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Fate and transport of quinolones at iron oxides / water interface

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Abstract

Due to their extensive use, many emerging contaminants, such as quinolone antibiotics, are released into the environment. Because their environmental fate is largely controlled by their interactions with mineral surfaces, such as iron oxides, this thesis project aimed to develop predictive models of quinolones adsorption to iron oxides under environmental relevant conditions (pH, redox potential, presence of ubiquitous cations and anions, etc.) and their reactive transport processes. To address these issues, an innovative approach combining kinetic and thermodynamic data, *in situ* spectroscopic measurements and surface complexation modeling, was applied in the two sections of this manuscript.

In the first section, magnetite and goethite were chosen as model iron oxides to investigate adsorption process under a wide range of environmentally relevant conditions. Nalidixic acid (NA) and oxolinic acid (OA) were chosen as representative quinolones because they are widespread in the environment. Surface complexation modeling was applied to describe the interactions between these iron oxides and quinolones. Firstly, investigations of NA adsorption on magnetite in slightly reducing environments revealed that magnetite stoichiometry (Fe(II)/Fe(III) ratio) played a crucial role on the binding property of magnetite. NA adsorption strongly increased with increasing stoichiometry of the magnetite. Magnetite stoichiometry was influenced by pH, oxidation, or Fe(II)-amendment, which drastically affect NA adsorption. Secondly, OA adsorption onto goethite in the presence of major $(Mg^{2+} and SO_4^{2-})$ and trace (Cu^{2+}) ions naturally occurring in seawater was investigated under both static and water saturated flow-through conditions, to evaluate OA transport in costal sediments. The competitive and synergetic effects of different ions on OA adsorption can be well predicted with a mechanistic surface complexation model (CD-MUSIC). In addition, the transport of OA in goethite-coated sand columns under flow-through conditions can also be well predicted through coupling hydrodynamic parameters and surface complexation constants obtained under static conditions.

In the second section, the binding mechanisms of Leonardite humic acid (LHA, a representative hydrophilic natural organic matter) onto goethite and the effects of LHA loading on the hydrophilicity of goethite surfaces were studied using microgravimetry and FTIR spectroscopy. At low LHA loading (C/Fe < 0.1), a greater proportion of LHA moieties were involved in ligand exchange or hydrogen

bonding to goethite surfaces. This resulted in potentially important configurational changes in LHA structure, exposing hydrophobic portions of the molecule to the goethite surface and thus decreased water binding capacity. At high loadings, LHA-LHA interactions dominated the adsorption of LHA onto goethite. Only a small fraction of the LHA moieties were directly bound to goethite surface, leaving excess LHA reacting with water in a similar manner to pure LHA. As a consequence, high loadings of LHA increased water binding. The LHA coating on mineral surface is then expected to alter the surface reactivity and affect the fate of quinolones. LHA underwent molecular fractionation during its interactions with goethite under flow-through conditions, where aromatic compounds were preferentially and primarily adsorbed, followed by bigger LHA compounds. The presence of LHA facilitated NA transport, but this influence depended on the LHA loading and/or preloading in column. When LHA was present as a mineral coating, a fast breakthrough of NA was observed where NA retention was dominated by interactions to the organic coating. When both LHA and NA were simultaneously injected in the column, the mobility of NA was enhanced, where both ligand exchange with goethite surface sites and interactions with LHA-covered goethite controlled NA transport.

The present study investigated molecular-level interactions between quinolones and iron oxides and reactive transport processes under a wide range of environment relevant conditions. In addition, this thesis will help to incorporate multiscale chemical and physical heterogeneities in reactive transport modeling studies and significantly improve our ability to accurately predict the fate and transport of quinolones in the environment.

Keywords: Quinolones; iron oxide; adsorption; transport; modeling.

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Chapter 1 Bibliography

1.1 Antibiotics in the environment

1.1.1 Occurrence and environmental risks of antibiotics

Antibiotics have been extensively used in human and veterinary medicine, as well as in commercial animal rearing operations to treat infections and improve growth and feed efficiency.^{1,2} Antibiotic consumption worldwide is steadily increasing. Reardon³ reported global antibiotic consumption grew by 30% between 2000 and 2010. Klein et al.⁴ analyzed the trends and drivers of antibiotic consumption from 2000 to 2015 in 76 countries and found that antibiotic consumption increased by 65% and the antibiotic consumption rate increased by 39% during 2000 and 2015. Based on that, they estimated that global antibiotic consumption in 2030, assuming no policy changes, will be up to 200% higher than that estimated in 2015. Van Boeckel et al.⁵ reported global antimicrobial consumption of antimicrobials will increase by 67%, from 63,151 \pm 1,560 tons to 105,596 \pm 3,605 tons. Impacts of antibiotics overuse on the environment have aroused worldwide concerns.⁶

Antibiotics can enter the environment through different pathways: inappropriate disposal of unused or expired compounds, excreted wastes, manufacturing plants, overland flow runoff and irrigation with effluents.⁷ Antibiotics can be only partially metabolized by humans and animals. Most of the non-metabolized fractions are excreted into environment and retain the anti-bacterial activities.⁸ Most of the antibiotics are water-soluble and therefore about 90% of one dose can be excreted in urine and up to 75% in animal faeces.^{2,9} The excreted wastes from animals are used as manure supplement or fertilizer in agricultural field, and eventually are directly exposed to the environment, as shown in Figure 1.



Figure 1. Principal routes of antibiotics into the environment.¹⁰

The accumulated antibiotics concentration can be as high as several thousand ng per L^{11–13} and they have emerged as aqueous micropollutants in surface waters, groundwaters and soils, which pose potential risks to human health and ecosystem.^{14–16} It is widely reported that antibiotics hampered microbial community structure and function in different ways.^{9,15,17–19} Antibiotics can be selectively toxic to specific microorganisms and causes a reduction in natural microbial biodiversity, thus disrupt ecological functions such as biomass production and nutrient transformation.^{9,15} Moreover, intensive exposure of antibiotics can result in potential promotion of resistance, which can influence various physiological activities and cause disadvantages in the therapeutic use of antimicrobials.^{15,17–19} Furthermore, resistant bacteria can enter the food chain directly through irrigation and fertilizing,¹⁷ and pose detrimental risks on human health.

1.1.2 Quinolones

Quinolone antibiotics, broad-spectra antimicrobial agents with quinolone structure (Figure 2), are some of the most widely used antibiotics. They have a dual ring structure with a nitrogen atom at position 1, a carbonyl group at position 4, and a carboxyl group attached to the carbon at the 3 position of the first ring (Figure 2). The first clinically useful quinolone, nalidixic acid (NA), was discovered in

1962 and marks the beginning of five decades of quinolone development and use (Figure 3).¹ Further research and experimentation showed that the addition of a fluorine molecule at C6 position enhanced activity of the quinolones and prompted the emergence of the fluoroquinolones.



Figure 2. Quinolone generic structure.



Figure 3. Quinolones: decades of discovery and use. *withdrawn.¹ Reproduced with the permission from Oxford University Press.

Quinolones are intensively used in aquaculture and livestock industries worldwide.^{20,21} Most of the quinolones release into waters and/or accumulate in marine and freshwater sediments.²⁰⁻²² Due to their frequent use in fish farming, concentrations of quinolones can be as high as hundreds of ppm in pond sediments.^{21,22} Nalidixic acid (NA) and oxolinic acid (OA), belonging to first and second generation of quinolones, respectively, have been intensively used and then accumulated in environmental systems. They have been used as representative antibiotics in the present manuscript.

1.1.3 Fate and transport of quinolones in the environment

Once released into the environment, quinolones can be transported to different water bodies

through leaching and runoff, and thus be present in virtually all aquatic environments.⁷ The fate and transport of quinolones in nature are controlled by different physical and chemical processes, such as sorption, transport, biodegradation, hydrolysis and photodegradation.^{2,7,23} Quinolones were reported to be quite persistent in activated sludge and were not biodegraded in sediments.^{17,23} Hence, the major removal pathway of quinolones was adsorption rather than degradation.^{24,25} Most quinolones are very chemically stable to hydrolysis and to high temperatures but are photolyzed by UV light.²⁶ Sturini et al.²⁷ studied photodegradation of quinolones, and found that the direct photolysis of quinolones under solar light caused fluorine substitution and reductive elimination, but that occurred at a very low kinetic rates. In addition, quinolones can also be degraded at Fe/Mn oxide surfaces. Martin et al.²⁸ revealed that the sorbed ciprofloxacin on hematite decayed to other surface species over a period of at least 65 h and oxidation proceeded through an opening of piperazine ring via N-dealkylation. Li et al²⁹ reported that over 91% of levofloxacin (initial concentration 40 μ M) were removed with 8 mM manganese oxide within a 35-day treatment period through oxidation and dealkylation.

Because most of the quinolones are quite persistent and accumulate in the environment,^{2,17,30} adsorption to immobile sediment minerals (clays, Fe/Al/Ti/Si oxides, etc.) and mobile colloids (e.g. dissolved organic matter) are the most important processes governing the fate and mobility of quinolones in the environment.^{31–40} The physico-chemical properties of the quinolones, such as water solubility, hydrophobicity, acid-base properties and speciation determine the adsorption process.^{7,41} In addition, aqueous solution composition, such as coexisting cations and anions, also influence adsorption. Some cations (e.g. Ca(II), Mg(II), Cu(II) and Al(III)) can form stable complexes with quinolones and affect the fate and transport of quinolones in soils.^{42–44} Anions (e.g. phosphate, silicates, carbonate, sulfate, natural organic matter (NOM), etc.) may cause competitive effects on adsorption.^{35,45–47} Moreover, sorption processes also depend on the surface properties of reactive minerals, which depend on the composition, size, crystallographic structure and morphology of the mineral (nano)particles.^{48,49}

1.2 Iron oxides

Among these reactive minerals, iron oxides (including oxides, hydroxides and oxyhydroxides), in particular, received much attention owing to their widespread abundance in nature and high surface

reactivity. Iron oxides have been widely used for environmental remediation through adsorption, precipitation and redox reactions. The interactions between iron oxides and surrounding microorganisms, nutrients, metals, and organic compounds profoundly impact global biogeochemical cycles, rock weathering and diagenesis, and microbial activity.⁵⁰⁻⁵²

Moreover, iron oxides have been specifically shown to play an important role in the transport and mobility of quinolone antibiotics in soils and groundwater.^{31,41,53–55} There are several iron oxides in nature, including goethite (α -FeOOH), lepidocrocite (γ -FeOOH), akaganeite (β -FeOOH), hematite, magnetite, maghemite, green rust, etc.⁵⁶ Goethite is the most thermodynamically stable iron oxyhydroxide at ambient temperature and widespread in soils and sediments,⁵⁷ while magnetite is an important iron oxide in reducing environments. In this work, goethite and magnetite were chosen as model minerals to represent adsorption process at a wide range of environmental relevant conditions.

1.2.1 Goethite

Because of its ubiquity, many studies have been dedicated to goethite. Hence, goethite is an ideal model phase for fundamental molecular-level interfacial studies due to its identified crystal structure, hydroxyl groups and density of sites.^{58–61} The synthetic goethite particles are often acicular in shape and dominated by structurally analogous (110) and (100) planes (*Panm* group) as well as the terminal (021) plane (*Panm* group), as shown in Figure 4.⁶² The BET surface area of goethite is in the range of 16-110 m²/g.⁶³ Goethite surface sites consist of different hydroxyl groups, such as singly (=FeOH^{-0.5}), doubly (=Fe₂OH) and triply (=Fe₃O^{-0.5} and =Fe₃OH^{+0.5}) coordinated sites with underlying Fe atoms, as shown in Figure 5.^{64–67} Two types of triply-coordinated sites are denoted as Fe₃O₁H^{+0.5} and Fe₃O_{II^{-0.5}, because the former site is considered to have a strong affinity for protons whereas the latter has a weak affinity for protons, due to their different local chemical environment.⁶⁷}



Figure 4. (a)TEM image of goethite particles and (b) idealized particle morphology.⁶² Reproduced

with the permission from American Chemical Society.



Figure 5. Schematic representation of the distribution of functional groups on the (a) (110) and (b) (001) planes.^{66,67} Reproduced with the permission from Elsevier.

Besides the crystal structure and sorption sites, another key parameter that affects adsorption process is the point of zero charge (pzc), which is the pH value where the net surface charge is zero. The pH_{pzc} of goethite is about 9,^{31,55,68,69} the goethite surface is positively charged at pH lower than pH_{pzc} and it is negatively charged at pH higher than pH_{pzc}. Since the goethite-water interface has been extensively studied,^{31,55,68,69} the crystal structure, reactive sites, and protonation-deprotonation property have been thoroughly understood. This is, therefore, a perfect model mineral to investigate quinolone adsorption at the molecular scale.

1.2.2 Magnetite and maghemite

Magnetite is ferrimagnetic mineral containing both Fe^{2+} and Fe^{3+} .⁵⁶ Magnetite crystallizes in the inverse spinel structure. The oxygen ions closely pack face-centred cubic lattices and iron ions locate in the interstices between oxygen ions. There are two different types of interstices, tetrahedral sites and octahedral sites, as shown in Figure 6. Tetrahedral sites are occupied by Fe^{3+} cations and octahedral sites by a 50:50 mixture of Fe^{2+} and Fe^{3+} cations.



Figure 6. (a)The inverse spinel structure of Fe_3O_4 face-centred cubic spinel structure of magnetite. (b) Magnification of one tetrahedron and one adjacent octahedron sharing an oxygen atom.⁷⁰

In the stoichiometric magnetite, the Fe^{2+}/Fe^{3+} ratio is 0.5. Therefore, its formula is $Fe^{2+}Fe_2^{3+}O_4$. The Fe^{2+} cations in magnetite can be partially or fully transformed to Fe^{3+} by oxidation, to get nonstoichiometric magnetite. This is followed by structural rearrangement leaving vacancy sites. Maghemite (γ -Fe₂O₃), with Fe^{2+}/Fe^{3+} ratio of 0, is the end member of the magnetite-maghemite solid-solution, with only Fe^{3+} in both tetrahedral and octahedral sites.⁷¹ Maghemite (γ -Fe₂O₃) has a structure similar to that of magnetite in which a fraction of the octahedral sites are vacant ($Fe_{8/3}\Box_{1/3}O_4$).

The surface acid-base properties of stoichiometric magnetite and maghemite have been studied through potentiometric titrations.^{72,73} The intrinsic equilibrium constants of magnetite and maghemite are very similar, their pH_{pzc} is about 6.5; the surface site density determined using Gran plot methodology,⁷⁴ were 1.50 sites/nm² for magnetite and 0.99 sites/nm² for maghemite.^{72,73} However, the surface properties of magnetite, Fe^{2+}/Fe^{3+} ratio in the range of 0-0.5, are much less known than that of goethite. To the best of our knowledge, its crystal phase, sites density and reactivity on each face as well as their relationship with the Fe^{2+}/Fe^{3+} ratio are scarcely investigated, especially in the case of magnetite nanoparticles.

Magnetite has been widely used in environmental remediation owing to its reduction capacity.^{75,76} The Fe^{2+}/Fe^{3+} ratio of magnetite has been reported to control the redox reactivity of magnetite in natural systems.^{77–79} However, the influence of Fe^{2+}/Fe^{3+} ratio on the binding mechanism of contaminants are rarely studied.

1.2.3 Hematite

Hematite is iso-structural with corundum and it is the most thermodynamically stable ferric oxide. The hematite structure (Figure 7) contains two formula unite per unit cell, the trigonal-hexagonal and the primitive rhombohedral unit cells.^{80,81} In each hexagonal unit, oxygen atoms are located in a hexagonal closed-packed lattice along the [001] direction and iron atoms occupied two-thirds of the octahedral interstices. This arrangement leads to pairs of FeO₆ octahedra that share edges with three neighboring octahedra in the same plane and one face with an octahedron in an adjacent plane.⁸⁰



Figure 7. Schematic illustration of the α -Fe₂O₃ (a) hexagonal unit cell and (c) the rhombohedral primitive cell. (b) and (d) show the face-sharing octahedra in (a) and (c) respectively. Color scheme: Fe = grey and O = red.⁸⁰

The BET surface area of hematite is reported to be in the range of 10-90 m^2/g^{82} and the pH_{pzc} is between 8.8 and 9.5.^{28,83} Hematite surface structure determines the densities and distributions of reactive hydroxyl groups.⁸⁴ The hematite crystals have different morphologies, such as rhombohedral, platy and rounded. In addition, crystal faces may have imperfections, and the surface composition in terms of surface sites is therefore difficult to determine.⁸⁵

1.2.4 Ferrihydrite

Ferrihydrite or hydrous ferric oxide is nanocrystalline. It is commonly designated as "two-line" or "six-line" according to the number of scattering bands observed in x-ray diffraction (XRD) patterns. Its particle size can be extremely small, in the order of 2-6 nm, leading to very high reactive surface

area, in a range of 530–710 m²/g.^{86–88} Ferrihydrite contains hexa-coordinated and tetrahedrally coordinated Fe sites. The mineral core is defect-free and the surface is depleted as an "inter-phase" and the surface structure is size dependent.^{86,88} Because of the small size, exact ferrihydrite surface structure is still on debate. Recently, Michel et al. ⁸⁹ proposed a single phase periodic structure to describe synthetic ferrihydrite based on pair distribution function (PDF) derived from direct Fourier transformation of the total X-ray scattering. The chemical formula for ferrihydrite in its ideal form can be described as $Fe_{10}O_{14}(OH)_2$, and the amount of additional surface-bound water is particle-size dependent.⁸⁹

1.3 Surface reactions at oxide/water interfaces

Antibiotics strongly interact with iron oxides through adsorption and redox reactions.^{28,31,90,91} The surface reactions are controlled by the physico-chemical properties of the studied antibiotics and iron oxides as well as aqueous solution composition, as detailed below.

1.3.1 Adsorption

Adsorption to reactive oxide minerals is major process affecting the transport and fate of quinolone antibiotics in the environment and the interactions between antibiotics and mineral surfaces have been the subject of extensive research for several decades.^{92–95} Different underlying adsorption mechanisms, especially at the molecular level scale, are detailed in the following paragraphs.

Surface complexation reaction

Surface complexation is the key process controlled the interactions between ligand and mineral surfaces. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy can be used to identify the binding mechanisms, as illustrated in the case of acetate (CH₃COO⁻; Figure 8, from Norén and Persson⁹⁶). The –COO⁻ group can directly coordinate and form chemical bonds with surface Fe sites, forming a metal-bonded (MB) complex, which has pronounced effect on the vibration frequencies of the C-O bonds. It can also interact with the protonated surface site via hydrogen bonds to form a hydrogen-bonded (HB) complex, which broadens the vibration frequencies of the C-O bonds in water. This can be demonstrated by performing the same experiment with D₂O as a solvent: the formation of deuterium bonds affects the C-O vibration frequency because of the larger atomic weight

of D compared to H. In addition, the ligand can coordinate through purely electrostatic attractions to form outer sphere (OS) complex, in which the ligand keeps its first hydration sphere. As a consequence, although adsorption can be measured at the macroscopic scale, the IR spectrum of the adsorbed molecule is identical to the truly dissolved one. The MB complex can be described as inner sphere complex since the ligand interact directly with the metal to the surface and the adsorption processes is referred to as specific adsorption. In contrast, HB and OS complexes do not involve a direct interaction with the surface site the adsorption process is referred to as non-specific adsorption.⁹⁷ The ratio of MB, HB and OS strongly depends on the experimental conditions, especially pH and ionic strength. In addition, different species have different formation kinetics. It has been reported that sorption rate of HB complex is faster than that of MB complex.⁹⁸ HB complex acts like transient species, the firstly formed HB complex can transform to the MB complex over time.



Figure 8. Molecular models of three principal bonding modes of acetate on goethite: (a) solvent-surface hydration-separated ion pair or outer sphere complex (OS); (b) surface hydration-shared ion pair or H-bonded complex (HB); (c) contact ion pair or inner-sphere complex or metal-bonded complex (MB).⁹⁶ Reproduced with the permission from Elsevier.

Typically, carboxylic-containing ligands may bind to the surface by different binding modes and form surface complex with different geometries. Depending on the structure of the formed surface complex, binding modes of a carboxylate can be classified into monodentate and bidentate modes. A monodentate surface complex forms when a single ligand oxygen atom binds to the surface, while a bidentate surface complex forms when two oxygen atoms from the ligand involve in the complex. If both oxygen atoms of the bidentate complex bind to the same metal center in the surface, the complex

is termed bidentate chelate or mononuclear bidentate complex; if each oxygen is coordinated to two different surface centers, it is termed binuclear bidentate complex.^{99,100}

Like acetate, the carboxylate group of quinolones can bind to the surface and via the formation of monodentate, bidentate chelate or bridging bidentate surface complexes, as illustrated in the case of levofloxacin and shown in Figure 9. In addition, the keto group of quinolones can also be involved in the complexation, as illustrated in the case of oxolinic acid (Figure 10, Marsac et al.³¹). The keto group and one['] oxygen of the carboxylate group can bind to iron oxide surface and form MB, HB and OS complexes, the surface can involve one or two surface Fe atoms.



Figure 9. Proposed structures for levofloxacin complexation on the surface of goethite.¹⁰¹ Reproduced with the permission from Elsevier.



Figure 10. Possible surface complexes of OA at goethite surface.³¹ Reproduced with the permission from American Chemical Society.

In the case of ciprofloxacin binding to goethite, three surface sites were involved in adsorption: two sites form bidentate surface complexes with carboxylic group and a third site forms H-bonding with the adjacent keto group (Figure 11).¹⁰²



Figure 11. Proposed surface complexation species of ciprofloxacin onto goethite surfaces.¹⁰² Reproduced with the permission from Elsevier.

Hydrophobic interactions

Hydrophobic interactions drive hydrophobic organic compounds out of aqueous solution, with weak surface interactions resulting from van der Waal forces. The hydrophobic interactions controlled predominately the fate of nonpolar aromatic compounds. It has been reported that the organic coating on hematite made the surface hydrophobic and hydrophobic interaction was the dominant mode of hydrophobic organic compound binding.¹⁰³ The binding enthalpies involved in hydrophobic interactions are considered negligible.¹⁰⁴ The hydrophobic interactions are positively correlated to the *n*-octanol-water partition coefficients (K_{ow}) and inversely correlated to the water solubility (S_w) of the compounds.¹⁰⁵

Polar interactions

Marco et al.¹⁰⁶ investigated the polar interactions between molecules with aromatic moieties attach to organic and minerals. They found that aromatic pi-systems within organic compounds have the capacity to adsorb to minerals through specific sorptive forces other than hydrophobic interactions, as shown in Figure 12.



Figure 12. Schematic representation of aromatic interactions involving the π -system (indicated by •••-lines).¹⁰⁶ Reproduced with the permission from American Chemical Society.

The cation- π interaction can be conceptualized as the electrostatic attraction of a positively charged ion on the mineral surface with the negative electrostatic potential surface of the aromatic π -donor system. It is a noncovalent interaction and the bonding strength positively related to the size of the cyclic aromatic π -system¹⁰⁷ and the amount of electron-donating groups¹⁰⁸.

Hydrogen- π Interactions was proposed by Ringwald et al.¹⁰⁹ to explain the different binding behaviors of benzene, toluene, and picoline onto silica. The interaction between benzene or toluene and silica occurs via weak hydrogen- π bonding, with the face of electron-rich π -systems of benzene and toluene and the H of silanol groups at dehydrated silica surfaces, while in the case of picoline, the hydrogen- π Interactions is much stronger involving the lone pair electrons on the N atom.

 $n-\pi$ EDA Interactions was proposed by Haderlein and Schwarzenbach.¹¹⁰ It described the attractive forces between nitroaromatic compounds (π -acceptors) and the nonbonding electrons (n-donors) of the surface. The electron donor-acceptor (EDA) complexes between surface oxygens of the siloxane surface and a given nitroaromatic compounds were suggested to contribute significantly to the overall binding energy.¹¹⁰

1.3.2 Redox transformation

Stone¹¹¹ and Lakind et al.¹¹² studied the oxidation of organics on oxide surfaces, and proposed that redox reactions occurred via the following reaction steps: (i) surface precursor complex formation between the organic molecule and oxide surface site, (ii) electron transfer between the metal and organics within this surface complex, (iii) breakdown of the successor complex and release of the oxidized product into solution. Some antibiotics are also susceptible to oxidation by iron oxides.^{28,113–115} For example, Zhang et al¹¹³ studied the adsorption and oxidation of fluoroquinolones with goethite and found that piperazine ring of quinolones is critical for oxidation.

To quantify the contribution of redox reactions on the removal of NA or OA by goethite, desorption tests (pH = 11) were carried out under various experimental conditions to check the mass balance of quinolones. The results showed that NA or OA, which does not exhibit a piperazine ring, was removed only by adsorption and that redox transformation did not occur under the experimental conditions.^{31,55}

1.3.3 Factors affecting quinolones adsorption

In addition to surface properties, speciation of quinolones in aqueous solution also governs the surface complexation process. Physicochemical properties of the quinolones especially their solubility in water, pK_a and metal complex stability constants are key parameters that determine their aqueous

speciation.

Quinolones solubility in water changes with pH and determines whether precipitation may occur during the removal process. For example, Figure 13 shows solubility of oxolinic acid (OA) increased with pH. Marsac et al.³¹ used surface complexing modeling to study the interactions between oxolinic acid and goethite, and found more than 50% of oxolinic acid was removed by precipitation at acidic pH and high initial OA concentration (50 μ M). Precipitation did not occur for [OA] = 10 μ M because adsorption decreased OA final concentration below its solubility limit. Quinolone solubility is also affected by their molecular structure: NA solubility is about 10 times larger than that of OA (Figure 13).³²



Figure 13. Experimental OA or NA Solubility in 100 mM NaCl versus pH. The equilibrium OA concentration ($[OA]_{aq}$) in contact with 50 m²/L goethite for $[OA]_{tot} = 10$ and 50 µM in 100 mM NaCl are also plotted. Data from Xu et al. and Marsac et al^{31,55} with permission from American Chemical Society.

The pK_a of quinolones describe the acid-base properties and determine the chemical speciation of quinolones. Figure 14 shows the speciation of ciprofloxacin (CIP) at different pH. With pK_{a, 1}= 5.46 and pK_{a, 2} = 7.67, CIP exists mainly as cationic forms at pH lower than 5.46 and as anionic forms at pH higher than 7.67, and as zwitterionic forms at pH between 5.46 and 7.67.



Figure 14. Distribution of ciprofloxacin (CIP) at various pH values with molecular structures of different CIP species. The species distributions are calculated with PHREEQC using the acidity constants of CIP.

Quinolones can also form stable aqueous complexes with metals, which will change their solubility and speciation and therefore their adsorption processes. In addition, the coexisting cations or anions and natural organic matters will have different effects on quinolones adsorption, as will be detailed in the following paragraphs.

Synergistic adsorption

Quinolones adsorption may be increased through cation $\operatorname{bridging}^{116-121}$ and intermolecular interactions.^{32,55} Cation bridging, a covalent molecular interaction where a cation (Cu²⁺, Ca²⁺, Cd²⁺, Pb²⁺ etc.) acts as bridge to link ligand and mineral surfaces. Figure 15 shows coadsorption of Cu²⁺ and ciprofloxacin onto goethite involved two surface sites, in which Cu²⁺ works as a bridge ion to form a six-member ring with the carboxylic group and carbonyl oxygen of ciprofloxacin.¹²¹ Generally the cation bridging effects increase the adsorption of both cations and ligands due to the formation of a surface-cation-ligand ternary complex.^{116–121}



Figure 15. Proposed surface complexation species of ciprofloxacin onto goethite surface with Cu(II).¹²¹ Reproduced with the permission from Elsevier.

Our group^{32,55} studied the adsorption of nalidixic acid (NA) and niflumic acid (NFA) at goethite (α -FeOOH) surfaces both in single and binary systems and revealed cooperative binding caused by intermolecular interactions, as illustrated in Figure 16. The NFA-NA dimer stabilized by intermolecular hydrogen bonding and van der Waals interactions could be responsible for this phenomenon.



Figure 16. NA and NFA molecules coadsorbed on the diaspore surface, with NA adsorbed as inner sphere.³² Reproduced with the permission from American Chemical Society.

Competitive adsorption

Coexisting cations and anions that can bind to surface on the same sites as quinolones can decrease the adsorption of quinolones. The binding mechanism and concentration of coexisting cations and anions determine the competitive effects. Generally, cations and anions that strongly bind to a surface will be more competitive and higher concentration of cations and anions leads to more significant competition. Mg^{2+} and Ca^{2+} are common cations that decreased quinolones adsorption.^{25,35} Phosphate, and sulfate are common competitive anions that will decreased the adsorption of organic compounds onto iron (hydro) oxides.^{35,122} The presence of phosphate significantly decreased the adsorption of levofloxacin on goethite,³⁵ while sulfate only affects organic acid adsorption at low pH,⁴⁷ which results from the different binding mechanisms of phosphate and sulfate to goethite. Phosphate binding mechanisms on iron oxides have been intensively studied and different surface complexes, such as bidentate mononuclear, bidentate binuclear and monodentate mononuclear surface complexes have been proposed.^{35,123} Kim et al.¹²⁴ used ³¹P static spin-echo mapping NMR experiments to investigate the local environments of the phosphates on surfaces, and found that phosphate ions binding to the goethite surface via a binuclear bidentate complex (*i.e.*, one involving binding of two phosphate oxygen atoms to two adjacent Fe³⁺surface sites) predominates, as shown in Figure 17. Silicate is ubiquitous in surface- and ground-waters and interacts with iron oxides. The binding of silicates to iron oxides is concentration dependent. At low Si loading, monomer complex dominates the reaction, at high Si loadings, oligomerization and polymerization reactions occur and lead to the formation of trimer and tetramer complexes, as shown in Figure 18. However, the effects on silicates on quinolones binding are scarcely studied.



Figure 17. Binding mechanims between Phosphate and goethtie.¹²⁴ Reproduced with the permission from Royal Society of Chemistry.



Figure 18. Optimized geometries of the three representative Si complexes that have been revealed with CD modeling of the Si adsorption data.¹²⁵ Reproduced with the permission from Elsevier.

Effect of natural organic matter (NOM)

NOM, a polydisperse mixture of organic molecules varying in molecular size and chemical compositions (see Figure 19), is ubiquitous in soils and aquatic systems.^{126–128} Due to its abundant functional groups, especially carboxylic and phenolic groups, NOM can bind to minerals through different mechanisms, primarily as electrostatic attraction and ligand exchange, as shown in Figure 20.^{129,130} The NOM coating on minerals will modify the surface properties, such as surface charge density and aggregation state.^{131,132} The aggregation state of the surface will affect accessible reactive surface sites and therefore affect adsorption of other ligands.

Both NOM and quinolones can bind to minerals, therefore, NOM will compete with quinolones for sorption sites and decreased quinolones adsorption. On the other hand, NOM can also bind directly with quinolones via H-bonds, hydrophobic interactions or pi-type bonds.^{133–136} Therefore, NOM can pose both positive and negative effects on quinolone adsorption under various experimental conditions, e.g. different concentration,¹³⁷ solution pH,¹³⁸ and ionic strength and the coexisting cations.¹³⁹



Existence of weak attraction forces in a supramolecular conformation

Figure 19. Hypothetical primary structure of a leonardite humic acid. This figure is from Erro et al.¹⁴⁰



Figure 20. Schematic depicting different interactions between NOM and mineral surfaces.¹²⁹ Reproduced with the permission from Royal Society of Chemistry.

NOM has a supramolecular structure, different fractions of NOM have different affinity and

adsorption kinetics to mineral surfaces, thus lead to molecular fractionation, as shown in Figure 21, NOM adsorption to goethite shows three sequential stages of discrete molecular composition, in which aromatic compounds was preferentially adsorbed, followed by secondary lignin-like and tertiary aliphatic. compounds.¹⁴¹ Due to the heterogeneous characteristics of NOM and different experimental conditions, the impacts of NOM on antibiotics adsorption still remain inconclusive and warrant further study.



Figure 21. Conceptual model of sequential NOM adsorption onto goethite.¹⁴¹ Reproduced with the permission from American Chemical Society.

1.3.4 Interactions at the mineral/water interface under flow-through conditions

The adsorption of quinolones on iron oxide have been intensively studied in batch mode (a perfectly stirred closed reactor), namely under static conditions.^{31,35,55,102,142,143} However, adsorption under flow-through conditions, namely dynamic columns, have been less studied. The basic principle of a column experiment involves the packing of the column with the relevant geologic material and pumping water with a specific contaminant to flow through the column under controlled flow conditions, namely saturated or unsaturated conditions. In saturated conditions, columns are characterized as no air or gaseous phase present in their pore spaces and typically used to reproduce the conditions found in an aquifer; while unsaturated column have both gas and liquid phase in their pores spaces and resemble conditions found in the vadose zone.¹⁴⁴

Both static batch and dynamic column tests contribute to reveal the quantitative and macroscopic sorption behavior of contaminants. Batch study is often a result of static and equilibrium process, while the adsorption in the column is often a result of dynamic, non-equilibrium process and gives rise to a spatial profile of adsorption. In addition, column tests have the advantage of being conducted under conditions approximating field conditions, provide results at different liquid-to-solid (L/S) ratios and time-dependent transport of ligands.^{145,146}

Transport processes

In a column, there are many different physico-chemical processes controlling the solute transport, such as advection, hydrodynamic dispersion and retardation processes. The direct observation and distinction of these processes in column are difficult, and the retardation of a breakthrough curve (BTC) is commonly used as an indicator of these processes as shown in Figure 22, and detailed below.



Figure 22. Effect of advection, dispersion, and retardation on the BTC of a substance in a continuous injection mode. PV is the number of injected pore volumes (adapt from Banzhaf et al.¹⁴⁷).

Advection is the transport process where solutes flow with the bulk water. It is driven by the gradient in the total mechanical energy of the solution. The advective flux, J_{adv} (M L⁻²T⁻¹) can be expressed by eq.1:

$$J_{adv} = qC \tag{1}$$

where C is the solute concentration (M L^{-3}), q is the Darcy velocity (L T^{-1}) and can be quantified
using Darcy's law:

$$q = \phi v = -\mathbf{K}\nabla h \tag{2}$$

where ϕ is the porosity of porous medium, v is the average pore water velocity (L T⁻¹); $\nabla h(L)$ is the hydraulic head gradient, and K is the hydraulic conductivity (L T⁻¹).

Hydrodynamic dispersion includes both diffusion and mechanical dispersion processes. The diffusion is driven by concentration gradient and is described by Fick's first Law:

$$J_{diff} = -D_e \frac{\partial C}{\partial z} \tag{3}$$

where C is the solute concentration (M L⁻³), J_{diff} is the diffusive mass flux per unit area (M L⁻² T⁻¹); D_e is the effective molecular diffusion coefficient in water $(L^2 T^{-1})$; and z is the spatial coordinate (L).

The impact of diffusion on mass transport decreases with velocity and scale. Diffusion is strong if a column experiment is operated at low flow velocities or at a very small scale and becomes insignificant as the velocities and scale increase.¹⁴⁷

Mechanical dispersion described the mixing of a solute due to fluctuations around the average velocity and it is caused by velocity and flow path variations within column and involves both lateral dispersion (i.e., a spreading of the solute perpendicular to the flow direction) and longitudinal dispersion. The mechanical dispersion coefficient in porous media is typically defined as the product of the average fluid velocity and dispersivity α :

$$D_m = \alpha v \qquad (4)$$

where D_m is the dispersion coefficient (L² T⁻¹), **v** is the average flow velocity (L T⁻¹) and α refers to the dispersitivity (L).

The spreading of the solute mass as a result of diffusion and dispersion is similar to diffusion, and therefore the hydrodynamic dispersion process can be described by the Fick's first Law:

$$J_{disp} = -D \frac{\partial C}{\partial z} \qquad (5)$$

Its partial differential equation can be used to predict how dispersion causes the concentration to change with time according to Fick's second law:

$$\frac{\partial C}{\partial t} = -\frac{\partial J_{disp}}{\partial z} = D \frac{\partial^2 C}{\partial z^2}$$
(6)

where D is the hydrodynamic dispersion coefficient defined as the sum of effective diffusion coefficient D_e and mechanical dispersion coefficient D_m . t is the time (T).

Retardation is the delay in the transport of solute, and adsorption of solutes onto solid surfaces is the main mechanisms for the retardation. Different adsorption processes, such as surface complexation, hydrophobic interactions, cation exchange may take place in the column. The retardation factor of the solute can be estimated as: ¹⁴⁸

$$R = 1 + \frac{\rho}{\theta} K_d \tag{7}$$

where K_d is the distribution coefficient between the solid and liquid phases; ρ is the bulk density and θ is the porosity of the medium. K_d is a macroscopic description of the adsorption that can, in principle, be derived from surface complexation models.

Degradation is the transformation and mineralization of compound. A reactive substance can undergo chemical or biological degradation during transport, which involves redox reactions between solute and medium. The degradation will reduce the solute and thus affects the breakthrough behavior.¹⁴⁷

The transport of solutes in porous media is subject to physical and/or chemical nonequilibrium processes, which lead to non-sigmoidal and asymmetrical breakthrough curves with tailing. Chemical nonequilibrium results from rate-limited chemical reactions between solute and interface. Physical nonequilibrium occurs as a result of diffusion resistance within the porous particles of the column. This can be caused by unsaturated flow, aggregated medium, and existence of immobile water zone.¹⁴⁹ Under unsaturated conditions, macro-pores may be filled with air and rely on diffusion processes to attain equilibrium with the displacing solution; aggregation increased the amount of immobile water while the diffusion pathway becomes longer, resulting in more intensive tailing of the breakthrough curve.¹⁴⁹

Interactions in batch vs column

The sorption behavior in dynamic column may disagree with that in batch due to the different experimental conditions in these two systems: solid/liquid (S/L) ratio, kinetic behavior of adsorption, loss of sorbent particles through transport, variations in column flow and moisture content, accessible sorption sites,¹⁵⁰ which will be detailed as follows.

Each batch experiment provides results at single S/L ratio, while column experiment under flow-through condition has very wide S/L ratios. S/L ratio affects adsorption, it has been reported that batch sorption coefficient decreased with increasing S/L ratio.¹⁵¹

Kinetic limitations of sorption may take place in the column under hydrodynamic conditions due to chemical nonequilibrium, which can be confirmed by comparing the sorption kinetic rates and the residence time of solute in the column. Therefore, flow rate has a big effect on adsorption behavior in a column.¹²² Increase in flow rate will decrease the residence time, and thus cause chemical nonequilibrium.

Flow-through conditions can induce some mobilization of sorbent particles. In a system of iron oxide coated quartz sand, Gu et al¹⁵² showed that NOM adsorption could reverse surface charge and cause a stabilization of iron oxide colloids, which resulted in mobilization of iron oxide, as observed by analyzing the total iron in the effluent. Similarly, Hofmann et al.¹⁵³ reported that citrate adsorption could mobilize ferrihydrite colloids through repulsive force and release them in solution.

Variations in column flow and moisture content will affect the dispersion process and thus the physical nonequilibrium. As the moisture content decreased in the media, changes in orientation of low paths and pore-water velocity distribution will take place, thus lead to different dispersivity.¹⁵⁴ Padilla et al¹⁵⁵ also reported that at lower water contents, the medium has a greater fraction of immobile water, higher dispersion, and slower mass transfer between the mobile and immobile regions.¹⁵⁵

The accessible sorption sites in batch and column may be different. Compared to a batch system, intra-aggregate diffusion and diffusion through a stationary liquid film may be more significant because of a less turbulent regime in the column system. Therefore the intra-aggregate pores may hinder accessibility of sorption sites to solute and decrease the mass transfer kinetics between mobile and immobile phases. The accessible sorption sites are hard to identify, however, model simulations suggested that decreased external mass transfer between solution and surface may play a significant role under flow through conditions.¹⁵⁰

1.4 Numerical modeling

Adsorption process in batch has been empirically described by Langmuir or Freundlich isotherms,

and pseudo-first-order or pseudo-second-order kinetic models; and in column by Thomas, Yan and Yoon–Nelson models. In order to better understand the chemical processes occurring at the mineral/water interface, mechanistic models that can predict the uptake of organic contaminants on minerals are important. This section deals with the surface complexing models and transport models relative to adsorption process tested in this study.

1.4.1 Surface complexation model

Surface complexation models (SCMs) provide molecular descriptions of adsorption using a thermodynamic equilibrium approach that defines surface species, chemical reactions, mass balances, and charge balances. In SCMs, the reactive -OH surface sites on the mineral surface can act as a ligand to complex cations, or can be substituted by ligands that can bind to the underlying metal ion. Ion adsorption to the mineral surface was analogous to the formation of solution-phase complexes with definite stoichiometry and equilibrium constants.^{156–159} The sorption/desorption of ions will change the charge and electrical potential of surface, thus affect the free energy of the adsorption process. Therefore, the electrostatic effects of the surface are accounted for in the model. The free energy and electrostatic effects,^{156–159} therefore, the adsorption process is composed of two parts, chemical (intrinsic) free energy and electrostatic effects.

Surface sites and chemistry

In SCMs, there are different configurations and representation of surface sites. The reactive surface can be described using an amphoteric surface site (\equiv SOH) that can uptake and release of protons.¹⁶⁰

SOH + H⁺
$$\rightleftharpoons$$
 SOH₂⁺ (K_{a1}, protonation reaction) (8)
SOH \rightleftharpoons SO⁻ + H⁺ (K_{a2}, deprotonation reaction) (9)

where K_{a1} and K_{a2} are the intrinsic acidity constants for the protonation and deprotonation reactions. Point of zero charge (pzc) is the pH value where the net surface charge is zero. It can be determined by potentiometric titration method. The relationship between pH_{pzc} and surface acidity constants is given in eq.10.

$$pH_{pzc} = 0.5(pK_{a,1} + pK_{a,2})$$
(10)

In the thesis project, surface complexation modeling was used to provide a semiquantitative

evaluation of how much magnetite binding capacity toward quinolones is affected by its stoichiometry. Because of the possible presence of various types of $Fe^{II/III}O(H)$ groups at magnetite surfaces, full mechanistic description of binding mechanisms using a complete approach would have required fitting of many parameters, and then generated large errors on simulated phenomena. Therefore, the 2-pK_a approach developed by Jolsterå et al.^{72,73} was used to describe the surface of magnetite and maghemite.

The MUlti-SIte Complexation (MUSIC) model accounts for surface heterogeneity by using crystallographic information to describe surface sites and surface acidity of dominant crystal planes of minerals.^{161,162} In the case of goethite, singly (\equiv FeOH^{-0.5}), doubly (\equiv Fe₂OH) and triply (\equiv Fe₃O_I^{-0.5} and \equiv Fe₃O_{II}^{-0.5}) coordinated oxygens are outcropped at the goethite surface on the (100), (110) and (021) planes, which represent 27%, 63% and 10% of the total surface, respectively, in the case of goethite particles exhibiting a surface area of 80-100 m² g^{-1.163} The site density of these surface sites on each plane can be calculated based on the crystallographic structure of the goethite. The acidity constants of the different surface sites can be predicted based on the Fe-O distances in the crystal structure.⁶⁷ It is possible to simplify the MUSIC model. Because \equiv Fe₂OH groups remain neutral and \equiv Fe₃O_{II}^{-0.5} ones remain negatively charged at pH 2 to 11, their contributions from the multisite approach predictions can be ignored. This leads to the 1-pK approximation.⁶⁷ Moreover, the (100) and (110) planes show a similar reactivity for H⁺ and mean site densities may be considered.¹⁶⁴ To sum up, the reactive site densities of goethite in this model can be described as: $[=FeOH^{-0.5}] = 3.12$ sites nm⁻² and $[=Fe_3O^{-0.5}] =$ 3.12 sites nm⁻² on (001)/(101) planes (90% of the surface area), and $[=\text{FeOH}^{-0.5}] = 7.4$ sites nm⁻² on (021) plane (10% of the surface area). The protonation constants of these groups are set to that of the pH_{pzc}. This MUSIC approach has not been established for magnetite yet because of limitations in precise identifying its surface sites and reactivity.

Electrostatic models

Many models have been developed to describe the electric double layer (EDL) and electrostatic effects. The most frequently used electrostatic models include, the diffuse layer model (DLM), the constant capacitance model (CCM), the basic stern model (BSM), the triple layer model (TLM) or the triple plane model (TPM).^{157–159,161,165} These models differ in complexity according to the number of adjustable parameters. The description of the mineral-water interface varies among models depending

on different simplifications regarding ions distribution on specific planes, the corresponding charge distribution, and the charge-potential relationship in the electric double layer, as demonstrated in Figure 23.^{157,158,165}



Figure 23. Schematic representation of the electric potential (ψ) versus distance (*x*) from the surface for different models. Adapted from Hayes et al.¹⁶⁵ and Koretsky¹⁶⁶ The counter ions are distributed on or in blue region to ensure the electroneutrality of the interface.

Diffuse Layer Model (DLM)

The DLM considers an electrically charged surface plane (0-plane) and a diffuse plane (d-plane), in which counter-ions accumulate to neutralize the surface charge. All specifically sorbed ions are modeled as inner-sphere surface complexes binding directly to the mineral surface plane and no ion-pairing occurs on the surface. None specifically adsorbed ions, as well as background electrolytes are located on the diffuse layer and cannot form surface complexes.¹⁶⁷ The potential of the 0-plane (ψ_0) is equivalent to the potential of the d-plane (i.e., ψ_d), which can be calculated from charge density of the diffuse plane (σ_d) according to Gouy-Chapman theory.¹⁶⁸ The DLM is often used in combination with the 2-pK_a approach, and needs at least 4 parameters to describe the adsorption of proton and the ion of interest: 2 pK_a values, the sorption equilibrium constant of the ion (K), and the surface sites density (Ns).

Constant Capacitance Model (CCM)

The DLM has usually been restricted to modeling low ionic strength.¹⁵⁸ At high ionic strength solution (>0.1M), the diffuse layer is compressed and the electric double layer can be approximated as a plate capacitor.^{158,160} The CCM considers only one electrostatic plane (0-plane) on the mineral surface and a layer of constant capacitance (C) between surface and bulk solution. The relationship between surface charge (σ_0) and potential of the 0-plane (ψ_0) is simply described by $\sigma_0=C\psi_0$. All specific adsorbed ions are located on the 0-plane as inner-sphere complexes, and no ion-pairing occurs. Compared to DLM, the CCM requires an additional fitting parameter (C) to model the ion adsorption. The CCM has been applied to describe the reactions on the magnetite/water and maghemite/water interfaces and successfully predicted the adsorption of silicate and Mg²⁺.^{72,73}

Basic Stern model (BSM)

The BSM is a combination of the DLM and the CCM. It assumes the presence of a surface plane (0-plane) and a diffuse plane (d-plane). Contrast to DLM and CCM, the BSM considers the adsorption of background electrolyte ions. The empty space between the surface and the head end of the diffuse layer (stern plane), also called "stern layer", is treated as a plate condenser with a capacitance C. H^+ and inner-sphere complexes are located on the 0-plane, out-sphere complexes and ion pairs are located on the stern plane, and counter ions are placed on the diffuse plane.^{169,170} Compared to CCM, the BSM includes two additional parameters, two electrolyte surface-binding constants, K_{An} and K_{cat}.

Three plane Model (TPM)

The TPM divides the mineral – water interface into three electrostatic layers, i.e., 0-plane, 1-plane (or β -plane), and 2-plane (or d-plane). The stern layer is split into two parallel plate capacitors in series with capacitance values of C₁ and C₂, respectively, with $1/C_{stern} = 1/C_1 + 1/C_2$. H⁺, OH⁻ and metal-bonded surface complex are located at the 0-plane; hydrogen-bonded complex are located at the 1-plane, outer-sphere surface complexes are located at the 2-plane; the diffuse layer plane (d-plane) represents the boundary distance of approach to the surface for counter ions in solution.^{31,164,171} The TPM has at least seven adjustable parameters; pH_{pzc} (in the 1-pK_a approach), two capacitance parameters (C₁, C₂), surface affinity constant for the ion of interest (K), site density (Ns), and two electrolyte surface-binding constants, K_{An} and K_{cat}.

The triple layer model (TLM) is very similar to TPM, they differ in the distribution of ions. In TLM,

 H^+ , OH^- and strongly-bound ions are located at the 0-plane; ion pair adsorption of cations and anions associated with the background electrolyte as well as other outer-sphere surface complexes are located at 1-plane.^{158,165} The TLM is often used in combination with the 2-pK_a approach while the TPM often uses the 1-pK_a approach.

Charge Distribution (CD)

The CD model defines EDL identical to the TLM or TPM, but this model allows charge distribution between two different electrostatic planes.¹⁶¹ The CD values can be related to the structure of the surface complexes, Ideally, the CD values chosen can be based on a simple Pauling bond valence analysis and quantum chemical computations of the geometry of the surface complex.^{161,172} In most cases, the CD value is treated as an adjustable parameter to obtain a good description of experiment data. Figure 24 shows charge distribution of silicates (H₄SiO₄) binding to goethite (sorption sites FeOH^{-0.5}). Δz_0 and Δz_1 represent respectively the overall change of charge in the 0- and 1-plane upon the adsorption of uncharged H₄SiO₄. The overall charge of the bidentate silicon complex is -1, it distributed on the 0- and 1-plane respectively in Figure 24a and Figure 24b, while it distributed on both planes in Figure 24c.¹⁷²



Figure 24. The charge distribution of a bidentate silicon complex bound to goethtie. (a) The Si-charge is equally distributed based on the Pauling bond valence concept. (b) The Si-charge is asymmetrically distributed that fully neutralizes the surface. (c) charge distribution derived from adsorption experiments.¹⁷² Reproduced with the permission from Elsevier.

All the surface complexation models described above can be used with the geochemical

speciation code PHREEQC (version 2)¹⁷³

1.4.2 Transport model

The transport of solutes in column is subject to nonequilibrium processes. These nonequilibrium processes have been considered in the transport models. The models can be classified into three groups, (i) physical nonequilibrium transport models, including the Mobile-Immobile Water Model, Dual-Porosity Model, Dual-Permeability Model, and Dual-Permeability Model with Immobile Water; (ii) chemical nonequilibrium transport models, including the One Kinetic Site Model, the Two-Site Model, and the Two Kinetc Sites Model; and (iii) physical and chemical nonequilibrium transport models including Dual-Porosity Model with One Kinetic Site and the Dual-Permeability Model with Two-Site Sorption.¹⁷⁴ All of these models have been incorporated in Hydrus-1D program,¹⁷⁴ and modeling parameters can be obtained by fitting the transport data of the solutes.

Uniform Flow Model

Water flow in the numerical model is described by Richards equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(\theta) \left(\frac{\partial h}{\partial z} + 1 \right) \right] \tag{11}$$

where *K* is the hydraulic conductivity; h is the pressure head (L) *z* is the vertical coordinate (L), θ is the volumetric water content (L³ L⁻³), and *t* is time (T).

The transport of solute in column can be described by the advection-reaction-dispersion equation, the governing equation can be expressed as follows:

$$\frac{\partial C}{\partial t} + \frac{\partial S}{\partial t} = -\nu \frac{\partial C}{\partial z} + D \frac{\partial^2 C}{\partial z^2}$$
(12)

where *C* is the solution concentration (M L⁻³), *S* is the sorbed concentration of solute in the solid phase (M M⁻¹), *t* is time (T), *v* is the pore water flow velocity (L³ L⁻³), *z* is spatial coordinate (L), *D* is the hydrodynamic dispersion coefficient (L² T⁻¹).

In HYDRUS-1D, the sorption term $\partial S/\partial t$ is often described as Langmuir or Freundlich isotherm, or linear sorption. Here we assume only linear adsorption of the form for simplicity:

$$S = K_d C \tag{13}$$

where K_d is the distribution coefficient (L³ M⁻¹).

PHREEQC also can be used to model several one-dimensional transport processes by combining with equilibrium and kinetic chemical reactions.¹⁷³ The transport part of equation 13 is solved with an explicit finite difference scheme that is forward in time, central in space for dispersion, and upwind for advective transport.¹⁷³ The 1D column is divided into a series of cells with the same pore volume. The time step and shifts must be defined. The time step gives the length of time associated with each advective shift or diffusion period, the shift is the number of times the solution in each cell will be shifted to the next higher or lower numbered cell; the velocity of water in each cell can be calculated as the length of the each cell divided by the time step. The sorption term $\partial S/\partial t$ is calculated separately from the transport part for each time step. At each shift, advective transport is firstly calculated, with flux-type boundary conditions, the dispersion steps follow the advective shift, thereafter all equilibrium and kinetically controlled chemical reactions, which is followed again by advection.¹⁷³

Physical nonequilibrium transport models

The physical nonequilibrium models derived from the uniform flow model by considering variable pore water flow in the medium, as shown in Figure 25. The most common physical nonequilibrium model is the Mobile-Immobile Model, which assumed that there are two regions in pore space, namely mobile zone (macropores or inter-aggregate pores and fractures) and immobile zone (matrix or intra-aggregate pores). Water in the immobile zone is stagnant and dissolved solutes can move into and out of this immobile zone by molecular diffusion.¹⁷⁵ The governing solute transport equations are as follows¹⁷⁶:

$$\theta_{m} \frac{\partial C_{m}}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} + \rho_{b} \frac{\partial S}{\partial t} = \theta_{m} D_{m} \frac{\partial^{2} C_{m}}{\partial z^{2}} - \theta_{m} \upsilon_{m} \frac{\partial C_{m}}{\partial z}$$
(14)
$$\theta_{im} \frac{\partial C_{im}}{\partial t} + \rho_{b} \frac{\partial S_{im}}{\partial t} = \alpha (C_{m} - C_{im})$$
(15)
$$\theta = \theta_{m} + \theta_{im}$$
(16)

where θ is the volumetric water content (L³ L⁻³), the subscripts m and im refer to the mobile and immobile region, *C* is solute concentration in the aqueous phase (M L⁻³), *S* is the solid phase concentration of solute (M M⁻¹), ρ_b is the dry soil bulk density (M L⁻³), *D* is the dispersion coefficient

(L² T⁻¹), *v* is the pore-water velocity (L T⁻¹), α is a coefficient for mass transfer between mobile and immobile region (T⁻¹), *z* is vertical coordinate (L), and *t* is time (T).



Figure 25. Conceptual physical nonequilibrium models for water flow and solute transport.¹⁷⁴ Reproduced with the permission from Soil Science Society of America.

The Mobile-Immobile Model can be further expanded to Dual-Porosity and Dual-Permeability Models. The Dual-Porosity Model allows for water flow in the immobile zone; while the Dual-Permeability Model allows the transfer of both water and solutes between the two pore regions.¹⁷⁴ The Dual-Permeability Model can be further refined by assuming that an additional immobile region exists inside the matrix domain which solute can move through molecular diffusion.¹⁷⁴

In some porous media, chemical nonequilbrium prevails on the physical effects.^{177,178} The nonequilibrium transport is mainly due to chemical effects and chemical nonequilibrium transport models will be detailed in the following paragraphs.

Chemical nonequilibrium transport models

Chemical nonequilibrium transport models are shown in Figure 26. The One Kinetic Site Model assumes that sorption is kinetically limited and can be described as a first-order process. This model can be expanded into two site sorption model by dividing the sorption sites into two fractions with different sorption kinetics.



Figure 26. Conceptual chemical nonequilibrium models for reactive solute transport. Grey and cyon area represent respectively solid and aqueous phase. θ is the water content, *c* are concentrations of the corresponding regions, *S*^{*e*} and *S*^{*k*} are sorbed concentrations in equilibrium and kinetic sites, respectively.¹⁷⁴ Reproduced with the permission from Soil Science Society of America.

The One Kinetic Site Model assumed one kind of sorption site and the sorption is time dependent on this site and follows first-order kinetics, its governing equations can be expressed as follows:

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S^{k}}{\partial t} = D \frac{\partial^{2} C}{\partial z^{2}} - \nu \frac{\partial C}{\partial z}$$
(17)
$$\frac{\partial S^{k}}{\partial t} = \alpha (K_{d}C - S^{k})$$
(18)

where *C* is the concentration of the adsorbate in the effluent in the column (M L⁻³), *t* is time (T), ρ is the bulk density of medium (M L⁻³), θ is the volumetric water content (L³ L⁻³). *D* is the dispersion coefficient (L² T⁻¹), *v* is the average pore water velocity (L T⁻¹), α is the first-order rate coefficient associated with the kinetic site (T⁻¹). *K_d* is the linear isotherm adsorption coefficient (L³ M⁻¹).

The Two-Site Model¹⁷⁹ assumed the existence of two types of sorption sites: an equilibrium site and a kinetic site. Sorption is instantaneous on the equilibrium site and described by a sorption isotherm (Type 1, equilibrium). While sorption is time dependent on the kinetics site and follows first-order kinetics (Type 2, kinetic).¹⁷⁹ The final governing equations of the model are given as follows:

$$\frac{\partial C}{\partial t} + \left(\frac{\rho}{\theta}\right) \left(\frac{\partial S^e}{\partial t} + \frac{\partial S^k}{\partial t}\right) = D \frac{\partial^2 C}{\partial z^2} - \nu \frac{\partial C}{\partial z}$$
(19)

$$\frac{\partial S^k}{\partial t} = \alpha \left[(1 - f) K_d C - S^k \right]$$
(20)

where S^e and S^k are sorbed-phase concentration of solute on the equilibrium sites and kinetic nonequilibrium sites (M M⁻¹), respectively, *f* is the fraction of equilibrium sites.

The Two Kinetic Sites Model assumed the existence of two types of kinetic sorption sites and is usually used to simulate transport of colloids, where the two kinetic processes represented colloid chemical attachment and physical straining respectively.¹⁸⁰ The final governing equations of the model can be expressed using the attachment–detachment approach:

$$\frac{\partial C}{\partial t} + \left(\frac{\rho}{\theta}\right) \left(\frac{\partial S_1^k}{\partial t} + \frac{\partial S_2^k}{\partial t}\right) = D \frac{\partial^2 C}{\partial z^2} - \nu \frac{\partial C}{\partial z}$$
(21)

$$\rho \frac{\partial S_1^k}{\partial t} = k_{a1} \theta C - k_{d1} \rho S_1^k \tag{22}$$

$$\rho \frac{\partial S_2^k}{\partial t} = k_{a2} \Theta C - k_{d2} \rho S_2^k \tag{23}$$

where S_1^k and S_2^k are sorbed concentrations of the first and second fractions of kinetic sorption sites (M M⁻¹), respectively; k_{a1} and k_{a2} are attachment coefficients for the first and second fractions of kinetic sorption sites (T⁻¹), respectively; k_{d1} and k_{d2} are detachment coefficients for the first and second fractions of kinetic sorption sites (T⁻¹), respectively.

Physical and chemical nonequilibrium transport models

Physical and chemical nonequilibrium models integrate both physical and chemical nonequilibrium processes. The Dual-Porosity Model with One Kinetic Site divided the porous medium into mobile and immobile zones, and divided the sorption sites in contact with the mobile zone into equilibrium and kinetic sorption sites. The Dual-Permeability Model with Two-Site Sorption assumed applicability of the dual-permeability model and divided the sorption sites in both the macropre and micropore regions into equilibrium and kinetic sites.

for field-scale processes where complicated physical and chemical processes may contribute to the nonequilibrium flow and transport.

1.5 Objectives of the thesis and plan

Due to the widespread use of antibiotics, their impacts on the environment are becoming of serious concern.⁶ In addition, the overuse and misuse of antibiotics are key factors contributing to antibiotic resistance, which becomes one of the most pressing health issues. Therefore, it is necessary to evaluate the transport and mobility of quinolones under various chemical and physical conditions from the molecular scale to larger scales and ultimately their ecological impacts. However, the lack of quantitative data on the transport and mobility of quinolones and gaps in translating molecular information to larger scales hinder our ability to develop valuable models to assess their fate in various environmental systems.

This thesis aimed to investigate molecular-level interactions of quinolones at the mineral/water interface and under a wide range of environment relevant conditions. The adsorption experiments were conducted both in static batch and dynamic column conditions, and surface complexation and hydrodynamic transport models were developed for accurate description of adsorption/transport behavior.

The structure of the thesis is shown in Figure 27. It consists of two sections. The first section (Chapters 2 and 3) investigate the binding mechanisms of quinolones (nalidixic acid and oxolinic acid were chosen because of their intensive use and high residual levels in environmental systems) onto iron oxides (goethite and magnetite were chosen because they represent important reactive surfaces toward organic ligands in soils and sediments) under environmentally relevant conditions relative to reducing and seawater conditions. The second section (Chapters 4 and 5) investigate the interactions of goethite with natural organic matter and their impacts on the quinolone mobility/transport.



Figure 27. Work scheme of this thesis.

Chapter 2 aims to examine the adsorption process of organic contaminants on iron oxides in slightly reducing environments. Magnetite was used as a representative adsorbent in reducing environments. The effects of magnetite stoichiometry (i.e., Fe(II)/ Fe(III) ratio) on its reducing reactivity has been extensively studied, while little is known about the influence of stoichiometry of magnetite on its binding properties. This study, for the first time, demonstrates that the stoichiometry strongly affects the binding capacity of magnetite to bind not only quinolone antibiotics such as nalidixic acid and flumequine, but also salicylic acid, natural organic matter, and dissolved silicates. A surface complexation model was used to describe the observed behavior and reveal the binding mechanisms of ligand sorption upon Fe(II)-recharge.

Chapter 3 aims to predict adsorption and transport of quinolones under seawater conditions to understand the behavior of quinolones in costal sediments. Oxolinic Acid (OA) was chosen as the model quinolone because of its widespread use in aquaculture, goethite was chosen because it is the most common diagenetic iron oxyhydroxide in marine sediments. The adsorption of quinolones in the presence of major (Mg^{2+} and SO_4^{2-}) and trace (Cu^{2+}) ions of synthetic seawater and under both static and water saturated flow-through conditions were investigated. TPM combined with CD-MUSIC model is applied to predict binding mechanisms and the reactive transport under flow-through conditions.

Chapter 4 aims to study the effects of NOM coating on mineral surface reactivity. Leonardite humic acid (LHA) was chosen as representative hydrophilic NOM, and goethite was chosen as a model mineral. Water binding on initially dry LHA-goethite assemblages was monitored using Fourier Transform InfraRed (FTIR) spectroscopy and gravimetry by Quartz Crystal Microbalance (QCM). Water adsorption capacity, indicating the surface hydrophilicity, is LHA loading dependent.

Chapter 5 studys the fractionation of Leonardite Humic Acid (LHA, a representative hydrophilic NOM) and its impacts on the sorption and transport of Nalidixic Acid (NA, a widely used quinolone antibiotic) by column experiments and reactive transport modeling. The fractionation of LHA and its impact on NA transport was investigated in goethite-coated sand (GCS) columns over a wide concentration range of LHA (0-50 mg/L). A transport model that accounts for adsorption kinetics was used to predict the breakthrough behavior of NA. The results of this work showed that LHA fractionation alters sorption mechanisms and kinetics of NA, which in turn affected their fractionation.

Finally the conclusions, implications and perspectives are given.

The combined analysis of data obtained from these different experimental approaches and techniques may help in accurate description of quinolones binding at mineral-water interface, and may have strong implications in the prediction of fate and mobility of quinolones in the environment. From a fundamental point of view, the original ideas and achieved results in this thesis will help to incorporate multiscale chemical and physical heterogeneities in reactive transport modeling studies and will significantly improve the modeling of the fate and transport of contaminants. In addition, outcomes of this thesis will help to develop decision support tools for risk assessments and for strategies of remediation based on minimizing risks to the environment and human health.

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Summary

This part of the thesis summarizes the first section of results studying the binding mechanism of quinolones onto iron oxides under environmentally relevant conditions relative to reducing and seawater conditions. The section is composed of two articles. One aimed to examine the adsorption process of organic contaminants on iron oxides at slightly reducing environments, and the other aimed to predict adsorption and transport of quinolones under seawater conditions to understand the behavior of quinolones in costal sediments. Main findings are reported here and readers should refer to the articles for details. Following are the titles of these articles presented in this section:

• Influence of Magnetite Stoichiometry on the Binding of Emerging Organic Contaminants

• Adsorption of Quinolone Antibiotics to Goethite under Seawater Conditions: Application of a Surface Complexation Model

In the first part of this section (see Figure 1), organic contaminants adsorption onto magnetite were studied. Magnetite is a mixed Fe(II)-Fe(III) oxide and is common in reducing environments. It shows high reduction capacity due to the presence of structural Fe(II). The stoichiometry of the magnetite (i.e., Fe(II)/Fe(III) ratio that can vary from 0 to 0.5) governs the reactivity of magnetite in natural systems. It has been extensively reported that the stoichiometry strongly influences the reduction reactions. The effecs of stoichiometry of magnetite on its binding properties has never been studied and merits investigation. In this study, ligand adsorption and Fe(II) dissolution as a function of pH for magnetites exhibiting different Fe(II)/Fe(III) ratio, prepared as such, or through Fe(II) recharge of nonstoichiometric magnetite suspensions were examined. Mass balance showed that ligands were removed only by adsorption. Nalidixic acid (NA, a widely used quinolone) adsorption increased with the stoichiometry of the magnetite, and Fe(II)-amendement of nonstoichiometric magnetite led also to an enhancement in NA adsorption. At pH between 6 and 10, all magnetites exhibiting similar Fe(II)/Fe(III) ratio in the solid phase showed similar adsorption properties. This enhancement in binding capability of magnetite for NA is still observed in the presence of naturally occurring ligands (e.g., 10 mg L^{-1} of humic acid or 100 μ M of silicates). NA adsorption was also examined in the presence of other divalent cations (Mn(II), Ni(II)) and compared with that of Fe(II). The different adsorption behavior of NA in the presence of Fe(II) with respect to other divalent transition metals

indicated the adsorption enhancement for NA is mainly controlled by the $(Fe(II)/Fe(III))_{bound}$ ratio in magnetite, rather than by NA-Fe(II) complexation in solution or ternary surface complexation. Surface complexation modeling was used to describe the observed behavior, and the NA-magnetite complexation constant remains constant for Fe(II)/Fe(III)bound below 0.40, but increases sharply when Fe(II)/Fe(III) increases from 0.40 to 0.50. The existence of a threshold may be related to the surface amount of magnetite bound-Fe(II) required to trigger the enhancement of NA binding with magnetite surfaces. The increase in NA sorption with Fe(II)/Fe(III)bound ratio may result from the creation of new binding sites upon Fe(II)-recharge, or changes in the intrinsic surface reactivity of amended magnetite.



Figure 1. Graphic illustration of influence of magnetite stoichiometry on NA adsorption

In the second part of this section (see Figure 2), Oxolinic acid (OA, a widely used quinolone in aquaculture) adsorption onto goethite was studied under seawater conditions. Goethite is chosen as a model mineral because it is the most thermodynamically stable Fe-oxyhydroxide mineral and widespread in coastal soil and sediments. Despite the widespread use of quinolones in fish farming, the effect of cations and anions found in seawater on their solubility and adsorption behavior to suspended mineral particles or mineral sediments has received little attention. In this study, interactions of OA with goethite in the presence of two major ions (e.g., Mg^{2+} , SO_4^{2-}) and one trace cation (Cu²⁺ used as a model trace metal in seawater) have been studied under a wide range of ion concentrations and pH values. Mg^{2+} was found to strongly reduce OA-goethite binding and increase OA solubility via the formation of aqueous complex with OA, SO_4^{2-} decreased slightly OA adsorption at low pH due to

competition for sorption sites, while Cu^{2+} could strongly increase OA binding by forming a ternary metal-ligand surface complex. The effects of different ions on OA adsorption to goethite can be well predicted with three plane model (TPM). Possible antagonistic or synergetic effects on OA adsorption have also been investigated in the presence of mixtures of Mg^{2+} , SO_4^{2-} and Cu^{2+} and in synthetic seawater. OA adsorption in multicomponents system can be well predicted by including a ternary surface goethite-Cu-sulfate complex in the present model and without further parameter adjustment. Finally, column experiments were carried out at different pH and flow rates to assess OA transport under seawater conditions. The transport of OA in flow-through columns can be well predicted through coupling hydrodynamic parameters and surface complexation constants obtained under seawater conditions.



Figure 2. Graphic illustration of OA adsorption onto goethite under seawater conditions

Results of this study suggest binding mechanism of quinolones onto iron oxides under different conditions can be described with surface complexation modeling. This study has important implications for assessment and prediction of the fate of quinolones in different environmentally relevant systems.
Chapter 2 Influence of magnetite stoichiometry on the binding of emerging organic contaminants

Abstract

While the magnetite stoichiometry (i.e. Fe(II)/Fe(III) ratio) has been extensively studied for the reductive transformation of chlorinated or nitroaromatic compounds, no work exists examining the influence of stoichiometry of magnetite on its binding properties. This study, for the first time, demonstrates that the stoichiometry strongly affects the capacity of magnetite to bind not only quinolone antibiotics such as nalidixic acid (NA) and Flumequine (FLU), but also salicylic acid (SA), natural organic matter (humic acid, HA) and dissolved silicates. Fe(II)-amendment of non-stoichiometric magnetite (Fe(II)/Fe(III) = 0.40 and Fe(II)/Fe(III) = 0.42) led to similar sorbed amounts of NA, FLU, SA, silicates or HA as compared to the stoichiometric magnetite (i.e. Fe(II)/Fe(III) = 0.50). At any pH between 6 and 10, all magnetites exhibiting similar Fe(II)/Fe(III)ratio in the solid phase showed similar adsorption properties for NA or FLU. This enhancement in binding capability of magnetite for NA is still observed in presence of environmentally relevant ligands (e.g. 10 mg L^{-1} of HA or 100 μ M of silicates). Comparison with other divalent cations (e.g. Ni(II) and Mn(II)) suggests that the driving mechanism in increase of ligand adsorption upon Fe(II)-recharge of magnetite does not correspond with a common ternary surface-metal-ligand complexation. Using surface complexation modeling, it was shown that the NA-magnetite complexation constant does not vary with Fe(II)/Fe(III) between 0.24 and 0.40, but increases by 4 orders of magnitude when Fe(II)/Fe(III) increases from 0.40 to 0.50. Thus, to account for the influence of the stoichiometry of magnetite on the fate of organic contaminants in environmental systems, the potential Fe(II)-enrichment or Fe(II)-depletion of magnetite should be appropriately considered in reactive transport studies.

1 Introduction

Magnetite is an ubiquitous mixed Fe(II)–Fe(III) oxide in soils and sediments, and is very efficient in environmental remediation owing to its reduction capacity.^{1,2} For this reason, the reactivity of magnetite to reduce various organic^{3–7} and inorganic contaminants^{8–11} has been extensively studied. The stoichiometry of the particles (*i.e.* Fe(II)/Fe(III) ratio that can vary from 0 to 0.5) is one of the most important factors in the reduction reaction, and could govern the reactivity of magnetite in natural systems.^{6,10,11} Exposing non-stoichiometric magnetite (i.e. low Fe(II)/Fe(III) ratio) to a source of Fe(II) can restore the 0.5 ratio (i.e. perfectly stoichiometric magnetite) through oxidation of adsorbed Fe(II), accompanied by reduction of the octahedral Fe(III) in the underlying magnetite to octahedral Fe(II).^{5,6} Therefore, investigations to recharge magnetite surfaces by Fe(II) in order to enhance its reactivity as well as the effect of magnetite stoichiometry on the reduction of contaminants have attracted great attention.^{4–7} However, very little is known about the impact of Fe(II)-recharge on adsorption properties of the magnetite surface. Although the magnetite adsorption capacity was evaluated for different compounds including heavy metals and radionuclides,^{2,12,13} oxyanions^{14,15} and organic ligands,¹⁶ none has attempted to assess the influence of Fe(II)/Fe(III) ratio on the mechanism and extent of binding of these compounds on magnetite surfaces.

In this work, we elucidate these effects in different magnetite suspensions containing Nalidixic Acid (NA) or Flumequine (FLU) (see their structures and species in Figure S1). Because of their growing use in human and veterinary medicine and continuous release into the environment, quinolone antibiotics such as NA and FLU have been detected in surface waters, groundwaters and sediments at concentrations levels ranging from ng L⁻¹ to μ g L⁻¹.^{17–19}As the mobility of these compounds in the environment can be strongly affected by interactions with surfaces of soil and sediment mineral particles,^{18,19} a thorough understanding of their sorption behavior is essential. Magnetite and more generally iron (oxy)(hydr)oxides represent important reactive surfaces toward organic ligands in soils and sediments.

Here, we examined both ligand adsorption and Fe(II) dissolution as a function of pH for magnetites exhibiting different Fe(II)/Fe(III) ratio, prepared as such, or through Fe(II) recharge of non-stoichiometric magnetite suspensions. The binding capability of magnetite with respect to

Fe(II)/Fe(III) ratio was also examined in presence of naturally occurring ligands (e.g. salicylic acid (SA), silicates and humic acid (HA)). The implication of ternary surface complexation (i.e. surface-metal-ligand complex) in enhancement in ligand adsorption was assessed by investigating the impact of other divalent cations (Mn(II), Ni(II)) on NA adsorption, where metal binding with no electron transfer is supposed to occur on magnetite. We then used surface complexation modeling to describe the observed behavior, and to gain further insights into the mechanisms responsible for enhancing ligand sorption upon Fe(II)-recharge. The present work notably revealed a considerable impact of the magnetite stoichiometry on the sorption capability of magnetite surfaces.

2 Materials and methods

2.1 Chemicals

If not mentioned, chemicals (all pro analytical quality or better) were obtained from Sigma Aldrich. Leonardite Humic Acid standard (LHA) was purchased from the International Humic Substances Society (IHSS). Solutions were prepared with ultrapure "MilliQ" water (specific resistivity, 18.2 MΩ cm⁻¹) purged with N₂ for 4 h. Magnetite (ideal formula: Fe₃O₄) was synthesized applying a procedure involving a room temperature aqueous precipitation method in an anaerobic chamber (JACOMEX). A 0.3 M HCl solution containing a FeCl₂:FeCl₃ 1:2 molar ratio was introduced into an N₂-sparged 25% w/v ammonium (NH₄OH) solution, with continuous stirring at 1400 rpm, leading to instantaneous precipitation of magnetite particles. Because washing steps can lead to the loss of Fe(II),⁶ no washing step was applied to obtain the stoichiometric magnetite (M0.50; the number refers to Fe(II)/Fe(III) ratio). The solid concentration was 25 g L⁻¹ and the pH was 8.3. Other magnetites, Fe(II)-depleted, were obtained from M0.50. By applying one or three washing steps to a fraction of M0.50 suspension with N₂-purged ultrapure water and then centrifuged for 5 min at 4000 rpm, M0.44 and M0.40 were obtained, respectively. This procedure was repeated to obtain another suspension of M0.40, but M0.42 was obtained, which shows that this synthesis method has little uncertainty. By exposing the M0.50 during 24h to a known amount of H₂O₂ (following the procedure of Gorski et al.⁶), a second suspension of M0.42 (denoted as M0.42-H₂O₂) and M0.33 were obtained. By exposing the M0.50 during 24h to ambient air, M0.24 was obtained.

2.2 Characterization of magnetite nanoparticles

The mineral identify was confirmed by X-ray diffraction (see XRD pattern in Figure S2). According to TEM micrographs (Figure S2), the synthetic magnetite particles are 10 to 15 nm in diameter (12.5 nm on average based on site distribution). Similar XRD patterns were found for the different magnetites investigated here, and no notable influence of the stoichiometry of the particles on particle size was observed. Accordingly, B.E.T. surface area did not significantly differ between the magnetites used in this study ($89 \pm 4 \text{ m}^2 \text{ g}^{-1}$). Using the assumption that all magnetite particles are spherical in shape (density = $5.15 \times 10^6 \text{ g m}^{-3}$)¹, TEM surface area was determined to be 93 m² g⁻¹, close to the BET one.

An aliquot of each magnetite suspension was taken and digested in N₂-sparged 5 M HCl inside the glovebox overnight with shaking. Dissolved Fe(II) and Fe(III) concentrations were then determined using the phenanthroline method.²⁰ This bulk Fe(II) content was found very close to that determined by acid digestion on the filtered solid, as previously reported.^{5,6} The amount of magnetite bound-Fe(II) ([Fe(II)]_{bound} = [Fe(II)]_{tot} – [Fe(II)]_{aq}) was used to calculate the effective Fe(II)/Fe(III) ratio (denoted as (Fe(II)/Fe(III))_{bound}) in magnetite which was shown to vary with pH (see results and discussion section). [Fe(II)]_{tot} is the total concentration of Fe(II) in the suspension (solid + solution) and [Fe(II)]_{aq} is the dissolved concentration of Fe(II), measured after filtration (0.2 µm, Whatman) of the magnetite suspention.

2.3 Adsorption experiments

Adsorption batch experiments were carried out in 15 mL polypropylene tubes under anaerobic conditions (glovebox). NaCl concentration was set to 10 mM for all experiments. The effect of dissolved Fe(II) on NA or FLU adsorption to magnetite was investigated by adding small amounts of 100 mM FeCl₂ solution (dissolved in 0.1 M HCl). pH was adjusted using 0.1 M NaOH/HCl solutions. After 24h reaction time, an aliquot was taken and filtered (0.2 µm, Whatman) for high performance liquid chromatography analysis with UV-vis detection (HPLC-UV) and dissolved Fe(II) analysis by the phenanthroline method. Aqueous concentrations of NA or FLU were determined using HPLC (Waters 600 Controller) equipped with a reversed-phase C18 column (250 mm×4.6 mm i.d., 5 µm) and a UV-vis detector (Waters 2489). The mobile phase was mixture of acetonitrile/water (60/40 v/v)

contained 0.1% formic acid. The flow rate was set at 1 ml min⁻¹ in isocratic mode. The UV detector was set to 258 nm for NA and 246 nm for FLU. Note that kinetic experiments at pH = 8.5 revealed that (i) NA binding to magnetite (M0.50 and M0.42) and Fe(II) uptake by M0.42 occurred within less than 5 minutes and (ii) the adding sequence (i.e. preequilibrated M0.42 with Fe(II) then addition of NA or preequilibrated M0.42 with NA then addition of Fe(II)) had no impact on the binding data after 1h (Figure S3).

The same procedure was applied to test the effect of Mn(II) and Ni(II) on NA adsorption to M0.40. Dissolved Mn(II) and Ni(II) concentrations were determined by atomic absorption spectroscopy (AAS, Shimadzu). The effect of 10 mg L⁻¹ HA or 100 μ M silicates on the adsorption of 20 μ M NA to magnetite was also investigated, applying the same procedure. HA concentrations in solution were monitored using an organic carbon analyzer (Shimadzu TOC-VCSH). SA concentration was determined using UV-Visible spectrophotometer at 297 nm. Silicates concentrations were determined by the molybdenum-blue colorimetric method.²¹

2.4 Surface Complexation Modeling

The geochemical speciation code PHREEQC (version 2)²² and the "minteq" database provided with this code were used. At infinite dilution, the pK_a of NA and FLU equal 6.19 and 6.31, respectively, and the logarithm of the formation constant of NA-Fe⁺(aq) and FLU-Fe⁺ (aq) equal 3.99 and 4.23, respectively, as calculated from reported conditional constant values and the Davies equation.^{23,24} The surface complexation models developed by Jolsterå et al.²⁵ for magnetite and maghemite were used to predict NA and FLU adsorption to magnetite with different stoichiometry. Maghemite γ -Fe^{III}₂O₃ is considered as an extreme example of a nonstoichiometric magnetite (Fe^{II}₁Fe^{III}₂O₄), with only Fe^{III} in both tetrahedral and octahedral sites.¹

Surface site protonation is formulated as follows (2-pK_a approach):

$$\equiv \text{FeOH}_2^+ \rightleftharpoons \equiv \text{FeOH} + \text{H}^+; \text{pK}_{a,1} \qquad (1)$$

$$\equiv \text{FeOH} \rightleftharpoons \equiv \text{FeO}^- + \text{H}^+; \text{pK}_{a,2}$$
(2)

Charge-potential relationship is described according to the constant capacitance model (CCM). Model parameters for magnetite and maghemite are reported in SI Table S1. The CCM is not implemented in PHREEQC, but it can be used via a three plane model (TPM; available in PHREEQC), in which one capacitor and the diffuse layer are suppressed, following the procedure detailed in Marsac et al.²⁶

3 Results and discussion

3.1 Binding capacity vs magnetite stoichiometry

Nalidixic acid (NA) adsorption to four magnetites exhibiting different Fe(II)/Fe(III) ratio (0.40, 0.42, 0.44 and 0.50) showed that NA adsorption was strongly related to the stoichiometry of the particles (*i.e.* Fe(II)/Fe(III) ratio vary from 0.40 for non-stoichiometric magnetite, to 0.50 for stoichiometric magnetite; Figure 1a). NA adsorption to M0.40 decreased with increasing pH, as typically encountered for anionic ligands, and became negligible for pH > 7.5. Indeed, adsorption of anionic ligands to mineral oxides is typically greatest under acidic to circumneutral pH, and lowest under alkaline conditions, with maximum adsorption generally observed at a pH near the pK_a (i.e. 6.19 for NA).^{27–31} At higher stoichiometry (0.42, 0.44 or 0.50), pH dependence of NA sorption was significantly altered. NA adsorption increased from pH 6 to 7 < pH < 8 and then decreased with increasing pH, thereby shifting the maximum NA adsorption to larger pH values than the pK_a. Note that adsorption of NA to M0.42 prepared either by washing or oxidizing (with H₂O₂) M0.50 was similar. The data are merged in Figure 1a (see Figure S4 for more details).

Fe(II)-amendement of non-stoichiometric magnetite (M0.40 and M0.42) led also to an enhancement in NA adsorption (Figure 1a). Indeed, the pH-adsorption curve of NA shifted to larger pH values with increasing added amounts of dissolved Fe(II), a result suggesting that NA binding was closely related to the Fe(II) content or Fe(II)/Fe(III) ratio in magnetite. The Fe(II) recharge of non-stoichiometric magnetite provided the same adsorption capability as for the corresponding magnetite with higher stoichiometry on the whole pH-range investigated (i.e. Fe(II)/Fe(III) = 0.42 for M0.40 + 100 μ M Fe(II) and M0.42 ; Fe(II)/Fe(III) = 0.44 for M0.40 + 200 μ M Fe(II) and M0.44 ; Fe(II)/Fe(III) = 0.50 for M0.40 + 500 μ M Fe(II), M0.42 + 400 μ M Fe(II) and M0.50).

Because of Fe(II) dissolution, the amount of bound-Fe(II) in magnetite can vary depending on pH, which may affect the NA adsorption. Indeed, $[Fe(II)]_{aq}$ increased with decreasing pH (no dissolved Fe(III) was found), due to the H⁺ promoted dissolution of magnetite,^{32,33} but also with magnetite stoichiometry (i.e. M0.40 < M0.44 < M0.50) (Figure 1b). Exposing a non-stoichiometric magnetite (M0.40) to 200 or 500 μ M Fe(II) led to similar Fe(II) aqueous concentration as those measured with

M0.44 or M0.50, respectively. Note that only up to ~10% of magnetite could dissolve in our experiments (i.e. for M0.50 at pH = 6). Therefore, the effect of magnetite dissolution on NA adsorption can be neglected.



Figure 1. (a) NA adsorption data versus pH for 50 m² L⁻¹ suspensions of M0.24, M0.33, M0.40, M0.42, M0.44, M0.5 and Fe(II)-amended M0.40 and M0.42 versus pH in a 10 mM NaCl + 20 μ M NA solution, after 24h reaction time. Lines correspond to surface complexation modeling results (see text for more

details). (b) Final Fe(II) aqueous concentration ($[Fe(II)]_{aq}$) and (c) calculated (Fe(II)/Fe(III))_{bound} the corresponding experiments. The same legend is used in (a), (b) and (c).

As expected, (Fe(II)/Fe(III))_{bound} increased with Fe(II)-recharge of non-stoichiometric magnetite and pH (Figure 1c). Variation in (Fe(II)/Fe(III))_{bound} appeared fully consistent with the magnetite ability to bind NA. For instance, all magnetites exhibiting similar (Fe(II)/Fe(III))_{bound} values showed similar NA sorbed amounts whatever the investigated pH, though the dissolved Fe(II) amounts are different (especially at low pH values < 7.5) (Figure 1b). For instance, M0.50 shows the same binding capability for NA as for the corresponding Fe(II)-amended magnetite (i.e. M0.40 + 500 μ M Fe(II) and M0.42 + 400 μ M Fe(II)), and therefore similar surface properties with respect to NA adsorption. This is also true for M0.40 + 200 μ M Fe(II) *vs* M0.44, and further illustrated in Figure S5, where variations of NA sorbed amounts at pH 7.7 as a function of (Fe(II)/Fe(III))_{bound} followed the same trend for both stoichiometric magnetite (M0.5) and Fe(II)-amended non-stoichiometric magnetites (M0.40 and M0.44). Likewise, enhancement in FLU adsorption was observed with increasing amounts of added Fe(II) to M0.40 or (Fe(II)/Fe(III))_{bound} (Figure S6). Desorption tests were conducted by adjusting pH to 11 after the system reached equilibrium and then stirred for around 2 h, and mass balance showed that NA or FLU was removed only by adsorption and that transformation by, for example, reduction, did not occur under the experimental conditions of this study.



Figure 2. (a) Uptake data of 200 μ M Mn(II), Fe(II) or Ni(II) on M0.40 and (b) corresponding NA adsorption data versus pH. Experimental conditions: 50 m² L⁻¹ suspensions of magnetite, 10 mM NaCl, 20 μ M NA, 200 μ M Mn(II), Fe(II) or Ni(II), 24h reaction time. Negative values for Fe(II) uptake at low pH are due to magnetite dissolution.

Formation of ternary surface complexes (i.e. surface-metal-ligand complex) generally entails more ligand adsorption when complexing cation concentration increases,³⁴ which might explain the enhancement in NA or FLU binding to magnetite. To test this hypothesis, impacts of the presence of two divalent cations (Mn(II) and Ni(II)) on NA adsorption to M0.40 were investigated and compared with that of Fe(II). Because the redox potential of the Mn^{II}/MnO₂(s) couple at pH 7 is much larger than that of Fe^{II}/Fe₃O₄(s), Mn(II) oxidation by magnetite is not expected.³⁵ According to the Irving-Williams series,³⁶ cation adsorption data³⁵ and aqueous complexation with NA,^{23,37} ternary

surface complexation of Mn(II), Fe(II) and Ni(II) with NA on magnetite are supposed to follow the order: Mn(II) < Fe(II) < Ni(II)³⁴ (assuming that no electron transfer occurs between Fe(II) and the solid). This ranking is, however, observed neither for metal uptake nor for NA adsorption to M0.40 (Figure 2). Indeed, more Fe(II) uptake than Ni(II) is achieved (Figure 2a), whereas maximum NA adsorption was obtained at pH \approx 7.5 for Fe(II) and pH \approx 8.5 for Mn(II) and Ni(II). This observation is also confirmed at higher metal concentration (e.g., 500 µM, SI Figure S7), thereby underscoring a different adsorption behavior of NA in the presence of Fe(II) with respect to other divalent transition metals.

Taken together, these findings suggest that the adsorption enhancement for NA is mainly controlled by the $(Fe(II)/Fe(III))_{bound}$ ratio in magnetite, rather than by NA-Fe(II) complexation in solution at low pH or ternary surface complexation. As a matter of fact, the enhanced binding of ligands to stoichiometric magnetite with respect to non-stoichiometric one may result from the creation of new binding sites upon Fe(II)-recharge, or changes in the intrinsic surface reactivity of amended magnetite.

3.2 Description of enhancement sorption capacity

As an attempt to describe the relationship between (Fe(II)/Fe-(III))bound and ligand adsorption, we used a surface complexation modeling approach. The aim of the present modeling exercise was to provide a semiquantitative evaluation of how much magnetite surface reactivity toward quinolones is affected by its stoichiometry. Because of the possible presence of various types of $\Box Fe^{II/III}O(H)$ groups at magnetite surfaces, full mechanistic description of binding mechanisms using a complete approach would have required fitting of many parameters, and then generated large errors on simulated phenomena. Therefore, we used the 2-pKa-CCM approach developed by Jolsterå et al.²⁵ Using acid-base titration method, they have calculated site densities of 1.50 site nm⁻² and 0.99 site nm⁻² for magnetite (91 m² g⁻¹) and maghemite (86 m² g⁻¹), respectively. As shown in SI Figure S8, fitting experimental adsorption isotherms of NA on M0.50 and M0.42 at pH 7 with Langmuir equation results in a maximum binding capacity of 0.95 and 0.71 NA molecule nm-2, respectively. Previous studies on quinolones binding to iron (hydr)oxides evidenced that one molecule binds to two surface hydroxo groups,^{29,38,39} by involving its carboxylate and its keto-group as following:

$$2 \equiv FeOH + 2H^{+} + NA^{-} \rightleftharpoons (\equiv Fe)_2 NA^{+} + 2H_2O; \qquad {}^{S}K$$

Hence, the maximum binding of NA to magnetites corresponds to 1.90-1.42 site nm⁻², which are relatively close to those determined by Jolsterå et al.²⁵ As the present modeling exercise aimed to determine surface complexation constant (SK) to each magnetite, we focused only on the pH edge curve (obtained at low surface coverage) and thus used the same site density for all magnetites (1.50 site nm⁻²). Measured total dissolved Fe(II) concentration in solution at the end of each adsorption experiment was used as input parameter to account for ligand-Fe(II) complexation in solution. However, decreasing ligand adsorption with decreasing pH (i.e., at high [Fe(II)]aq) could not be well predicted, further suggesting that effects of variation of (Fe(II)/Fe(III))bound were more important than the ligand-Fe(II) aqueous complexation. Therefore, we only focused on data at high pH values, where (Fe(II)/Fe(III))bound is maximal and constant (see Figure 1c; e.g. pH > 8 for M0.50, pH > 6.5for M0.40). As shown in Figure 1a (NA) and SI Figure S6 (FLU), a relatively good fit to the adsorption data versus pH was found (unsuccessful extrapolations at lower pH are shown as dotted lines in Figure 1a and SI Figure S6). When plotting log ^SK for NA versus (Fe(II)/Fe(III))bound (Figure 3), a linear relationship was found ($R^2 = 0.99$). Data for FLU are also included and show a comparable behavior. Values of ^SK increased by almost 8 orders of magnitude with increasing (Fe(II)/Fe(III))bound from 0.40 to 0.50, suggesting that stoichiometric magnetite (Fe(II)- enriched) may have a much stronger affinity for NA or FLU than partially oxidized magnetite (Fe(II)-depleted). Such large variation in log ^sK cannot be attributed to potential modification in surface site density that was neglected by using the same site density for all magnetites. As more amount of Fe(II) at the magnetite surface is expected upon Fe(II) recharge, we may suppose that \Box Fe^{II}O(H) sites are more reactive than Fe^{III}O(H) for NA or FLU binding.



Figure 3. Surface complexation modeling results. Logarithm of ligand-magnetite surface complexation constant (log ^SK) versus (Fe(II)/Fe(III))_{bound} determined at pH \geq 8 (where (Fe(II)/Fe(III))_{bound} is constant).

To test the binding capacity of magnetite with lower stoichiometries, we prepared M0.33 and M0.24 (similar to magnetites found in some natural samples^{40,41}), by exposing the M0.50 during 24h to (i) a known amount of H₂O₂ (following the procedure of Gorski et al.⁶) and (ii) ambient air, respectively. Both oxidized magnetites exhibited similar NA adsorption, whereas [Fe(II)]aq were found very low (Figure 1b). For pH \leq 7, more pronounced NA adsorption was observed on M0.33 and M0.24 as compared to M0.40, a result that can be attributed to the complete suppression of dissolved Fe(II) at low pH. Consistently, the best fitting values of SK were found very close for M0.24, M0.33 (log ^SK = 17.7) and M0.40 (log ^SK = 17.5). It is worth noting that the calculated surface complexation constant SK remains constant for 0.23 < Fe(II)/Fe(III))bound < 0.40, and then sharply increased after 0.40 (Figure 2). The existence of a threshold may be related to the surface amount of magnetite bound-Fe(II) required to trigger the enhancement of NA binding with magnetite surfaces.



Figure 4. NA adsorption data versus pH for 50 m² L⁻¹ suspensions of M0.40 and Fe(II)-amended M0.40 in a 10 mM NaCl + 20 μ M NA solution, after 24h reaction time, in presence of (a) silicates (100 μ M) or (b) HA (10 mg L⁻¹).Empty symbols represent NA adsorption without Si and HA.

Because nonstoichiometric magnetites may have oxidized magnetite/maghemite-like structure at the outermost surface (oxidation of magnetite particles is supposed to take place from the surface to the core²⁵), NA adsorption to magnetites with Fe(II)/Fe(III) ≤ 0.42 was also evaluated using the surface complexation model developed for maghemite (i.e., fully oxidized magnetite). Because of the little variation in site density, surface area and acid-base properties, log SK (for NA and FLU) determined using magnetite model or maghemite model were found to be very similar (Figure 4, log ^SK = 17.8 ± 0.2).

This modification in binding properties is not specifically limited to NA or FLU molecule, since the adsorption of naturally occurring ligands such as salicylate (1-hydroxybenzoic acid, SA), humic acid (HA) and silicates (Si) was also considerably enhanced by the addition of dissolved Fe(II) to a nonstoichiometric magnetite M0.40 (see SI Figures S9-S11). Consequently, the stoichiometry of magnetite is not only a key parameter for Fe(II) uptake⁵ and contaminant reduction^{6,10,11} but also for the binding of emerging organic contaminants and naturally occurring ligands. Because emerging contaminants binding to magnetite might be affected by naturally occurring ligands, competitive experiments between NA and HA or Si were conducted. The presence of 100 µM Si decreased NA binding to magnetite due to ligand competition, though the effect of Si on NA adsorption to M0.40 is insignificant (Figure 4a). However, the impact of 10 mg L⁻¹ HA on NA binding implies both competitive (i.e., antagonistic effect) and cooperative (i.e., synergetic effect) mechanisms (Figure 4b). Indeed, at high Fe(II)/Fe(III), HA effectively decreases NA binding whereas, at low Fe(II)/Fe(III), NA binding is enhanced in the presence of HA. The latter may arise from intermolecular interactions between HA and NA, as previously observed between NA and other organic compounds at goethite surfaces,^{38,39} and supported by a quinolone-HA binding study.⁴² While further investigations are required to understand the different competitive and cooperative effects, this data further supports

that (i) binding properties of magnetite is affected upon Fe(II)-recharge, and (ii) this change toward adsorption of emerging contaminants is still observed in the presence of naturally occurring ligands.

4 Environmental implications

Magnetites of differential composition and stoichiometry may exist in natural systems depending on the local redox and chemical conditions, particularly in Fe-rich subsurface environments or temporary flooded soils (e.g. wetlands experiencing redox potential fluctuation).^{1,2,38,39} Given its higher solubility and surface area-to-volume ratio, Fe(II) release and/or surface oxidation may occur for the nanosized magnetite, commonly found in environmental systems¹. On the other hand, different kinds of magnetite can be obtained depending on the synthesis method, as reported in water remediation studies using magnetite as sorbent.^{27,31,32} Consequently, the stoichiometry of magnetite and its potential Fe(II)-enrichment or Fe(II)-depletion in reaction medium should be taken into account in sorption assessment studies. It is worth noting that the changes in binding properties of magnetite upon Fe(II)-recharge are still observed in the presence of environmentally relevant ligands, emphasizing the importance of the presently evidenced mechanisms in environmentally relevant conditions. Therefore, these findings call for refinements in current day modeling approaches used in the prediction of fate of organic contaminants in Fe-rich subsurface environments or magnetite-based remediation processes.

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Supporting information

Influence of magnetite stoichiometry on the binding of emerging organic

contaminants

1) FLU and NA speciation in solution



Figure S1. Distribution of (a) NA and (b) FLU at various pH values with molecular structures of different NA and FLU species. Ionic strength: 10 mM NaCl.

2) XRD and TEM analyses





Figure S2. XRD and TEM data for synthesized magnetite Fe_3O_4

3) Kinetics

Figure S3 shows kinetics of 400 μ M Fe(II) adsorption onto M0.42 (Figure S4a) and 20 μ M NA adsorption onto M0.5 and Fe(II)-amended magnetite (i.e. M0.42 + 400 μ M Fe(II)) with different adding sequence(Figure S4b) at pH 8.5. The kinetics of Fe(II) adsorption by M0.42 is very fast and Fe(II) concentration in solution decreased to 0 in a few minutes. The kinetics of NA adsorption achieves equilibrium immediately and NA uptake by M0.5 is the same with that of M0.42+ 400 μ M Fe(II). Morover, the kinetics and uptake of NA is independent of adding sequence.



Figure S3. Kinetics of (a) 400 μ M Fe(II) adsorption onto M0.42 and (b) 20 μ M NA adsorption onto magnetite. Experimental conditions: pH = 8.5, 50 m² L⁻¹ magnetite, 10 mM NaCl.

4) Comparison between M0.42 and M0.42-H₂O₂

Figure S4 compares pH edges and isotherm adsorption of M0.42 and M0.42- H_2O_2 . They have very close pH edges in the presence or in the absence of Fe(II) and they have almost the same isotherm, which confirms that it is the real bulk stoichiometry of Fe(II)/Fe(III) ratio that dominated the different adsorption equilibrium rather than introducing artificial treatment that selectively altered the surface of magnetite.



Figure S4. (a) pH edges and (b) isotherm of M0.42-H₂O₂ and M0.42 at pH 7. Experimental conditions: 20 μ M NA for pH edges and 20-300 μ M NA for isotherm , 50 m² L⁻¹ magnetite, 10 mM NaCl, 24 h reaction time.

5) NA adsorption versus Fe(II)/Fe(III) at pH 7.7



Figure S5. NA adsorption versus (Fe(II)/Fe(III))_{bound} for M0.50, Fe(II)-amended M0.40 ($0 \le added$ [Fe(II)] $\le 500 \mu$ M) and Fe(II)-amended M0.44 ($0 \le added$ [Fe(II)] $\le 300 \mu$ M). Experimental conditions: pH = 7.7; 20 μ M NA, 50 m² L⁻¹ magnetite, 10 mM NaCl, 24 h reaction time.





Figure S6. FLU adsorption data versus pH for M0.40, M0.50 and Fe(II)-amended M0.40 ($0 \le$ added [Fe(II)] $\le 500 \ \mu$ M). Lines correspond to surface complexation modeling results. Experimental conditions: 20 μ M FLU, 50 m² L⁻¹ magnetite, 10 mM NaCl, 24 h reaction time.

7) Comparison between Fe(II), Mn(II) and Ni(II)

Figure S7 compares the uptake of 500µM of Fe(II), Mn(II) and Ni(II) (Figure S7a) by M0.40 and their impacts on NA adsorption to M0.40 (Figure S4b). Fe(II) uptake by M0.40 is much larger than that of Ni(II) and Mn(II). Furthermore, pH-edges of Mn(II) and Ni(II) exhibit a break at pH \approx 8.5, suggesting Ni/Mn-(hydr)oxides precipitation at higher pH values. Finally, NA adsorption is much larger in presence of Fe(II) than Mn(II) or Ni(II). This confirms the strong disagreement with the Irving-Williams series (Mn(II) < Fe(II) < Ni(II)) discussed in the main text.



Figure S7. (a) Uptake data of 500 μ M Mn(II), Fe(II) or Ni(II) on M0.40 and (b) corresponding NA adsorption data versus pH. Experimental conditions: 50 m² L⁻¹ suspensions of magnetite, 10 mM NaCl, 20 μ M NA, 200 μ M Mn(II), Fe(II) or Ni(II), 24h reaction time.

8) isotherm adsorption of magnetite

Figure S8 compares NA adsorption isotherm onto M0.42 and M0.5 at pH 7. Langmuir model was used to fit the isotherm data, which can be expressed as follows:

$$[NA]_{sorbed} = Q_{\max} \frac{K_L \times [NA]_{aq}}{1 + K_L \times [NA]_{aq}}$$

Sorption isotherms can be fitted well with Langmuir equation and the calculated maximum NA uptake for M0.5 and M0.42 are 1.575 and 1.33 μ M m⁻², respectively, namely 0.95 and 0.80 site nm⁻², which is close to the reported site density of magnetite and maghemite in literature³⁸.



Figure S8. Isotherms of M0.42 and M0.50. Lines correspond to Langmuir modeling results. Experimental conditions: pH = 7, 50 m² L⁻¹ magnetite, 10 mM NaCl, 20 - 300 μ M NA, 24h reaction time.

9) Salicylate adsorption data



Figure S9. Salicylate adsorption versus pH for M0.40, M0.50 and Fe(II)-amended M0.40 (added [Fe(II)] = 1 mM). Experimental conditions: 100 µM salicylate, 100 m² L⁻¹ magnetite, 10 mM NaCl, 24 h reaction time.



10) Humic acid adsorption data

Figure S10. Humic acid (HA) removal data versus pH for M0.40, M0.50 and Fe(II)-amended M0.40 $(0 \le \text{added} [\text{Fe(II)}] \le 500 \,\mu\text{M})$. Experimental conditions: 10 mg L⁻¹ humic acid, 50 m² L⁻¹ magnetite, 10 mM NaCl, 24 h reaction time. M0.40 and M0.40+200 μ M Fe(II) exhibit almost a similar trend, probably due to the strong complexation of HA with Fe(II) in aqueous phase.

11) Silicates adsorption data



Figure S11. Silicates removal data versus pH for M0.40, M0.50 and Fe(II)-amended M0.40 ($0 \le$ added [Fe(II)] $\le 500 \ \mu$ M). Experimental conditions: 100 μ M silicates, 50 m² L⁻¹ magnetite, 10 mM NaCl, 24 h reaction time.

Aqueous		
reactions		log K
$FLU^{-} + H^{+} =$		
FLUH		6.3
$NA^- + H^+ =$		
NAH		6.19
$FLU^{-} + Fe^{2+} =$		
$FLUFe^+$		4.23
$NA^{-} + Fe^{2+} =$		
$NAFe^+$		3.99
surfa	ce reactions ^a	
Fe(II)/Fe(III)	log	log
ratio	K _{NA}	K _{FLU}
0.24	10.3	/
0.33	10.3	/
0.4	10.1	11.1
0.42	11.3	12
0.44	12.7	12.7
0.484	13.9	/
0.5	14.3	14.15
^a The site densities of	magnetite	is 1.5 sites/m

Table S1. Summary of the surface complexation model parameters used in this study.

Chapter 3 Adsorption of Quinolone Antibiotics to Goethite under Seawater Conditions: Application of a Surface Complexation Model

Abstract

The assessment of antibiotics mobility under seawater conditions has been rarely studied, since an accurate description of such multicomponent systems is quite challenging. In this study, the adsorption of a widely used quinolone antibiotic in aquaculture, Oxolinic acid (OA), to a synthetic goethite (α -FeOOH) was examined in presence of major (e.g. Mg²⁺, SO₄²⁻) and trace (e.g. Cu²⁺) ions naturally occurring in seawater. The OA adsorption can be successfully predicted using a charge distribution multi-site complexation model (CD-MUSIC) coupled with the three plane model (TPM). This modeling approach allowed a quantification of the competitive and synergetic effects of different ions in seawater over a large range of environmentally relevant conditions. Finally, the mobility of OA in dynamic column tests can be well predicted through coupling aqueous transport and batch sorption parameters obtained in synthetic seawater. These results may have strong implications for assessment and prediction of the fate of quinolones in sediment/seawater interface systems.

1 Introduction

Quinolone antibiotics, broad-spectra antimicrobial agents, are widely used in the treatment and prevention of bacterial diseases of fish.^{1,2} Among them, oxolinic acid (OA) is commonly used as a prophylactic, or, as a chemotherapy agent.^{1,2} Due to its frequent use, great amounts of OA can be disseminated into the environment, which poses potential risks to human health and aquatic life.³ As a result, high residual levels of OA were detected in affected environments, *i.e.* in concentration ranging from 2.50 ppm in fresh or saline surface waters to 426 ppm in pond sediments.^{4–6} Due to the rapid growth of aquaculture in different countries, impacts of antibiotics overuse on the environment are becoming of big concern.⁷ Therefore, it is necessary to evaluate the transport and mobility of quinolones in marine ecosystems and ultimately their ecological impacts.

In marine environments, mineral particles present in suspension or in sediments are able to bind quinolones, which may affect their mobility and bioavailability in water.⁸ Among these reactive mineral surfaces, goethite (α -FeOOH) is the most thermodynamically stable iron oxyhydroxide mineral and the most common diagenetic iron oxyhydroxide in both marine and lake sediments.⁹ Recently, goethite has been shown to strongly sorb OA across a wide range of salinity (10–1000 mM NaCl) including seawater-like one.⁸ However, cations and anions existing in seawater environments naturally or due to anthropogenic activities, could affect the mobility of OA in marine ecosystems. This may proceed through (i) complexation with divalent transition metals in aqueous solution^{10,11} and (ii) competitive or cooperative binding to mineral surfaces.^{12–16}

Despite the widespread use of quinolones in fish farming, the effect of cations and anions found in seawater on their solubility and adsorption behavior to suspended mineral particles or mineral sediments has received little attention. In this study, interactions of OA with goethite in presence of two major ions (e.g. Mg^{2+} , SO_4^{2-}) and one trace cation (Cu^{2+} used as a model trace metal in seawater) have been studied under a wide range of ion concentrations and pH values. Possible competitive or synergetic effects on OA adsorption have also been investigated in the presence of mixtures of Mg^{2+} , SO_4^{2-} and Cu^{2+} , and in synthetic seawater. The ability of the three plane model (TPM) to predict competitive or cooperative interactions on goethite surfaces has been evaluated under a wide range of pH (4-10). Finally, this thermodynamic adsorption model was used to predict the breakthrough

behavior of OA in a goethite-packed column under water-saturated conditions.

Given the complexity of the seawater matrix where a wide array of cations and anions exist, a quantitative framework for assessing competitive or synergetic interactions both under static and hydrodynamic conditions is quite challenging. For the first time, TPM combined with the charge distribution multisite complexation (CD-MUSIC) model is successfully applied to predict binding mechanisms of contaminants on mineral particles in the presence of major and trace ions of seawater, and then the reactive transport under flow-through conditions.

2 Materials and Methods

2.1 Materials

All reagents were purchased from Sigma-Aldrich and used without further purification. All solutions were prepared with ultrapure water. An OA (purity >99%) stock solution was prepared by dissolving 30 mg (115 μ moles) OA in 20 mL of 1 M NaOH, then diluted to 1 L with ultrapure water.

2.2 Synthesis and Characterization of Goethite Particles

Goethite was synthesized as described in previous studies.^{8,17} Briefly, 400 mL of a 2.5 mol L⁻¹ sodium hydroxide solution was mixed with 500 mL of a 0.5 mol L⁻¹ ferric nitrate solution (Fe(NO₃)₃·9H₂O) at a fixed rate of 1 mL min⁻¹ with stirring under nitrogen atmosphere. The obtained hydroxide slurry was aged at 60 °C for 72 hours in an oven. The precipitate obtained was then dialyzed (Spectra/Por membrane 2) against Milli-Q water. The water was changed every day until its conductivity was close to 0 μ S cm⁻¹. The suspensions were stored in polypropylene containers at 4 °C for further use. The purity of goethite was confirmed by X-ray diffraction (XRD) and the B.E.T. specific surface area of the synthetic goethite was 80±1 m² g⁻¹ and the point of zero charge (PZC) of goethite, determined at 298 K in 0.01, 0.1 and 1 M NaCl solutions by the potentiometric titration method, was pH 9.1. Goethite coated sand (GCS) was prepared by coating goethite onto sieved Fontainebleau quartz sand (100–150 µm) as previously detailed.¹⁸

2.3 Batch adsorption experiments.

Because pH measurements will be affected by high background electrolyte solutions, the pH electrode was calibrated to measure the molarity of the proton (-log [H⁺], noted as pHc) using

solutions of known $[H^+]$ (10⁻⁵-10⁻² M) in 480 mM NaCl, and the results are provided in this form in this study. The procedure was repeated in the presence of other ions (Mg²⁺, SO₄²⁻, Cu²⁺).

OA solubility experiments (undersaturation direction) were conducted by suspending solid OA (~3-5 mg) in 10 mL of 480 mM NaCl with different concentrations of Mg²⁺ and adjusting pHc from 4 to 8 using HCl and NaOH. The suspensions were equilibrated for 24 h (long enough for drug release¹⁹), after that the supernatants were filtered (0.2 µm) and OA concentrations were measured with high pressure liquid-chromatography coupled with UV detection (HPLC-UV).

All batch experiments were carried out under $N_{2(g)}$ atmosphere to avoid effects of carbonates and bicarbonates on the adsorption of OA onto goethite. Batch adsorption experiments were carried out in 15 mL polyethylene tubes at a total volume of 10 mL solution with 10 μ M OA, 480 mM NaCl and 50 m² L⁻¹ goethite. MgCl₂ (10 and 50 mM), CuCl₂ (10, 50 and 100 μ M) and/or Na₂SO₄ (1, 10 and 29 mM) were added to the solutions in order to study the effects (and combined effects) of Mg²⁺, SO₄²⁻ and/or Cu²⁺ on OA adsorption. The solution compositions are listed in Table S1. The pHc was then adjusted to the desired value (4 < pHc < 10) with HCl or NaOH solutions. The tubes were sealed by caps and then shaken continuously on a platform shaker at 200 rpm and 25 °C. After equilibrating for 24 h, pHc was measured again before filtration (0.2 μ m) and OA was analyzed by HPLC-UV. Desorption tests (pHc = 11) were carried out under various experimental conditions to check the mass balance of OA (Table S2).

To study OA adsorption in conditions closer to the marine environment, an artificial seawater was synthesized according to the method of Kester et al.²⁰ Table S3 shows the major elements present in the synthetic seawater. However, batch experiments were conducted in absence of NaHCO₃ in order to avoid the potential complication of competing carbonate adsorption.

Aqueous OA concentrations were determined using a high performance liquid chromatography (Waters 600 Controller) equipped with a UV detector (Waters 2489) and a reversed-phase C18 column (250 mm×4.6 mm i.d., 5 μ m). The mobile phase (1 mL min⁻¹) was a mixture of acetonitrile/water (60:40 v/v) contained 0.1% formic acid. The detector was set to 259 nm for OA. Concentrations of Cu²⁺ and Mg²⁺ were analyzed by Varian AA140 Atomic Absorption Spectrometer. The sulfate concentration was measured by DIONEX IX Chromatograph DX-120.
2.4 Column adsorption experiments.

Breakthrough column experiments were conducted according to Hanna et al.^{18,21} Briefly, 15 g of dry GCS was packed into glass chromatographic columns of 1.6 cm internal diameter to give a porous bed length of 4.7 cm. After packing to a uniform bulk density $(1.59 \pm 0.05 \text{ g cm}^{-3})$, the column was wetted upward with a synthetic seawater solution at a constant flow rate. Once the column was water saturated, the flow characteristics of the porous bed were determined by a nonreactive tracer experiment, as previously described.^{18,21} The classical convection dispersion equation (CDE) was applied to describe the 1D transport of a non-reactive solute (bromide) under steady-state water flow. The fitting result provided estimations of the volumetric water content (θ) and dispersion coefficient (D) that characterize flow homogeneity. The dispersivity λ was calculated according to $\lambda = D\theta/q$, neglecting the molecular diffusion. At a flow rate of 0.5 mL min⁻¹, the Darcy velocity (q) was 0.25 cm min⁻¹, dispersion coefficient D = 0.009 cm² min⁻¹ and the dispersivity λ was 151 µm within order of magnitude of particle size of the used sand. The Péclet number (Pe = vL/D, L is total column length) in the column was higher than 300, indicating the predominance of a convective regime. Similarly, these parameters were also calculated for 0.1 mL min⁻¹ as flow rate.

Two different conditions of inflow solution, with or without carbonates, were tested. In both tests, a mixture of 10 μ M OA and 10 μ M Cu²⁺ was injected in the column at a constant flow rate (0.5 mL min⁻¹ or 0.1 mL min⁻¹). OA concentrations in the collected fractions were measured by HPLC/UV.

2.5 Surface Complexation Modeling

Predictions of OA adsorption to goethite were made using the multisite complexation (MUSIC) model approach.²² The geochemical speciation code PHREEQC (version 2)²³ was used for surface complexation calculations. The charge of the goethite/water interface was treated by using the three plane model (TPM). Charges of the adsorbates were distributed among the 0 (H⁺, metal-bonded OA), 1 (hydrogen-bonded OA), and 2 (Na⁺, Cl⁻) planes of the TPM. Although not required for OA binding to goethite,⁸ a charge distribution (CD) term was used in the present work to describe the adsorption of other ions on goethite. Singly (\equiv FeOH^{-0.5}), doubly (\equiv Fe₂OH) and triply (\equiv Fe₃O^{-0.5} and \equiv Fe₃OH^{+0.5}) coordinated oxygens outcrop the goethite surface, depending on the crystal face. A simplified 1-pK

surface charging model, neglecting the contributions of doubly- and part of the triply-coordinated oxygens, was used. The reactive site density in this model are detailed in our previous paper and in SI:⁸ [\equiv FeOH^{-0.5}] = 3.12 sites nm⁻² and [\equiv Fe₃O^{-0.5}] = 3.12 sites nm⁻² on (001)/(101) planes (90% of the surface area), and [\equiv FeOH^{-0.5}] = 7.4 sites nm⁻² on (021) plane (10% of the surface area). The protonation constants of these groups are set to that of the pHpzc (1-pK approach of MUSIC model). Equilibrium constants of all surface species are reported in Table 1. PhreePlot²⁴ was used to determine parameters for OA sorption to goethite. All equations and parameters describing goethite surface (e.g. pK_a, capacitances) and OA-goethite binding were taken from our previous work.⁸

PHREEQC can use various equations to account for the non-ideality of aqueous solutions. In this study, a modified version of the Debye-Hückel equation so-called WATEQ was used with the "minteq.v4" database provided with PHREEQC:

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + Ba_i^0 \sqrt{I}} + b_i I \tag{1}$$

Where γ_i and z_i are, respectively, the activity coefficient and the charge of the ion *i*, A and B are temperature dependent parameters (A=0.5095 and B=0.3284×10⁸ at 25°C), a_i^0 and b_i are fitted ion-specific parameters. This equation is valid up to I values of about 2 in dominantly chloride solutions.²⁵ Because these parameters are missing for OA aqueous species, Ba_i^0 was systematically set to 1.5 (i.e., $a_i^0 = 4.57 \times 10^{-8}$), as commonly adopted in the specific ion interaction theory (SIT²⁶), a more advance model than the WATEQ equation. All necessary parameters are available in the "minteq.v4" database except for OA species. $b_{OA-} = b_{OAH} = 0$ was used, as in our previous study.⁸ b_{OAMg^+} was fitted using Phreeplot and OA solubility data in presence of Mg²⁺. b_{OACu^+} and b_{OACa^+} were assumed equal to b_{OAMg^+} .

All experimentally studied ions were included in the calculations, and PHREEQC calculated the ionic strength according to the composition of the solution. As shown below, surface complexation of almost all ions were taken into account except Br⁻ and H₃BO₃. Br⁻ is expected to behave similarly to Cl⁻, but is about 660 times less abundant than Cl⁻ in seawater. To our knowledge, no CD-MUSIC parameters are available to describe H₃BO₃ sorption to goethite. Therefore, the adsorption of Br⁻ and

H₃BO₃ was neglected as a first approach.

Precipitation of $Mg(OH)_{2(s)}$, $Ca(OH)_{2(s)}$ and $Cu(OH)_{2(s)}$ were taken into account in the calculations. Only $Mg(OH)_{2(s)}$ could form under alkaline conditions, which had little effect on the adsorption behavior and interpretations.

PhreePlot²⁴ was used when parameter adjustment was required. It also provides a statistical uncertainty for the estimated parameters (see Table 1). Parameters were fitted separately from independent data sets in simple (binary) systems, and then kept constant for simulations in more complex systems. For instance, bOAMg⁺ was determined using OA solubility data in the presence of Mg²⁺ and kept constant afterward. Goethite-OA and goethite-Mg²⁺ surface complexation constants were determined in previous studies dedicated to the corresponding binary system.^{8,27} Then, simulations were made (with no parameter adjustment) in the ternary goethite- Mg²⁺-OA system. This step-by-step procedure was used in all systems, hence limiting the uncertainties on newly adjusted model parameters.

3 Results and Discussion

3.1 OA solubility and binding to goethite in 480 mM NaCl

The OA solubility was first calculated with PHREEQC using the acidity constant (K_a) value from the IUPAC stability constant database and the solubility constant (K_s) previously determined (with

$$b_{OA^{-}} = b_{OAH} = 0):^{\circ}$$

$$OAH_{(s)} \rightleftharpoons OAH_{(aq)}; \log K_{s} = -5.06$$

$$OAH_{(aq)} \rightleftharpoons OA^{-} + H^{+}; \log K_{a} = 6.92$$
(2)
(3)

The experimental solubility values are very close to the calculated ones (Figure S1a). In 480 mM NaCl, OA solubility increased with increasing pH.

OA adsorption shows typical anion adsorption character on goethite surfaces, i.e. adsorption reaches a maximum value at acidic to circumneutral pH and then decreases with increasing pH (Figure S1b).⁸ According to previous infrared spectroscopic investigations,⁸ OA binds to goethite predominantly through a metal-bonded (MB) complexes with surface Fe sites and a strong hydrogen-bonded (HB) complexes (surface hydration shared ion pair) with surface hydroxo groups. MB surface complex formed at the goethite (101)/(001) and (210) planes involving OA keto group and

one oxygen of the carboxylate group:

$$2 H^{+} + 2 \equiv FeOH^{-0.5} + OA^{-} \rightleftharpoons (\equiv Fe)_{2}(OA)^{0} + 2 H_{2}O; \qquad \log K_{MB}$$

$$\tag{4}$$

Only singly coordinated (\equiv FeOH^{-0.5}) surface sites are considered to be involved in the reaction given the propensity for ligand exchange of these sites. Eq.4 does not denote the number of Fe(III) octahedra in a complex but only the number of \equiv FeOH^{-0.5} sites that may or may not be of the same Fe(III) octahedron.²⁸ Ideally, the steric constraints at the dominant (101)/(001) planes should promote bridging between two Fe atoms separated by 3 Å from one another,²⁹ while at the (210) plane, two \equiv FeOH^{-0.5} should be located on the same Fe(III) octahedron, hence our preference for modeling OA binding as a 1:2 OA/ \equiv FeOH^{-0.5} species.

Hydrogen-bonded (HB) complexation with singly \equiv FeOH^{-0.5} sites was also proposed:

$$2 \operatorname{H}^{+} + 2 \equiv \operatorname{FeOH}^{-0.5} + \operatorname{OA}^{-} \rightleftharpoons (\equiv \operatorname{FeOH}_{2})_{2}^{+1 + \Delta z 0 \dots} (\operatorname{OA})^{\Delta z 1}; \quad \log K_{\operatorname{HB}}$$
(5)

In our previous work,⁸ the CD approach was not used and OA negative charge was placed at the 1-plane ($\Delta z_0 = 0$; $\Delta z_1 = -1$). In general, within the CD-MUSIC framework, 0.2 bond valence unit can be assigned to each H-bond. Because OA binds to goethite surface via two H-bonds (one with each of two adjacent =FeOH₂^{+0.5} sites), a CD value of 0.4 was used ($\Delta z_0 = -0.4$; $\Delta z_1 = -0.6$). In fact, this had a minor effect on the prediction of OA-goethite binding and as shown in Figure S1b, the model predicts well the OA adsorption onto goethite at high salt concentration (i.e. 480 mM NaCl).

3.2 Effect of Mg²⁺ on OA solubility and binding to goethite

The equilibrium constant of the formation of the aqueous OAMg $^+$ complex has previously been reported at I = 0.1 M:¹⁰

$$OA^{-} + Mg^{2+} \rightleftharpoons OAMg^{+}; \quad \log K_{OA-Mg}$$
 (6)

In the present study, Mg-OA complexation in 480 mM NaCl was investigated via measurements of OA solubility at different MgCl₂ concentrations (Figure 1a). As expected, OA apparent solubility increased with increasing $[Mg^{2+}]$ due to the formation of OAMg⁺ aqueous complex. The formation constant of OAMg⁺ was determined at infinite dilution (log K_{OA-Mg} = 3.51) using previously reported constant at I = 0.1 M.¹⁰. An accurate prediction of OA apparent solubility in presence of Mg²⁺ (Figure

1a) can be achieved by adjusting b_{OAMg^+} (= 0.5) using PhreePlot.

Figure 1b shows OA adsorption to goethite in 480 mM NaCl at different Mg²⁺ concentrations (0,

10 and 50 mM). The presence of Mg^{2+} decreased OA adsorption to goethite at all pH values and shifted the sorption edge to lower pH values. As previously reported, ^{12,13} the effect of Mg^{2+} could be explained by the formation of an aqueous complex and/or competition effects towards surface sites. Mg^{2+} adsorption to goethite is weak and could not be detected at as high $[Mg^{2+}]$ as in the present work. This is also in agreement with a previous report,²⁷ where Mg^{2+} adsorption became only detectable at pH >8 and at lower $[Mg^{2+}]$ (\leq 0.4 mM) in 0.1 M NaNO₃. At such pH value, there is almost no OA adsorption in our experiments, ruling out possible competitive effect with Mg^{2+} . Accounting for OAMg⁺ formation in the OA adsorption model agreed with our experimental values. Including Mg^{2+} -goethite surface complex²⁷ did not affect the simulations, thereby confirming the predominant contribution of the aqueous complex OAMg⁺ (Figure 1b).



Figure 1. (a) OA solubility in 480 mM NaCl at different MgCl₂ concentrations. (b) OA (10 μ M) adsoption to goethite (50 m² L⁻¹) in 480 mM NaCl versus pHc at different MgCl₂ concentrations after 24h reaction time. Lines are modeling results.

3.3 Effect of SO₄²⁻ on OA binding to goethite

Figure 2a shows OA adsorption to goethite at different SO_4^{2-} concentrations (0, 1, 10 and 29 mM).

At 1 mM of SO_4^{2-} , there is almost no effect on OA adsorption. For larger $[SO_4^{2-}]$, OA adsorption is only decreased at low pH values (pHc < 6.5), with no significant influence at higher pH (Figure 2a).

To maximize sensitivity to residual sulfate concentration determination, $SO_4^{2^-}$ adsorption was only determined at the lowest $[SO_4^{2^-}]$ (i.e. 1 mM). Because ionic chromatography measurements of aqueous $[SO_4^{2^-}]$ are subjected to large error due to interferences caused by Cl⁻, an adsorption experiment was investigated at both 10 and 480 mM NaCl concentrations (Figure 2b). As typically observed for anion adsorption to iron oxides, sulfate adsorption decreased with increasing pH.^{30–33} According to several vibrational spectroscopy studies,^{31,34,35} both inner-sphere complexes and outer-sphere complexes are supposed to form between $SO_4^{2^-}$ and the goethite surface. Therefore, a monodentate MB complex (eq.7) and a monodentate HB surface (eq.8) complex can be proposed to describe the adsorption data as follows:³⁶

$$H^{+} + \equiv FeOH^{-0.5} + SO_{4}^{2-} \rightleftharpoons \equiv FeO^{-0.5 + \Delta z0} - SO_{3}^{\Delta z1} + H_{2}O; \quad \log K \equiv FeOSO_{3}$$
(7)
$$H^{+} + \equiv FeOH^{-0.5} + SO_{4}^{2-} \rightleftharpoons \equiv FeOH_{2}^{-0.5 + \Delta z0} \dots \Delta z^{1}O - SO_{3}^{\Delta z2}; \quad \log K \equiv FeOH_{2}SO_{4}$$
(8)

The charge of SO_4^{2-} is distributed over the 0- and 1-plane for the MB complex, and between the 1and 2-plane for the HB complex. By fitting only the surface complexation constants in the present investigation (see Table 1), our model satisfactorily described sulfate adsorption versus pH and ionic strength (Figure 2b) and successfully predicted competitive effects of sulfate on OA at pH<7, though underestimated OA adsorption at high pH (Figure 2a). This experimental and modeling data confirm the sulfate competition for OA adsorption at low pH values.



Figure 2. (a) OA removal from solution for $[OA]_{tot} = 10 \ \mu\text{M}$ on 50 m² L⁻¹ goethite in 480 mM NaCl versus pHc at different Na₂SO₄ concentrations and (b) Sulfate removal for $[Na_2SO_4] = 1 \ \text{mM}$ and $[OA]_{tot} = 10 \ \mu\text{M}$ at two NaCl concentrations on 50 m² L⁻¹ goethite versus pHc after 24h reaction time. Lines are modeling results.

3.4 Effect of Cu²⁺ on OA binding to goethite

The equilibrium constant of the formation of the aqueous OACu⁺ complex has been reported to be much larger than that of OAMg⁺ complex at I = 0.1 M:¹⁰

$$OA^{-} + Cu^{2+} \rightleftharpoons OACu^{+}; \quad \log K_{OA-Cu}$$

$$\tag{9}$$

By using the WATEQ Debye-Hückel equation and setting $b_{OACu^+} = b_{OAMg^+} = 0.5$, log K_{OA-Cu}

was found equal to 6.61. Figure 3a shows that copper adsorption to goethite increases with pH, for the three tested concentrations (10, 50 and 100 μ M). Based on previous report,³⁷ four equations can be proposed to describe the binding of Cu²⁺ to goethite:

$$2 \equiv \text{FeOH}^{-0.5} + \text{Cu}^{2+} \rightleftharpoons (\equiv \text{FeOH})_2^{-1+\Delta z_0} \text{Cu}^{\Delta z_1}; \quad \log K_{(\equiv \text{FeOH})_2 \text{Cu}}$$
(10)

$$2 \equiv \text{FeOH}^{-0.5} + \text{Cu}^{2+} + \text{H}_2 \text{O} \rightleftharpoons (\equiv \text{FeOH})_2^{-1+\Delta z_0} \text{Cu}(\text{OH})^{\Delta z_{1-1}} + \text{H}^+; \quad \log K_{(\equiv \text{FeOH})_2 \text{Cu}(\text{OH})}$$
(11)

$$2 \equiv \text{FeOH}^{-0.5} + 2\text{Cu}^{2+} + 2\text{H}_2 \text{O} \rightleftharpoons (\equiv \text{FeOH})_2^{-1+\Delta z_0} \text{Cu}_2(\text{OH})_2^{\Delta z_1} + 2\text{H}^+; \log K_{(\equiv \text{FeOH})_2 \text{Cu}_2(\text{OH})_2}$$
(12)

$$2 \equiv \text{FeOH}^{-0.5} + 2\text{Cu}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons (\equiv \text{FeOH})_2^{-1 + \Delta z0} \text{Cu}_2(\text{OH})_3^{\Delta z1 - 1} + 3\text{H}^+; \log K_{(\equiv \text{FeOH})_2\text{Cu}_2(\text{OH})_3}$$
(13)

Using this model, our Cu^{2+} uptake data in 480 mM NaCl can be well predicted by only adjusting log K(=FeOH)₂Cu(OH), while keeping all other parameters equal to literature values.³¹

The presence of Cu^{2+} significantly enhanced OA adsorption at all pH values, whereas OA adsorption increased with increasing Cu^{2+} concentration (Figure 3b). As previously reported, ^{14,37–40} the formation of a surface- Cu^{2+} -organic ligand ternary complex may explain the enhancement in OA adsorption. Indeed, Cu^{2+} may act as a bridge ion to form a six-member ring with the carboxylic and carbonyl groups.³⁸ Accordingly, accounting for a ternary goethite- Cu^{2+} -OA complex (eq.14) allows an accurate prediction of OA binding to goethite in the presence of Cu^{2+} (Figure 3b):

 $2 \equiv \text{FeOH}^{-0.5} + \text{Cu}^{2+} + \text{OA}^{-} \rightleftharpoons (\equiv \text{FeOH})_2^{-1 + \Delta z0} \text{CuOA}^{\Delta z1}; \log K_{(\equiv \text{FeOH})_2 \text{CuOA}}$ (14)

This phenomenon is favored by (i) the great $OA-Cu^+$ aqueous complexation and (ii) the overlapping in pH-edges of OA and $Cu^{2+,41}$ Note that all other parameters were kept constant while fitting log K(=FeOH)₂CuOA.



Figure 3. (a) Cu^{2+} and (b) OA removal from solutions for $[OA]_{tot} = 10 \ \mu\text{M}$ on 50 m² L⁻¹ goethite in 480 mM NaCl versus pHc at different CuCl₂ concentrations after 24h reaction time. Lines are modeling results.

3.5 OA-goethite binding in presence of Mg²⁺, SO₄²⁻ and Cu²⁺

As shown in Figure 4a, OA-goethite pH-edge in presence of mixture of Mg^{2+} and SO_4^{2-} exhibits the previously observed features, i.e. Mg^{2+} decreased OA adsorption and shifted sorption edge to lower pH, while SO_4^{2-} decreased only significantly OA adsorption at low pH values. Interestingly, our SCM has well predicted the experimental data without further parameter adjustment.

As expected, the presence of 10 μ M Cu²⁺ increased OA-goethite binding even in presence of 50 mM Mg²⁺ and/or 29 mM SO₄²⁻ (Figure 4b). However, the model overestimated OA (Figure S2a) and underestimated Cu²⁺ (Figure S2b) adsorption to goethite at low pH, respectively. As an attempt to improve the description of our experimental data, we include a ternary surface goethite-Cu-sulfate complex in the present model, as previously suggested:⁴²

$$2 \equiv \text{FeOH}^{-0.5} + \text{Cu}^{2+} + \text{SO}_4^{2-} \rightleftharpoons (\equiv \text{FeOH})_2^{-1+\Delta z0} \text{CuSO}_4^{\Delta z1}; \quad \log \text{K}_{(\equiv \text{FeOH})_2 \text{CuSO}_4}$$
(15)

We assumed Cu^{2+} charge to be distributed at the 0 plane and SO_4^{2-} charge distribution is similar to the MB complex in eq. 7 (i.e. -0.5 charge at the 0-plane, -1.5 at the 1-plane). This equation has permitted to enhance Cu-goethite binding and limit the goethite-Cu-OA surface complex formation, thereby considerably improving the prediction of both Cu^{2+} (Figure S2c) and OA adsorption to goethite (Figure 4b).

It is worth noting that no further parameter adjustment was made in the following sections, which aim at testing the capability of the present model to predict OA adsorption and transport under conditions closer to marine environments.



Figure 4. OA removal from solutions for $[OA]_{tot} = 10 \ \mu\text{M}$ on 50 m² L⁻¹ goethite in 480 mM NaCl versus pHc at 50 mM MgCl₂ and /or 29 mM Na₂SO₄ after 24h reaction time in presence of (a) 0 μ M CuCl₂ (b) 10 μ M CuCl₂. Lines are modeling results. Same legends for (a) and (b).

3.6 OA adsorption in synthetic seawater

OA adsorption edges in synthetic seawater are similar to that obtained in presence of 50 mM MgCl₂ and 29 mM Na₂SO₄ at 480 mM NaCl (Figure S3), suggesting that Mg²⁺ and SO₄²⁻ are the most influencing ions in synthetic seawater. Other ions such as F, Br⁻, BO₃³⁻ and Ca²⁺ have no significant impact on OA adsorption due to their lower concentrations in synthetic seawater. When the aqueous complexation of Ca²⁺ and OA:¹⁰

$$OA^{-} + Ca^{2+} \rightleftharpoons OACa^{+}; \quad \log K_{OA-Ca}$$
 (16)

and surface complexation of Ca^{2+} to goethite²⁷ and F⁻ to goethite⁴³ are introduced in the present model (see more details in Table 1), only a slight difference in the predicted OA-goethite binding is observed, as compared to that simulated in presence of only Mg²⁺ and SO₄²⁻ (Figure S3).

The presence of Cu^{2+} in synthetic seawater overrides partially the negative effects of major ions and, thus, increased OA adsorption (Figure 5). Cu^{2+} adsorption to goethite in seawater or in presence of 50 mM MgCl₂ and 29 mM Na₂SO₄ at 480 mM NaCl did not exhibit a significant difference (Figure S4). The model predicted quite well OA and Cu^{2+} adsorption to goethite in seawater without further parameter adjustment (Figure 5 and Figure S4).



Figure 5. OA removal from synthetic seawater for $[OA]_{tot} = 10 \ \mu\text{M}$ on 50 m² L⁻¹goethite versus pHc with or without 10 μ M CuCl₂ after 24h reaction time. Lines are modeling results.

3.7 OA transport under seawater conditions

To assess the OA binding to goethite surfaces under flow-through conditions, dynamic experiments were carried out using goethite-coated sand (GCS) packed column. Column saturation has been made using synthetic seawater to emulate water-saturated marine sediments.

In a first experiment, the column was injected with 10 μ M OA and 10 μ M Cu²⁺ dissolved in synthetic seawater as used in batch experiments (Table S3 without carbonates), at a water velocity of 0.5 mL min⁻¹. The pH of inflow solution was found to be at 7.4 ±0.1, and then slightly increased in the column system (exp 1-0.5 mL/min in Figure 6a). The breakthrough curve (BTC) of OA is sigmoidal in shape and shows a slight tailing. The breakthrough point of OA lies at 5 V/Vp, while total breakthrough occurs at ~18 injected pore volumes (PV). The total adsorbed amount at complete OA breakthrough (~0.03 µmol m⁻²) is close to that expected from the batch experiments (Figure 5). However, the predicted breakthrough using batch-derived parameters overestimated OA sorption in the column system and showed a large retardation (see Figure 6b). Then the experiment was repeated at 0.1 mL/min (exp 1-0.1 mL min⁻¹ in Figure 6a), the breakthrough point of OA lies at 7 V/Vp and total breakthrough occurs at ~13 injected pore volumes (PV). Lower flow rate promoted the retention of OA in the column, moreover, the predicted breakthrough using batch-derived parameters described quite well OA sorption in the column at 0.1 mL/min (see Figure 6b). The fast OA transportation at high flow

rate could possibly be related to the lack of local geochemical equilibrium in the column, as previously observed in numerous reports.^{21,44–47} The steepness of the BTC of OA as compared to that of bromide (i.e. the BTC of OA is more tilted than that of the tracer) as well as the short tail observed in the BTC of OA suggests that sorption kinetic limitations might take place in the column. To test this possibility, an additional flowthrough experiment was performed at a lower flow rate (0.1 mL min⁻¹) using the same conditions of exp 1 (i.e., 10 μ M OA, 10 μ M Cu²⁺, pH_{in} 7.4 ± 0.1) (Figure 6a). The experimental breakthrough curve becomes more sigmoidal in shape at 0.1 mL min⁻¹ and shows no extended tailing. A higher residence time promotes more OA retention in the column and pushes the breakthrough point to ~7 injected pore volumes (PV) compared to ~3 PV at 0.5 mL min⁻¹, proving that the sorption equilibrium was not reached within the time scale of the column experiment. Interestingly, very good agreement between the experimental and calculated breakthrough curves is observed at 0.1 mL min⁻¹ (Figure 6b).

In a second experiment, 10 μ M OA and 10 μ M Cu²⁺ dissolved in synthetic seawater containing 2.3 mM of NaHCO₃ (full composition displayed in Table S3), closer to the real seawater at pH 8.2,²⁰ was injected at 0.5 mL/min. Due to the higher pH value (Figure 6a), lower adsorption and faster breakthrough were obtained, which is in agreement with the batch data. The breakthrough point of OA lies at 1.5 V/Vp, while total breakthrough occurs at ~4 injected PV. The model using batch-derived parameters can predict quite well the breakthrough curve of OA (Figure 6b). Carbonate-goethite binding was accounted using parameters derived by Rahnemaie et al.⁴⁸ (Figure S5). Since the adsorption extent is relatively low at seawater-like conditions, sorption kinetic limitations did not significantly affect the simulation results. This data confirm that transport modeling using hydrodynamic parameters can be successfully used to predict adsorption of quinolone antibiotics onto goethite under salt water conditions and at two environmentally relevant pH values (7.4 and 8.2).



Figure 6. (a) Experimental breakthrough curves of OA (solid symbols) and pH (empty symbols) at two inflow conditions. exp 1: injection of 10 μ M OA and 10 μ M Cu²⁺ in synthetic seawater as in batch experiments. exp 2: injection of 10 μ M OA and 10 μ M Cu²⁺ in synthetic seawater containing carbonates as for the real seawater (see Table S3) (b) Calculated BTC of OA.

Table 1. Sur	face Comp	lexation Model
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Aqueous solutions	log K		b _i		ref.
$OAH_{(s)} \rightleftharpoons OAH_{(aq)}$	-5.06		0		8
$OA^{-} + H^{+} \rightleftharpoons OAH$	6.92		0		8
$OA^{-} + Mg^{+2} \rightleftharpoons OAMg^{+}$	3.51		0.5±0.1		10
$OA^{-} + Cu^{+2} \rightleftharpoons OACu^{+}$	6.61		$0.5(b_{OAMg^+})$		10
$OA^{-} + Ca^{+2} \rightleftharpoons OACa^{+}$	2.61		$0.5(b_{OAMg^+})$		10
Surface reactions	log K	Δz_0	Δz_1	Δz_2	
$\equiv Fe_{3}O^{-0.5} + H^{+} \rightleftharpoons \equiv Fe_{3}OH^{+0.5}$	9.1	+1	0	0	8
$\equiv Fe_3O^{-0.5} + H^+ + CI^- \rightleftharpoons \equiv Fe_3OH_2^{+0.5}CI^-$	8.1	+1	0	-1	8
$\equiv Fe_3O^{-0.5} + Na^+ \rightleftharpoons \equiv Fe_3OH^{-0.5}Na^+$	-1	0	0	+1	8
$\equiv \text{FeOH}^{-0.5} + \text{H}^+ \rightleftharpoons \equiv \text{FeOH}_2^{+0.5}$	9.1	+1	0	0	8
$\equiv FeOH^{-0.5} + H^+ + CI^- \rightleftharpoons \equiv FeOH_2^{+0.5}CI^-$	8.1	+1	0	-1	8
$\equiv FeOH^{-0.5} + Na^{+} \rightleftharpoons \equiv FeOH^{-0.5} Na^{+}$	-1	0	0	+1	8
$2 \text{ H}^+ + 2 \equiv \text{FeOH}^{-0.5} + \text{OA}^- \rightleftharpoons (\equiv \text{Fe})_2(\text{OA})^0 + 2 \text{ H}_2\text{O}$	20.6±0.1	+1	0	0	8
$2 \text{ H}^+ + 2 \equiv \text{FeOH}^{-0.5} + \text{OA}^- \rightleftharpoons (\equiv \text{FeOH}_2)_2^{+}\text{OA}^-$	20.6±0.1	+1.6	-0.6	0	8
$2 \equiv FeOH^{-0.5} + Mg^{+2} \rightleftharpoons (\equiv FeOH)_2Mg^+$	4.89	+0.71	+1.29	0	27
$2 \equiv FeOH^{-0.5} + Mg^{+2} + H_2O \rightleftharpoons (\equiv FeOH)_2MgOH + H^+$	-6.44	+0.71	+0.29	0	27
\equiv FeOH ^{-0.5} + Ca ⁺² $\rightleftharpoons \equiv$ FeOHCa ^{+1.5}	2.85	0	+2	0	27
\equiv Fe ₃ O ^{-0.5} + Ca ⁺² $\rightleftharpoons \equiv$ Fe ₃ OCa ^{+1.5}	2.85	0	+2	0	27
\equiv FeOH ^{-0.5} + Ca ⁺² $\rightleftharpoons \equiv$ FeOHCa ^{+1.5}	3.69	+0.32	+1.68	0	27
$\equiv \text{FeOH}^{-0.5} + \text{Ca}^{+2} + \text{H}_2\text{O} \rightleftharpoons \equiv \text{FeOHCaOH}^{+1.5} + \text{H}^+$	-9.17	+0.32	+0.68	0	27
H^+ + ≡FeOH ^{-0.5} + SO ₄ ⁻² \rightleftharpoons (≡Fe) (SO ₄) ^{1.5-} + H_2O	8.0±0.2*(9.37)	+0.5	-1.5	0	36
H^{+} + ≡FeO $\mathrm{H}^{-0.5}$ + SO ₄ ⁻² \rightleftharpoons (≡Fe) (SO ₄) ^{1.5-} $\mathrm{H}_2\mathrm{O}$	9.7±0.2*(11.06)_	+1	-1.84	-0.16	36
$2 \equiv FeOH^{-0.5} + Cu^{+2} \rightleftharpoons (\equiv FeOH)_2Cu^+$	9.18	+0.84	+1.16	0	37
$2 \equiv FeOH^{-0.5} + Cu^{+2} + H_2O \rightleftharpoons (\equiv FeOH)_2CuOH + H^+$	4.6±0.1*(3.6)	+0.84	+0.16	0	37
$2 \equiv FeOH^{-0.5} + 2 Cu^{+2} + 2 H_2O \rightleftharpoons (\equiv FeOH)_2Cu_2(OH)_2^+ + 2 H^+$	3.65	+0.84	+1.16	0	37
$2 \equiv FeOH^{-0.5} + 2 Cu^{+2} + 3 H_2O \rightleftharpoons (\equiv FeOH)_2Cu_2(OH)_3 + 3 H^+$	-3.1	+0.84	+0.16	0	37
$2 \equiv FeOH^{-0.5} + OA^{-} + Cu^{+2} \rightleftharpoons (\equiv FeOH)_2CuOA$	18±0.1	+1.3	-0.3	0	P.W.
$2 \equiv \text{FeOH}^{-0.5} + \text{Cu}^{+2} + \text{SO}_4^{-2} \rightleftharpoons (\equiv \text{FeOH})_2 \text{CuSO}_4^{-1}$	12.6±0.2	+1.5	-1.5	0	P.W.
$\equiv FeOH^{-0.5} + H^+ + F^- \rightleftharpoons \equiv FeF^{-0.5} + H_2O$	9.6	+0.4	-0.4	0	43
2 H ⁺ + 2 ≡FeOH ^{-0.5} + CO ₃ ⁻² \rightleftharpoons (≡Fe) ₂ (CO ₃) ⁻¹ + 2 H ₂ O	22.01	+0.62	-0.62	0	48
2 H ⁺ + 2 ≡FeOH ^{-0.5} + CO ₃ ⁻² +Na ⁺ \rightleftharpoons (≡Fe) ₂ (CO ₃ Na) ⁰ + 2 H ₂ O	22.03	+0.62	+0.38	0	48
$H^+ + \equiv FeOH^{-0.5} + CO_3^{-2} \rightleftharpoons \equiv FeOH_2CO_3^{-1.5}$	10.22	+1	-2	0	48
$\mathrm{H}^{+} + \equiv \mathrm{Fe_3O^{-0.5}} + \mathrm{CO_3^{-2}} \rightleftharpoons \equiv \mathrm{Fe_3OHCO_3^{-1.5}}$	10.22	+1	-2	0	48

*adjusted from the original work. Log K values are given at I = 0. Parameter "b_i" is used in the

WATEQ Debye-Hückel equation. The original constants from literature are in the brackets.

4 Environmental Implications

We have notably demonstrated that TPM can be successfully used to predict adsorption of quinolone antibiotics onto goethite over a large range of environmentally relevant conditions in seawater. In addition, the mobility of OA in seawater can be well predicted through coupling aqueous transport and sorption parameters obtained under static conditions. This modeling approach allowed a quantification of the effects of different ions naturally present in seawater on OA retention. Although SO_4^{2-} is known as a strong competitor for anions, its effect on OA-goethite binding at seawater relevant pH was found to be almost negligible. Other less abundant ions such as F⁻, Br⁻, BO₃⁻³⁻ and Ca²⁺ did not exhibit a significant impact. However, at seawater relevant concentrations, Mg²⁺ was found to strongly decrease OA-goethite binding via the formation of aqueous complex with OA. Furthermore, trace metals (e.g. Cu²⁺ used here as a model metal) naturally occurring in seawater could strongly increase OA binding by forming a ternary metal-ligand surface complex. It is worth noting that the presence of natural organic matter in marine and/or estuary ecosystems could also alter the binding mechanism of quinolones onto minerals and then their mobility in marine ecosystems. This last point stresses the need for a more detailed study to assess the application of surface complexation model (SCM) in real seawater containing natural organic matter. These findings may have strong implications in the prediction of transport of quinolones antibiotics, and thus assessment of ecological impacts of aquaculture induced pollution in marine systems.

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Supporting information

Adsorption of Quinolone Antibiotics to Goethite under Seawater Conditions:

Application of a Surface Complexation Model

Surface complexation modeling

PHREEQC includes the three plane model (TPM), where charges of the adsorbates can be distributed between the 0-, 1- and 2- planes. The solution-side part of the interface is described according to the Gouy-Chapman equation. The total (Stern) capacitance of the oxide/water interface is split into the capacitances of the charge-free layers in between the 0- and 1-planes:

 $C_s^{-1} = C_1^{-1} + C_2^{-1}$

For goethite, $C_1 = 2.3 \text{ F/m}^2$ and $C_2 = 1.07 \text{ F/m}^2$ ($C_s = 0.73 \text{ F/m}^2$).

The multisite complexation (MUSIC) model takes into account the crystallographic distribution of surface sites on the dominant crystal planes of particles. Synthetic goethite exhibited a plane distribution of 27% (001) and 63% (101). Singly- (\equiv FeOH^{-0.5}), doubly- (\equiv Fe₂OH), and two distinct types of triply- (\equiv Fe₃O₁^{-0.5} and \equiv Fe₃O₁₁^{-0.5} with high and low affinity for H⁺, respectively) coordinated sites are present on both crystal planes of the goethite particles. Sites densities for the (001) and (101) planes are, respectively, 3.34 and 3.03 sites nm⁻² for \equiv FeOH^{-0.5}, \equiv Fe₂OH and \equiv Fe₃O₁₁^{-0.5}; 6.68 and 6.06 sites nm⁻² for \equiv Fe₃O₁^{-0.5}. Because \equiv Fe₂OH groups remain neutral and \equiv Fe₃O₁₁^{-0.5} ones remain negatively charged at pH 2 to 11, their contributions from the multisite approach predictions can be ignored. This leads to the 1-pK approximation. Moreover, the (001) and (101) planes show a similar reactivity for H⁺ and mean site densities may be considered. To sum up, only singly- (\equiv FeOH^{-0.5}; 3.12 sites nm⁻²) and triply- (\equiv Fe₃O₁^{-0.5}; 3.12 sites nm⁻²) coordinated sites are considered and they have the same protonation constant. The (021) plane (10% of the surface area) is characterized by alternating rows of singly and doubly coordinated surface groups. The site density of each type of group on this (021) plane is about 7.4 sites nm⁻², but the doubly coordinated groups can be neglected.

Experiments [*]	NaCl	Na ₂ SO ₄	MgCl ₂	CuCl ₂	$\mathbf{O}^{\mathbf{A}}$
	(mM)	(mM)	(mM)	(µM)	UA
	480	-	0	-	3~5 mg
Ι	480	-	10	-	3~5 mg
	480	-	50	-	3~5 mg
	480	-	0	-	10 µM
Π	480	-	10	-	10 µM
	480	-	50	-	10 µM
	480	1	-	-	10 µM
TT	480	10	-	-	10 µM
111	480	29		-	10 µM
	10	1	-	-	10 µM
	480	-	-	10	10 µM
IV	480	-	-	50	10 µM
	480	-	-	100	10 µM
V	480	29	50	-	10 µM
VI	480	29	50	10	10 µM

Table S1. Composition of batch experiments with NaCl

*Experiment I studies the effect of Mg^{2+} on OA solubility. Experiments II, III and IV study the effects of Mg^{2+} , SO_4^{2-} and Cu^{2+} on OA adsorption onto goethite. Experiments V and VI study the effects (and combined effects) of Mg^{2+} , SO_4^{2-} and/or Cu^{2+} on OA adsorption

Desorption tests

According to the pH edge of OA, adsorption of OA was negligible at pH = 10. Therefore, desorption test was conducted by adjusting pH to 11 after the system reached equilibrium, and then stirred for around 2 h. As can be seen from Table S2, an average recovery of $100 \pm 2\%$ for OA in various systems was obtained.

system	рН			
	4	6	8	
OA + 480 mM NaCl	99.99	100.90	101.99	
OA + 29 mM SO ₄ ²⁻ + 480 mM NaCl	102.42	103.22	98.43	
OA + 50 mM Mg ²⁺ + 480 mM NaCl	99.49	100.85	100.83	
$OA + 100 \ \mu M \ Cu^{2+} + 480 \ mM \ NaCl$	97.41	100.81	95.43	
$OA + 10 \ \mu M \ Cu^{2+} + synthetic seawater$	101.71	101.28	99.81	

Table S2. Desorption data (%) of OA in various systems

Salt	Concentration	Concentration	
	(g /Kg)	(mM)	
NaCl	23.926	409.392	
Na_2SO_4	4.008	28.217	
KCl	0.677	9.081	
KBr	0.098	0.823	
H ₃ BO ₃	0.026	0.420	
NaF	0.003	0.071	
MgCl ₂	5.027	52.798	
$CaCl_2$	1.141	10.281	
NaHCO ₃	0.196	2.333	

Table S3. Compositions and concentrations of major elements in synthetic seawater¹

¹Kester, D. R.; Duedall, I. W.; Connors, D. N.; Pytkowicz, R. M. Preparation of Artificial Seawater. Limnol. Oceanogr. 1967, 12 (1), 176–179.



Figure S1(a) OA solubility and (b) OA removal from solution for $[OA]_{tot} = 10 \ \mu\text{M}$ on 50 m² L⁻¹ goethite in 480 mM NaCl versus pHc = $-\log [H^+]$ after 24 h reaction time. Lines are modeling results. MB and HB refer to metal- and hydrogen-bonded OA, respectively.



Figure S2 (a) OA and (b) (c) Cu^{2+} removal from solutions for $[OA]_{tot} = 10 \ \mu\text{M}$, $[Cu^{2+}] = 10 \ \mu\text{M}$ on 50 m² L⁻¹ goethite in 480 mM NaCl versus pHc at 29 mM Na₂SO₄ and 50 mM MgCl₂ after 24h reaction time. (b) Lines are modeling results without goethite-Cu-sulfate ternary complex. (c) Lines are modeling results with goethite-Cu-sulfate ternary complex.



Figure S3. OA removal from synthetic seawater and OA removal in presence of 50 mM MgCl₂ and 29 mM Na₂SO₄ for $[OA]_{tot} = 10 \ \mu\text{M}$ on 50 m² L⁻¹ goethite in 480 mM NaCl versus pHc after 24h reaction time. Lines are modeling results.



Figure S4. Cu^{2+} removal from synthetic seawater and Cu^{2+} removal from 480 mM NaCl with 50 mM MgCl₂ and 29 mM Na₂SO₄ for [OA]_{tot} = 10 μ M, [Cu²⁺]= 10 μ M on 50 m² L⁻¹ goethite versus pHc after 24h reaction time. Lines are modeling results.



Figure S5. The model simulation of carbonate equilibrium concentrations versus pH at different added total carbonate levels. The data are from Rasoul Rahnemaie et al. *J. Colloid Interface Sci.* 297, 379–388 (2006).



Summary

This part of the thesis studied interactions of goethite with ubiquitous ligands, NOM, silicate and phosphate, and their impacts on the quinolones adsorption and transport. The section is composed of two articles. In the first article, the adsorption of NOM on goethite and carbon loading effects on the surface hydrophobicity were studied; in the second article, the fractionation of NOM and its effects of on nalidixic acid (NA) transport were studied under flow-through conditions. The impacts of inorganic ions, silicate and phosphate on NA transport was also studied in column. Main findings are reported here and readers should refer to the articles for details. Following are the titles of these articles presented in this section:

- Water Vapor Binding on Organic Matter-Coated Minerals
- Natural Organic Matter Controls on Quinolone Antibiotic Retention and Transport

NOM is a polydisperse mixture of organic molecules with supramolecular structure. It can interact directly with both minerals and quinolones, thus may pose different effects on the adsorption of quinolones onto minerals. In addition, different fractions of NOM have different affinity and adsorption kinetics to mineral surfaces and NOM may undergo fractionation after interacting with minerals. The molecular fractionation of NOM and its effects on quinolones transport under flow-through conditions have rarely been studied. This study used leonardite humic acid (LHA) as a representative hydrophilic NOM, goethite as model mineral and nalidixic acid (NA) as representative quinolones. The interactions of LHA with goethite and the effects of LHA on the adsorption and transport of NA under flow-through conditions were studied.

In the first part of this section (Figure 1), the binding mechanisms of LHA onto goethite and the effects of LHA loading on the hydrophobicity of goethite surface were studied. Different amounts of LHA and goethite were mixed to achieve C/Fe (w/w) ratios in the 0.005-5 range. After equilibrated at pH 5 for 48h, the suspension was centrifuged, and the wet pastes were analyzed by FTIR, and the supernatants were filtered and analyzed for soluble carbon concentrations. The adsorption isotherm of LHA characterized as an adsorption regime at low LHA concentrations, and a precipitation-like regime at high LHA. The interaction mechanism of LHA-goethite can be interpreted by FTIR spectroscopy. At low LHA loading (C/Fe < 0.1), the intensity of hydroxo groups of goethite surface decreased and

LHA functional groups increased with LHA loading, indicating the ligand exchange and hydrogen bonding mechanisms. The goethite surface was already covered in LHA at total C/Fe > 0.05. Further increase in LHA loading triggered LHA- LHA interactions through van der Waals hydrophobic interactions and caused the precipitation of LHA. The effects of LHA loadings on goethite surface hydrophobicity can be revealed by its water binding behavior. Water binding on initially dry LHA-goethite assemblages was monitored using FTIR spectroscopy, and gravimetry by quartz crystal microbalance (QCM). The water loadings of different samples increased in the order: low LHA loading (C/Fe = 0.005-0.1) < goethite< high LHA loading (C/Fe = 1.25-5) < LHA. The LHA-loading dependence on water binding can be explained in the following manner. At low LHA loadings (C/Fe = 0.005-0.1), a greater proportion of LHA moieties involved in ligand exchange or hydrogen bonding to goethite surface. This results in potentially important configurational changes in LHA structure, exposing hydrophobic portions of the molecules on the goethite surface. While at high loadings, a smaller fraction of the moieties is dedicated to binding with goethite, leaving excess LHA reacting with water in a similar manner to pure LHA. Therefore, low loadings of LHA increased surface hydrophobicity and high loading of LHA decreased surface hydrophobicity.



Figure 1. Graphic illustration of water vapor binding on organic matter-coated minerals

In the second part of this section (Figure 2), the impacts of LHA on the sorption and transport of NA were investigated over a wide concentration range of LHA (0 - 50 mg/L). LHA underwent fractionations during its interactions with goethite under flow-through conditions, with aromatics and

lower Mw fractions preferentially adsorbed, and replaced by higher Mw components of LHA. The presence of LHA alters NA adsorption mechanism and kinetics. When LHA and NA were simultaneously injected to clean GCS, NA and aromatics compounds of LHA competed for sorption sites, and NA could be also adsorbed onto LHA by nonspecific interactions; When NA was injected to the LHA preloaded GCS, NA transport was governed by van der Waals-type hydrophobic interactions between NA and preloaded LHA.



Figure 2. Graphic illustration of the influence of LHA on NA transport

In addition to NOM, we have also tested the impacts of other naturally occurring ligands, like inorganic ligands, phosphate and silicates. We have got interesting results. However, due to the lack of time, we cannot complete the experimentation and modeling, we choose not to show the data in the present thesis.

Results from this study improve our understanding on the adsorption and transportation of quinolones in the presence of naturally occurring ligands, and may have strong implications for assessment of the fate of quinolones in nature.

Chapter 4 Water vapor deposition on organic matter-coated minerals
Abstract

Atmospheric water vapor binding to soils is a key process driving water availability in unsaturated terrestrial environments. Using a representative hydrophilic iron oxyhydroxide, this study highlights key mechanisms through which water vapor (i) adsorbs and (ii) condenses at mineral surfaces coated with Leonardite humic acid (LHA). Microgravimetry and vibrational spectroscopy showed that liquid-like water forms in the three-dimensional array of mineralbound LHA when present at total C/Fe ratios exceeding ~73 mg C per g Fe (26 C atoms/nm²). Below these loadings, minerals become even less hydrophilic than in the absence of LHA. This lowering in hydrophilicity is caused by the complexation of LHA water-binding sites to mineral surfaces, and possibly by conformational changes in LHA structure removing available condensation environments for water. An empirical relationship predicting the dependence of water adsorption densities on LHA loadings was developed from these results. Together with the molecular-level description provided in this work, this relationship should guide efforts in predicting water availability, and thereby occurrences of water-driven geochemical processes in terrestrial environments.

1 Introduction

Soil hydrophobicity is a key parameter that describes the extent to which water-based geochemical reactions can proceed, and can be used in environmental monitoring and soil quality assessment.¹ This concept is a manifestation of the ability to which water vapor flowing through unsaturated soils (e.g., vadose zones) can form thin water films and droplets at and between mineral grains. Knowledge of the propensity of formation of these aqueous environments is consequently essential for predicting water availability, as well as geochemical aqueous reactions taking place within the microscopic solvation environments of water films and droplets.

Understanding the fate of water deposition in soils also requires knowledge of the intervening roles of natural organic matter (NOM). Of common occurrence in soils,^{2–4} NOM strongly reacts with mineral surfaces via chemical and/or physical adsorption reactions involving their hydrophilic functional groups (*e.g.* carboxylates, phenolates, amines), as well as by van der Waals hydrophobic interactions, and cation bridging.^{5–9} These organic coatings have a strong propensity to alter the hydrophilicity of mineral surfaces, the extent to which could be determined by the type and concentration of functional groups exposed at the mineral-organic/water vapor interface. Mineral-bound NOM can also alter surface properties of minerals,⁵ and have direct consequences on the mobility and fate of other contaminants, such as organic contaminants and heavy metals,^{10–14} through an interconnected network of water films/droplets localized on organic-coated mineral grains.

Although the concept of soil mineral hydrophobicity is well recognized and its influence on organic compound transport studied,^{1,11,15} its underlying mechanisms remain misunderstood. Still, strong correlations between soil hydrophobicity and soil organic matter¹⁶ or mineral-sorbed humic substances have been identified.¹⁵ Building upon our recent work on water vapor deposition on minerals^{17–22} and the thermochemical stability of NOM mineral coatings,²⁰ this work uses microgravimetry and vibrational spectroscopy to explain the strong NOM-loading dependence on the deposition of water vapor on minerals. This was achieved by focusing on a model system consisting of Leonardite humic acid (LHA), a representative hydrophilic NOM, and goethite (α -FeOOH), a mineral with key roles in NOM and contaminant mobility in terrestrial and aquatic environments.^{23–26}

2 Materials and methods

2.1 Materials

Goethite was synthesized by hydrothermal conversion of a freshly precipitated ferric oxyhydroxide at 60 °C for 72 h.^{27,28} The starting material was made by drop-wise (1 mL/min) addition of 500 mL of a 0.5 M ferric nitrate solution (Fe(NO₃)₃·9H₂O) to a continuously stirred 400 mL of 2.5 M sodium hydroxide solution in a N₂(g) atmosphere. The resulting goethite was dialyzed (Spectra/Por membrane 2) against ultrapure water. The water was changed every day until its conductivity was lower than 1 μ S/cm. The suspensions were stored in polypropylene containers at 4 °C for further use. Goethite purity was confirmed by X-ray diffraction (XRD) with a PANalytical X'Pert Pro X-ray diffractometer with Cu Ka radiation (c = 1.5406 Å) at 20 range = 10–65° (Figure S1).The B.E.T. specific surface area of the synthetic goethite (89.6 m²/g) was determined on a Micromeritics AutoPore IV 9500 surface area analyzer, and was calculated from 90-point adsorption/desorption N₂(g) isotherms before degassing overnight at 105°C under a stream of dry N₂(g).

Leonardite Humic Acid Standard (1S104H) was purchased from the International Humic Substance Society. A LHA stock solution (2 g/ L, 1276 mg C/L) was prepared by dissolving 2 g LHA in 100 mL of 1 M NaOH, then diluted to 1 L with ultrapure water.

2.2 NOM batch adsorption experiments

All NOM adsorption experiments were conducted in the absence of background electrolyte ions, and under an atmosphere of humidified $N_2(g)$. This minimized any competitive adsorption reactions that would occur under dry conditions.

A 320 μ L aliquot of a goethite (24.80 g/L, specific surface area: 89.6 m²/g) aqueous suspension was mixed with 19.6 mL diluted LHA solutions (1.276 to 1276 mg C/L) in 50 mL polyethylene centrifuge tubes to achieve C/Fe (w/w) ratios in the 0.005–5 range. The suspensions were then adjusted to pH 5.0 with a pH meter by addition of small volumes of 1.0 M HCl or NaOH and equilibrated on an end-to-end rotator at 25 ± 1 °C for 48 h. Next, the suspension was centrifuged at ~2000 g for 15 min, the supernatants were filtered (0.2 µm) and the final soluble C concentrations were analyzed using a TOC analyzer (Shimadzu TOC-VCSH). The centrifuged wet pastes were

analyzed by FTIR as described in Section 2.3.

2.3 Water Vapor Deposition by Dynamic Vapor Sorption

The Dynamic Vapor Sorption (DVS) technique was used to trigger water vapor deposition on initially dry LHA-goethite assemblages. Water deposition was monitored in two sets of independent experiments using (1) Fourier Transform InfraRed (FTIR) spectroscopy, and (2) gravimetry by Quartz Crystal Microbalance (QCM).

For both experiments, water vapor was generated by mixing humid $N_2(g)$ and dry $N_2(g)$ in different proportions using mass flow controllers (MKS, 179A). The total flow rate was always 200 standard cubic centimeters per minute (sccm), and water vapor pressures were continuously measured using a Non Dispersible InfraRed device (LI-7000, Licor Inc). Preliminary FTIR and QCM experiments demonstrated that a 30 min equilibration period under a constant water vapor pressure was well sufficient to achieve equilibrium with respect to water vapor deposition on the LHA-goethite assemblages.

2.3.1 FTIR

Centrifuged wet pastes were transferred onto a diamond window of an Attenuated Total Reflectance (ATR) cell (Golden Gate, single-bounce) and dried in the analytical chamber of a FTIR spectrometer under a flow of 200 sccm dry $N_2(g)$. FTIR spectra were collected during the drying period until all O–H stretching and bending modes of free water disappeared. Water vapor deposition experiments were then carried out on the resulting dry mineral film in a closed-loop flow-through reaction cell, and exposed to water vapor pressures from 0 to 19 Torr (80% R.H.) at 25 ± 1 °C.

FTIR spectra were continuously collected in-situ with a Bruker Vertex 70/V FTIR spectrometer, equipped with a DLaTGS detector. All spectra were collected in the $600 - 4000 \text{ cm}^{-1}$ range at a resolution of 4.0 cm⁻¹ and at a forward/reverse scanning rate of 10 Hz. Each spectrum was an average of 250 scans. The Blackman-Harris 3- term apodization function was used to correct phase resolution.

2.3.2 QCM

A gold-coated quartz resonator operating at 10 MHz was used for QCM measurements (eQCM 10M, Gamry Instruments Inc.). The time-independent serial resonance frequency (f_s) of the quartz resonator exposed to a flow of 200 sccm dry N₂(g) was first measured to obtain the correct baseline

of the empty cell. A dilute aqueous suspension of the LHA-goethite assemblage was pipetted on the gold area of the resonator, then dried under the same flow of $N_2(g)$. The resulting f_s was used to obtain the mass of the dry sample. A DVS experiment was then initiated to expose the sample to water vapor pressures from 0 to 19 Torr.

Changes in frequency (Δf) of the quartz resonator were converted to changes in sample mass (Δm) using the Sauerbrey equation:²⁹

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q \mu_q}} \Delta m \quad (1)$$

In this equation f_0 is the resonant frequency of empty cell, A is the piezoelectrically active crystal area of the gold-coated quartz crystal (0.205 cm²), ρ_q is the density quartz (2.648 g/cm³) and μ_q is shear modulus of quartz (2.947 × 10¹¹ g/cm·s²).

2.3.3 Adsorption/Condensation Modeling

Water adsorption at goethite/LHA surface sites and condensation in (nano)/(micro)pores in samples was modeled using an adaptation of the water condensation model of Do & Do³⁰, which we had previously³¹ shown to adequately predict water uptake in mineral powders:

$$C_{\mu} = S_{o} \frac{\kappa_{f} \sum_{1}^{n=\beta+1} n p_{W}^{n}}{1 + \kappa_{f} \sum_{1}^{n=\beta+1} p_{W}^{n}} + C_{\mu s} \frac{\kappa_{\mu} \sum_{1}^{n=\alpha+1} p_{W}^{n}}{\kappa_{\mu} \sum_{1}^{n=\alpha+1} p_{W}^{n} + \sum_{1}^{n=\alpha+1} p_{W}^{n-1}}$$
(2)

This equation predicts the total water deposition (C_{μ}) as a function of the reduced partial pressure of water ($p_w=p/p_{sat}$; where p_{sat} is the saturation pressure) in terms of the aforementioned *adsorption* (left-hand term) and *condensation* (right-hand term) regimes. Parameters for each regime include water-binding site densities for *adsorption* (S_o) and *condensation* ($C_{\mu s}$) with their respective association constants (K_f , K_{μ}) and hydration numbers (β , α).

The *adsorption term* is a B.E.T.-type equation³² which is however forced to plateau at $p_w \rightarrow 0$ by setting $\beta = 2$. This value denotes that a (hydr)oxo group can be involved in 2 (donating and/or accepting) hydrogen bonds, which is average hydration number that we retrieved in previous molecular modeling of water adsorption on various metal (oxy)hydroxides.³¹ The *condensation* pertains, in turn, to the condensation of water in the nano/micro-porous environments of the mineral-LHA mixture. It is triggered only when a nominal population of water (nano)clusters (e.g., $\alpha = 8$) is exceeded.³⁰ While the data on hand could not be used to unambiguously constrain condensation

parameters of eq. 2, the shape of the modeled curve nonetheless provide the possibility to extract the adsorption term, which is central for understanding the intrinsic affinity of water to LHA-bound goethite. Finally, we also used this equation to decompose the adsorption isotherm of LHA on goethite.

3 Results and discussions

LHA binding at goethite surfaces follows a Type II³³ adsorption isotherm loading (Figure 1), that can be characterized as an adsorption regime at low LHA concentrations, and a precipitation-like regime at high LHA. Maximal adsorption values under the adsorption regime are the equivalent of ~56 C atoms/nm², or ~3.7 times the total crystallographic oxygen site density (~15 sites/nm²).^{27,34,35} From these results, we estimate that the goethite surface should be already covered in LHA at total C/Fe > 0.05. The highest LHA loadings (C/Fe = 5 corresponding to 220 C atoms/nm²) suggest a precipitation-like regime triggered by LHA-LHA interactions, and therefore in the establishment of LHA bulk environments entirely covering the goethite surface.



Figure 1. LHA binding on goethite after equilibration at pH 5. Total C/Fe ratios are expressed in terms of adsorption and precipitated LHA. The model was generated using Eq.2, here adapted for the case of LHA binding and precipitation on goethite.

All water vapor binding on goethite follows Type II^{33} adsorption isotherms (Figures 2a,b), and is strongly affected by LHA loadings. LHA loadings in the C/Fe = 0.005-0.01 range decreased goethite

hydrophilicity, while loadings above this this range increased hydrophilicity. Water uptake of unbound LHA is highest due to its heterogeneous structure and abundant hydrophilic functional groups. As a result, increasing excess LHA loadings promotes water uptake.

These changes can be appreciated further by decomposing these adsorption isotherms in terms of (1) *adsorption* and (2) *condensation* regimes (Figure 2a), using Do & Do³⁰ theory presented in Section 2.3.3. In this framework, *adsorption* pertains to the attachment of water molecules to mineral surface and LHA functional groups via hydrogen bonding, followed by growth in the neighborhood of the adsorption site, very much in the manner described by B.E.T. theory.³² *Condensation*, on the other hand, pertains to water-water interactions leading to growth and coalescence of water (nano)droplets in (nano)/(micro)pores between goethite particles and within the LHA bulk.³¹

Modeling of the water adsorption isotherms reveals first shows that maximal densities achieved under the adsorption regime on LHA-free goethite are equivalent to the total crystallographic O surface density (~15 H₂O/nm²),^{27,34,35} and therefore ~1-1.5 H₂O monolayers. These loadings are however strongly affected by LHA loadings, as shown by the relationship of Figure 2c. This correlation expresses the decreased hydrophilicity of goethite at C/Fe below ~0.24 and of the increased hydrophilicity above these loadings. A mechanistic interpretation of these results can be developed by understanding the nature of organic-mineral interactions and of the hydrogen bonding of water on LHA-coated goethite. This can be gained by following the changes in the availability of the hydrophilic hydroxyl functional groups of the goethite as well as those of LHA (Figure 3), as will be detailed in the following paragraphs.





Figure 2. QCM-derived masses of water deposited on LHA and goethite. (**a**) Typical Type II water adsorption isotherm on pure goethite. (**b**) Adsorption isotherms for pure goethite, LHA and goethite-LHA assemblages, reported as total C/Fe (w/w). (**c**) Relationship between water site density

 $(S_0 \text{ of Eq. } 2)$ and total carbon loading on goethite (C/Fe). Values for pure goethite and LHA are shown for reference.



Figure 3. (a). Schematic representation of crystal habits of goethite (GT) particles under study, obtained from a snapshot of a MD simulation.¹⁸ (b-c) FTIR spectra of LHA-Goethite samples equilibrated at pH 5 then dried under N₂(g). (c) Difference spectra of the 1200-1800 cm⁻¹ region, with contributions from the goethite bulk ($\delta_{OH} + \gamma_{OH} = 1659 \text{ cm}^{-1}$; $\delta'_{OH} = 1794 \text{ cm}^{-1}$) removed (Figure S1 for raw data). Arrows in 1.3 adsorbed C atoms/nm² point to collection of bands.

Changes in the availability of hydrophilic hydroxo groups populating the goethite surface (Figure 3a) can be revealed by vibrational spectroscopy (Figure 3b), a detailed account of which is given in a series of articles from our group.^{17–19,22,36,37} Briefly, the goethite surface is predominantly populated by rows of singly-coordinated –OH, doubly-coordinated μ –OH, and triply-coordinated μ_3 –OH groups (Figure 3). About 50% of these –OH donate a hydrogen bond to a neighboring –OH, while all accept a hydrogen bond from an underlying $\mu_{3,1}$ –OH, as in the goethite bulk.^{17–19,22,36,37} The intensities and positions of O-H stretching bands of –OH groups (3661 cm⁻¹) and of the less reactive μ –OH and $\mu_{3,1}$ –OH groups (3648 cm⁻¹) are especially sensitive indicators of ligand exchange and hydrogen bonding reactions. Variations in the intensities of the triply-coordinated $\mu_{3,1}$ –OH sites (3543 cm⁻¹ and 3491 cm⁻¹) are, in turn, a direct response of the coordination changes in –OH due to the presence of a hydrogen bond between these two groups ($\mu_{3,1}$ –OH...OH–). Finally, we note that while the minor (021) face also exposes - OH and μ -OH groups they are so strongly hydrogen-bonded that they generate no resolvable O-H stretch, as described in Song and Boily.¹⁷

The loss in intensity of these O-H stretching bands in the C/Fe 0-0.1 range confirms the loss of hydrophilic -OH groups via ligand exchanges and/or the loss of the hydrophilic activity of these groups via hydrogen bonding with LHA functional groups.^{25,38-40} These changes correlate with the appearance of LHA functional groups in the range of 1200-1800 cm⁻¹ (Figure 3c), which we interpret as the appearance of a mixture of protonated ($v_{C=O carboxyl} = 1705 \text{ cm}^{-1}$, $v_{C-O-H} = 1261 \text{ cm}^{-1}$) and deprotonated ($v_{COOs} = 1381 \text{ cm}^{-1}$) groups as well as aromatic backbone of LHA ($v_{C=C}$ aromatic = 1600 cm⁻¹). They also reveal that the LHA-reacted goethite surface exposes a mixture of -OH groups and of LHA. At C loadings greater than the crystallographic density of goethite surface oxygens (> 26 C atoms/nm²; C/Fe > 0.1), all intensities of the -OH band are lost due to direct ligand exchange with LHA and a red-shift in the stretching frequency of hydrogen-bonded group to a broad range of values below 3661 cm⁻¹. The O-H spectral signature is then characterized by a blue-shift in the band of $\mu_{3,1}$ -OH from the weakening of its hydrogen bond with -OH, as well as from the appearance of OH groups of sorbed LHA. Additionally, because LHA loadings increased under conditions where all -OH groups have been occupied, LHA binding must have been driven by additional mechanisms such as van der Waals-type hydrophobic bonding. This mechanism could be responsible for the precipitation of LHA at the highest loadings considered in this work (Figure 1).



Figure 4. Baseline-subtracted FTIR spectra of C/Fe = 0.005 exposed to 0-60% R.H. (a) O-H stretching region responding to -OH and μ_{3I} -OH groups. The 3699 cm⁻¹ band is likely from geminal water bound directly to Fe sites, but is outside the scope of this work. (b) The 1200-1900 cm⁻¹ region. This region shows the appearance of liquid-like water through the growth of the bending band of water (v₂). The δ 'OH 1794 cm⁻¹ band is a bending overtone of the goethite bulk, and therefore not affected by water binding.



Figure 5. (**a-b**)Baseline-subtracted FTIR spectra of C/Fe = 5 exposed to 0-60 % R.H. (**c**) FTIR spectra of LHA first equilibrated at pH 5, then exposed to water vapor.

Exposure of water vapor to LHA-coated goethite (Figures 4 & 5) also induced systematic changes in the vibration spectra of goethite and LHA functional groups, and generated bands strongly indicative of the formation of liquid-like water. ^{41,42} While this can first be appreciated by the appearance of the bending (v_2 ; Figure 4b) and of the broad O-H stretching (Figure 5c) bands of water deposited within the three-dimensional framework of LHA (see also Figs S3 & S4), the spectral signature of hydrophilic OH groups provide greater details on water deposition mechanisms.

Samples with the lowest LHA loadings (C/Fe = 0.005) provide insight into the mechanisms of water binding at goethite surfaces exposing a mixture of (i) nonreacted - OH groups and (ii) adjacently bound LHA molecules. While our results (Figure 2) showed that water loadings were lower than on LHA-free goethite, vibration spectra (Figure 4) suggest that water binding mechanisms were not altered by LHA-binding.¹⁸ This can be appreciated in the loss and red-shift of the 3661 cm⁻¹ band of - OH with water loading, as well as in the blueshift of the 3490 cm⁻¹ band of $\mu_{3,1}$ -OH to a triplet at 3512, 3555, and 3582 cm⁻¹, also seen in LHA-free goethite.¹⁸ We note that this triplet results from a weakening of the H-bonding strength between $\mu_{3,1}$ -OH and -OH sites by water through the formation of hydrogen bonding networks of the type: $\mu_{3,1}$ -OH...-OH₂ and/or $\mu_{3,1}$ -OH...-OH₂. As water-binding mechanisms remain unchanged by LHA, lower water loadings are likely to result from the consumption of hydrogen bonding. This could also imply that the intrinsic LHA bulk structure (e.g., intramolecular hydrogen bonding network) has undergone changes that, for example, expose

hydrophobic sites to the outer portion of the macromolecules. This concept can be supported further in the 1200-1800 cm⁻¹ region (Figure 3c) revealing a combination of bands that is not manifested at larger LHA loadings. Previous work²⁰ from our group even showed that these conformational changes could be responsible for increasing the thermal stability of mineral-bound NOM.

This scenario diverges starkly with water binding to samples of high C/Fe loadings which, again, promote greater water loadings than in LHA-free goethite (Figure 2). In this case, the aforementioned triplet (Figure 4a) is readily transformed to a broad singlet, which is characteristic of a broad distribution of hydrogen bonding environments (Figure 5a). We also note that the water vapor pressure dependence of the 1200-1800 cm⁻¹ region is also considerably less sensitive than that of pure LHA (Figure 5). This suggests that LHA functional groups directly bound to goethite remain largely unaffected by hydration. It also implies that while water condensation in the three-dimensional array of pure LHA facilitates high water loadings, LHA binding to goethite limits this intrinsic capability to accommodate water.

To summarize, we can explain the strong LHA-loading dependence on water binding in the following manner. LHA binding at low loadings (1.3-26 C atoms/nm²; C/Fe = 0.005-0.1) involves a greater proportion of LHA moieties for ligand exchange or hydrogen bonding to goethite surfaces. This results in potentially important configurational changes in LHA structure, perhaps even exposing hydrophobic portions of the molecule at the goethite surface. This, with the decrease in accessible hydrophilic groups of the goethite surface, collectively lowers water binding on goethite reacted LHA loadings below ~73 mg C per g Fe. Water affinities become, in turn, substantially larger at high C/Fe loadings because a smaller fraction of the moieties is dedicated to binding with goethite, leaving excess LHA reacting with water in a similar manner to pure LHA.

Finally, we note that while this work on water deposition in NOM-reacted minerals was limited to a model system, we anticipate that its findings should be applicable to a wider range of representative systems. Recognition of the NOM loading dependency on the hygroscopic properties of solid materials in nature should not only be of importance to the study of terrestrial environments but also in the study of atmospheric clouds and rain formation phenomena^{43,44} Additionally, the molecular-scale knowledge of water vapor deposition in organic-mineral assemblages should serve to consolidate our understanding of natural photocatalytic reactions⁴⁵ where co-adsorbed water is an essential ingredient

in photodegradation processes.⁴⁶

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Supporting information

Water vapor deposition on organic matter-coated minerals



Figure S1. XRD pattern of the synthesized goethite



Figure S2. The raw 1200-1800 cm⁻¹ region, with contributions from the goethite bulk ($\delta_{OH} + \gamma_{OH} = 1659 \text{ cm}^{-1}$; $\delta'_{OH} = 1789 \text{ cm}^{-1}$) reveals a mixture of protonated ($v_{C=O \text{ carboxyl}} = 1705 \text{ cm}^{-1}$; $\delta_{C-O-H} = 1261 \text{ cm}^{-1}$) and unprotonated ($v_{C=O} = 1381 \text{ cm}^{-1}$) carboxyl groups of goethite-bound LHA, aromatic backbone of LHA ($v_{C=C \text{ aromatic}} = 1600 \text{ cm}^{-1}$, as well as combination ($\delta_{OH} + \gamma_{OH} = 1659 \text{ cm}^{-1}$) and overtones ($\delta'_{OH} = 1794 \text{ cm}^{-1}$) of bulk goethite .



Figure S3. Difference FTIR spectra of (a) C/Fe = 0.005 and (b) C/Fe =5 exposed to 0-60 % R.H. obtained by subtraction of spectrum at 0% R.H. Subtraction effectively removes contributions from combination ($\delta_{OH} + \gamma_{OH} = 1664 \text{ cm}^{-1}$) and overtones ($\delta'_{OH} = 1794 \text{ cm}^{-1}$) of bulk goethite. The resulting spectra show the increase in the bending mode of liquid-like water (v_2).



Figure S4. Difference spectra of LHA in the 1200-1800 cm⁻¹ region, obtained by subtraction of spectrum at 0% R.H, show the increase in the bending mode of liquid-like water (v_2) and uncompletely removed LHA functional groups.

	$C_{\mu s}$		S_0			
Sample	(mg/g)	K_{μ}	(mg/g)	$ m K_{f}$	α	β
Goethite	1504.8	10.5	36.3	3.8	8.0	2
C/Fe 0.005	711.8	10.5	23.3	3.9	8.1	2
C/Fe 0.05	734.1	10.5	30.7	3.1	8.1	2
C/Fe 0.1	869.5	10.5	34.0	2.8	7.9	2
C/Fe 1.25	3751.7	10.5	45.1	8.2	8.1	2
C/Fe 2.5	3916.3	10.5	47.1	6.0	8.1	2
C/Fe 5	2307.8	10.5	54.9	4.6	7.9	2
LHA	6323.5	10.5	78.5	4.3	8.1	2

Table S1. Parameters of Do & Do model for different samples

Chapter 5 Natural Organic Matter Controls on Quinolone Antibiotic Retention and Transport

Abstract

Although natural organic matter (NOM) is one of the most widespread and ubiquitous components in aquatic and terrestrial environments, its influence on the binding of quinolones to mineral surfaces and transport behaviour have been scarcely investigated. In this study, the sorption and transport of a widely used quinolone antibiotic, Nalidixic acid (NA), were investigated in goethite-coated sand (GCS) columns over a wide concentration range (5 - 50 mg/L) of Leonardite humic acid (LHA), a representative hydrophilic NOM. Simultaneous injection of NA and LHA in GCS columns accelerated NA breakthrough only at very high LHA loadings (50 mg/L). NA and LHA compounds bind and interact onto goethite surfaces, which mutually alter transport of each other, *i.e.* NA mobility and LHA molecular fractionation. Preloading of GCS column with LHA dramatically facilitated the transport behaviour of NA, where nonspecific interactions with LHA-covered goethite surfaces controlled NA mobility. Simulations using a two-site nonequilibrium model showed that a modified sorption rate constant was required to accurately describe the breakthrough curves of NA under these conditions. This altered rate constant points to nonspecific interactions of NA on bound LHA as an additional binding mechanism affecting adsorption kinetics. These results improve our understanding of quinolone transport in the presence of NOM and may have important implications for an accurate assessment of the fate of these types of antibiotics in the environment.

1 Introduction

Quinolone antibiotics are broad-spectra antimicrobial agents that are widely used in human and veterinary medicine to treat and prevent infectious bacterial diseases.¹ Due to their extensive uses and incomplete metabolisms *in vivo*, they can be disseminated into terrestrial and aquatic environments at concentrations as high as several hundred ng per L.² Adsorption to immobile soil/sediment minerals and/or mobile colloids is one of the key processes governing the fate and mobility of quinolones in environment.^{3–5} This process is strongly related to goethite (α -FeOOH), a common occurrence in the Earth's near-surface environment.⁶

Quinolone binding and transformation on minerals can however be strongly influenced by Natural Organic Matter (NOM).^{7–10} Although NOM may interact strongly with both minerals¹¹ and antibiotics,^{12,13} little is known about these co-occurring molecular interactions in natural settings where water migrates through soils and sediments.^{14–17} This is complicated by the complex nature of NOM — which consists of a polydisperse mixture of organic molecules of varying molecular size and chemical composition — and by its molecular fractionation resulting from its association to mineral surfaces. Currently available studies on the subject^{14–17} were limited to batch experiments, and little is known about the influence of NOM on binding and transport of antibiotics under flow-through conditions. Accounting for dynamic flow on nonequilibrium sorption of quinolones is particularly relevant when multiple mechanisms (*e.g.* binding, co-binding and NOM molecular fractionation) concurrently impact breakthrough.

In this study, we addressed these concerns by studying the mobility of Nalidixic acid (NA), a model quinolone antibiotic, over a wide concentration range (5 - 50 mg/L) of Leonardite humic acid (LHA), a representative hydrophilic NOM. Transport was studied in goethite-coated sand (GCS) columns, which are chosen to emulate the natural environments affecting contaminant migration and transformation.¹⁸ NA transport was studied in (i) clean and (ii) LHA-preloaded goethite-coated sand columns. In both cases, molecular fractionation of LHA and NA breakthrough were monitored by liquid chromatography, UV-Vis spectrophotometry and TOC analyses of column effluents. A transport model that accounts for adsorption kinetics was used to predict the adsorption and desorption fronts of the breakthrough behavior of NA. Changes in sorption kinetics can result from modifications in

binding mechanisms and thus explain how NA transportation is facilitated in the presence of LHA.

2 Materials and methods

2.1 Materials

All reagents except Leonardite humic acid were purchased from Sigma-Aldrich and were used without further purification. All solutions were prepared with ultrapure water. Leonardite Humic Acid Standard (1S104H) was purchased from the International Humic Substance Society. A LHA stock solution (2 g/L, 1276 mg C/L) was prepared by dissolving 2 g LHA in 100 mL of 1 M NaOH, then diluted to 1 L with ultrapure water. A 1 mM stock solution of Nalidixic acid (NA) (purity >99%) was prepared by dissolving 1 mmole NA in 20 mL of 1 M NaOH, then diluted to 1 L with ultrapure water.

2.2 Synthesis of Goethite-coated sand (GCS)

Goethite was prepared as described in previous studies,^{3,19} and coated onto cleaned Fontainebleau quartz sand (100-150 μ m) as previously detailed.^{20,21} All sample preparation and characterization procedures are in the Supporting Information (SI). All synthetic solids were washed with doubly distilled deionized water to remove soluble Fe and electrolyte ions. The solids were then stored in an anaerobic N₂(g) chamber at ambient temperature.

Previous work^{20,22} from our group confirmed that the coating procedure did not alter goethite particles and no silicates were released from quartz sand. The goethite content deposited on the sand surface, measured by acid digestion analysis, was 0.99 g/100 g of sand.

2.3 Breakthrough Column Experiments

Breakthrough column experiments were conducted at constant flow rate and under water-saturated conditions. Briefly, 15 g of dry goethite-coated sand was packed into a glass chromatographic column of 1.6 cm internal diameter to give a porous bed length of 4.7 cm. After packing to a uniform bulk density $(1.59 \pm 0.05 \text{g/cm}^3)$, the column was wetted upward with a 0.01 M NaCl solution at pH_{in} 5 and 0.5 mL/min. The pore volume (V_P) was estimated by weight differences between the saturated and dry column. Once the column became water saturated, the flow characteristics of the porous bed were determined by a nonreactive tracer (bromide) experiment and described by the classical advection dispersion equation (ADE). The fitting parameters of the bromide elution confirmed the flow

homogeneity and predominance of a convective regime in the column.

A LHA solution (5, 10 or 50 mg/L) in 0.01 M NaCl at pH_{in} 5 was thereafter injected into the column with a continuous mode at 0.5 mL/min. The effluent of the column was collected and stored at 4°C for further analyses. After the complete breakthrough of LHA, 10 μ M NA with the corresponding LHA (5, 10, 50 mg/L) in 0.01 M NaCl at pH_{in} 5 was injected in the same column at the same constant flow rate. NA concentrations in the collected fractions were measured by HPLC/UV. In another experimental series, 10 μ M NA and different concentrations of LHA (0, 5, 10, 50 mg/L) were equilibrated in 0.01 M NaCl at pH_{in} 5 and then injected simultaneously into column at 0.5 mL/min. LHA and NA concentrations in the effluents were measured. After total breakthrough of NA/LHA, desorption was initiated by injecting 0.01 M NaCl at pH_{in} 5 into column at 0.5 mL/min. After the desorption of NA/LHA, the solid was transferred to 0.1 M NaOH and shaken for 1 week. Then the supernatants were filtered (0.2 μ m), and analyzed by UV-Vis spectrometry and TOC analyzer.

The concentration of LHA in the effluent solution was determined by a total organic carbon (TOC) analyzer (Shimadzu TOC-VCSH). The UV absorbance of LHA samples were recorded in the range of 200 - 800 nm with a UV–visible spectrophotometer using 1 cm quartz cell. The following specific UV absorbance parameters were calculated as indicators of NOM fractionation. The relative absorbance ratio E_2/E_3 is defined as the ratio of absorbance at 250 nm and 365 nm. E_2/E_3 has been reported to inversely correlate with the molecular weight (Mw) and aromaticity of NOM.^{23–25} Specific ultraviolet absorbance of LHA at 280 nm (SUVA₂₈₀) was used to estimate NOM aromaticity by dividing the molar absorptivity at 280 nm (m⁻¹) by the TOC concentration (mg/L) in the solution.^{23,26} The parameter S_R (slope ratio) is the ratio of the slope of the shorter wavelength region (275 nm – 295 nm) to that of the longer wavelength region (350 nm – 400 nm).²⁷ S_R is reported to be negatively correlated with the Mw.^{27,28}

Aqueous NA concentrations were determined by high performance liquid chromatography (Waters 600 Controller) using a UV detector (Waters 2489) and a reversed-phase C18 column (250 mm×4.6 mm i.d., 5 μ m). The mobile phase (1 mL/min) was a mixture of acetonitrile/water (60:40 v/v) contained 0.1% formic acid. The detector was set to 258 nm for NA.

2.4 Model approach

The transport of NA both in the presence and absence of LHA through the columns was simulated

using a one-dimensional advection-dispersion model coupled with two-site nonequilibrium adsorption model.²⁹ The two-site nonequilibrium model is based on the assumption that two types of sorption sites exist, an equilibrium site and a kinetic site. Sorption is instantaneous on the equilibrium site and described by a sorption isotherm (Type 1, equilibrium), and time dependent on the kinetics site and follows first-order kinetics (Type 2, kinetic).²⁹ The final governing equations of the model are given by:

$$\frac{\partial C}{\partial t} + \left(\frac{\rho}{\theta}\right) \left(\frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t}\right) = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x}$$
(1)

$$S_I = K_d C^\beta \tag{2}$$

$$\frac{\partial S_2}{\partial t} = \alpha \left[(1 - f) K_d C^\beta - S_2 \right]$$
(3)

In these equations, *C* is the concentration of the adsorbate (NA) (μ M), *t* is time (h), ρ is the bulk density of goethite-coated sand in the column (g/cm³), θ is the volumetric water content (cm³/cm³), and it equals to the porosity of the saturated column, *S*₁ and *S*₂ are sorbed-phase concentrations of NA on the equilibrium and kinetic nonequilibrium sites (μ mol/g), respectively, *D* is the dispersion coefficient (cm²/h), *x* is distance (cm), *v* is the average pore water velocity (cm/h), *f* is the fraction of equilibrium sites (Type 1), α is the first-order rate coefficient associated with the kinetic site (h⁻¹), and *K*_d is the Freundlich isotherm adsorption coefficient (cm³/g) related to the sorption capacity, and β is the Freundlich exponent that characterizes the degree of nonlinearity.

Hydrus-1D program was used to obtain the model parameters for the two-site nonequilibrium model. The values of θ and D were obtained by fitting the breakthrough data of the Br⁻ tracer, and the values of β , K_d , f and α were obtained by fitting the transport data of NA. The best fitted f value to describe the mobility of NA alone was at 0.6. This value was then kept constant for all simulations, which allows a reducing of the number of estimated parameters. A complete sensitivity analysis, including the modeling approach used in the present work, is provided in the Supporting Information (SI).

3 Results and discussion

3.1 Mutual effects of LHA fractionation on the NA sorption

Simultaneous injection of NA and LHA in goethite-coated sand column alters NA mobility. This can be seen through the increased steepness of asymmetrical breakthrough curve of NA at larger LHA concentrations while the breakthrough point remained constant (Figure 1). The latter was shifted down only with the highest concentration of LHA (i.e. 50 mg/L), leading to a rapid breakthrough of NA. While the NA retention did not vary the outflow pH, the presence of LHA caused pH variations in the initial stage. The increase in pH indicated that the COO- groups of LHA replaced the surface OH on goethite³⁰ (Figure 1).



Figure 1. Breakthrough curves of NA (solid symbols) and pH (empty symbols) with the presence of different concentrations of LHA. 10 μ M NA with the corresponding LHA and 0.01 M NaCl at pH_{in} 5 was injected. Lines are modeling results.

Since both NA and LHA can bind to goethite through ligand-exchange and hydrogen bonding,^{4,31} competing for surface sorption sites could occur during simultaneous injection. Oxygenated polycyclic aromatics and carboxylic compounds, which generally contain in DOM of high oxidation state and high aromaticity, tend to have higher affinities for iron oxyhydroxides than alcohols, ethers and aliphatics.^{31–34} As LHA exhibits high chemical heterogeneity with higher aromaticity (i.e. carbon aromaticity of 0.58)³⁵ and lower aliphatic carbons contents, we expect a molecular fractionation caused by selective adsorption of LHA to goethite.^{34,36} This falls in line with the breakthrough

behavior of LHA in goethite-coated sand column, particularly in terms of the discrepancy between TOC and UV (Figure 2 for LHA without NA).



Figure 2. (a) Breakthrough curves of LHA based on TOC and UV_{254} measurements (b) $SUVA_{280}$, (c) E_2/E_3 , (d) S_R of different effluent concentrations of LHA as a function of V/V_p . The purple dashed line shows the corresponding value of inflow LHA.

Higher TOC values with respect to UV absorbance at 254 nm were observed during the first adsorption stage, before both of the two parameters followed each other to reach their inflow values. This can also be seen by the low SUVA₂₈₀ values observed at the first stage (lower PV values), suggesting that aromatics were primarily and preferentially adsorbed to goethite in the column. In addition, E_2/E_3 (Abs_{250nm}/Abs_{365nm}) and S_R of outflow solution were first lower than the initial value of LHA and then increased sharply, and finally decreased to reach the initial value (Figure 2c,d). This

confirms that LHA compounds with smaller molecular size were preferentially retained, leading to higher Mw fractions in the column effluent (lower E_2/E_3 and S_R than the initial LHA). The increase in both parameters above the initial value suggested that outflow solution contained lower Mw fractions with higher aromaticity, while higher Mw fractions were adsorbed in the column. Note that different reports have contrast results for humic acids fractionation onto Fe-oxides, which is likely related to the HA nature/source.^{23,37-40} Higher molecular weight were preferentially adsorbed and then replaced by lower ones in solution for commercial HA (Sinopharm Chemical Reagent Co. Ltd. China.) to goethite,²³ while in other reports lower Mw molecules of NOM are firstly adsorbed onto iron oxides and successively replaced by higher Mw fractions.^{37–40} The preferential adsorption of relatively small size fractions can be explained by their fast diffusion to the mineral surface, while the bigger HA compounds containing more reactive groups can exhibit stronger overall binding, and thus replace the lower Mw fractions during the adsorption process⁴¹. The primary adsorption of lower Mw of LHA aromatic components were also confirmed under batch conditions, where fast and simultaneous decrease in TOC and UV was observed over the first 15 min of contact time (Figure S1a). Higher TOC values relative to UV were observed during adsorption kinetics, while E_2/E_3 and S_R values tend to exceed the initial value after 6 h of contact time, suggesting that the lower Mw of LHA components first adsorbed may be replaced by the larger LHA components on the goethite surface. This is consistent with a recent kinetic study³⁴ showing a rapid primary phase adsorption of aromatic and polycyclic aromatic compounds to goethite at the first stage, followed by lignin-like and aliphatic compounds.

On the other hand, LHA fractionation under simultaneous injection with NA is illustrated using the relative UV absorbance at 254 nm (ΔA_{250}) and 400 nm (ΔA_{400}) of outflow solutions for the three LHA concentrations (empty symbols in Figure 3). Except at the highest LHA loading (50 mg/L), the breakthrough curves display a first step where high absorbance values were observed following by a classical breakthrough step, whereby ΔA_{400} gradually increased from zero and tend to 1 (complete breakthrough). The beginning of a second step coincides with the NA breakthrough, suggesting that NA adsorption at the first step may influence LHA retention and thus mobilize some LHA compounds. Compounds that are flushed out early have greater A_{400}/A_{254} ratios than in raw LHA (Figure 3 and Figure S2). The greater absorbance at 400 nm is attributed to π - π * transitions of polycyclic aromatic

compounds.⁴² This suggests that the smaller aromatic compounds are preferentially adsorbed compare to multiple benzene ring structures at the first stage of breakthrough. This result is also consistent with the fractionation of LHA in column where lower Mw fractions were preferentially adsorbed (lower E_2/E_3 and S_R than the initial LHA in Figure 2).

It is worth noting that this early breakthrough of aromatics is not observed in LHA transport experiments in the absence of NA (See UV absorbance at 400 nm in Figure S3), confirming the impact of NA retention on the LHA molecular fractionation in column. NA likely increased the mobility of some LHA compounds through competitive binding with goethite surfaces. The full breakthrough behavior of LHA in goethite-coated sand columns was also found affected by the co-existing NA (See Figure S4).



Figure 3. Breakthrough curves of NA and LHA when simultaneously injecting 10 μ M NA and (a) 5 mg/L, (b) 10 mg/L, or (c) 50 mg/L LHA. NA was analyzed by HPLC. Full breakthrough curve (empty symbols) of LHA was based on relative UV absorbance at 400 nm where NA does not absorb and LHA concentrations show linearity with respect to absorbance (Figure S5). The red dots in (a) and (b) are relative UV absorbance at 254 nm (Abs of outflow solution/Abs of influent LHA) for samples collected before the beginning of NA breakthrough. Lines are modeling results.

At low LHA loadings (5 or 10 mg/L), both NA and LHA compounds bind to surface sites of goethite and the breakthrough was only altered in the adsorption front (Figure 1). In contrast, at higher LHA loading (50 mg/L), NA simply follows the LHA breakthrough. This rapid breakthrough of NA is likely ascribed to strong competitive adsorption of LHA compounds to goethite, as well as intermolecular interactions between NA and unbound LHA that decreased NA retention. This was

confirmed further by a fluorescence test shown in Figure S6.

This breakthrough behavior can be understood in terms of the competitive binding of NA and carboxylic/aromatics compounds of LHA to the same surface sites of goethite.^{31,39} In particular, ligand exchange reaction with singly-coordinate –OH sites of goethite³¹ is likely to drive the first step in the breakthrough curve as our previous spectroscopic work⁴⁴ shows that NA binds both as metal- and hydrogen-bonded complexes on these sites. Therefore, competitive binding of NA and carboxylic/aromatics compounds of LHA on -OH sites occur at the first step, followed probably by further adsorption of NA to LHA covered goethite. We note that low amount of reactive phase (i.e. goethite ~ 1wt %) in the column as well as the low amount of adsorbed NA (0.06-0.24 μ mol/m²) hinder our ability to directly assess possible modifications in binding mechanisms in the column system. As a theoretical tool to examine the possibility of different mechanisms involved during the simultaneous injection of NA and LHA, a model integrating a sorption kinetic term was used to describe the influence of LHA on NA adsorption. The model adequately predicted NA adsorption ($r^2 \ge 0.9823$, Table 1) using a lower K_d but a higher α at high LHA concentrations, thus suggesting the modification of sorption mechanisms. The lower K_d indicates smaller NA surface loadings, whereas the total amount of NA adsorbed was positively correlated with K_d (Figure S7). Moreover, the higher α value indicates faster kinetics, as suggested by the less tailing of NA in the presence of LHA (Figure 1). The long tailing observed in the breakthrough curve of NA without LHA was likely caused by chemical kinetic limitations, as previously reported,^{45,46} and confirmed here for NA by the tailing mitigation obtained when a lower flow rate (0.1 mL/min) was applied (See Figure S8). To test whether modification of sorption kinetics takes place when NA interacts with LHA-covered goethite, injection of NA in LHA preloaded columns was investigated, as detailed in the following section.

3.2 Sorption of NA in LHA preloaded columns

Preloading of goethite-coated sand columns with LHA dramatically changed the transport behavior of NA in terms of both retardation factor and breakthrough curve shape (Figure 4). Asymmetrical curve shape with an extensive tailing became sigmoidal when NA was injected in LHA preloaded columns. Increasing in LHA concentrations (from 0 to 50 mg/L) advanced the breakthrough point, yet the latter remained very close for the three tested LHA concentrations. Overall, the preliminary loading of column with LHA considerably facilitated the transport of NA, with a very





Figure 4. Breakthrough curves of NA onto different concentrations of LHA preloaded column, 10 μ M NA with the corresponding LHA and 0.01 M NaCl at pH_{in} 5 was injected. Inset is the breakthrough curves in the initial stage. Lines were generated by the model. Very little variation in outflow pH values was observed independently of the LHA loading (See Figure S9).

As LHA ligand exchange predominantly involves ~ 3.3 sites/nm² of the reactive –OH groups,³¹ it becomes useful to express breakthrough results in terms of surface loadings. Based on our previous work,³¹ goethite surfaces expose a mixture of non-reacted –OH groups and bound LHA at C/Fe ratios below 0.1 (namely, 26 C/nm²). All -OH groups are, on the other hand, consumed above this ratio.³¹ Using the TOC and UV absorbance of column effluents (Figure 2a), the integrated area above the breakthrough curve shows that the total LHA adsorbed in the column was ~75 mg C/g goethite, which is equivalent to ~42 C atoms/nm² and therefore ~3 times the total crystallographic density of all surface oxygens (~15 sites/nm²).^{31,47}

Under these conditions, NA retention was mainly driven by weak van der Waals-type hydrophobic interactions, and/or through π - π electron coupling interactions with LHA-covered goethite surfaces. These interactions could govern the transport behavior in preloaded columns, independently on the LHA preloading concentration. This hypothesis was further confirmed in the simulation results using a nonequilibrium model of the breakthrough curves of NA in LHA-preloaded columns. Similar adsorption parameters (K_d , α and β) described the breakthrough curve of NA for the three preloading LHA concentration (Figure 4, Table 1). The first-order rate coefficient associated with the kinetically

limited site (α) increased when column is previously loaded with LHA, suggesting the modification of NA sorption kinetics. This phenomenon is also observed under batch conditions where the presence of LHA affected the adsorption kinetics of NA (Figure S10).

Experiment	K_d	β	α	R^2
NA	39.77	0.89	0.00095	0.9961
Preloaded 5 mg/L LHA	5.65	0.8649	0.00766	0.9928
Preloaded 10 mg/L LHA	4.39	0.9	0.01063	0.9960
Preloaded 50 mg/L LHA	3.72	1.1545	0.00968	0.9982
NA-5mg/L LHA	34.55	0.765	0.00313	0.9978
NA-10mg/L LHA	24.63	0.7662	0.01859	0.9893
NA-50mg/L LHA	7.6	0.7402	0.058	0.9995

 Table 1. Fitted parameters of two-site nonequilibrium sorption model

3.3 Impact of LHA on the breakthrough behavior of NA

Dynamic adsorption experiments in column provided relevant data on the dual binding mechanisms of NA, *i.e.* adsorption to (i) goethite in competition with carboxylic/aromatics LHA compounds, and (ii) LHA-covered goethite through nonspecific interactions, together with the molecular fractionation of LHA. To highlight the impact of LHA on the NA mobility/transport in the column system, full breakthrough curve consisting of both adsorption/desorption fronts was determined for NA alone and NA in presence of 50 mg/L LHA.


Figure 5. Full breakthrough curves for (a) NA alone and (b) NA in the presence of 50 mg/L LHA onto clean goethite coated sand. Lines are modeling results. 10 μ M NA with the corresponding LHA and 0.01 M NaCl at pH_{in} 5 was injected for adsorption and 0.01 M NaCl at pH_{in} 5 was injected for desorption at 0.5 mL/min. No pH variation was observed during the desorption stage.

As shown in Figure 5a, the full breakthrough curve of NA is asymmetrical, and exhibits tailing both in adsorption front and elution-wave, confirming the rate-limited sorption/desorption process of NA on goethite surfaces. Interestingly, the desorption front can be well predicted with the same parameters used for the adsorption, suggesting a reversible sorption process. As expected from previous column tests, the presence of LHA alters the desorption front, making the full breakthrough

curve of NA more symmetrical, with less tailing in both adsorption and desorption fronts (Figure 5b and S11). As it is difficult to directly access molecular-level information in the NA/LHA/goethite system, we have used a nonequilibrium model as for the previous column experiments, to describe the influence of LHA on NA mobility. If the same adsorption parameters (i.e. α , k_d, β) were used for full BTC description, the calculated curve failed to describe the desorption tailing (Simulation#1 in Figure 5b). Attempt to describe better the latter by changing α (see Table S1) provided a curve where adsorption front is shifted down with respect to the experimental data (Simulation#2). An accurate description of the full breakthrough curve required two different values of α for adsorption and desorption fronts (Simulation#3, See Table S1). Indeed, lower α for desorption than adsorption was needed, thereby underscoring possible modification of surface reactions. Due to the very slow and incomplete desorption of LHA compounds in column, the amount of LHA desorbed in the effluent solution becomes below detection limit after 5 PV (Figure S12), and extension up to 800 PV had no influence on the amount of LHA desorbed (data not shown). Solid-phase extraction conducted on the GCS solid after termination of the column experiment revealed that at least 80 % of total sorbed LHA are still present on the solid (total LHA adsorbed in the column was ~75 mg C/g goethite or ~42 C atoms/nm²). This can also be observed visually since the solid kept its brown color (due to the attachment of LHA), confirming the incomplete LHA desorption under our experimental conditions and over the whole breakthrough time. This is consistent with previous works^{30,48} where the slow desorption kinetics and low desorption extent of NOM at oxide surfaces have been attributed to the complex nature of NOM compounds (though different NOM were used in these studies) and their multiple interactions involving multiple binding sites with oxide surfaces.^{30,48} While NA desorption is almost complete, most of sorbed LHA compounds remained attached to goethite surfaces. Nonspecific interactions between NA and bound LHA compounds may influence desorption process and thus kinetics, as suggested by the simulation results.

4 Environmental implications

NOM is ubiquitous in natural aquatic and terrestrial environments, and can affect the mobility and fate of emerging contaminants. Here, we have considered two situations where target contaminants (i) are present together with NOM in groundwater and surface waters, then bind to mineral surfaces, and (ii) where they interact with NOM coatings on minerals. In both scenarios, NOM strongly affected quinolone binding to goethite, and thus transport behavior in dynamic column experiments. We notably demonstrated that LHA facilitated NA transport in columns but this effect depends on how organic matter is contacted to mineral surfaces. When LHA was present as a mineral coating, van der Waals-type hydrophobic interactions governed NA transport. However, when both LHA and NA were initially present in the influent solution, the breakthrough was characterized first by a primary step involving competitive adsorption of NA and carboxylic/aromatics compounds, and a second step involving nonspecific adsorption of NA to LHA-covered goethite. This two-step process controls both NA retention and LHA molecular fractionation in the column.

Our work thereby shows that NOM fractionation alters sorption mechanisms and kinetics of quinolone antibiotics, which in turn affect their fractionation. The slow and incomplete desorption of LHA compounds from goethite surfaces alters the desorption front and thus the NA mobility. More generally, this study shows how molecular interactions between the NOM and soil materials control the migration of contaminants within surface and subsurface environments. This calls for in-depth consideration of molecular characteristics of binding mechanisms in assessment studies of contaminant fate. These findings can have strong implications on the prediction of transport of quinolone antibiotics, and of their ecological impacts in the environment.

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Supporting information

Natural Organic Matter Controls on Quinolone Antibiotic Retention and Transport Synthesis and Characterization of Goethite Particles. 400 mL of a 2.5 mol L⁻¹ sodium hydroxide solution was mixed with 500 mL of a 0.5 mol L⁻¹ ferric nitrate solution (Fe(NO₃)₃·9H₂O) at a fixed rate of 1 mL min⁻¹ with stirring under nitrogen atmosphere. The obtained hydroxide slurry was aged at 60°C for 72 hours in an oven. The precipitate obtained was then dialyzed (Spectra/Por membrane 2) against Milli-Q water. The water was changed every day until its conductivity was close to 0 μ S cm⁻¹. The suspensions were stored in polypropylene containers at 4°C for further use. The purity of goethite was confirmed by X-ray diffraction (XRD) and the B.E.T. specific surface area of the synthetic goethite was 89.6 m² g⁻¹ and the point of zero charge (PZC) of goethite, determined at 298 K in 0.01, 0.1 and 1 M NaCl solutions by the potentiometric titration method, was pH 9.1.

Synthesis of Goethite coated sand (GCS). Fontainebleau quartz sand $(100-150 \ \mu m)$ was used. The quartz sand was cleaned with 1 M HCl for 48 hours, and then rinsed with pure water. The sand was placed in oven at 100°C for 1 day, and then rinsed repeatedly with pure water. The quartz sand was also cleaned with H₂O₂ to remove organic matter then rinsed with pure water. Possible sand dissolution was checked by measuring dissolved silica (ICP-AES). All the measurement tests confirmed the absence of Fontainebleau sand (100-150 μm) dissolution in our experimental conditions. Goethite coating was obtained by shaking a suspension containing the goethite and the silica sand. The purified quartz sand was then added to the goethite suspension containing 10 mM NaCl brought to pH 5 with HCl and the mixture was agitated again for 24 h. After that, the coated sand was washed with deionized water until the runoff was clear, and then it was dried for 24 h. The final goethite-coated sand was stored at ambient temperature until further use.

Batch experiments. Batch adsorption kinetics was carried out under $N_2(g)$ atmosphere to avoid effects of carbonates and bicarbonates on the adsorption of NA onto GCS. Suspensions were prepared in 15 mL polyethylene tubes at a total volume of 10 mL solution with 10 μ M NA, 0.01 M NaCl, 0.2 g GCS and different concentrations of LHA (0, 5 and 10 mg/L). The pH was maintained at 5.0 \pm 0.1 by adding 0.01 M HCl or NaOH. The tubes were sealed by caps and then shaken continuously on a platform shaker at 200 rpm and 25 °C. Every sample was filtered (0.22 μ m) after a specified time interval and the amount of residual NA was analyzed by HPLC-UV.

The similar procedure was applied to test the kinetics of NA (10 μ M) adsorption onto goethite (50

m²/L) in the presence of different silicates concentrations (100, 500, 1000 μM).



Figure S1. (a) LHA adsorption kinetics based on UV absorbance at 254 nm and TOC measurement and SUVA₂₈₀, and (b) E_2/E_3 and S_R variations with time. Experimental conditions: 50 m²/L goethite, 50 mg/L LHA, 0.01 M NaCl, pH 5. The dashed lines show the initial value of E_2/E_3 and S_R .



Figure S2. (a)(b) UV spectra of samples collected before NA breakthrough. Numbers indicate Number of injected PV. Simultaneous injection of 10 μ M NA and (a) 5 mg/L, or (b) 10 mg/L LHA.(c) UV spectra of raw LHA at different concentrations. (d) The UV absorbance ratio of 400 to 254 nm as a function of V/V_p when simultaneous injection of 10 μ M NA and different concentration of LHA. The solid line shows the A₄₀₀/A₂₅₄ value of raw LHA.



Figure S3. BTCs of different concentrations of LHA based on UV absorbance at 400 nm in absence of NA.



Figure S4. Breakthrough curves (based on UV measurement at 400 nm where no absorption for NA) of LHA in the absence and in the presence of 10 μ M NA.



Figure S5. Relationship between UV absorbance at 400 nm and LHA concentration.



Figure S6. Fluorescence quenching of 2 µM NA by different concentrations of LHA.



Figure S7. K_d versus the amount of NA adsorbed in different systems.



Figure S8. BTCs of NA normalized by its retardation factor to that of the bromide (tracer), at two flow rates. Inflow conditions: 10μ M NA, 0.01 M NaCl, pH_{in} 5.



Figure S9. Breakthrough curves of NA (solid symbols) and pH (empty symbols) with different LHA preloading concentrations, 10 μ M NA with the corresponding LHA and 0.01 M NaCl at pH_{in} 5 was injected. Lines were generated by the model.



Figure S10. NA adsorption kinetics in the presence of different concentrations of LHA. Lines are modeling results based on the pseudo-first-order kinectic model and k_1 is the rate constant (h⁻¹). Experimental conditions: 0.2 g GCS,10 μ M NA, 0.01 M NaCl, pH 5.



Figure S11. (a) full breakthrough curve of NA and (b) desorption curves of NA. 10 μ M NA with the corresponding LHA and 0.01 M NaCl at pH_{in} 5 was injected for adsorption and 0.01 M NaCl at pH_{in} 5 was injected for desorption at 0.5 mL/min. No pH variation was observed in the desorption stage.



Figure S12. Desorption of LHA in the presence of NA based on UV absorbance at 400 nm and TOC measurement.

modeling test	f	K_d	β	adsorption rate α	desorption rate α
simulation#1	0.6	7.6	0.7402	0.058	0.058
simulation#2	0.6	7.6	0.7402	0.00386	0.00386
simulation#3	0.6	7.6	0.7402	0.058	0.00386

Table S1. Modeling parameters of two-site nonequilibrium sorption model for full breakthrough curve of NA in the presence of 50 mg/L LHA.

Test S1. Sensitivity test

Estimation of fraction f. In the single system (e.g. NA alone), sorption parameters (including fraction of equilibrium-site *f*, Freundlich sorption isotherms K_d and β , first-order kinetic rate α for kinetic sorption site) of NA were first estimated by inverse modeling of step-input type experiment, and then validated by forward modeling of pulse-input type experiment.

In two-site equilibrium/kinetic model, the variation of parameter f will significantly influence the range of the other 3 parameters. In order to evaluate the potential range of parameter f, a rough estimation was first conducted by adjusting the 4 parameters mentioned above simultaneously to fit the experimental sorption front. Afterwards, obtained parameters were used to model the experimental BTC containing both sorption-wave and elution-wave. From the results (Figure 1 & Table 1), simulated BTC fitted very well the sorption-wave tailing, but failed in fitting the elution-wave.



Figure 1. Validation of simulated BTC from inverse modeling.

Variable	Value	S E Cooff	95% confidence limits	
Vallable	value	3.L.COEN	Lower	Upper
K _d (mol ^{1-β} cm ^{3β} g ⁻¹)	4,56E+01	8,70E-01	4,38E+01	4,74E+01
f	5,03E-01	9,94E-03	4,82E-01	5.23E-01
β (-)	8,30E-01	1,50E-02	7,99E-01	8,61E-01
α (min⁻¹)	7,18E-04	4,25E-05	6,31E-04	8,06E-04

Table.1 Parameter estimated from step-input type experiment of NA.

In a second time, a new fitting procedure was employed by setting a range of f (from 0.4 to 0.7) and adjusting the other 3 parameters simultaneously. The variation interval of f was 0.05, i.e. close to 95% confident interval (Table 1). Similarly, the pulse-input type experiment was used for validation. From the results (Figure 2), the tailing of both sorption-wave and elution wave becomes less pronounced with the increase of f. However, all simulated BTC slightly underestimated the beginning of elution wave. According to the goodness of fit both in sorption and desorption fronts, the set of parameters when f equals 0.6 was chosen. At that condition, 95% confidence intervals of the other 3 parameters were reasonable. In conclusion, the results of parameter estimation were quite close, indicating that parameter non-uniqueness is minimal here.



Figure 2. Simulated BTC by forward-modeling

Sensitivity analysis of K_d , β and α . A further sensitivity analysis was conducted to see how parameter β (the index constant determining the linearity or nonlinearity of sorption isotherm), K_d (empirical distribution coefficient) and α (first-order kinetic sorption rate) affect the shape of BTC. For example, we set a range of β (0.75~1.1) and kept the other 2 parameters same with the values of NA simulation. Similar procedures were also applied for α (0.0001~0.01 min⁻¹) and K_d (15~75 mol^{1- β}cm^{3 β}g⁻¹).



Figure 3. Sensitivity analysis of calculated BTC of NA by varying K_d , β or α

As shown in Figure 3, the influence caused by variation of β is mainly displayed by slight change in the slope of early breakthrough part. As expected, the increase of K_d shift up the full BTC, causing extended tailing in the elution wave. The parameter α controls the slopes of both adsorption and desorption fronts including tail parts.

The sorption and elution waves of BTC can be symmetrical or asymmetrical. Extended tailing in the elution wave may be caused by rate-limited sorption/desorption, and so adjusting first-order kinetic rate α may be required to better describe the BTC.

Chapter 6 Conclusions and perspectives

The impacts of quinolone antibiotics overuse on the environment is becoming of special concern given their extensive use and the severe threats they may cause to humans and ecosystem health.¹ Therefore, it is necessary to investigate the transport and mobility of quinolones in environment in order to accurately assess their ecological impacts. Major challenges in understanding the processes controlling quinolones behavior in the environment include the complexity of the soil and the large spatial scales over which these processes occur. Currently, the lack of quantitative data on the fate and mobility of quinolones and gaps in translating molecular information to larger scales hinder our ability to develop valuable models to assess their fate in environmental systems. This thesis aimed at understanding quinolones binding mechanisms to iron (hydr)oxides under a wide range of environment relevant conditions. The molecular-level interactions between quinolones and iron (hydr)oxides were thoroughly studied by combing batch adsorption, column adsorption, surface complexation model, hydrodynamic transport model and vibrational spectroscopy.

1 Conclusions

Chapter 2 examined the potential fate of quinolones in the subsurface, Fe(II)-rich, environments by investigating the influence of stoichiometry of magnetite on its binding properties. It is the first work that demonstrates that the stoichiometry strongly affects the capacity of magnetite to bind not only quinolone antibiotics such as Nalidixic acid (NA) and Flumequine (FLU), but also salicylic acid (SA), natural organic matter (humic acid, HA) and dissolved silicates. Fe(II)-amendment of non-stoichiometric magnetite (Fe(II)/Fe(III) = 0.40 and Fe(II)/Fe(III) = 0.42) led to similar sorbed amounts of NA, FLU, SA, silicates or HA as compared to the stoichiometric magnetite (i.e. Fe(II)/Fe(III) = 0.50). At any pH between 6 and 10, all magnetites exhibiting similar Fe(II)/Fe(III) ratio in the solid phase showed similar adsorption properties for NA or FLU. This enhancement in binding capability of magnetite for NA is still observed in presence of environmentally relevant ligands (e.g. 10 mg L⁻¹ of HA or 100 μ M of silicates). Comparison with other divalent cations (e.g. Ni(II) and Mn(II)) suggests that the driving mechanism in increase of ligand adsorption upon Fe(II)-recharge of magnetite does not correspond with a common ternary surface-metal-ligand complexation. Using a 2-pKa-CCM surface complexation model, it was shown that the NA-magnetite complexation constant does not vary with Fe(II)/Fe(III) between 0.24 and 0.40, but increases by 4

orders of magnitude when Fe(II)/Fe(III) increases from 0.40 to 0.50. Thus, to account for the influence of the stoichiometry of magnetite on the fate of organic contaminants in environmental systems, the potential Fe(II)-enrichment or Fe(II)-depletion of magnetite should be appropriately considered in reactive transport studies.

Chapter 3 aimed at predicting quinolone antibiotics mobility under seawater conditions, mimicking costal sediments. In this study, the adsorption of a widely used quinolone antibiotic in aquaculture, oxolinic acid (OA), to a synthetic goethite (α - FeOOH) was examined in the presence of major (e.g., Mg^{2+} , SO_4^{2-}) and trace (e.g., Cu^{2+}) ions naturally occurring in seawater. Although SO_4^{2-} is known as a strong competitor for anions, its effect on OA-goethite binding at seawater relevant pH was found to be almost negligible. Other less abundant ions such as F^- , Br^- , BO_3^{3-} , and Ca^{2+} did not exhibit a significant impact. However, at seawater relevant concentrations, Mg^{2+} was found to strongly decrease OA-goethite binding via the formation of an aqueous complex with OA. Trace metals (e.g., Cu²⁺ used here as a model metal) naturally occurring in seawater could strongly increase OA binding by forming a ternary metal-ligand surface complex. The OA adsorption could be successfully predicted using a charge distribution multisite complexation model (CD-MUSIC). This was the first time that the adsorption of an organic ligand to a mineral surface could be predicted with this highly mechanistic model under seawater conditions, by quantifying the effects of different ions naturally present in seawater on OA retention. Moreover, the transport of OA in flow-through columns could be well predicted through coupling hydrodynamic parameters and surface complexation constants obtained in static (batch) conditions. These results may have strong implications for assessment and prediction of the fate of quinolones in sediment-seawater interface systems, and thus assessment of ecological impacts of aquaculture-induced pollution in marine systems.

Chapter 4 examined the binding mechanisms of LHA onto goethite and the effects of LHA loading on the hydrophobicity of goethite surface through quantifying water binding capacity of different LHA-goethite assemblages. Microgravimetry and FTIR spectroscopy revealed the strong LHA-loading dependence on water binding. LHA binding at low loadings (C/Fe = 0.005-0.1) involves a greater proportion of LHA moieties for ligand exchange or hydrogen bonding to goethite surfaces. This results in potentially important configurational changes in LHA structure, perhaps even exposing hydrophobic portions of the molecule to the goethite surface. This, with the decrease in accessible

hydrophilic groups of the goethite surface, collectively lowers water binding on goethite reacted LHA loadings and increased surface hydrophobicity. Water affinities become, in turn, substantially larger at high C/Fe loadings (C/Fe > 0.1) because a smaller fraction of the moieties is dedicated to binding with goethite, leaving excess LHA reacting with water in a similar manner to pure LHA. Therefore, high loading of LHA decreased water hydrophobicity. An empirical relationship predicting the dependence of water adsorption densities on LHA loadings was developed from these results. Together with the molecular-level description provided in this work, this relationship should guide efforts in predicting water availability, and thereby occurrences of water-driven geochemical processes in terrestrial environments. Furthermore, the NOM coating modified the mineral surface reactivity and may affect the fate and mobility of other contaminants.

Chapter 5 Studied fractionation of LHA and its impacts on NA transport in goethite coated sand (GCS) columns under flow-through conditions. LHA underwent fractionations during its interactions with goethite, with aromatics and lower Mw compounds preferentially adsorbed, and replaced by higher Mw compounds. LHA fractionation alters sorption mechanisms and kinetics of NA, which in turn affect their fractionation. LHA facilitated NA transport in columns and this effect depends on how the LHA is contacted to mineral surfaces When LHA and NA were simultaneously injected to clean GCS, NA and aromatics compounds of LHA competed for sorption sites, and NA could be also adsorbed onto LHA by nonspecific interactions. When NA was injected to the LHA preloaded GCS, NA transport was facilitated significantly and the impact of preloaded NOM concentration was negligible, where NA transport was governed by van der Waals-type hydrophobic interactions between NA and preloaded LHA. These findings may have strong implications in the prediction of transport of quinolones antibiotics in environment with NOM.

2 Implications

This thesis revealed molecular-level binding mechanism of quinolones to iron oxides under a wide range of environmentally relevant conditions, such as reducing conditions, the marine system and natural environment with NOM and silicates. Findings from this thesis may improve our understanding of the transport of quinolone antibiotics, and thus assessment of ecological impacts of aquaculture-induced pollution in environment. From fundamental point of view, the original ideas and achieved results in this thesis will help to incorporate multiscale chemical and physical heterogeneities in reactive transport modeling studies and will improve the modeling ability of the fate and transport of contaminants. In addition, outcomes of this thesis will help to develop decision support tools for risk assessments and for strategies of remediation based on minimizing risks to the environment and human health.

3 Perspectives

The current study can be extended in many directions. Some examples are discussed below.

3.1 Perspectives in the short term

Although the scope of this study was limited to magnetite and goethite, similar approach can be applied to other reactive minerals and clays, for example, gibbsite, kaolinite and montmorillonite, etc. In addition, different minerals and clays coexist and form complex heterogeneous assemblages in the environment. It is necessary to study the mobility and fate of contaminants in single mineral vs mixed assemblages. Further studies are required to examine antibiotics adsorption onto different minerals to get a better understanding of fate and transport of antibacterial agents in soils and sediments.

This current work studied the adsorption and transport of a single antibiotic, however, many different antibiotics coexist in nature. In multicomponent systems, coexisting antibiotics can compete for surface binding sites, or cooperatively bind by co-neutralization of surface charge and/ or by direct molecular interactions.² In such a case, it is necessary to investigate the adsorption and transport of multiple antibiotics in mixed systems to identify the competitive or cooperative effects on adsorption. In addition, different parameters, such as solid/solution ratio, pH, ionic strength, coexisting ligands, flow rates etc. should be studied systematically to fully understand the hydrodynamic transport behavior of antibiotics at different environment relevant conditions.

NOM is ubiquitous in soils and aquatic systems and is reported to play import roles in the mobility and fate of other contaminants.^{3–7} This study used leonardite humic acid (LHA) as model NOM to study the fraction of NOM in column and its effects on antibiotic transport under flow-through conditions. However, NOM from different origins may have various characteristics, such as different aromaticity, molecular weight, redox potential, functional groups, surface charge, hydrophobicity etc. and so distinct effects on antibiotics transportation are expected. It will be important to investigate

adsorption and fractionation properties of different NOM. Although the present thesis provides valuable information of the structure of the complex goethite/NOM/water interface, as well as the impact of NOM on quinolones adsorption to goethite under flow though conditions, mechanistic modeling approach could not be applied because of the extreme complexity and heterogeneity of NOM. Further studies are required to investigate NOM fractionation mechanisms in order to incorporate these information into surface complexation models based, for example, on the humic-ion binding Model VII⁸ or the Ligand Charge Distribution model.^{9,10} Indeed, both models consider NOM as indivisible macromolecules, and cannot account for NOM fractionation. Moreover, it is also necessary to combine molecular and hydrodynamic modeling coupling flow, transport, and chemical reactions to predict explicitly interactive flow and reaction processes at complex mineral/NOM/water interfaces. In addition to NOM, it is also necessary to test the impacts of other naturally occurring ligands on the adsorption and transport of antibiotics.

The transport and mobility of contaminants are strongly related to reactive oxide minerals through adsorption and redox reactions.^{11–15} It will thus important to study the redox transformation of redox-sensitive quinolones at mineral-water interfaces.

The present study investigated transport of NOM and quinolones at fixed flow rate and under water saturated conditions, since different chemical, physical and hydrodynamic properties can affect solute transport, it is also necessary to study the transport process under water-unsaturated and different hydrodynamic conditions. Further studies are required to conduct at various hydraulic conductivity, flow rate, pH, etc. In addition, the effects of physical processes (dispersion, diffusion, dual porosity, flow heterogeneity, microporosity/macroporosity, etc.) on transport process as well as on surface chemical reactions (sorption/desorption and redox reactions) should be studied.

3.2 Perspectives in the long term

Almost all of the studies about fate and mobility of antibiotics in soils have been conducted under ideal laboratory conditions.^{11,16,17} However, it is unknown under which conditions the results obtained in the laboratory can be applied to the field situation. Adsorption and transport processes between contaminants and minerals are more complicated at field scale than that in laboratory. The complexity may come from the existence of a wide range of zones at field scale with different chemical, physical and hydrodynamic properties. The soil properties, such as organic carbon content, moisture, texture

and pH etc. as well as the microbes in soils will affect the transformation and the transport of contaminants and preferential flow phenomena may be common in coarse-textured soil at the field scale. Field experiments should be carried out to better understand the fate and mobility of contaminants in real environments (e.g. soils, sediments, groundwater, etc.). In addition, more investigates should be studied to reveal how data from the bench scale is applied to field scale simulations, and how to incorporate scaling behaviors in reactive transport models to describe the distribution and fate of contaminants in the field.

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Titre: Devenir et transport des quinolones à l'interface oxydes de fer / eau

Mots clés : Quinolones, Oxydes de fer, Adsorption, Transport, Modélisation numérique

Résumé: En raison de leur utilisation accrue, de nombreux contaminants émergents, comme les antibiotiques de type quinolone sont retrouvés dans l'environnement. Leur devenir étant fortement contrôlé par leur interaction avec surfaces minérales, cette thèse a eu pour objectif de comprendre et prédire l'adsorption de quinolones sur des minéraux dans des conditions environnementales variées (pH, salinité, présence de cations et d'anions naturels, etc...) et de développer des modèles de transport réactif. Une approche innovante a alors été développée, combinant des données cinétiques et thermodynamiques, des mesures spectroscopiques in situ et de la modélisation de la complexation de surface. Cette thèse est divisée en deux sections. La première a eu pour but de déterminer les mécanismes de complexation de quinolones sur des oxydes de fer (goethite et magnétite) dans des conditions réduites

et dans l'eau de mer. La stœchiométrie de la magnétite (Fe(II)/Fe(III)) s'est avéré être un facteur majeur de contrôle de l'adsorption de l'acide nalidixique (NA). Les effets compétitifs et coopératifs de différents ions présents dans l'eau de mer ont pu être prédits avec précision en réacteur fermé et en colonne (conditions de flux). La deuxième partie de la thèse s'est penchée sur les interactions entre goethite avec des ligands ubiquistes dans l'environnement, comme la matière organique naturelle (MON), et leur impact sur le transport de quinolones. L'adsorption de NA sur la goethite en présence et en l'absence de MON, ainsi que le fractionnement de la MON, ont été étudiés en colonne. Ces résultats pourraient permettre de mieux comprendre et prédire le devenir des quinolones dans l'environnement.

Title: Fate and transport of quinolones at iron oxides /water interface

Keywords : Quinolones, Iron Oxide, Adsorption, Transport, Numerical Modeling

Abstract : Due to their extensive use, many emerging contaminants, such as quinolone antibiotics, are released to the environment. Because their environmental fate is largely controlled by their interaction with mineral surfaces, such as iron oxides, this thesis aimed to assess quinolones adsorption onto minerals under environmental relevant conditions (pH, ionic strength, presence of ubiquitous cations and anions, etc.) and develop reactive transport models. To address these issues, an innovative approach combining kinetic and thermodynamic data, in situ spectroscopic measurements and surface complexation modeling, was proposed. This thesis manuscript consists of two parts. The first part investigated the binding mechanisms of quinolones onto iron oxides (goethite and magnetite) under reducing or seawater conditions. Considerable impact of the magnetite stoichiometry (Fe(II)/Fe(III)) on its sorption capability towards nalidixic acid has been demonstrated. Competitive and synergetic effects of different seawater ions on quinolone adsorption to goethite were accurately predicted under static and water saturated flow-through conditions. The second part investigated the interactions of goethite with naturally occurring ligands such as natural organic matter (NOM) and their impacts on the mobility/transport of quinolones. Interactions of NOM and goethite and effects on the surface hydrophilicity were first investigated. Then, nalidixic acid adsorption to goethite and to NOM-covered goethite and NOM fractionation were examined under flow-through conditions. These results may have important implications for assessment and prediction of the fate of quinolones antibiotics in the environment.