

# THE SPECIATION OF CADMIUM AND ZINC FROM PULP AND PAPER MILL EFFLUENT WITH INORGANIC LIGANDS

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## Abstract

The effluents from Webuye pulp and paper mill were analysed chemically using AAS to obtain the stoichiometric concentrations of the major anions and cations. However, this does not indicate how the components are distributed amongst possible species. The speciation calculation was performed using the available equilibrium constants for all the metal – ligand and proton – ligand species identified. The stoichiometric concentrations were used to construct a pH dependent model with corrected IUPAC stability constants using the SPECIES computer program. 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. The equilibrium distribution calculations showed that inorganic speciation behaviour was of three types; (a) Cd speciation was dominated by free Cd<sup>2+</sup><sub>(aq)</sub> with 62.68% distribution. Bicarbonate complexes could only form to significant levels at high [HCO<sub>3</sub><sup>-</sup>]<sub>T</sub> and high ionic strength. (b) Chloro-complexes of Cd that formed were CdCl<sup>+</sup>, CdCl<sub>2(aq)</sub> and CdCl<sub>3</sub><sup>-</sup>. Zn formed ZnCl<sup>+</sup>, ZnCl<sub>2(aq)</sub>, ZnCl<sub>3</sub><sup>-</sup> and ZnCl<sub>4</sub><sup>2-</sup>. All these complexes were weak. (c) No hydroxo-complex of Cd<sup>II</sup> formed because Cd<sup>II</sup> has a comparatively low affinity for oxygen donor ligands. These results indicated that for reliable speciation calculations of Cd<sup>II</sup> and Zn<sup>II</sup> in environmental systems, the accuracy of thermodynamic data is crucial. Discharge of effluent into the river was significant in speciation of Cd<sup>II</sup> and Zn<sup>II</sup>.

**Key words:** Model, inorganic, speciation, ligand, complex

## 1.0 Introduction

The speciation of a metallic element in an aqueous ecosystem depends on different chemical forms that may be encountered depending on the metal characteristics of the environment. This will depend on the physical-chemical conditions such as temperature, redox potential, pH, chemical complexity of the species that are present (Mizuike, 1987). Subsequently in surface waters, a metal may participate in countless chemical reactions balance from its point of emission up to its place of residence. The chemical forms of an element have different ecotoxicological properties, so its speciation determines its reactivity and its degree of nuisance. The chemical risk management and the choice of a method for rehabilitating a polluted site by a toxic metal do not depend only on the total concentration of the metal but also on its chemical speciation.

Most heavy metals are transition elements with incompletely filled d-orbitals. The d-orbitals provide heavy-metal cations with the ability to form complex compounds, which may or may not be redox-active. Thus, heavy metal cations play an important role as 'trace elements' in sophisticated biochemical reactions. The speciation of a metal in natural aquatic environments is affected by a large number of different, simultaneously occurring processes. This web of processes comprises various complexation reactions in the aqueous phase, precipitation and dissolution reactions, sorption at surfaces of particulate matter and so on. Trace metal speciation in natural waters has been based on the use of two different techniques: experimental measurements and computer modelling. The first approach is still limited by the lack of experimental techniques sufficiently sensitive and selective to detect individual species at the concentrations normally found in natural systems (Andren A. W., Robert T. W., 1993).

## 2.0 Materials and Methods

### 2.1 Experimental Procedures

Effluent (EFF) was collected as a composite samples 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 was 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 250 m 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 temperature, pH, alkalinity, chloride and heavy metals Cd and Zn. 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 was determined by titration. Chloride was analyzed by titration. The water was analyzed for metals Cd and Zn by AAS. 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.

### 3.0 Results and Discussion

Table 1: Average concentrations of physico-chemical parameters

Parameter	Temp	pH	Alkalinity (mg CaCO <sub>3</sub> /L)	Cl <sup>-</sup> mg/L
EFF	28.0	8.5	265.0	78.73
APD	27.5	8.0	110.5	62.67
*STDEV	0.0548	0.5	12.71	10.14

Key –APD- After point of discharge, EFF- Effluent, \*STDEV – Standard deviation

Temperature downstream was normal with no significant difference having an average of 27.5° C. The fluctuation of pH in the samples was from 7.6 to 8.5 which was within the prescribed limit. Effluent had alkalinity of 265.0 mg CaCO<sub>3</sub>. Downstream alkalinity ranged from 9.5 to 255.0 mg CaCO<sub>3</sub>. The average level of total alkalinity downstream was 110.5 mg CaCO<sub>3</sub>/l. This is below the prescribed limit for total alkalinity of 120.0 mg/ l (UNEP, 1992).

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 are found below the permissible value set at 250 mg/l in the study area.

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

Heavy metal	Cd (mg/L)	Zn (mg/L)
EFF	0.1317	0.5518
APD	0.1215	0.4627
*STDEV	0.0028	0.0341

\*Standard Deviation (±)

Key –APD- After point of discharge, EFF- Effluent

From Table 2; Cd and Zn were of average levels of 0.1317 and 0.5518 mg/L respectively in the 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 Cd and Zn downstream were 0.1215 and 0.4627 mg/L respectively. Water downstream is used for irrigation of many 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 much lower than the total levels.

### 3.1 Chemical modelling using the SPECIES computer program Cadmium

Table 3: Carbonato and bicarbonato complexes of Cadmium and their stability constants

Reactions for complex formation	<sup>1</sup> IUPAC stability constant values	<sup>2</sup> Corrected stability constant values (0.031 M) using the SPECIES computer program
$Cd^{2+} + CO_3^{2-} \rightleftharpoons CdCO_{3(aq)}$	$K_1 = 4.4 \pm 0.2(P)$	$K_1 = 4.08$
$Cd^{2+} + 2CO_3^{2-} \rightleftharpoons Cd(CO_3)_2^{2-}$	$\beta_2 = 6.37 \pm 0.1(P)$	$\beta_2 = 6.37$
$Cd^{2+} + HCO_3^- \rightleftharpoons CdHCO_3^+$	$K = 0.84 \pm 0.1(P)$	$K = 1.00$

<sup>1</sup>IUPAC Provisional (P) values for the  $Cd^{2+} + CO_3^{2-}, HCO_3^-$  systems at 298.15K, 1 bar and  $I_m = 0 \text{ mol Kg}^{-1}$

Figure 1 shows a speciation diagram for the  $Cd^{2+} + CO_3^{2-}, HCO_3^-$  system. The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows:

#### Concentration ( $\text{mmol}^{-1}$ )

$Cd^{2+}$  - 1.080855

$HCO_3^-$  - 4.30328

$CO_3^{2-}$  - 0.50

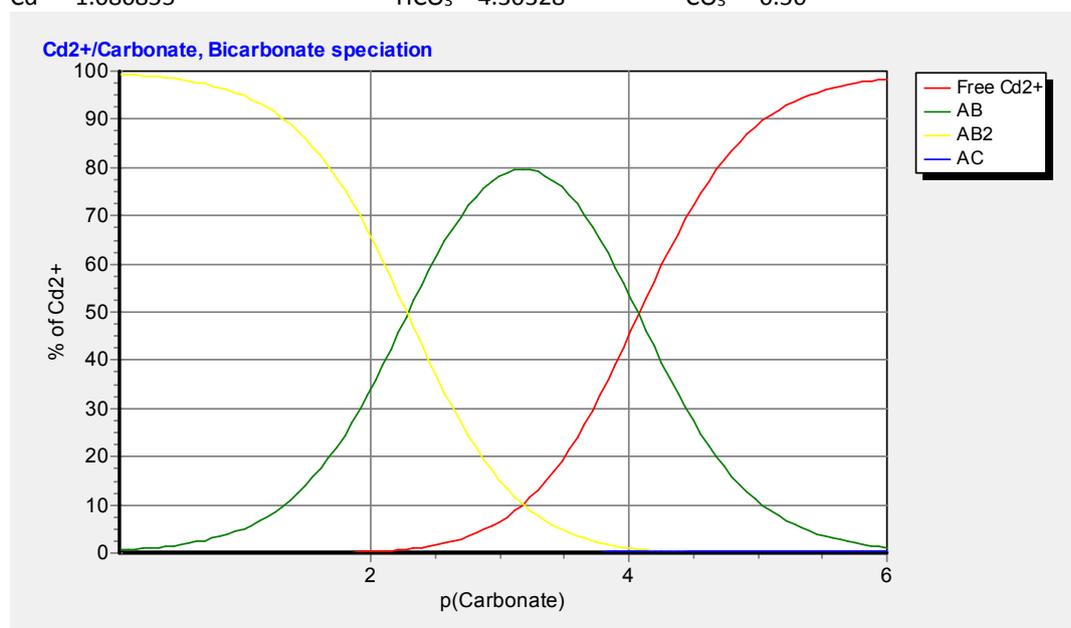


Figure 1: Speciation diagram for the  $Cd^{2+} + CO_3^{2-}, HCO_3^-$  system at 27.5<sup>o</sup> C in simulated river water as a function of Carbonate concentration [denoted by the symbol  $p$  (carbonate)] at pH 8.0. The total concentration of  $Cd^{II}$  was set at  $2.0 \text{ mmol dm}^{-3}$ ,  $[CO_3^{2-}]$  and  $[HCO_3^-]$  were allowed to vary between  $0.0 - 4.5 \text{ mmol dm}^{-3}$

**Note:** For all the modelled species in this paper, it was assumed that the system was at equilibrium with air having a  $CO_2$  fugacity of  $10^{-3.5}$  bar (1 bar =  $10^5$  Pa).  $\text{Log}_{10} [CO_{2(g)} = CO_{2(aq)}] = -1.5$  (Morel and Hering, 1993).

The chart legend at the extreme right of the speciation diagram represents the following complexes;

#### Complex % distribution at pH 8.0, $I_m = 0.00453 \text{ M}$ and $[CO_3^{2-}]/[HCO_3^-] = 4.30328 \text{ mmol}^{-1}$

Free  $Cd^{2+}_{(aq)}$  62.68

AB –  $CdCO_{3(aq)}$  36.97

AB2 –  $Cd(CO_3)_2^{2-}$  < 1

At  $[HCO_3^-]_T$  of  $4.30 \text{ mmol}^{-1}$  (which was the concentration of bicarbonate ions in the river) and pH 8.0, the speciation of  $Cd^{II}$  was dominated by  $Cd^{2+}_{(aq)}$  ions with a distribution of 62.68% indicating the toxicity of the

system. This agrees with Powell et al., (2011), that in weakly alkaline fresh water solutions  $7.5 < -\log_{10} \{[H^+] / C^0\} < 8.6$ , the speciation of Cd<sup>II</sup> is dominated by Cd<sup>2+</sup><sub>(aq)</sub>. At the same [HCO<sub>3</sub><sup>-</sup>]<sub>T</sub> of 4.30 mmol<sup>-1</sup>, the species CdCO<sub>3(aq)</sub> had a distribution of 36.97% and Cd(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> had < 1% distribution. However, despite increasing the [HCO<sub>3</sub><sup>-</sup>]<sub>T</sub>, no Cd<sup>II</sup> – bicarbonate complex formed. This is because there's considerable uncertainty in the equilibrium constant for the formation of the species CdHCO<sub>3</sub><sup>+</sup> and consequently the Cd<sup>II</sup> – bicarbonate complex will probably be less stable than those of Cu<sup>II</sup> and Pb<sup>II</sup> (Powell et al., 2009).

Table 4: Chloro complexes of cadmium and their stability constants

Reactions for complex formation	<sup>1</sup> IUPAC stability constant values	<sup>2</sup> Corrected stability constant values (0.031 M) using SPECIES computer program
$Cd^{2+} + Cl^- \rightleftharpoons CdCl^+$	$K_1 = 1.98 \pm 0.06(R)$	$K_1 = 2.14$
$Cd^{2+} + 2Cl^- \rightleftharpoons CdCl_{2(aq)}$	$\beta_2 = 2.64 \pm 0.09(R)$	$\beta_2 = 2.32$
$Cd^{2+} + 3Cl^- \rightleftharpoons CdCl_3^-$	$\beta_3 = 2.3 \pm 0.21(R)$	$\beta_3 = 3.03$

<sup>1</sup>IUPAC Recommended (R) values for the Cd<sup>2+</sup> / Cl<sup>-</sup> systems at 298.15K, 1 bar and  $I_m = 0$  mol Kg<sup>-1</sup>

Figure 2 shows a speciation diagram for the Cd<sup>2+</sup> / Cl<sup>-</sup> system. The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows:

#### Concentration (mmol<sup>-1</sup>)

Cd<sup>2+</sup> - 1.080855

Cl<sup>-</sup> - 1.7678

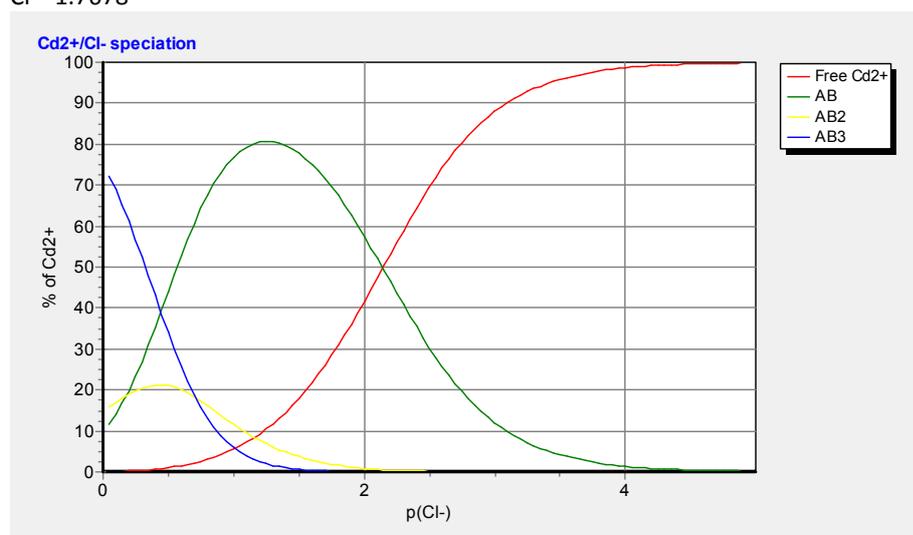


Figure 2: Speciation diagram for the Cd<sup>2+</sup> + Cl<sup>-</sup> system at 27.5<sup>o</sup> C in simulated river water as a function of Chloride concentration [denoted by the symbol p ( Cl<sup>-</sup> ) at pH 8.0. The total concentration of Cd<sup>II</sup> was set at 2.0 mmol dm<sup>-3</sup>, [Cl<sup>-</sup>] was allowed to vary between 0.0 - 2.0 mmol dm<sup>-3</sup>.

The chart legend at the extreme right of the speciation diagram represents the following complexes.

#### Complex% distribution at pH 8.0, $I_m = 0.00453$ M and [Cl<sup>-</sup>] = 1.7678 mmol<sup>-1</sup>

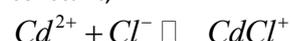
AB – CdCl<sup>+</sup> 69.37

Free Cd<sup>2+</sup><sub>(aq)</sub> 29.93

AB2 – CdCl<sub>2(aq)</sub> 1.76

AB3 – CdCl<sub>3</sub><sup>-</sup> < 1

Cd<sup>II</sup> forms three consecutive chloro – complexes in aqueous solution each with a well characterized stability constant;





All these complexes were weak and could best be studied in media of high  $[Cl^{-}]_T$ , high  $[Cl^{-}]_T : [Cd^{II}]_T$  ratios, and high ionic strength (Powell et al., 2011). At  $[Cl^{-}]_T$  of  $1.76 \text{ mmol}^{-1}$  (which was the concentration of chloride ions in the river), the dominant species was  $CdCl^{+}$  with a distribution of 69.37%. This species was therefore the main contributor to the  $Cd^{II}$  speciation. At this concentration the other species were free  $Cd^{2+}_{(aq)}$  with 29.93% distribution,  $CdCl_{2(aq)}$  with 1.76% abundance. The species  $CdCl_{3}^{-}$  also formed but in insignificant amounts. Most studies on the  $Cd^{2+} + Cl^{-}$  report the formation of the complex 1:3 complex ( $CdCl_{3}^{-}$ ). However, high concentrations of chloride ions are necessary for  $CdCl_{3}^{-}$  to form in sufficient amounts (Powell et al., 2011). There is an equilibrium established between  $CdCl^{+}$  with free  $Cd^{2+}$  at  $[Cl^{-}]_T$  of  $2.14 \text{ mmol}^{-1}$  with 50.0% distribution,  $CdCl^{+}$  with  $CdCl_{3}^{-}$  at  $0.44 \text{ mmol}^{-1}$  (39.79%),  $CdCl^{+}$  with  $CdCl_{2(aq)}$  at  $0.16 \text{ mmol}^{-1}$  (17.96%),  $CdCl_{3}^{-}$  with  $CdCl_{2(aq)}$  at  $0.70 \text{ mmol}^{-1}$  (18.31%) and  $CdCl_{3}^{-}$  with free  $Cd^{2+}_{(aq)}$  (5.99%). Figure 9 indicates that the predominance areas for the  $Cd^{2+}$  - chloro complexes overlap significantly.

Table 5: Hydroxo complexes of cadmium and their stability constants

Reactions for complex formation	<sup>1</sup> IUPAC stability constant values	<sup>2</sup> Corrected stability constant values
$Cd^{2+} + H_2O \rightleftharpoons CdOH^{+} + H^{+}$	$K_1 = -9.80 \pm 0.10(R)$	$K_1 = -9.64$
$Cd^{2+} + 2H_2O \rightleftharpoons Cd(OH)_{2(aq)} + 2H^{+}$	$\beta_2 = 7.81 \pm 0.13(R)$	$\beta_2 = 7.49$
$Cd^{2+} + 3H_2O \rightleftharpoons Cd(OH)_{3}^{-} + 3H^{+}$	$\beta_3 = -33.5 \pm 0.5(R)$	$\beta_3 = -32.77$
$Cd^{2+} + 4H_2O \rightleftharpoons Cd(OH)_{4}^{2-} + 4H^{+}$	$\beta_4 = -47.28 \pm 0.15(P)$	$\beta_4 = -47.49$

<sup>1</sup>IUPAC Recommended (R), Provisional (P) values for the  $Cd^{2+} / OH^{-}$  systems at 298.15K, 1 bar and  $I_m = 0 \text{ mol Kg}^{-1}$

Figure 3 shows a speciation diagram for the  $Cd^{2+} / OH^{-}$  system. The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows:

#### Concentration ( $\text{mmol}^{-1}$ )

$Cd^{2+}$  - 1.080855

$OH^{-}$  - 0.0011765

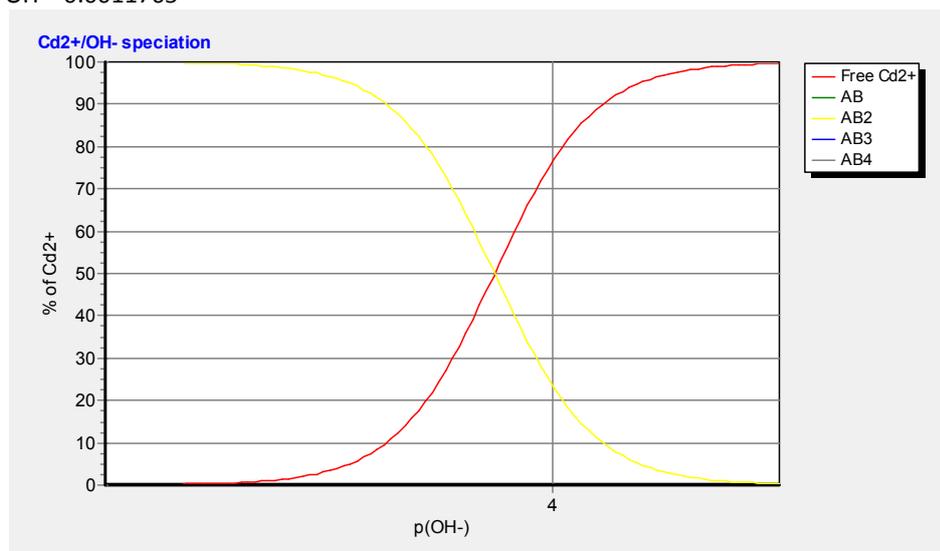


Figure 3: Speciation diagram for the  $Cd^{2+} / OH^{-}$  system at  $27.5^{\circ} C$  in simulated river water as a function of Hydroxide concentration [denoted by the symbol  $p(OH^{-})$ ] at pH 8.0. The total concentration of  $Cd^{II}$  was set at  $2.0 \text{ mmol dm}^{-3}$ ,  $[OH^{-}]$  was allowed to vary between  $0.0 - 1.0 \text{ mmol dm}^{-3}$

The chart legend at the extreme right of the speciation diagram represents the following complexes.

**Complex% distribution at pH 8.0,  $I_m = 0.00453\text{ M}$  and  $[\text{OH}^-] = 0.0011765\text{ mmol}^{-1}$**

AB2 – Cd(OH) <sub>2(aq)</sub>	100
AB – CdOH <sup>+</sup>	< 1
AB3 – Cd(OH) <sub>3</sub> <sup>-</sup>	< 1
AB4 – Cd(OH) <sub>4</sub> <sup>2-</sup>	< 1

At  $[\text{OH}]_{\text{T}}$  of  $0.0011765\text{ mmol}^{-1}$  (which was the concentration of OH<sup>-</sup> in the model water) at pH 8.0, the dominant species was Cd(OH)<sub>2(aq)</sub> with 100% distribution. Cd(OH)<sub>2(aq)</sub> was therefore the main contributor of Cd<sup>II</sup> speciation in the river. However there is an equilibrium established between Cd(OH)<sub>2(aq)</sub> and Cd<sup>2+(aq)</sup> at  $[\text{OH}]_{\text{T}}$  of  $3.75\text{ mmol}^{-1}$  with both having 50% abundance. Increase in  $[\text{OH}]_{\text{T}}$  results in a decrease of Cd(OH)<sub>2(aq)</sub> and an increase in Cd<sup>2+(aq)</sup>. This is however at high  $[\text{OH}]_{\text{T}}$ . This was possibly due to the formation of metastable Cd<sup>II</sup> – hydroxide colloidal suspensions and / or precipitates. All the hydroxo complexes of cadmium, that is, Cd(OH)<sub>2(aq)</sub>, CdOH<sup>+</sup>, Cd(OH)<sub>3</sub><sup>-</sup> and Cd(OH)<sub>4</sub><sup>2-</sup> are destabilized as shown by their large negative stability constant values. The aqueous chemistry of Cd<sup>II</sup> is dominated by its high affinity for sulphur and other “soft” donors. Thus, Cd<sup>II</sup> has a comparatively low affinity for the oxygen donor ligand: OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> as reflected in its stability constants with these ligands. Unlike Cu<sup>II</sup> and Pb<sup>II</sup>, Cd<sup>II</sup> has a rather weak tendency to form polymeric hydroxo- species in aqueous solution (Powell K. J, 2011).

**Zinc**

Table 6: Carbonato and bicarbonate complexes of zinc and their stability constants

Reactions for complex formation	<sup>1</sup> MINTEQA2 stability constant values	<sup>2</sup> Corrected stability constant values
$\text{Zn}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{ZnCO}_3(\text{aq})$	$K_1 = 5.30^{(*)}$	$K_1 = 4.98$
$\text{Zn}^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Zn}(\text{CO}_3)_2^{2-}$	$\beta_2 = 9.63^{(*)}$	$\beta_2 = 9.63$
$\text{Zn}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{ZnHCO}_3^+$	$K = 2.07^{(*)}$	$K = 2.39$

<sup>1</sup>These stability constant values are contained in the thermodynamic database of the MINTEQA2 model for the Zn<sup>2+</sup> + CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> systems.

Figure 4 shows a speciation diagram for the Zn<sup>2+</sup> + CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> system. The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows:

**Concentration (mmol<sup>-1</sup>)**

Zn<sup>2+</sup> - 7.07601

CO<sub>3</sub><sup>2-</sup> - 0.50

HCO<sub>3</sub><sup>-</sup> - 4.30328

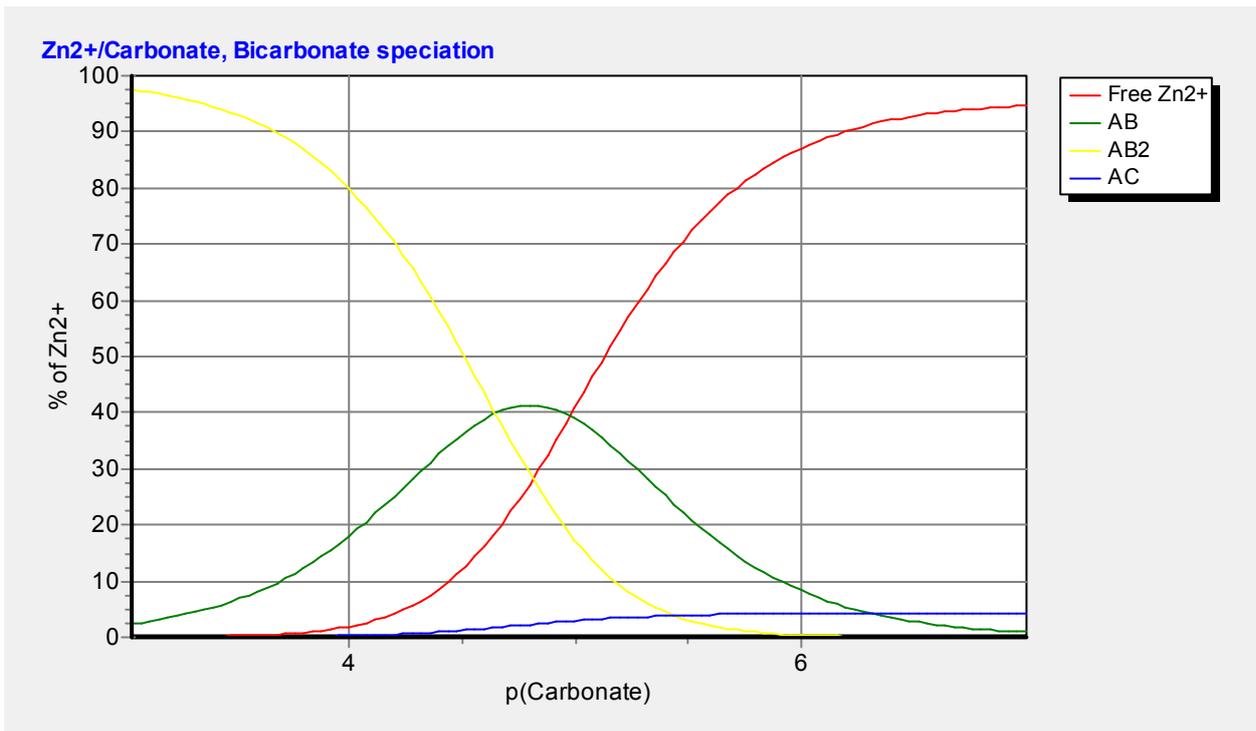


Figure 4: Speciation diagram for the  $Zn^{2+} + CO_3^{2-}, HCO_3^-$  system at 27.50 C in simulated river water as a function of carbonate and bicarbonate concentration [denoted by the symbol  $p(CO_3^{2-})$  at pH 8.0. The total concentration of  $Zn^{II}$  was set at  $8.0 \text{ mmol dm}^{-3}$ ,  $[CO_3^{2-}]$  and  $[HCO_3^-]$  were allowed to vary between  $3.0 - 7.0 \text{ mmol dm}^{-3}$

The chart legend at the extreme right of the speciation diagram represents the following complexes.

**Complex % distribution at pH 8.0,  $I_m = 0.00453 \text{ M}$  and  $[CO_3^{2-}]/[HCO_3^-] = 4.30328 \text{ mmol}^{-1}$**

AB – $ZnCO_{3(aq)}$	28.52
AB <sub>2</sub> – $Zn(CO_3)_2^{2-}$	64.44
Free $Zn^{2+}_{(aq)}$	5.99
AC – $ZnHCO_3^+$	1.41

At  $[HCO_3^-]_T$  of  $4.30 \text{ mmol}^{-1}$  (which was the concentration of the bicarbonate ions in the river) and at pH 8.0, the speciation of  $Zn^{II}$  was dominated by the species  $Zn(CO_3)_2^{2-}$  with a distribution of 64.44%. This is because  $Zn(CO_3)_2^{2-}$  was the most stable complex with a high stability constant value of 9.63. The stability of this complex is also attributed to the two carbonate ligands that are coordinated to the zinc metal. As the  $[CO_3^{2-}]_T$  and  $[HCO_3^-]_T$  were increased, the species  $Zn(CO_3)_2^{2-}$  decreased in abundance and was overtaken at  $[CO_3^{2-}]_T$  and  $[HCO_3^-]_T$  of  $4.63 \text{ mmol}^{-1}$  with the species  $ZnCO_{3(aq)}$ . This implies that the species  $ZnCO_{3(aq)}$  can only dominate speciation in freshwater at high  $[CO_3^{2-}]_T$  and  $[HCO_3^-]_T$  and high ionic strength since it is not very stable as shown by its low stability constant value of 4.98. However, increasing the  $[HCO_3^-]_T$  results in the formation of only one bicarbonate species,  $ZnHCO_3^+$  which formed at  $[HCO_3^-]_T$  of  $4.23 \text{ mmol}^{-1}$  with 0.70% and increased gradually upto a maximum of 3.17% at  $[HCO_3^-]_T$  of  $4.98 \text{ mmol}^{-1}$  beyond which its distribution curve levels off probably as a result of using an exact stability constant for the model system. Increased water hardness at pH < 8.5 when zinc is in suspension increases toxicity associated with increased suspended  $ZnCO_3$ . Suspended zinc carbonate may also be toxic, although its toxicity decreases under conditions suitable to zinc hydroxide formations. Zinc toxicosis affects freshwater fish by destruction of gill epithelium and consequent tissue hypoxia. The steady increase in the fraction of free  $Zn^{2+}_{(aq)}$  is probably as a result of the dissociation of organozinc complexes which are not stable and under reducing conditions may liberate  $Zn^{2+}$  (Spear 1981).

Table 7: Chloro complexes of zinc and their stability constants

Reactions for complex formation	<sup>1</sup> MINTEQA2 stability constant values	<sup>2</sup> Corrected stability constant values (0.031 M) using SPECIES computer program
$Zn^{2+} + Cl^{-} \rightleftharpoons ZnCl^{+}$	$K_1 = 0.43$	$K_1 = 0.59$
$Zn^{2+} + 2Cl^{-} \rightleftharpoons ZnCl_{2(aq)}$	$\beta_2 = 0.45$	$\beta_2 = 0.21$
$Zn^{2+} + 3Cl^{-} \rightleftharpoons ZnCl_3^{-}$	$\beta_3 = 0.5$	$\beta_3 = 1.23$
$Zn^{2+} + 4Cl^{-} \rightleftharpoons ZnCl_4^{2-}$	$\beta_4 = 0.199$	$\beta_4 = 0.85$

<sup>1</sup>These stability constant values are contained in the thermodynamic database of the MINTEQA2 model for the Zn<sup>2+</sup> / Cl<sup>-</sup> system.

Figure 5 shows a speciation diagram for the Zn<sup>2+</sup> / Cl<sup>-</sup> system. The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows;

#### Concentration (mmol<sup>-1</sup>)

Zn<sup>2+</sup> - 7.07601

Cl<sup>-</sup> - 1.7678

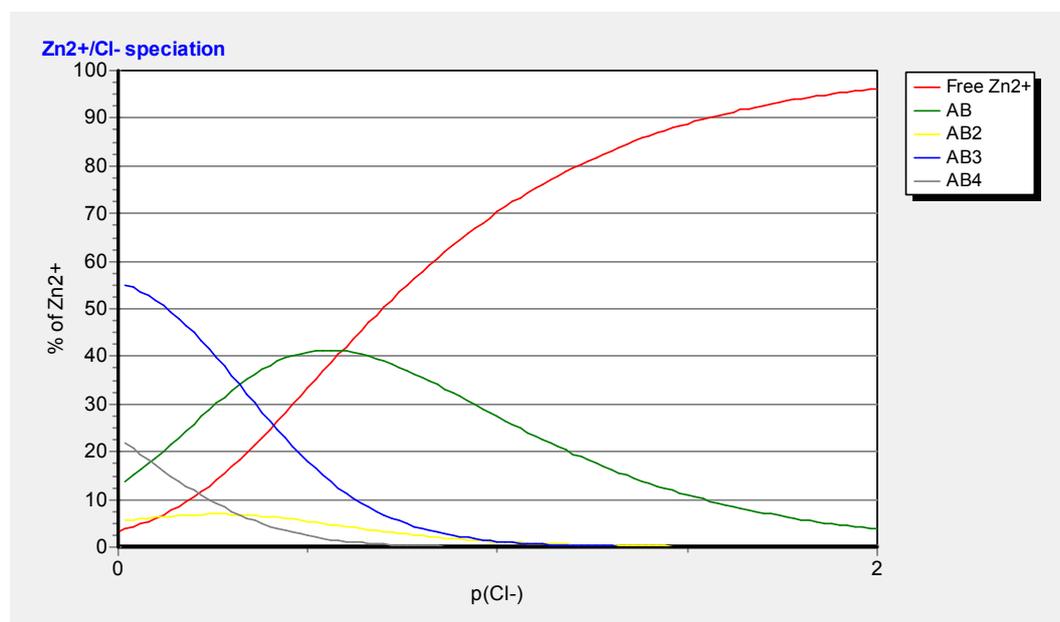


Figure 5: Speciation diagram for the Zn<sup>2+</sup> / Cl<sup>-</sup> system at 27.5<sup>o</sup> C in simulated river water as a function of Chloride concentration [denoted by the symbol p (Cl<sup>-</sup>) at pH 8.0. The total concentration of Zn<sup>II</sup> was set at 8.0 mmol dm<sup>-3</sup>, [Cl<sup>-</sup>] was allowed to vary between 0.0 - 2.0 mmol dm<sup>-3</sup>

The chart legend at the extreme right of the speciation diagram represents the following complexes.

**Complex**                      % distribution at pH 8.0, I<sub>m</sub> = 0.00453 M and [Cl<sup>-</sup>] = 1.7678 mmol<sup>-1</sup>

Free Zn<sup>2+</sup><sub>(aq)</sub>                      94.01

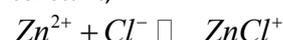
AB – Zn Cl<sup>+</sup>                      5.63

AB2 – ZnCl<sub>2(aq)</sub>                      < 1

AB3 – ZnCl<sub>3</sub><sup>-</sup>                      < 1

AB4 – ZnCl<sub>4</sub><sup>2-</sup>                      < 1

Zn<sup>II</sup> forms upto four consecutive chloro-complexes in aqueous solution each with a well characterized stability constant;





All these complexes are weak and are best studied in media of high  $[\text{Cl}^-]_T$ , high  $[\text{Cl}^-]_T : [\text{Cd}^{II}]_T$  ratios, and high ionic strength. At  $[\text{Cl}^-]_T$  of  $1.76 \text{ mmol}^{-1}$  (which was the concentration of chloride ions in the river), the dominant species was the free  $\text{Zn}^{2+}_{(aq)}$  with a distribution of 94.01%. Also the steady increase in the fraction of free  $\text{Zn}^{2+}_{(aq)}$  could be attributed to the dissociation of organozinc complexes which are not stable, and under reducing conditions may dissociate liberating  $\text{Zn}^{2+}_{(aq)}$  (Spear, 1981). Zinc is a potent inducer of metallothioneins. The pancreas and bone seem to be primary targets of zinc intoxication in birds and mammals; gill epithelium is the primary target site in fish.  $\text{Zn}^{2+}_{(aq)}$  species was therefore the main contributor of  $\text{Zn}^{II}$  speciation, resulting in increased bioavailability of the free metal ion and increased bioconcentration by resident organisms (Nugedoda and Rainbow, 1989). At  $[\text{Cl}^-]_T$  of  $1.76 \text{ mmol}^{-1}$ , the other species were  $\text{ZnCl}^+$  with 6.69% distribution. At low salinities  $\text{ZnCl}^+$  predominate. The species  $\text{ZnCl}_{2(aq)}$ ,  $\text{ZnCl}_3^-$  and  $\text{ZnCl}_4^{2-}$  also formed but in insufficient amounts. This indicates that for these complexes to form in sufficient amounts, high concentrations of chloride ions are necessary. Furthermore, the solubility of  $\text{ZnCl}_{2(s)}$  is comparatively high and therefore  $\text{ZnCl}_{2(s)}$  would not influence the speciation of  $\text{Zn}^{II}$  in natural fresh water.

Table 8: Hydroxo complexes of zinc and their stability constants

Reactions for complex formation	<sup>1</sup> MINTEQA2 stability constant values	<sup>2</sup> Corrected stability constant values (0.031 M) using SPECIES computer program
$\text{Zn}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{ZnOH}^+ + \text{H}^+$	$K_1 = 5.038$	$K_1 = 5.20$
$\text{Zn}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Zn(OH)}_{2(aq)} + 2\text{H}^+$	$\beta_2 = 11.097$	$\beta_2 = 10.77$
$\text{Zn}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Zn(OH)}_3^- + 3\text{H}^+$	$\beta_3 = 13.595$	$\beta_3 = 13.35$
$\text{Zn}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Zn(OH)}_4^{2-} + 4\text{H}^+$	$\beta_4 = 14.793$	$\beta_4 = 15.44$

<sup>1</sup>These stability constant values are contained in the thermodynamic database of the MINTEQA2 model for the  $\text{Zn}^{2+} / \text{OH}^-$  system.

Figure 6 shows a speciation diagram for the  $\text{Zn}^{2+} / \text{OH}^-$  system. The actual concentrations of the parameters that were fed into the SPECIES computer program were as follows;

**Concentration ( $\text{mmol}^{-1}$ )**

$\text{Zn}^{2+}$  - 7.07601

$\text{OH}^-$  - 0.0011765

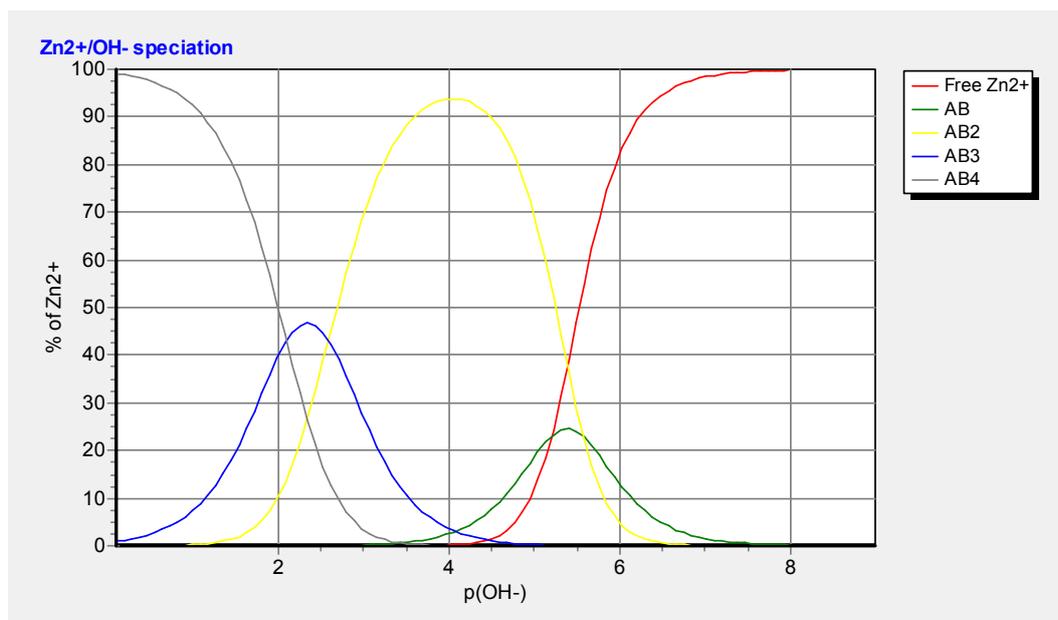


Figure 6: Speciation diagram for the  $Zn^{2+} / OH^-$  system at  $27.5^{\circ}C$  in simulated river water as a function of Hydroxide concentration [denoted by the symbol  $p(OH^-)$  at pH 8.0]. The total concentration of  $Zn^{II}$  was set at  $8.0 \text{ mmol dm}^{-3}$ ,  $[OH^-]$  was allowed to vary between  $0.0 - 8.0 \text{ mmol dm}^{-3}$

The chart legend at the extreme right of the speciation diagram represents the following complexes.

**Complex% distribution at pH 8.0,  $I_m = 0.00453 \text{ M}$  and  $[OH^-] = 0.0011765 \text{ mmol}^{-1}$**

AB – $ZnOH^+$	2.44
AB2 – $Zn(OH)_{2(aq)}$	93.50
AB3 – $Zn(OH)_3^-$	3.66
AB4 – $Zn(OH)_4^{2-}$	< 1
Free $Zn^{2+}_{(aq)}$	< 1

The dominant hydrolysis species is  $Zn(OH)_{2(aq)}$  at  $[OH^-]_T$  of  $4.0 \text{ mmol}^{-1}$  with a distribution of 93.50%. In typical river waters, 90% of the zinc is present as aquo ion (Spear, 1981). Higher-order polymeric species;  $Zn(OH)_3^-$  and  $Zn(OH)_4^{2-}$  also formed but could best be studied under conditions of high ionic strength. The dominance of the species  $Zn(OH)_{2(aq)}$  indicated low levels of zinc toxicity in the river since  $Zn(OH)_{2(aq)}$  is relatively non-toxic. The system was potentially safe upto  $[OH^-]_T$  of  $5.39 \text{ mmol}^{-1}$  beyond which it started becoming polluting due to the emergence to significant levels of free  $Zn^{2+}_{(aq)}$  ions. Infact at  $[OH^-]_T$  of  $7.99 \text{ mmol}^{-1}$  free  $Zn^{2+}_{(aq)}$  ions attain a maximum of 100% abundance which is highly toxic to the system.

### 3.0 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. The speciation calculations indicate that in freshwater systems in equilibrium with atmospheric  $CO_2$ , at pH 8.0 – 9.0 in the absence of organic ligands, the speciation of Cd was dominated by the free  $Cd^{2+}_{(aq)}$  indicating Cd toxicity in river Nzoia. All chloro-complexes for Cd were weak and could best be studied in media of high  $[Cl^-]_T$  and high ionic strength. Free  $Cd^{2+}_{(aq)}$  dominated hydroxo-complexes since Cd<sup>II</sup> has a comparatively low affinity for oxygen donor ligands. About 93% of  $Zn^{II}$  existed as zinc hydroxide.

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## References

- Andren, A. W., Bober, T. W. (1993). Transport, fate and effects of silver in the environment.
- APHA – AWWA – WPCF (1985). Standard Methods for the Examination of Water and Wastewater, ALPHA – AWWA-WPCF, Washington DC.
- Mizuike, A. (1987). Recent developments in trace metal speciation in fresh water, *Pure & Appl. Chem.*, **59** (4), pp 555-564.
- Nugedoda, D. and Rainbow, P. S. (1988b). Salinity, Osmolality and zinc uptake in *Palaemonetes* (Crustacea: Decapoda). *Marine Ecology Progress Series*, **55**, pp 149-157.
- Pettit, L., Pettit, G. (2009). A more realistic approach to speciation using the IUPAC Stability Constants Database.
- Powell, K. J. (2011). Chemical Speciation of Environmentally Significant Metals with Inorganic ligands (IUPAC Technical Report).
- Spear, P. A. (1981). Zinc in the Aquatic environment: chemistry, distribution and toxicology. National Research Council of Canada Publication NRCC 17589. 145 pp.
- Trivedi, R. K. and Goyal, P.K. (1986). Chemical and Biological Methods for water Pollution Studies, Environmental publications, Karad.
- UNEP (1992). Saving Our Planet Challenges and Hopes, United Nations Environment Programme, Nairobi, 1-8.
- USEPA (1980). Environment Protection Agency Ambient Water Quality Criteria for Cadmium Spring field.