

METAL CONCENTRATIONS OF PAINT EFFLUENT, METAL DUMP SITE SOIL AND ASSOCIATED NICOTIANA TABACUM LEAVES FROM A CROWN CAPS INDUSTRY

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(Received, November 15, 2004)

ABSTRACT

The levels of minor metals: Sn, Mn, Zn, Cu, Cr, Cd, Pb, Fe, As, Ti, Al and major metals: Na, K, Ca and Mg were determined in the paint effluent, metal dump site and the associated leaves of *Nicotiana tabacum* plant from a Crown caps industry. Levels of Al, Mg, Na, K, As, Cr, Cd, Ti and Ca were all correspondingly higher in the *N. tabacum* leaves than the soil, this could be due to the metal bioaccumulation of the metals in the leaves. With the exception of As (with 231.5 ppm) all the values in the plant and the dump site were higher than the values in the paint effluent. The correlation coefficient between the metal dump and tobacco leaves was significantly, high ($r_{xy} = 0.68$) with a low index of forecasting efficiency (26.7%). Since all the samples were high in the metals determined (particularly the trace metals) the industrial environment was polluted and would need constant monitoring.

Key words:- Metal concentrations, paint effluent, dump site *Nicotiana tabacum* leaves, Crown caps industry.

INTRODUCTION

Industrialization is vital to nation's socio-economic development as well as its political stature in the international committee of nations. It provides ready employment opportunities for a good percentage of the population in medium to highly developed economics. Although industrialization is inevitable, various devastating ecological and human disasters which have continuously occurred over the last three decades or so implicate industries as major contributors to environmental degradation and pollution problems of various magnitudes. Rapid industrial development in developed and developing countries has increased hazardous wastes generation several fold.

By way of explanation, environmental pollution is the contamination of air, water, land and food in a way that will result to real or potential harm or threat to human health and damage to non-human nature without any justification. It is, therefore, very imperative for us to know the sources of these pollutants/contaminants to our environments.

Industrial effluents, wastes and emissions, contain toxic and hazardous substances most of which can be detrimental to human health¹. These include heavy metals such as Pb, Cd, Hg, Co, etc. and toxic organic chemicals. For instance, there was the case of Minamata disease in Japan in the 1960's caused by mercury poisoning of consumers of fish from Minamata Bay, Japan², which had received untreated efflu-

ents from a plastic factory. Then there was a case of Itai - Itai poisoning from ingestion of rice irrigated with effluent containing the toxic metal cadmium³. Many people from Abakaliki mining district of Anambra State, Nigeria suffer from lead poisoning resulting from the contamination of their water source by lead⁴. Adeyeye and Ayejuyo⁵ had advised the inhabitants of Ado-Ekiti, Nigeria and consumers of cassava tubers around a textile farmland on the danger of consuming excessive mineral elements from such location.

Since pollution through trace heavy metals has become increasingly more in recent years, not only because people are more sensitive on this subject but also because the amount of pollution has increased markedly. Therefore, there is need for continuing assessment, surveillance, research and public information less these unknown dangers create irreparable environmental damage which in turn results in widespread human suffering in the future. This work reports the metal concentrations (both minor and major) from the paint effluent, metal dump site and associated *Nicotiana tabacum* (L.) leaves from a Crown caps industry based in Akure, Ondo State, Nigeria.

MATERIALS AND METHODS

Collection and treatment of samples :-

All samples were collected in the vicinity of Omotosho Crown Caps Industry, Akure, Ondo State, Nigeria. The soil in the scrap metal dump site was collected to the depth of 10 cm manually. The tobacco leaf samples were plucked from the tobacco plant which was less than one meter from the dump site. The paint effluent was collected from its dump site. The paint effluent contained organol-acquer, white enamel and varnish.

The soil sample was air dried, turned into powder and sieved using 850mm mesh. The tobacco leaves were also air dried, turned into powder and preserved. A representative mixture of the paint waste was

also obtained. The metal scraps were normally mixed with chemicals and burnt at the dump site while paint effluents were normally discharged into a gutter or burnt with the metal scraps.

Digestion of samples :- Wet ashing procedure was employed to prepare all the samples for mineral analyses⁶. The weight of samples taken for digestion ranged from 0.5g (leaf), 0.51 g (soil) and 0.96g (paint) and addition of 5ml of HNO_3 , 5ml HClO_4 and 5ml of HF to each sample respectively in 50 ml berzelius beaker each and heated. After cooling the contents were filtered into a 100 ml standard flask and made up to the mark with distilled de-ionized water for each sample.

Mineral analysis:- The minerals were analyzed from solutions obtained by means of atomic absorption spectrophotometer (PYE Unicam Sp 9, Cambridge, UK)⁷.

RESULTS AND DISCUSSION

Crown caps are metallic, protective cover used to seal the top of a bottle containing liquid drinks or syrups as its content. There were fourteen Crown Caps Industries in Nigeria as at 1979. The number got reduced to nine in 1983. This number had got reduced to only five in 2002; this five includes the industry we are reporting upon. The raw materials normally used in the industry included: tin plates (Gold coated plate), tin free steel (Silver coated), polyvinyl chloride (PVC), lacquer, blanket, ink, vanish, white enamel, paper cartons. With this array of raw materials there is bound to be some waste that could be deleterious to man, hence the need to assess the waste products.

Table 1 depicts the metals analyzed for in *N. tabacum* and metal dump site soil. The minor metals analyzed for were Fe, Zn, Mn, Cu, Sn, Al, Pb, As, Cr, Cd and Ti while

the major metals were Mg, Na, K and Ca. These same metals were also analysed for in the paint effluents as shown in Table 2. The metals which were highly concentrated in both the soil and tobacco leaves were Fe, Zn, Mn, Cu, Pb, Cr, Na, As, Mg and K while Sn, Al, Ti and Ca were comparatively low in values. The following metals were high in the paint effluents: Mg, Na, K, Pb, As and Cr. In Table 1, these metals were higher in the tobacco leaves than the soil: Al, Mg, Na, K, As, Cr, Cd, Ti and Ca; this could be due to bioaccumulation of such metals in the tobacco leaves⁸. The coefficient of variation percent (CV%) values in Table 1 showed that Fe was the most varied between the dump site soil and the tobacco leaves while Na was the least varied. The correlation coefficient was high ($r_{xy} = 0.68$) and significant while regression coefficient (Rc) showed that for every overall unit increase in the tobacco leaf metal value, there was an increase of 0.77 in the dump site soil value; this meant that the tobacco leaves had overall higher concentration of the metals. The coefficient of alienation (CA) was high (0.733 or 73.3%) while the index of forecasting efficiency (IFE) was low (26.7%); that is, the reduction in the error of prediction between the metal values in the dump site soil and tobacco leaves was just 26.7%.

Cadmium is one of the primary respiratory poisons and has higher lethal potential than most other heavy metals⁹. Cadmium poison has extremely long life in the human body, about 16-33 years¹⁰. One ingested, cadmium is transported to all parts of the body via the blood stream, with high concentration in the liver and kidney but low concentration in the pancreas and spleen¹¹. Cadmium poison causes the damage of the kidney and particularly the renal tubules, softens bones and results in cough, diarrhoea and nausea¹¹. Both the tobacco leaves and the metal dump site soil contained high levels of cadmium.

The pathological effects of lead are varied, but in general reflect the tendency of lead to interact with proteins, especially those containing sulfhydryl groups and hence to damage tissue and interfere with the proper functioning of enzymes¹². Lead ingestion could cause damage to the Central Nervous System, induce miscarriage in pregnant women and anemia by causing a shortening of the life of red blood cells due to disruption of the red blood cell membrane¹². All our samples contained high levels of lead.

Zinc is an essential metal and plays important roles in enzyme activity. It protects the body against lead and cadmium poisoning¹³. However too much of zinc oxide in the body usually blocks the ducts of sebaceous glands. Symptoms of zinc toxicity in humans include abdominal pain, dizziness, vomiting, dehydration, lethargy and lack of muscular co-ordination¹⁴. The zinc levels were high in the tobacco leaves and dump site soil, such levels are not known to constitute hazards to man.

Manganese has been associated with enzymes system particularly oxidation processes, activating enzymes involved in the transfer of phosphate and hydroxyl groups as well as some dehydrogenation reaction¹⁵. Chronic manganese poisoning has both psychiatric and neurological manifestation, the most crippling of which has been related to extrapyramidal system of the brain¹⁶.

Chromium is essential to life. Trivalent chromium (Cr^{3+}) is essential for glucose and lipids metabolism. Its deficiency results in diabetic mellitus and increases the toxicity of lead¹⁶. It is very poorly absorbed from the digestive system and it combines with protein in skin to form a superficially stable insoluble complex¹⁶. All our samples contained high levels of chromium with some with some evidence of bioaccumulation in the tobacco leaves.

Our results contain low level of iron in the paint, slightly high level in the tobacco

leaves but very high in the metal dump site soil. The result in the tobacco leaves showed low level bioaccumulation. Approximately 1 mg of iron is usually absorbed daily while the total loss of iron from an adult is about 1 mg daily and is distributed in hair, sweat, urine and faeces. This means there is need for iron balance in the human body¹³. It is also needed by all plants being an essential component of the catalyst involved in the formation of chlorophyll¹⁷. Our sample iron results were below the deleterious levels.

Copper is a necessary element in animal metabolism. The adult human body contains 100-150mg of copper. Copper is also required for the growth and reproduction of lower plant form such as algae and fungi, although larger amount are toxic¹³. Copper toxicity tends to accumulate in the liver. Hypotheses concerning the effect of zinc-to-copper ratios in the diet as a determining factor of plasma cholesterol levels have been made¹³. Our copper level in the tobacco leaves was less than half of the soil value, it was also low in paint effluent.

Arsenic was higher in both the paint effluent and the tobacco leaves than the metal dump site soil. No role in natural bio-geological phenomena has been found for arsenic. Although the element may be present in sea water to the extent of 0.006-0.03ppm¹³, it may be ten times as high in estuaries. Shellfish tend to accumulate arsenic from the large amount of sea water with which they come in contact. Oysters may contain 3-10ppm. Its lack of function in the human body is suggested by the fact that it tends to accumulate in the hair and nail which are essentially non-living.

Titanium is used extensively in the Chemical industries for handling some of the most corrosive process liquors. The food and drug processing industries find that titanium is unaffected by their products and by the strongest cleaning agent they employ. A large variety of products are processed without apparent contamination. Titanium level

was low in all the samples analysed but showed some level of bioaccumulation in the tobacco leaves.

Aluminium is used in many phases of life such as healing of severe burns¹³. Because of its corrosion resistance and relatively low cost, it is used widely for food processing equipment, food containers, food packaging foils and numerous vessels for the processing of chemicals. No ill effects on life processes have been established for aluminium. Because of the presence of aluminium in soils and rocks, there are natural traces of the element in nearly all foods. While processing of foods in copper vessels will cause destruction of vitamins, aluminium does not accelerate the degradation of vitamins. Aluminium compounds have been greatly used in medical applications: its hydroxide is administered by mouth as a gel in the treatment of indigestion, gastric and duodenal ulcers and reflux oesophagitis¹⁸. Values of aluminium were relatively low in all the samples, bioaccumulation existed in the tobacco leaves.

The tin levels were low in the samples analysed: 3.9 ppm (*N. tabacum*), 7.8 ppm (metal dump site soil) and 12.5ppm in the paint effluent. There are no published records of any human fatalities from ingesting metallic tin; in fact, tests have shown that considerable quantities of tin can be consumed without effect on the human system¹⁹. Small amounts are present in most liquid canned products; the agreed limit of tin content in foods is 300 mg/kg in the U.S.A. and 286ppm in the U.K., which far exceeds the amount found in canned products of good quality²⁰. Although there have been statements that tin compounds are excreted as rapidly as absorbed at low levels, Kehoe *et al.*²¹ have demonstrated that tin is stored in nearly all organs of the human body. The levels range from undetermined amounts in the brain to 80mg/100g in the long bones.

Potassium is the third macrometal

Table 1. Minor and major metal concentrations (ppm) in metal dump site soil and *Nicotiana tabacum* leaves (dry weight) from the Crown caps industry

Element	<i>N. tabacum</i>	Metal dump soi	Mean SD ^a		CV% ^b	r _{xv} ^c	Rc ^d	CA ^g	IFE% ^h
Fe	208.8	1962.8	1085.8	1240.2	114.2				
Zn	509.5	862.8	686.2	249.8	36.4.				
Mn	170.4	221.4	195.9	36.0	18.4				
Cu	205.5	445.9	325.7	170.0	52.2				
Sn	3.9	7.8	5.9	2.8	48.2				
Al	69.2	39.3	54.2	21.2	39.0				
Mg	1630.8	1152.0	1391.4	338.6	24.3				
Na	1542.9	1530.1	1536.5	9.1	0.6	0.68	0.77	0.733	*26.7
K	1517.3	1487.5	1502.4	21.0	1.4				
Pb	563.0	630.0	596.5	47.4.	8.0				
As	222.3	108.9	165.6	80.2	48.4				
Cr	237.3	132.9	185.1	73.8	39.9				
Cd	293.9	287.6	290.8	4.4	1.5				
Ti	16.7	13.1	14.9	2.6	17.1				
Ca	187.2	169.3	178.2	12.7	7.1				

^aStandard deviation.^bCoefficient of variation percent.^cCorrelation coefficient.^ddegression coefficient.^eCoefficient of alienation.^fIndex of forecasting efficiency.

Table 2. Minor and major metal concentrations (ppm) in the paint effluent in the Crown caps industry

Element	Paint effluent
Fe	67.0
Zn	16.1
Mn	17.8
Cu	31.4
Sn	12.5
Al	24.7
Mg	479.3
Na	790.9
K	845.9
Pb	427.7
As	231.5
Cr	88.3
Cd	2.0
Ti	1.7
Ca	29.8

required for plant growth. In man, potassium is highly useful being universally present in all foods. Potassium level was high in all the samples, although it is not known to cause pollution.

Sodium is required by plants for growth and in man it controls body water balance and has a role in muscle contraction. Our sodium values were high in all the samples but slightly more concentrated in the tobacco leaves than the soil (as it was the case in potassium). When absorbed by clay colloids at high concentration it can cause displacement of potassium and calcium, leading to deterioration of soil texture²².

Most economic crops yield best in soils where the exchange complex is dominated by Ca^{2+} . High Ca^{2+} indicates a near - neutral pH, which is desirable for most plants. Representative levels of calcium in the soil solution of temperature region soils are 30 to 300 ppm; our metal dump site soil fell within this range. In soils of higher rainfall areas, soil solution calcium concentration will range from 8 to 45ppm, and usually averages about³³ ppm²³. The calcium level in the tobacco leaves showed some level of bioaccumulation.

Magnesium was high in all the samples but higher in the tobacco leaves than the metal dump site soil showing reasonable level of bioaccumulation. Magnesium is the key element in the chlorophyll molecule and it is involved in protein, DNA and RNA syntheses in man. Bray²⁴ stated that most soils containing less than 4536 kg of exchangeable magnesium will probably produce magnesium deficiency symptoms in -plant. As early as 1858, Thomas Green Clemson wrote of magnesium "Its presence in the soil is a requisite to fertility, and its addition, of manifest necessity wherever it may be wanting".

Tobacco, derived from *N. tabacum* L. and *N. rustica* L, is one of the American gifts to the people of the Old World. In pre-Columbian times, American Indians used tobacco in much the same way as it is used ■today and believed that it possessed medicinal virtues. Tobacco was used in their religious ceremonies such as the smoking of 'the pipe of peace'²⁵.

The results of this work showed that the Crown Caps environment needs constant monitoring. Also it is recommended that an underground dump site, with concrete base and line should be provided for the disposal of the waste metals and paints. Dolomite should also be added to avoid plant mineral uptake.

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