The Speciation of Environmentally Significant Metals from Pulp and Paper Mill Effluent with Selected Inorganic Ligands and their Impact on Water Quality of River Nzoia, Kenya

Amayi James
Department of Chemistry and Biochemistry, School of Science, University of Eldoret, P.O. Box 1125, Eldoret, Kenya
jamesamayi@gmail.com; jamesamayi@yahoo.com

Titus M. Muthoka
Department of Chemistry and Biochemistry, School of Science, University of Eldoret, P.O. Box 1125, Eldoret, Kenya.

Kituyi Lusweti
Department of Chemistry and Biochemistry, School of Science, University of Eldoret, P.O. Box 1125, Eldoret, Kenya.

Omindo Charles
Department of Chemistry, School of Pure and Applied Sciences, Kenyatta University, P. O. Box 43844, Nairobi, Kenya

Sherry Oluchina
School of Nursing and Midwifery, Masinde Muliro University of Science and Technology, P. O. Box 190-50100, Kakamega, Kenya

Abstract

The effluents from Webuye paper mill were analysed chemically using Atomic absorption spectroscopy to obtain the stoichiometric concentrations of the major anions and cations. However, this does not indicate how the components are distributed amongst possible species. pH was measured with pH meter previously calibrated with pH buffer, alkalinity was determined by titration using phenolphthalein indicator and 0.010 M HCl, chloride was analyzed by titration using potassium chromate indicator and standardized 0.014 N mercuric (II) nitrate solution. A pH dependent model for the speciation of divalent Pb and Cu ions downstream was constructed with corrected IUPAC stability constants using SPECIES computer program. Modelling results showed that inorganic speciation behaviour was of three types; (a) Pb and Cu were dominated by carbonato- complexes at pH 8.0, $PbCO_{3(aq)}$ having 66.06% and $CuCO_{3(aq)}$ 90.45% abundance. Bicarbonato complexes could only form to significant levels at high $[HCO_3^-]_T$ and high ionic strength. (b) Chloro-complexes of Pb and Cu that formed were $PbCl^+$, $PbCl_{2(aq)}$, $PbCl_2^{2-}$, $CuCl^+$ and $CuCl_{2(aq)}$. All these complexes were weak and could best be studied in media of high $[Cl^-]_T$, high $[Cl^-]_T$: $[Metal]_T$ ratios and high ionic strength. The fraction of free aquo ions (Pb^{2+} and Cu^{2+}) dominated speciation with increase in $[Cl^-]$ and pH. (c) Hydroxo- complexes of Pb were dominated by carbonato- complexes over a wide range of solution conditions.

Key Words: *Model, Inorganic, Speciation, Ligand, Complex*

INTRODUCTION

Although trace elements contribute negligibly to the total salt content of river water, they do play an important role in aquatic systems. Certain trace metals, such as zinc and copper, are essential for the growth of aquatic organisms, although others such as cadmium and lead may be toxic to life in the river. The uptake of trace metals and the paths by which they travel from source to sediment depend on their chemical state in the aquatic environment. The complexation reactions involving trace metals in natural water systems are so diverse and complex that the calculations of the equilibrium concentrations of different forms of any element are difficult and burdened with uncertainties. Nevertheless, much of our understanding of aquatic trace metal chemistry depends on such calculations since direct measurement of many species is impossible by any presently known analytical techniques (Ferguson, 1990).Most dissolved metals bear the potential to coordinate with a large number of naturally occurring dissolved ligands. Stability constants and anionic concentrations vary so enormously, however, that under any given conditions the metal is usually present in one or two heavily predominant forms with all other forms present only in insignificant quantities. The diversity of dissolved trace metal species may therefore be considered rather limited at any instant in a natural aquatic system but becomes much more complicated through time because the predominant coordination complexes change markedly under different conditions. In this work, the metals Pb and Cuwere chosen because of their importance in the biosphere and because some experimental information regarding their speciation was available.

MATERIALS AND METHODS

Experimental Procedures

Effluent (EFF) was collected as composite sample at the point of discharge (PD) into the river at 15 minutes interval over a period of four hours. At each time of effluent collection two separate sets of samples were collected, one for the determination of heavy metals and the second for the determination of other physico- chemical parameters. The point of discharge was chosen as a reference point. Water samples were collected downstream after the point of discharge (APD) of the effluent at five different sampling locations at 250m intervals. At each sampling location the surface water sample was collected at the middle of the river and stored in clean polyethylene bottles that had been pre-washed with nitric acid and thoroughly rinsed with deionized water. The water samples were analyzed for pH, alkalinity, electrical conductivity, chloride, sulphate, phosphate, TDS and heavy metals Pb and Cu. The water chemical analysis was done using standard analytical methods of water analysis (Trivedi and Goyal, 1986; APHA-AWWA-WPCF,1985; USEPA, 1980). pH which was a non-conservable parameter was determined at the time of sampling in the field. The pH of the sample was measured with a pH meter that had been previously calibrated. Alkalinity and chloride were determined by titration. Sulphate was determined turbidimetrically, TDS gravimetrically and phosphate colorimetrically. The water was analyzed for metals Pb and Cu by atomic absorption spectroscopy. Each sample was analyzed in duplicate and the average of the results reported. General laboratory quality assurance measures were always observed to prevent sample contamination and instrumental errors. The water used throughout the experiment was doubly distilled in an all glass distiller before it was deionized.

RESULTS AND DISCUSSION

Table 1. Average concentrations of physico-chemical parameters

Parameter	**Temp**	**pH**	**Alkalinity ($CaCO_3$ mg/L)**	**EC (µmhos/cm)**	**Cl^- (mg/L)**	**SO_4^{2-} (mg/L)**	**PO_4^{3-} (mg/L)**	**TDS (mg/L)**
UPS	27.5	7.6	9.1	69.68	44.97	120.16	15.35	62.71
***STDEV**	0.0894	0.4	0.8	27.40	5.58	23.57	2.75	31.73
EFF	28.0	8.5	265.0	865.25	78.73	195.10	35.10	778.73
APD	27.5	8.0	110.5	117.88	62.67	169.16	28.73	106.10
***STDEV**	0.0548	0.5	12.71	7.45	10.14	14.11	3.95	7.02

KEY – UPS-Upstream, APD- After point of discharge, EFF- Effluent, *STDEV – Standard deviation

Temperature of water upstream and downstream was normal with no significant difference having an average of 27.5^0 C. The fluctuation of pH in the samples was from 7.6 to 8.5 which was within the prescribed limit. Alkalinity upstream ranged from 8.5 to 10.5 mg $CaCO_3$/L with an average level 9.1 $CaCO_3$/L while the effluent had alkalinity of 265.0 mg/L $CaCO_3$. Downstream alkalinity ranged from 9.5 to 255.0 mg $CaCO_3$/L. The average level of total alkalinity downstream was 110.5 mg $CaCO_3$/L. This was below the prescribed limit for total alkalinity of 120.0 mg/ L (UNEP, 1992).

Chloride concentration upstream ranged from 34.82 to 49.10 mg/L with an average level of 44.97 mg/L. Downstream chloride concentration ranged from 44.96 to 73.12 mg/L with an average level of 62.67 mg/L. Chlorides have been associated with pollution as an index and are found below the permissible value set at 250 mg/l in the study area. The average level of phosphate (35.10 mg/L) in the effluent was slightly high and of great concern. The discharge of this effluent into the river increased the level of phosphate downstream to an average of 28.73 mg/L. High levels of phosphate could lead to eutrophication and outgrowth of alga, which could further deplete the dissolved oxygen levels of the river. From table 2; Pb and Cu were of average levels of 1.4921 and 0.0893 mg/L, respectively in the effluent.

Table 2: Average levels of heavy metals at the sampling points

Heavy metal	**Pb (mg/L)**	**Cu (mg/L)**
UPS	0.0452	0.0253
*STDEV	0.0120	0.0198
EFF	1.4921	0.0893
APD	1.2809	0.0686
*STDEV	0.1469	0.0102

*Standard Deviation (±)

KEY – UPS-Upstream, APD- After point of discharge, EFF- Effluent

The sources of heavy metals in the effluent could probably be from chlorine bleaching process where a chelating agent (EDTA) is added to bind the metal ions contained in the pulp and preventing them from decomposing the peroxide. The average levels of Pb, and Cu upstream were 0.0452 and 0.0253 mg/L, respectively while their corresponding average levels downstream were 1.2809 and 0.0686 mg/L. Water downstream is used for horticultural irrigation of vegetables and other food crops along the bank of the river because of its high nutrient contents. Accumulation of heavy metals by crops receiving such contaminated water for irrigation is common and metals could be biomagnified along food chain to a higher trophic level. Consumption of such food crops could expose man to untold heavy metal hazards. The dissolved metals were, however, much lower than the total levels.

Chemical Modelling of Pb^{2+} + CO_3^{2-}, HCO_3^-Systems based on the Corrected Stability Constants Recorded in Table 3 using the SPECIES Computer Program

Table 3: CO_3^{2-} and HCO_3^{2-} complexes of Pb and their stability constants

Reactions for complex formation	**[1]IUPAC stability constant values**	**[2]Corrected stability constant values using the SPECIES computer program**
	$K_1 = 6.45 \pm 0.72(\mathrm{I})$	$K_1 = 6.13$
	$\beta_2 = 10.13 \pm 0.24(P)$	$\beta_2 = 10.13$
	$K = 1.86 \pm 0.12(P)$	$K = 2.02$

[1] IUPAC Provisional (P) and Indicative (I) values for the Pb^{2+} + CO_3^{2-}, HCO_3^- systems at 298.15K, 1 bar and $I_m = 0$ mol

Note: The following applies to all the corrected stability constant values in tables 3, 4, 5, 6, 7 and 8;

[2] Corrected stability constants as a function of ionic strength [corrected 0.031 M] for the metal-ligand systems used for the modelling of the equilibrium distribution of metal complexes in the dissolved phase, using the SPECIES computer program. The $\log_{10}\beta_{p,q,r}$ and $\log_{10}K_n$ values are at 300.5 K.

The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows;

Parameter	Pb^{2+}	CO_3^{2-}	HCO_3^-
Concentration ($mmoL^{-1}$)	12.03627	0.50	4.30328

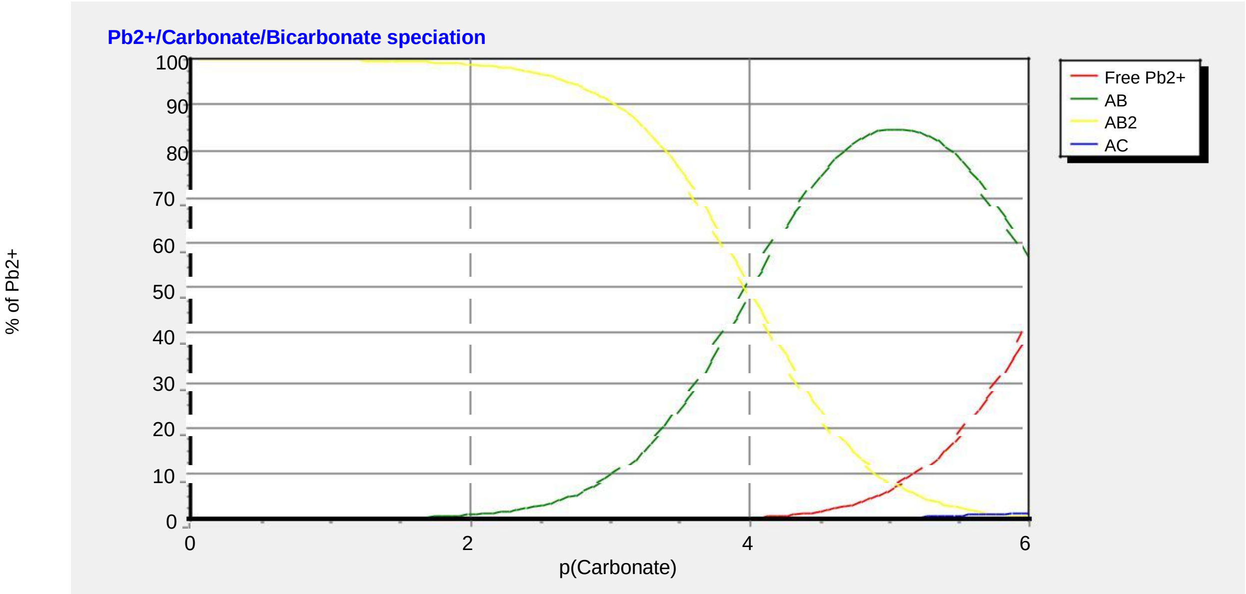

Figure 1: Speciation diagram for the Pb^{2+} + CO_3^{2-}, HCO_3^- system at 27.5^0 C in simulated river water as a function of $[CO_3^{2-}]$ [denoted by the symbol p (carbonate) at pH 8.0

Figure 1 represents the following species;

Symbol	*Complex*	*% distribution*
AB	$PbCO_{3(aq)}$	66.06
AB	$Pb(CO_3)_2^{2-}$	32.93
	Free $Pb^{2+}_{(aq)}$	< 1
AC	$PbHCO^+$	< 1

[These % distribution values are obtained real-time from the SPECIES computer program].

Note: The following apply to all the modelled systems (speciation diagrams) in this paper;

1. All formation constants were dependent on ionic strength hence corrections were made to 0.031 M.
2. It was assumed that the systems were at equilibrium with air having a CO_2 fugacity of $10^{-3.5}$ bar (1 bar = 10^5 Pa). Log_{10} $[CO_{2(g)} = CO_{2(aq)}] = -1.5$ (Morel and Hering, 1993).

At $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ of 4.30 $mmoL^{-1}$ (which was the concentration of CO_3^{2-} and HCO_3^- in the river water) at pH 8.0, the speciation of Pb^{II} was dominated by $PbCO_{3(aq)}$ with 66.06% distribution and increased up to a maximum of approximately 85% at $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ of 5.0 $mmol^{-1}$. At 4.30 $mmol^{-1}$, $Pb(CO_3)^{2-}$ had a distribution of 32.93% (real time value). The distribution of free $Pb^{2+}_{(aq)}$ was, however, negligible at 1.22%. Therefore carbonato- complexes dominated speciation of Pb^{II}in the river indicating high levels of Pb toxicity. $PbC_{O3(aq)}$ is harmful ecotoxicologically since it limits plant chlorophyll synthesis. It also bio accumulates in the food chain. This agrees with Powell and Pettit (2009), that in the absence of inorganic ligands, in weakly alkaline solutions, $8.0 < -\log_{10} \{[H^+]/c^0\} < 9.0$, the speciation of Pb^{II} is dominated by $PbCO_{3(aq)}$ with its maximum corresponding to 74% of $[Pb^{II}]_T$ at $-\log_{10} \{[H^+]/c^0\} = 8.35$ for the conditions; $I_m = 0$ mol kg^{-1}, $t=25^0$ C and f $(CO_2) = 10^{-3.5}$ bar (1 bar = 10^5 Pa). The difference of ≈ 7.94% between this study and Powell and Pettit (2009) could be attributed to the differences in ionic strength and temperature used in both studies. The species $PbHCO_3^+$ did not form at the $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ of 4.30 $mmol^{-1}$ of the river. It could only form to significant levels at high $[HCO_3^-]_T$ and high ionic strength. Therefore, at $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ of 4.30 $mmol^{-1}$, free $Pb^{2+}_{(aq)}$ ions become significant hence potential polluting ability of the solution.

Chemical Modelling of Pb^{2+} $+Cl^-$ System using Corrected Stability Constants

Table 4. Cl^- complexes of Pb and their stability constants

Reactions for complex formation	**[1]IUPAC stability constant values**	**[2]Corrected stability constant values using the SPECIES computer program**
	$K_1 = 1.50 \pm 0.03(R)$	K_1 =1.66
	$\beta_2 = 2.10 \pm 0.05(R)$	β_2 =1.78
	$\beta_3 = 2.00 \pm 0.10(R)$	β_3 =1.76

[1] IUPAC Recommended (R) values for the Pb^{2+} + Cl^- systems at 298.15K, 1 bar and $I_m = 0$ mol Kg^{-1}

The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows;

Parameter	Pb^{2+}	Cl^-
Concentration ($mmoL^{-1}$)	12.03627	1.7678

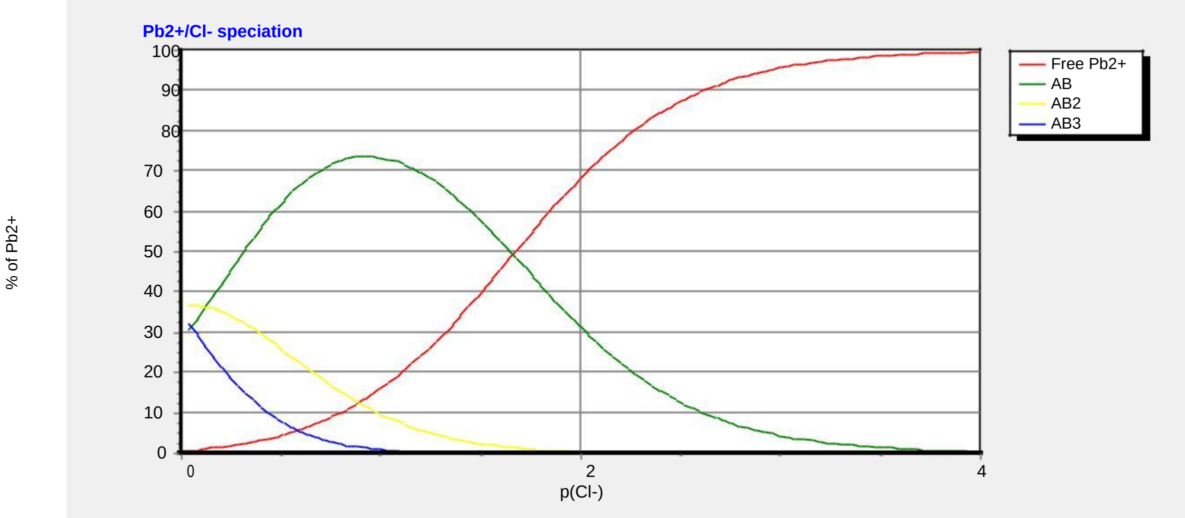

Figure 2: Speciation diagram for the Pb^{2+} + Cl^- system at 27.5^0 C in simulated river water as a function of chloride [denoted by the symbol p (Cl^-) at pH 8.0

Figure 2 represents the following species;

Symbol	*Complex*	*% distribution*
	Free $Pb^{2+}_{(aq)}$	58.10
AB	$PbCl^+$	42.25
AB_2	$PbCl_{2(aq)}$	< 1
AB_3	$PbCl_3^-$	< 1

[These % distribution values are obtained real-time from the SPECIES computer program]. Pb^{II} appears to form up to four consecutive chloro- complexes in aqueous solution;

In this model only three complexes formed; $PbCl^+$, $PbCl_{2(aq)}$ and $PbCl_3^-$. All these complexes were weak and are best studied in media of high $[Cl^-]_T$, high $[Cl^-]_T : [Pb^{II}]_T$ ratios and high ionic strength. Cl^- plays a negligible role in speciation (Powell and Pettit, 2009). The dominant species were free $Pb^{2+}_{(aq)}$ with 58.10% distribution at $[Cl^-]_T$ of 1.80 $mmol^{-1}$ (which was the concentration of Cl^- in the river). Pb interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, reproductive and nervous systems. At $[Cl^-]_T < 1.8$ mmol^{-1}, the system had the species $PbCl^+$, $PbCl_{2(aq)}$ and $PbCl_3^-$ as the only chloro species. At $[Cl^-]_T$ of 1.8 mmol^{-1}, the system became potentially toxic due to the emergence of the free $Pb^{2+}_{(aq)}$ ions.

Chemical Modelling of Pb^{2+} + OH^- System using [2]Corrected Stability Constants

Table 5: OH^- complexes of Pb and their stability constants

Reactions for complex formation	[1]IUPAC stability constant values	[2]Corrected stability constant values using the SPECIES computer program
	$K_1 = -7.46 \pm 0.06(R)$	$K_1 = -7.30$
	$\beta_2 = -16.94 \pm 0.09(R)$	$\beta_2 = -16.94$
	$\beta_3 = -28.03 \pm 0.06(R)$	$\beta_3 = -28.27$
	$\beta_{3,4} = -23.01 \pm 0.07(R)$	$\beta_{3,4} = -19.77$

[1] IUPAC Recommended (R) values for the Pb^{2+} + OH^- systems at 298.15K, 1 bar and $I_m = 0$ mol Kg^{-1}

The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows;

Parameter	Pb^{2+}	OH^-
Concentration (mmoL^{-1})	12.03627	0.0011765

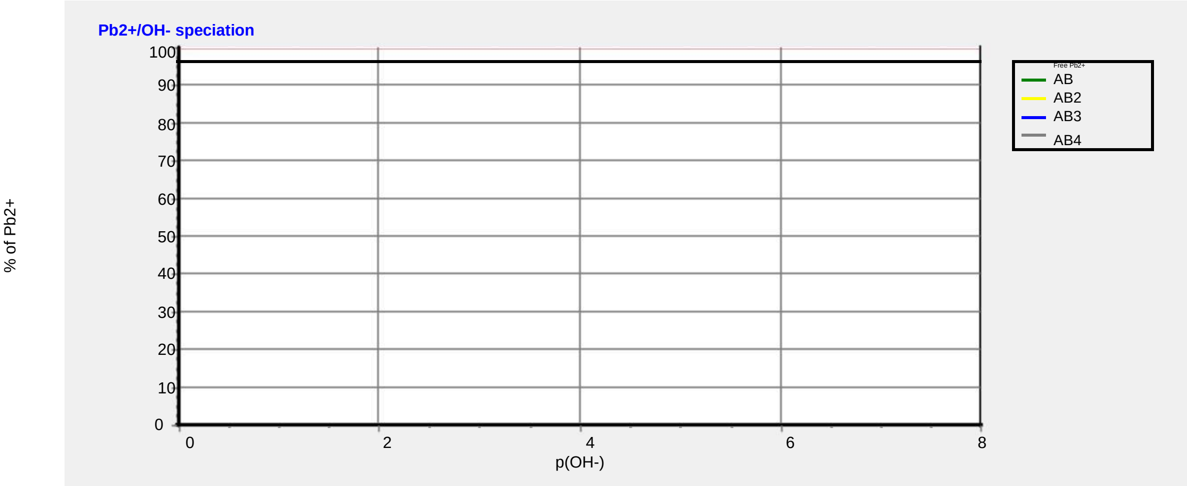

Figure 3: Speciation diagram for the Pb^{2+} + OH^- system at 27.5^0 C in simulated river water as a function of $[OH^-]$ denoted by the symbol p (OH^-) at pH 8.0

Graphs for complexes are not shown in figure 3 because all the complexes that formed had less than 1% distribution. These species are however as shown below:

Symbol	*Complex*	*% distribution*
AB	$PbOH^+$	< 1
AB_2	$Pb(OH)_{2\ (aq)}$	< 1
AB_3	$Pb(OH)_3^-$	< 1
AB_4	$Pb_3(OH)_4^{2+}$	< 1

[These % distribution values are obtained real-time from the SPECIES computer program].

In this model, at pH 8.0, the speciation diagram for the Pb^{2+} + OH^- system did not show any hydroxo complexes that formed since they were highly destabilised as evident from their negative stability constant values shown in table 5. This is also because the system was assumed to be at equilibrium with air having a CO_2 fugacity of $10^{-3.5}$ bar (1 bar = 10^5 Pa). Now, in such a system, carbonato-complexes dominate speciation of hydroxo-complexes on a wide range of solution conditions unless $f(CO_2)$ is significantly lower than the atmospheric levels (Powell and Pettit, 2009). Otherwise, at $[Pb^{II}]_T$ of 12.03627 mmol dm^{-3} (which was the concentration of Pb in the river) and $[Pb^{II}]_T < 1$ mg dm^{-3} (a condition typical of environmental systems), the dominant hydrolysis species that form in aqueous solution are monomeric $PbOH^+$, $Pb(OH)_{2\,(aq)}$ and $Pb(OH)_3^-$. Higher-order monomeric species $Pb(OH)_4^{2-}$ and $Pb(OH)_6^{4-}$ have been postulated at pH > 13 (Ferri and Branica, 1989) but remain controversial (Perera et al., 2001).

Chemical Modelling of Cu^{2+} + CO_3^{2-}, HCO_3^- Systems using Corrected Stability Constants

Table 6: CO_3^{2-} and HCO_3^- complexes of Cu and their stability constants

Reactions for complex formation	[1]IUPAC stability constant values	[2]Corrected stability constant values
	$K_1 = 6.75 \pm 0.03(R)$	$K_1 = 6.43$
	$\beta_2 = 10.3 \pm 0.1(R)$	$\beta_2 = 10.30$
	$K = 1.84 \pm 0.1(R)$	$K = 2.00$

[1] IUPAC Recommended (R) values for the Cu^{2+} + CO_3^{2-}, HCO_3^- systems at 298.15K, 1 bar and $I_m = 0$ mol Kg^{-1}

The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows;

Parameter	Cu^{2+}	CO_3^{2-}	HCO_3^-
Concentration ($mmolL^{-1}$)	1.079533	0.5	4.30328

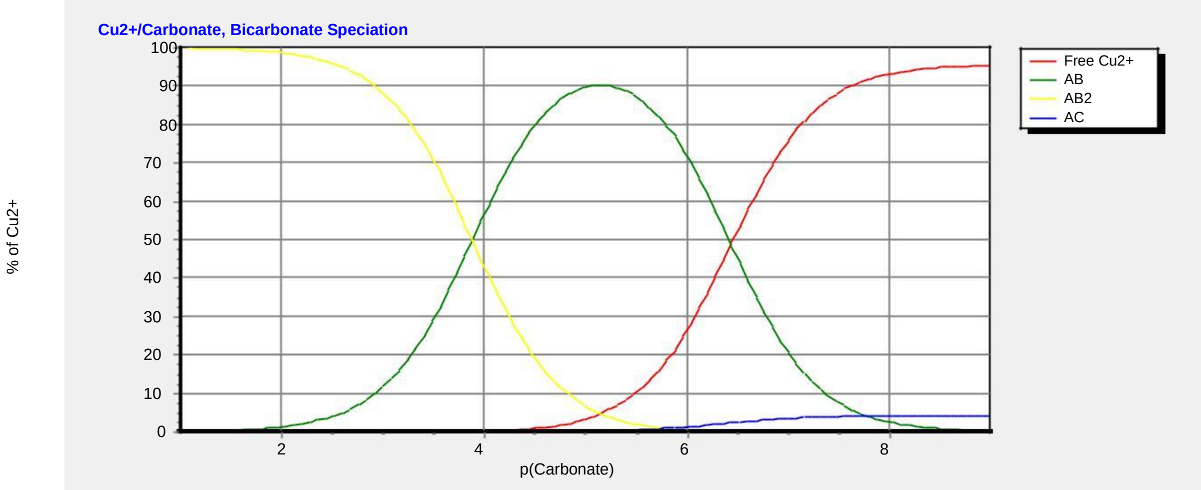

Figure 4: Speciation diagram for the Cu^{2+} + CO_3^{2-}, HCO_3^- system at 27.5^0 C in simulated river water as a function of $[CO_3^{2-}]$ [denoted by the symbol p (carbonate)] at pH 8.0

Figure 4 represents the following species;

Symbol	*Complex*	*% distribution*
AB	$CuCO_{3\,(aq)}$	90.45
AB_2	$Cu(CO_3)_2^{2-}$	4.93
	Free $Cu^{2+}_{(aq)}$	4.93
AC	$CuHCO_3^+$	4.07

[These % distribution values are obtained real-time from the SPECIES computer program].

At $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ of 1.10 mmol dm^{-3} the species $Cu(CO_3)_2^{2-}$ was therefore the main contributor of Cu^{II} speciation. As $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ increased, the species $Cu(CO_3)_2^{2-}$ diminished in abundance as the species $CuCO_{3(aq)}$ started to increase in abundance. $Cu(CO_3)_2^{2-}$ and $CuCO_{3(aq)}$ were in equilibrium at $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ of 3.87 mmol dm^{-3} with 49.80% distribution. Beyond this concentration, the species $CuCO_{3(aq)}$ dominated speciation of Cu^{II}. $CuCO_{3(aq)}$ attained a maximum distribution of 90.45% at $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ of 5.12 mmol dm^{-3}, slightly above the value reported by (Powell, 2007) of 82% at $I_m = 0$ mol kg^{-1}, t = 25^0 C and $f(CO_2) = 10^{-3.5}$ bar and pH 8.1. This was probably due to differences in temperature and ionic strength used in this model. As $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ increased $CuCO_{3(aq)}$ started to diminish as the free $Cu^{2+}_{(aq)}$ ions started to form and increased in distribution. Free $Cu^{2+}_{(aq)}$ ions was at equilibrium with $Cu(CO_3)_2^{2-}$ at $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ of 6.43 mmol dm^{-3} with 50.20% abundance. Beyond this concentration, free $Cu^{2+}_{(aq)}$dominated speciation. This is because CO_3^{2-} forms ion pairs to a significant extent with Na^+, Mg^{2+} and Ca^{2+} in natural waters. In this model, the species $CuHCO_3^+$ formed at $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ of 5.27 mmol dm^{-3} and attained a maximum distribution of 4.07%, then the distribution curve became uniform throughout all the pH and concentration ranges. This was as a result of using the exact stability constants for $CuHCO_3^+$ with an accurate model for the system (Pettit and Pettit, 2009). $CuHCO_3^+$ formation constants are sufficiently so small that, $CuHCO_3^+$ is unlikely to be a significant environmental species. It can, however, become a significant species in studies conducted at high levels of bicarbonate (Grenthe et al., 1992). Therefore, at $[CO_3^{2-}]_T$ and $[HCO_3^-]_T$ of 4.30328 mmol^{-1} and below, the system was safe. But beyond this concentration, the system could be highly polluting due to the significant levels of the free $Cu^{2+}_{(aq)}$ ions.

Chemical Modelling of Cu^{2+} / Cl^-Systems using [2]Corrected Stability Constants

Table 7. Cl^- complexes of copper and their stability constants

Reactions for complex formation	[1]IUPAC stability constant values	[2]Corrected stability constant values using the SPECIES computer program
	$K_1 = 0.83 \pm 0.09(R)$	$K_1 = 0.99$
	$\beta_2 = 0.6 \pm 0.3(P)$	$\beta_2 = 0.28$

[1]IUPAC Recommended (R), Provisional (P) values for the Cu^{2+} / Cl^- systems at 298.15K, 1 bar and $I_m = 0$ mol Kg^{-1}

The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows;

Parameter	Cu^{2+}	Cl^-
Concentration (mmolL^{-1})	1.079533	1.7678

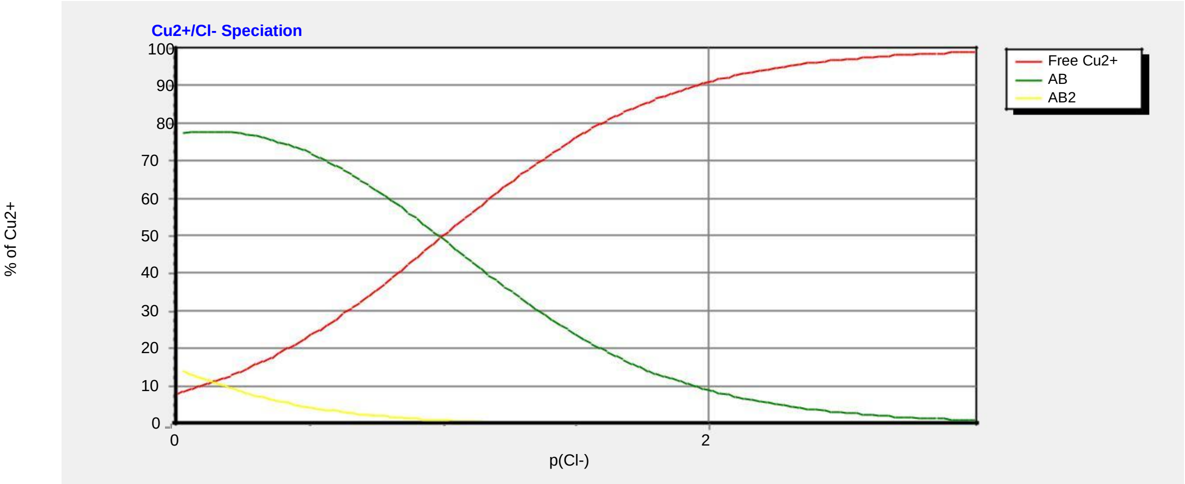

Figure 5: Speciation diagram for the Cu^{2+} / Cl^- system at 27.5^0 C in simulated river water as a function of $[Cl^-]$ [denoted by the symbol $p(Cl^-)$ at pH 8.0

Figure 5 represents the following species;

Symbol	*Complex*	*% distribution*
	Free $Cu^{2+}_{(aq)}$	85.16
AB	$CuCl^+$	14.43
AB_2	$CuCl_{2(aq)}$	< 1

[These % distribution values are obtained real-time from the SPECIES computer program].

Cu^{II} is thought to form four consecutive chloro – complexes in aqueous solution;

In this model, two chlo-complexes formed; $CuCl^+$ and $CuCl_{2(aq)}$. Since the concentrations required for the formation of these complexes is well above those in environmental systems at low ionic strength, they will not contribute significantly to Cu speciation in non-saline systems (Powell et al., 2011). At $[Cl^-]_T$ of 1.76 $mmol^{-1}$ (which was the concentration of Cl^- of the river), the species $CuCl^+$ had a distribution of 14.43%. The distribution of $CuCl_{2(aq)}$ at this $[Cl^-]_T$ was < 1% while the free Cu^{2+} ions had a distribution of 85.16% which was high, indicating potential polluting ability of the system. The species $CuCl^+$ and $CuCl_{2(aq)}$ did not contribute significantly to speciation of copper. Furthermore these complexes are weak. The complex $CuCl_{2(aq)}$ is less stable than $CuCl^+$. $CuCl_{2(aq)}$ formed at $[Cl^-]_T$ of 0.03 $mmol^{-1}$ (which was less than the concentration of Cl^- in the river) with a distribution of 14.02%. It diminished to < 1% at $[Cl^-]_T$ of 1.31 $mmol^{-1}$.

Chemical Modelling of Cu^{2+} / OH^- Systems using Corrected Stability Constants

Table 8: OH^- complexes of copper and their stability constants

Reactions for complex formation	[1]IUPAC stability constant values	[2]Corrected stability values using the SPECIES computer program
	$K_1 = -7.95 \pm 0.16(R)$	$K_1 = -7.79$
	$\beta_2 = -16.20 \pm 0.2(P)$	$\beta_2 = -16.52$
	$\beta_3 = -26.60 \pm 0.09(R)$	$\beta_3 = -25.87$
	$\beta_4 = -39.74 \pm 0.18(P)$	$\beta_4 = -39.09$

[1] IUPAC Recommended (R), Provisional (P) values for the Cu^{2+} / OH^- systems at 298.15K, 1 bar and $I_m = 0$ mol Kg^{-1}

The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows;

Parameter	Cu^{2+}	OH^-
Concentration ($mmoL^{-1}$)	1.079533	0.0011765

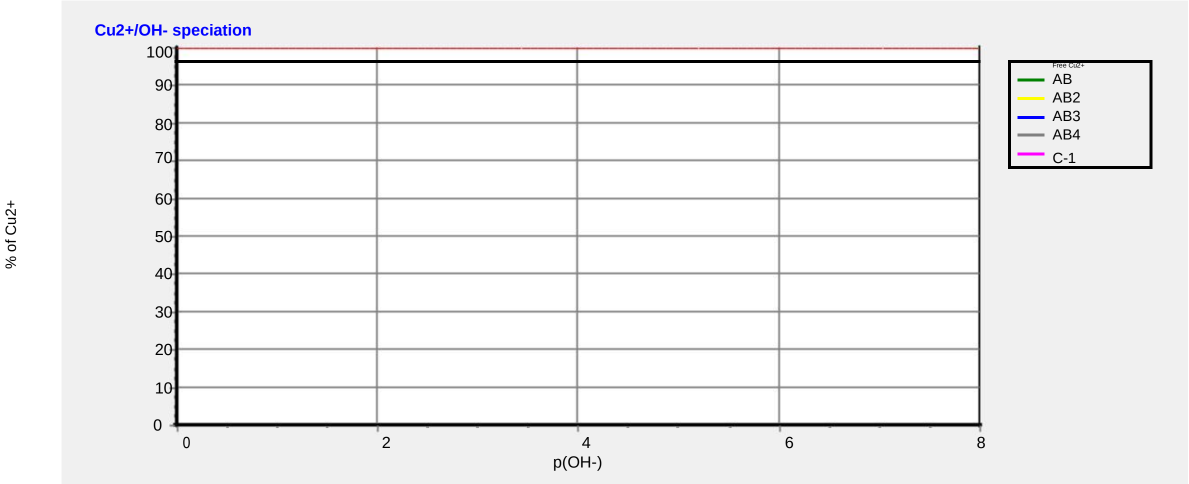

Figure 6: Speciation diagram for the Cu^{2+} / OH^- system at 27.5^0 C in simulated river water as a function of $[OH^-]$ [denoted by the symbol p (OH^-) at pH 8.0

Graphs for complexes are not shown in figure 6 because all the complexes that formed had less than 1% distribution. These species are however as shown below:

Symbol	***Complex***	***% distribution***
AB	$CuOH^+$	< 1
AB_2	$Cu(OH)_{2(aq)}$	< 1
AB_3	$Cu(OH)_3^-$	< 1
AB_4	$Cu(OH)_4^{2-}$	< 1

[These % distribution values are obtained real-time from the SPECIES computer program].

Figure 6 shows a speciation diagram for the Cu^{2+} + OH^- system, based on the corrected stability constants recorded in table 8. In this model (and at pH 8.0), no hydroxo species formed because they are highly destabilized as shown by the large negative values of the stability constants. This is because the values for the formation constants are strongly divergent (Pettit and Powell, 2005). The proposed speciation schemes even do not agree about the number and stoichiometry of the mono- and / or poly-nuclear complexes formed. Indeed, the identification and quantification of the mononuclear $Cu(OH)_n^{(2-n)+}$ complexes (n = 1,2) is difficult due to the formation of di- and trinuclear complexes even at quite modest values of $[Cu^{II}]_T$. Furthermore, the formation of (possibly metastable) —Cu^{II} – hydroxide‖ colloidal suspensions and / or precipitates in slightly hydrolyzed solutions adds complexity in terms of measurement, accuracy and data interpretation (Powell et al., 2011).

CONCLUSION

Metals in aqueous systems can generate chemical species that may exist in different quantities. These species cannot be identified by a simple analysis of water samples and could only be calculated using the results obtained by analyzing all the physical and chemical parameters determined by the SPECIES program. Speciation calculations indicate that in fresh water systems in equilibrium with atmospheric CO_2, at pH 8.0 – 9.0 and in the absence of organic ligands, the speciation of Pb and Cu was dominated by the carbonato species $PbCO_{3(aq)}$and $CuCO_{3(aq)}$ with moderate contributions from $Pb(CO_3)_2^{2-}$, $Cu(CO_3)^{2-}$, $Pb^{2+}_{(aq)}$ and $Cu^{2+}_{(aq)}$. $PbCO_3$ is harmful ecotoxicologically since it limits plant chlophyl synthesis. Chloro-complexes of Pb and Cu were weak, therefore, the free metal ions $Pb^{2+}_{(aq)}$ and $Cu^{2+}_{(aq)}$ dominated speciation. This showed high levels of toxicity of the river.

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BIO-DATA

James Amayi is currently a Chemistry teacher at Matsakha High School-Kakamega, Kenya. He is also a postgraduate student at university of Eldoret finalizing his Msc in Chemistry. He is also a part-time lecturer at Mount Kenya University where he teaches analytical chemistry. He is involved in extensive research in the fields of water chemistry and bioinorganic chemistry and has published widely in these areas.