Influence of Cu and Ca cations on ciprofloxacin transport in saturated porous media

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HIGHLIGHTS

- Quartz sand effectively sorbed ciprofloxacin (CIP) with Fe/Al oxides on surface being important.
- Aqueous Ca and Cu significantly promoted CIP transport in clean sand.
- Neither Cu nor Ca was effective in mobilizing pre-sorbed CIP from native sand.
- Mathematical model successfully simulated CIP transport in sand media.

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ABSTRACT

Emerging contaminant ciprofloxacin (CIP) has been frequently detected in soils and groundwater; however, impacts of cations on its transport in the environment remain largely unknown. We examined CIP transport in saturated sand media under the influence of Cu/Ca by either mixing CIP with Cu/Ca in solution or preloading CIP onto sand then using Cu/Ca solution to mobilize CIP. Though the amount of Fe/Al oxides on native sand surface was limited, it significantly impeded CIP transport, delaying CIP breakthrough curve from 30 to >100 PV. In clean sand where Fe/Al oxides were removed, Ca and Cu significantly promoted CIP transport by reducing the retardation factor R from 22 to <2. In native sand, due to CIP’s strong complexation with Fe/Al, only Cu promoted CIP transport. When CIP was pre-sorbed onto sand, neither Cu nor Ca was effective in mobilizing CIP from native sand. However, Cu effectively mobilized 90% CIP whereas Ca mobilized 30% CIP from clean sand. A mathematical model based on advection–dispersion equation coupled with equilibrium and kinetic reactions successfully simulated CIP transport in saturated sand media. Our results suggested that cations in aqueous solution and on solid phase are important to better understand CIP transport in soils.

1. Introduction

Ciprofloxacin (CIP), one of the most widely prescribed fluoroquinolones (FQs) antibiotics, is widely used in health care and agricultural industries to treat human and animal diseases. It is refractory to biodegradation and effective at low doses [1], so it is persistent in the environment and imposes a risk to the ecosystems. CIP has been frequently detected in streams and groundwater [2,3], with the concentrations ranging from ng L⁻¹ to mg L⁻¹ [4]. It has high sorption affinity onto soils [5–8], so up to ppm levels of CIP can accumulate in soils. Therefore, soil can act as a reservoir of CIP [9]. Hence, it is important to examine the fate and transport behaviors of CIP in soil and water system.

The ability of FQs to form complexes with metal cations is important for their antibiotic activity [10], so metal cations are expected to influence their fate and transport in the environment. The high affinity of soil matrix for FQs has been attributed to their complexation with cations [7,11–14] and the attraction of their protonated piperazine moiety (NH₃⁺) to the negatively-charged mineral surface [15]. Interaction between FQs and soil minerals are strong even silica shows substantial sorption ability for FQs [15]. Minerals like Fe/Al oxides can develop both positive and negative surface charge [19,20], even present in limited quantity in soils, they are the major sorption sites for CIP [8,11]. However, the interactions between FQs and metal cations are reversible and controlled by the type of metal cations [10,16]. The impacts of metal cations on CIP sorption onto minerals have been studied in batch experiments [17,18], however, little information is available regarding their impacts on CIP transport. It is expected that metals in both aqueous and solid...
phase greatly influence the fate and transport of CIP in porous media and soils.

The objective of this study was to provide insights into how metal cations influence CIP transport in porous media to better understand its chemodynamic behaviors in soils and receiving waters, which is essential for comprehensive assessment of their potential environmental risk. We hypothesized that cations both in aqueous phase and on solid phase were critical factors controlling CIP transport in saturated porous media. To test the hypothesis, column experiments using saturated quartz sand were conducted to compare the transport behavior of CIP in two sands and in presence of two cations. The specific objectives were to: (1) evaluate the effects of Fe/Al coating on sand surface on CIP transport in porous media, (2) compare the effects of Cu and Ca cations on retention and transport of CIP in porous media; (3) compare the effects of Cu and Ca cations on mobilization of CIP presorbed on porous media; and (4) apply solute transport models to simulate the retention and transport of CIP in porous media.

2. Materials and methods

2.1. Materials

Ciprofloxacin (ACS 85721–33–1) was purchased from Applichem (Darmstadt, Germany) (Table 1). All other chemicals were of analytical grades from Fisher Scientific (Pittsburgh, PA). CIP stock solution (40 mg L⁻¹) was prepared in deionized (DI) water and stored at 4 °C in darkness. All solutions were prepared in DI water at pH 5.6 and glassware was acid-washed before use.

Quartz sand from Standard Sand & Silica Co. (Davenport, FL) was sieved to size range of 0.5–0.6 mm. To remove Fe/Al coating from the sand surface, the native sand was first washed with tap and DI water, and then heated in 70% nitric acid at 90 °C for 5 h at 1:1.5 sand to acid ratio. The acid-washed sand was then washed with DI water to remove the acid and was referred to as clean sand. The point of zero charge was determined by potentiometry titration method [21] (Table 2). The elemental composition of the sand was determined by ICP-MS after digesting with HNO₃/H₂O₂ using hot-block digestion procedure [22].

2.2. Column and batch experiments

The sand was wet-packed into an acrylic column of 1.5 cm × 10 cm (d × h) according to Chen et al. [23]. Sand was gradually poured gently into 8 mL of DI water standing in the column until the sand surface was slightly below the water level. A polypropylene stir-rod was used to stir the sand to remove air bubble and ensure uniformity. This procedure was repeated several times until the column was fully packed with ~32 g of sand with a porosity of 0.42. A peristaltic pump (Masterflex L/S, Cole Parmer instrument) was used to regulate the upward flow at a constant rate of 0.2 cm min⁻¹. DI water was first pumped through the saturated column for ~2 h to remove impurities and then followed by working solutions for column experiment. Bromide was added to the column as a conservative tracer for the breakthrough studies.

2.2.1. Impacts of aqueous Ca and Cu on CIP transport in sand media

To test the impacts of aqueous Ca and Cu on CIP transport in sand media, 0.2 mg L⁻¹ CIP (0.7 nM) was mixed with DI water, 1 μM CaCl₂ or 1 μM CuCl₂. Once the outflow was stabilized, the experiment was then terminated. Effluent samples were collected from the column top with a fraction collector (IS-95 Interval Sampler, Spectrum Chromatography) during sample injection and column flushing to analyze CIP concentrations. All experiments were performed in duplicate.

To determine the impacts of Ca and Cu on CIP sorption onto sand, batch experiments in triplicate with the same CIP and Ca or Cu concentration was conducted using 50 mL polytetrafluoroethylene centrifuge tubes. Each vessel was filled with 3.00 g of sand and 30 mL of 0.7 nM CIP with DI water, 1 μM CaCl₂ or 1 μM CuCl₂. The vessels were shaken for 24 h. Preliminary experiment showed that it reached equilibrium within 24 h (data not shown). The suspensions were centrifuged at 5000 × g for 10 min to separate the solids from the liquid phase. Aliquots of supernatant were withdrawn to determine CIP concentrations, and CIP concentrations on solid phase were obtained through mass balance calculations [22].

2.2.2. Impacts of aqueous Ca and Cu on mobilization of CIP presorbed onto sand media

In the previous experiment, CIP and Cu or Ca was transported simultaneously in the column. To determine the ability of aqueous Ca and Cu in mobilizing CIP presorbed onto sand media, CIP was applied to the column at a 5 PV pulse, and then the column was flushed with DI water, 1 μM CaCl₂, or 1 μM CuCl₂. Experiment was terminated when outflow stabilized or after 100 PV. Effluent samples were collected from column top with a fraction collector during flushing with Ca or Cu solution to analyze CIP concentrations. All column experiments were performed in duplicate.

Since Ca/Cu was ineffective in mobilizing CIP presorbed onto sand column, a column study was conducted. For each experiment, CIP was applied to the columns at a 5 PV pulse, and then the columns was flushed with 5 PV of DI water, 1 μM CaCl₂, or 1 μM CuCl₂. At the end of flushing, the column was separated into 10 sections to determine CIP concentrations retained onto the sand as a function of column depth. The sand was excavated under saturated conditions

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Table 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>MW</th>
<th>pKₐ</th>
<th>Charge of functional group at pH 5.6</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image_url" alt="Image" /></td>
<td>311.4</td>
<td>pKₐ1 = 6.2, pKₐ2 = 8.8</td>
<td>COOH (80%), COO⁻ (20%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NH₄⁺ (100%)</td>
</tr>
</tbody>
</table>

2.2. Column and batch experiments

- The sand was wet-packed into an acrylic column of 1.5 cm × 10 cm (d × h) according to Chen et al. [23]. Sand was gradually poured gently into 8 mL of DI water standing in the column until the sand surface was slightly below the water level. A polypropylene stir-rod was used to stir the sand to remove air bubble and ensure uniformity. This procedure was repeated several times until the column was fully packed with ~32 g of sand with a porosity of 0.42. A peristaltic pump (Masterflex L/S, Cole Parmer instrument) was used to regulate the upward flow at a constant rate of 0.2 cm min⁻¹. DI water was first pumped through the saturated column for ~2 h to remove impurities and then followed by working solutions for column experiment. Bromide was added to the column as a conservative tracer for the breakthrough studies.

Table 2

<table>
<thead>
<tr>
<th>Cation exchange capacity (meq kg⁻¹)</th>
<th>Point of zero charge</th>
<th>Fe (mg kg⁻¹)</th>
<th>Al (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean sand</td>
<td>0.05</td>
<td>5.0</td>
<td>1.30</td>
</tr>
<tr>
<td>Native sand</td>
<td>0.28</td>
<td>5.1</td>
<td>157</td>
</tr>
</tbody>
</table>
from top to bottom with a spatula in 1 cm increment and each increment was placed into a small vial with 4 mL of H₂PO₄/Na₂HPO₄ buffer and acetonitrile solution (i.e., 27.2 g KH₂PO₄ + 1.35 mL H₃PO₄ in 1 L water with 1:1 acetonitrile) [24]. The excavated sand was then washed three times with the same amount of extraction solution. CIP concentrations in the solutions were determined with HPLC. The CIP retention was then calculated for each sand section.

2.3. Chemical analysis

CIP concentration was determined by HPLC (Waters 2695, Milford, MA) equipped with a fluorescence detector (Waters 2475, Milford, MA). The CIP detection limit was 10 µg L⁻¹. Concentrations of sorbed Ca or Cu on the sand, and elemental concentrations in sand were analyzed by ICP-MS (NexION 300, Perkin-Elmer Corp., MA) after digestion with HNO₃/H₂O₂ using hot-block digestion procedure [22]. The detection limits for all elements were <0.5 µg kg⁻¹. The concentration of bromide, a conservative tracer for column experiment, was determined by ion chromatograph (ICS-90, Dionex Corporation).

2.4. Modeling CIP transport in saturated porous media

One dimensional advection-dispersion equation coupled with reaction terms was used to simulate CIP transport in water-saturated sand columns. We assumed that the interactions between CIP and sand grains in the column were affected by both reversible-equilibrium and irreversible-kinetic reactions [25]. The governing equation can be written as:

\[
\frac{dC_W}{dt} = D \frac{d^2C_W}{dx^2} - v \frac{dC_W}{dx} - kC_W
\]

where \(C_W\) is the CIP concentration in pore water (mg L⁻¹); \(R\) is the retardation factor, which reflects the extent of equilibrium reactions in sand column; \(D\) is the dispersion coefficient (cm² min⁻¹); \(v\) is the velocity of pore water (cm min⁻¹); and \(k\) is the kinetic reaction rate constant (min⁻¹).

We solved the governing equation of the transport model numerically for a zero initial concentration, a pulse-input boundary condition at the column inlet, and a zero-concentration-gradient boundary condition at the outlet. The model was first applied to the bromide breakthrough data to estimate dispersion coefficient \((D)\) (Br: \(R = 1, k = 0\)). We assumed that the \(D\) for CIP was the same as that of the bromide tracer in the column. CIP transports in the columns were quantified by identifying the best-fit values of \(R\) and \(k\).

3. Results and discussion

3.1. CIP species in solution and characteristics of sand

The charged species of CIP's functional groups are important as they impact its interactions with Ca, Cu and sand. CIP can exist in three forms (cationic, zwitterionic, and anionic forms) in DI water [23]. At pH 5.6, 100% of piperazinyl groups existed as \(-\text{NH}_2\) and 20% of carboxyl groups presented as \(-\text{COO}^-\) (Table 1). In comparison, \(\sim 99\%\) of Ca and Cu were present as free cations based on Visual-MINTEQ (data not shown). When coexisting with metal cations in solution, CIP can complex with Cu or Ca via its carboxyl and keto groups to form metal-CIP or metal-CIP complexes. The complexation constants of Cu-CIP and Ca-CIP are 11.3 and 14.7 (Table 3) [10]. In this study, since the amounts of Cu or Ca (1 µM) used were much greater than CIP (0.7 µM), only 1:1 metal-CIP was important (Fig. 1A). It is expected that CIP-cation complexation reactions in solution were reversible, especially when cations with high complexation ability (e.g., \(\equiv\text{Fe/Al}\)) compete with cations with low ability (e.g., Ca) [10,16].

In this experiment, the net surface charge for clean sand at pH 5.6 was negative with its PZC being 5.0–5.1 (Table 2). With the majority of negative sites being from broken edges of silicon oxides (\(\equiv\text{SiO}^-\)), CIP sorption onto sand was primarily via electrostatic attraction of its piperazinyl groups (Fig. 1B). Different from clean sand, native sand was coated with Fe/Al (157 and 904 mg kg⁻¹ Fe and Al) (Table 2), the key component for CIP sorption. The PZC for Fe/Al oxides is 10 [26] so locally their broken edges carried positive charges (\(\equiv\text{FeOH}^+\) and \(\equiv\text{AlOH}^+\)). The broken edges of Fe/Al oxides with high energy are highly reactive and can complex with CIP, forming \(\equiv\text{Fe}-\text{CIP}\) and \(\equiv\text{Al}-\text{CIP}\) (Fig. 1C). In addition, Fe/Al oxides can also sorb Ca (\(\equiv\text{Fe/AlO}^-\text{Ca}^-\)) or Fe/Al (\(\equiv\text{Fe/AlO}^-\text{Cu}^-\)) (Fig. 1C). Trivedi et al. [12] demonstrated that Cu is more likely to bind to high affinity site on goethite whereas Ca binds to low affinity site [12,19].

3.2. CIP transport in saturated sand media

The breakthrough curve (BTC) of CIP transport in clean sand column in DI water was significantly delayed compared to that of bromide, the conservative tracer (Fig. 2A). After applied to the clean sand column, CIP was first detected in the effluent at \(\sim 30\) PV. The BTC then slowly climbed to a peak value at \(-60\) PV and stayed there during further CIP injection (Fig. 2B). Compared to the bromide BTC, the delayed CIP transport indicated significant CIP retardation, which was consistent with Chen et al. [23]. The normalized peak concentration \((C/C_0)\) of CIP was \(\sim 70\%\). The breakthrough experiment demonstrated that CIP interacted with the clean sand. At pH of 5.6, CIP carried both positive and negative charge (Table 1). This interaction was attributed to the electrostatic attraction between positively-charged CIP piperazinyl group (\(\equiv\text{NH}_2\)) and negatively-charged clean sand (\(\equiv\text{SiO}^-\cdot\equiv\text{CIP}\)) [28,29] (Fig. 1B). Our data were consistent with the literature where many studies have observed the low mobility of CIP in soils [30,31].

Simulated transport model matched well with the BTC of CIP transport in clean sand with \(R^2 = 0.99\) (Fig. 2B) and the best-fit retardation factor \(R\) being 21.7 (Table 4). The best-fit kinetic reaction rate

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Stability constant (log k) of CIP with Cu, Ca, Fe and Al [10].</th>
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<tbody>
<tr>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>M(CIP)</td>
<td>11.2</td>
</tr>
<tr>
<td>M(CIP)₂</td>
<td>28.5</td>
</tr>
<tr>
<td>M(CIP)₃</td>
<td>49.6</td>
</tr>
</tbody>
</table>

When Fe/Al coating from native sand were removed, it was referred to as clean sand.

<table>
<thead>
<tr>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18</td>
</tr>
<tr>
<td>0.016</td>
</tr>
<tr>
<td>0.22</td>
</tr>
</tbody>
</table>

When Fe/Al coating from native sand were removed, it was referred to as clean sand.

\(R\) is the retardation factor, which reflects the magnitude of equilibrium reactions in the sand column; \(k\) is the kinetic reaction rate constant (min⁻¹); and \(D\) is the dispersion coefficient (cm² min⁻¹).

CIP transport in native sand column when DI water (No. 2) or 1 µM Cu (No. 4) was applied showed no breakthrough response after prolonged injection as much as 100 PV.
A) CIP forms stronger complex with Cu than Ca in solution
\[
\begin{align*}
HN-\text{COOH} + Cu^{2+} & \rightarrow HN-\text{COOCu}^{+} + H^+ \\
HN-\text{COOH} + Cu^{2+} & \rightarrow HN-\text{COOCu}^{+} + H^+
\end{align*}
\]

B) Electrostatic attraction of CIP, Ca and Cu onto clean sand surface
- H-OH
- Si-O
- Si-OH
- Si-O-\text{Ca}^+
- Si-O-\text{Cu}^+
- Si-O

C) Complex of CIP with Fe/Al and electrostatic attraction of Ca and Cu onto Fe/Al coating on native sand surface
- Al-O-OH
- Fe-O-\text{Cu}^+
- Al-O
- Fe-O
- Al-O-\text{Ca}^+

Fig. 1. Possible interactions of ciprofloxacin (CIP) with clean and native sand where HN-\text{COOH} \rightarrow CIP

The strong CIP retention in native sand column was consistent with the literature examining its sorption behaviors in soils [7,11,34,35]. As discussed above, CIP sorption onto sand under DI water was mainly controlled by two mechanisms: (1) weak electrostatic attraction between CIP and sand [36] (Fig. 1B), and (2) strong complexation between CIP carboxyl groups and Fe/Al oxides on sand surface [7] (Fig. 1C). These two mechanisms were confirmed in the literature through batch and spectroscopic studies of CIP sorption onto Fe/Al oxides and aluminosilicates [7,11,15,37].

3.3. When co-existing with CIP, aqueous Cu and Ca promoted CIP transport in clean sand

When CIP was mixed with Cu^{2+} and Ca^{2+} in solution, CIP existed primarily as Cu--CIP^{+} and Ca--CIP^{+}, with little free CIP in solution.

Fig. 2. Transport of bromide and CIP (ciprofloxacin) in saturated sand media when DI water was applied. When Fe/Al coating from native sand were removed, it was referred to as clean sand.
(Fig. 1A). This was due to the high complexity ability of CIP with Ca and Cu (log \( k = 11.3 \) and 14.7) as well as the excess amount of Ca and Cu added (Table 3) [10]. As a result, excess amounts of free Cu\(^{2+}\) and Ca\(^{2+}\) (1 \( \mu \)M) relative to Cu–CIP* and Ca–CIP* (0.7 nM) were also present in the solution. Compared to CIP transport experiment, the presence of aqueous Cu or Ca with CIP in solution significantly promoted CIP transport in clean sand (Fig. 3A and B). The BTC of CIP transport in the clean sand in presence of aqueous Cu (i.e., CIP = 0.7 nM and Cu = 1 \( \mu \)M) was only slightly retarded than the BTC of bromide (Fig. 2A). After the Cu and CIP solution was applied to the sand column, CIP was detected in the effluent at \( \approx 1.5 \) PV (Fig. 3A) compared to 30 PV under DI water (Fig. 2B). The BTC then quickly climbed to a peak value at \( \approx 4 \) PV and stayed there during further injection (Fig. 3A). Similar to Cu, the presence of aqueous Ca also significantly increased CIP transport in clean sand (Fig. 3B). CIP was detected in the effluent after applying \( \approx 1.5 \) PV of Ca and CIP solution; it then quickly reached peak value at \( \approx 5 \) PV. The C/C\(_{0}\) of CIP was \( \approx 0.70 \) (Fig. 3B), which was 25% less than that in presence of aqueous Cu (C/C\(_{0}\) = 0.95) (Fig. 3A), indicating that Ca was less effective than Cu in enhancing CIP transport in clean sand when co-existing with CIP.

This was consistent with the fact that clean sand sorbed more Cu than Ca (2.99 vs. 0.03 mg kg\(^{-1}\); Table 5). At pH 5.6, during CIP transport in clean sand, piperazine groups of CIP was effectively attracted to sand surface (=SiOH; Fig. 2). However, when 0.7 nM CIP was mixed with 1 \( \mu \)M Cu or Ca, the sand was ineffective in sorbing Cu–CIP* or Ca–CIP*. This was probably because the high concentration of aqueous Cu\(^{2+}\) and Ca\(^{2+}\) outcompeted Cu–CIP* or Ca–CIP* to be sorbed onto sand surface, leaving more CIP in the solution.

Different from kinetic transport experiment, batch experiment emphasizes equilibrium conditions in different sorbate–sorbent systems. Although different, they are governed by fundamental interactions between sand and CIP. To further test the hypothesis that aqueous Cu\(^{2+}\) and Ca\(^{2+}\) outcompeted Cu–CIP* and Ca–CIP* during transport experiment, batch experiment using 1 \( \mu \)M of Cu or Ca and 0.7 nM CIP was conducted. The ability of clean sand in sorbing CIP was reduced from 0.5 to 0.03 mg kg\(^{-1}\) in the presence of aqueous Cu and from 0.5 to 0.38 mg kg\(^{-1}\) in the presence of aqueous Ca (Table 5). In this aspect, clean sand was more effective in sorbing Cu than Ca, with CIP probably being the least effective among the three (Fig. 1B).

Though aqueous Cu and Ca effectively increased CIP transport when they co-existed with CIP, CIP BTC in the presence of either Ca or Cu showed some delay, indicating slight retardation of CIP in clean sand. This was probably due to the attraction of Cu–CIP* or Ca–CIP* onto sand surface. Simulations of the transport model matched well with CIP BTC in the presence of Ca or Cu, with R\(^2\) of 0.93 and 0.97, respectively (Table 4). The R was 1.71 (Ca) and 1.17 (Cu) and the k was 0.016 min\(^{-1}\) (Ca) and 0.0031 min\(^{-1}\) (Cu), suggesting some CIP was retained in the sand column through kinetic reactions with more in the presence of Ca than Cu. The modeling results further confirmed that Cu was more effective than Ca in enhancing CIP transport in clean sand when co-existing with CIP in solution.

3.4. When co-existing with CIP, aqueous Cu promoted CIP transport in native sand

When eluted under DI water, no CIP was detected even after 100 PV in native sand (data not shown). After applying 1 \( \mu \)M Cu and 0.7 nM CIP solution to the native sand column for \( \approx 30 \) PV, CIP was detected in the effluents (Fig. 3C). Its BTC then slowly climbed to a peak value and stayed there during further injection. The C/C\(_{0}\) of CIP was \( \approx 1 \) after 60 PV compared to \( \approx 1 \) after 4 PV in clean sand. Clearly, it was much easier for Cu–CIP* to be sorbed onto native sand where besides quartz sand, Fe/Al coating was also present. With stronger complexation of CIP to Fe/Al than Cu [11], Fe/Al coating on native sand surface enhanced CIP sorption onto sand (Fig. 1C). Since native sand showed stronger interaction with CIP than clean sand (1.4 vs. 0.5 mg kg\(^{-1}\); Table 5), it took much longer for CIP to come out from native sand than clean sand column (60 vs. 5 PV). Simulations of the transport model matched well with the experimental breakthrough data (Table 4). The k was 0.0054 min\(^{-1}\), suggesting some CIP was retained in the native sand column through irreversible-kinetic reactions. The R for CIP in native sand was 22, which was lower than the estimated R of 41 based on K\(_{eq}\) of 10 based on batch experiment. This is because the K\(_{eq}\) from batch experiment included both reversible and irreversible interactions between sand and CIP whereas only reversible interaction between sand and CIP was reflected in the R simulated based on the column experiment.

Unlike Cu, when Ca was present in the solution, CIP could not be detected even after applying 100 PV of Ca and CIP solution (data not shown), indicating much weaker complexation of Cu with CIP. This was because Cu–CIP* was 3-order magnitude stronger than Ca–CIP* [10]. As a result, it was easier for CIP to disassociate from Ca–CIP*, leaving CIP to be sorbed onto sand via strong complexation with Fe/Al on the surface. This was supported by the batch data where 1.7 and 1.0 mg kg\(^{-1}\) CIP was sorbed onto native sand in the presence
of Ca and Cu (Table 5). Our result indicated that the presence of metals in aqueous phase and surface chemistry of porous media were both important in controlling CIP retention and transport in sand media.

3.5. Aqueous Cu and Ca increased transport of presorbed CIP in clean sand

In the previous experiment, CIP was mixed with Cu or Ca in solution. Here CIP was presorbed onto sand and then leached with aqueous Cu or Ca. Both Cu and Ca mobilized CIP presorbed on clean sand surface (Fig. 4). After 1 μM Cu was applied to sand column presorbed with CIP, CIP was detected around 1.5 PV, then quickly climbed to peak ~2 PV. CIP was also detected after applying ~1.5 PV of Cu+CIP solution (Fig. 3B), indicating CIP desorption from clean sand surface was reversible. The C/C_0 of CIP was ~1.8, which was greater than unity because presorbed CIP onto sand column was released in short period when Cu was applied in the column. Mass balance calculations showed that 90% of CIP was remobilized from sand column. This was attributed to the fact that the interaction between CIP and clean sand was mostly via electrostatic attraction. When excess amount of aqueous Cu (1 μM) was applied to the column, Cu^{2+} effectively replaced the CIP on the sand surface since they were both positively charged (Fig. 1B). This was similar to the experiment where Cu^{2+} was mixed with CIP, with Cu being more effective being sorbed onto clean sand surface than CIP.

Similar to Cu, after 1 μM Ca was applied to sand column with presorbed CIP, CIP was detected ~1.5 PV, then quickly climbed to peak at ~3 PV (Fig. 4). The C/C_0 of CIP was ~0.25. Mass balance calculations showed that 30% of CIP was remobilized from sand column compared to 90% by 1 μM Cu. This was consistent with

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Cu/Ca in solution (mg L⁻¹)</th>
<th>CIP sorbed (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clean</td>
<td>Native</td>
</tr>
<tr>
<td>DI water</td>
<td>2.99 ± 0.02</td>
<td>21.7 ± 1.40</td>
</tr>
<tr>
<td>1 μM Cu</td>
<td>0.03 ± 0.03</td>
<td>0.21 ± 0.06</td>
</tr>
</tbody>
</table>

Table 5: Sorption of CIP onto clean and native sand after shaking 3 g of sand with 0.7 mM CIP (ciprofloxacin) plus water, 1 μM Ca or 1 μM Cu for 24 h.

the fact that clean sand was more effective in sorbing Cu than Ca (Table 5).

3.6. Aqueous Cu and Ca didn’t enhance transport of presorbed CIP in native sand

When CIP was mixed with 1 μM Cu, CIP was detected in the effluent ~30 PV after applied to the native sand column (Fig. 3C). However, when CIP was presorbed onto native sand column, no CIP was detected even after applying 100 PV of 1 μM Ca or 1 μM Cu (data not shown). This indicated that CIP sorption onto native sand was not as reversible as those onto clean sand, indicating different sorption mechanism.

To understand CIP distribution in sand column, a separate profile study was conducted. Analysis of the retained CIP profile in the sand column after 5 PV of DI water flushing showed that ~95% of the CIP was retained in the first 1-cm of the column and 5% in the second 1-cm layer from the inlet (Fig. 5), suggesting strong interactions between CIP and the native sand (Fig. 1C). Similar to DI water, analysis of the retained CIP profile in the sand column after flushing with 1 μM Ca solution showed that 94% the CIP was retained in the first 1-cm layer and 6% in the second 1-cm layer from the inlet (Fig. 5). This suggested the limited effect of Ca on mobilizing presorbed CIP on native sand surface. Unlike Ca, analysis of the retained CIP profile in the sand column after 5 PV of 1 μM Cu solution flushing showed that 88% 10%, and 2% CIP was retained in the first, second, and third 1-cm layer from the inlet (Fig. 5).

The results were consistent with the hypothesis that CIP sorption onto native sand via complexation with Fe/Al was stronger and more effective than that via electron static attraction onto SiO₂ of clean sand. Once sorbed onto Fe/Al surface, Ca or Cu was unable to replace CIP. However, the sorbed CIP on SiO₂ surface can be replaced by Ca (~1%) or Cu (~7%). Therefore more likely, those

![Fig. 4. Mobilization of presorbed CIP (ciprofloxacin) in clean sand columns after flushing with DI water, 1 μM Ca, and 1 μM Cu for 5 pore volumes. When Fe/Al coating from native sand were removed, it was referred to as clean sand.](image)

![Fig. 5. Distribution of sorbed CIP (ciprofloxacin) in different layers of the saturated native sand column after flushed with DI water, 1 μM Ca, and 1 μM Cu for 5 pore volumes.](image)
mobilized CIP was from $\equiv$SiO– surface. Though limited in quantity, $\equiv$Fe/Al was more effective in sorbing CIP than $\equiv$SiO– as supported by the batch data where 1.4 mg kg$^{-1}$ CIP was sorbed by native sand compared to 0.5 mg kg$^{-1}$ by clean sand (Table 5).

4. Conclusions

Limited information is available regarding CIP interaction with cations in aqueous and on solid phase. This study showed that while surface Fe/Al coating was effective in immobilizing CIP in soils, aqueous phase Ca and Cu facilitated CIP transport in sand media. Important factors controlling CIP transport included: 1) the type of metal cations, which controls the stability of CIP complex formed; 2) the concentration of metals present; and 3) whether the cations are in aqueous phase or on solid phase.

Although only aqueous Cu and Ca were investigated here, CIP could form complexes with majority of metal cations in soils [38], suggesting other metals could have similar effect on CIP transport in this environment. In addition, almost all FQs share the same carboxyl, keto and piperazine reactive functional group like CIP. Similar chemodynamics process is expected for other FQs. Therefore, other major cations in aqueous and soil environment should also be evaluated to better understand the chemodynamics of FQs in soils and receiving waters, which is critical for comprehensive assessment of the potential environmental risk of FQs.

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References