepted Standards for wastewater sludge application on farmland; Many researchers and governmental agencies have made different suggestions for standards based on heavy metals, but none has been accepted universally. As a result of this, different countries have different standards for sludge application to suit their environment and the type of crops or seeds planted on farmland.

In United States of America, the Environmental Protection Agency, (EPA) in 1977 gave the total amount of sludge metals allowed on agricultural land as shown in table I of the appendix. Different values of amount of metal are given as a result of the difference is soil Cation Exchange Capacity (CEC).

In Finland, Norway and Sweden the annual maximum applications of sludges allowed on agricultural lands are 4 tonnes per hectare, 2 tonnes per hectare and 1 tonne per hectare respectively.

In Denmark, the rate is variable depending on the nitrogen balance and Cadmium concentration. Scandinavian countries have maximum allowable levels of heavy metals. In Denmark and Finland the maximum allowable amount of lead (Pb) in sludge is 1,200mg/kg. While in Norway and Sweden it is 300mg/kg.

Maximum allowable amount of Cadmium in sludge in Denmark and Finaland is 30mg/kg while in Norway and Sweden is 15mg/kg.

In Netherlands farmers are advised to use sludges containing not more than 2,000 mg/L (Zn) 500mg/L (Cu) and 50mg/L (Ni) and 10mg/L (Cd)

Some researchers also suggested that no application of sludge on farm land should be greater than 250ppm Zinc equivalent for soil with P^H greater than 6.5[7]

Zinc equivalent = (Zn)+ 2(Cu) + 8 (Ni)[7] where the

amounts of zinc, copper and nickel are in ppm or mg/kg.

Other researchers like Chaney and Wisconsin gave the standards for maximum allowable sludge application rate for soils with P^H 6.5 as

$$\text{TOTAL Sludge Application (dry ton/acre)}^{(7)} = \frac{16,300 \ (\text{CEC})^*}{(Zn) + 2\,(Cu) + 4\,(Ni) - 300}$$

and $$\frac{32,500\ (\text{CEC}^*)}{(Zn) + 2(Cu) + 4(Ni)}$$

Chaney did not only give the maximum application of sludge but also suggested the maximum heavy metal concentrations in sludge as shown on table (2) of the appendix.

Another standard for annual application rate of sludge on land based on heavy metals is given by the equation below.

$$\text{Tons Sludge/hectare} = \frac{X \text{ kg metal/hectare}}{\text{ppm metal in sludge} \times 0.002}\ ^{(8)}$$

Where x is the maximum amount of the metal allowed on agricultural land.

In Nigeria no such standards have been formulated.

*CEC = Cation Exchange Capacity.

The lack of this standard is probably either due to the ignorance of the government on the use of wastewater sludge as means of increasing soil fertility or the assumption that the level of pollution arising from wastewater sludges is very insignificant since the level of industrial development which contribute most of the hazards inherent in sludge is low.

1.7 RESEARCH OBJECTIVE

In developed countries wastewater sludges have been applied on farmlands to increase the fertility of the soil and consequent yield in crop production. Victor Hugo in les Miserables (9) reported that the most fertilizing and effective manures is the human manure. Woodward in the same vein maintained in his report in England in 1699 that plants grew much better in sewer waters and water to which such things as garden mould has been added then in rain water(10).

Although the wastewater sludges are applied on farmland to increase the fertility of the soil, nevertheless, they are not indiscrimentely applied. Before wastewater sludges are applied on farmlands chemical analysis is carried out to determine the amount of nutrients and toxic metal present

in the sludge, because presence of toxicants may delay the germination periods of seeds or even posion the seed or crops as indicated earlier. Sometimes the effect of the toxic metal may not express itself in the plant but on animal that eats the plant. For instance cadmium a toxic metal to animal or man does not affect the growth of plants, but render them a health hazard when consumed by humans and animals (11)

R.M. Sterritt and J.N. Lester(12,13, 14) were of the opinion that the amount of toxic metals in sewage sludge should be determined in order to ascertain the amount of the sludge that should be applied on agricultural land because toxic metals such as cobalt,manganese etc. in sludges have caused an increase in their accumulation by crops and in some cases adverse effects on crops yield have been observed.

K.C. Thompson and K. Wagstaff suggested the monitoring of the level of toxic metals in sewage sludges before they are ultimately disposed to the land or soil which may contain lower level of the metals (15,16).

The reason for monitoring the level of these metals is to know which crops or seed should be planted on sludge

amended soil for some plants can easily pick up some toxic metals than other plants. For instance potato, Lettuce and corn were planted on a sludge amended soil. The sludge contained some certain amounts of Manganese (Mn), Copper (Cu), Cadmium (Cd), Lead (Pb), Chromium (Cr) and Nickel (Ni). When harvested and analysed for the presence of these metals it was found than Mn, Zn Cu, Cd, Pb were present in potato tubers, Lettuce leaf and corn grain. Chromium and nickel were not detected (17) (See table 3 in the appendix).

In Nigeria sludge application on farmland has not assumed any wide dimension because of non-participation of any arm of the government. Wastewater sludge are used on small scale farming by local farmers, especially in the Northern parts of Nigeria, living around the urban cities as a source of water supply for their crops during the dry season and not necessarily as a source of food nutrients or toxicants for the crops or seeds planted.

From the foregoing expositions it is my desire not only to dermine the amounts of macro nutrients such as magnesium calcium, sodium and potassium,

but, also to monitor the level of amounts of toxic metals present in sludges found in some parts of Kaduna and Zaria. Successful completion of the excerise will serve as guide to the farmers who may wish to use wastewater sludges for soil amendment.

CHAPTER TWO

COLLECTION AND ANALYSIS OF SAMPLES

2.1 SAMPLES TUDIED

The samples studied were from Kaduna and Zaria. A total of eighteen different samples were collected and analysed. Nine of the samples were from Kaduna and its environs while the remaining ones were from Zaria and its environs. Most of the samples were domestic wastewater sludges while few were industrial and municipal wastewater sludges.

Each sample collected was designated with a different letter of the alphabets as shown in table 2.1 below. The area of collection is also shown.

Table 2.1: Designation and area of collection of samples.

Sludge Designation	Area of Collection
A	Barnawa low cost houses, Kaduna.
B	Narayi Village, Kaduna.
C	Angwarimi low Cost Houses, Kaduna.
D	Badarawa Village, Kaduna.
E	Malali Low Cost Houses, Kaduna.
F	Fertilizer Industry, Kaduna.
G	Textile Industry, Kaduna.

Sludge Designation	Area of Collection
H	Peugeot Factory, Kaduna.
I	Kano Road, Kaduna.
J	Student Cafeteria, Ahmadu Bello University, Zaria.
K	Warri Street, Zaria.
L	Along Sokoto Road, Samaru, Zaria.
M	Funtual Road, about 18 Kilometres from Zaria town.
N	Nigeria Tobaco Company,(NTC) Zaria.
O	Under the bridge between Samaru and I.A.R.
P	Military School, Zaria.
Q	Between Alexander Hall and Kashim Ibrahim Library, Ahmadu Bello University, (MAIN CAMPUS).
R	University dam, Zaria.

2.2 SAMPLING

The aim of sampling before analysis is to obtain a good representative of the whole since it is not possible to handle the whole at a time. The sample taken should as far as possible reflect the character of the bulk of material.

2.3 METHOD OF SAMPLING

Along the line of flow of wastewater sludges samples were taken at different points using plastic cup riveted to a long stick. The samples collected were mostly at points of high turbulence which ensured a high degree of mixing of the surface layers of the inorganic material, suspension, emulsion and large dense materials.

2.4 PRESERVATION OF SAMPLES

It is a well known fact that wastewater sludges (domestic, industrial or municipal) undergo both chemical and biological degradation on standing even for a few minutes. Certain chemical changes alter the chemical structure of the constituents of the sludge that are a function of physical conditions. Cations may change their Oxidation States (although this is not important in Atomic

Absorption method of Analysis for what is important is the number of metal ions or atoms in the ground State) or they form Oxides, hydroxides or even complexes, which might make it impossible to obtain good result during analysis. Some of the metals may even adsorb on the walls of the containing vessels.

Micro organisms, especially the saprophytes attack the wastewater sludges leading to their decomposition.

To minimise these effects, for they cannot be completely guided against, samples collected were put in clean plastic containers previously leached in 10% V/V nitric acid.and acidified with 100ml of another 10% V/V of nitric acid.

The treatment makes the wastewater sludge acidic thereby reducing or preventing the adsorption of the Cations. Since some of the samples collected were not analysed on the very day of collection they were stored in a refrigerator at a termperature of about $4^{o}C$. At this temperature any change that occurred was small.

2.5 ANALYSIS OF SAMPLES

Neutron activation analysis, fluorimetry, colorimetry and flame photometry are among the analytical methods

applied in the dermination of metals in environmental samples. However, atomic-absoption spectroscopy is the method mostly used for this type of analysis because of its speed of analysis, availability as well as its relative freedom from inter-element effect.

Except for the determination of the amount of sodium and potassium in which flamephotometer was used the amounts of other metals were dermined by atomic absorption spectroscopy.

Metals analysed included Ca, Mg, Cu, Pb, Ni, Cr, Cd, Zn,Mn and Co.

2.6 EXPERIMENTAL

2.6.1. APPARATUS

ATOMIC ABSORPTION SPECTROPHOTOMETER AND FLAMEPHOTOMETER:

A Unicam SP 1900 atomic-absorption spectrophotometer and Corning : EEL flame photometer were used in the analysis.

LAMPS: The lamps used for the atomic absorption spectrosopy were pye Unicam hollow Cathode lamps.

Digestion apparatus; The digestions were carried out in 750 ml conical flasks with long neck. Electric heating block, heatrae served as source of heat supply

and stand for the conical flask.

OVEN: A thermostatically controlled electric Gallenkamp oven Bs Model was used.

2.6.2. REAGENTS

Except for samples C,D and E digested with Aristar-grade nitric acid, other samples were digested using analytical grade nitric acid. All solutions were prepared with deionised water and analytical reagent grade material unless otherwise stated. The de-ionised water used to make up the solution during preparation of of stock solutions and serial dilutions were acidified to 1% V/V with nitric acid.

Nitric acid, Sp gr, 1.42

BDH sulphuric acid, 98, Sp gr. 1.84

Hydrochloric acid (36% m/m)

2.7 PREPARATION OF DRIED SLUDGE SAMPLES FROM 50 ML OF THE WET SLUDGE

Table 2.2 lists the sludge studied and also gives the dry mass in grammes. The dry mass of each sludge was obtained by gentle evaporation to dryness of the 50ml of the wet sample in an oven kept at constant temperature of 110°C for 24 hours. The mass of the residue left after evaporation is the dry mass.

TABLE 2.2 DESCRIPTION OF SLUDGE INVESTIGATED

Sludge Designation	Types of Sludge	Dry mass* (gramme) at 110°C
A	Raw	154.99×10^{-2} g
B	"	4.4×10^{-2} g
C	"	41.6×10^{-2} g
D	"	204.64×10^{-2} g
E	"	126.75×10^{-2} g
F	"	9.5×10^{-2} g
G	"	10.62×10^{-2} g
H	"	15.93×10^{-2} g
I	"	5.46×10^{-2} g
J	"	137.14×10^{-2} g
K	"	11.48×10^{-2} g
L	"	5.75×10^{-2} g
M	"	67.45×10^{-2} g
N	"	28.83×10^{-2} g
O	"	90.11×10^{-2} g
P	"	15.84×10^{-2} g
Q	"	49.75×10^{-2} g
R	"	4.22×10^{-2} g

* Average of two determinations each dried at constant mass.

2.8 LABORATORY SAMPLING TECHNIQUE

The wastewater sludge in the plastic containers was shaken vigorously for about three minutes to ensure thorough mixing. 50ml of the sludge were quickly measured out using a 50ml measuring cylinder. The contents of the measuring cylinder were carefully poured into a 750 ml conical flask and remaining residues were washed from the measuring cylinder into the 750ml conical flask using a wash-bottle with a very fine jet. Then the appropriate digestion reagents were added and the digestion carried out. This process was repeated three, four or five times (as the case may be) for the same sample.

2.9 DIGESTION METHOD

There are many conventional procedures that are used to digest wastewater sludges. Nitric acid digestion technique has been recommended as rapid and safe dissolution technique for the routine atomic absorption determination of Cadmium, chromium, copper, nickel lead and zinc in sewage sludges, because all nitrates of these metals are competely soluble in water.

2.9,1 DIGESTION PROCEDURE

Five replicates, sometimes three or four replicates of each wastewater sludge were digested simultaneously on a thermostatic heating block, heatree.

Each replicate of 50ml wet sludge in 750ml conical flask was digested almost to dryness with 35ml of 70% analytical reagent grade nitric acid, or Aristar grade nitric acid as the case may be.

After digestion the flask and contents were allowed to cool. 100ml of acidified de-ionised water were added. The flask and contents were shaken for about five minutes.

The solution was filtered into a 100ml volumetric flask.

After filtration, the filtrate was then transferred to a clean dry polytene container, corked and stored in refreigerator for latter analysis. The filtration was necessary to aviod blockage of the nebuliser of the atomic absorption spectrophotometer and that of the flamephotometer.

2.10 PRINCIPLES OF FLAME SPECTROPHOTOMETRIC ANALYSIS

2.10.1 ATOMIC ABSORPTION SPECTROSCOPY, AAS.

The principle governing the use of atomic absorption spectroscopy as the most effective analytical tool for the determination of amount of metal ions in solution is the ability of the atoms of the same metal in the ground

state to absorb radiation of specific wavelength, characteristic of the metals. The number of atoms of the metal present in the ground state determines the extent of absorption of the radiation emitted from the hollow cathode tube. The amount of absorption of the radiation by the atoms in the ground state is a measure of the amount of the metal ions in solution.

Advantages of atomic absorption spectrophotometric method of analysis are the high degree of sensitivity, accuracy and its relative freedom from inter-element effect. Others are its non-discrimination in the oxidation states of metal in determining the amount of metal in solution and the ease of availability of the instrument.

2.10.2 FLAME PHOTOMETER

Unlike the AAS, flame photometer works on the principle of emission of radiation by excitation of the electrons in the atoms from the ground state to a higher energy level. The elctrons on falling back to the ground state emits radiation characteristics of the wavelength of the difference between the ground state and the excited State. The amount of excited atoms and hence concentration is temperature dependent. Unless temperature is kept constant, concentration will always vary.

This method is usually used to determine the amounts of sodium and potassium because of their low excitation energy.

2.11 EXPERIMENTAL CONDITIONS FOR THE FLAME SPECTROPHOTOMETRIC ANALYSIS

During all the analysis using the Unicam Sp 1900 atomic absorption spectrophotometer, the curvature and scale expansion were at the 000 mark while slit width and sensitivity were at 125 and 513 respectively. For the flame photometer the air and fuel pressure was 11lb/in^2. Flame used was non-luminous for both methods of analysis.

For the metals determined, the wavelength, that is resonance lines, and working ranges are as detailed below.

2.11.1 NICKEL

The principal resonance line used for the determination of nickel in all samples was 232nm[19]. Working range standards from 0.8 to 10ppm were prepared from the stock solution. Air-acetylene flame was used for the atomization.

The hollow cathode tube which supplied the resonance line was the pye Unicam type. The lamp current used was 12 milliamperes.

2.11.2 LEAD

The wavelength used was 283.3mm. Working range standards were from 2ppm to 10ppm. Air-acetylene flame was used for the atomization. Lamp current was 4 milliamperes.

2.11.3 CALCIUM

Principal resonance line used was 422.67nm. Working range standard solutions were from 0.5 ppm to 5.0 ppm. Air-acetylene flame was used. Lamp current of 8 milliamperes was used. 0.5% lanthanum chloride solution was added to each of the standard solution to suppress inter-element effect.

2.11.4 MAGNESIUM

Wavelength of most sensitive absorption was used. The wavelength was 285.21nm, working standard solutions ranged from 0.2 ppm to 1.0ppm. Lamp current used was 4 milliamperes Air-acetylene flame was used.

2.11.5 IRON

Principal resonance line used was 248.33nm. Working standard solutions ranged from 0.5ppm to 5.0ppm. Lamp current was 12 milliamperes. Air-acetylene flame was used.

2.11.6 CADMIUM

Wavelength of 228.8nm was used. Hollow Cathode lamp current supplied was 4 millianperes. Working range was between 0.1 ppm and 0.6 ppm. Air-acetylene flame was used.

2.11.7 COBALT

The resonance line used for cobalt determination was 240.72nm. Working range for cobalt was between 0.5 ppm to 5.0 ppm. Lamp current used 40 milliamperes. Air-acetylene flame was used.

2.11,8 COPPER

Wavelength used was 324.75nm. Working range was between 2ppm and 10ppm. Lamp current used was 4 milliamperes. Airacetylene flame was used.

2.11.9 MANGANESE

Wavelength of most sensitive absorption which was 279.48 nm was used. Lamp current used was 10 milliamperes The flame used was air-acetylene flame. A working range of standard solution from 0.5 ppm to 3.0 ppm was used. Air-acetylene flame was used.

2.11.10 ZINC

The Wavelength used for the determination of Zinc in standard solutions and samples was 213.86 nm. Air-acetylene

flame was used. A working range of standard solutions from 0.02ppm to 0.2 ppm was prepared from metal stock solution.

2.11.11 CHROMIUM

Principal resonance line used for chromium determination was 357.87nm. Fuel rich air-acetylene flame was used. Lamp current used was 8 milliamperes. Working range was from 0.5 ppm to 5.0 ppm.

2.11.12 POSTASSIUM

A working range of standard solutions from 2ppm to 8ppm was used Potassium filter was used. The Flamephotometer was calibrated using de-oinised water and 10 ppm of standard solution of potassium. The de-oinised water was used to bring the reading to zero scale while the 10ppm was used to adjust to maximum scale reading. Air-acetylene flame non-luminous was used. The pressure of vacuum pump used was 11ib/in^2.

2.11.13 SODIUM

Working range of standard solutions from 2 ppm to 8 ppm was used. Sodium filter was used. The calibration was done with de-ionised water and 10 ppm of standard solution of sodium.

Air-acetylene flame flame was used and the pressure supplied was 11 ib/in^2.

2.12 PREPARATION OF STANDARD SOLUTIONS

All metal stock solutions were prepared from analytical reagent grade materials using acidified deionised water. Serial dilutions to get the required working range standards were done using acidified de-ionised water which was prepared by diluting 7 ml of 70% BDH HNo_3 to 1 litre using de-ionised waster.

2.12.1 CALCIUM STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTIONS

The stock solution was prepared by dissolving 2.497g of $CaCo_3$ with a little excess of dilute nitric acid and made up to 1 litre with 1% acidified de-ionised water. The amount of Calcium present in the solution was determined by standardisation with 0.01 M EDTA[20] using Eriochrome Black T as the indicator. The amount was determined to be 1000 ppm. Serial dilutions to get a warking range between 0.5 ppm and 5.0 ppm were made by taking appropriate volumes of the stock solutions and making up to 100 ml mark.

2.12.2 LEAD STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTIONS

1.598g of lead nitrate was dissolved in dilute HN_3 acid (1:100) and made up to 1 litre. The amount of lead present in the solution was determine by standardisation with 0.05 MEDTA[21]

using Xylenol Orange as the indicator. The amount was determined to be 1000 ppm. Serial dilutions to get a working range of standard solutions between 2ppm to 10 ppm were made by taking appropriate volume from the stock solution and making up to the 100 ml mark with acidified de-ionised water.

2.12.3 COPPER STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTIONS

1.00g of copper turnings were dissolved in 25ml of 70% nitric acid and evaporated almost to dryness. It was then diluted with de-ionised water to make a litre. The actual amount of copper present was determined to be 1000 ppm after standardisation with 0.02 MEDTA[21] solution using pyrocatechol violet as the indicator. Serial dilutions were done to get a working range between 2 ppm and 10ppm by taking appropriate volumes from the stock solution.

2.14.4 MANGANESE STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTION

1.00 g of metallic manganese was dissolved in 10ml of 70% nitric acid and made up to 1 litre with de-ionised water. It was standardised using 0.05 MEDTA[21] solution and Erio. T as the indicator. The amount of manganese

in the solution was 1000 ppm. Serial dilutions of appropriate volumes were done to obtain working range standard solutions between 0.5 ppm and 3.00 ppm.

2.15.5 ZINC STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTIONS

1.000 g of zinc dust was dissolved in a slight excess of dilute hydrochloric acid and made up to the 1 litre mark of the Volumetric flask. The amount of zinc present in the solution was determined by standardisation with 0.1 MEDTA solution using Eriochrome Black T as the indicator[21]. The amount of zinc was approximately 1000 ppm, that is, 1000 mg/litre. Serial dilutions of appropriate volumes of stock solution were done to obtain working range standard solutions between 0.02 ppm and 0.2 ppm.

2.12.6 NICKEL STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTIONS

1.000 g of metallic nickel was dissolved in dilute nitric acid and then made up to 1 litre mark with de-ionised water. Standardisation of the solution with 0.1MEDTA[21] using murexide indicator gave the amount of Nickel present in the 1 litre solution as approximately 1000 ppm. Working

range standard solutions of 0.8 ppm to 10 ppm were obtained by serial dilutions of the appropriate volumes of standardised stock solution.

2.12.7 MAGNESIUM STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTIONS

1.000 g of magnesium ribbon was dissolved in 100ml of dilute hudrochloric acid (1:100) and diluted to 1 litre mark with de-ionised water. It was then standardised using 0. IMEDTA[21] and Eriochrome Black T as an indicator The amount of Magnesium present in the solution after the standardisation was approximately 1000 ppm.
Working range standard solutions of 0.2 to 10 ppm were obtained by serial dilutions of appropriate volumes from the stock solution.

2.12.8 IRON STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTIONS

4.9552 g of Ferrous sulphate heptahydrate, $FeSO_4.7H_2O$ was dissolved with 1% nitric acid and made up to one litre with the 1% nitric acid solution. The iron solutions was standardised with $N.K_2Cr_2O_7$ solution [22] using diphenylamine as an indicator. Serial dilutions were done to get working range standard solutions of 0.5 ppm to 5.0 ppm by

by taking the appropriate volumes of the stock solution and diluting them to 100ml mark.

2.12.9 CHROMIUM STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTIONS.

5.124 g of chromium chloride were dissolved in 2 MH cl and made up to 1 litre with de-ionised water to obtain 1000 ppm stock solution of chromium. Working range standards between 0.5 and 5.0 ppm were obtained by serial dilution of the appropriate volumes from the stock solutions.

2.12.10 COBALT STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTIONS

4.940 g of Cobalt nitrate was dissolved in '2MHcll and made up to 1 litre with de-ionised water. Standardisation of the solution with 0.05 M EDTA solution using Xylenol Orange indicator gave the amount of cobalt present in the 1 litre solutions as 1000 ppm. Serial dilutions of the appropriate volumes from the stock solution were done to obtain working range standard solutions from 0.5 to 5.0 ppm.

2.12.11 CADMIUM STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTIONS

2.0314 g of cadmium chloride were dissolved in 1% nitric acid and made up to the 1 litre mark with acidified de-ionised

This solution was standardised with 0.05M EDTA[21] solution using xylenol Orange indicator. The amount of cadmium in the solution was determined to be 1000 ppm. Working range range standard solutions of 0.1 ppm to 0.6 ppm were obtained by serial dilutions of the appropriate volumes from the stock solution.

2.12.12 POTASSIUM STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTION

1000 ppm of potassium stock solution were prepared by dissolving 1.9070g of dried (at 110°c) potassium chloride with acidified de-ionised water and then made up to 1 litre. Working range standard solutions between 2 ppm and 10 ppm were obtained by serial dilution of the appropriate volumes from the stock solution.

2.12.13 SODIUM STOCK SOLUTION AND WORKING RANGE STANDARD SOLUTION

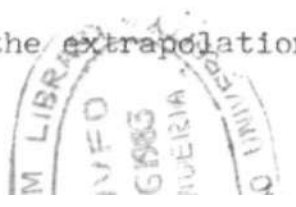
Stock solution of 1000 ppm of sodium was prepared by dissolving 2.542 g of dried (at 110°c) sodium chloride with 1% nitric acid acidified de-ionised water. Working range standard solutions of 2 ppm to 10 ppm were obtained by serial dilution of the appropriate volumes from the stock solution.

2.13 DETERMINATION OF METAL-ION IN THE DIGESTATES

Standard working range solutions of the metal ions to be determined in the digestates were prepared as already indicated.

The absorbances (by using atomic absorption spectroscopy and emission intensities (using flame emission spectroscopy) of these standard solutions were determined. Graphs of absorbances (A) versus amount of metal in ppm and graphs of emission Intensities against amount of metal in ppm were plotted. These graphs obeyed Beer-lambert law hence straight line curves were obtained passing through the origin.

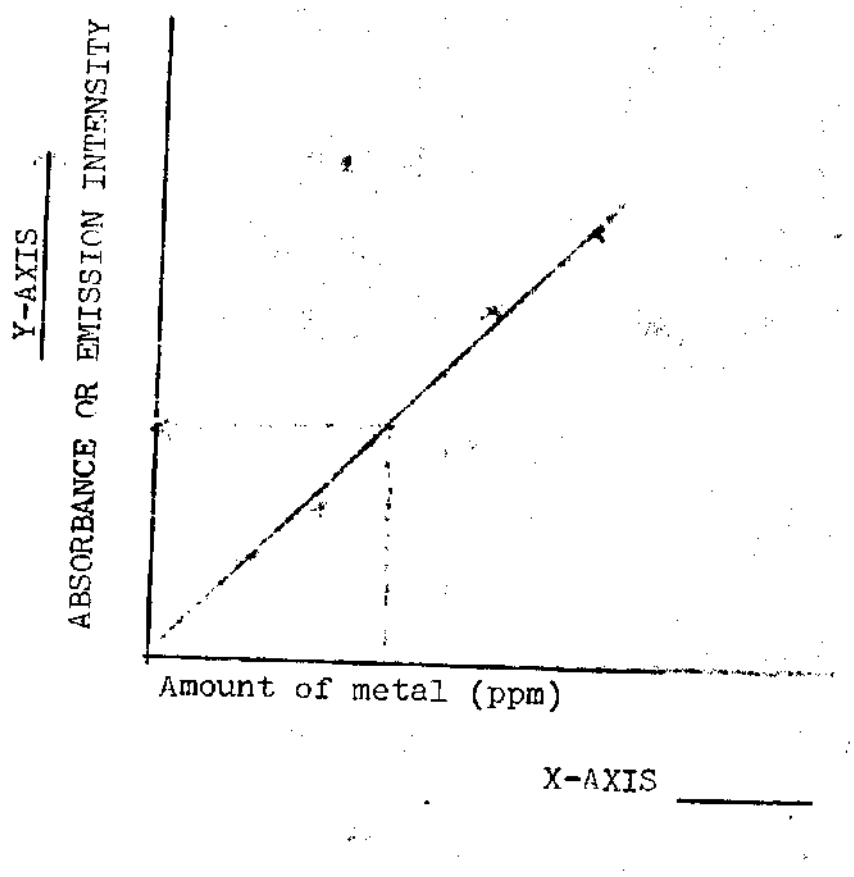
The absorbances of the digestates for the metal ions considered in this analysis other than sodium and potassium were determined and their corresponding amounts determined by extrapolation from the y-axis at the point of the absorbance until it reached the standard straight line graph. From the point on the straight line graph it was further extrapolated to the x-axis. The point of interception on the x-axis gave the amount of the metal ion corresponding to the absorbance from which the extrapolation started.



Similarly, the amounts of sodium and potassium in the digestates were determined by plot of emission intensity (I) against the amount of metal in (rpm) .

The point of interception of the x-axis after extrapolation gave the amount corresponding to the emission intensity.

The diagram below illustrates how the amounts of the metals in the digestates were determined.



2.13.1 EQUATION USED IN CALCULATING THE CONCENTRATIONS OF METAL IONS IN MILLIGRAM PER KILOGRAM (Mg/Kg)

Let the weight of dried sludge equivalent to 50ml wet sludge be W. The volume (ml) of extract after digestion = V. Concentration of metal ion from the absorbance or emission intensity vs concontration curve = a. Concentration of blank solution = b

The metal content expressed in milligram per 1000 g. that is, milligram per kilogram (mg/kg

$$= \frac{(a-b) \times V}{W} \quad (23)$$

The weights (w) of the drv masses of the wastewater sludges equivalent to 50ml of wet sludge are shown in table 2.2. The volume of each extract after digestion was 100ml. a and b were determined from the calibration curves.

2.13.2 CALCULATION OF STANDARDS FOR APPLICATION OF WASTEWATER SLUDGES ON FARMLAND.

The equations used for the calculation of standard were based on(i) Zinc equivalent, (ii) tonne of sludge per hectare and (iii) sodium absorption ratios(SAR). For (i) the equation is

$$\text{Zinc Equivalent (ppm)} = (Zn)^{*} + 2\,(Cu) + 8\,(Ni) \quad (24)$$

*( ) means concentration

(ii) Two equations are used, one is

Total sludge application (dry ton/hectare)

$$= \frac{32500 \quad (CEC^*)}{(Zn)+2(Cu)+4\ Ni} \quad (25)$$

Where CEC* is the Cation Exchange Capacity of the soil. Table 3.15 gives the values obtained by using this equation.

The second is

Tonnes of Sludge/hectare.

$$= \frac{X\ Kg\ metal/hectare}{ppm\ metal\ X\ 0.002} \quad (26)$$

Where X is the upper limit for a particular metal addition on land. The values of X for Pb, Zn, Cu, Ni and Cd are given on table 1.1 of the appendix.

In using this equation the amount of sludge in tonnes per hectare to be applied on the land is limited by one of these metals above that gives the lowest amount of tonnes of sludge. (See table 3.16 for values obtained by applying this equation) (iii) Sodium Adsorption Ratio (SAR). Even though sodium (Na), potassium (k), Calcium (Ca) and Magnesium (mg) are not frequently known to pose a problem in wastewater sludges used for soil amendment and in plant germination, sometimes their presence in wastewater sludges may be determental to soil structures and ultimate reduction in the inflitration rate of the soils (17).

To avoid this effect sodium adsorption ratio (SAR) which considers the amount of these metals in wastewater is used as a guide to their application on land.

Wasterwater sludges with SAR Values greater than 15 should be avoided.[27] . The equation used for calculating (SAR) is given below.

$$SAR = \frac{Na/\ 23\ meq\ Na}{\sqrt{\frac{(Ca)\ /20\ meq\ Ca + (Mg)/12\ meq\ Mg}{2}}} \quad (27)$$

CHAPTER THREE

RESULTS AND DISCUSSION

3. 1 RESULTS

The results showing the amounts of the metal ions in mg/kg; standard deviations; and relative standard deviations as well as the values which should determine the application of sludge or otherwise on farm lands are shown on tables 3.1-3.17

TABLE 3.1 RESULTS OF DETERMINATION OF POTASSIUM BY FLAME EMISSION SPECTORS COPY

AMOUNT OF METAL/mg kg-1

SLUDGE DESIGNATION	NUMBER OF DIGESTIONS	MEAN	STANDARD DEVIATION	RELATIVE STANTANDARD DEVIATION %
A	5	1.903	64.97	3.4
B	5	4.597	130.9	2.8
C	5	4.695	149.2	3.2
D	5	2.404	54.1	2.3
E	5	1.963	82.3	4.2
F	5	5.498	202.3	3.6
G	5	11.139	606.4	5.4
H	3	9.915	111.5	1.1
I	3	12.996	331.	2.5
J	3	1.384	328	2.4
K	3	11.002	196.5	1.8
L	3	12.625	781	6.2
M	3	8.895	556	6.2
N	3	7.374	655.8	2.1
O	3	4.604	659	14.3
P	3	9.002	141.7	1.6
Q	3	7.035	0.00	0.00
R	3	6.951	273.7	3.9

TABLE 3.2 RESULTS OF DETERMINATION OF SODIUM BY FLAME EMISSION SPECTORS COPY

AMOUNT OF METAL/mg kg^{-1}

SLUDGE DESIGNATION	NUMBER OF DIGESTIONS	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION %
A	5	1,661	56	3.4
B	5	9.646	488.5	5.1
C	5	4.836	109.6	2.3
D	5	2.165	46.0	2.1
E	5	1.540	53.1	3.4
F	5	83.789	2745.	3.3
G	5	07.156	6658	3.2
H	3	20.925	365.5	1.7
I	3	40.048	846.0	2.1
J	3	948	36.5	3.7
K	3	13.066	435.5	3.3
L	3	28.406	1328.3	4.7
M	3	24.216	856	3.5
N	3	13.123	200	1.5
O	3	6,658	0.00	0.00
P	3	17.677	631.3	3.6
Q	3	14.908	290	1.9
R	3	15.482	273	1.8

TABLE 3.3 RESULTS OD DETERMINATION OF MAGNESIUM BY ATOMIC ABSORPTION SPECTORS COPY

AMOUNT OF METAL/mg kg^{-1}

SLUDGE DESIGNATION	NUMBER OF DIGESTIONS	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION %
A	5	656	1.7	0.26
B	5	1168	26.5	2.3
C	5	1275	15.0	1.2
D	5	693	2.3	0.3
E	5	792	4.9	0.6
F	5	1522	15.2	1.0
G	5	1416	26.8	1.9
H	5	1724	40.1	2.3
I	5	2823	71.6	0.8
J	5	542	5.2	0.9
K	5	2268	21.2	0.9
L	4	2479	36.6	1.5
M	5	1559	12.5	0.8
N	4	571	24.0	4.2
O	4	1406	18.1	1.3
P	4	1299	3.7	0.3
Q	4	1463	4.8	0.3
R	4	2528	0.00	0.00

TABLE 3.4 RESULTS OF DETERMINATION OF CALCIUM BY ATOMIC ABSORPTION SPECTROSCOPY

AMOUNT OF METAL/mg kg^{-1}

SLUDGE DESIGNATION	NUMBER OF DIGESTIONS	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION %
A	5	53	1.3	2.5
B	5	470	37.5	8.0
C	5	106	6.0	5.7
D	5	139	2.2	1.6
E	5	90	5.4	6
F	5	13,988	215.0	1.5
G.	5	2149	30.6	1.5
H	5	4.143	188.4	4.5
I	5	4.483	414.7	9
J	5	350	14.8	4.2
K	5	616	21.6	3.5
L	4	3.788	762.9	20
M	4	1.160	20.3	1.75
N	4	42	2.1	5
O	4	3,001	206.0	6.9
P	4	2.614	213.0	8.2
Q	3	163	5.8	3.8
R	4	2.125	16.4	0.8

TABLE 3.5 RESULTS OF DETERMINATION OF LEAD BY ATOMIC ABSORPTION SPECTROSCOPY

AMOUNT OF METAL/mg kg^{-1}

SLUDGE DESIGNATION	NUMBER OF DIGESTIONS	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION %
A	5	34	6.4	18.1
B	5	n.d	-	-
C	5	29	7.2	24.9
D	5	21	2.6	12.4
E	5	32	2.7	8.3
F	5	n.d	-	-
G	5	n.d	-	-
H	5	8.4	0.5	-
I	5	285	70.5	24.7
J	5	10	0.9	9.4
K	5	n.d	-	-
L	5	n.d	-	-
M	5	117	10.0	8.5
N	3	42	6.7	15.0
O	3	89	5.6	6.3
P	3	n.d	-	-
Q	3	18	7.8	43.2
R	3	n.d	5.6	6.3

nd means "not detected"

TABLE 3. RESULTS OF DETERMINATION OF ZINC BY ATOMIC ABSORPTION SPECTROSCOPY

AMOUNT OF METAL/mg kg^{-1}

SLUDGE DESIGNATION	NUMBER OF DEGISTION	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION-%
A	5	136	5.7	4.2
B	5	n.d	-	-
C	5	96	4.1	4.3
D	5	91	0.9	1.1
E	5	58	3.7	6.3
F	5	n.d	-	-
G	5	71	6.8	1.7
H	5	224	7.1	3.2
I	5	1982	52.0	2.6
J	5	120	0.7	0.6
K	5	119	2.3	1.9
L	5	250	18.2	7.3
M	5	31.9	9.0	2.8
N	5	75	1.2	1.6
O	5	297	2.5	0.3
P	4	40	0.8	2.0
Q	3	132	9.9	7.5
R	3	56	2.4	4.3

nd Means "not detected".

TABLE 3.7 RESULTS OF DETERMINATION OF CADMIUM BY ATOMIC ABSORPTION

SLUDGE DESIGNATION	NUMBER OF DIGESTIONS	AMOUNT OF METAL/mg kg^{-1} MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION-%
A	5	n.d	-	-
B	5	n.d	-	-
C	5	n.d	-	-
D	5	n.d	-	-
E	5	1.0	0.1	8
F	5	n.d	-	-
G	5	n.d	-	-
H	3	n.d	-	-
I	3	n.d	-	-
J	3	0.33	0.056	17.5
K	3	n.d	-	-
L	3	n.d	-	-
M	3	2.0	0.30	12.5
N	3	n.d	0.0	24
O	3	2.4	0.82	34
P	3	n.d	-	-
Q	3	1.0	4.0	-
R	3	n.d	-	-

n.d Means "not detected"

TABLE 3.8 RESULTS OF DEPTERMINATION OF AMOUNT OF CHROMIUM BY ATOMIC ABSORETION

AMOUNT OF METAL/mg kg^{-1}

SLUDGE DESIGNATION	NUMBER OF DIGESTIONS	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION-%
A	5	21,2	1.2	5.8
B	5	n.d	-	-
C	5	n.d	-	-
D	5	15	2.4	15.8
E	5	23	3.4	14.7
F	3	n.d	-	-
G	3	n.d	-	-
H	3	n.d	-	-
I	3	n.d	-	-
J	3	7	0.9	12.7
K	3	n.d	-	-
L	4	n.d	-	-
M	4	15	-	-
N	4	n.d	-	-
O	4	2.3	3.3	14.5
P	4	n.d	-	-
Q	4	n.d	-	-
R	4	n.d	-	-

TABLE 3.9 RESULTS OF DETERMINATION OF IRON BY ATOMIC ABSORPTION

AMOUNT OF METAL/mg kg^{-1}

SLUDGE DESIGNATION	NUMBER OF DIGESTIONS	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION %
A	5	2,839	59.0	2.1
B	5	107,154	1422.0	1.3
C	5	25,740	212.4	0.8
D	5	1,734	35.0	2.0
E	5	2,567	94.0	3.7
F	5	10,645	378.6	3.6
G	5	n.d	-	-
H	4	8,549	218.8	2.6
I	4	3,630	142.8	3.9
J	4	4,784	88.9	1.9
K	4	21,061	548.6	2.6
L	4	10,330	937.0	9.0
M	4	13,788	76.8	0.6
N	5	8,843	114.1	1.3
O	3	13,172	104.7	0.8
P	3	7,365	243.0	3.2
Q	3	10,218	125.9	1.2
R	3	29,621	1612.0	5.4

TABLE 3.10 RESULTS OF DETERMINATION OF MAINGANESE BY ATOMIC ABSORPTION SPECTROSCOPY

AMOUNT OF METAL/mg kg^{-1}

SLUDGE DESIGNATION	NUMBER OF DIGESTIONS	MEAN	STANDARD DEVIATON	RELATIVE DEVIATION-%
A	5	52	9.6	18.9
B	5	631	24.7	3.9
C	5	123	6.3	5.4
D	5	97	14.10	14.5
E	5	89	5.8	6.6
F	5	n.d	-	-
G	5	169	21.7	12.8
H	5	97	6.7	6.8
I	5	3,984	406.0	10.2
J	5	108	7.3	6.8
K	5	257	33.0	12.8
L	5	178	8.7	4.9
M	5	54	1.8	3.4
N	5	22	1.7	8.0
O	5	143	2.8	2.0
P	5	301	6.0	2.0
Q	5	127	11.6	9.0
R	5	592	22.8	3.8

TABLE 3.11 RESULTS OF DETERMINATION OF COPPER BY ATOMIC ABSORPTION

AMOUNT OF METAL/mg kg^{-1}

SLUDGE DESIGNATION	NUMBER OF DIGESTIONS	MEAN	STANDARD DEVIATION	RELATIVR STANDARD DEVIATION-%
A	5	48	4.0	8
B	5	n.d	-	
C	5	13	3	23.4
D	5	7	0.3	4.6
E	5	14	1.3	9.4
F	5	n.d	-	-
G	5	n.d	-	-
H	4	n.d	-	-
I	4	n.d	-	-
J	4	8	0.4	4.6
K	4	31	6.7	21.7
L	4	85	6.7	7.9
M	4	36	3.3	9.2
N	4	11	1.4	12.6
O	4	45	1.5	3.3
P	4	n.d	-	-
Q	4	8.9	0.8	9.1
R	4	n.d	-	-

TABLE 3.12 RESULTS OF DETERMINATION OF NICKEL BY ATOMIC ABSORPTION

AMOUNT OF METAL/mg kg^{-1}

SLUDGE DESIGNATION	NUMBER OF DIGESTIONS	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION %
A	5	31	4.4	14.3
B	5	n.d	-	-
C	5	n.d	-	-
D	5	n.d	-	-
E	3		2.3	17.3
F	3	n.d	-	-
G	3	n.d	-	-
H	3	n.d	-	-
I	3	11	0.6	5.4
J				
K	3	n.d	-	-
L	3	n.d	-	-
M	3	57	4.9	8.7
N	3	35	0.0	-
O	3	56	2.0	-
P	3	63	0.0	-
Q	3	32	0.0	-
R	3	n.d	-	-

TABLE 3.13 RESULTS OF DETERMINATION OF COBALT BY ATOMIC ABSORPTION SPECTROSCOPY

AMOUNT OF METAL/mg kg^{-1}

SLUDGE DESIGNATION	NUMBER OF DIGESTION	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION %
A	4	n.d	-	-
B	4	n.d	-	-
C	4	n.d	-	-
D	4		0.40	5.2
E	4	9.1	0.8	8.8
F	4	n.d	-	-
G	4	n.d	-	-
H	4	n.d	-	-
I	4	n.d	-	-
J	4	4.7	0.3	6.0
K	4	n.d	-	-
L	4	n.d	-	-
M	4	n.d	-	-
N	4	n.d	-	-
O	4	13	1.1	8.6
P	4	n.d	-	-
Q	4	n.d	-	-
R	4	n.d	-	-

TABLE 3.14 ZINC EQUIVALENT (PPM) RESULTS USING CHUMBLY'S FORMULA

SLUDGE DESGINATION	ZINC EQUIVALENT (ppm)
A	480
B	-
C	122
D	105
E	190
F	-
G	71
H	224
I	1982
J	224
K	181
L	420
M	847
N	377
O	835
P	544
Q	406
R	56

TABLE 3.15 TOTAL SLUDGE APPLICATION USING WISCONSIN'S FORMULA.

SLUDGE DESIGNATION	(DRY TONNE PER HECTARE)*
A	1826
B	-
C	5328
D	6190
E	4710
F	-
G	9155
H	2902
I	328
J	3611
K	3591
L	1548
M	1050
N	2743
O	1064
P	2226
Q	2340
R	11607

TABLE 3.16 TONNES OF SLUDGE APPLICABLE PER HECTARE OF LAND

SLUDGE DESIGNATION	TONNES/HECTARE.	LIMITING METAL
A	3676	Zn
B	--	-
C	5208	Zn
D	5494	Zn
E	8621	Zn
F	-	-
G	7042	Zn
H	2232	Zn
I	252	Zn
J	4167	Zn
K	4202	Zn
L	2000	Zn
M	1567	Zn
N	6667	Zn
O	1684	Zn
P	3968	Ni
Q	2783	Zn
R	8929	Zn

TABLE 3.17 SODIUM ADSORPTION RATION (SAR) VALUES FOR THE SLUDGES INVESTIGATION

SLUDGE DESIGNATION	SAR
A	13.4
B	53.5
C	28.0
D	11.8
E	8.0
F	179.2
G	849.7
H	68.7
I	121.8
J	7.6
K	54.2
L	87.6
M	108.5
N	114.1
O	25.0
P	70.5
Q	81.0
R	53.4

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3.2 DISCUSSION AND COMMENTS

3.2.1 From the tables of results, it is easily seen that the amounts of sodium, potassium and iron in allthe samples they were detected are high. Sample G has an exceptionally high value for sodium. Recall that sample G is from Textile factory which I understand makes a great use of sodium salts in their manufacturing process. With the exception of samples, A, D E, J from Barenawa low cost, Badarawa village, Malali low cost and student cafeteria of Ahmadu Bello University, Zaria, respectively, the amounts of sodium in all other samples are higher than those of postassium. This reason may be due to higher domestic use of sodium than potassium.

Iron in table 3.9 shows high amounts in the samples it was detected. In fact, with exception of sample D and G where potassium has higher amounts than Iron and in samples D, F, G, H, I, K, L, M, O, P,Q, where sodium amounts are higher than those of iron, all other samples contain higher amounts of iron than potassium and sodium. Magnesium and Calcium, although have high amounts in most of the samples, nevertheless, the amounts are not as high as these of sodium, potassium and iron. The highest amount of calcium which is 13,988 mg/kg. from sample F is higher than those of iron

and potassium in the same sample F. This is so, because of the source of F which is the Fertilizer Industry that makes use of calcium phosphate rock as one of the raw materials.

A look through the tables shows that sodium, potassium, magnesium and calcium are present in all samples. Iron and manganese are also present in all the samples except in sample G that Iron is not present and sample F that manganese is not present.

Zinc is not present in two samples B and F.

The abundance of these metals, K, Na, Ca, Mg, Fe and Zn shows the great extent to which they are put into use in various ways.

Although zinc is almost present in the samples, the amount present in the wastewater. sludges do not exceed the maximum amount allowed. The maximum amount of zinc allowed in sludge or farmland is 200mg/kg or 1,000 kg/hectare at soil Cation Exchange Capacity greater than 15[24] (See tables 1.1 and 1.2 of the appendix).

In samples B,F, G, K, L, P and R lead was not detected. In other samples where lead was detected the amounts of lead were very low compared to the maximum amount allowed.

Cadmium was detected only in five out of the eighteen

samples analysed. The amounts of cadmium in each of the five samples did not exceed the maximum allowed level of 15mg/kg in any sludge. (See tables 1.1 and 1.2 in the appendix and table 3.7 for comparison).

Table 3.8 shows the amounts of chromium in the samples it was detected. None of the amounts exceeded the maximum allowed value of 1000 mg/kg. Only in five samples were chromium detected. Cobalt and Nickel were detected in four and eight samples respectively.

In all the samples these metals were detected, their amounts were very low when compared to the maximum amount allowed in wastewater sludges.

The amounts of copper in all the samples were far below the maximum allowed level of 1,000 mg/kg.

In general consideration, the amounts of the heavy metals Zn, Cd, Cu, Ni, Pb, Cr and Co in the wastewater sludges analysed were far below the maximum allowed amount given by Chaney (See table 1.2 in the appendix).

3.22 PROBABLE INFLUENCE OF SAMPLING AND DIGESTION ON RESULTS

A look through the columns of the standard deviations shows that no mean value of the replicate amounts of metals

fell outside the range of plus or minus four times its corresponding standard deviation. Again the relative standard deviations of a particular metal in all the samples were almost in good agreement.

In some of the few cases where the relative standard deviations were high the reasons may be due to problem of homogeneously sampling of 50ml of the wastewater sludges.

Another reasons may be due to losses in some replicates during the digestion process. For instance, at the centre of the heating block some particles of the samples were lost owing to bumping and adherence on the walls ot the conical flask. The centre of the block heated the samples faster than the sides.

3.2.3 STANDARDS FOR SLUDGE APPLICATION ON FARMLAND

As earlier indicated there is no universally accepted standard for sludge application on land. This is because of the limiting factors already mentioned in chapter one.

Based on Chumbly's formula for application of sludge on land whose PH is greater than 6.5, the zinc equivalent values for the sludges analysed are shwon on table 3.14. From Chumbly's recommended zinc equivalent value which should not exceed 250 ppm, only sludges C, D, E, G, K and R are suitable for application on farlmland. B and F are without values because of non detection of elements

which limit the determination of zinc equivalent. They can therefore, be applied on farmland.

All other samples have their zinc equivalent values greater then 250 ppm.

From Wisconsin's Formula, the total amounts of sludge application of the samples analysed are shown on table 3.15. Table 3.16 also shows the total amounts of sludge samples that should be applied on farmland using equation (ii) already metioned.

Table 3.17 shows the sodium Adsorption Ration (SAR) which also determines the sludge that should be applied on soil.

From tables 3.15 and 3.16 all the sludges can be applied on farmlands provided the amount in tonnes of sludge per hectare of land or equivalent ratio is not exceed.

The zinc equivalent (ppm) and sodium, adsorption ratio (SAR) show that not all the wastewaters sludges can be applied on farmland or soil.

3.3 COMMENT AND SUGGESTION

A comparison of the levelof amount of the heavy metals in wastewater sludges analysed with the values given by Chaney in appendix 1.2, shows that the wastewater sludges

From Kaduna and Zaria are adequate for use on farmland. But from the tables regarding the applications of the wastewater sludges on farmland based on their zinc equivalent and sodium adsorption rations, only wastewater sludges, D,E, J meet all the requirements considered suitable for sludge application on farmland.

There are some of the sludges, C, G, K, R that are within the recommended zinc equivalent value of 250 ppm, but fail to satisfy the sodium adsorption ratio, Sludge A falls within allowed SAR Value, but failed in its zinc equivalent value.

The problem now is how to reconcile these two parameters to see the effect they have on seeds and crops planted using the wastewater sludges. For this reason, I am suggesting that research be carried out with these sludges on plants to actually ascertain the tolerable level of thse metals by Nigerian plants.

This will help not only to formulate Nigerian standards for sludge application on farmland but also determine those plants or crops that should be planted on sludge amended soil.

APPENDIX

TABLE 1.1 TOTAL AMOUNT OF SLUDGE METALS ALLOWED ON AGRICULTURAL LAND (EPA, 1977*) WHOSE SOIL p^H 6.5

	SOIL CATION EXCHANGE CAPACITY meq/100g		
	0-5	5-15	15
METAL	AMOUNT OF METAL (kg/ha)		
Pb	500	1,000	2,000
Zn	250	500	1,000
Cu	125	250	5,000
Ni	125	250	5,000
Cd	5	10	20

Source: P. AARNE VESILIND, Treatment and Disposal of Wastewater Sludges, revised Edition, 1979.

TABLE 1.2 MAXIMUM OF HEAVY METAL CONCENTRATIONS BY CHANEY

METAL	MAXIMUM CONCENTRATION (mg/kg)
Zn	2,000
Cu	1,000
Ni	200
Cd	15 or 1% of Zn
Pb	1,000
Cr	1,000

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TABLE 1.3 UPTAKE OF HEAVY METALS BY POTATOES, LETTUCE AND CORN

SLUDGE APPLIED tonne/heactare (ha)	ELEMENTS (PPm) Mn	Zn	Cu	Cd	Pb
	Potatoes (tubers)				
0	9	24	8.6	0.12	0.4
112	6	31	12.8	0.11	0.4
225	7	41	15.8	0.21	0.4
450	7	53	19.0	0.23	0.6
	Lettuce (Leaf)				
0	133	21	1.6	1.6	1.10
112	84	94	5.4	1.28	1.4
225	77	155	8.1	1.72	0.7
450	79	225	11.9	2.69	0.8
0	Corn	Grain			
0	12	41	2.0	0.02	0.2
112	8	47	2.9	0.02	0.2
225	9	48	0.5	0.03	0.2

Note: Sludge applied contained 1,070 ppm Zn, 245 ppm Cu, 545 ppm Mn, 515 ppm Pb, 64 ppm Cr, 24 ppm Ni and 7.4 ppm Cu Ibid page 271.

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