Chemical Speciation, Stability and Toxicity of Sulphate and Phosphate Salts of Copper

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Abstract

Chemical modelling involves use of published stability constant data to predict equilibrium distribution of metal species under various conditions of water quality together with known concentrations of various ions and suspended solids in the water and to complete the equilibrium concentrations (or activities) of the various species. An extensive thermodynamic data consisting of bank of all conceivable stability constants for a system is needed.To model the speciation of Cu with the common environmental ligands SO_4^{2-} *and* PO_4^{3-}*method. Cu was analysed by atomic absorption spectrophotometer. Turbidimetric method using a Uv-visible spectrophotometer, Spectroscan 30 calibrated was used to study* SO_4^{2-}*at 420 nm providing a light path of 2.5 to 100 nm. Phosphate was determined with a spectrophotometercalibrated at 690 nm using ammonium molybdate, concentrated sulphuric acid, stannous chloride reagent and standard phosphate solution. Chemical modelling was performed using the specific ion interaction theory (SIT). SIT uses an extended Debye-Hückel expression and goes beyond the more simple Davies equation. It does this by adding medium specific properties and by including ion-pairing between the medium ions and the species involved in the equilibrium reaction.Results:The distribution of* $CuSO_{4\,(aq)}$ *was 19.37 % with the free sulphate distribution at 80.28%.*$CuSO_{4(aq)}$ *is stable while at pH 8.0 and* $[Cu^{2+}]_T$ *=1.078533 mmo/L, the maximum concentration of* $CuHPO_{4\,(aq)}$ *occurs at pH 8.0; it reaches 31.69 % of* $[Cu^{II}]_T$ *when* $[PO_4^{3-}]_T$ *= 0.44892 mmol*$^{-1}$*and a maximum of 62.32 % when* $[Cu^{II}]_T$ *= 0.09 mmol/L.* $CuHPO_{4(aq)}$ *is unstable.*

Keywords: Speciation, SIT, modeling

INTRODUCTION

Heavy-metal toxicity could be affected by climate change. For copper, the LC_{50} (the concentration lethal to half of any given species over a certain time) decreases with temperature — meaning that toxicity increases. The effect is so strong that if Earth continues to warm at the current rate, the LC_{50} for one species she has studied, fathead minnows (*Pimephales promelas*), will be only half as much in 2060 as it is now. "This has some pretty severe implications for water-quality criteria (Lovett, 2010).

Syntheses of the classical complexes are carried out in aqueous solution by taking a metal ion in solution and adding the ligands. Whenever a metal ion is present in aqueous solution, it is surrounded by a number of water molecules. The number of water molecules x surrounding a metal ion is known as its hydration sphere and this depends on the charge and size of the metal ion. Some of these water molecules are bonded to the metal ion through coordinate linkage. The number of water molecules *n* that are bonded to a metal ion is its coordination number. The exact value of *n* of a metal ion in aqueous solution can be obtained by looking at their electron spectra and magnetic moment and comparing them with those of the aquo complexes whose structure and coordination number are definitely known from their crystal structure determined by X-ray diffraction in the solid state (Chakrabarty, 2012).

MATERIALS AND METHODS

Experimental procedures

Sulphate

Sulphate was determined by turbidimetric method using a Uv-visible spectrophotometer, Spectroscan 30. The apparatus used were a magnetic stirrer with stirring bars, spectrophotometer at 420 nm providing a light path of 2.5 to 100 nm, a stopwatch and a measuring spoon of capacity 0.2 to 0.3 ml. The reagents used were;

(a) Conditioning reagent, prepared by mixing 50 ml glycerol with a solution containing 30 ml concentrated HCl, 300 ml distilled water, 100 ml 95% ethyl alcohol and 75 g NaCl.
(b) Barium chloride crystals, 20-30 mesh.
(c) Stock sulphate solution, prepared by dissolving 1.4798 g anhydrous Na_2SO_4 in distilled water and diluting to 1000 ml. 1 ml = 1 mg SO_4^{2-}.
(d) Standard sulphate solution, prepared by diluting 10 ml of stock solution to 100 ml with distilled water, 1 ml = 0.1 mg SO_4^{2-}.

To construct the calibration curve, in 250 ml conical flask was measured 10.0, 20.0, 30.0, 40.0, 50.0 ml of standard sulphate solution and diluted to 100 ml. A 5.0 ml conditioning reagent was added and mixed well using magnetic stirrer. The speed of stirring was the same for both standards and samples. As stirring continued, about 0.5 g $BaCl_2$ crystals were added and stirring continued for one minute. Immediately after the one minute, 10 ml of the solution was poured into the absorption cell and the optical density measured at 420 nm at 30 seconds intervals for four minutes while taking the maximum turbidity which was after a period of 2 minutes after completion of stirring. A reagent blank was carried out using distilled water. Then a calibration curve was prepared for sulphate concentration v/s absorbance. The sample measurement was done by measuring in a 250 ml conical flask a suitable quantity of the sample and diluting to 100 ml and repeating the procedure as for standards as already explained. The calculation was done using the formula;

SO_4^{2-} (mg / l) = Concentration of mg/l, obtained after comparison with calibration curve X D where

D = dilution factor

Phosphate

The apparatus used was a Uv-visible spectrophotometer calibrated at 690 nm and glassware washed with HCl and rinsed well with distilled water. The reagents used were;

(a) Phenolphthalein indicator aqueous solution.
(b) Strong acid solution, prepared by slowly adding 300 ml concentrated H_2SO_4 to about 600 ml distilled water. It was cooled and then 4.0 ml concentrated HNO_3 was added and diluted to 1 litre.

(c) Ammonium molybdate reagent, prepared by dissolving 25g $(NH_4)_6 MO_7 O_{24}. 4H_2O$ in 175 ml distilled water. A 280 ml concentrated H_2SO_4 was cautiously added to 400 ml distilled water, cooled and molybdate solution added and diluted to 1 litre.

(d) Stannous chloride reagent,prepared bydissolving 2.5g fresh $SnCl_2. 2H_2O$ in 100 ml glycerolwas then heated in a water bath and stirred with a glass rod to hasten dissolution.

(e) Standard phosphate solution, prepared bydissolving 219.5 mg anhydrous KH_2PO_4 in distilled water and diluting to 1000 ml; 1.0 ml = 50.0 mg PO_4^{3-} - P.

(f) Working phosphate solution, prepared by taking 10 ml of standard phosphate solution into 100 ml volumetric flask and making up to 100 ml. This was 5 ppm PO_4^{3-} - P.

Preliminary sample treatment was done by adding 0.05 ml (1 drop) phenolphthalein indicator to 100 ml sample containing not more than 200 mg P and free from colour and turbidity. When the sample turned pink a strong acid solution was added drop wise to discharge the colour. A calibration curve was prepared in the range of 0 – 0.6 mg/l PO_4^{3-} - P by diluting 2, 4, 6, 8, 10 and 12 ml of working standard solution to 100 ml. This was equal to the concentration of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mg/l PO_4^{3-}-P. Colour development was achieved by adding with thorough mixing after each addition, 4.0 ml molybdate reagent and 0.5 ml (10 drops) stannous chloride reagent. Rate of colour development and intensity of colour depended on the temperature of the final solution. Hence, samples and standards for reagents were held within 2 °C of one another and the temperature range between 20 ^{0}C and 30 °C.

Colour measurement was carried out within a time interval of 10-12 minutes, using the same specific interval for all determinations. The colour was measured photometrically at 690 nm and compared with a calibration curve using distilled water blank. Light path length was increased for lower concentrations. A blank of reagents and distilled water was always run because the colour at first develops progressively and later fades. Equal timing conditions for sample and standards were maintained. At least one standard with each set of samples were prepared or once each day that tests were made. The calibration curve deviated from a straight line at the upper concentrations of the 0.3 to 2.0 mg / l range. Calculation was done by comparing the reading of absorbance of samples with calibration curve and noting down the concentration as mg / l PO_4^{3-} - P. The presence of any dilution was multiplied with the observed concentration and the final concentration noted down as PO_4^{3-}- P mg / l.

Copper

Copper was determined by digesting a known volume of water sample with analytical grade HNO_3. The digested sample was filtered into a 20 ml standard flask, made up to the mark with distilled deionized water and stored in a nitric acid pre-washed polyethylene bottle in the refrigerator prior to the chemical analysis. 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. Wavelengths setting of the spectrometer used were done daily by the standard instrumental procedures and other equipment used was always calibrated against reference standards. The digested samples were analysed by atomic absorption spectrophotometer.

RESULTS

Chemical modelling of the Cu^{2+} - SO_4^{2-} system based on the corrected stability constants using specific ion interaction theory (SIT)

Table 1: Sulfato complexes of copper and their stability constants

Reactions for complex formation	[1]IUPAC stability constant values	Corrected stability constant values at I_m = 0.00453 M using SIT
$Cu^{2+} + SO_4^{2-} \rightleftharpoons CuSO_{4(aq)}$	$K_1^0 = 2.35 \pm 0.05$ (R)	$K_1^0 = 2.598$

[1]IUPAC Recommended (R) values for the Cu^{2+} / SO_4^{2-} systems at 298.15K, 1 bar and $I_m = 0$ molkg^{-1}

[2]Corrected stability constant values at I_m = 0.00453 M using SIT using the following real-time data:

Medium – $NaClO_4$
Ionic strength – 0.00453 M
Temperature – 28^0 C
Cation – Cu^{2+}
Anion – SO_4^{2-}
Cation SIT parameter – 0.32 ± 0.02
Anion SIT parameter - -0.14 ± 0.06
Equation $Cu^{2+} + SO_4^{2-} \rightleftharpoons CuSO_{4(aq)}$
log K (c) = 2.35 (molar)
log K (m) = 2.348 (Molal)
Molality (mol kg^{-1}) = 0.005
Molarity (mol dm^{-3}) = 0.005
log K^0 = 2.597
$\sum z^2 = -8$
$\sum \varepsilon = -0.18$
D = 0.0312

Figure 1 shows the changes in stability constant (K_1) as a function of molality and molarity.

Molality —— ✕ log K^0 =2.598 ✕ Starting point
Molarity ——

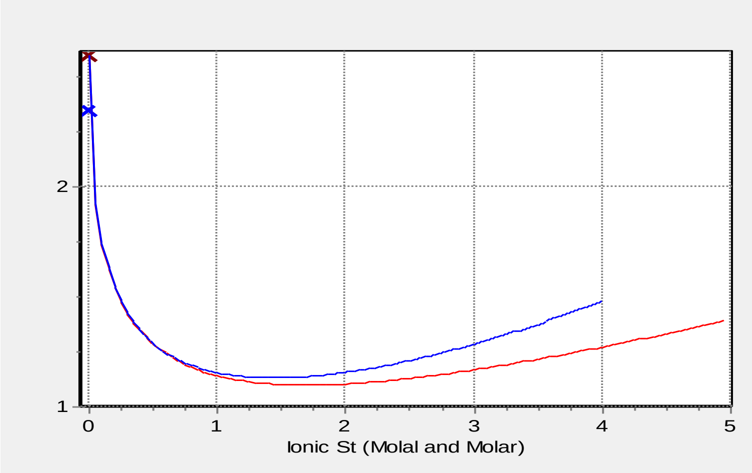

Figure 1: Log K as a function of molality and molarity

Table 2: Stability constants corrected using SIT forthe reaction;

$Cu_{(aq)} + SO_4^{2-}{}_{(aq)} \rightleftharpoons CuSO_{4(aq)}$ at 28^0C NaClO$_4$

Ionic Strength (molal)	(Molar)	log K(m)	log K(c)
0.000	0.000	2.598	2.598
0.050	0.050	1.922	1.924
0.100	0.099	1.738	1.741
0.150	0.149	1.622	1.626
0.200	0.198	1.538	1.544
0.250	0.246	1.473	1.480
0.300	0.295	1.421	1.428
0.350	0.343	1.378	1.386
0.400	0.392	1.341	1.351

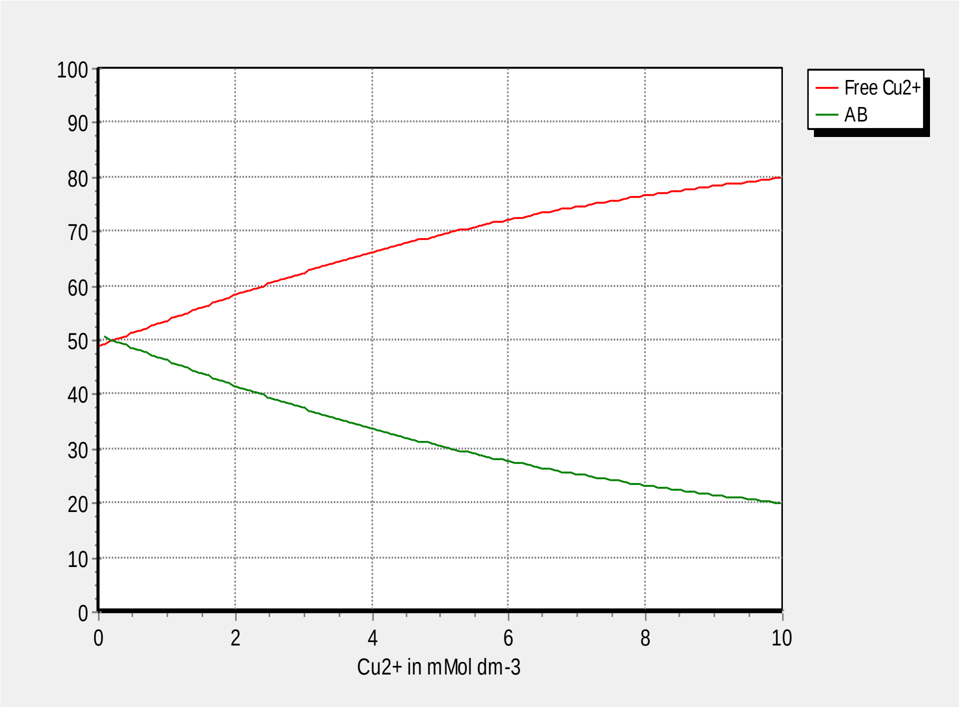

Figure 2: Speciation diagram for the Cu^{2+} + SO_4^{2-} system at 27.5 ^{0}C in simulated river water with total concentrations $[Cu^{2+}]_T$ = 1.0795 mmol^{-1}, $[SO_4^{2-}]_T$ = 2.64 mmol/L.

The total concentration of Cu^{2+} was set to 1 mmol/L, and it was assumed that the system was in equilibrium with air having a CO_2 fugacity of $10^{-3.5}$ bar (1 bar = 10^5 Pa). Log $K_{10}[CO_2(g) = CO_2(aq)]$ =-1.5 (Morel and Hering, 1993).

Figure 3 shows the speciation diagram of Cu^{2+} + SO_4^{2-} system when varying the concentration of $[SO_4^{2-}]_T$ and maintaining constant the concentration of $[Cu^{2+}]_T$ =1.078533 mmol/L.

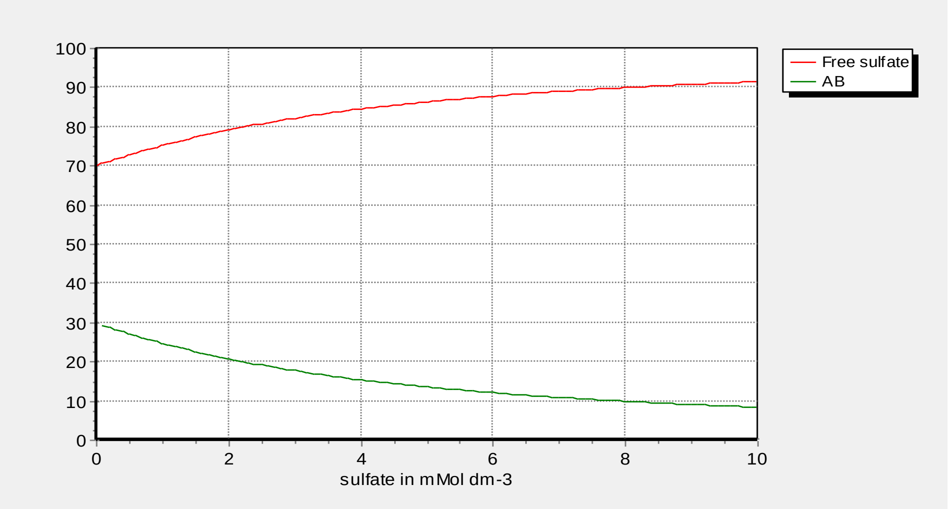

Figure 3: Speciation diagram for the Cu^{2+} + SO_4^{2-} system at 27.5 ^{0}C in simulated river water as a function of SO_4^{2-} with total concentrations $[Cu^{2+}]_T$ = 1.0795 mmol/L, $[SO_4^{2-}]_T$ = 2.64 mmol/L

The total concentration of SO_4^{2-} was set to 3 mmol/L, and it was assumed that the system was in equilibrium with air having a CO_2 fugacity of $10^{-3.5}$ bar (1 bar = 10^5 Pa). Log $K_{10}[CO_2(g) = CO_2(aq)]$ =-1.5 (Morel and Hering, 1993).

Copper Phosphate

Table 3: Phosphato complexes of copper and their stability constants

Reactions for complex formation	^{1}IUPAC stability constant values	Corrected stability constant values at I_m =0.00453 M using SIT
$Cu^{2+} + HPO_4^{2-} \rightleftharpoons CuHPO_{4(aq)}$	$K_1^0 = 3.52 \pm 0.2$ (R^1)	$K_1^0 = 2.598$

^{1}IUPAC Recommended (R) values for the Cu^{2+} / PO_4^{3-} systems at 298.15K, 1 bar and $I_m = 0$ molkg^{-1}

^{2}Corrected stability constant values at I_m = 0.00453 M using SIT using the following real-time data:

Medium – $NaClO_4$
Ionic strength – 0.00453 M
Temperature – 28 ^{0}C
Cation – Cu^{2+}
Anion – PO_4^{3-}
Cation SIT parameter – 0.32 ± 0.02
Anion SIT parameter - -0.25 ± 0.03
Equation $Cu^{2+} + HPO_4^{3-} \rightleftharpoons CuHPO_{4(aq)}$
log K (c) = 3.25 (molar)
log K (m) = 3.248 (molal)
Molality (mol kg^{-1}) = 0.005
Molarity (mol dm^{-3}) = 0.005
log K^0 = 3.624
$\sum z^2 = -8$
$\sum \varepsilon = -0.18$

D = 0.0312

Figure 4 and table 3 show the changes in stability constant (K1) as a function of molality and molarity.

Molality ——— ╳ log K^0 =2.59 ╳ Starting point
Molarity ———

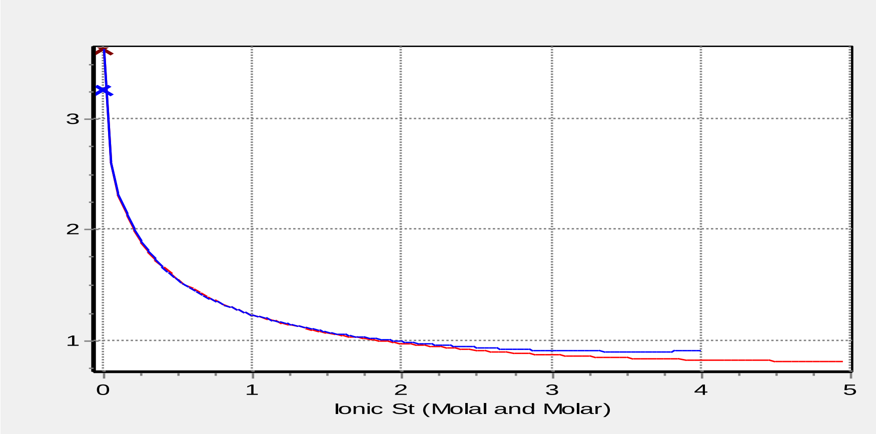

Figure 4: Log K as a function of Molality and Molarity

Table 4: Stability constants corrected using SIT for the reaction

$Cu^{2+}_{(aq)} + HPO_4^{3-} \rightleftharpoons CuHPO_{4\,(aq)}$ at 28°C $NaClO_4$

Ionic Strength (molal)	(Molar)	log K(m)	log K(c)
0.000	0.000	3.624	3.624
0.050	0.050	2.599	2.602
0.100	0.099	2.314	2.317
0.150	0.149	2.130	2.134
0.200	0.198	1.994	1.999
0.250	0.246	1.887	1.893
0.300	0.295	1.798	1.806
0.350	0.343	1.724	1.732
0.400	0.392	1.659	1.668
0.450	0.440	1.602	1.612
0.500	0.487	1.552	1.563

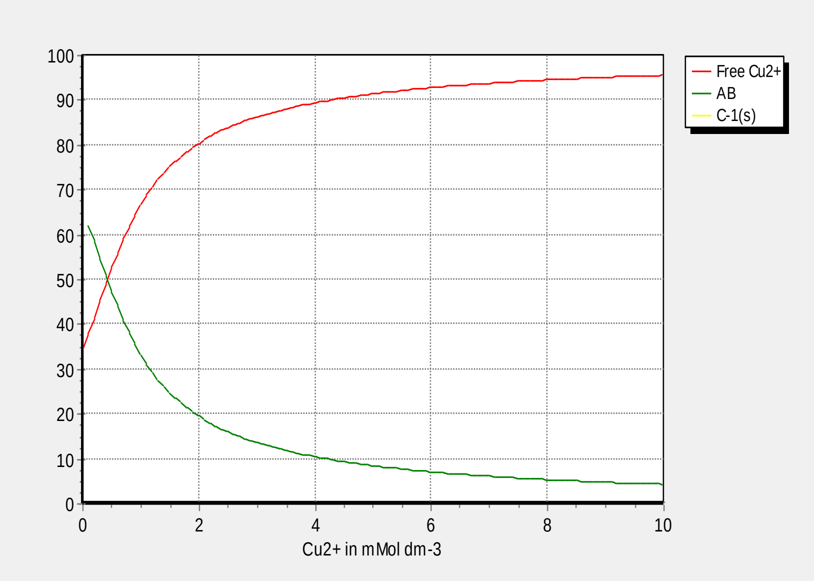

Figure 5: Speciation diagram for the Cu^{2+} + HPO_4^{3-} system at 27.5 ^{0}C in simulated river water with total concentrations $[Cu^{2+}]_T$ = 1.0795 $mmol^{-1}$, $[HPO_4^{3-}]_T$ = 0.44892 $mmol^{-1}$.

The total concentration of Cu^{2+} was set to 1 mmol/L, and it was assumed that the system was in equilibrium with air having a CO_2 fugacity of $10^{-3.5}$ bar (1 bar = 10^5 Pa). Log $K_{10}[CO_2(g) = CO_2(aq)]$ =-1.5 (Morel and Hering, 1993).

DISCUSSIONS

Figures 1 and 4 show that there was a rapid decrease in K_1 with increasing I_m and therefore the calculations were truncated at $[SO_4^{2-}]$ = 11.05 mM and $[PO_4^{3-}]_T$ = 1.076 × 10^{-6}mol dm^{-3}. However, even at this low $I_{m,}$ there was a significant activity coefficient effect [$\log_{10} K_1$ = 2.597 at I_m = 0.00453 M] for $[SO_4^{2-}]_T$ and K_1=3.498 at I_m= 0.00453M for $[PO_4^{3-}]_T$.

The speciation diagram in Figure 2 indicates that at pH 8.0 and $[Cu^{2+}]_T$ =1.078533 $mmol^{-1}$, $[SO_4^{2-}]$= 11.05mM the percentage of copper present as $CuSO_{4(aq)}$ was 46.13%. The "best" estimate for the formation of $CuSO_{4(aq)}$ was $\log_{10}$ = 2.598. In a similar study conducted by (Powell et al., 2007), the "best" estimate for the formation of $CuSO_{4(aq)}$ is $\log_{10}$ = 2.35 ± 0.05. $CuSO_{4(aq)}$ at I_m = 0.00453 M has a stability constant K_1^0 = 2.598, indicating that it is quite stable in a fresh water environment. Sulphate salts of copper (II) are chelate compexes. A chelate complex is more stable. The reason for this may be traced to increased entropy as attachment of a chelating ligand releases more number of water molecules and hence increases entropy. This increases its bioavailability and uptake by living organisms affecting biodiversity. From figure 2, it is evident that increasing the ionic strength of water will significantly reduce the concentration of $CuSO_{4(aq)}$. This can serve as a remedial measure to remove $CuSO_{4(aq)}$ from water bodies.

Figure 3 shows that on varying the concentration of $[SO_4^{2-}]_T$ and maintaining the concentration of $[Cu^{2+}]_T$ =1.078533 mmol/L constant the distribution of $CuSO_{4\ (aq)}$ was 19.37 % with the free sulphate distribution at 80.28%. In a similar study (Powell et al.,

2005) reported that at pH 6.5 and $[Cu^{2+}]_T = 10^{-9}$ mol dm^{-3}, the percentage of copper present as $CuSO_{4(aq)}$ is 46 % at $-\log_{10} [SO_4^{2-}] = 2.4$ and 18 % at $-\log_{10} [SO_4^{2-}] = 3.0$. Since this modelling was performed at basic pH of 8.0, the large fraction of free sulphate could be attributed to the "basic" sulphates such as antlerite, $Cu_3(OH)_4SO_{4(s)}$ and bronchantite, $Cu_4(OH)_6SO_{4(s)}$ that are sparingly soluble in basic media and thus may become important under certain conditions. $CuSO_4$ binds to organic matter and could be another reason why there is an increase in the fraction of free Cu^{2+} ions. These results indicate that $SO_4^{2-}{}_{(aq)}$ plays a major role in Cu^{II} speciation with inorganic ligands in weakly basic or strongly basic waters in equilibrium with CO_2. $CuSO_{4\ (aq)}$ is stable. SO_4^{2-} plays a minor role in Cu^{II} speciation with inorganic ligands in weakly acidic or near-neutral fresh waters in equilibrium with CO_2 (Powell *et al.,* 2007)

The speciation diagram in figure 5 indicates that at pH 8.0 and $[Cu^{2+}]_T = 1.078533$ mmol^{-1}, the maximum concentration of $CuHPO_{4\ (aq)}$ occurred at pH 8.0; it reached 31.69 % of $[Cu^{II}]_T$ when $[PO_4^{3-}]_T = 0.44892$ mmol/L and a maximum of 62.32 % when $[Cu^{II}]_T = 0.09$ mmol^{-1}. PO_4^{3-} is the most basic $H_nPO_4^{(3-n)-}$ species, and is therefore expected to be the strongest phosphate ligand. However, formation of $Cu(PO_4)_x^{(2-3x)+}$ complexes at higher pH is prevented, (or possibly accompanied) by metal ion hydrolysis. Phosphorous ligand form very stable complexes. They are σ donors, but can act as π acceptors that can accept *d* electrons form the metal into their π^* orbital. A definite trend is noticed when log k_f is plotted gainst the atomic number in the M^{2+} ions of the first transition series complexing with a ligand L. It is found that a maximum is reached at Cu^{2+} after which it decreases. This is known as the *Irving-Wallace series.* There are two reasons for this increase in stability. One is the electrostatic effect that depends on the size of the cation, and the other is the crystal field stabilization energy (CFSE). The sharper increase from d^6 to d^9 is due to additional CFSE. One thing that needs further explanation is that the Cu^{2+} complex is more stable than the corresponding Ni^{2+} complex, although the former has one more electron in the e_a level. This is because of strong Jahn-Teller distortion of the Cu^{2+} complex. The tetragonal distortion increases the bond strength of the four M-L bonds lying on the square plane that lead to higher stability (Chakrabarty, 2012).

The formation of copper-phosphate complexes is not significant (< 1 %) at typical environmental concentrations of $[Cu^{II}]_T = [PO_4^{3-}]_T = 10^{-6}$ mol dm^{-3}. This is due to the relatively low stability of phosphate complexes. Consequently, the measured pH changes in potentiometric studies are small for typical reactant concentrations ($0.001\ M \leq c_M, c_L \leq 0.01\ M$). This can be overcome by use of a large excess of metal ion or ligand. However, the stoichiometry of complexes formed in significant amount is constrained by the use of excess component, while the pH change upon complex formation becomes negligible in the case of excess phosphate (Powell *et al.,* 2005) Since $CuHPO_{4\ (aq)}$ is less stable, it does not contribute to speciation of copper and therefore has little impact on aquatic biodiversity.

CONCLUSIONS AND RECOMMENDATIONS

$CuSO_{4(aq)}$ is stable and will have a significant influence on Cu^{II} speciation in waters having a pH of 8.0 and above. $CuHPO_{4(aq)}$ is a weak complex and therefore unstable. The study of this complex burdened with difficulties due to the competing effects of Cu^{II} hydrolysis reactions. $CuHPO_{4(aq)}$ is not a significant species in waters with pH greater than 8.0 and therefore will not influence speciation of Cu^{II}. Several factors contribute to our understanding of the toxic effects of environmental exposure to chemical mixtures:

(a) Many of the effects of exposure are subtle and difficult to quantify.

(b) Many environmental contaminants are changed to metabolites of conjugates in the body, and these new products may also have biologic activity that may not be similar to the parent compound. Thus, even a single compound may become a functional mixture.

(c) A single environmental contaminant may lead to different effects when exposure occurs at different ages. Researchers need to design studies that will evaluate long-term, delayed, and potential trans-generational health effects resulting from environmental or occupational exposures.

(d) Humans may be exposed to nearly infinite number of combinations of conatminants, and we do not know what dose rnages or which biologic endpoints should be studied.

ACKNOWLEDGEMENT

The authors are indebted to Kenyatta University and University of Eldoret for use of their facilities for experimental work.

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