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Bioaccumulation Of Heavy Metals In Crabs At Bundu-Ama Community, Port Harcourt.

UMUNNAKWE JOHNBOSCO.E [1]* OGAMBA ADINDU STEVE [2]
1. DEPARTMENT OF ENVIRONMENTAL TECHNOLOGY, FEDERAL UNIVERSITY OF TECHNOLOGY OWERRI, IMO STATE NIGERIA.
2. Fugro Nigeria Limited, Port Harcourt Rivers State, Nigeria.
* E-mail of Corresponding Author: jnboscokwe@yahoo.com

Abstract

The potential bioaccumulation of heavy metals in crabs collected from Bundu-Ama environs using X-Ray Fluorescence spectrophotometer was investigated. Bundu Ama creeks, rivers and soil support subsistent and commercial crab harvest. Industrial activities and municipal waste discharges into the environment of the community have contributed to possible high concentrations of trace metals. The mean concentration of the heavy metals from the four sampled stations were as follows: Chromium 8.85mg/kg, Copper 196mg/kg, Barium 403mg/kg, Lead < 1.00,Nickel 25.8mg/kg, Arsenic 0.83mg/kg, Cadmium <2.00mg/kg, Mercury <1.00mg/kg, Selenium < 0.50mg/kg and Vanadium 11.3mg/kg. The concentrations of Chromium, Copper, Barium, Nickel, Arsenic and Vanadium exceeded the standard limits of USEPA, WHO and Nigerian Industrial Standard (NIS) for drinking water quality. The analysis report suggests that activities in the area have contributed to high sediment contributions of these contaminants and consumption of the crabs may be considered unsafe.

Keywords: Bundu-Ama, Crab, Heavy metal, Bioaccumulation**.**

INTRODUCTION:

Crabs are crustaceans that are abundant in the sea, freshwater; a few are common in moist land environments (Cubbage, 1991). They are part of invertebrate organisms in aquatic environment, and are also benthic organism. The crabs in Bundu-Ama are mainly the swimming crab locally called **Epa** and are often omnivores, scavengers or predators partly because they eat small plants and animals. Crabs are consumed by many animals including humans and are rich in proteins (Ghiselin, 2009). Crabs take in hazardous materials such as heavy metals, PCB, chlorinated paraffins, PAHs, pesticides (Sea On Screen, 1988). The body either stores or excretes it. By storing it the concentrations of those toxic materials in the body can increase and become greater than in the surrounding environment. This phenomenon is called bioaccumulation (Olowu et al., 2010). Heavy metals accumulate in organisms as a result of direct uptake from the surroundings across the body wall, from respiration and from food (Heip,1997). There is an increasing concern about the health effect in human due to continuous consumption of food contaminated with heavy metals (Chukwujindu et al., 2008). Heavy metals are introduced in an aquatic environment through domestic and industrial waste discharge into water body. It is rather of great concern that over 80% of the industries in Nigeria discharge their solid, liquid and gaseous effluents containing toxic concentration of heavy metals into the environment without any prior treatment while just only 18% undertake rudimentary recycling prior to disposal (Odukoya and Ajayi, 1987:, Jibrin and Adewuji 2008 and Oyewo, 2003).

Several researches revealed heavy metal content in crustaceans and the effects on man who in turn consume the crustacean (Baird and Ulanowics, 1999). A research on heavy metal bioaccumulation in tropical crab from River Aponwa, Ado Ekiti revealed that Cu, Cd, and Zn are evidently bioaccumulated and biomagnified (Falusi and Olanipekun, 2007). Another study on heavy metals in crab and prawn in Ojo River Lagos indicated that the mean concentration of copper and Zinc have higher concentrations above the range of NAFDAC standard for water and aquatic foods (Olowu et al., 2009). Cubbage, (1991) in his study on bioaccumulation of contaminants in crabs and clams in Bellingham Bay showed that industrial and municipal discharges into the bay have contributed to high sediment concentrations of mercury and PCBs. Sediments have been reported to form the major repository of heavy metals in aquatic systems (Adeniyi et al, 2008). The landscape of Port Harcourt sited 66km from the Atlantic Ocean comprises the coastal plains criss-crossed by a maze of swamps, creeks, rivers and waterways (Umeuduji and Aisuebeosun, 1999). Bundu-Ama, a heavily populated community is one of the shanties in Port Harcourt and the people also live in squalid environment (Ikaderinyo, 2012). It is enclosed by a network of rivers and creeks traversing, dissecting the landmass; prominent among them is the Dockyyard

Creek, Primrose Creek, Dick Fibresima Creek and Isaka River all linked to Bonny River which is the largest river in the area with an average width of 0.5km (Aisuebeogun, 1995). The community is host to many multinational industries and establishments, such as PZ Cussons, MI Drilling Fluids, Ibeto Cement Company, Oando, National Oil, Union Dicon Salt, African Petroleum, Conoil, Sun and Gas Oil among others. The indiscriminate waste effluents dumped into the water bodies and poor domestic waste management pollute the area (Ajayi and Osibanjo, 1981 and Oguzie, 2000).The study aims to investigate potential bioaccumulation of heavy metal in crabs of Bundu-Ama environs and their possible health effect on man .

METHODOLOGY

Study Area:

The city of Port Harcourt had a humble beginning in 1913 as a fishing settlement with an initial population of 5000 persons (Oyegun, 1999). The current population of the metropolis (Port Harcourt and Obio-Akpor) according to the official gazette of the 2006 census final results is 1,000,908 (Fed. Republic of Nigeria official gazette of the 2009). The rapid growth of the city and its region has spatial and socio-economic implications. The Port Harcourt city, capital of Rivers State (Fig 1) is also the hub of the oil and gas industry in Nigeria with Bundu-Ama playing host to many industries in the downstream sector of the petroleum industries.

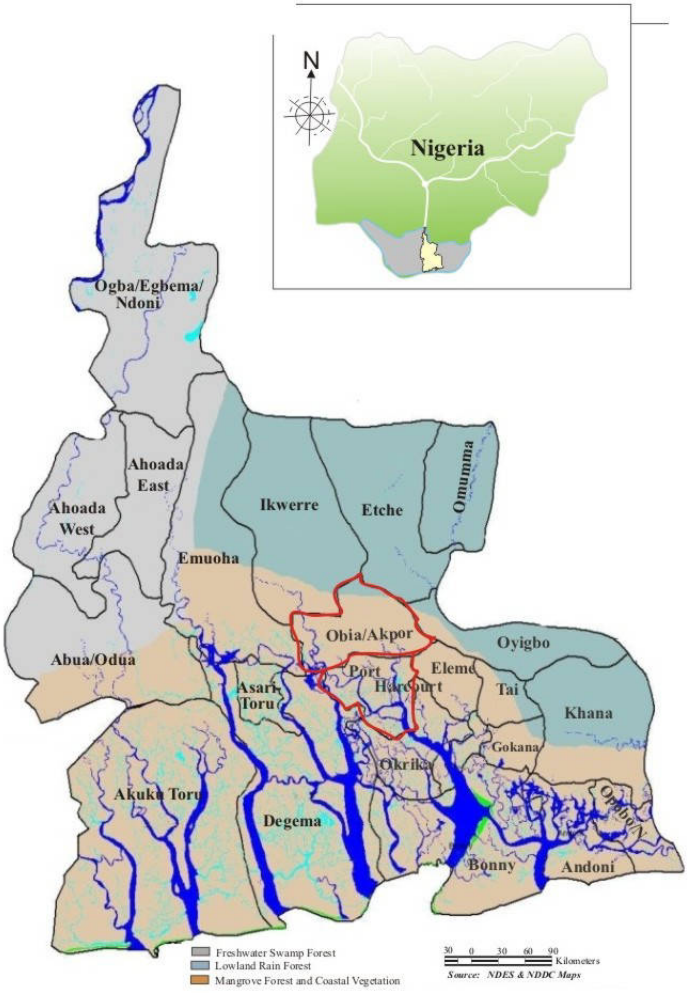


FIG 1: MAP OF RIVERS STATE SHOWING PORT HARCOURT METROPOLIS

Bundu-Ama community experiences the injection of large quantities of effluents due to the activities of industries on one hand and improper domestic waste management that create poor sanitary conditions. The weather and climate of the region show that the mean annual temperature is 28^0C with an annual range of 3.8^0C while humidity is 85% (Oyegun and Adeyemo 1999). One of the most striking features of the city is the uniqueness of its surface drainage which is poor, essentially due to a combination of low relief, high water table and high rainfall (Areola, 1983). The largest river in the area is Bonny River with an average width of 0.5km. The low relief of the city results in strikingly gentle slopes with major rivers and creeks traversing and draining the old Port Harcourt Township and Borokiri areas. In this poorly drained area, the dockyard creek makes a unique network with swamps and several other creeks including Isaka River and Dick Fibresima Creek. It should be pointed out also that there is the flow reversal of ebb and flow tides associated with the semi-diurnal tidal regime of the city (Aisuebeogun, 1995).

Design of Sample Collection Procedure

Four sample stations were established after a reconnaissance visit to the area. The criterion for the choice of the sampling stations was to ascertain the contribution of the activities at each of them to the levels of the heavy metals present. Station one is the Ibeto cement company premises close to Dick Fibresima Creek from where crabs were picked with fishing drag net into a plastic container. The activities taking place in this station is cement bagging, also some residents bath in the water body. Station two is Bundu waterside drained by Dockyard Creek. Domestic waste products are often dumped here and residents use the water body as public lavatory. Station three is Macoba Drilling Fluid Company, MI that lies close to Primrose Creek and Isaka River. Here drilling fluids and engineering activities take place. Station four is the Union Dicon Salt which is close to a jetty where petroleum products are offloaded. Bagging of salts also take place here. The water body where it lies is also a section of Primrose Creek.

Each crab was properly cleaned by rinsing with distilled water after collection to remove debris, sand, planktons and other external adherent before taking the containers to the laboratory for analysis.

Digestion of Crab and Analysis.

The samples of crab were collected from four stations weekly for three weeks using containers and wooden gear from their holes**.** Each crab was properly cleaned by rinsing with distilled water to remove debris, sand, and other external adherents. Prior to analysis, the crab was digested by drying it in oven with foil plate, crushed inside the mortar with pestle. 2g of the sample was weighed and 5ml HNo_3 added. It was digested on steam bath or low temperature hot plate until it dissolved and evaporated to dryness. Another 2ml HNO_3 was added and warmed without drying. The dried samples were transferred into 50ml volumetric flask with hot water using a filter paper made in the form of a funnel. The beaker containing the dried samples and filter paper were continuously rinsed with hot water until it makes up the 50ml mark of the flask. The filter paper was weighed. The digested sample was filtered into a graduating cylinder and the filtrate was made up to 50ml using distilled water. The concentration of the crab in mg/kg was analyzed using X – Ray fluorescence spectrophotometer.

RESULT AND DISCUSSION

The concentrations of the heavy metals determined in the crabs from the Bundu – Ama study locations were indicated in table 1.

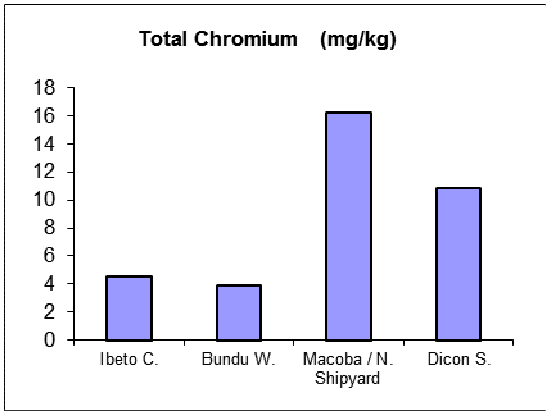
Parameter	Method	Result			
		Crab from Ibeto Cement Company	Crab from Bundu Waterside	Crab from Macoba, M I	Crab from Union Dicon Industry
Total Chromium (mg/kg)	USEPA 6200	4.50	3.90	16.2	10.8
Copper (mg/kg)	USEPA 6200	188	197	159	240
Barium (mg/kg)	USEPA 6200	301	241	515	554
Lead (mg/kg)	USEPA 6200	<1.00	<1.00	<1.00	<1.00
Nickel (mg/kg)	USEPA 6200	25.0	25.0	27.3	25.8
Arsenic (mg/kg)	USEPA 6200	0.70	<0.50	0.80	1.30
Cadmium (mg/kg)	USEPA 6200	<2.00	<2.00	<2.00	<2.00
Mercury (mg/kg)	USEPA 6200	<1.00	<1.00	<1.00	<1.00
Selenium (mg/kg)	USEPA 6200	<0.50	<0.50	<0.50	<0.50
Vanadium (mg/kg)	USEPA 6200	2.90	6.70	20.4	15.1

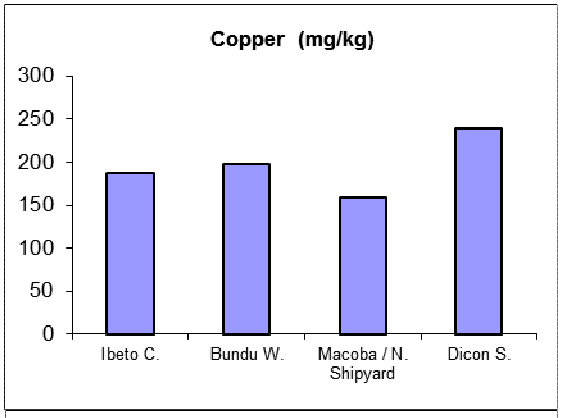
.USEPA = United States Environmental Protection Agency

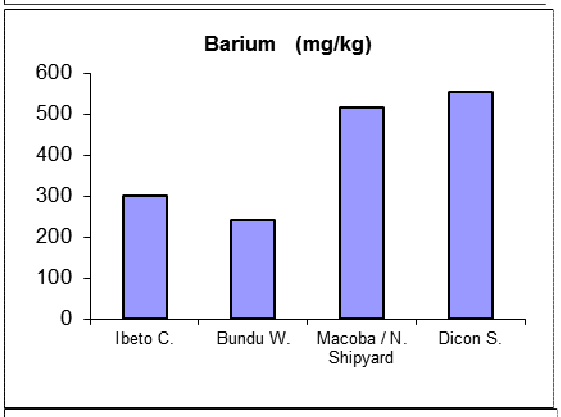
From the results, the heavy metals ranged as follows: Total chromium (3.90 - 16.20) ; Copper (159 – 240) ; Barium (241 – 554) ; Lead (<1,00) ; Nickel (25.0 – 27.3) ; Arsenic (<0.50 -1.36) ; Cadmium (<2.00) ; Mercury (<1.00) ; Selenium (<0.50) and Vanadium (2.90 – 20.4).

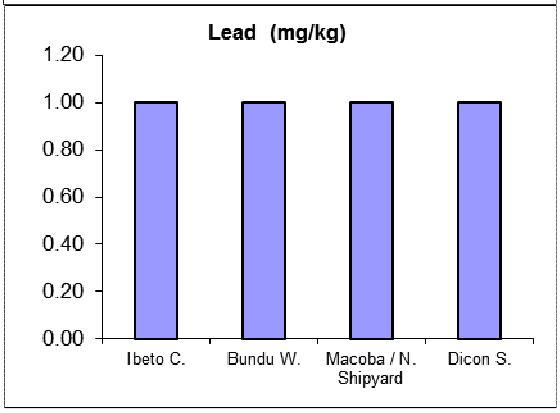
The ten heavy metals investigated were detected in all the stations studied though at varying concentrations. This is because of industrial activities taking place at those locations and poor municipal waste management (Olowu et al., 2011). Crabs are bottom feeders and pick up particulate matter from surrounding water and sediments while feeding (Okoye et al 1991). The concentration of total Chromium was highest at Macoba, M I, industry and lowest at the Bundu water side. Macoba, M I, industry is a mud drilling serving company in the Nigeria petroleum industry. Since Chromium is used in metal alloys and pigment for materials, this may account for its prevalence in Macoba and Union Dicon where massive industrial activities take place. Low exposure to Chromium can irritate the skin and cause ulceration; while long term exposure cause kidney and Liver damage including circulatory and nerve tissues. The chromium concentration in all the four sampled stations exceeded the acceptable limit of Nigerian Industrial Standard, NIS, for drinking water quality. The concentration of Copper is highest at Union Dicon industry followed by Bundu water side while the least was observed at Macoba, M I. copper is released to the atmosphere during the combustion of fossil fuels, wind-blown dust, decaying vegetation, sea spray and ends up mainly in soil. Copper is found in waste disposal site and also released through Phosphate fertilizer production in Agriculture. At Union Dicon, there is contamination of the environment with refined hydro carbon products due to loading activities during their loading operations at the jetty while municipal wastes are dumped at Bundu. The concentration of Copper exceeded the limits of WHO, USEPA, and NIS at the sampled stations. The concentration of Barium is highest compared to other heavy metals (241ml/kg – 554ml/kg). The measured concentrations exceeded tolerable limit of NIS standard at all the sampled stations. Long exposure to Barium leads to hypertension (NIS, 2007). Lead was detected in all the sampling points but at uniform concentration (1.00). Though it occurs naturally in the environment, most lead concentrations that are found in the environment are as a result of human activities such as fuel combustion, industrial processes and solid waste. Lead accumulates in the bodies of aquatic organisms, soil organisms, and in Crabs even when the concentrations are low. The accumulation of lead in food chains can give rise to health effects such as disruption of biosynthesis of hemoglobin and anemia, decline in fertility, brain and Kidney damage among others. Nickel exceeded the maximium tolerable limit at the four sampled stations with Macoba, M I having the highest concentration (207.3 ml/kg). Nickel is released into the air by power plants and trash incinerators and can also be found in surface water when it is a part of waste water stream. Nickel is not known to accumulate in plants and in animal and as result will not biomagnify up the food chain. Arsenic has the highest concentration at Union Dicon and the lowest at Bundu waterside (range: < than 0.50

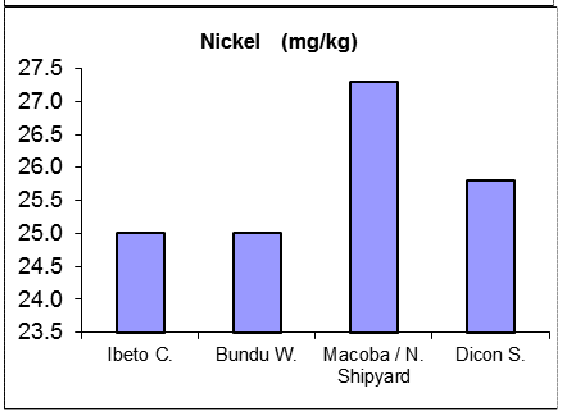
t0 1.30). A study on bio accumulation of contaminants in Crabs in Bellingham Bay reported the range of 1.9 to 5.6 As (Cubbage, 1991).

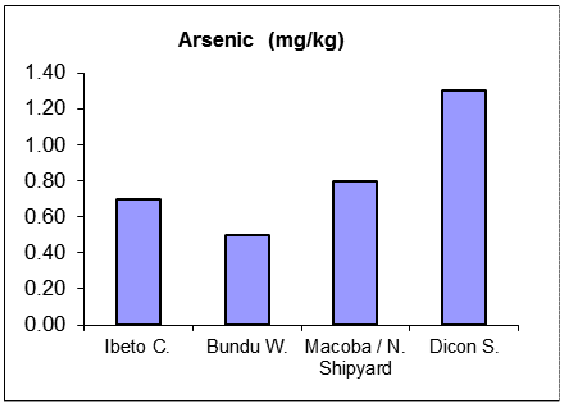


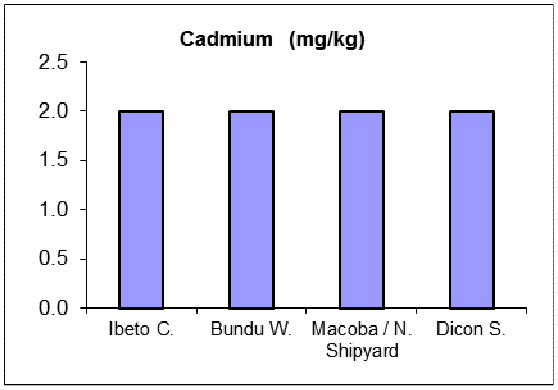


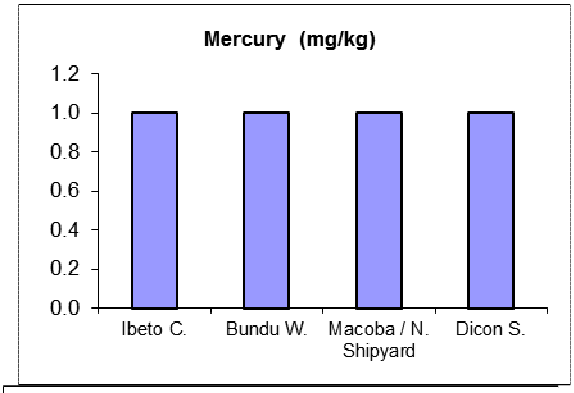


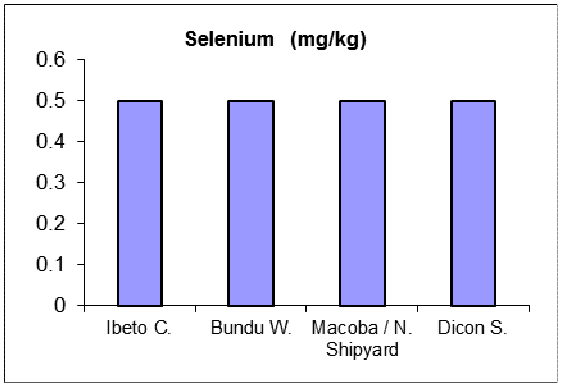


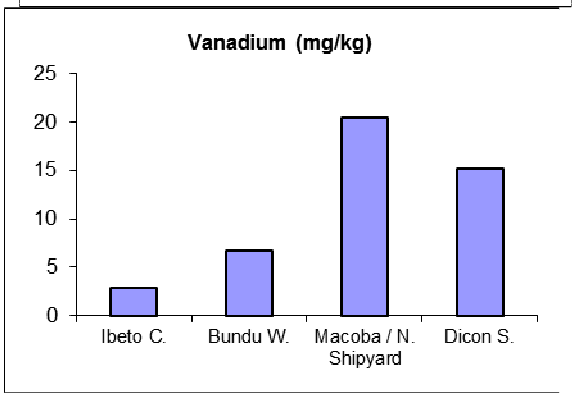












Cadmium, Mercury and Selenium were detected but the concentration (cd: < 2,00; Hg < 1.00 and Se < 0.50) were not specific. A high exposure of Cadmium occurs with people who live near hazardous waste sites or factories that release Cadmium into the air by burning of fossil fuels. Cadmium waste stream from the industries mainly ends up in soils and uptake through food e.g Crab will increase. Soils that are acidified enhance Cadmium up take by plants. In aquatic ecosystem, cadmium can bio accumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to Cadmium can vary greatly between aquatic organisms. Salt water organisms are known to be more resistant to Cadmium poisoning than freshwater organisms. Cadmium acceptable limit lies between 0.003mg/1 – 0.005mg/ (Hergenreder, 2011). Vanadium is abundant in most soils, in variable amount and it is taken up by plants at levels that reflect its availability. In Crabs, Vanadium strongly bioaccumulsates, which can lead to concentration of about 10^5 to 10^6 times greater than the concentration that are found in waste water. Vanadium can have a number of affects on human health, when the uptake is too high.

CONCLUSION

The result of the analysis indicated that all the heavy metals investigated were all detected in the Crabs from Bundu – Ama environs. These crabs accumulated more total Chromium, Copper, Barium, Nickel, Arsenic and Vanadium above NIS, WHO and USEPA tolerable and consumable standard for food. The concentration of lead, Cadium, Mercury and Selenium detected were not very specific with regards to their allowable limits. However, their continuous accumulation shows potential tendencies to exceed tolerable limits. The consumption of Crabs from Bundu – Ama pose negative health and environmental effects. The consumption of Crabs by the inhabitants can expose them to health impacts such as gastro intestinal disorder, Cancer, Kidney, Liver, Brain damage, hypertension and hindrances to development of infants. The need for continuous monitoring to prevent bioaccumulation is necessary. Good waste management practices and remediation of the area are recommended.

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APPENDIX

TEST METHOD FOR HEAVY METALS USING X-RAY FLUORESCENCE (XRF).

USEPA 6200: XRF Measurement (Cd, Zn, Mn, Fe, Ni, Cr, Co, As, Hg, Pb, Ba, V, Cu, etc)

2.1 Equipment/Apparatus

- X-Ray Fluorescence (XRF) spectro xepos
- Mixer Mill MM400
- Grinding Jars, Balls and Screen Insert rings
- Evacuable Pellet Die with the components
- Hydraulic Press
- Analytical Balance, precise to within 0.1mg
- Oven
- Crucibles
- Fume Cupboard
- Sample Cups (32mm, 40mm)
- Prolene Film 4µm Roll and Precutted
- Dust Protection Foil
- Sample Cup Liquid Protect
- Tool Snap Ring Sample Cup
- Handling Tool
- Cotton Wool
- Scissors
- Glass Beads (FLX-SP1&2)

2.2 Reagent/Materials

- Hochstwax HWC (binder)
- Cleaning Agent (methanol)
- Standard Reference Material (SRM)

- Spike Blank

2.3 Preparation of Standard Reference Material for Calibration Curve

The spectrometer must be calibrated using an appropriate reference element(s) at a minimum frequency as recommended by the manufacturer.

- Prepare the 32mm sample cup using prolene film roll
- Weigh 3.00g of a given concentration of SRM
- Run the SRM in the XRF unit
  - Copy and paste the result of the standards from the result window into the calibration window
- Enter the given concentration of the various elements
- 'Enable all' standards for calibration
- Select 'calculate' to determine the correlation coefficient
- The correlation coefficient for the standard curve should be at least 0.990

Note: check/uncheck 'calibration with offset' in the calibration window to determine the slope. If it prompts 'incorrect slope', never accept or end calibration at that point but still work on the calibration to get a correct slope. The new calibration curve can last for two years and above.

2.4 Preparation of Standard Reference Material for Q.C. purpose

- Prepare 32mm sample cup by carefully placing a ply of prolene film on one end of the cup, placing the inner cup on the film, and gently pushing down the inner cup to form a smooth closure at the other end.
- Weigh 3.00g of the chosen standard reference material (SRM) for QC
- Cover the sample cup with the lid
- Place the sample cup into the liquid protect
- Place all into the sample chamber- sample is ready for analysis
- Carry out the analysis using the XRF

3.0 TESTING PROCEDURE

USEPA 6200

3.1 Sample Preparation

- Sample blank: collect a substantial amount of a soil/sediment sample and burn off at a 1000^{o}C to remove all the metal analytes. Run the sample in the XRF unit to check if there are analytes. If the sample is free of metal analytes, use as sample blank. If not, carry out acid digestion of the sample, wash and dry, then use as blank.
- Prepare the sample cup using prolene film
- Weigh 3.00g of the sample (pulverized using the Mixer Mill as in3.2 below) into the prepared cup
- Place the sample cup in the measuring chamber
- Carry out the analysis using the XRF

3.2 Using the Mixer Mill

- Dust the equipment before usage and power on
- Feed the grinding jars with sample up to 8mm and tighten with the screw top design
- Fix the grinding jars in the appropriate position in the mixer mill
- Bring down the pin-like knob on top of the black head knob, then screw and tighten using the black head knob for a safe operation
- Grinding time: press the "on" button, set the oscillation frequency to 30Hz/min, set the time to 1min, then press the "green" or "start" button to start milling
- Pour out the sample in a foil, the sample is expected to have a maximum reproducibility

Note; the frequency and time are dependent on the sample's nature. Expected grind size is 5µm.

3.3 Using the Evacuable Pellet Die

- Place the base of the die onto a work surface
- Assemble the die cylinder body onto its appropriate base

- Take one of the stainless steel polished pellets and place it (polished side up) into the bore of the cylinder
- When the first steel pellet is in position, you can now fill the die with a prepared sample powder
- Using a spatula, pour a well ground and mixed powder (5g sample in 1g HWC binder mixture) to be compacted into the bore of the cylinder body
- Tap the side of the die lightly so that the powder is evenly distributed across the face of the polished steel pellet (can use a spatula to smooth over the surface if tapping of the die is insufficient)
- Take the second stainless steel pellet and push (polished face first) into the bore of the cylinder body
- Insert the plunger, non-chamfered edge end first in the cylinder body
- Ensure that the O-ring seal is in place around the plunger and seated in the chamfer of the cylinder body
- The die is now ready to be placed in the press for compaction of the sample powder

3.4 Using the Hydraulic Press

- Make sure that the die is central on the piston pressing face of the press.
- There should be a gap of no more than 2-3mm between the piston pressing face and the top surface of the sample to be compressed
- Turn on by pressing the power on/off button
- Press ''accept'' (or button 16) to highlight ''pump up to 3.0T''
- Increase load to 18.0T using button 15
- Press button 16 to accept/enter again
- Press ''start'' (or button 11) to apply load
- After 20s, press ''stop'' or button 12 to release the load
- Then remove the die from the press
- Remove the base of the die
- Put the die back to the press, manually press/apply load on the plunger turning the press piston
- The pellet sample drops out
- Put the pellet sample in a 40mm sample cup and label properly
- Place the pellet sample in the sample plate of the XRF using the handling tool
- Then analyze

Note; when started, the load builds up or is applied. The mixture is pressed with a pressure of 18tons for 20s

3.5 Equipment Operation

Using the XRF

- Connect all components to the UPS (unit, pc, monitor, etc)
- Turn on the power supply connection with ''on/off'' button
- Switch on the UPS using the ''on/off'' button
- Turn the key switch behind the unit/instrument to the horizontal position
- Press the ''on/off'' button behind the instrument
- Switch on the computer and wait for the operating system to boot up
- The ups is now installed
- Click on ''x-labpro 5.1 communication server'' below in the menu bar
- Type in the password ''xlabpro'' and enter to log into the software
- The XRF unit initializes
- Enter the standby mode by clicking ''yes'' on the pop up message box
- Open the chamber lid and place the prepared sample on the sample tray
- Close the sample chamber lid
- Click on the sample position in the sample data table on the screen
- Enter the sample data and sample method respectively
- Turn on the helium gas, ensure that only such samples present on the sample tray are measured under the same condition
- Start the measurement using the ''start button''

- Accept ''the samples to be measured with gas flush' if you are using helium gas, or continue the measurement after pressing the start button if you are measuring in air
- Switching off the unit – if the unit is in standby mode, shut down the standby mode first using the corresponding switch
- Select the ''file'' menu and the ''exit'' command, the program is terminated
- Turn the key switch
- Press the ''on/off'' button
- Select the ''start'' menu in the windows operating surface and the ''exit'' command, the computer is turned off
- The unit is now switched off
- Select the ''on/off'' button of the ups
- Finally turn off the power supply

3.6 Quality Control

- Always start by analysing QC sample
- A sample of known concentration is chosen as the quality control (QC) standard. Prepare and analyse it after every 10 samples or each batch of samples, whichever is less.
- Measure a reference sample daily for quality checking
- Enter the first QC result from the analysis sequence into the QC notebook and plot this value on the means control chart
- Run the MCA glass tablet recalibration once a week and global recalibration once every two months to correct for instrument drift, use FLX-SP1&2 for both sensitivity and baseline drift. This is MCA and Global Recalibration.
- The acceptable co-efficient from the calibration curve is 0.99
- If the value of the QC sample exceeds the control limit on means control chart, check the expiry date of the stock standard/QC sample. Prepare a fresh sample if necessary and repeat the QC analysis. If it still exceeds the control limit, identify source of the error and rectify.
- If the QC value is within the control limit, then six successive points within the control limit can be either above or below the central line but the seventh point should not be on the same side. If the seventh point is on the same side, discontinue analysis and rectify problem.
- Only one plotted point should be above the warning limit on one side, either above or below the central limit. For three sets of points, if two out of three successive points exceed the warning limit (WL), repeat the QC analysis. If the repeated QC is within warning limit, continue analysis. If not discontinue analysis and rectify problem
- If the mid-point standard after every ten samples or batch of samples fall outside 90-110% of the expected concentration, repeat analysis of mid-point standard. If result is still outside the above limit, discontinue analysis and rectify the problem.
- In every 10 samples or each batch of samples, whichever is less, analyse one of the samples in duplicate, the relative percent difference (RPD) of the duplicate analysis should not be more than 90-110%. If the duplicate analysis exceeds the stated limit, repeat the analysis. If it still exceeds the limit, discontinue analysis and rectify the problem.
- If acceptable, enter the first duplicate analysis in the analysis sequence into the QC notebook.

Note: Relative percent difference (RPD) = $\frac{\text{(sample result – duplicate result)}}{\text{(Sample result +duplicate result)/2}} \times 100\%$

- Ensure that at least a spiked sample is analysed in every batch of samples. The percentage recovery of the spiked sample should be between 90-110% of the expected concentration

4.0 Data Processing and Reporting

Record results in analytical notebook stating the date of analysis, project number, type of sample, analysis required method and results transcribed into hand filled report sheet.

4.1 Data Processing

Results are calculated automatically by the unit since the sample name, method, job, dilution mass, sample mass, sample diameter, sample type, sample state and Prolene foil sizes have been imputed in the X-LabPro Routine Dialog and Method Administration.

4.2 Reporting

Results are reported in mg/kg
Values greater than 100 should be reported to the nearest whole number
Values between 10 and 100 should be reported to one decimal place
Values less than 10 should be reported to two decimal places
Values less than the Limit of Detection (LOD) should be reported as less than the LOD