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The effect of pH, calcium, phosphate and humic acid on cadmium availability and speciation in artificial groundwater

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Abstract. The interface between the ions in groundwater affects the biogeochemical behaviour of metal, and metal bioremediate by bacteria. Therefore, this study was aimed to predict the influence of pH, calcium, phosphate and humic acid on cadmium availability in artificial groundwater (AGW). Speciation and the thermodynamic calculation (MINTEQ program) were used to predict this in AGW theoretically. In results, cadmium availability diminished with an increase in pH, increase of calcium concentration and the addition of phosphate and humic acid of AGW. According to MINTEQ program, cadmium binds to some cations leaving fewer free cadmium ions available in AGW such as $CdHCO_3^+$, $Cd(SO_4)_2^{2-}$, $CdCl^+$, $CdHPO_4$, HA1-Cd, FA1-Cd, FA2-Cd, and HA2-Cd. It is suggested though that pH in AGW is maintained at pH 4.00 for best availability of cadmium and bioremediate by bacteria.

Keywords. Availability, cadmium, calcium, groundwater, humic acid, pH, phosphate, speciation.

1. Introduction

The Metals speciation and availability in environments and their biogeochemical activities are the main area of research for biochemistry and ecotoxicology of metals [1]. This is important since chemical or mineral speciation is a crucial factor inducing; the solubility, mobility, bioavailability, bioaccumulation, biodegradability, persistence and toxicity [2]. Metals can occur in environments as free metal ions and/or complexed with inorganic components or organic ligands. Is typically, the dissolved and transferrable forms of metals are well-known as bioavailable. Comparably, the fraction of a metal that forms as a portion of the solid-phase minerals may not be bioavailable [3]. Therefore, it is impossible to measure the total metal concentration as its concentration is often insufficient to clarify its ions. Expecting metal speciation has increasingly gained inclusive application as an active constituent of environmental chemistry in enhancing our knowledge of studies such as agriculture, pollution risk assessment or remediation. Cadmium is considered as a serious environmental issue because of its toxicity, non-biodegradability and bioaccumulation [4]. The contamination of groundwater with cadmium has become a global challenge, and more effective methods for removing cadmium are required. The bioavailability and toxicity of cadmium in water are strongly affected by the cadmium forms. Predication of metal speciation aids our understand of metal performance in water and few analytical techniques are used to estimate metal speciation in water such as sorption onto C18 columns, anodic stripping voltammetry, ion-selective electrodes and competitive ligand equilibration/adsorptive stripping cathodic voltammetry [5]. Nevertheless, these methods are acknowledged as very time consuming in sample preparation. Alternatively, the use of geochemical speciation software programs offers a rapid method to establish metal speciation such as Visual PHREEQC, CHEAQS, ORCHESTRA, ECOSAT, CHESS and MINTEQ. These geochemical speciation software programs can predict metal speciation theoretically. This study, aimed to predict the cadmium speciation in typical groundwater without any contamination; AGW was prepared in the laboratory, and cadmium speciation was then predicated under the contamination of a change in pH, an increase of calcium concentration and the addition of phosphate and humic acid.

2. Materials and Methods

2.1. Cadmium precipitation and speciation

2.1.1. Uncontaminated AGW

The component of AGW is specified in Table 1 (first column, Cd-AGW), according to [6]. To theoretically assess the experimental conditions of Cd-AGW, the inorganic chemical speciation at 22°C was calculated using the geochemical speciation software Visual MINTEQ, version 3.1 [7]. The input file contained the components and concentrations of AGW, with a nominated concentration of 10 µM Cd at pH 7.00; (Table 1), oversaturated solids were allowed to precipitate, ionic strength was calculated, and activity corrections were performed after Davies. Redox calculations were not performed.

2.1.2. Contaminated AGW: Chang the pH, increase of calcium concentration and the addition of phosphate and humic acid

The inorganic Cd speciation at different pH values (fixed at pH 4.00, 7.00, 7.50, and 8.50, respectively) was calculated. At pH 8.50, calcium carbonate species (e.g., calcite) and Cd carbonate (otavite) were predicted to precipitate, and the proportion remaining in the AGW was 84.9% of Ca2+, 4.8% of Cd2+, and 76.5% of CO32-. The otavite precipitation predicts that only 0.48 µM remained in AGW as Cd2+. Consequently, the experiment was not run at pH 8.50. The concentration of calcium in AGW was increased from 1.75 to 17.5 mM, applied as CaCl2. Similarly, the effects of the higher concentration of the anion on the cadmium speciation were studied by adding phosphate (10 mM), which does not consist of AGW. Phosphate (10 mM) consisted of two components of 6.15 mL of K2HPO4 (1 M) and 3.85 mL of KH2PO4 (1 M) in a litre. Humic acid constitutes the significant fractions of OM in natural water, which consists of 90% of the total dissolved organic carbon (DOC) [8]. Thus, humic acid (Sigma-Aldrich) was added at the concentration of 10 mg/L to Cd-AGW. This concentration of humic acid was chosen as the average concentration is presented in natural water [9]. With the addition of humic acid (10 mg/L), the NICA-Donnan model in Visual MINTEQ was used. It was found that the parameters and constants for a ‘generic’ fulvic acid were assumed to be 82.5% of the input; dissolved organic carbon (DOC) consists of fulvic acid with a carbon content of 50% (the portion designated ‘active’ concerning metal complexation because humic acid is assumed not to be dissolved in solution), as described by [10]. Fifty percent was in a DOC: DOC ratio of 1.65, which is an average based on stream and lake sediments from the Swedish environmental monitoring network. However, default parameters were used for VMINTEQ for humic acid: 1.4. The total molar concentration of DOC was10 mg/L (gave 551% C in HA), which is equal to 459 µM. Therefore, the input parameter for humic acid is 459 µM (Table 1).

Table 1. The input file of software Visual MINTEQ contained the components and their concentrations in AGW with a concentration of 10 µM Cd at pH 7.00 under the increase of calcium concentration (17.5 mM) and the addition of a phosphate (10 mM) and humic acid (10 mg/L).

Component	Concentration (µM)			
	Cd-AGW	Increase of $CaCl_2$	Addition of phosphate	Addition of humic acid
Ca^{2+}	1750	17500	1750	1750
Cd^{2+}	10	10	10	10
Cl^-	1750	17500	1750	1750
CO_3^{2-}	1162	1162	1162	1162
K^+	103	103	103	103
Mg^{2+}	448	448	448	448
Na^+	1144	1144	1144	1144
NO_3^-	44	44	44	44
PO_4^{3-}	*	*	10000	*
SO_4^{2-}	448	448	448	448
Humic acid	*	*	*	459

*No component added.

2.2. Statistical analysis

ANOVA followed by Tukey post hoc was performed on the data of Cd species distribution of AGW with a concentration of 10 µM Cd, which predicted using Visual MINTEQ to find the differences under the effect of different factors on the percentages of Cd species.

3. Results and Discussion

3.1. Cadmium precipitation

At pH 7.50, the calculations revealed the precipitation of otavite (80% of the added Cd concentration), as shown in Table 2, leaving a dissolved concentration of 2 µM in AGW. At pH 7.00, the calculations indicated that the precipitation of otavite (57.7% of the added Cd concentration), leaving a dissolved concentration of 4.22 µM in AGW. It has been recently reported by [11] that cadmium could be precipitated at alkaline pH (>8.00). The calculations revealed the potential loss of Cd from the solution, as the initial concentration in the AGW was 10 µM Cd. At pH 4.00, the calculated saturation index for all species was negative, and Cd was not predicted to precipitate.

Table 2. Effect of pH on the percentages of dissolved and precipitated components in AGW with a concentration of 10 µM Cd. The percentages of values were predicted using Visual MINTEQ.

Component	pH 4.00		pH 7.00		pH 7.50	
	Dissolved (%)	Precipitated (%)	Dissolved (%)	Precipitated (%)	Dissolved (%)	Precipitated (%)
Ca^{2+}	100	0.00	100	0.00	100	0.00
Cd^{2+}	100	0.00	42	57.7	19.5	80
Cl^-	100	0.00	100	0.00	100	0.00
CO_3^{2-}	100	0.00	99	0.40	99	0.40
K^+	100	0.00	100	0.00	100	0.00
Mg^{2+}	100	0.00	100	0.00	100	0.00

Na^{+}	100	0.00	100	0.00	100	0.00
NO_3^{-}	100	0.00	100	0.00	100	0.00
SO_4^{2-}	100	0.00	100	0.00	100	0.00

However, when CaCl2 was increased from 1.75 mM to 17.5 mM (for the removal process under cation competition), the calculated saturation index for all species was negative, and no precipitation was predicted (Table 3). The dissolved Cd concentration at the beginning of the experiment can be assumed as 10 µM, and the initial measured concentration was approximately 10 µM. Also, the addition of a phosphate (10 mM) showed no potential precipitation of Cd in AGW (Table 3). The NICA-Donnan model indicated that there was no Cd precipitated (Table 3), leaving a dissolved concentration of 10 µM in the test AGW. The measured and predicted dissolved Cd concentrations were the same, due to the low concentration of humic acid, which explains the lack of Cd complexation with the humic acid. [12] used 200 mg/L of humic acid, which is higher than the concentration in this study, and they found that the log activities of binding of $Cd(OH)_2$ and $CdOH^{+}$ with humic acid were -9.5 and -8.4 mol/L, respectively. While, in this study, the log activities for the same species of Cd were low -11.5 and -8.5 mol/L, respectively.

Table 3. Effect of increased calcium (17.5 mM), additional phosphate (10 mM), and humic acid (10 mg/L) on the percentages of dissolved and precipitated components in AGW with a concentration of 10 µM Cd. The percentages were predicted using Visual MINTEQ.

	Calcium (17.5 mM)		Phosphate (10 mM)		Humic acid (10 mg/L)	
Component	Dissolved (%)	Precipitated (%)	Dissolved (%)	Precipitated (%)	Dissolved (%)	Precipitated (%)
Ca^{2+}	100	0.00	0.59	99.4	100	0.00
Cd^{2+}	100	0.00	100	0.00	100	0.00
Cl^{1-}	100	0.00	100	0.00	100	0.00
CO_3^{2-}	100	0.00	100	0.00	100	0.00
K^{1+}	100	0.00	100	0.00	100	0.00
Mg^{2+}	100	0.00	100	0.00	100	0.00
Na^{1+}	100	0.00	100	0.00	100	0.00
NO_3	100	0.00	100	0.00	100	0.00
PO_4^{3-}	*	*	94.7	5.21	*	*
SO_4^{2-}	100	0.00	100	0.00	100	0.00
FA1	*	*	*	*	100	0.00
FA2					100	0.00
HA1					100	0.00
HA2					100	0.00

* No component added.

3.2. Cadmium speciation

Predicting Cd speciation in AGW versus pH showed that Cd^{2+} was the dominant type in AGW with a concentration of 10 µM Cd at a different pH (**Error! Reference source not found.**A, $^{a}p<0.05$), compared to other dissolved Cd species. Similarly, $CdCl^{+}$ recorded no differences at different pH values (**Error! Reference source not found.**A). The appearance of $Cd(SO_4)_2^{2-}$ at pH 4.00 and 7.00, which disappeared at pH 7.50, showed no significant differences between pH 4.00 and 7.00. The occurrence of $CdHCO_3^{+}$ was the unique species predicted at pH 7.00 and 7.50 (**Error! Reference source not found.**A, $^{c}p<0.05$). The effect of increased Ca concentration (17.5 mM) of Cd speciation in AGW at pH 7.00 showed Cd^{2+} was lower than the value recorded at a natural concentration of Ca (1.75 mM). However, Cd^{2+} was the dominant species and showed significant differences (**Error!**

Reference source not found.B, [a]p<0.05) compared to other Cd species. However, $CaCl^+$ was predicted to be 41%, which was higher than the percentage recorded at the initial concentration of $CaCl_2$ (1.75 mM). Moreover, both species of $CdHCO_3^+$ and $Cd(SO_4)_2^{2-}$ were predicated at an increase of Ca as a natural concentration of Ca (1.75 mM), without any differences between them (**Error! Reference source not found.**B, [c]p<0.05). While the addition of a phosphate (10 mM) showed that the domain of Cd species was $CdHPO_4$ (89%), the presence of other Cd-species was rare. Fraction Cd^{2+} was the highest predicted percentages (9.2%) among $CdCl^+$, $Cd(SO_4)_2^{2-}$, $CdHCO_3^+$, and $CdCO_3^+$ (**Error! Reference source not found.**C). Similarly, as Cd^{2+} was the dominant species in AGW at pH 7.00, with the addition of humic acid (10 mg/L) into the AGW, Cd^{2+} was the dominant species (84%), followed by $CdCl^+$ (10%, Figure 1D).

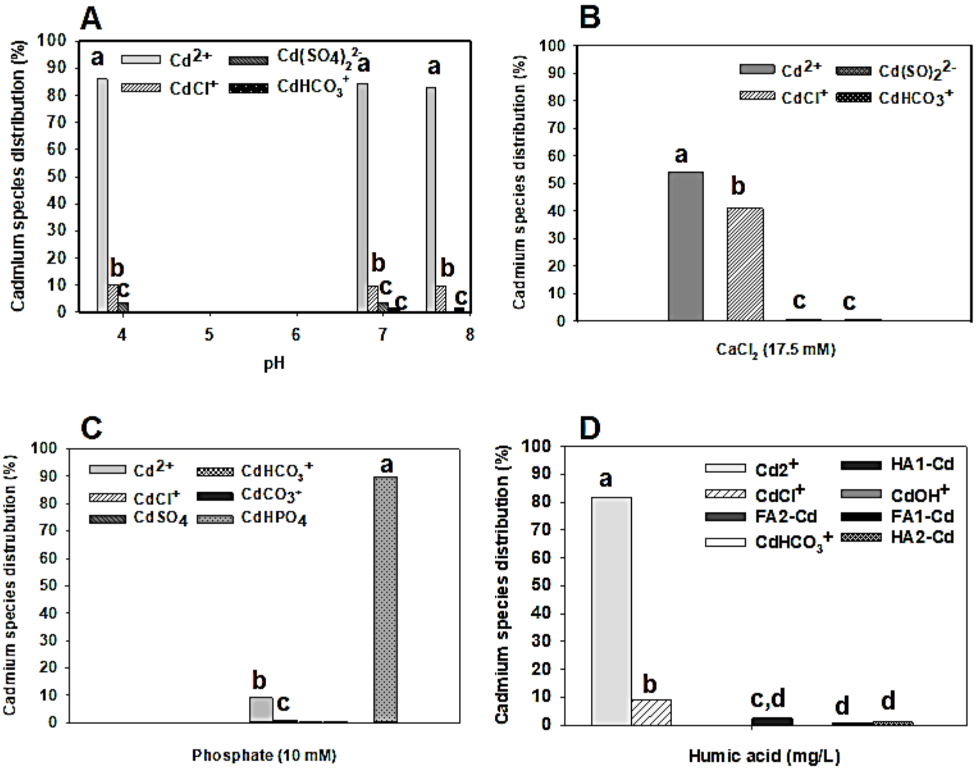

Figure 1. The effect of different factors on the percentages of Cd species distribution of AGW with a concentration of 10 µM Cd, predicted using Visual MINTEQ. (A) At pH 4.00, 7.00, and 7.50, (B) increase of calcium (17.5 mM), additions, (C) phosphate (10 mM), and (D) humic acid (10 mg/L) on Cd speciation in AGW. The Cd species were subjected to two-way ANOVA, Tukey *post hoc* test, and a different letter indicates a significant difference between Cd species under different factors.

With the use of two types of Cd-binding with fulvic and humic acids in the NICA-Donnan model, complex HA1-Cd occurred in addition to other complexes in rare percentages (FA1-Cd, FA2-Cd, and HA2-Cd) as well as the occurrence of fractions $CdHCO_3^+$ and $CdOH^+$. The complexation of Cd with humic acid (Cd-HA) was predicted as this complex is the most formed complex with Cd [13].

4. Conclusion

The ions of cadmium diminished with increase in pH of AGW, in which cadmium binds to cations present in water, leaving less availability of cadmium ions. Increase of calcium concentration and the addition of phosphate and humic acid formed of insoluble cadmium species that appeared in the water. It is recommended though that free cadmium ions were available at a pH of 4.00, which would make cadmium soluble, available and toxic.

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