Chemical Poisoning And Heavy Metals Concentration In Kulön River Estuary In Southern Nigeria

William Ubi

Thomas Okweche

Department of Science and Technology, National Open University of Nigeria, Calabar Study Centre

Godwin Michael Ubi

Department of Genetics and Biotechnology, University of Calabar, Nigeria

Imaobong Sunday Essien

Department of Environmental Pollution and Toxicology, University of Calabar, Nigeria

Abstract: Studies were carried out in January to April of 2015 and 2016 to determine the levels of heavy metals concentration in Kulön river estuary, after chemical poisoning with "Gamalin 20" and a native "Yosee" leaf paste for a period of four months of each year. A total of 320 litres of Gamalin 20 was applied at 80 litres every 1st of the month from January to April for each year fitted into a 20 x 20m latin square convering the estuary of the river. At every month's application (January to April), sampling stations A_1, A_2, A_3, and A_4 were established, where water samples were collected and analyzed for heavy metals concentration and their values compared with the critical values recommended by World Health Organization (WHO). A control water sample was collected from the upper part of the estuary where no chemical was applied. The ten metals involved in this study includes: Lead (Pb), Nickel (Ni), Vanadium (V), Iron (Fe), Copper (Cu), Cadmium (Cd), Mercury (Hg), Chromium (Cr), Arsenic (Ar) and Zinc (Zn). The results showed that all the metals differ in their various concentrations and at varying sampling stations. All the metals had their maximum concentration in sampling station A_4 and in the month of April. The highest values recorded for Pb, Ni, V, Cd, and Hg were 0.30g, 0.384, 0.242, 0.138 and 0.166mg/l respectively. These values exceeded the critical value of 0.05mg/l for each, recommended by WHO (1991). The values of Cu (0.469mg/g), Cr (0.171mg/l) and Ar (0.676mg/l) had their critical values of 1.0mg/l; 0.5mg/l and 0.01mg/l respectively while Fe (0.479mg/l) has a critical value of 0.3mg/l, indicating their toxicity at higher levels of concentration. The concentration of some of these metals from the results are above these critical levels thus making the water dangerous for use by human and aquatic animals compared with the control. The pH of the water at all sampling stations was moderately acidic 4.3 at station A_1 and January, to acid in A_4 sampling station and April. Decreasing the pH consistently increased the concentration of the metals, indicating that levels of concentration were pH dependent. The magnitude of variability of these metals between the months and between the sampling stations had their coefficient of variability (cv%) higher in station A_4 and the month of April than in others under similar experimental conditions.

Keywords: Water pollutants, chemical poisoning, below detectable levels, "Yosee"

I. INTRODUCTION

Human activity in the use of chemical poisoning to kill fish and other aquatic animals has increased tremendously especially in rural communities. Among the commonest chemicals used are "Gamalin 20" (a chemical used to spray cocoa trees against black pod disease), and a native leaf called "Yosee". Many rural communities have no other source of

drinking water except the natural rivers, streams and springs located at varying distances from their communities. When the water levels are low during the dry season, many of the communities either as a group or a few individuals adopt chemical poisoning in these drinking rivers, streams and springs in attempt to catch some fish and other aquatic animals for sale to public and for domestic consumption, leading to water poisoning. This problem has persisted and has become a yearly means of fish catching inspite of government intervention, and has become very pertinent that adequate focus be placed on its control to avoid disaster which may be similar to the incidence of methyl mercury poisoning which occurred in Japan (Christian *et al.,* 1974; Young and Blevins, 1981). The composition of some of these chemicals contain heavy metals such as nickel, lead, mercury, copper, zinc, arsenic glutin and chromium compounds, cadmium, titanium, vanadium are among the several compounds that could be found in chemically poisoned waters. It is difficult to be sure of the possible long term effect, but the toxins that accumulate have nowhere else to go; the river, stream and spring become its ultimate sink, (Appel and Ma, 2002).

Complex biotic societies are typically adaptable to changing conditions, but no one can guarantee that the organisms of the rivers, springs and streams, including human beings drinking from these sources will continue to survive the present rate of influx of exotic chemical poisoning, (Hudges *et al.,* 1977; Torr *et al.,* 1982). However, Stanley (1992) suggested standard for drinking water in form of maximal allowable concentration of various substances, including copper, lead, zinc, manganese, arsenic, chromium silver, selenium, barium, cadmium, cyanides, nitrates, fluorides, phenols, alkyl benzene sulfonates, and total organic substances.

The pollution of water supplies is probably responsible for more human illness than any other environmental influence. The diseases so transmitted are chiefly due to micro organisms and parasites, such as cholera (an illness caused by ingestion of the bacterium vibrio cholerae) is an illness characterized by intense diarrhea which results rapidly in massive fluid depletion and death of a very large percentage of untreated patients.

Schistosomiasis is another group of disease caused by worms transmitted through contamination of water supplied. Other bacteria illness are salmonelloses (of which typhoid fever is a leading example), and viral infection like poliomyelitis and hepatitis may also be disseminated this way. Some of these diseases are dropped into the drinking water, feces of infected individuals (Smith, 1998). Koli and Whitemore (1983) have through their various works on the contamination of fishes, found that pollutants, especially heavy metals can cause serious damage to aquatic lives. Others have indicated certain process that could be affected by heavy metal levels in fish to include: physiological balance and respiratory processes Hemmandez and Diaz (1986) , cardiac respiration rhythms, Skidmoll (1970), oxygen, consumption of gill tissue and enzymatic activities, Hughes and Aversy (1977), Tort *et al.* (1982) and these effects on fish according to Jacki (1974) have a high tendency of manifesting in human. This study was undertaken to assess the impact of chemical poisoning of water and the level of concentration of heavy metals in Kolön River, in Biase local government area of Cross River State, Nigeria.

II. MATERIALS AND METHODS

A. STUDY AREA

Kulön River (Fig. 1) lies within latitude $8°14'N$ and $8°20'E$, longitude $5°14'N$ and $5°18'E$, with a rainfall of over 2,000mm in the rainforest vegetation. The river is called "Kulön", which originated from Ikom and forms part of Ikom River in the central senatorial district of Cross River State. It traverses mainly sedimentary terrains which develop into a river before emptying into the Atlantic Ocean through Cross River. The river is turbid due to high qualities of suspended and dissolved solids. Between Agoi Ibami, Agoi Ekpo and Idomi where it passes, there are sandy beaches found in some parts of the river before getting to Abini, but most of the shorelines are fringed with tidal mudflats and waterlogged soils in which Guinea grass (Panicum maximum S112), Northern gamba grass (Andropogon gayanus) and panicum repens were dominant floral species. It has been a routine for fishermen in this area to chemically poison the river with "Gamalin 20" and native leaves called "yosee" with high lead content in an attempt to catch fish and other aquatic animals for sale to the public and for domestic consumption. In this study, 80 litres of "Gamalin 20" together with 1000kg of the "yosee" leaves were mixed thoroughly with sand and released into the marked area of 50 x 5m Latin Square, every first of the month, beginning from January to April of 2015.

B. EXPERIMENTAL TREATMENTS

✓ "Gamalin 20" (320 litres) (application was 80 litre per month, for four months, January to April and was done on the 1st of every month for the two years).
✓ "Yosee" leaves 1000 kg (The fresh leaves of "yosee" were pounded in a mortar to form a paste and then mixed with "Gamalin 20" and sand).
✓ Control sample where no treatment was given (Both "Gamalin 20" and "Yosee" heavy metals contents and other chemical pollutants were not determined in this study. Treatment were applied in the exact way the communities do it).

C. SAMPLING STATIONS AND MONTHS OF TREATMENTS/SAMPLING

Treatments of the marked area 50 x 5 Latin Square was carried out every first day of the month from January to April. Sampling was taken seven days after treatment. Sampling stations were designated thus:

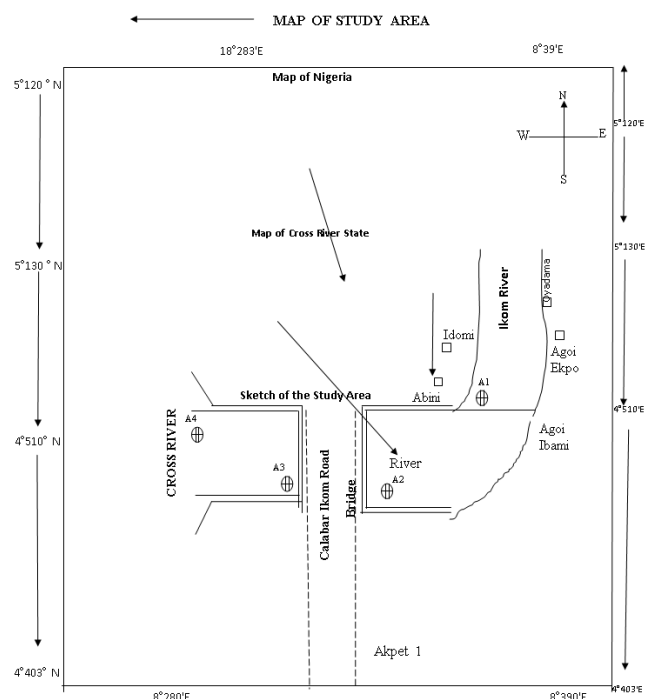| Symbols	Meaning
A_1	River Upstream at Kulön
A_2	Stubbs Creeks before the bridge
A_3	Gate to Estuary
A_4	River Estuary
mg/l	Milligram per litre

Figure 1: Water pollution by chemical poisoning (Distribution of heavy metals in Kulön Estuary)

D. SAMPLING METHOD

Sampling was done for four months beginning from January to April in 2014, spanning the beginning of the wet and dry seasons of the year. Water samples were collected at the four designated points using white plastic bottles, and filling them 3.0 litres (Fig. 1). The bottles were rinsed three or four times with the water sample and then carefully filling them to avoid trapping of air bubbles in the bottles (Polpraset, 1982). The samples were preserved by acidification with 1ml concentration HNO_3, before moving them to the University of Calabar labouratory for chemical analysis. Activities of chemical poisoning of water in this area usually starts from December to April evolving 80 litres of "Gamalin 20" mixed with "Yosee" and sand randomly poured into the river. Insecticides, fungicides and herbicides are toxic chemical and water pollutants (Mills, 1971). This study was undertaken from January to April being the period that chemical poisoning/pollution takes place in Kulön estuary. A control sample in which no treatment was applied was taken at the upper part of the river which was 10 metres away from the experimental site.

E. STATISTICAL ANALYSIS

Data was analyzed using analysis of variance (ANOVA) and means compared using coefficient of variability (cv%) (Little and Hills, 1978).

F. INSTRUMENTATION, HEAVY METAL DETERMINATION AND ANALYSIS

A total of ten heavy metals (Pb, Ni, V, Fe, Cu, Zn, Cd, Ti, Ch and Ar) were analyzed using the procedures of Milner and Whitefield (1981) and atomic absorption spectrophotometer (AAS) Unicam 919 model. The sampled solutions were aspirated into the air acetylene flame of the AAS. A calibration curve of the metal was prepared before analysis of the samples. And this was done by using standard stock solution of the metal analyzed. From the curve, the concentration of the metal in sample was determined (Whiteside, 1979). All analysis was done in triplicates to ensure that accurate results are obtained. The pH of the water was measured with a pH meter ECE model M3 in a water suspension, using a glass electrode.

III. RESULTS AND DISCUSSION

A. CHEMISTRY OF WATER

Water contains eight parts of oxygen to one part of hydrogen by weight. The atomic weight of oxygen is 16, that of hydrogen is 1. Thus oxygenation is 16 times as heavy as a hydrogen atom. The composition of water and the atomic weight of oxygen and hydrogen are reconciled by the formular H_2O. The sum of the atomic weight, $1+1+16 = 18$, is the molecular weight of water. Weight ratio =

$$\frac{0}{1+2} = \frac{16}{1+1} = \frac{16}{2} = \frac{8}{1}$$

Thus water is structured:
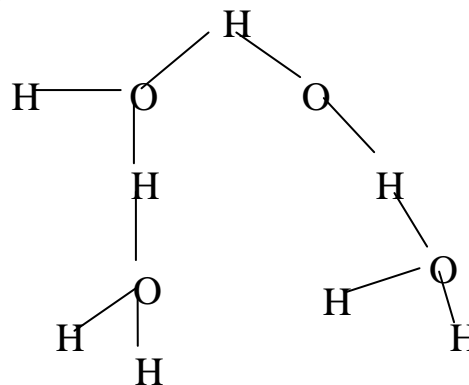
This strong aggregation accounts for the fact that water remains a liquid up to 100^oC normal pressure, in sharp contrast to the behaviour of other substances of similar or even higher molecular weight (Jocki, 1974). The pollution of water is the addition of undesirable foreign matter which deteriorates the quality of water. Thus water quality may be defined as its fitness for the beneficial uses by man and animals. One of the consequences of the unique physical and chemical properties of water is that it invites or accepts pollution readily, a time through unexpected mechanisms (Ashraf *et al.,* 1992).

B. CONCENTRATION OF THE TEN HEAVY METALS IN KULON ESTUARY

The concentration of the ten metals: lead, Nickel, Vanadium, Iron, Copper, Cadmium, Mercury, Chromium, Arsenic and Zinc are presented in tables 1-4 respectively. The highest concentration of lead (Pb) in January 0.220mg/l was from sample A₄, taken from the Estuary, while the least

0.065mg/l came from sample A_3 (Table 1). This value of lead recorded in January was higher than all other values on lead, recorded for either February, or March and those of April, (Udosen *et al.,* 1990).

The concentration of lead in the water was higher in the dry season than in the rainy season. Equally the highest value of Nickel (Ni) was higher in January from sample A_4 and this value tended to be higher than all other mean values recorded for February, March and April under similar experimental condition. The lowest value of Nickel 0.027mg/l was recorded in March from sample A_1 (Table, 3). The highest value of vanadium 0.119mg/l was recorded from A_1 in the month of February while the lowest value 0.023mg/l came from A_2 sample in April (Tables 2 and 4). The highest iron (Fe) content 0.231mg/l was obtained from A_4, in April while the lowest value 0.028mg/l came from A_2 in April (Table 4). The highest concentration of copper 0.186mg/l came from A_4 in April, while the lowest 0.017mg/l came from station A_1 in January. The highest concentration of cadmium (Cd) 0.071mg/l was recorded from sample A_4 in April while the lowest 0.016mg/l came from sample A_3 in March. The highest concentration of mercury 0.076mg/l was recorded from sample A_4 in January while the lowest value 0.012mg/l was recorded from A_2 in April (Table 4). The highest concentration of chromium 0.087mg/l was highest in A_1 in February while the lowest 0.012mg/l came from A_2 in the month of February. The highest value of Arsenic 0.035 was recorded from A_4 in January, while the lowest value was 0.016mg/l recorded from sample A_3. The highest Zn concentration 0.593mg/l was obtained from A_2 in January while the lowest value 0.023mg/l came from A_1 in January (Warren, 1981).

C. MAGNITUDE OF HEAVY METALS VARIABILITY FOR THE DIFFERENT MONTHS AND SAMPLING STATIONS

The magnitude of variability of the metals for different months and sampling stations are presented in Tables 5 and 6 in which the metals had their maximum values at different months and different sampling stations.

a. VANADIUM

This is a very rare metal in soil water solution and it high concentration can cause irritation of the respiratory tract, hemorrhage, coughing characteristics, nausea, occasional vomiting, dizziness and late nervousness (Brook and Jacobs, 1958). In this study, the concentration of vanadium was highest in sampling station A_4 (0.242mg/l) with coefficient of variability 52.09%, while April recorded the variability of 52.18%. Coefficient of variability was lowest in A_3 26.55%, and January 22.16%. These results reported in this study were similar to those of Takahashi and Basset, (1965). However, Ebong *et al.* (2004) in a similar study, reported the vanadium values to be below detectable levels. It is suggested that the gradient of the river flow could influence the volume of contaminants/metals carried and the quantity dropped at any given place and time variations could be influenced by season and the pH (Ashraf *et al.,* 1991).

b. IRON

Iron occurs mostly in the forms of Chalcocite (Cu_2S), Chalcopyrite ($CuFeS_2$), Cuprites (Cu_2O), Melaconite (Cuo) and Malaclinte (Cu_2COH_2). Other forms are $FeTio_4$, Fe_3O_4, $FeTio_3$, Fe_2O_3, $Fe_2O_3 Tio_2$ and $Fe_2O_2 Tio_2$ indicating that iron ranks second, if not first among the metals and fourth among all elements in earth crust (Nebergall *et al.,* 1975; Sienko and Plane, 1976; Basta *et al.,* 2001; Srivastava *et al.,* 2005). Coefficient of variation, 48.63% was highest in station A_4 and in April 69.36% while the lowest 25.16% came from A_1 and 31.22% came from month of January (Tables 5 and 6). The high concentration of iron in sampling station A_4 was in line with earlier reports (Takahashi and Basset, 1965; WHO, 1991; Ebong *et al.,* 2004).

c. LEAD

The coefficient of variation indicates the distribution pattern of the metals for the different months and different sampling stations. The results obtained showed that lead has its highest coefficient variability of (54.12%) during the onset of wet season in April while the lowest percentage (36.18%) occurred in January, (Heidmann *et al.,* 2005). High concentration of lead in wet season in April had earlier been reported, (Ebong *et al.,* 2004; Thilini *et al.,* 2008). It may be suggested from this results that high level of lead in this river has relationship of the season and volume of water in this river. The coefficient of variation of lead was higher in sampling station A_4, (48.59%) being the last sampling stations to the estuary, suggesting that there could be downward movement of lead, some of which might have reacted with phosphorous to form insoluble lead phosphate at the depth of the river. This is because P is ubiquitous in soil water. The metal exists in many forms in the earth's crust and the WHO critical level is 0.05mg/l for drinking water. The concentration in this study ranged between 0.060 to 0.150mg/l which tends to be on the high side and could be detrimental to human and other organisms in water, (Mills, 1971). Lead is accumulative poison, and even small quantity if continually present in drinking water may cause serious illness or death, (Heltiarachchi, 2001).

d. NICKEL

The degree of variability of nickel was very high (62.75%) in station A_4 and (49.68%) in April, with the lowest values of 13.14 and 33.27% respectively. The range of nickel 0.054 to 0.526mg/l reported in this study was higher than 0.05mg/l critical level, recommended by WHO, (1991). In this study, the highest concentration of nickel 0.526mg/l came from the sampling station A_4 near the estuary while the month of January had the highest value of 0.384mg/l significant higher than values of all other months with coefficient of variability of 53.27%. Sharma, (1992) reported a critical level of nickel to be 0.05, earlier reported by WHO, (1991). Any level above this critical level can cause cancer of the lungs. The high concentration of nickel recorded at station A_4 was attributed to location of sampling station A_4 which serves as a sink where are received (Polprasert, 1982; Vavuz *et al.,* 2003).

e. COPPER

The degree of variability of Cu was very high with station A_4 (49.46%) while the lowest came from stations A_1 and A_3 each having 31.40%. Also, observed in Table 6, is that the concentration of Cu in the month of April was higher with coefficient of variation of 60.19%.

The distribution of copper tended to be higher in sampling station A_4 like other metals because this station is closer to the estuary in which heavy concentrations of wastes and metals are collected as Sink earlier reported (Frieden, 1965; Ebong et al., 2004). According to WHO (1991), the recommended critical level for copper for drinking water is 1.00mg/l. The values obtained in this study are much less than the critical level of 1.00mg/l indicating that copper level reported in this study will not be toxic to human or aquatic animals (Cahalam and Jacob, 1973). Copper exists in nature in many forms, such as Chalocites (Cu_2S), Chalcopyrite, ($CuFeS_2$), Cuprites (Cu_2O), Melaconite (Cuo) and Malachite (Cu_2) $(OH)_2Co_3$), (Cahalan, 1973). High copper level produces harmful effects such as nausea, vomiting, pallor, diarrhoea, with symptoms of collapse and heart failure on human (Brooks and Jacobs, 1958; Christian et al., 1974; Hemmandz and Diaz, 1986; Goldsmith and Hildrad, 1988).

f. CADMIUM

The degree of variability of cadmium was high with sampling station A_4 having the highest percentage (54.95%), and April with (44.31%) indicating that this was a period of onset of rains in the study area, in which metal from the treatments on the air, land and upper part of the river was washed down to the river, increasing the concentration, (Ebong et al., 2004). Inspite of the significance of cadmium as a component of haemoglobin of the blood, a concentration above 0.3mg/l in water will cause toxicity in animals including aquatic animals (WHO, 1991). In this study, the high concentration of cadmium recorded in April during the onset of rains could be attributed to the impact of the treatment with rains carrying high concentration of these pollutants and contaminants in which large amount of cadmium could be part of these components, deposited at A_4 near the estuary which acts as the receiving sink (Wag and Xing, 2002).

g. MERCURY

The degree of variability of the metal in the area of study was high with station A_4 recording the highest percentage (47.09%) and the month of April recording the highest percentage (44.31%) indicating that this metal appears in abundance during the wet season and carried by run-off in large quantity towards to the estuary at sampling station A_4, (Ebong et al., 2004). Mercury poisoning has been one of the greatest problems of metallic pollution (Sarkor et al., 2000). It is the only metal that is liquid at ordinary temperature, hence, the other name is "quicksilver". Its vapour is basically poisonous and at high temperatures, it can vaporize rapidly enough to be deadly. Until recently, mercury was not considered a dangerous water pollutant because though it is distributed over the earth, it generally occurs only in trace concentrations. Natural waters contain typically less quantity. Metallic mercury itself although poisonous in vapour form, is not particularly hazardous when taken by mouth as a liquid. Hence, the use of mercury as a component of dental fillings has been shown to be harmless. Many mercy compounds are very highly insoluble, for instance it was calculated that it would require about 88 litres of water to dissolve one molecule of mercuric sulphide (HgS). This consideration implies that mercury in water is not a potential pollutant. Moreover, the mercury in a fish was present in organically-bound forms that especially hazardous to man. These compounds are all related to methyl mercury, $H_3C.Hg.CH_3$. Such mercury compounds are sometimes used as pesticides and fungicides, and the discharge of these residues in waters may therefore be serious hazard. Following this episode, research led to the disturbing finding that metallic mercury and inorganic mercury compounds can be methylated (converted to methyl mercury) by anaerobic bacteria in the mud of the river banks and bottom, and therefore cannot be regarded as inert sludge. They are potential sources for biochemical conversion into forms of mercury that can enter and pass through the food chain in increasing concentration and thus become poison for man as was earlier reported (Koli and Whitemore, 1983).

h. CHROMIUM

The coefficient of variation was high at station A_4 (36.17%) and in the month of April (49.36%), while the lowest (20.26%) was recorded for station A_2 and 25.29% for the month of February. The recommended value for drinking was by WHO, (1991) was 0.50mg/l, which was quite above the values obtained in this study, indicating their concentrations in the sampled areas in this study were not dangerous and will not be detrimental to both human and aquatic life (Takahashi and Bassett, 1965; Sastry and Tyagi, 1982).

i. ARSENIC

Arsenic which always occurs in natural waters like that of the study area is considered to be accumulative poison to both human and aquatic animals. The save limit in drinking water for both lead and arsenic recommended by WHO, (1991) is 0.01mg/l. The range obtained for arsenic in this study was between 0.076 to 0.143mg/l, giving 88.16% unit difference $\frac{0.143 - 0.076}{0.076} \times \frac{100}{1}$ comparing concentrations of April with that of January. The implication is that the rains of April influenced the concentration of this metal through accumulation of compounds of several pollutants. Equally, sampling station A_4 with 0.157mg/l and the coefficient of variability (27.36%) recorded higher value of arsenic than all other values obtained under similar experimental condition. The concentration of arsenic in running water is often influenced by arsenic bearing minerals and could be suggested to be the cause of high concentration of this metal during the wet season in April and a similar concentration at the estuary in sampling station A_4 (Polprasert, 1982).

j. ZINC

Variations in concentration of zinc among the months (January to April) were glaring in which the coefficient of variation (49.69%) showed the highest percentage in April while the lowest percentage (29.12%) came from the month of January (Koli and Whitemore, 1983). The mineral soil particles from the treatment, among the contaminants drifting down the estuary in April during the onset of wet season must have accounted for the high concentration of this mineral in station A_4, this of course, tended to be the same for other metals. The amount of contaminants in water, the pH and season tended in one way or the other to influence the metal concentration at any particular time (AWWA, 1980; Warren, 1981). The critical level for zinc content for drinking water is 1.0mg/l (WHO, 1991). The values obtained in this study tended to be lower than the critical levels considering the water not poisonous for use by human and aquatic animals. It is surprising therefore to realize that although the potential for diseases production from this source exists, but the actual accounts of major illness due to chemically contaminated water are few. We must recognize that water molecules have no memory, and therefore it is somewhat unreasonable to talk about the numbers of times that the drinking water has been polluted.

D. PH (ACIDITY AND ALKALINITY)

Hydrogen ions (H^+) render water acidic. A hydrogen ion or proton designated H^+ cannot exist as an independent entity in water because it is strongly attracted or chemically bonded to the oxygen atom of the water molecule. The resulting hydrated proton is formulated as H (H_2O) $^+$, or H_3O^+. When the hydrogen ion concentration is greater than 1.0×10^{-7} moles per liter at $25^{\circ}C$, the solution is acidic. Hydrogen ion concentration are usually expressed logarithmetrically as pH values, where pH = $-\log_{10}$ (hydrogen ion concentration). Recall that the logarithm of a number "to the base 10" is simply the number of times 10 is multiplied by itself to give the number. The pH of the samples of water taken from different sampling stations (A_1 to A_4) and different months (January to April) are presented in Tables 5 and 6. The highest pH value 4.3 came from sampling station A_1 while the lowest (3.1) came from the sampling station A_4 with a mean of 3.7. Equally, sampling among the months from January to April showed that the highest pH value (4.1) was recorded in January when the water volume was low while the lowest (3.2) came from April, with a mean of 3.6. The results showed that the sampling station A_4 and the month of April with higher concentration of these metals had the highest pH, while stations with higher pH had lower metallic concentration. The implication is that the concentration of metals in the study area was pH dependent which of course was influenced by treatment. Each of the metals increasing with increase in pH level, such that their availability and level of concentration was pH dependent (Ashraf et al., 1991).

Metal (mg/l)	A_1	A_2	A_3	A_4
Control Sample	*BDL	*BDL	*BDL	*BDL
Lead	0.080±0.003	0.083±0.003	0.065±0.002	0.220±0.001
Nickel	0.118±0.002	0.064±0.002	0.043±0.001	0.298±0.002
Vanadium	0.068±0.002	0.071±0.001	0.018±0.002	0.086±0.002
Iron	0.051±0.002	0.058±0.002	0.029±0.003	0.134±0.003
Copper	0.017±0.002	0.072±0.002	0.018±0.001	0.046±0.002

Metal (mg/l)	A_1	A_2	A_3	A_4
Cadmium	0.039±0.003	0.051±0.003	0.041±0.002	0.029±0.001
Mercury	0.048±0.003	0.064±0.001	0.035±0.002	0.076±0.001
Chromium	0.037±0.001	0.085±0.002	0.019±0.003	0.038±0.002
Arsenic	0.019±0.002	0.066±0.002	0.016±0.001	0.085±0.002
Zinc	0.023±0.002	0.593±0.001	0.025±0.002	0.142±0.003

*BDL = Below Delectable Level

Table 1: Heavy metals concentration in water samples in Kulön River Estuary in January after application of treatment. Results are means of duplicates measurements/determination for two years

Metal (mg/l)	A_1	A_2	A_3	A_4
Control Sample	*BDL	*BDL	*BDL	*BDL
Lead	0.071±0.002	0.056±0.002	0.078±0.001	0.113±0.002
Nickel	0.035±0.002	0.038±0.002	0.039±0.002	0.032±0.002
Vanadium	0.119±0.001	0.050±0.002	0.052±0.002	0.039±0.002
Iron	0.146±0.002	0.146±0.002	0.143±0.003	0.138±0.002
Copper	0.065±0.001	0.073±0.003	0.098±0.002	0.149±0.002
Cadmium	0.039±0.002	0.050±0.002	0.036±0.002	0.015±0.001
Mercury	0.074±0.002	0.061±0.002	0.029±0.001	0.018±0.002
Chromium	0.087±0.001	0.012±0.003	0.041±0.002	0.035±0.001
Arsenic	0.048±0.002	0.032±0.002	0.056±0.003	0.029±0.002
Zinc	0.139±0.002	0.057±0.002	0.019±0.002	0.137±0.003

*BDL = Below Delectable Level

Table 2: Heavy metals concentration in water samples in Kulön River Estuary in February after application of treatments. Results are means of duplicates measurements/determination for two years

Metal (mg/l)	A_1	A_2	A_3	A_4
Control Sample	*BDL	*BDL	*BDL	*BDL
Lead	0.038±0.002	0.082±0.001	0.086±0.002	0.052±0.002
Nickel	0.038±0.002	0.098±0.002	0.037±0.001	0.036±0.002
Vanadium	0.043±0.002	0.053±0.001	0.062±0.002	0.028±0.001
Iron	0.086±0.001	0.105±0.003	0.108±0.001	0.079±0.002
Copper	0.075±0.002	0.073±0.002	0.049±0.002	0.082±0.002
Cadmium	0.033±0.001	0.063±0.001	0.016±0.002	0.048±0.003
Mercury	0.029±0.001	0.049±0.001	0.023±0.001	0.066±0.001
Chromium	0.041±0.002	0.028±0.002	0.048±0.002	0.041±0.002
Arsenic	0.054±0.001	0.019±0.002	0.017±0.001	0.027±0.002
Zinc	0.056±0.002	0.087±0.003	0.082±0.002	0.072±0.001

*BDL = Below Delectable Level

Table 3: Heavy metals concentration in water samples in Kulön River Estuary in March after application of treatments. Results are means of duplicates measurements/determination for two years

Metal (mg/l)	A_1	A_2	A_3	A_4
Control Sample	*BDL	*BDL	*BDL	*BDL
Lead	0.051±0.002	0.121±0.002	0.071±0.001	0.216±0.002
Nickel	0.036±0.002	0.116±0.002	0.058±0.002	0.184±0.003
Vanadium	0.049±0.001	0.023±0.002	0.036±0.001	0.091±0.001
Iron	0.039±0.002	0.028±0.001	0.046±0.003	0.231±0.001
Copper	0.068±0.001	0.056±0.001	0.037±0.002	0.186±0.002
Cadmium	0.019±0.001	0.024±0.002	0.017±0.002	0.071±0.001
Mercury	0.016±0.002	0.012±0.002	0.016±0.001	0.032±0.002
Chromium	0.022±0.002	0.020±0.001	0.024±0.002	0.021±0.002
Arsenic	0.026±0.001	0.018±0.002	0.025±0.001	0.028±0.001
Zinc	0.047±0.002	0.102±0.001	0.086±0.002	0.086±0.002

*BDL = Below Delectable Level

Table 4: Heavy metals concentration in water samples in Kulön River Estuary in April after application of treatments. Results are means of duplicates measurements/determination for two years

Metal (mg/l)	A_1			A_2			A_3			A_4		
	Mean(x)	SD	CV%	Mean(x)	SD	CV%	Mean(x)	SD	CV%	Mean(x)	SD	CV%
Lead	0.060	0.02	33.24	0.150	12.0	39.21	0.150	0.03	35.12	0.250	0.07	48.59
Nickel	0.054	0.08	13.14	0.288	14.14	43.47	0.128	0.07	27.15	0.526	0.24	62.75
Vanadium	0.141	12.0	31.42	0.159	0.07	29.86	0.179	0.06	26.55	0.242	0.08	52.09
Iron	0.219	14.0	25.16	0.293	13.10	28.15	0.316	10.12	32.91	0.479	0.21	48.63
Copper	0.174	0.08	26.33	0.219	10.12	32.91	0.174	0.08	31.40	0.351	13.74	49.46
Cadmium	0.097	0.06	26.33	0.110	14.56	31.14	0.116	0.05	34.26	0.369	0.05	54.95
Mercury	0.091	0.07	28.45	0.140	0.06	24.70	0.155	0.05	33.21	0.179	0.08	47.09
Chromium	0.098	0.08	20.26	0.136	0.05	23.56	0.151	0.05	25.29	0.171	0.05	36.17
Arsenic	0.072	0.07	25.15	0.123	0.07	28.92	0.072	0.05	29.27	0.157	0.06	37.36
Zinc	0.0161	0.07	28.38	0.198	27.12	59.12	0.566	0.09	36.93	0.676	0.28	57.18
pH	4.3	-	-	3.5	-	-	3.5	-	-	3.2	-	-

Table 5: The magnitude of heavy metal variability with sampling stations

Metal (mg/l)	Jan.			Feb.			March			April		
	Mean(x)	SD	CV%	Mean (x)	SD	CV%	Mean(x)	SD	CV%	Mean(x)	SD	CV%
Lead	0.298	0.13	36.18	0.233	12.4	42.36	0.219	10.12	47.91	0.309	12.1	54.12
Nickel	0.384	0.16	33.27	0.120	0.07	25.21	0.165	0.08	28.97	0.256	12.14	49.68

Vanadium	0.341	12.98	22.16	0.231	12.2	47.17	0.165	0.08	28.97	0.131	0.05	52.18
Iron	0.171	0.08	31.22	0.172	0.20	47.52	0.319	13.72	48.81	0.469	0.08	69.36
Copper	0.119	0.06	27.08	0.208	13.0	41.78	0.218	10.13	42.92	0.273	9.10	60.19
Cadmium	0.094	0.05	23.98	0.124	0.05	23.51	0.137	0.07	26.15	0.138	0.05	44.3
Mercury	0.052	0.07	28.96	0.137	0.05	23.51	0.118	0.06	27.06	0.166	0.08	33.01
Chromium	0.071	0.07	26.17	0.127	0.07	25.29	0.149	0.07	27.14	0.151	0.05	49.36
Arsenic	0.076	0.07	25.04	0.097	0.06	24.18	0.122	0.05	35.23	0.143	0.06	48.75
Zinc	0.677	0.27	29.12	0.249	12.0	52.72	0.243	12.1	51.43	0.257	12.14	49.66
pH	4.1	-	-	3.6	-	-	3.4	-	-	3.2	-	-

Table 6: Magnitude of heavy metals variability with months (Jan-April)

Metal	For domestic use	For drinking
Cd	-	0.05
Fe	1.00	0.30
Ni	-	0.05
Pb	-	0.05
Cr	-	0.50
Co	-	0.05
Cu	1.50	1.00
Zn	-	-
Mn	1.50	1.50

Table 7: World Health Organization Recommendation for Water (1991)

IV. CONCLUSION

From the findings of this study we are able to establish the distribution pattern of 10 heavy metals as influenced by treatment, analyzed for their various concentrations between sampling stations and between months. Their various concentrations in relation to their various critical levels spelt out by WHO, (1991) was noted. However, some metals have been found to be above the widely acceptable standards, thereby constituting menace and chemical poisoning in the study area. This levels are believed to be caused by the treatment, which reduced the pH of the water in the study area. The lower the pH of a body of water, the more prone it is to be corrosive and toxic, thereby making it polluted with metallic compounds resulting to metallic poisonings, which of course form a serious environmental hazard for both human and aquatic animals in developed and developing countries. The ions of metallic elements are electrically positive. These ions are attracted to the negative ends of the water molecules (oxygen atoms). Therefore, rivers with highly charged metal ions tend to be acidic and our study area features well in this case.

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