



Effect of Cl^- , SO_4^{2-} , and fulvate anions on Cd^{2+} free ion concentrations in simulated rhizosphere soil solutions

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ABSTRACT

The binding between heavy metals and corresponding ligands affects their chemical behavior and toxicity in soil environments. The mechanisms of competitive complexation and/or chelation between Cd^{2+} free cations and preferential concentrations of Cl^- , SO_4^{2-} , and fulvate anions were investigated in simulated soil solutions at pH 4.00, 5.00 and 6.00. The Cd^{2+} concentrations were calculated by a proposed equation, simulated by MINTEQ software, and directly determined by ion chromatography (IC). When Cl^-/Cd or Cl^-/Cd with $\text{SO}_4^{2-}/\text{Cd}$ molar ratios of 3.18 and 4.05, the differences among Cd^{2+} concentrations calculated by equation, simulated by MINTEQ software, and directly determined by IC were not significant, but their differences were pH independent for considering Cl^-/Cd molar ratio and pH dependent for Cl^-/Cd and $\text{SO}_4^{2-}/\text{Cd}$ molar ratios. When Cl^-/Cd , $\text{SO}_4^{2-}/\text{Cd}$, and additional FA/Cd molar ratios of 3.18 and 4.05, the Cd^{2+} concentrations calculated by equation were significantly larger than those simulated by MINTEQ and determined by IC because in simulation and determination of Cd^{2+} concentrations by IC, the complexation of Cd^{2+} with ligands to form CdCl^+ , CdSO_4 , FACd^+ and FA_2Cd had been considered, whereas in calculation this complexation aspect was ignored. Though IC can be used to determine Cd^{2+} concentration in rhizosphere soil solutions ion chromatographic peak of Cd^{2+} in 0.1 M HCl saturation extract of slightly acidic soil and in deionized distilled water saturation extract of acidic soils still may be shielded by the vicinal chromatographic peaks of Mg^{2+} and Mn^{2+} , respectively. The Cd^{2+} concentrations in rhizosphere soil solutions of acidic or slightly acidic soils calculated by equation and/or simulated by Model may thus be used as potential alternatives for those determined by IC.

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1. Introduction

Most of the toxic heavy metals in soil solution and associated environmental solutions were in the form of free ions, complex ions and neutral molecules. The behavior of heavy metals in soil solution including mobility and bioavailability can thus not be predicted and evaluated by their total concentrations. Total cadmium (Cd) concentration in soils or water is in most cases poorly related to bio-uptake by organisms instead of specific speciation [1]. The toxicity and bioavailability of cadmium is mainly controlled by its dissolved free Cd^{2+} ion concentration, which is expected to be the most stable ion in solution [2]. However, the corresponding inorganic and organic ligands present in the solution binding with heavy metals have an important influence on the free metal-ion activity [3,4]. Smolders and McLaughlin [5] investigated the effect of Cl^- concentrations (0.01–120 mM) on the absorption of Cd by Swiss sugar chard. They reported that Cd contents in the aboveground parts and in roots of Swiss chard increased as Cl^- concentration increased in culture

solution. This indicates that Cl^- promoted the absorption of Cd by Swiss chard. Consequently, the complexation of Cl^- with Cd^{2+} to form the complex $\text{CdCl}_n^{(2-n)}$ may increase Cd bioavailability. Further, McLaughlin et al. [6] reported that the amendment of sulfate (SO_4^{2-}) in the range of 0–24 mmol kg^{-1} to Cd contaminated soil also significantly promoted Cd uptake by Swiss chard. Zhao et al. [7] studied the effect of different forms and rates of applied potassium fertilizers (KNO_3 , KCl, and K_2SO_4) on Cd uptake by two cultivars of spring wheat (*Triticum aestivum*, L.). The results showed the role of paired inorganic anions Cl^- , SO_4^{2-} , and NO_3^- of the three forms of potassium fertilizers in influencing the uptake of Cd by spring wheat. In soil solutions dissolved organic matter has group of complexing agents such as humic acids (HAs) and fulvic acids (FAs). The complexation of the metal ions, Cd^{2+} and Ca^{2+} , with several FAs were examined using ^{113}Cd NMR. The results indicate that Cd^{2+} predominately binds to the oxygen containing functional groups of the FAs [8].

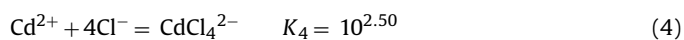
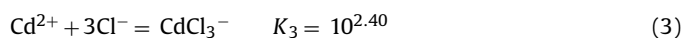
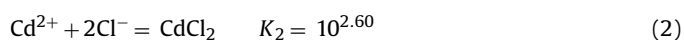
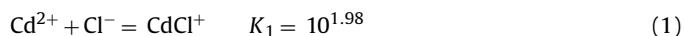
Attempts have been focused for measuring Cd^{2+} activity/concentration in soil solution. Workman and Lindsay [9] used a competitive chelation technique in soil solutions with an added solid phase PbCO_3 to measure Cd^{2+} activities and reported that pCd^{2+} values were in the range of 9.5–6.5 in eight uncontaminated

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alkaline soils. Salam and Helmke [10] used an ion exchange membrane technique to determine free Cd^{2+} activity in two slightly contaminated soils containing 1.5 and 0.5 mg of Cd kg^{-1} . The results showed that free ionic Cd^{2+} activity was negatively correlated with soil pH when soil pH was in the range of approximately 4.0–7.0. Zwonitzer et al. [11] studied the effects of phosphorus additions on lead, cadmium, and zinc bioavailability in a metal-contaminated soil. They found that Cd^{2+} activities estimated with MINTEQA2 and those measured with ion selective electrode (ISE) were not in good agreement. Growth studies with a soil alga (*Chlorococcum* sp.) were conducted by Krishnamurti et al. [12] on a growth medium and pore water of Cookes Plain soil (Paleuxeralf), spiked with Cd as $\text{Cd}(\text{NO}_3)_2$. They studied speciation of the Cd in pore water, and in growth medium using the MINTEQA2 computer model incorporating updated values of the stability constants of Cd-DOM (dissolved organic matter) complexes, as well as using anodic stripping voltammetry. Analysis of the toxicity data showed that Cd present as Cd-citrate as well as Cd-DOM complexes is bioavailable and contributes toward the toxicity of alga. The recently developed Donnan Membrane Technique (DMT) was used by Cancés et al. [13] to measure free metal (Cd, Pb, and Zn) concentrations in the soil solution and compare the results with those obtained from model calculations. They reported that speciation of Cd, Zn, and Pb in the soil was controlled by organic matter and metallic oxides.

In agricultural soils, inorganic anions such as Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , and PO_4^{3-} are very common species in their corresponding soil solutions. Taylor and Percival [14] investigated Cd concentrations in soil solutions from a transect of soils. They used the Model GEOCHEM-PC [15] to simulate Cd speciation in soil solutions and reported that Cd in soil solution was less than 1% of soil total Cd and Cd^{2+} in soil solution accounted for 55–90% of Cd in soil solutions. In addition, though inorganic anions NO_3^- and PO_4^{3-} are considerably high, Cl^- and SO_4^{2-} preferentially react with Cd^{2+} to form complex and/or ion pair in soil solutions.

McBride [16] pointed out that the binding of metals (including heavy metals) with respective ligands affected chemical behavior and toxicity of heavy metals in soil environment. Depending on the variation of soil solution composition, the soluble heavy metals usually react with organic as well as inorganic ligands in soil solution to form complexes. For example, McBride [16] proposed that 1 mol Cd^{2+} ultimately complexes with 4 mol of Cl^- . The mechanistic stepwise reactions are expressed as following equations.



For each equilibrium constant, K_n can be expressed as the following general equation.

$$K_n = \frac{[\text{CdCl}_n^{(2-n)}]}{[\text{Cd}^{2+}][\text{Cl}^-]^n} \quad (5)$$

where $\text{CdCl}_n^{(2-n)}$, Cd^{2+} , and Cl^- are expressed in concentrations. Accordingly, total dissolved Cd expressed as [Cd] is the sum of all dissolved forms of Cd in solution which can be denoted as below.

$$[\text{Cd}] = [\text{Cd}^{2+}] + [\text{CdCl}^+] + [\text{CdCl}_2^0] + [\text{CdCl}_3^-] + [\text{CdCl}_4^{2-}] \quad (6)$$

By combining Eqs. (1)–(4), [Cd] can be denoted by the three terms $[\text{Cd}^{2+}]$, $[\text{Cl}^-]$, and K_n as follows.

$$[\text{Cd}] = [\text{Cd}^{2+}] + K_1[\text{Cd}^{2+}][\text{Cl}^-] + K_2[\text{Cd}^{2+}][\text{Cl}^-]^2 + K_3[\text{Cd}^{2+}][\text{Cl}^-]^3 + K_4[\text{Cd}^{2+}][\text{Cl}^-]^4 \quad (7)$$

By extracting the common term $[\text{Cd}^{2+}]$ in the right-hand side of Eq. (7), the $[\text{Cd}^{2+}]$ term can be denoted by the following equation.

$$[\text{Cd}^{2+}] = \frac{[\text{Cd}]}{1 + K_1[\text{Cl}^-] + K_2[\text{Cl}^-]^2 + K_3[\text{Cl}^-]^3 + K_4[\text{Cl}^-]^4} \quad (8)$$

This clearly indicates that various degrees of complexes formed by Cl^- substantially affect the activity as well as concentration of Cd^{2+} . The known values of equilibrium constants K_1 , K_2 , K_3 , and K_4 and the determined concentration of Cl^- can be used to calculate the concentration of free ion Cd^{2+} as well as the fraction of Cd^{2+} accounted for the total dissolved Cd in solution by using Eq. (8). For example, if determined concentration of Cl^- is 0.01 M, the calculated free $[\text{Cd}^{2+}]$ accounts for 50% of total dissolved Cd and the remaining Cd is almost in the form of CdCl^+ . The aim of this study was thus to investigate the effect of Cl^- and SO_4^{2-} inorganic and fulvate organic anions on Cd^{2+} free ion concentration in simulated rhizosphere soil solutions by comparing the results obtained from existing methods (a) calculated by the proposed equation, (b) simulated by using software package MINTEQ [17], and (c) determined by using ion chromatography (IC). In addition, Cd^{2+} concentrations of simulated rhizosphere soil solutions of a heavy metals contaminated soil and a Cd spiked soil were also calculated by equation, simulated by software, and measured by IC to identify the applicability of this study.

2. Materials and methods

To simulate the reaction systems involving Cd^{2+} and related species in soil solutions, three categories of reaction systems were prepared. In addition, simulated rhizosphere soil solutions of a heavy metals contaminated soil and a Cd spiked soil were extracted. The solutions were then subjected to the determination of Cd^{2+} free ion concentrations by calculation, simulation, and ion chromatography.

2.1. Preparation of Cd solution containing Cl^- anion

Analytical grade solid $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Riedel-de Haën) and stock solution $\text{Cd}(\text{NO}_3)_2$ ($1000 \pm 2 \text{ mg L}^{-1}$ of Cd) (Merck) were used to prepare 0.074 and 0.057 mM Cd solutions, respectively. 90 mL of each solution was added with adequate amount of analytical grade NaCl (Merck, 99.5–100.5% purity) to make Cl^-/Cd molar ratios of 3.18 and 4.05, respectively. For each constant molar ratio of solution, 12 solutions were separately prepared and divided into three sets. These three sets of solutions were separately adjusted to pH 4.00, 5.00, and 6.00 with diluted HCl (Riedel-de Haën) or with NaOH (Riedel-de Haën) solution and then diluted with deionized distilled water to 100 mL. For each pH set of one constant molar ratio, there were thus four replicated solutions. Finally, the concentrations of Cd in solutions originally prepared from analytical grade $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and stock solution $\text{Cd}(\text{NO}_3)_2$ were 0.067 and 0.052 mM, respectively.

2.2. Preparation of Cd solution containing Cl^- and SO_4^{2-} anions

To study the effect of Cl^- and SO_4^{2-} on Cd^{2+} concentration the procedure followed for the preparation of Cd solution containing Cl^- was similar to the procedure described in Section 2.1. To the Cd solution, adequate amounts of analytical grade Na_2SO_4 (Merck, 99% purity) were added to make Cl^-/Cd and $\text{SO}_4^{2-}/\text{Cd}$ molar ratio of 3.18 with Cd using analytical grade $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and Cl^-/Cd and $\text{SO}_4^{2-}/\text{Cd}$ molar ratio of 4.05 with Cd using stock solution $\text{Cd}(\text{NO}_3)_2$.

2.3. Preparation of Cd solution containing Cl^- , SO_4^{2-} , and fulvate anions

Fulvic acids including compounds with $\text{MW} > 1000$ and $\text{MW} < 1000$ were extracted from top layer (0–30 cm in depth) of an uncultivated high mountain soil. Subsequently, the extraction and fractionation of fulvic acid ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$) and their purification were conducted in our laboratory. The details of the collection of soil, extraction of humic substances, and their subsequent fractionation, purification, and characterization are described by Wang et al. [18]. The uncultivated high mountain soil was collected from top layer (0–30 cm) of 10 sites within the selected area and made a composite soil sample. The soil sample was air-dried and ground to pass through a 2-mm sieve or a 0.15-mm sieve. The soil sample with particle size less than 2 mm was used for pH and electrical conductivity (EC) measurements and determination of organic C, N, H, O, and S contents. The C, N, H, O, and S contents of soil sample were determined using a Heraeus CHN-O-rapid elemental analyzer and Tacussel coulomax 78 automatic coulometric titrator. The soil sample with particle size less than 0.15 mm was used for the extraction of humic substances. The soil sample was extracted repeatedly with 0.1 M HCl at 1:10 (w/v) ratio to extract acid soluble humic substances until the extract was clear and then washed with deionized distilled water once at 1:10 (w/v) ratio. The 0.1 M HCl extracts and washing for the soil were combined and stored for further purification of FAs. Then the extracted residue for the soil was extracted repeatedly with 0.1 M NaOH at 1:10 (w/v) ratio until the extract was clear. The 0.1 M NaOH extracts were combined and acidified to pH 1.0 with 6 M HCl. The acidified solution was equilibrated at room temperature for 24 h and then centrifuged at $2000 \times g$ to separate the humic acid fraction (precipitate) from the FA fraction (supernatant). The HA fraction was stored for further purification in another experiment. The stored 0.1 M HCl extract with washing described above and the supernatant containing FA fraction were combined. The FA solution was purified by using an XAD-8 adsorption resin, and the 0.1 M NaOH alkaline eluate was passed through H^+ -saturated cation exchange resin. The purified H^+ -saturated FA solution was concentrated using a rotary evaporator to an adequate volume. The concentrated FA solution was transferred to dialysis tube with a molecular weight cutoff of 1000 to separate the fraction FA ($\text{MW} > 1000$) from that of FA ($\text{MW} < 1000$). The equilibrated solution outside the dialysis tubes was then concentrated by using a rotary evaporator to collect the fraction FA ($\text{MW} < 1000$). All FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$) fractions were freeze-dried and their yields were determined. In addition, based on the functional groups of FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$) reaction with metals (including heavy metals), total acidities of both FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$) were determined according to the method proposed by Schnitzer and Khan [19]. An amount of 50–100 mg of FA ($\text{MW} > 1000$) or FA ($\text{MW} < 1000$) was taken in a 125-mL ground-glass stoppered Erlenmeyer flask and to this 20 mL of 0.10 M $\text{Ba}(\text{OH})_2$ solution was added. Simultaneously a blank consisting of 20 mL of 0.10 M $\text{Ba}(\text{OH})_2$ only was set up. Air in each flask was displaced by N_2 , and the flask was stopped carefully and shaken for 24 h at room temperature. Following this, the suspension was filtered, and then the residue was washed thoroughly with CO_2 -free deionized distilled water. The filtrate plus washing was titrated potentiometrically (glass-Ag/AgCl electrode) with standard 0.5 M HCl solution to pH 8.4. Then the total acidities of FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$) were calculated. The determined total acidities of FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$) were 12.1 and 15.9 mmol g^{-1} , respectively. In this study, we assumed that total acidities of FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$) were reaction functional group to react with cations including metals and proton in reaction solution. Therefore, according to the determined

total acidities of FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$), 1.75 mg of FA ($\text{MW} > 1000$) or 1.33 mg of FA ($\text{MW} < 1000$) contained around 0.0212 mmol of reaction function group. For the solution with Cl^-/Cd as well as $\text{SO}_4^{2-}/\text{Cd}$ molar ratio of 3.18 or 4.05 containing 1.75 mg of FA ($\text{MW} > 1000$) or 1.33 mg of FA ($\text{MW} < 1000$), 12 solutions were separately prepared and divided into three sets. These three sets of solutions were separately adjusted to pH 4.00, 5.00, and 6.00 with diluted HCl (Riedel-de Haën) or NaOH (Riedel-de Haën) solution and then diluted with deionized distilled water to 100 mL. For each pH set of solutions with Cl^-/Cd as well as $\text{SO}_4^{2-}/\text{Cd}$ molar ratio of 3.18 or 4.05 containing FA ($\text{MW} > 1000$) or FA ($\text{MW} < 1000$) were thus four replicates. Because in 100 mL solution, the amount of Cd was 0.0067 or 0.0052 mmol as described in Section 2.1, the FA/Cd molar ratio in each prepared solution containing Cl^- and SO_4^{2-} was also 3.18 or 4.05.

2.4. Extraction of simulated rhizosphere soil solutions

A soil contaminated by heavy metals (201589 mE, 2662350 mN; Erhlin soil series, Changhua Township) and a red soil (220653 mE, 2662068 mN; Wufong Township, Taichung County) were selected to extract the rhizosphere soil solutions. The bulk soil pH and aqua regia soluble Cd contents of the heavy metals contaminated soil and the red soil were 6.24 and 4.15 (in deionized distilled water, w/v = 1:1), and 31.7 and 0.38 mg kg^{-1} , respectively. Hence, in order to simulate lower pH of rhizosphere soil than that of bulk soil, the heavy metals contaminated soil was saturated with both 0.1 M HCl and deionized distilled water to extract the saturation extracts. However, the red soil was spiked with four different amounts of Cd as $\text{Cd}(\text{NO}_3)_2$ solution. Each of the required amounts of $\text{Cd}(\text{NO}_3)_2$ was separately dissolved in deionized distilled water which is equivalent to 33.3 kPa moisture tension of a certain amount of red soil. The four amounts of Cd as $\text{Cd}(\text{NO}_3)_2$ spiked to the red soil were 5.08, 10.2, 20.3, and 30.5 mg kg^{-1} . After the Cd spiked red soil was air-dried to the constant weight, the four sets of Cd spiked red soil were subjected to four cycles of wetting-and then-drying under room temperature in order to expedite the aging process. For each wetting-and then-drying cycle, the four sets of red soil were separately added with a certain amount of deionized distilled water, which was equivalent to the amount of water of 33.3 kPa of soil moisture tension (field capacity), and then the four sets of Cd spiked red soil were let to equilibrate with atmosphere until air-dried. Upon completion of four cycles of wetting-and then-drying, the four sets of Cd spiked red soil were then subjected to the extraction of deionized distilled water saturation extract.

2.5. Calculation, simulation and determination of Cd^{2+} concentrations

Cd^{2+} and their related species concentrations in the three prepared solution systems and in deionized distilled water and 0.1 M HCl saturation extracts of the heavy metals contaminated soil and in deionized distilled water saturation extract of the red soil described above were measured by three different existing methods: (a) Cd^{2+} concentration calculated by equation proposed by McBride [16], (b) Cd^{2+} concentration simulated by using software package MINTEQA [17], and (c) Cd^{2+} concentration determined by using IC equipped with cation separation column.

Each constant pH and correspondingly different Cl^-/Cd , $\text{SO}_4^{2-}/\text{Cd}$, as well as FA/Cd molar ratio solutions, and deionized distilled water and 0.1 M HCl saturation extracts of the heavy metals contaminated soil, and deionized distilled water saturation extract of the red soil were subjected to the determination of total dissolved Cd and Na concentrations using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo Electron Corporation, IRIS Intrepid II XSP). Further, each solution was subjected

to the determination of Cl^- and SO_4^{2-} concentrations by IC. The obtained Cl^- and Cd concentrations and the known equilibrium constants for K_1 , K_2 , K_3 , and K_4 from Eqs. (1)–(4) were substituted in Eq. (8) as described above to calculate the concentration of Cd^{2+} . This is the concentration calculated from Eq. (8) proposed by McBride [16]. Moreover, the obtained concentrations of Cl^- as well as SO_4^{2-} and NO_3^- determined by IC, and the obtained concentrations of Cd and Na determined by ICP-OES for each constant pH and corresponding Cl^-/Cd , $\text{SO}_4^{2-}/\text{Cd}$, and FA/Cd molar ratio solution and those in deionized distilled water and 0.1 M HCl saturation extracts of the heavy metals contaminated soil and in deionized distilled water saturation extract of the red soil were used to simulate the Cd^{2+} concentration and CdCl^+ , CdSO_4 , FACd^+ , and FA_2Cd percentages by using MINTEQ software package [17]. This is the Model simulated concentration. Further, each constant pH and correspondingly different Cl^-/Cd , $\text{SO}_4^{2-}/\text{Cd}$, and FA/Cd molar ratio solutions, and deionized distilled water and 0.1 M HCl saturation extracts of the heavy metals contaminated soil and deionized distilled water saturation extract of the red soil were subjected to the determination of Cd^{2+} using IC equipped with cation separation column and electrical conductivity detector. This is the determined Cd^{2+} concentration. The cation separation column used was MIC GEL SCK01 (Mitsubishi Ltd., Japan). The injection volume of each sample solution was 20 μL and the mobile phase (eluent) used was a single solvent containing 1.5 mM $\text{C}_4\text{H}_6\text{O}_6$ (tartaric acid) and 0.8 mM $\text{C}_2\text{H}_8\text{N}_2$ (ethylenediamine) for isocratic elution. The eluent pH was 3.88.

3. Results and discussion

On the basis of the maximum complexation of Cl^- with Cd^{2+} leading to the formation of CdCl_4^{2-} proposed by McBride [16], Cl^-/Cd ratios were thus prepared as less than and close to 4.00 using molar ratio of 4.00 as the reference point. For three solution systems as described above, additional Cl^- was added while adjusting the solution pH to 4.00, the calculated Cl^-/Cd , Cl^-/Cd and $\text{SO}_4^{2-}/\text{Cd}$, or Cl^-/Cd , $\text{SO}_4^{2-}/\text{Cd}$, and FA/Cd ratios for FA (MW > 1000) or FA (MW < 1000) of 3.18 and 4.05, the determined ratios for these anions were presented in their respective Tables 1–4. The corresponding calculated, simulated, and determined Cd^{2+} concentrations in the prepared three solution systems, in the deionized distilled water and 0.1 M HCl saturation extracts of the heavy metals contaminated soil, and in the deionized distilled water saturation extract of the red soil were shown in Tables 1–6.

3.1. Cd^{2+} concentration in the presence of Cl^-

The determined concentrations of Cd by ICP-OES for Cl^-/Cd ratios of 3.18, 3.44 and 4.05 were shown in Table 1 and their differences in the pH range of 4.00–6.00 were not statistically significant. Correspondingly, the results of the Cd^{2+} concentrations (Table 1) calculated by Eq. (8) proposed by McBride [16], for the same Cl^-/Cd ratios also showed that their differences in the pH range of 4.00–6.00 were not statistically significant. The concentration of hydrolyzed species of Cd^{2+} such as CdOH^+ mainly increases with increasing pH in the pH range of 4.00–6.00 [20], showing the competition of Cl^- with OH^- with varying degrees to react with Cd^{2+} in the reaction systems. However, the concentration of Cd^{2+} calculated by Eq. (8) proposed by McBride [16] was shown pH independent (Table 1).

The concentrations of Cd^{2+} simulated by Model MINTEQ [17] (Table 1) were also not statistically significant in the pH range of 4.00–6.00 though the effect of pH were considered. The differences between the concentrations of Cd^{2+} calculated by Eq. (8) and simulated by Model MINTEQ [17] were not statistically significant for

each corresponding pH and Cl^-/Cd ratio. This indicates that $[\text{OH}^-]$ (or pH) may not play a role in affecting the estimation of Cd^{2+} concentration in the pH range of 4.00–6.00. The concentrations of CdCl^+ simulated by Model MINTEQ [17] were statistically different in the pH range of 4.00–6.00 for Cl^-/Cd ratios of 3.18 and 3.44, but for Cl^-/Cd ratio of 4.05 their differences were not statistically significant (Table 1). The concentration of CdCl^+ for Cl^-/Cd ratio of 3.44 and at pH 4.00 was significantly larger than those for Cl^-/Cd ratio of 3.18 and at pH 5.00 and 6.00. This may be due to the fact that higher pH promotes the competition between Cl^- and OH^- to react with Cd^{2+} in reaction system, leading to less formation of CdCl^+ or more formation of CdOH^+ and/or $\text{Cd}(\text{OH})_2$. However the concentrations of CdCl^+ were not comparable to those of Cd^{2+} at each corresponding pH and Cl^-/Cd ratio.

The concentrations of Cd^{2+} determined by IC with cation exchange column were not statistically significant in the pH range of 4.00–6.00 for Cl^-/Cd ratios of 3.18, 3.44, and 4.05 (Table 1). Comparisons of the concentration of Cd^{2+} determined by IC to those calculated by Eq. (8) and simulated by Model MINTEQ [17] at each corresponding pH and for Cl^-/Cd ratios were not statistically significant. This clearly indicates that concentration of Cd^{2+} calculated from Eq. (8) considering solely the effect of complexation of Cl^- with Cd^{2+} and that simulated by Model MINTEQ [17] can accurately estimate Cd^{2+} concentration as that directly determined by IC in the pH range of 4.00–6.00 for Cl^-/Cd ratios of 3.18, 3.44, and 4.05. Moreover, based on the concentration of Cd^{2+} determined by IC and the Cd^{2+}/Cd weight percentages the most speciation of Cd at Cl^-/Cd ratios of 3.18, 3.44, and 4.05 in the pH range of 4.00–6.00 was in the form of Cd^{2+} (Table 1). Further, at each corresponding pH, the Cd^{2+} concentrations were significantly larger for Cl^-/Cd ratios of 3.18 and 3.44 than for Cl^-/Cd ratio of 4.05 (Table 1) (statistical labels not shown), indicating that Cl^-/Cd molar ratio of stoichiometric parameter plays an important role in influencing the complexation of Cd^{2+} with Cl^- in the reaction system.

3.2. Cd^{2+} concentration in the presence of Cl^- and SO_4^{2-}

In addition to Cl^- , SO_4^{2-} is also one of the most abundant anions and potentially affects the absorption of Cd by crop roots in soil and associated environments [7]. In the reaction system of this study, SO_4^{2-} was thus amended along with Cl^- to investigate its effect on the concentration of Cd^{2+} in solution.

The determined concentrations of Cd by ICP-OES for Cl^-/Cd and $\text{SO}_4^{2-}/\text{Cd}$ ratios of 3.18 and 3.45 showed that their differences were not statistically significant (Table 2), but for Cl^-/Cd and $\text{SO}_4^{2-}/\text{Cd}$ ratio of 4.05 the determined concentration of Cd was significantly larger at pH 4.00 than at 6.00 (Table 2). This indicates that Cd may complex with ligands to form precipitation which cannot be determined by ICP-OES as total dissolved Cd in supernatant of aqueous solution at pH 6.00.

The Cd^{2+} concentrations calculated by Eq. (8) showed that their differences were also not statistically significant (Table 2) in the pH range 4.00–6.00 for Cl^-/Cd and $\text{SO}_4^{2-}/\text{Cd}$ ratios of 3.18 and 3.45, but for Cl^-/Cd and $\text{SO}_4^{2-}/\text{Cd}$ ratio of 4.05 the Cd^{2+} concentration was significantly larger at pH 4.00 than at 6.00 showing the same behavior as that of Cd described above (Table 2). The formation of hydrolyzed species of Cd^{2+} such as CdOH^+ and $\text{Cd}(\text{OH})_{2(\text{aq})}$ as well as $\text{Cd}(\text{OH})_{2(\text{s})}$ mainly increases with increasing pH in the pH range 4.00–6.00 [20], indicating the competition of Cl^- with OH^- with varying degrees to react with Cd^{2+} in the reaction systems. Consequently, the determined concentration of total dissolved Cd will be decreased when the species $\text{Cd}(\text{OH})_{2(\text{s})}$ was formed in the reaction system. This thus resulted in less calculated concentration of Cd^{2+} using Eq. (8) when K_1 , K_2 , K_3 , and K_4 and the determined concentration of Cl^- (denoted as $[\text{Cl}^-]$) were constants (Table 2).

Table 1Comparison of calculated, simulated, and determined Cd²⁺ in the reaction solutions containing Cd(NO₃)₂ and NaCl with different Cl⁻/Cd molar ratios and at different pH^a.

Cl ⁻ /Cd	pH	Determined Cd (mg L ⁻¹)	Equation calculated Cd ²⁺ (mg L ⁻¹)	Model simulated		Determined Cd ²⁺ (mg L ⁻¹)	Cd ²⁺ /Cd (%)
				Cd ²⁺ (mg L ⁻¹)	CdCl ⁺ (mg L ⁻¹)		
3.44	4.00	7.53a	7.33Aa	7.35Aa	0.24a	7.27Aa	96.5a
3.18	5.00	7.23a	7.10Aa	7.11Aa	0.16b	7.01Aa	97.0a
3.18	6.00	7.21a	7.07Aa	7.08Aa	0.17b	6.98Aa	96.9a
4.05	4.00	5.76a	5.66Aa	5.58Aa	0.11a	5.26Aa	91.9a
4.05	5.00	5.36a	5.26Aa	5.21Aa	0.10a	5.10Aa	95.4a
4.05	6.00	5.37a	5.27Aa	5.23Aa	0.10a	5.04Aa	94.0a

^a Means within each column of each Cl⁻/Cd molar set followed by same lower case letter and those within each row followed by same upper case letter, are not significantly different at 5% level by least significant difference (LSD) test.

Table 2Comparison of calculated, simulated, and determined Cd²⁺ in the reaction solutions containing Cd(NO₃)₂, NaCl, and Na₂SO₄ with different Cl⁻/Cd and SO₄²⁻/Cd molar ratios and at different pH^a.

Cl ⁻ /Cd	SO ₄ ²⁻ /Cd	pH	Determined Cd (mg L ⁻¹)	Equation calculated Cd ²⁺ (mg L ⁻¹)	Model simulated			Determined Cd ²⁺ (mg L ⁻¹)	Cd ²⁺ /Cd (%)
					Cd ²⁺ (mg L ⁻¹)	CdCl ⁺ (mg L ⁻¹)	CdSO _{4(aq)} (mg L ⁻¹)		
3.45	3.18	4.00	7.50a	7.34Aa	7.14Aa	0.19a	0.41a	7.08Aa	94.4a
3.18	3.18	5.00	7.29a	7.16Aa	6.96Aa	0.14b	0.41a	6.92Aa	94.9a
3.18	3.18	6.00	7.30a	7.17Aa	6.97Aa	0.14b	0.41a	6.89Aa	94.4a
4.05	4.05	4.00	5.84a	5.74Aa	5.59Aa	0.10a	0.26a	5.36Aa	91.8a
4.05	4.05	5.00	5.42ab	5.32Aab	5.18Aab	0.09a	0.24a	4.97Aab	91.8a
4.05	4.05	6.00	5.37b	5.27Ab	5.13Ab	0.10a	0.25a	4.92Ab	91.6a

^a Explained in Table 1.

Table 3Comparison of calculated, simulated, and determined Cd²⁺ in the reaction solutions containing Cd(NO₃)₂, NaCl, Na₂SO₄, and FA (MW > 1000) with different Cl⁻/Cd, SO₄²⁻/Cd, and FA/Cd molar ratios and at different pH^a.

Cl ⁻ /Cd	SO ₄ ²⁻ /Cd	FA/Cd	pH	Determined Cd (mg L ⁻¹)	Equation calculated Cd ²⁺ (mg L ⁻¹)	Model simulated					Determined Cd ²⁺ (mg L ⁻¹)	Cd ²⁺ /Cd (%)
						Cd ²⁺ (mg L ⁻¹)	CdCl ⁺ (%)	CdSO _{4(aq)} (%)	FACd ⁺ (%)	FA ₂ Cd (%)		
3.44	3.18	3.18	4.00	6.79a	6.63Aa	6.23Ba	1.95a	2.88a	1.56c	0.01c	6.20Ba	91.3a
3.18	3.18	3.18	5.00	6.32b	6.22Ab	5.57Bb	1.34b	2.81b	4.72b	0.09b	5.53Bb	87.4b
3.18	3.18	3.18	6.00	6.06b	5.95Ab	5.00Bc	1.26b	2.64c	9.31a	0.42a	4.93Bc	81.3c
4.05	4.05	4.05	4.00	5.42a	5.32Aa	5.03ABa	1.28a	2.35a	1.34c	0.01c	4.96Ba	91.6a
4.05	4.05	4.05	5.00	4.97b	4.88Ab	4.42Bb	1.17b	2.28b	4.38b	0.10b	4.49Bb	90.4ab
4.05	4.05	4.05	6.00	4.61c	4.54Ac	3.83Bc	1.10c	2.11c	9.36a	0.47a	4.03Bc	87.3b

^a Explained in Table 1.

Table 4Comparison of calculated, simulated, and determined Cd²⁺ in the reaction solutions containing Cd(NO₃)₂, NaCl, Na₂SO₄, and FA (MW < 1000) with different Cl⁻/Cd, SO₄²⁻/Cd, and FA/Cd molar ratios and at different pH^a.

Cl ⁻ /Cd	SO ₄ ²⁻ /Cd	FA/Cd	pH	Determined Cd (mg L ⁻¹)	Equation calculated Cd ²⁺ (mg L ⁻¹)	Model simulated					Determined Cd ²⁺ (mg L ⁻¹)	Cd ²⁺ /Cd (%)
						Cd ²⁺ (mg L ⁻¹)	CdCl ⁺ (%)	CdSO _{4(aq)} (%)	FACd ⁺ (%)	FA ₂ Cd (%)		
3.63	3.18	3.18	4.00	7.08a	6.90Aa	6.63Aa	2.04a	2.91a	0.65c	N.A. ^b	6.56Aa	92.8a
3.20	3.18	3.18	5.00	6.24b	6.13Ab	5.73Bb	1.39b	2.91a	2.33b	0.04b	5.70Bb	91.3a
3.18	3.18	3.18	6.00	6.13b	5.95Ab	5.52Bb	1.47b	2.86b	3.98a	0.18a	5.62Bb	91.7a
4.05	4.05	4.05	4.00	5.54a	5.45Aa	5.24Aa	1.27a	2.32a	0.57c	N.A.	5.07Aa	91.4a
4.05	4.05	4.05	5.00	4.85b	4.76Ab	4.42Bb	1.22b	2.29b	1.99b	0.04b	4.54Bb	93.8a
4.05	4.05	4.05	6.00	4.86b	4.78Ab	4.32Bb	1.21b	2.25b	3.89a	0.19a	4.36Bb	89.8b

^a Explained in Table 1.

^b Not applicable.

Table 5Comparison of calculated, model simulated, and determined Cd²⁺ in deionized distilled water and 0.1 M HCl saturation extracts of a heavy metals contaminated soil (Erhlin soil series, Changhua Township)^a.

Saturation extract	pH	Soil solution Cd (mg kg ⁻¹)	Equation calculated Cd ²⁺ (mg kg ⁻¹)	Model simulated Cd ²⁺ (mg kg ⁻¹)	Determined Cd ²⁺ (mg kg ⁻¹)
Deionized distilled water	6.24a	0.039Ab	0.028Bb	0.005Cb	N.D. ^b
0.1 M HCl	4.37b	9.84Aa	0.26Da	1.07Ca	9.13B

^a Means within each column followed by same lower case letter and those within each row followed by same upper case letter, are not significantly different at 5% level by least significant difference (LSD) test.

^b Chromatographic peak of Cd²⁺ was not observed and detected by the sensitivity threshold of IC. The method detection limit (MDL) of Cd²⁺ concentration in deionized distilled water saturation extract determined by IC is 0.85 mg L⁻¹.

Table 6
Comparison of calculated, model simulated, and determined Cd²⁺ in deionized distilled water saturation extracts of a red soil (Wufong Township, Taichung County) spiked with various amounts of Cd as Cd(NO₃)₂.

Amount of Cd spiked (mg kg ⁻¹)	pH	Soil solution Cd (mg kg ⁻¹)	Equation calculated Cd ²⁺ (mg kg ⁻¹)	Model simulated Cd ²⁺ (mg kg ⁻¹)	Determined Cd ²⁺ (mg kg ⁻¹)
5.08	3.76a	0.69Ad	0.68Ad	0.58Bd	N.D. ^b
10.2	3.50b	2.53Ac	2.48Ac	2.27Bc	1.07Cc
20.3	3.25c	8.08Ab	7.85Bb	7.32Cb	4.72Db
30.5	3.03d	14.2Aa	13.6Ba	12.7Ca	5.49Da

^a Explained in Table 5.

^b Explained in Table 5.

The concentrations of Cd²⁺ simulated by Model MINTEQ [17] showing the same trend as that of determined Cd and calculated Cd²⁺ as described above for Cl⁻/Cd and SO₄²⁻/Cd ratios in the pH range of 4.00–6.00 (Table 2). The comparison between the concentration of Cd²⁺ calculated by Eq. (8) and that simulated by Model MINTEQ [17] were not statistically different at each corresponding pH and for Cl⁻/Cd and SO₄²⁻/Cd ratios. The concentrations of CdCl⁺ simulated by Model MINTEQ [17] were statistically different between pH 4.00 and 5.00 as well as 6.00 for Cl⁻/Cd and SO₄²⁻/Cd ratios of 3.18 and 3.45 (Table 2). However, for Cl⁻/Cd and SO₄²⁻/Cd ratio of 4.05 the differences of CdCl⁺ and CdSO_{4(aq)} concentrations were not statistically significant in the pH range of 4.00–6.00. The concentrations of CdCl⁺ and CdSO_{4(aq)} were not comparable to those of Cd²⁺ at each corresponding pH for Cl⁻/Cd and SO₄²⁻/Cd ratios. The concentration of CdCl⁺ for Cl⁻/Cd ratio of 3.45 and at pH 4.00 was significantly larger than those for Cl⁻/Cd ratio of 3.18 and at pH 5.00 and 6.00. This may be due to more formation of CdCl⁺ in the reaction system for Cl⁻/Cd ratio of 3.45 at pH 4.00 than those for Cl⁻/Cd ratio of 3.18 at pH of 5.00 and 6.00. The simulated concentrations of CdSO_{4(aq)} at pH 4.00, 5.00, and 6.00 showed the formation of appreciable amount of ion pair CdSO_{4(aq)} in the reaction systems especially for Cl⁻/Cd and SO₄²⁻/Cd ratios of 3.18.

The concentrations of Cd²⁺ determined by IC were not significantly different in the pH range of 4.00–6.00 for Cl⁻/Cd and SO₄²⁻/Cd ratios of 3.18 and 3.45. However, for Cl⁻/Cd and SO₄²⁻/Cd ratio of 4.05 the concentration of Cd²⁺ was significantly larger at pH 4.00 than at pH 6.00 (Table 2). This indicates that both stoichiometric ratio of Cl⁻/Cd as well as SO₄²⁻/Cd and pH affect the concentration of Cd²⁺ in the reaction system. Comparisons of the concentration of Cd²⁺ determined by IC to those calculated by Eq. (8) and simulated by Model MINTEQ [17] considering the formation of CdSO₄ at each corresponding pH and for Cl⁻/Cd and SO₄²⁻/Cd ratios were not statistically significant (Table 2). This clearly indicates that concentration of Cd²⁺ calculated by Eq. (8) considering solely the effect of complexation of Cl⁻ with Cd²⁺ and that simulated by Model MINTEQ [17] can accurately estimate Cd²⁺ concentration as that directly determined by IC with cation separation column in the pH range of 4.00–6.00 for Cl⁻/Cd and SO₄²⁻/Cd ratios. Further, based on the concentration of Cd²⁺ determined by IC and the Cd²⁺/Cd weight percentages the most species of Cd for Cl⁻/Cd and SO₄²⁻/Cd ratios of 3.18, 3.45 and 4.05 and in the pH range of 4.00–6.00 was in the form of Cd²⁺ (Table 2).

3.3. Cd²⁺ concentration in the presence of Cl⁻, SO₄²⁻, and fulvic acid

Cd potentially reacted with both FA (MW > 1000) and especially with FA (MW < 1000) derived from swine manure-based compost at pH 4.00 and especially at pH 6.50 [21]. In this reaction system, FA (MW > 1000) or FA (MW < 1000) was thus amended to study its effect on the concentration of Cd²⁺ in solution.

The determined concentrations of Cd by ICP-OES for Cl⁻/Cd, SO₄²⁻/Cd as well as FA/Cd ratios of 3.18, 3.44, and 4.05 in the pH

range 4.00–6.00 were shown in Table 3. The concentration of Cd significantly decreased with increasing pH and particularly Cd concentration was higher for Cl⁻/Cd, SO₄²⁻/Cd as well as FA/Cd ratios of 3.18 and 3.44 at pH 4.00 than at pH 5.00 and 6.00 (Table 3). This indicates that Cd may complex with various ligands to form precipitation which cannot be determined by ICP-OES as total dissolved Cd in supernatant of aqueous solution at pH 5.00 and 6.00.

The Cd²⁺ concentrations calculated by Eq. (8) showed the same trend as that of Cd for each Cl⁻/Cd, SO₄²⁻/Cd as well as FA/Cd ratio, and pH as described above (Table 3) and the dependence of Cd²⁺ concentration calculated by Eq. (8) on pH in this reaction system was different from the reaction system in the absence of FA (MW > 1000) (Tables 2 and 3). This is mainly attributed to the dissociation of FA (MW > 1000) at higher pH, leading to the formation of complex species FACd⁺ and FA₂Cd, which in turn causes lower concentration of Cd²⁺ calculated at higher pH. Moreover, the formation of hydrolyzed species of Cd²⁺ such as CdOH⁺ and Cd(OH)_{2(aq)} as well as Cd(OH)_{2(s)} mainly increase with increasing pH in the range of 4.00–6.00 [20], indicating the competition of Cl⁻ with OH⁻ with varying degrees to react with Cd²⁺ in the reaction systems. Consequently, the determined concentration of total dissolved Cd will be decreased when the species Cd(OH)_{2(s)} was formed in the reaction system. This thus resulted in less calculated concentration of Cd²⁺ (Table 3) using Eq. (8) when K₁, K₂, K₃, and K₄ and the determined concentration of Cl⁻ (denoted as [Cl⁻]) were constants.

The concentrations of Cd²⁺ simulated by Model MINTEQ [17] for Cl⁻/Cd, SO₄²⁻/Cd, and FA/Cd ratios of 3.44, 3.18 and 4.05 and in the pH range of 4.00–6.00 decreased with increasing pH (Table 3). This indicates that [OH⁻] (or pH) plays a role in affecting the estimation of Cd²⁺ concentrations for Cl⁻/Cd, SO₄²⁻/Cd, and FA/Cd ratios of 3.44, 3.18, and 4.05 and in the pH range of 4.00–6.00 by the formation of complex species FACd⁺ and FA₂Cd resulted from the dissociation of FA (MW > 1000). Consequently, for each corresponding pH the concentration of Cd²⁺ simulated by Model MINTEQ [17] was thus significantly less than that calculated by Eq. (8), which only considers the concentration of inorganic ligand Cl⁻ reacting with Cd²⁺ in Eq. (8). The percentage of CdCl⁺ or CdSO_{4(aq)} significantly decreased with increasing pH while that of FACd⁺ or FA₂Cd significantly increased with increasing pH in the pH range of 4.00–6.00 (Table 3). The reverse trend of the change of percentage with pH between CdCl⁺ as well as CdSO_{4(aq)} and FACd⁺ as well as FA₂Cd may be mainly attributed to higher pH resulting in larger deprotonation of FA (MW > 1000) and leading to more formation of FACd⁺ and FA₂Cd and less formation of CdCl⁺ and CdSO_{4(aq)} in the reaction system.

The concentrations of Cd²⁺ determined by IC were significantly decreased with increasing pH in the range of 4.00–6.00 for Cl⁻/Cd, SO₄²⁻/Cd, and FA/Cd ratios of 3.18, 3.44 and 4.05 (Table 3). As mentioned above, higher pH promotes the dissociation of FA (MW > 1000) leading to much more formation of complex species FACd⁺ and FA₂Cd and thus less amount of Cd²⁺ left in the reaction system. The concentration of Cd²⁺ determined by IC as well as simulated by Model MINTEQ [17] was significantly less than

that calculated by Eq. (8) at each corresponding pH and for Cl^-/Cd , $\text{SO}_4^{2-}/\text{Cd}$, and FA/Cd ratios (Table 3). This clearly indicates that concentration of Cd^{2+} simulated by Model MINTEQ [17] considering the formation of CdCl^+ , $\text{CdSO}_4(\text{aq})$, and FACd^+ as well as FA_2Cd can accurately estimate Cd^{2+} concentration as that directly determined by IC with cation separation column in the pH range of 4.00–6.00 for Cl^-/Cd , $\text{SO}_4^{2-}/\text{Cd}$, and FA/Cd ratios. Moreover, based on the concentration of Cd^{2+} determined by IC and the Cd^{2+}/Cd weight percentages (91.6–81.3%), the most species of Cd were in the form of Cd^{2+} for Cl^-/Cd , $\text{SO}_4^{2-}/\text{Cd}$, and FA/Cd ratios of 3.18, 3.44 and 4.05 and in the pH range of 4.00–6.00 (Table 3). Further, the concentration of determined Cd^{2+} as well as the percentage of Cd^{2+}/Cd decreased with increasing pH can also be attributed to the pH-dependence of deprotonation of FA ($\text{MW} > 1000$) and the subsequent formation of FACd^+ as well as FA_2Cd .

The characteristics of FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$) related to their reaction with cations including metals and proton are mainly of total acidity, and carboxyl and phenolic OH contents, which were of 12.1 and 15.9, 3.15 and 2.04, and 8.95 and 13.9 mmol g^{-1} , respectively. Moreover, the distribution percentages of characteristic carbons in cross-polarization magic-angle spinning ^{13}C nuclear magnetic resonance (CPMAS ^{13}C NMR) spectra (not shown) showed that C in carboxylic group of FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$) were 16.2% and 14.2%, respectively. Their difference was statistically significant and followed the trend revealed by functional group analysis described above. Because the characteristic differences between FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$) related to their reaction with cations including metals and proton were statistically different, the calculated Cl^-/Cd of 3.18 was determined as 3.63 and 3.20 at pH 4.00 and 5.00, respectively, of FA ($\text{MW} < 1000$) reaction system, which were different from those of FA ($\text{MW} > 1000$) (Tables 3 and 4). The concentration of Cd determined by ICP-OES, that of Cd^{2+} calculated by Eq. (8), that of Cd^{2+} and percentage of CdCl^+ simulated by MINTEQ [17], and the concentration of Cd^{2+} determined by IC were significantly larger at pH 4.00 than at pH 5.00 and 6.00 for $\text{SO}_4^{2-}/\text{Cd}$ and FA/Cd molar ratios of both 3.18 and 4.05 (Table 4). This trend is different from that of FA ($\text{MW} > 1000$) reaction system to some extent (Tables 3 and 4), which can be attributed to statistically significant differences of characteristics between FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$) described above. Moreover, except for Model simulated percentage of FACd^+ , the trend for statistically significant differences in the percentages of CdSO_4 or FA_2Cd of FA ($\text{MW} < 1000$) reaction system was different from that each of FA ($\text{MW} > 1000$) reaction system in the pH range of 4.00–6.00 for $\text{SO}_4^{2-}/\text{Cd}$ and FA/Cd molar ratios of both 3.18 and 4.05 (Tables 3 and 4). Further, though the percentage of Cd^{2+}/Cd also showed that Cd^{2+} was the main species in FA ($\text{MW} < 1000$) reaction system, the trend for statistically significant differences in the percentages of Cd^{2+}/Cd was different from that of FA ($\text{MW} > 1000$) reaction system (Tables 3 and 4), which can also be ascribed to statistically significant differences of characteristics between FA ($\text{MW} > 1000$) and FA ($\text{MW} < 1000$).

FAs are the fraction of humic substances that are soluble under all pH conditions [22]. FAs and their correspondingly dissociated form fulvates anion can thus be regarded as typically dissolved organic carbon (DOC) in soil and associated solutions. As seen from Tables 1–4, DOC derived from FAs as well as their corresponding fulvate organic anion was much more potentially in the reduction of Cd^{2+} free ion concentrations than Cl^- and SO_4^{2-} inorganic anions in the reaction systems. The estimation of Cd^{2+} concentration calculated by equation, simulated by Model, or determined by IC thus strongly depends on the presence of potential Cl^- and SO_4^{2-} inorganic anions and especially DOC in soil and associated solutions though Cd^{2+} still accounted for more than 80% of dissolved Cd in common pH range.

3.4. Calculation, simulation, and determination of Cd^{2+} concentrations of rhizosphere soil solutions

Because the pH of deionized distilled water saturation extract of the heavy metals contaminated soil was high to 6.24, Cd concentration in this extract determined by ICP-OES was very low to 0.039 mg kg^{-1} (converted to soil weight basis). Consequently, the Cd^{2+} concentrations calculated by Eq. (8) and simulated by Model MINTEQ [17] were also very low. Moreover, Cd^{2+} concentration determined by IC was even lower than method detection limit (MDL) (Table 5). However, the differences of the concentrations among soil solution Cd, and equation calculated and Model simulated Cd^{2+} were significant. To simulate rhizosphere soil solution, the pH of 0.1 M HCl saturation extract of the heavy metals contaminated soil was low to 4.37. The Cd concentration in this saturation extract of the soil was 9.84 mg kg^{-1} (converted to soil weight basis). Correspondingly, the Cd^{2+} concentration determined by IC was significantly less than the Cd concentration in 0.1 M HCl saturation extract of the heavy metals contaminated soil (Table 5). However, the Cd^{2+} concentrations calculated by Eq. (8) and simulated by MINTEQ [17] were significantly lower than that determined by IC (Table 5). This is probably because very high concentration of Cl^- was present in 0.1 M HCl saturation extract of the heavy metals contaminated soil and the Cl^- concentration was used to substitute into Eq. (8) and Model MINTEQ [17] to calculate and simulate Cd^{2+} concentrations, respectively.

The pH values of deionized distilled water saturation extract of the red soil spiked with various amounts of Cd as $\text{Cd}(\text{NO}_3)_2$ were in the range of 3.76–3.03 (Table 6); hence the deionized distilled water saturation extracts can be regarded as the solutions close to rhizosphere soil solutions. The determined soil solution Cd concentrations converted to soil weight basis were much lower than the amounts of spiked Cd of the red soil. This can be ascribed to the spiked Cd reacting with soil organic and inorganic components leading to the formation of complexes containing Cd, which were not dissolved in deionized distilled water saturation extract. When the amount of spiked Cd of the red soil was 5.08 mg kg^{-1} , the concentrations of determined soil solution Cd and equation calculated Cd^{2+} were significantly larger than that of simulated Cd^{2+} concentration, while IC determined Cd^{2+} concentration was lower than MDL (Table 6). The pH of deionized distilled water saturation extract decreased with increasing the amount of spiked Cd as $\text{Cd}(\text{NO}_3)_2$. This may be due to acidic characteristic of $\text{Cd}(\text{NO}_3)_2$ reacting with soil components of the red soil. Moreover, the pH of deionized distilled water saturation extract was inversely proportional to the concentrations of soil solution Cd, equation calculated Cd^{2+} , Model simulated Cd^{2+} , and IC determined Cd^{2+} . When the amount of spiked Cd was 10.2 mg kg^{-1} , the soil solution Cd concentration and equation calculated Cd^{2+} concentration were significantly larger than Model simulated Cd^{2+} concentration and IC determined Cd^{2+} concentration (Table 6). However, when the amounts of spiked Cd as $\text{Cd}(\text{NO}_3)_2$ were 20.3 and 30.5 mg kg^{-1} , the differences among the concentrations of soil solution Cd, equation calculated Cd^{2+} , Model simulated Cd^{2+} , and IC determined Cd^{2+} were significant. This trend is very close to that of simulated soil solutions described above containing potentially influencing Cl^- , SO_4^{2-} inorganic anions and fulvate organic anion in the pH range of 4.00–6.00. On the other hand, the percentages of Cd^{2+}/Cd at the amounts of spiked Cd of 10.2, 20.3, and 30.5 mg kg^{-1} were not as high as those of simulated soil solutions (Tables 1–4 and 6). This is probably because of the dissolved Cd^{2+} reacting with soil components of the red soil.

The four replicated ion chromatographs for the determination of Cd^{2+} concentrations in four 0.1 M HCl or in four deionized distilled water saturation extracts of the heavy metals contaminated soil (Erhlin soil series, Changhua Township) or in four deionized

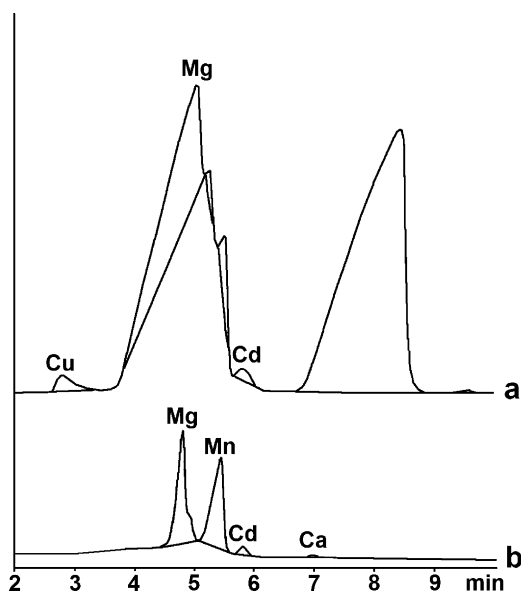


Fig. 1. Ion chromatograms of (a) 0.1 M HCl saturation extract of a heavy metals contaminated soil, and of (b) after the pH of 0.1 M HCl saturation extract adjusted to 5.00 and then added with Mg^{2+} equivalent oxalate as oxalic acid.

distilled water saturation extracts of the red soil (Wufong Township, Taichung County) were not significantly different. Therefore, one of each set of four chromatographs from various treatments of the heavy metals contaminated soil and of the red soil were shown in Figs. 1 and 2, respectively. Though the chromatographic peak of Cd^{2+} in 0.1 M HCl saturation extract of the heavy metals contaminated soil (Erhlin soil series, Changhua Township) was partially shielded by the vicinal chromatographic peaks and especially the peak of Mg^{2+} (Fig. 1a) the concentrations of Cd^{2+} and other cations including Ca^{2+} and Mg^{2+} still can be determined by interpolations. The Cd^{2+} concentration was thus shown in Table 5. In order to identify the accuracy of determined Cd^{2+} concentration by the chromatograph shown in Fig. 1a, a certain volume of 0.1 M HCl saturation extract was added with 1.0 M and then 0.1 M NaOH to adjust the solution pH to 5.00 and then an amount of Mg^{2+} equivalent oxalate as oxalic acid was added to precipitate Ca^{2+} and Mg^{2+} in 0.1 M HCl saturation extract. Subsequently, the final extract solution was diluted with deionized distilled water to volumetric volume and then subjected to the determination of Cd^{2+} concentration by IC. The chromatographic peaks of Mg^{2+} and especially Ca^{2+} were thus drastically subsided and chromatographic peak of Cd^{2+} was distinctly separated from the vicinal peaks in the chromatograph (Fig. 1b). The Cd^{2+} concentration interpolated and determined by the chromatograph Fig. 1b was not significantly different from that determined by the chromatograph Fig. 1a. However, from the evaluation of chromatographs Fig. 1a as well as Fig. 1b, it clearly indicates that the determination of Cd^{2+} concentrations in intrinsic rhizosphere soil solution or in acidified bulk soil solution as well as simulated rhizosphere soil solution of slightly acidic soils by IC may encounter the interferences of potential concentrations of some cations such as Ca^{2+} , Mn^{2+} , and especially Mg^{2+} . Under this situation, the Cd^{2+} concentrations in rhizosphere soil solutions may be alternatively calculated by Eq. (8) and/or simulated by Model MINTEQ [17] described above.

The Cd^{2+} concentration in deionized distilled water saturation extract of the red soil was not detectable and no chromatographic peak of Cd^{2+} was shown in Fig. 2a. After being spiked with various amounts of Cd as $Cd(NO_3)_2$, the chromatographic peak height of Cd^{2+} in IC chromatograph of deionized distilled water saturation extract of the red soil increased with increasing the spiked concen-

tration of Cd as $Cd(NO_3)_2$ (Fig. 2b–e). When 5.08 mg kg^{-1} of Cd as $Cd(NO_3)_2$ (soil weight basis) was spiked to the red soil, the Cd^{2+} chromatographic peak in IC chromatograph of deionized distilled water saturation extract showed only a weak shoulder (Fig. 2b). Consequently, the Cd^{2+} concentration was thus not detectable and lower than MDL (Table 6). However, when the amounts of spiked Cd as $Cd(NO_3)_2$ converted to soil weight bases were 10.2, 20.3, and 30.5 mg kg^{-1} , the chromatographic peaks of Cd^{2+} were distinctly separated from their vicinal chromatographic peaks of Mn^{2+}

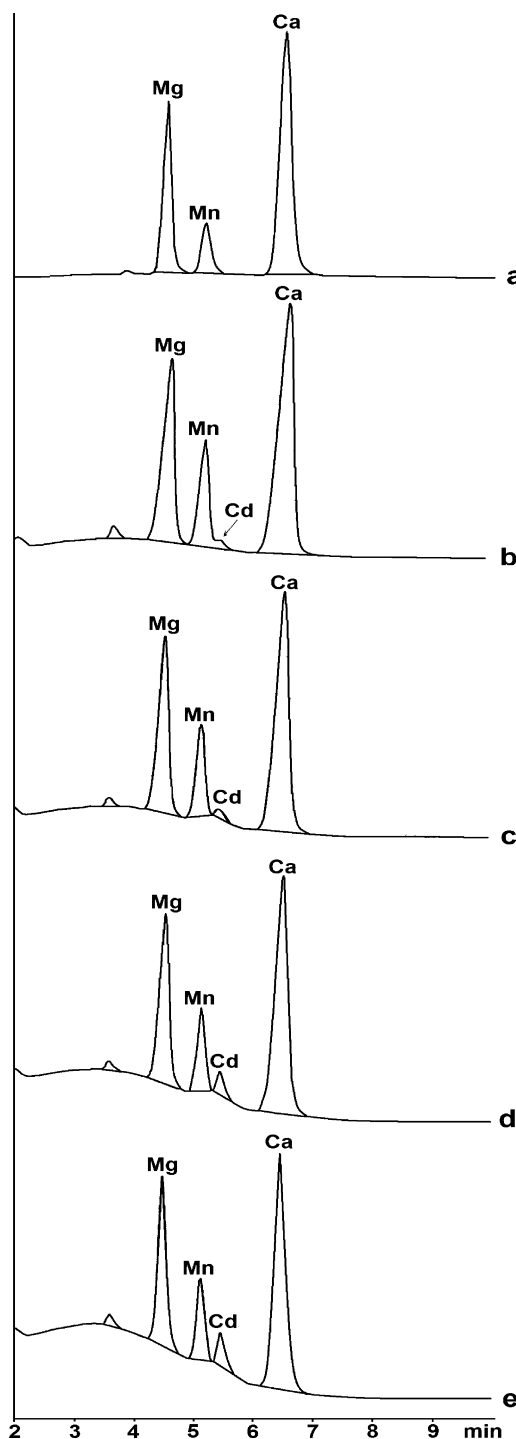


Fig. 2. Ion chromatograms of (a) deionized distilled water saturation extract of a red soil, and of deionized distilled water saturation extracts of the red soil spiked with (b) 5.08 mg kg^{-1} , (c) 10.2 mg kg^{-1} , (d) 20.3 mg kg^{-1} , and (e) 30.5 mg kg^{-1} Cd as $Cd(NO_3)_2$.

(Fig. 2c–e) and the Cd^{2+} concentrations in deionized distilled water saturation extracts of the red soil were thus interpolated and determined. Moreover, it was found that the baseline height of the IC chromatograph of deionized distilled water saturation extract of the red soil increased with increasing the spiked concentration of Cd as $\text{Cd}(\text{NO}_3)_2$ (Fig. 2a–e). This is probably because of the acidic characteristic of $\text{Cd}(\text{NO}_3)_2$ in deionized distilled water saturation extract of the red soil leading to the formation of hump-shape baseline and the dissolution of other cations. Because the red soil used in this study was moderately weathered, it thus has lower base saturation and higher concentration of dissolved Mn. Consequently, it is postulated that chromatographic peak of Cd^{2+} in intrinsic rhizosphere soil solution of highly weathered soils may not be shielded by the chromatographic peaks of Ca^{2+} and Mg^{2+} but by the chromatographic peak of Mn^{2+} in IC analysis. The Cd^{2+} concentrations in rhizosphere soil solutions of highly weathered soils calculated by Eq. (8) and/or simulated by Model MINTEQ [17] were also thus potential alternatives.

4. Conclusions

In simulated soil solutions in the pH range of 4.00–6.00 for Cl^-/Cd , $\text{SO}_4^{2-}/\text{Cd}$, and FA/Cd molar ratios of around 4, based on equation calculated, Model simulated, and directly determined by IC equipped with cation separation column, Cl^- and SO_4^{2-} inorganic anions and especially fulvate organic anions substantially affect Cd^{2+} free cation concentrations. Moreover, pH as well as OH^- concentration and related dissociation of FA affect Cd^{2+} concentrations calculated by equation, simulated by Model, and directly determined by IC in simulated soil solutions. The determination of Cd^{2+} concentration in simulated rhizosphere soil solution (0.1 M HCl saturation extract) of a heavy metals contaminated soil with slightly acidic bulk soil pH by IC revealed substantial interference of Mg^{2+} concentration which can be eliminated by the addition of Mg^{2+} equivalent amount of oxalate as oxalic acid. On the contrary, the determination of Cd^{2+} concentrations by IC in deionized distilled water saturation extracts of a moderately weathered acidic red soil spiked with Cd as $\text{Cd}(\text{NO}_3)_2$ showed the possibly potential interference of Mn^{2+} concentration. Therefore, based on the consideration of interferences in the determination of Cd^{2+} concentrations in soil solutions by IC, the Cd^{2+} concentrations in simulated rhizosphere soil solutions of acidic or slightly acidic soils can be calculated by equation and/or simulated by model. These calculated by equation and/or simulated by model values may be used as potential alternatives for those determined by IC.

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