SPECIATION OF SOME HEAVY METALS IN NGONG RIVER USING THE JOINT EXPERT SPECIATION SYSTEM (JESS)

DAMARIS MBUI[1], DUKE O. ORATA[2], GRAHAM E, JACKSON[3] & DAVID K. KARIUKI[4]

[1,2,4]Department of Chemistry, University of Nairobi, Kenya

[3]Department of Chemistry, University of Cape Town, South Africa

ABSTRACT

Ngong River, a tributary of Nairobi River in the Capital City of Nairobi in Kenya, was assessed for heavy metal and their species using atomic absorption spectroscopy (AAS) and the Joint Expert Speciation System (JESS) a computer program for equilibrium calculations. Six sampling points in the middle stream of Ngong River.

Physico-chemical parameters were analysed *insitu* while grab samples were analysed for seven metals and their species were predicted using JESS.The samples had pH values of about 7.5, except for sample no.3 which recorded a pH value of 8.3. Of the seven analyzed ions, the most abundant metal was iron with an concentration of 6.56 mg/L while some of the metals were below the detection limits in some sampling points.

The concentrations of the heavy metals were used to construct a speciation predicting model of the Ngong river using the JESS. Using this model, the major species in most of the samples were predicted to be $[Cr(OH)_2]^{1+}$, $[Fe(OH)_2]^{1+}$, $[Zn_4(OH)_4]^{4+}$, $Mn^{2+,}$ Cd^{2+}, $[Pb_4(OH)_4]^{4+}$ and $[Cu_3(OH)_4]^{2+}$ for Chromium, iron, zinc, manganese, cadmium, lead and copper respectively. It is also clear that some ions were found in labile state for example Zn^{2+}, Mn^{2+}, and Cd^{2+}, states that are considered to be more toxic than their combined states, a situation rendering the Ngong river water unsuitable for domestic use.

KEYWORDS: Ngong River, Pollution, Heavy Metal, Speciation, JESS

INTRODUCTION

Nairobi, the capital city of Kenya, is home to various multinational companies and organizations including the United Nations Environmental Programme (UNEP) heaquarters. It is a fast-growing industrial town and is currently ranked as the 13th largest city in Africa, based on population and fourth largest in infrastructure development and size.

Ngong River a tributary of Nairobi River passes through the industrial area of the city. In the early 20th Century, the Nairobi River supplied fresh water to the inhabitants of the town. Over time, however, due to industrial and population growth and lack of equivalent infrastructural growth, all that remains of a larger part of the river are foul – smelling and dark coloured water streams.

Figure 1: Section of Ngong River at Sampling Point No. 5

According to the Global Environment Assessment Report [1] in developing countries, untreated water is the most commonly-encountered health threat and causes about 25,000 deaths per day due to water-borne diseases. Nairobi residents have felt the impact of the degeneration of the Nairobi River through water borne diseases such a cholera, and general decrease in the city's social and economic decline. Studies by Keraka and Wamicha in 2003 indicated that in two weeks 12.9% of children living in slums adjacent to the Nairobi River are prone to diarrhoea, and 3.4% develop diarrhoea with blood [2]. A mortality rate of 66.1% children under five years has been reported [3]. There, however, are other less obvious effects of water pollution such as those caused by short or long term exposure to toxic substances. These may cause more harm as they are subtle, the effects more long term and the cure more difficult to administer. Heavy metals are one such possibility.

Metal ions are expected to be in effluents from industries due to their various uses in such activities as stainless steel formulations [4], use in batteries [5], anti-corrosion agents [6], as coloring elements [7], catalysis [8], piping and electrical applications among others.

Heavy metals in excess are known to be harmful in living systems, for example high levels of heavy metals are known to be toxic [9] and affect systems in the body [10]. They also cause kidney problems [11, 12], seizures, coma and death [13], affect reproductive and foetal health [14], cause learning disabilities, weight loss, and growth and hearing problems [15].

It is also known that some specific compounds of a particular substance may be more toxic than others. For example permanganate exhibits a higher toxicity than the manganese (II) compounds [16]. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish [17, 18]. Trivalent chromium (Cr^{3+}), in trace amounts, is essential in humans, and its deficiency is suspected to cause a disease called chromium deficiency [19], while, hexavalent chromium (Cr(VI) or Cr^{6+}) is very toxic and mutagenic when inhaled,[20] and is toxic and may be carcinogenic due to its oxidizing potential and easy permeation of biological membranes. [21]

Knowledge of the total concentration and speciation of heavy metal ions would be advantageous in establishing the risk factor posed by their presence. It may also assist in identification of point sources and thus contribute greatly to its subsequent minimization or elimination of pollutants. Thus, in addition to monitoring specific heavy metals, their speciation studies may be necessary. This is made possible by computational programmes such as the Joint Expert Speciation System (JESS)

Computational methods have been utilized for equilibrium calculations and the determination of equilibrium constants since the early 1960s [21, 22]. Whereas other programs like SYCHEM [23], DENDRAL [24], GEOCHEM [25, 26], MINEQL [27], PHREEQE [28], EQ3/6 [29], ECCLES [30] exist, users have encountered difficulties such as technical obstacles in preparing input data, as well as difficulty in obtaining reliable thermodynamic data. Work on JESS began in 1985 [31] and attempted to solve some of these difficulties primarily by accumulating critically selected data into a unified primary source, finding ways of estimating unmeasured equilibrium constants and encouraging informed feedback (making the program amenable to change), using a collection of a number of computer programs rather than a single one. In JESS, a model is set up by feeding the analytical data into the database together with the required conditions of concentration, temperature, pressure, ionic strength and pH. Various equilibrium calculations take place before the final output.

Cleaning up the Nairobi River has become an urgent task and has been given due priority by the Government of Kenya. UNEP, United Nations Habitat (UNHabitat), United Nations Development Progarm (UNDP) in conjuction with the government have already gone through three phases in Nairobi River clean up, through the Nairobi River Basin Program (NRBP). The National Environmetal Management Authority (NEMA) have also attempted to tackle the matter. Whereas cleaning up the river would do the city a lot of good, monitoring of pollutants, thus knowledge accumulation of the nature and concentrations of the pollutants as well as setting up systems to contain the pollutants before they are deposited into the water system would solve this problem in the long term.

Heavy metal ions have been known to exist in Ngong' River, but speciation of the same has not been carried out. In this study, analysis of some heavy metals at points along the Ngong' River have been performed using the Atomic Absorption Spectrometry, and speciation of the same assessed using the Joint Expert Speciation System (JESS).

EXPERIMENTAL SECTION

Six sampling points, along 1.8 km of the Ngong River were identified and mapped. This is section that runs through the city's industrial area. Sampling Points one and two are located just before the river gets to the industrial area. These may be said to be the control points before the river gets polluted by the industrial waste. Sample points number three, four and five were in the middle section of the industrial area, while sampling point number six is located just after the industrial area. An overview of the points is as shown in the map (figure 2) below:
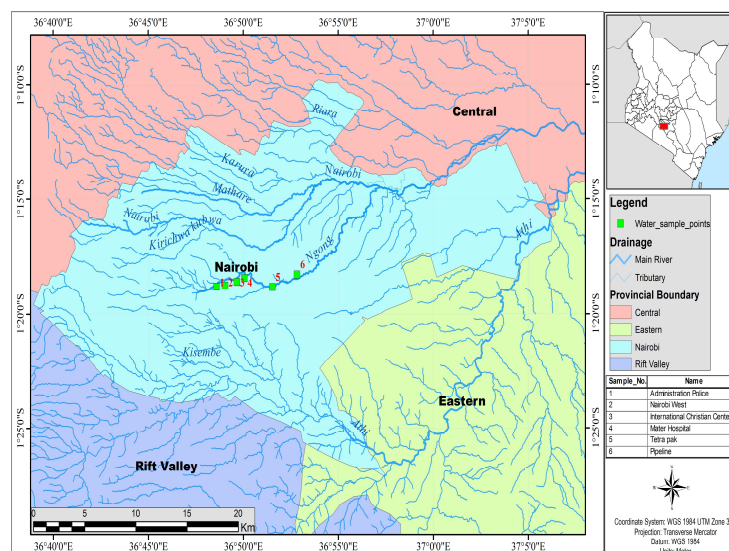

Figure 2: Map of Nairobi River Basin and Neighbouring Provinces

Sampling was carried out in the dry months of the year signifying the dry season. Water samples were obtained in 1- Litre plastic containers, previously rinsed with dilute hydrochloric acid (BDH chemicals), thoroughly washed with detergent and eventually rinsed with distilled water to minimise contamination and ensure reliability of data. Heavy metals were analysed using an atomic absorption spectrophotometer of the type Shimadzu AA-6300 at appropriate wavelengths. The samples were digested using the method described elsewhere [32].

The JESS model was created using data obtained from AAS together with other measured parameters, at a temperature of $25^{o}C$ and at the pH values obtained for the various water samples (table 2). This were fed into the JESS (v 7.3) program, simulations done and the speciation results obtained

RESULTS AND DISCUSSIONS

Table 1 below shows the data obtained from AAS;

Table 1: Concentrations of Heavy Metals in Ngong River

Metal	Who(Mg/L)	Concentration (Mg/L) In Sample Points					
		1	2	3	4	5	6
Cr	0.05	ND	ND	0.041	0.025	ND	0.577
Fe	*	1.512	0.989	0.760	1.819	4.053	6.559
Zn	4*	0.061	0.045	0.036	0.831	0.691	1.005
Mn	0.4	3.410	3.164	1.696	1.494	2.104	2.247
Cd	0.003	ND	ND	ND	ND	ND	0.002
Pb	0.01	0.063	0.002	0.071	0.022	0.059	0.233
Cu	2	0.003	ND	ND	0.033	0.049	0.104
Ni	0.07	ND	0.020	0.049	ND	ND	0.019

* No guidelines for drinking water, but above the indicated thresholds there are unpleasant characteristics like colour, bad taste, slimy feel, and stains on laundry and plumbing features.

Table 2: Conductivity and Ph

Sample No.	Conductivity(Ms)	Ph	Bod(Mg/L)	Cod(Mg/L)
1	0.600	7.5	150	50
2	0.628	7.3	150	50
3	0.493	8.3	150	75
4	0.586	7.4	200	100
5	0.603	7.3	300	175
6	0.888	7.0	375	200

It is worth noting that the concentration of lead, iron and manganese were found to be high in most of the sampling points. This is matter of great concern for the people living at the river banks, for example the slum, and may be tempted to use the water for domestic purposes. The high concentration of iron, highly colours the water and may stain laundry, corrode pipes (due to rust) and cause turbidity in the water; forcing the users to use a lot of detergent, which is expensive to an already economically strained populace.

RESULTS FROM JESS

The JESS programme was ran on the heavy metal concentrations using pH as corroborated by Korfali and Jurdi [31]. The heavy metals that were not detected (ND) were estimated to be 1.0×10^{-7} mg/l. The rationale being that, different species were observed along the water course, hence the heavy metals were present in very low concentrations.
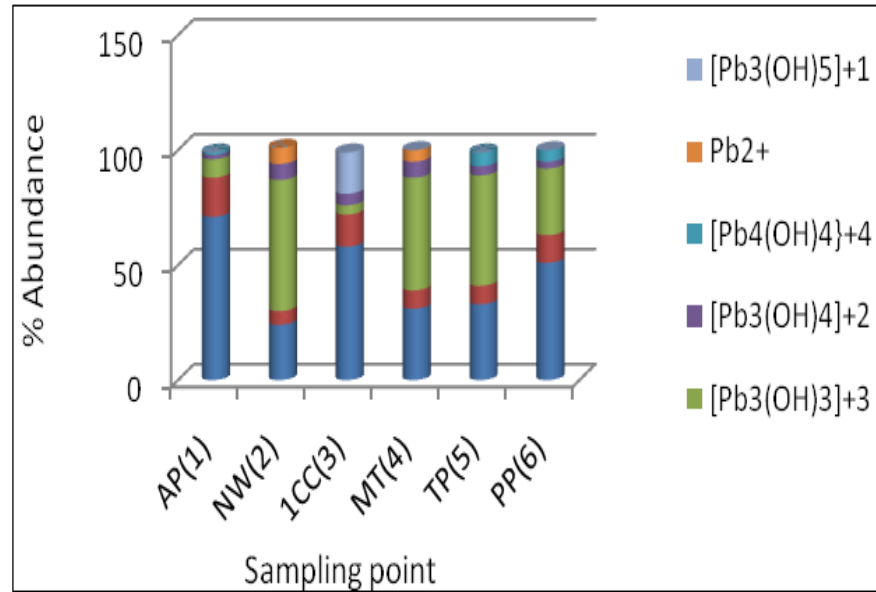
Lead

Figure 2: Speciation of the Lead in Ngong' River

Lead concentrations in all sampling points was found to be considerably higher than the WHO's recommended 0.01 mg/L value. This impllied that the people who use the water are predisposed to lead poisoning. Research shows that exposure of children to high levels of lead may cause learning disability.

In terms of speciation, lead was predicted to be prevalently in oxidation state two and of the hydroxide species. Free lead ion (Pb^{2+}) was predicted to be present in Sample Points 2 and 4. The univalent lead hydroxide complex ($[Pb_3(OH)_5]^{+1}$ was predicted to be only present in Sample Point 3, because this ion is only stable under slightly basic conditions as in this case where the water is pH 8.3. This corroborates with the UNEP findings [33] which reported that at higher pH, lead forms hydroxide complexes i.e, $[Pb(OH)_4]^{2-}$. The predominant lead species in Sampling Points 1, 3 and 6 were predicted to be the tetravalent lead hydroxide species $[Pb_4(OH)_4]^{4+}$ while that for Sampling Points 2, 4 and 5 were predicted to be the trivalent $[Pb_3(OH)_3]^{3+}$. This is most probably due to the fact that the concentration of lead ion in the Sampling Points 1, 3 and 6 were considerably higher compared to Sampling Points 2, 4 and 5.

Zinc

The total zinc concentration in Ngong' river was reported to be lower than the WHO allowable value of 4 mg/L. The amounts, however, varied from one sampling point to another, for example the concentration is highest at Sampling Point 6, most probably due to a point source at the industrial area. The relatively high level of zinc in Sampling Point1 may be due to dwellings made of corrugated iron sheet constructed close to the river bank. Increase in pH may trigger precipitation of zinc compounds, since zinc hydroxides and zinc sulphates dominate [34] and therefore less zinc to be detected in the water. However, when the pH reduced, the speciation of zinc was altered and the zinc complexes therein formed became more soluble thereby increasing zinc concentration in water after Sampling Point 3. The total zinc concentration increased from Sampling Points 4 to 6.
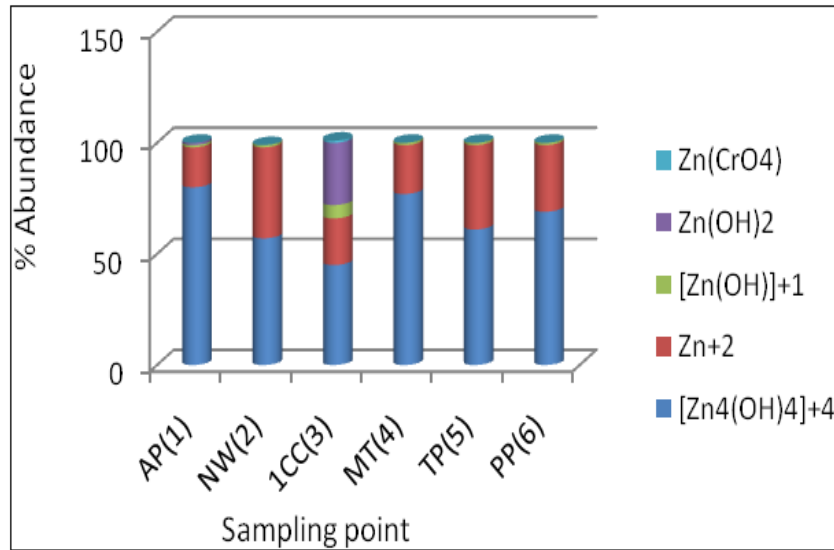
Figure 3: Speciation of Zinc in Ngong' River

Zinc was predicted to be predominantly in oxidation state II, which supports the observation by Petrucci and Harwood (1993) [35] with zinc hydroxide complexes and traces of the chromate ion in Zn (CrO_4), an indication of the presence of chromium (VI) ions. The free zinc ion Zn^{2+} was also predicted to be present in substantial quantities. This should serve as a warning to the people using this water for domestic purposes and for aquatic systems since free zinc ion is found to be particularly toxic.

Nickel

The total nickel concentrations in all the Sampling Points were lower than the WHO allowed value of 0.07mg/l (Table 1). There was an increase in the total nickel concentration at Sampling Points 2 and 3.
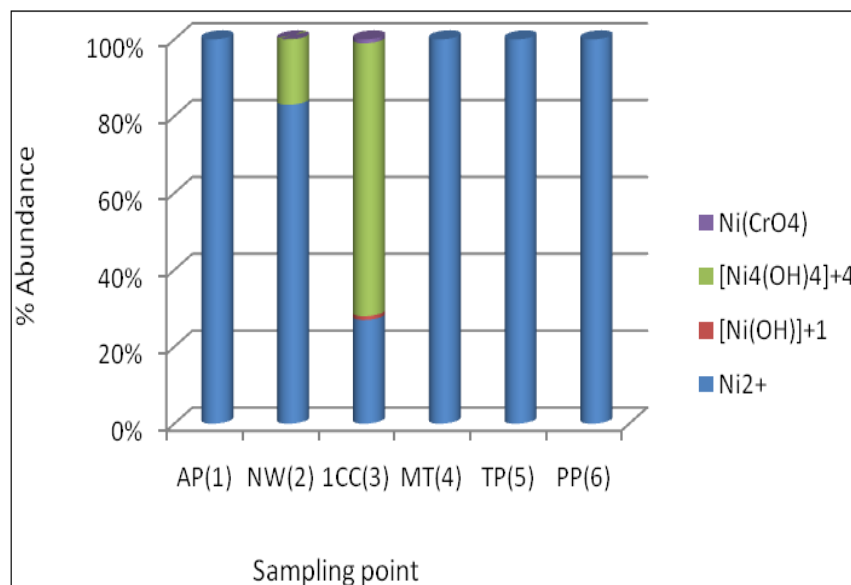

Figure 4: Speciation of Nickel in Ngong' River

Nickel was predicted to be in oxidation state II. Free Ni^{2+} ion was predicted to be predominant, especially when nickel levels are relatively low (figure 4). This is in agreement with observation by Martino et al. [36], that dissolved nickel fraction in fresh and sea water forms free hydrated Ni (II) cation and soluble nickel inorganic and organic complexes of different stability. In Sampling Points 2 and 3 there are traces of the chromate and hydroxide complexes with

nickel. This may be due to higher nickel concentrations in these two Sampling Points as well as the elevated pH in Sampling Point 3 whereby the tetravalent nickel hydroxide ion ($[Ni_4(OH)_4]^{4+}$ is predominant. Cornellis et al. [37] observed that the speciation of nickel in sea and fresh water depends on pH, redox conditions, ionic strength, type and concentration of inorganic ligands, pressure and temperature conditions among others.

Chromium

Total chromium concentration was also found to be within the WHO acceptable limits in all the Sampling Points except 6 (See Table 1). The speciation studies of chromium predicted that the univalent hydroxide species $[Cr(OH)_2]^{1+}$ was predominant except in Sampling Point 3, with hydroxide $[Cr_4(OH)_6]^{6+}$. Chromate ion (CrO_4^{2-}) complexing with manganese, nickel or zinc, was also predicted. The unique behavior at Sampling Point 3 is attributed to the high pH of 8.3. At this pH Cr (VI) ions are readily reduced to Cr (III) in the presence of organic matter [38]. The study shows in addition to knowledge of the total concentration, speciation of the elements is key in establishing water pollution.
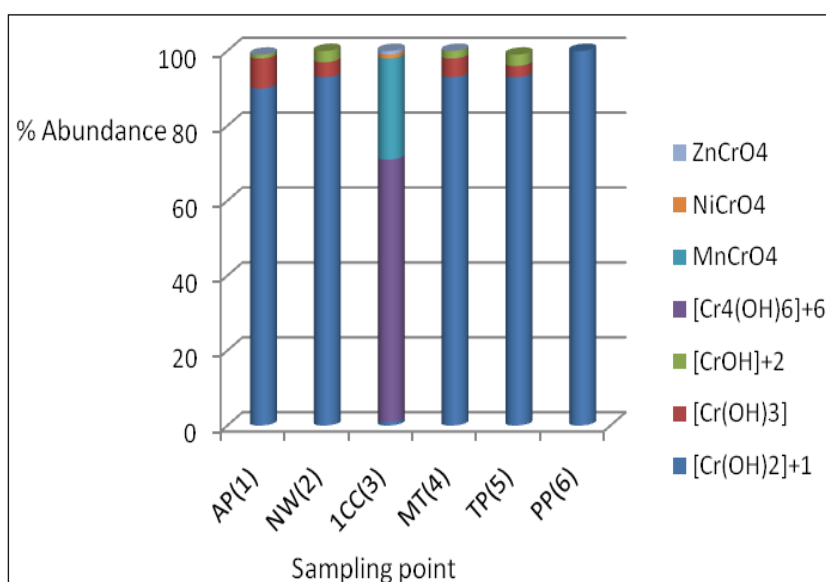

Figure 5: Speciation of Chromium in Ngong' River

Iron

Iron was found to be the most abundant heavy metal in the Nairobi River (Table 1). The concentration in all the Sampling Points was quite high implying that the Ngong' river water have colour, bad taste, may stain laundry and lead to rust covering pipes and tanks. Sampling Point 1 had the highest iron content and is surrounded by structures made of corrugated iron sheets and thus a direct source of iron. The concentration decreases in Sampling Points 2 and 3 before being elevated in Sampling Points 4 to 6. The influence of the man-made activities next to river courses is therefore quite significant.

The speciation predictions show that the ferric hydroxide is predominant in most of the Sampling Points (Figure 6), and that the free ferrous iron is also present in substantial amounts. The most predominant species of iron in all Sampling Points except Sampling Point 3, is $[Fe(OH)_2]^{+1}$(Figure 6). The ferric hydroxide species is predominant in Sampling Point 1. The ferric ion is predicted to be reduced to ferrous ion in Sampling Point 2 while the abundance of the univalent ferrous hydroxide ion $[Fe(OH)_2]^{1+}$ remained the same. In Sampling Points 4, 5 and 6 the Fe^{2+} concentration increased while that of $Fe(OH)_3$ decreased. This can be attributed to reducing agents from industrial effluents inflows near this Sampling Points. The oxygen demand was observed to increase across Sampling Points 4, 5 and 6 (Table 2).

The speciation in Sampling Point 3 was markedly different from all the others, with the species $[Fe_3(OH)_4]^{8+}$ being the most predominant.
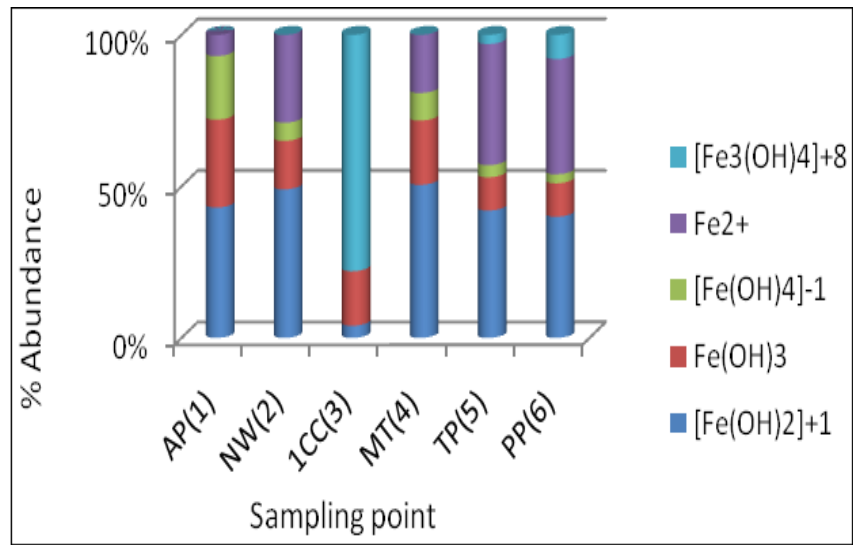

Figure 6: Speciation of Iron in Ngong' River

Manganese

The total manganese concentrations in all the Sampling Points exceeded the WHO acceptable value of 0.4 mg/l. Sampling Point 1was found to have Mn concentration. The concentration of Mn decreases in Sampling Points 2 to 4, then increases in Sampling Points 5 and 6.

Speciation predictions in all Sampling Points except 3 showed that the predominant species is the free aquo complex, Mn^{2+}. This also has been observed by Faulkner *et al* [40], who observed that only upon oxidation, are traces of the oxidized form, Mn^{4+} are observed. The water was quite deprived of oxygen given the oxygen demand values (Table 2) and therefore only Mn^{2+} was expected. They also noted that manganese oxidation is primarily biologically mediated but above pH 8, manganese oxidation is observed. This explains the difference in speciation in Sampling Point 3 which had a pH value of 8.3 (Table 2). Traces of the hydroxide and chromate were also envisaged in most of the sampling points (Figure 7).
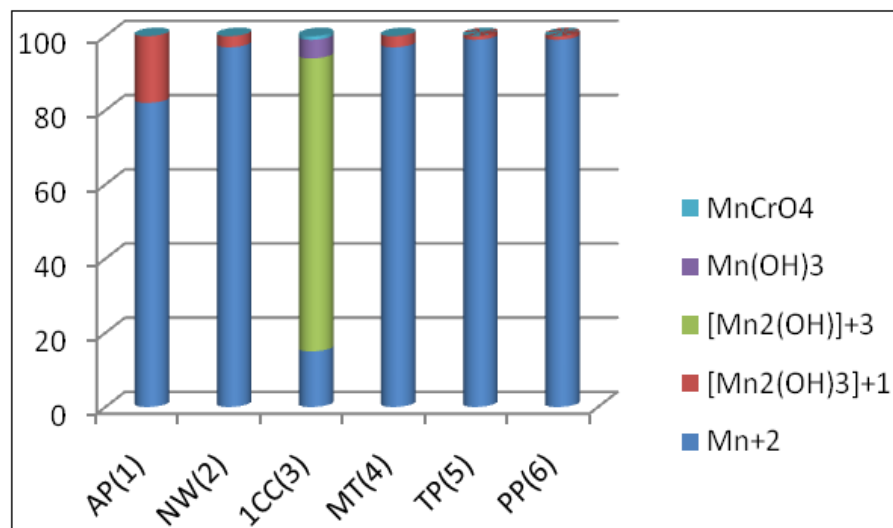

Figure 7: Speciation of Manganese in Ngong' River

Cadmium

A similar trend is observed for cadmium as that of manganese, with Cd^{2+} being the predominant species (Figure 8). At Sampling point 3 there are predictions of substantial quantities of cadmium in the form of $CdCrO_4$ and $[Cd(OH)]^{+1}$, which is most probably due to the elevated pH (Table 2). It has been previously observed [41] that complexation of Cd decreases with increase in pH. Thus at lower pH values (pH 7 ± 0.5), Cd^{2+} ions predominate, whereas at higher pH values (>pH 7.6), complexes of Cd form and Cd^{2+} becomes less dominant.
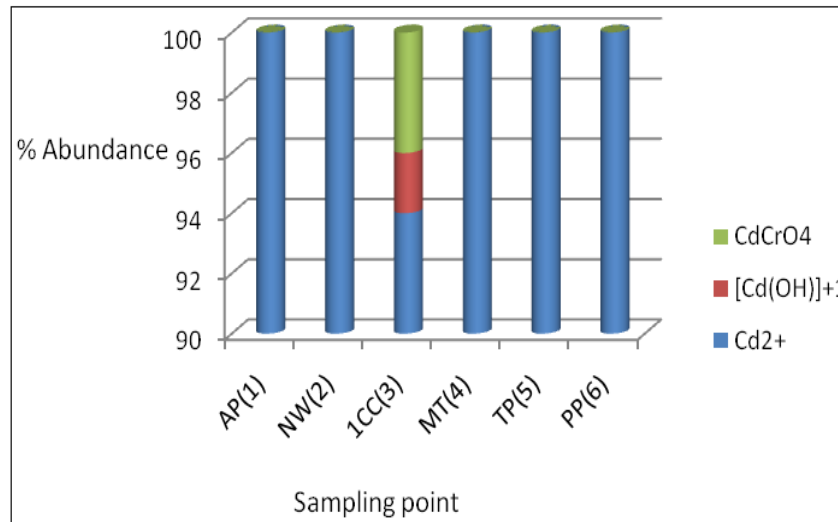

Figure 8: Speciation of Cadmium in Ngong' River

Copper

The total copper concentration in the river was generally below the WHO limit of 2 mg/l (Table 1). There was no detectable copper at Sampling Points 2 and 3. The concentration increases from Sampling Points 4 to 6.

Speciation predictions indicated that at higher copper concentrations the predominant species was the divalent copper hydroxide species $[(Cu_3(OH)_4]^{2+}$. The free copper II ion was observed to be predominant where total copper concentration is low (Figure 9). A different scenario is observed when the pH is high as in Sampling Point 3 (Table 1 and Figure 9) where the predominant species is the univalent copper hydroxide species $[Cu(OH)]^{+1}$.
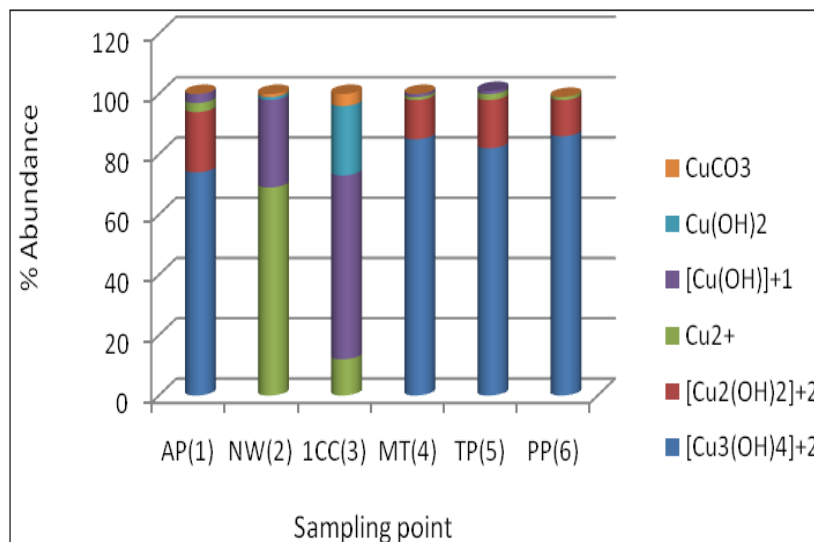

Figure 9: Speciation of Copper in Ngong' River

CONCLUSIONS AND RECOMMENDATIONS

Iron was found to have the highest with an average concentration of 8.87×10^{-5}M while the least was copper with an average concentration of 2.95×10^{-7}M. Using this model, the major species predicted in most of the Sampling Point were found to be $[Cr(OH)_2]^{+1}$, $[Fe(OH)_2]^{+1}$, $[Zn_4(OH)_4]^{+4}$, Mn^{+2}, Cd^{+2}, $[Pb_4(OH)_4]^{4+}$ and $[Cu_3(OH)_4]^{2+}$ for Chromium, iron, zinc, manganese, cadmium, lead and copper respectively. The samples had an average pH value of 7.4, except the sample from sampling point three which recorded a pH value of 8.3. The speciation predicted at Sampling Point 3 was considerably different from that from the other sampling points, due to its high pH value. The studies corroborate the findings of various authors that pH greatly affects speciation of the elements in the water and therefore is an important factor to take into account when considering whether or not water is suitable for domestic use. The conductivity of the water and the quantity of heavy metals implies that this water is unsuitable for drinking or other domestic use. These specification predictions can be traced to various point sources, and hence pollutants need to be mitigated at source, and pH of water bodies needs to be regulated. An investigation can also be carried out in conjunction with the health sector to identify any correlation between various conditions of residents of the City of Nairobi, especially those residing adjacent to the river.

REFERENCES

1. UNEP/GEMS. (1991). Freshwater Pollution. UNEP/GEMS Environmental Library No. 6. UNEP

2. Nyanchoka K. Margaret and Wamicha N. Wellington (Jan 2003). Child Morbidity and Mortality in Slum Environments along Nairobi River. *Eastern Africa Social Science Research Review*, **19** No. 1. pp 41-57

3. Kenya Demographic and Health Survey (1998)

4. Corathers, Lisa A. (2008). 2006 Minerals Yearbook: Manganese. Washington, D.C.: United States Geological Survey. Retrieved 2009-04-30;

5. Dell, R. M. (2000). Batteries fifty years of materials development. *Solid State Ionics* **134**: pp139–158

6. Garverick, Linda (1994). *Corrosion in the Petrochemical Industry*. ASM International

7. Leonard, Alvin R.; Lynch, Glenn (1958). "Dishware as a Possible Source for Lead Poisoning". *Calif. Med.* **89** (6): 414–416).

8. Weckhuysen, Bert M. (1999). "Olefin polymerization over supported chromium oxide catalysts". *Catalysis Today* **51** (2): 215–221

9. Rodrigues – Iznaga I., A. Gomez, G. Rodriguez – Fuentez and A. Benitez – Aguila (2002). Natural Clinoptilolite as an exchanger of Ni^{2+} and NH_4^+ ions under hydrothermal conditions and high ammonia concentration. *Microporous Mesoporous Mater.* **53** (1 – 3) pp 71 – 80.

10. Elbetieba and Al-Hammod (1997). Long term Exposure of Male and Female Mice to trivalent and hexavalent chromium compounds: Effect of Fertility. *Toxicology* **116** pp 19 – 47

11. Grant, L.D. (2009). Lead and compounds. in Lippmann, M. *Environmental Toxicants: Human Exposures and Their Health Effects, 3rd edition*. Wiley-Interscience

12. Nogawa, Koji; Kobayashi, E; Okubo, Y; Suwazono, Y (2004). Environmental cadmium exposure, adverse effects, and preventative measures in Japan. *Biometals* **17** (5): 581–587

13. Pearce, J. M. S. (2007). Burton's line in lead poisoning. *European Neurology* **57** (2): 118–119

14. Bellinger, D. (2005). Teratogen update: Lead and pregnancy. *Birth defects research. Part A, Clinical and molecular teratology* **73** (6) pp 409–420.

15. Nevin Rick (2000). How Lead Exposure relates to temporal changes in IQ, violent crime and unwed pregnancy. *Environmental Research*. **83** (1)

16. Young, R., Critchley, JA, Young, KK, Freebairn, RC, Reynolds, AP, Lolin, YI (1996). Fatal acute hepatorenal failure following potassium permanganate ingestion. *Human & Experimental Toxicology* **15** (3): 259

17. Eisler, Ronald (1993), "Zinc Hazard to Fish, Wildlife, and Invertebrates: A Synoptic Review" (PDF), *Contaminant Hazard Reviews* (Laurel, Maryland: U.S. Department of the Interior, Fish and Wildlife Service) (10)

18. Muyssen, Brita, T. A.; De Schamphelaere, Karel A. C.; Janssen, Colin R. (2006), Mechanisms of chronic waterborne Zn toxicity in Daphnia magna, *Aquatic Toxicology* **77**: 393

19. Merz, Walter (1 April 1993) Chromium in Human Nutrition: A review. *Journal of Nutrition* **123**(4): 626 – 636).

20. Katz SidneyA., Salem H. (1992).'The Toxicology of Chromium with respect to its Chemical Speciation: A review. *Journal of Applied Toxicology* **13** (3) 217 – 224.

21. Swietlik R. (1998). Speciation of Chromium in waters. *Polish Journal of Environmental Studies*. **7**. (5) 257 - 266

22. L. G Sille, *Acta Chem. Scand.*, 1962, **16**, 159;

23. N. Ingri and L.G. Sillen, *Acta Chem. Scand.,* 1962, **16**, 173

24. H. L. Gelernter, A. F. Sanders and D. L. Larsen, *Science*, 1977, **197**, 1041

25. B. G. Buchanan, D. H. Smith, W. C. White, R. J. Gritter, E. A. Feigenbaum, J. Lederberg amd C. Djerassi, *J. Am. Chem. Soc.*, 1976, **98**, 6168

26. S.V Mattigod and G. Sposito, in Am. Chem. Soc. Symp. Ser. 93 (1979), E. A. Jenne (ed.), pp. 837-856. ACS, Washington

27. J. C. Westall, J. L. Zachary and F. M. M. Morel (1976).Users Manual: MINEQL, *A Computer Program for the Calculation of Chemical Composition of Aqueous systems. Tech. Note 18, Dept. Civil Eng*., M. I. T., Cambridge, MA,

28. D. L. Parkhurst, D. C. Thorstenson and L. N. Plummer (1985). *Users Manual: PHREEQE, NTIS Tech. Rep., PB81-167801*, 1980. Revised

29. T. J. Wolery, K. J. Jackson, W. L. Bourcier, C. J. Briton, B. E. Viani, K. G. Krauss and J. M. Delany (1990) in *Am. Chem. Soc. Symp. Ser. 416*, D. C. Melchior and R. L. Basset (eds.), pp 104 – 116. ACS, Washington,

30. P. M. May, P. W. Linder and D. R. Williams (1977). *J. Chem. Soc. Dalton Trans*., 588

31. May M. Peter and Murray Kevin (1991). JESS, A Joint Expert Speciation System – I, Raison D'être. *Talanta*, **38**, No. 12 pp 1409 – 141

32. Greenberg, E. A., S. L. Cleseri and E. A. Eaton (1992). Standard Methods for Examination of Water and Wastewater, 18th ed.

33. Korfali, S.I and Jurdi, M.S. (2011) Speciation of Metals in Bed Sediments and Water of Qaraaoun Reservoir, Lebanon. *Environ monit assess* **178** (1), 563-579.

34. United Nations Environmental Programme (2010) Final Review of Scientific Information on Lead. Report to the Governing Council at its Twenty-sixth Session in Nairobi, Kenya.

35. Bjornsdottir, I. (1996) Metals and Metal Speciation in Waste Water from the Nesjavellir Geothermal Power Plant, Sw-iceland and Possible Effects on lake Thinvallavain. Msc thesis, Chalmers University of Technology.

36. Petrucci and Harwood (1993) General Chemistry Principles and Modern Applications.6th Edition. Macmillan Publishing Company, New York.

37. Martino M., A. Turner and M. Nimmo (2004). Distribution, Speciation and Particle-Water Interactions of Nickel in the Mersey Estuary, UK. *Marine Chemistry*. **88** (3-4). 161 – 177

38. Cornelis, R., Crews, H., and Caruso, J. (2005) Handbook of Elemental Speciation II: Species in the Environment, Food, Medicine and Occupational Health. John Wiley and son's ltd. Germany

39. Tetsushi S., E. McCurdy and S. Wilbur (2005). Ion Chromatography (IC) ICP-MS for Chromium Speciation in Natural Samples. Agilent Technologies, Inc. 2005, USA.

40. Hopkison B. M. and K.A. Barbeau (2007). Organic and redox speciation of iron in the eastern Tropical North Pacific Suboxic Zone. *Marine Chemistry*. **106**. 2 – 17

41. Faulkner S. P., R.P. Gambrell and S.L. Ashby (1996). Analytical Methods for Iron and Manganese Determinations in Reservoir Tailwaters: Laboratory Investigations. Water Quality Note PD-01.

42. Xu H. and L. Sigg (1998). Cadmium speciation and complexation by Natural Organic Ligands in Fresh Waters. *Analytica Chimica Acta*. **363**. 249 – 259.

43. Gao, Y., Kan, A.T., Thomson, M.B. (2003) Critical Evaluation of Desorption Phenomena of Heavy Metals from Natural Sediments. *Environ. Sci. Technol* **37**, 5566-5573.