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Variations of Heavy Metals in Agricultural Soils Irrigated with Tin Water in Heipang District of Barkin Ladi, Plateau State, Nigeria.

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ABSTRACT

Untreated tin mine water from tin mined ponds is mostly used for the irrigation of crops in Heipang District of Barkin Ladi, Plateau State, Nigeria, due to its easy availability, difficulties in reclaiming the shafts and scarcity of freshwater. Irrigation with mine water is known to contribute significantly to the heavy metals content of soil. This work assessed the pH values and the concentrations of eight heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Zn, and Pb) in surface soil, soil from the depth of 10cm, sediment and maize plant from June to August, 2010 in an irrigated area of Heipang using the inductively coupled plasma optical emission spectrophotometer (ICPOES). The pH of the soil and sediment in this work ranged from 5. 33 -7.00. Most of the pH values were acidic and below WHO permissive values. The analyses of samples for heavy metals revealed very high concentrations of Pb, Zn, Mn, Fe, Cr, and Cu and Ni except Cd which was not detected in most of the samples. The variations of the concentrations of metals in the samples did not follow any regular pattern for the three months studied. The accumulation of the metals in soils and sediment samples followed the sequence Fe>Zn>Mn>Cr>Pb>Cu>Ni>Cd. Cd was only detected in the plant (maize) sample with normal concentration range of 0.054 - 0.308 but showed concentrations higher than the toxic levels for Mn, Zn, Cu, whereas, Ni, Pb, and Cr concentrations in June exceeded the toxic levels and the concentrations for the other months were very close to the upper limits of their respective toxic concentrations. The acidic mine waters from the closed tin mines could be extremely dangerous pollutants of arsenic and heavy metals poisoning either by direct exposure during tin mining or through soil, water contamination and the food chain causing cancer and other heavy metals related illnesses. Control measures of pollution routes and remediation measures at the site are urgently required

Keywords: *Heavy metals, Agriculture soils, Tin mine water, irrigation*

I. INTRODUCTION

Barkin Ladi Local Government Area of Plateau State was well known even beyond the state for its mining activities. Tin mining has devastated vast portions of its land mass. This is evident by the presence of mounds and ponds scattered all over the local government. The unprofitable open – cast mining and ore processing activities are continuing by local miners and the pollution problems caused by the open pits and tailings are on the increase. The use of tin mine water for irrigation of agricultural crops could be a promising technology which could solve the problems relating to both shortage of irrigation water and disposal of effluents mine drainage (Annandale, Jovanovich, Pretorius, Lorentz s, Rothmans and Tanner, 2001), but the use of such water for irrigation exposes consumers as well as producers to various health risks. Srinivarsan and Ruddy (2009) found out that, significantly higher morbidity in the waste water (mining inclusive) irrigated villages compared to fresh water irrigated village and the cost of the treatment of the illnesses incurred by households is substantial. Whilst support for increase production and consumption of fresh vegetables is an important goal, citizens have a right to safe food and to ensure food available to them are not contaminated beyond safe acceptable limits (Marshal, Agarwal, Lintel and Bhupal, 2003).

The anthropogenic activities like mining, ultimate disposal of treated and untreated waste effluents containing toxic metals and metal chelates from industries and the indiscriminate use of heavy metals containing fertilizers and pesticides in agriculture results in the deterioration of water, air and soil quality, thereby, rendering serious environmental problems that is posing treat to humans. The deadlier diseases like, ochema of eyelids, tumor, congestion of nasal mucous membranes and pharynx, stuffiness of head and gastrointestinal, muscular, reproductive, neurological and genetically infection have been documented (Kar, Kur, Manual, Saha and Kale, 2008).

Metal - soil interaction is such that when metal is introduced at the surface, downward transport does not occur to any extent, unless the metal retention capacity of the soil is overloaded or metal interactions with associated waste matrix enhances the mobility of the metal (McLean and Blasé, 2000). Measurement of the total concentration of metals in soils is useful for determining the vertical and horizontal extent of contamination and for increasing net change (leaching to groundwater, surface run offs) in soil metal concentration over time. However, this does not give an indication as to the chemical form of the metal in the soil. The aim of this work is to determine the levels and the trend of a three months variation of eight heavy metals in maize, soils and sediment of mine pond used for agricultural applications in Heipang District of Barkin Ladi L. G. A of Plateau State.

II. METHODOLOGY

Study Area

Heipang is a district in Barkin Ladi L.G.A of Plateau State, Nigeria and hosts an Airport, the State's Polytechnic and a Railway passes through the town. The irrigated farms studied were some of the reclaimed tin mine areas. These areas were reclaimed by planting eucalyptus trees that restored the landscape. One of the unclaimed tin mine ponds is used by the Polytechnic as a source of raw water for its water treatment plant and farmers in the area also use it for irrigation.

Sample Collection, Treatment and Analysis

Surface soil, soil from 10cm dept (referred to as depth) and Maize's leaves from different stages of development were randomly collected from different locations on the irrigated farms from June to August, 2010. The soil and sediment samples were each collected using a plastic spoon, poured into already labelled polythene bags, and mixed thoroughly to give a representative fraction of the samples.

The sediment, soils and leaf samples collected were dried in an oven at temperature of 110ºC for 7 hours. Each sample was separately crushed using pestle and mortar and then sieved through a 3mm screen. One gram of each sample was weighed into a beaker . To each sample, 6ml of hydrochloric acid was added, 4ml of trioxonitrate (V) acid and 2ml of perchloric acid was added. The samples were heated on a sand bath in a fume cupboard for six hours until almost dry. 2ml of trioxonitrate (V) acid was then added to dissolve the almost dried samples and 10ml of distilled water was added and heated for 10minutes. After 10minutes, the sample was removed and allowed to cool, then filtered into a 100ml volumetric flask and made to the mark with distilled water. The solution of each sample was analyzed for eight heavy metals using inductively coupled plasma optical omission spectrophotometer (ICPOES).

III. RESULTS AND DISCUSSION

Table 1: The pH values of surface soil, soil from dept of 10cm and sediment for three months

S/No	Sample	Month	pH
1	surface soil	June	5.49
2		July	5.53
3		August	5.52
4	soil at 10cm Dept	June	5.44
5		July	6.12
6		August	5.54
7	sediment	June	7.00
8		July	6.77
9		August	5.33

WHO* pH range is 6.5 – 8.5 (Tabari, Azadeh, Jahangard and Alireza, 2007)

Figures (a) – (h): Comparison of Heavy Metal Concentrations (mg/kg) in Four Samples Analyzed from June to August, 2010.

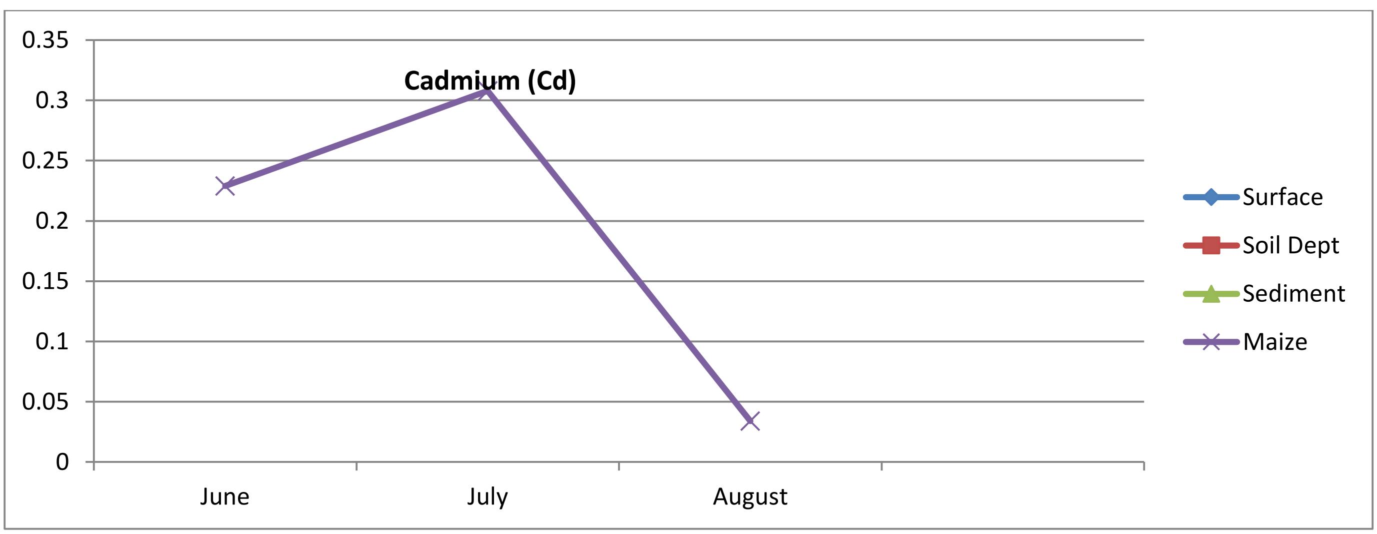

Fig (a): Three months' variations in measured concentration of cadmium in samples

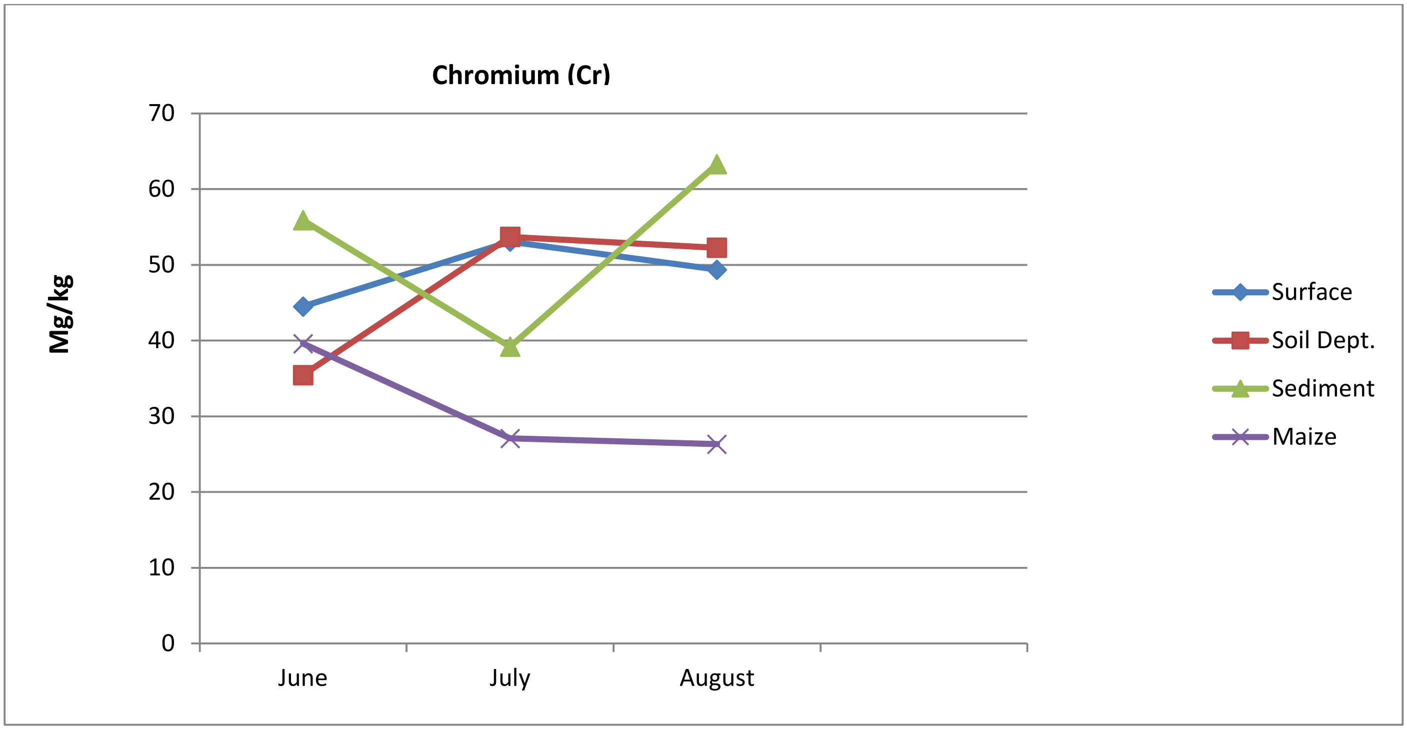

Fig (b): Three months' variations in measured concentration of chromium in samples

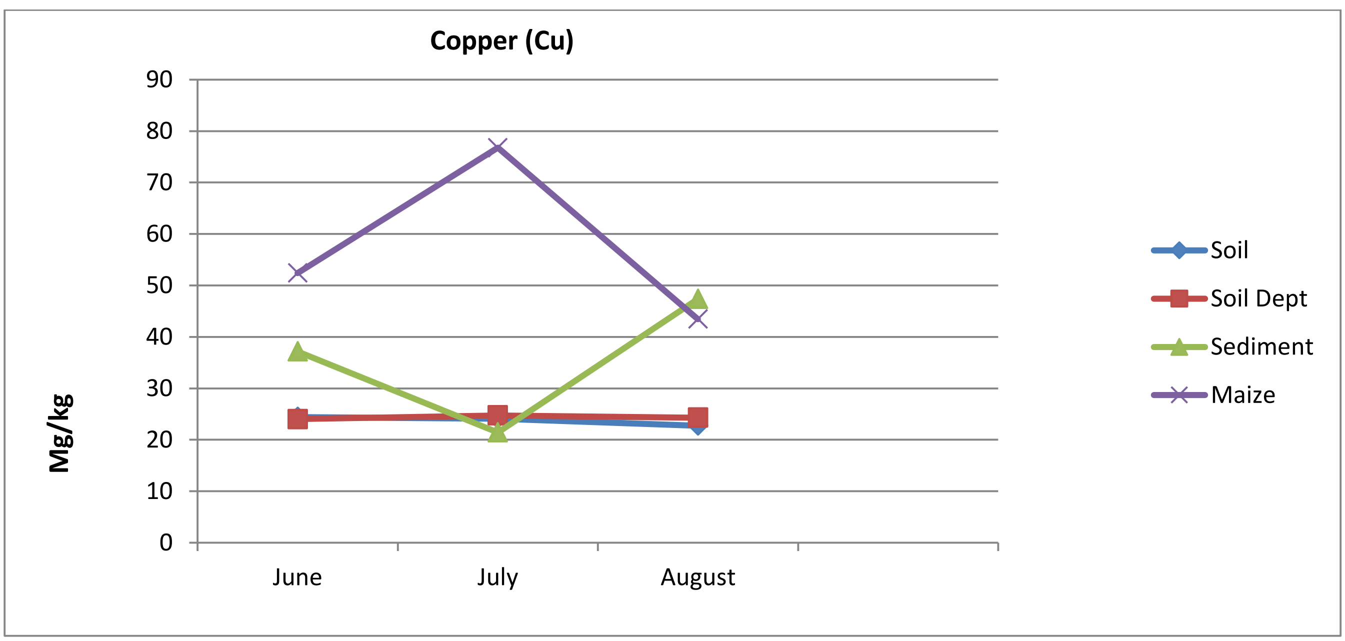

Fig (c): Three month's variations in measured concentration of copper in samples

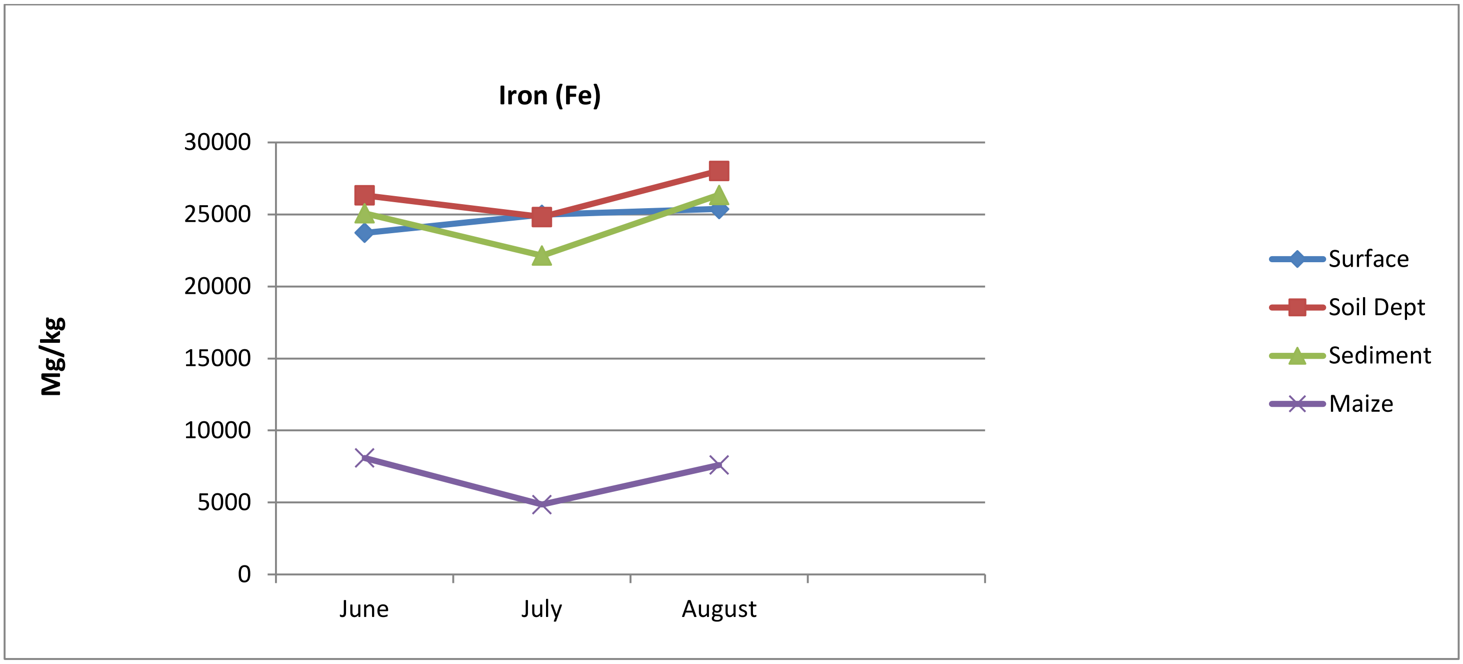

Fig (d): Three months' variations in measured concentrations of iron in samples

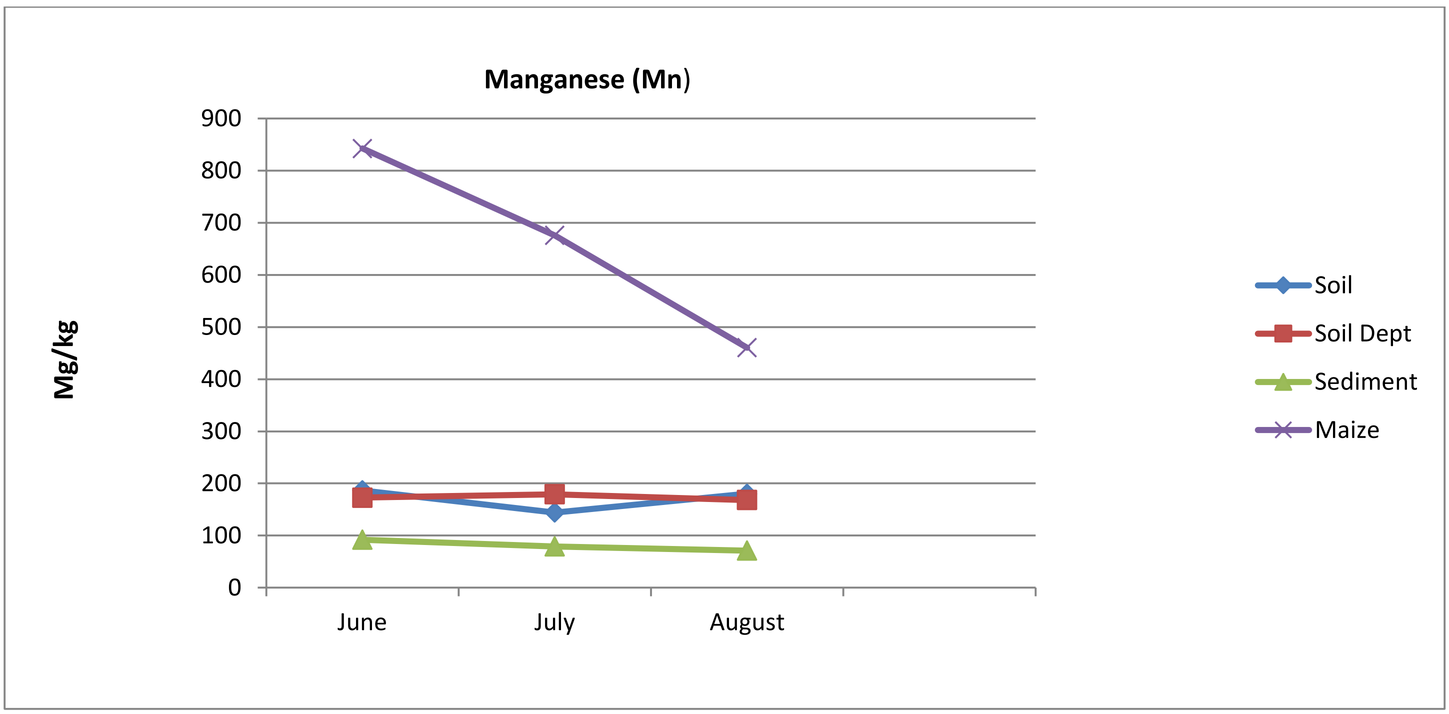

Fig (e): Three months' variations in measured concentrations of manganese in samples

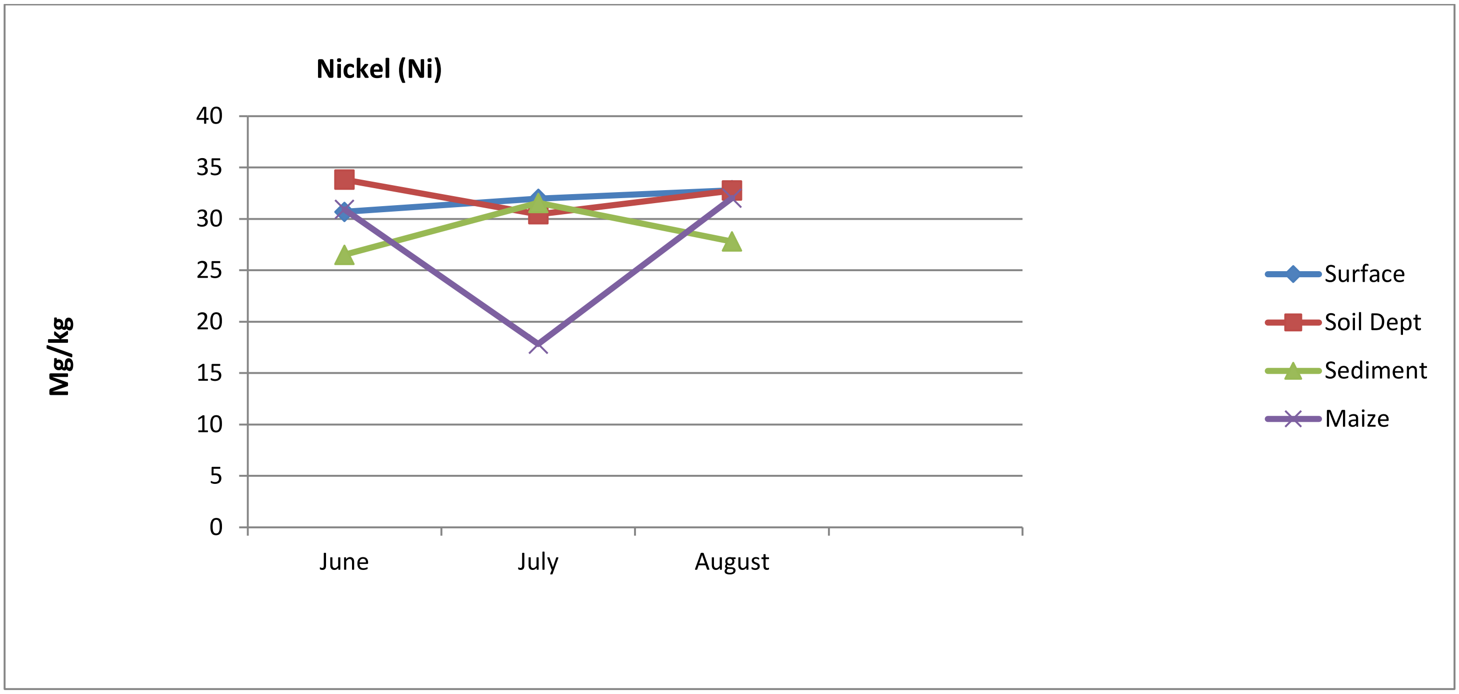

Fig (f) three months' variations in measured concentrations of nickel in samples

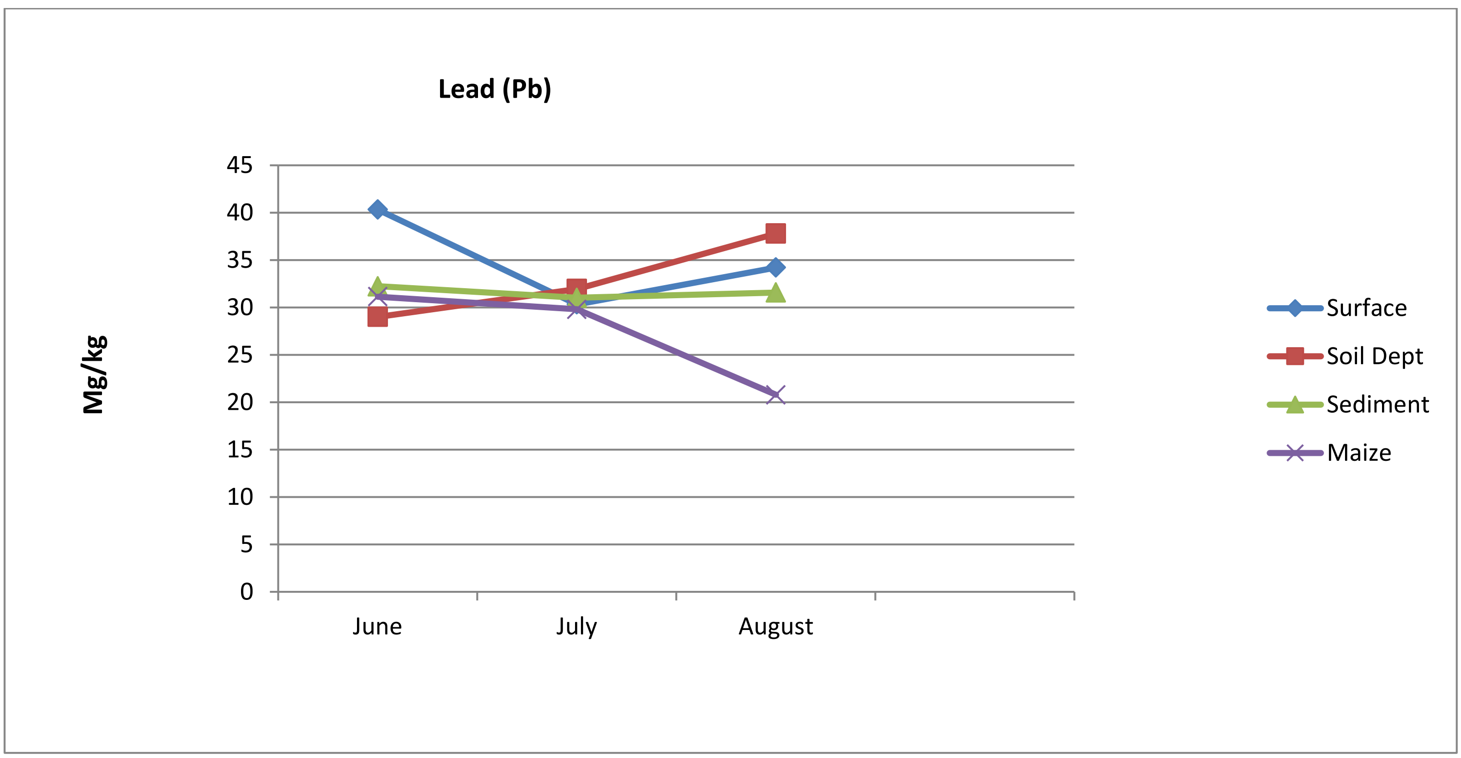

Fig (g): Three months' variations in measured concentrations of lead in samples

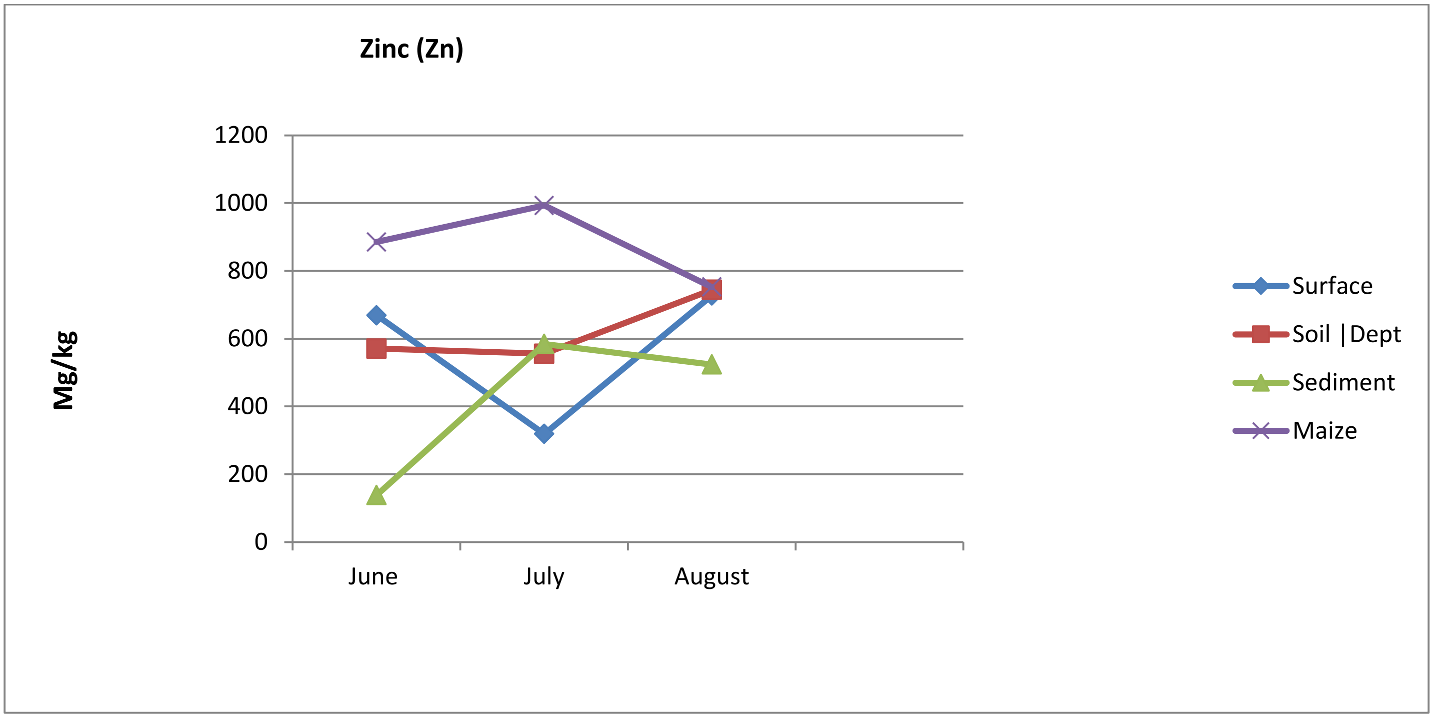

Fig (h): Three months' variations in measured concentrations of zinc in samples

Mining disturbances is a common source of exposed sulfide minerals; so acid drainage frequently referred to as acid mine drainage (AMD) associated with mining is responsible for the observed low pH in this work. Only the pH of the sediments in June and July were within WHO permissive values. Mine waters originated from active or closed mines AMD are extremely dangerous pollutants, polluting their environment for a very long period of time (Stankovic, Bozic, Gorgievski & Bogdanovic, 2009). Lower acidites allow metals which are associated with mining (such as Cadmium, Copper, Lead, and Zinc) to enter the solution phase and be transported from the system. However, low pH values do not need to be established for metals to be released from mine waste at extreme concentrations because near neutral pH (pH 6 - 7) have been established for metals such as Zn, Cd and As (Duruibe, ogwuegbu &Egwurugwu, 2007). These metals precipitate from the water column as pH increases, however the pH at which the potential for complete precipitation varies for different metals (Gaikwad & Gupta, 2008). Also, heavy metals in acidic drainage in the presence of organic matter and bacteria are methylated to yield the organic forms of the metals. These organic forms of the metals are very toxic and will adversely affect the water quality by seepage to underground water (Duruibe, Ogweuegbu & Egwurugwu, 2007).

The concentrations of the metals for the three months are shown in figures (a) to (h). The variations of the concentrations of metals in the samples did not follow any pattern for the three months studied. For some, there was steady decrease from June to August in the levels of the heavy metals in the irrigated soils and sediments but to various extents. This could be due to leaching, run offs and difference in mobilities of the metals. Others showed no appreciable change in their concentration throughout the months of study. Yet some of the heavy metals increase in July and again decrease in August indicating the combine effects of anthropogenic inputs, run offs and leaching. The results also showed that the irrigated soils and sediments were severely contaminated by heavy metals.

Labbe (2008) report that, abandoned metal mines that produce AMD have the potential to discharge arsenic (As) and heavy metals from a variety of sources. According to him, heavy metals and As may be transported in leachate from tailings, waste rocks, and contaminated soils or may be discharge from mine workings such as portals, shafts, and adits. He added that, heavy metals (As, Pb, Zn, Cu, Cr and Ni) contained in the tailings are mobilized, migrate to the surroundings and cause severe and widespread contamination of soils,suface and ground waters. For this reason, site specific factors are possibly the most important in determining how products of AMD are transported to the streams.

Cadmium (Cd) was not detected in soil, soil from depth of 10cm or in sediment but only in the maize plant. This might be due to fertilizer and pesticide applications to the farm. The metal in maize increased in July but dropped in August. The increase in July could be as a result of some anthropogenic activities in the area and the decrease could be due to leaching of the metals to the underground water and run offs. Soil pH is the principal factor governing the concentration of cadmium in the soil solution. Cadmium adsorption in soil particles is greater in neutral or alkaline soils than in acidic ones. As a consequence, plant uptake of cadmium decreases as the soil pH increases (WHO, 2007).

Chromium (Cr) concentration was fairly constant in the surface soil for the three months but Cr in soil from the depth of 10cm and in sediment decreased in July and in August. The metal concentration in maize decreased in July and remain constant in August. Cr exist as Cr^{3+} and Cr^{6+} forms but in normal soils, reduction of Cr^{3+} to Cr^{6+} is favoured. The environmental chemistry of Cr in soil is very complex and is generally difficult to extract some general patterns. The pH also affects the speciation, bioavailability and solubility of the metal but affects the different forms of the metal differently (Mclean and Blease, 2000).

The concentration of copper (Cu) in surface soil and soil from 10cm depth were faily constant throughout the study period but the metal in sediment decreased in July and increases in August, while in maize, the concentration increased in July but dropped drastically in August. Cu has concentration that range from 21. 74-52.42mg/kg in soil, soil from dept of 10cm and sediment. When Cu concentrations is greater than 20 mg/kg, in soil, it is considered contaminated soil (Alshaebi, Wan, Samsudin & Alsabahi, 2009). The soils and Sediment of this study are therefore contaminate with the metal. Cu is a significant cause of ecological degradation where it occurs in receiving concentration above about 0.5 $mg.1^{-1}$.

The concentration of iron (Fe) in the surface soil increased slightly from June to August but in soil dept of 10cm, sediment and maize decreased in July and increased in August. Iron is the most common pollutant of mine waters which commonly occurs at concentrations within a range from 3 to 200 $mg.1^{-1}$ with extreme concentration of iron reaching tens of thousands of $mg.1^{-1}$. The extreme concentrations are particularly where evaporative concentration of mine waters has occurred. In this work,the high concentration rage of Fe (22140 – 28020mg/kg) could be explain by the fact that samples were collected during the dry season when much water has evaporated. Even at relatively modest range of in soils and sediment concentrations of a few $mg.1^{-1}$ of dissolved iron can render waters unsuitable for supply purposes without extensive (and frequently expensive) prior treatment. The forms of dissolved iron vary with pH: ferrous iron (Fe^{2+}) is commonly found in solution across a wide range of pH values (typically 3-9), whereas the ferric form (Fe^{3+}) is only appreciably soluble under low-pH conditions (pH<4.5). At higher pH values, ferric iron rapidly becomes insoluble as its hydroxide ($Fe(OH)_3$), which forms the red/orange' ochre' precipitates which discolour the beds of streams impacted by mine water discharges. In more acidic waters, the 'ochre' tends to be lighter in colour (often being yellow in appearance) and is mineralogical dominated by ferric hydroxysulphate minerals such as schwertmannite and/or jarosite. Ochre deposition causes marked ecological degradation principally by prevention of photosynthesis where the benthos is smothered in precipitates (Jarvis and Younger,1997).

The concentration of manganese (Mn) was very high in maize and decrease from June to August. The concentration of the metal was fairly constant in soil, soil from dept of 10cm and sediment for the three months. Manganese is regarded as one of the four contaminants that are very commonly found in mine waters. Manganese as Mn^{2+} in solution is not ecotoxic, but can cause unsightly black staining of domestic plumbing and laundry where it enters public water supplies and becomes oxidized to Mn^{4+} precipitated as its oxide, MnO_2 (Younger, Banwart, & Hedin, 2002).

The concentration of nickel (Ni) in surface soil, soil from depth of 10cm, and sediment were fairly constant throughout the study period. The concentration in maize decreased sharply in July but increased sharply in August. Ni concentration in this work ranged between 30.68 -33.81mg/kg in soil and sediment and was far lower than those in the work of Alshaebi Wan, Samsudin A & Alsabahi (2009). Alshaebi Wan, Samsudin & Alsabahi (2009) states it's Ni contaminates the soil when its concentration is higher than 40mg/kg. The values for Ni in soil and sediment in this work are lower than 40mg/kg which indicated that, the soil and sediment have not been contaminated by Ni. They also reported that, highest concentration of Ni is normally associated with the layer of the soil that is rich in organic matter or with relatively high content of clay.

The concentration of lead (Pb) in the surface soil decreased in July but increased in August. The concentration of the metal in soil depth of 10cm increased from June to August but the concentration in sediment dropped in July but was fairly constant in August. The Pb concentration in this work ranged from 20.78 – 40.3mg/kg and had an average mean concentration of 40.82 in the work of Egila and Daniel (2012) conducted in 2001 in the area. These results showed that, there is no much difference in the Pb concentration between this present work and the previous one. Pb is said to be the most immobile of all the common heavy metals and strongly sorbed by soils under neutral to basic conditions, being particularly attracted to sulphur groups in humans. Lead introduced at the soil's surface will complex with organic matter causing lead to be bound in the soil within the top few centimeters, where organic matter content is highest (Ezeh and Chukwu, 2011). Alshaebi Wan, Samsudin & Alsabahi, 2009 assessed metals in abandoned tin mine pond in Malaysia and found Pb concentration to range from 149740.33 - 250311.33mg/kg in soil. This concentration is many times higher than what was obtained in this work. According to Niragu (1978) in Alshaebi, et al, (2009), the measure of the soil is uncontaminated when the concentration of Pb less than 20mg/kg. They also reported that Pb resides in large quantities with the remnants of mining activities and Pb is associated in large amounts with tin residues and is possible for high concentrations of Pb to be released to the environment.

The concentrations of zinc (Zn) in surface dropped in July and increased in August but in soil from depth of 10cm, the metal was fairly constant between June and July but increased in August. The concentrations of zinc in sediment dropped in July but remains fairly constant to August but increased in mass in July and dropped in August. Zn presented concentrations that ranged between 138.3-885.3mg/kg soil and sediment. These results demonstrated that there is the enrichment of soil and sediment with Zn when compared with the work of Egila and Daniel (2012) in the same area in 2001. It is likely that high concentrations of Zn could be due to oxidation of organic matter and sulfides in the soil in the presence of abundant oxygen (Alshaebi et al, 2009).

Maize (zea mays), which belongs to the cereal family, is a common, fast growing, seasonal plant and a stable food in the study area. Maize (zea mays) planted on the tin mine soil during irrigation had high levels of heavy metals. Normal and toxic concentrations of heavy metals (mg kg-1) are respectively considered to be 0.1-0.5 and 5-30 for Cr, 20-300 and 300-500 for Mn, 0.02-0.1 and 15-30 for Ni, 5-30 and 20-100 for Cu, 27-150 and 100-400 for Zn, 1.0-1.7 and 5-20 for Cd, and 5-10 and 30-300 for Pb, (Nguyen et al, 2001). The maize analysed showed concentrations higher than these toxic levels for Mn, Zn, and Cu whereas Ni, Pb, and Cd concentrations in June also exceeded the toxic levels and the concentration for the other months were very close to the upper limits of their respective toxic concentrations. Only Cd presented concentrations that were within the normal levels. Akhionbare, Ebe, Akhionbare, & Ac-Chukwuocha, (2010) in their work used Maize (zea mays) to phytoremediate copper, cadmium, chromium, lead, nickel, and zinc and found that Maize was able to accumulate these metals and also, was tolerant to the targeted metals and of a fast growth. They therefore classified Maize as a hyper accumulator. In this area of study, the maize cultivated during irrigation are mostly roasted and eaten when the Maize are still fresh. The concentration of most metals determined by Akhionbare et al, (2010) were far lower than what is obtained in this work. It therefore means that, the consumers of Maize grown in this area are at risk due to high metal contaminations. However, the health risk depends on the available forms of the metals and the consumption pattern of the people.

IV. CONCLUSION

The study revealed that the soils and the sediment were acidic indicating the mine water was also acidic and could possibly solubilise most metals associated with mining that could be transferred to humans through direct contact or food chains. The analyses of concentrations of heavy metals in the samples had high concentrations and presented an irregular trend for the three months studied and therefore, control measures of pollution routes and remediation measures at the site are urgently required studied. The knowledge of heavy metal content, their species and the leachability at various environmental conditions for the use of mine water for irrigation are a prerequisite for the assessment for reclamation and hazardous potential of the water. However, speciation and leacheabilty studies were not covered in this study.

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REFERENCES

Akhionbare, S.M.O., Ebe, T.E. Akhionbare, W. N. & Ac-Chukwuocha N. (2010). Heavy MetalUptake by Corn (Zea Mays) Grown on Contaminated Soil. *Research Journal of Agriculture and Biological Sciences*. *6(6): 993-997'*

Alshaebi F.Y., Wan Z.W. Y., Samsudin A. R & Alsabahi E. I. (2009). Risk *Abandoned Tin Mine In Sungai Lembing, Pahang, Malaysia EJGE*

Annadale J.G., Jovanovic N.Z., Pretorious J.J.B,, Lorentz S.A. Rethman N.F. & Tanner P.D.(2001). Gypsiferous Mine WaterUse in Irrigation on Rehabilitated Open Cast Land crop production, Water and Soil Balance. Ecological Engineering 17,153-164

Duruibe J.O., Ogwuegbu M.O.C. & Egwurugwu J.N. (2007). Heavy Metals *Pollution* andHuman Biotoxic Effects. *International Journal of physical Sciences, 2(5),112-118.*

Esakku, Obuli.P. K., Kurian J. and Nagendran R., Heavy Metal Fractional andLeachability studies on Fresh and Partially Decomposed Municipal solid waste.

Ezeh, H.N. and Chukwu E. (2011). Small Scale Mining and Heavy Metals Pollution of Agriculture Soils: The Case of Ishiagu Mining District, South of Geology and Mining Research 3(4). 87-104, Gaikwad R.W. Gupta D.V. (2008). Review on Removal of Heavy Metals From Acid Mine Drainage *Applied Ecology and Environmental Research 6(3): 81-98.*http://www.ecology

Jarvis,A.P. and Younger,P.L. (1997). Dominating chemical factors in mine water Induced impoverishment of the invertebrate fauna of two streams in the *Durham Coalfield. UK. Chemistry and Ecology, 13,249-270*.

Kar D; Sur P; S. Mandai; Saha K.T; Kole R.K.(2008). Assessment of Heavy *in Surface water Int.J. Environ. Sci. Tech, 5(1), 119-124,*

Labbe, R. (2008). Report as of FY2008 for 2007MT152B; “Sediment and Heavy Metals source Determination and Reduction at a Reclaimed Abandoned Mine Site, Alta Mine, Jefferson County, MT”.

Marshal F. Agarwal R,Lintel D.& Bhupal D.S (2003). Heavy Metals Contamination of Vegetables in Delhi.

Mclean J.E. & Bledsoe B.E. (1992). Groundwater Issue the behavior of Metals in Soils EPA

Nguyen T. H. H., Masayuki S. Saka S. & Mai T.N. (2011). Uptake of metals and metalloids by plants growing in a lead-zinc mine area, Northern Vietnam, *Journal of hazardous Materials 186 (2011) 1384-1391*

Srinivasan T.J. & Reddy R.V. (2009). Waste water Irrigation in India: An Analyais of its Heath Impact.A Conference paper of INSEE, Centre for Economic and social studies, Nizamiah observation Campus, Begumpet. Hyderabad

Stankovic V., Bozic D, Gorgievski M. & Bogdanovic G. (2009). Heavy Metal Ions Adsorption…*CI&CEQ 15 (4) 237-249,*

Tabari M, Azadeh S, Jahangard M. and Alireza A. Heavy Metal Contamiation of zn, Cu, Ni andPb in Soil an Leaf of *Robinta pseudoacacia irrigation* with Municipal wastewater in Iran

WHO. (2007). Health Risks of Heavy Metals from Long-Range Transboundry Air Pollution.

Younger, P.L., Banwart, S.A. and Hedin, R.S. (2002). *Mine water: hydrology,Pollution, Remediation*. Kluwer Academic publishers, Dordrecht. Aa

