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Evaluation of the Presence and Concentrations of Nine Heavy Metals: Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in Five Crops Harvested From Farms Located in Kpean and Zaakpon in Khana Rivers State Nigeria Using AAS and XRF

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Research Article

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ABSTRACT

The presence and concentrations of nine heavy metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb) were evaluated in five crops that were cultivated in two farmlands that had been impacted by oil spills over the years and a third farm that was 3 km away from an old oil location site using AAS and XRF. Most of the data analyses were carried out on results obtained from AAS. The XRF analysis was performed for comparison and it turned out to be a useful tool in this study. Both AAS and XRF results showed that the soil from the oil location farmland had the highest concentration values for all the metals detected.

INTRODUCTION

Background of study

Nigeria is one of the oil producing countries and is ranked 6th largest oil exporter in the world. Oil exploration and exploitation has uplifted nigerian economy leading to rapid development but the impacts on the environment are receiving less attention. Crude oil exploration has taken place in five major sedimentary basins namely: The niger delta, the anambra basin, the benue trough, the chad basin and the benin basin. The most prospective is the niger delta. The continuous exploration, production, processing of crude oil and its transportation exposes the environment to constant threat of oil pollution [1]. Heavy metals are one of the groups of pollutants in our environment and the nigerian crude oil is known to contain some of these heavy metals such as Zn, Ac, As, Ba, Fe, Pb, Co, Cu, Cr, Mn, Hg, Cd, Sb, Ni and V, therefore plants growing in crude oil impacted soils can accumulate the toxic metals at high concentrations causing serious risk to human health when consumed. Metals and metalloids may be naturally found in the crude oils and these could also be added during production, transportation and storage. These elements are present as inorganic salts (mainly as chlorides and sulphates of K, Mg, Na and Ca) or as organometallic compounds of Ca, Cu, Cr, Mg, Fe, Ni, Ti, V and Zn. The interactions between metals and solid phases of soils, water and air within and above the soil depend on a variety of chemical factors and the heavy metal transport [2]. Absorption of metals from soil water to soil particles is the most important chemical determinant that limits mobility in soils. Studies have shown that plants growing within the heavy metals contaminated areas usually take up heavy metals by absorbing them from deposits on the parts of the plants exposed to the air from polluted environments as well as from contaminated soils.

Purpose of the study

Though oil production in ogoni land has ceased, the entire gamut of oil operations in the land took place on soil which was very productive. According to the UNEP (2011) report, some oil facilities that were no longer in operation have never been formally decommissioned and some have been abandoned [3]. They have been left without maintenance and exposed to the elements making them vulnerable to corrosion and damage. It shows the site of an abandoned oil well head in the oil location.

The picture was taken during the rainy season which explains the water log. The soil is no longer as productive as it used to be but the farmers apply ample quantities of fertilizer to boost the yield. During the dry season the soil is dry, black and crusted. These abandoned facilities pose both environmental and safety risks.

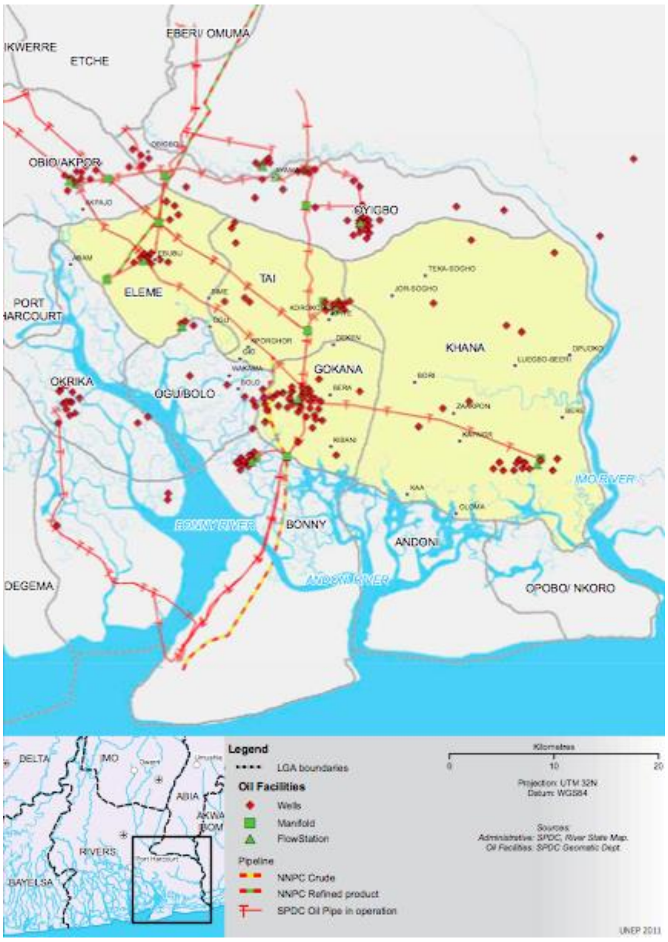
Corrosion of metallic objects leads to ground contamination by heavy metals. Investigated the concentration levels of some heavy metals in tuber crops grown around etelebou oil flow station in bayelsa state, nigeria. These tuber crops (cassava, plantain and cocoyam) were observed to have high concentrations of Fe, Zn, Cr, Cu, and Pb. Studies on heavy metal concentrations in food crops grown in crude oil impacted soils in olomoro, delta state, Nigeria revealed high metal concentrations of Cr, Cu, Fe, Pb, and Zn in cassava tubers and plantain fruits.

MATERIALS AND METHODS

Study area

Oil spills are frequent events in ogoni land. When oil reaches the root zone, plants begin to experience stress and in extreme cases death follows and one of the greatest problems associated with oil pollution is the constant exposure to high concentrations of heavy metals from oil [4]. According to the UNEP (2011) report the team observed that the oilfield in ogoni land is interwoven with the ogoni community with many families living close to oil field facilities. The three farmlands (100 m^2 each) used for this study are in khana local government area.

Figure 1. Map of ogoniland. Note: Courtesy: UNEP 2011 report.



Materials and farmlands

The three farms for this study are located in two different communities in khana local government area of rivers state. One farm had experienced oil spill in the year 2000 and is located in zaakpon. Another is an abandoned oil spill site (referred to as oil location by the indigenes) while the third farm (Kpean) is about 3km into the village away from the oil location farm [5]. Maize (grain) and four crops (cassava, white yam, three-leaved yam and water yam) were used for this study. These are major staple food crops for the indigenes.

Sample collection and planting

The four crops and maize were selected out of many crops and grains that the farmers in these communities plant for the purposes of this study. The crops and maize used were purchased at different market days. These were divided into two portions. One portion was dried and digested in duplicates with acid mixture and analysed as the baseline samples while the other portion was planted. The crops and the maize were planted without the addition of fertilizer to the soils. These crops have a shorter maturation period which enabled us plant, harvest and analyse our samples within the specified period of study. Maize was harvested 3 months after planting while the varieties of yams were harvested after 9 months of planting.

Monitoring of farms and crops

The farms were monitored weekly and clearing of the weeds were carried out frequently especially during the rainy season by farm helps engaged for purposes of this study [6]. Stunted growths were observed among the crops when compared with those in adjourning farms that had been planted with the addition of fertilizer.

Harvesting

From the three farms, samples were selected for maize after 3 months of planting for digestion and analysis using AAS and XRF. After 9 months of planting, the cassava, white yam, water yam and three-leaved yams were harvested, digested and analysed also. Portions of cassava were left in the three farms to be harvested at 12 months and 18 months after planting and processed into the edible form (garri). This is to simulate the farmer's full agricultural activity with respect to this particular crop from cultivation to consumption. The farms were monitored from time to time. The last harvesting of cassava was carried out at 18 months.

Sample preparation

At maturation, the samples were harvested from the three farms, peeled and sliced into little sizes (in the case of the crops) and kept in the open to air dry for 3 days. The drying was rapid because of the harmattan weather. The maize kernels were removed from the cob and also left to dry in the open to reduce moisture content [7]. The dried samples were ground into fine powder using polyurethane mortar and pestle, put into separate sample containers and labelled appropriately and set aside for digestion and analysis. The soil samples were air dried for 3 days to remove moisture and ensure constant aggregate weight.

Sample digestion

AAS analysis: About 1 g each of the soil samples was weighed into a beaker and extracted by shaking with 10 ml of the digestion mixture of perchloric acid and nitric acid (1:4 v/v) in pre-washed glass containers for 1 hr. The extracted solution was filtered using whatman filter papers and the filtrate was made up to mark in 50 ml volumetric flasks using deionized water [8]. The resultant solutions were put in sample bottles (10 ml) for analysis using AAS. For the crop samples and maize samples, 1 g were weighed out using analytical balance and 10 ml of the digestion mixture of perchloric acid and nitric acid (1:4 v/v) was added to the samples in breakers and the mixtures allowed to stand for 15 minutes. The contents were heated for 4 hrs to ensure complete digestion, allowed to cool and then filtered into 50 ml volumetric flasks and made up to mark with deionized water [9]. The resultant solutions were put in sample bottles (10 ml) for analysis using AAS.

XRF analysis: The soil samples were packaged in clean plastic sample containers and labelled appropriate for XRF analysis. Ground maize and crop samples were also packaged and labelled properly for the XRF analysis by the materials science and engineering laboratory of kwara state university, malete.

RESULTS AND DISCUSSION

The results from AAS and XRF analysis are presented in Tables 1 and 2.

Table 1. Concentration of the metals (mg kg^{-1}) in the baseline samples before planting (AAS)

Samples	Cr	Co	Mn	Fe	Ni	Zn	Cu	Cd	Pb
Cassava K_1	-	-	6.35	94.00	5.15	44.75	-	-	-
Cassava Z_1	-	-	6.35	62.70	9.85	34.20	-	-	-
Water Yam K_1	-	-	-	81.35	5.15	39.90	-	-	1.65
Water Yam Z_1	-	-	-	80.10	5.15	54.40	-	-	1.65
Maize K_1	-	-	4.45	25.35	5.15	88.70	-	-	-
Maize Z_1	-	-	11.35	31.95	2.80	89.60	-	-	-
Three-leaved Yam K_1	-	-	-	89.05	12.20	43.00	-	-	-
Three-leaved Yam Z_1	-	-	-	94.55	12.20	43.00	-	-	-
White Yam K_1	-	-	-	67.10	5.15	49.60	-	-	5.75
White Yam Z_1	-	-	-	72.60	5.15	64.55	-	-	5.75

Table 2. Concentrations of the metals in baseline samples before planting (XRF)

Sample	Cr	Co	Mn	Fe	Ni	Zn	Cu	Cd	Pb
Cassava K_1	0.001	-	0.006	0.141	0.092	0.212	0.355	-	-
Three-leaved yam K_1	0.006	-	0.002	0.139	0.091	0.180	0.159	-	-
Water yam Z_1	0.004	-	0.004	0.199	0.085	0.184	0.284	-	-
White Yam K_1	0.002	-	0.002	0.148	0.081	0.201	0.368	-	-
Maize K_1	0.005	-	0.004	0.157	0.104	0.224	0.227	-	-
Maize Z_1	0.003		0.009	0.342	0.096	0.243	0.261	-	-

Pb, Cd and Hg have been reported not to have any known function in human biochemistry or physiology. Dietary intake of these metals even at very low concentrations can be very harmful because they bio-accumulate and have been classified as carcinogens.

- Co is required in the manufacture of red blood cells and it is an integral component of vitamin B12. It is essential in minute quantities. Excessive intake of this metal may cause over production of red blood cells. At high levels, it exhibits mutagenic and carcinogenic effects.

- Mn promotes hepatorenal functions. It is important for the function of the pituitary gland. However, it is capable of causing brain and nerve damage and other health problems including carelessness when present in high concentration.

- Fe is very essential to almost all living things in humans its deficiencies lead to anaemia. It is the element needed in the formation of haemoglobin. Fe is absorbed rapidly in the gastrointestinal tract. Excessive level of Fe in the body is commonly referred to as iron-overload (hemochromatosis). It may cause conjunctivitis, choroditis, retinitis or siderosis.

- Ni activates some enzymes when present in trace quantities. It is involved in fat metabolism and functions as a biocatalyst required for body pigmentation in addition to Fe. At higher levels it is believed to be carcinogenic, cause skin irritation, heart and liver damage.

- Cu is a metal that occurs naturally in the environment, accumulates in plants and animals, it is a micronutrient required for monitoring good health. High levels can cause harmful effects such as irritation of the nose and eyes, nausea, diarrhoea and stomach cramps. It may also be linked to liver cancer and brain tumours. People with Wilson's disease are at a greater risk from overexposure to copper.

- Cd is toxic even at very low levels. Exposure to Cd leads to lung disease. It targets the liver, placenta, kidneys, brain and bones. It is also associated with bone defects, such as osteomalacia, osteoporosis, and spontaneous fractions. Long term exposure results in renal dysfunction, prostrate and ovarian cancers.

- Zn is considered to be relatively non-toxic especially if taken orally. The clinical signs of Zn toxicosis have been reported as vomiting, bloody urine, liver failure, kidney failure and anaemia. It has been reported to cause the same signs of illness as Pb and can easily be mistakenly diagnosed as Pb poisoning.

- Pb is not beneficial in any form. It is biotoxic and the serious effect of lead toxicity is its teratogenicity. Pb poisoning causes the inhibition of the synthesis of haemoglobin, dysfunctions in the kidneys, joints, reproductive systems, cardio vascular systems and chronic damage to the central and peripheral nervous systems.

CONCLUSION

Most of the data analyses were carried out on results obtained from AAS. The XRF analysis was performed for purposes of comparison and it turned out to be a useful tool in this study. Both AAS and XRF results showed that the soil from oil location had the highest concentration values for all the metals detected in this study. The order of the metal concentrations are Fe>Zn>Ni>Mn>Pb. The pollution load indices are greater than 1 for Fe and Ni which is an indication of heavy metals contamination in these soils. PCF indices for Mn, Ni and Pb were high for the tuberous crops while maize showed the highest PCF value for Zn from all the three farms. From this study, Yam has the highest concentration of the metals followed by cassava. The order is presented as white yam>Cassava>Three leaved yam>Water yam>maize. Daily consumption of white yam has to be reduced to a minimum so as to minimize the accumulation of some of these heavy metals to a toxic level. Processed cassava after 18 months of planting had lower values of Fe and Ni. However, Mn and Zn concentrations were higher. The metals Cr, Co, Cu, Cd and Pb were not detected in the processed Cassava at 18 months though they were present in the unprocessed raw cassava at 9 months.

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