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## Influence of magnetite stoichiometry on the binding of emerging organic contaminants

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1 **Influence of magnetite stoichiometry on the binding of emerging**  
2 **organic contaminants**

3

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17

## 18 **Abstract**

19 While the magnetite stoichiometry (*i.e.* Fe(II)/Fe(III) ratio) has been extensively studied for  
20 the reductive transformation of chlorinated or nitroaromatic compounds, no work exists  
21 examining the influence of stoichiometry of magnetite on its binding properties. This study,  
22 for the first time, demonstrates that the stoichiometry strongly affects the capacity of  
23 magnetite to bind not only quinolone antibiotics such as nalidixic acid (NA) and Flumequine  
24 (FLU), but also salicylic acid (SA), natural organic matter (humic acid, HA) and dissolved  
25 silicates. Fe(II)-amendment of non-stoichiometric magnetite (Fe(II)/Fe(III) = 0.40) led to  
26 similar sorbed amounts of NA, FLU, SA, silicates or HA as compared to the stoichiometric  
27 magnetite (*i.e.* Fe(II)/Fe(III) = 0.50). At any pH between 6 and 10, all magnetites exhibiting  
28 similar Fe(II)/Fe(III) ratio in the solid phase showed similar adsorption properties for NA or  
29 FLU. This enhancement in binding capability of magnetite for NA is still observed in  
30 presence of environmentally relevant ligands (e.g. 10 mg L<sup>-1</sup> of HA or 100 μM of silicates).  
31 Using surface complexation modeling, it was shown that the NA-magnetite complexation  
32 constant does not vary with Fe(II)/Fe(III) between 0.24 and 0.40, but increases by 8 orders of  
33 magnitude when Fe(II)/Fe(III) increases from 0.40 to 0.50.

## 34 I. Introduction

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

52 In this work, we elucidate these effects in different magnetite suspensions containing  
53 Nalidixic Acid (NA) or Flumequine (FLU) (see their structures and speciation in Fig. S1).  
54 Because of their growing use in human and veterinary medicine and continuous release into  
55 the environment, quinolone antibiotics such as NA and FLU have been detected in surface  
56 waters, groundwaters and sediments at concentrations levels ranging from  $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$ .<sup>17–</sup>  
57 <sup>19</sup> As the mobility of these compounds in the environment can be strongly affected by  
58 interactions with surfaces of soil and sediment mineral particles<sup>18–19</sup>, a thorough

59 understanding of their sorption behavior is essential. Magnetite and more generally iron  
60 (oxy)(hydr)oxides represent important reactive surfaces towards organic ligands in soils and  
61 sediments.

62 Here, we examined both ligand adsorption and Fe(II) dissolution as a function of pH for  
63 magnetites exhibiting different Fe(II)/Fe(III) ratio, prepared as such, or through Fe(II)  
64 recharge of non-stoichiometric magnetite suspensions. The binding capability of magnetite  
65 with respect to Fe(II)/Fe(III) ratio was also examined in presence of naturally occurring  
66 ligands (e.g. salicylic acid (SA), silicates and humic acid (HA)). Implication of ternary surface  
67 complexation (i.e. surface-metal-ligand complex) in enhancement in ligand adsorption was  
68 assessed by investigating the impact of other divalent cations (Mn(II), Ni(II)) on NA  
69 adsorption, where metal binding with no electron transfer is supposed to occur on magnetite.  
70 We then used surface complexation modeling to describe the observed behavior, and to gain  
71 further insights into the mechanisms responsible for enhancing ligand sorption upon Fe(II)-  
72 recharge. The present work notably revealed a considerable impact of the magnetite  
73 stoichiometry on the sorption capability of magnetite surfaces.

74

## 75 **II. Experimental**

76 **Chemicals.** If not mentioned, chemicals (all pro analytical quality or better) were obtained  
77 from Sigma Aldrich. Leonardite Humic Acid standard (LHA) was purchased from the  
78 International Humic Substances Society (IHSS). Solutions were prepared with ultrapure  
79 “MilliQ” water (specific resistivity,  $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) purged with  $\text{N}_2$  for 4 h. Magnetite (ideal  
80 formula:  $\text{Fe}_3\text{O}_4$ ) was synthesized applying a procedure involving a room temperature aqueous  
81 precipitation method in an anaerobic chamber (JACOMEX). A 0.3 M HCl solution containing  
82 a  $\text{FeCl}_2:\text{FeCl}_3$  1:2 molar ratio was introduced into an  $\text{N}_2$ -sparged 25% w/v ammonium  
83 ( $\text{NH}_4\text{OH}$ ) solution, with continuous stirring at 1400 rpm, leading to instantaneous

84 precipitation of magnetite particles. Because washing steps can lead to the loss of Fe(II),<sup>6</sup> no  
85 washing step was applied to obtain the stoichiometric magnetite (M0.50; the number refers to  
86 Fe(II)/Fe(III) ratio). The solid concentration was 25 g L<sup>-1</sup> (5g in 200 mL) and the pH was 8.3.  
87 Other magnetites, Fe(II)-depleted, were obtained from M0.50. By applying one washing step  
88 to a fraction of M0.50 suspension with N<sub>2</sub>-purged ultrapure water and then centrifuged for 5  
89 min at 4000 rpm, M0.44 was obtained. By applying three washing steps to M0.50, M0.40 or  
90 M0.42 can be obtained. By exposing the M0.50 during 24h to a known amount of H<sub>2</sub>O<sub>2</sub>  
91 (following the procedure of Gorski et al.<sup>6</sup>), M0.42 (denoted as M0.42-H<sub>2</sub>O<sub>2</sub>) and M0.33 were  
92 obtained. By exposing the M0.50 during 24h to ambient air, M0.24 was obtained.

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

101 An aliquot of each magnetite suspension was taken and digested in N<sub>2</sub>-sparged 5 M HCl  
102 inside the glovebox overnight with shaking. Dissolved Fe(II) and Fe(III) concentrations were  
103 then determined using the phenanthroline method.<sup>20</sup> This bulk Fe(II) content was found very  
104 close to that determined by acid digestion on the filtered solid, as previously reported.<sup>5,6</sup> The  
105 amount of magnetite bound-Fe(II) ( $[\text{Fe(II)}]_{\text{bound}} = [\text{Fe(II)}]_{\text{tot}} - [\text{Fe(II)}]_{\text{aq}}$ ) was used to calculate  
106 the effective Fe(II)/Fe(III) ratio (denoted as  $(\text{Fe(II)/Fe(III)})_{\text{bound}}$ ) in magnetite which was  
107 shown to vary with pH (see results and discussion section).  $[\text{Fe(II)}]_{\text{tot}}$  is the total concentration

108 of Fe(II) in the suspension (solid + solution) and  $[\text{Fe(II)}]_{\text{aq}}$  is the dissolved concentration of  
109 Fe(II), measured after filtration (0.2  $\mu\text{m}$ , Whatman) of the magnetite suspension.

110 **Adsorption experiments.** Adsorption batch experiments were carried out in 15 mL  
111 polypropylene tubes under anaerobic conditions (glovebox). NaCl concentration was set to 10  
112 mM for all experiments. The effect of dissolved Fe(II) on NA or FLU adsorption to magnetite  
113 was investigated by adding small amounts of 100 mM  $\text{FeCl}_2$  solution (dissolved in 0.1 M  
114 HCl). pH was adjusted using 0.1 M NaOH/HCl solutions. After 24h reaction time, an aliquot  
115 was taken and filtered (0.2  $\mu\text{m}$ , Whatman) for high performance liquid chromatography  
116 analysis with UV-vis detection (HPLC-UV) and dissolved Fe(II) analysis by the  
117 phenanthroline method. Aqueous concentrations of NA or FLU were determined using HPLC  
118 (Waters 600 Controller) equipped with a reversed-phase C18 column (250 mm $\times$ 4.6 mm i.d., 5  
119  $\mu\text{m}$ ) and a UV-vis detector (Waters 2489). The mobile phase was mixture of  
120 acetonitrile/water (60/40 v/v) contained 0.1% formic acid. The flow rate was set at 1 ml  $\text{min}^{-1}$   
121 in isocratic mode. The UV detector was set to 258 nm for NA and 246 nm for FLU.

122 Note that kinetic experiments at pH = 8.5 revealed that (i) NA binding to magnetite  
123 (M0.50 or M0.42) and Fe(II) uptake by M0.42 occurred within less than 5 minutes and (ii) the  
124 order of adding chemicals (i.e. addition of NA to 24h pre-equilibrated M0.42 with Fe(II) or  
125 addition of Fe(II) to 24h pre-equilibrated M0.42 with NA) had no impact on the binding  
126 behavior (See Fig. S3). NA adsorption isotherms on M0.50 and M0.42 were also investigated  
127 at pH = 7 ( $20 \leq [\text{NA}] \leq 300 \mu\text{M}$ ).

128 The same procedure was applied to test the effect of Mn(II) and Ni(II) on NA adsorption to  
129 M0.40. Dissolved Mn(II) and Ni(II) concentrations were determined by Atomic absorption  
130 spectroscopy (AAS, Shimadzu). The effect of 10 mg  $\text{L}^{-1}$  HA or 100  $\mu\text{M}$  silicates on the  
131 adsorption of 20  $\mu\text{M}$  NA to magnetite was also investigated, applying the same procedure.  
132 HA concentrations in solution were monitored using an organic carbon analyzer (Shimadzu



133 TOC-VCSH). SA concentration was determined using UV-Visible spectrophotometer at 297  
134 nm. Silicates concentrations were determined by the molybdenum-blue colorimetric method.<sup>21</sup>  
135 **Surface complexation modeling.** The geochemical speciation code PHREEQC (version 2)<sup>22</sup>  
136 and the “minteq” database provided with this code were used. At infinite dilution, the pK<sub>a</sub> of  
137 NA and FLU equal 6.19 and 6.31, respectively, and the logarithm of the formation constant of  
138 NA-Fe<sup>+</sup><sub>(aq)</sub> and FLU-Fe<sup>+</sup><sub>(aq)</sub> equal 3.99 and 4.23, respectively ; as calculated from reported  
139 conditional constant values and the Davies equation.<sup>23,24</sup> The surface complexation models  
140 developed by Jolsterå et al.<sup>25</sup> for magnetite and maghemite were used to predict NA and FLU  
141 adsorption to magnetite with different stoichiometry. Maghemite  $\gamma$ -Fe<sup>III</sup><sub>2</sub>O<sub>3</sub> is considered as  
142 an extreme example of a non-stoichiometric magnetite (Fe<sup>II</sup><sub>1</sub>Fe<sup>III</sup><sub>2</sub>O<sub>4</sub>), with only Fe<sup>III</sup> in both  
143 tetrahedral and octahedral sites<sup>1</sup>.

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



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

152

### 153 **III. Results and discussion**

154 **Binding capacity vs magnetite stoichiometry.** Nalidixic acid (NA) adsorption to four  
155 magnetites exhibiting different Fe(II)/Fe(III) ratio (0.40, 0.42, 0.44 and 0.50) showed that NA  
156 adsorption was strongly related to the stoichiometry of the particles (*i.e.* Fe(II)/Fe(III) ratio  
157 vary from 0.40 for non-stoichiometric magnetite, to 0.50 for stoichiometric magnetite; Fig.

158 1a). NA adsorption to M0.40 decreased with increasing pH, as typically encountered for  
159 anionic ligands, and became negligible for  $\text{pH} > 7.5$ . Indeed, adsorption of anionic ligands to  
160 mineral oxides is typically greatest under acidic to circumneutral pH, and lowest under  
161 alkaline conditions, with maximum adsorption generally observed at a pH near the  $\text{pK}_a$  (i.e.  
162 6.19 for NA).<sup>27-31</sup> At higher stoichiometry (0.42, 0.44 or 0.50), pH dependence of NA  
163 sorption was significantly altered. NA adsorption increased from pH 6 to  $7 < \text{pH} < 8$  and then  
164 decreased with increasing pH, thereby shifting the maximum NA adsorption to larger pH  
165 values than the  $\text{pK}_a$ . Note that adsorption of NA to M0.42 prepared either by washing or  
166 oxidizing ( $\text{H}_2\text{O}_2$ ) of M0.50 was similar. The data are merged in Fig. 1a (see Fig. S4 for more  
167 details).

168 Fe(II)-amendment of non-stoichiometric magnetite (M0.40 and M0.42) led also to an  
169 enhancement in NA adsorption (Fig. 1a). Indeed, the pH-adsorption curve of NA shifted to  
170 larger pH values with increasing added amounts of dissolved Fe(II), a result suggesting that  
171 NA binding was closely related to the Fe(II) content or Fe(II)/Fe(III) ratio in magnetite. The  
172 Fe(II) recharge of non-stoichiometric magnetite provided the same adsorption capability as  
173 for the corresponding magnetite with higher stoichiometry on the whole pH-range  
174 investigated (i.e.  $\text{Fe(II)/Fe(III)} = 0.42$  for M0.40 + 100  $\mu\text{M}$  Fe(II) and M0.42 ;  $\text{Fe(II)/Fe(III)} =$   
175  $0.44$  for M0.40 + 200 $\mu\text{M}$  Fe(II) and M0.44 ;  $\text{Fe(II)/Fe(III)} = 0.50$  for M0.40 + 500 $\mu\text{M}$  Fe(II),  
176 M0.42 + 400  $\mu\text{M}$  Fe(II) and M0.50).

177 Because of Fe(II) dissolution, the amount of bound-Fe(II) in magnetite can vary  
178 depending on pH, which may affect the NA adsorption. Indeed,  $[\text{Fe(II)}]_{\text{aq}}$  increased with  
179 decreasing pH (no dissolved Fe(III) was found), due to the  $\text{H}^+$  promoted dissolution of  
180 magnetite,<sup>32,33</sup> but also with magnetite stoichiometry (i.e.  $\text{M0.40} < \text{M0.44} < \text{M0.50}$ ) (Figure  
181 1b). Exposing a non-stoichiometric magnetite (M0.40) to 200 or 500  $\mu\text{M}$  Fe(II) led to similar  
182 Fe(II) aqueous concentration as those measured with M0.44 or M0.50, respectively. Note that

183 only up to ~10% of magnetite could dissolve in our experiments (*e.g.* for M0.50 at the lowest  
184 pH investigated, *i.e.* 6). Therefore, the effect of magnetite dissolution on NA adsorption can  
185 be neglected.

186 As expected,  $(\text{Fe(II)/Fe(III)})_{\text{bound}}$  increased with Fe(II)-recharge of non-stoichiometric  
187 magnetite and pH (Figure 1c). Variation in  $(\text{Fe(II)/Fe(III)})_{\text{bound}}$  appeared fully consistent with  
188 the magnetite ability to bind NA. For instance, all magnetites exhibiting similar  
189  $(\text{Fe(II)/Fe(III)})_{\text{bound}}$  values showed similar NA sorbed amounts whatever the investigated pH,  
190 though the dissolved Fe(II) amounts are different (especially at low pH values < 7.5) (Fig.  
191 1b). For instance, M0.50 shows the same binding capability for NA as for the corresponding  
192 Fe(II)-amended magnetite (*i.e.* M0.40 + 500  $\mu\text{M}$  Fe(II) and M0.42 + 400  $\mu\text{M}$  Fe(II)), and  
193 therefore similar surface properties with respect to NA adsorption. This is also true for M0.40  
194 + 200  $\mu\text{M}$  Fe(II) *vs* M0.44, and further illustrated in Fig. S5, where variations of NA sorbed  
195 amounts at pH 7.7 as a function of  $(\text{Fe(II)/Fe(III)})_{\text{bound}}$  followed the same trend for both  
196 stoichiometric magnetite (M0.5) and Fe(II)-amended non-stoichiometric magnetites (M0.40  
197 and M0.44). Likewise, enhancement in Flumequine (FLU) adsorption was observed with  
198 increasing amounts of added Fe(II) to M0.40 or  $(\text{Fe(II)/Fe(III)})_{\text{bound}}$  (Fig. S6). Desorption tests  
199 were conducted by adjusting pH to 11 after the system has reached equilibrium and then  
200 stirred for around 2 h. Mass balance showed that NA or FLU was removed only by adsorption  
201 and that transformation by, for example, reduction, did not occur under the experimental  
202 conditions of this study.

203 Formation of ternary surface complexes (*i.e.* surface-metal-ligand complex) generally  
204 entails more ligand adsorption when complexing cation concentration increases<sup>34</sup>, which  
205 might explain the enhancement in NA or FLU binding to magnetite. To test this hypothesis,  
206 impacts of presence of two divalent cations (Mn(II) and Ni(II)) on NA adsorption to M0.40  
207 were investigated and compared with that of Fe(II). Because the redox potential of the

208  $\text{Mn}^{\text{II}}/\text{MnO}_{2(\text{s})}$  couple at  $\text{pH} = 7$  is much larger than that of  $\text{Fe}^{\text{II}}/\text{Fe}_3\text{O}_{4(\text{s})}$ , Mn(II) oxidation by  
209 magnetite is not expected.<sup>35</sup> According to the Irving-Williams series,<sup>36</sup> cation adsorption  
210 data<sup>35</sup> and aqueous complexation with NA,<sup>23,37</sup> ternary surface complexation of Mn(II), Fe(II)  
211 and Ni(II) with NA on magnetite are supposed to follow the order:  $\text{Mn(II)} < \text{Fe(II)} < \text{Ni(II)}$ <sup>34</sup>  
212 (assuming that no electron transfer occurs between Fe(II) and the solid). This ranking is,  
213 however, observed neither for metal uptake nor for NA adsorption to M0.40 (Fig. 2). Indeed,  
214 more Fe(II) uptake than Ni(II) is achieved (Fig. 2a), whereas maximum NA adsorption was  
215 obtained at  $\text{pH} \approx 7.5$  for Fe(II) and  $\text{pH} \approx 8.5$  for Mn(II) and Ni(II). This observation is also  
216 confirmed at higher metal concentration (e.g.  $500\mu\text{M}$ , Fig. S7), thereby underscoring a  
217 different adsorption behavior of NA in presence of Fe(II) with respect to other divalent  
218 transition metals.

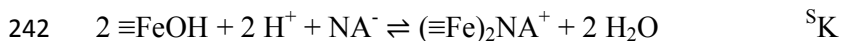
219 Taken together, these findings suggest that the adsorption enhancement for NA is mainly  
220 controlled by the  $(\text{Fe(II)}/\text{Fe(III)})_{\text{bound}}$  ratio in magnetite, rather than by NA-Fe(II)  
221 complexation in solution at low pH or ternary surface complexation. As a matter of fact,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

225

226 **Description of enhancement sorption capacity.** As an attempt to describe the  
227 relationship between  $(\text{Fe(II)}/\text{Fe(III)})_{\text{bound}}$  and ligand adsorption, we used a surface  
228 complexation modeling approach. The aim of the present modeling exercise was to provide a  
229 semi-quantitative evaluation of how much magnetite surface reactivity towards quinolones is  
230 affected by its stoichiometry. Because of the possible presence of various types of  
231  $\equiv\text{Fe}^{\text{II/III}}\text{O(H)}$  groups at magnetite surfaces, full mechanistic description of binding  
232 mechanisms using a complete approach would have required fitting of many parameters, and

233 then generated large errors on simulated phenomena. Therefore, we used the 2-pKa-CCM  
234 approach developed by Jolsterå et al.<sup>25</sup>. Using acid-base titration method, they have calculated  
235 site densities of 1.50 nm<sup>-2</sup> and 0.99 nm<sup>-2</sup> for magnetite (91 m<sup>2</sup> g<sup>-1</sup>) and maghemite (86 m<sup>2</sup> g<sup>-1</sup>),  
236 respectively

237 As shown in Figure S8, fitting experimental adsorption isotherms of NA on M0.50 and  
238 M0.42 at pH = 7 with Langmuir equation results in a maximum binding capacity of 0.95 and  
239 0.71 NA molecule nm<sup>-2</sup>, respectively. Previous studies on quinolones binding to iron  
240 (hydr)oxides evidenced that one molecule binds to two surface hydroxo groups,<sup>29,38,39</sup> by  
241 involving its carboxylate and its keto-group as following:



243

244 Hence, the maximum binding of NA to magnetites corresponds to 1.90 to 1.42 site nm<sup>-2</sup>,  
245 which are relatively close to those determined by Jolsterå et al.<sup>25</sup>. As the present modeling  
246 exercise aimed to determine surface complexation constant (<sup>S</sup>K) to each magnetite, we  
247 focused only on the pH-edge curve (obtained at low surface coverage) and thus used the same  
248 site density for all magnetites (1.50 nm<sup>-2</sup>). Measured total dissolved Fe(II) concentration in  
249 solution at the end of each adsorption experiment was used as input parameter to account for  
250 ligand-Fe(II) complexation in solution. However, decreasing ligand adsorption with  
251 decreasing pH (i.e. at high [Fe(II)]<sub>aq</sub>) could not be well predicted, further suggesting that  
252 effects of variation of (Fe(II)/Fe(III))<sub>bound</sub> were more important than the ligand-Fe(II) aqueous  
253 complexation. Therefore, we only focused on data at high pH values, where  
254 (Fe(II)/Fe(III))<sub>bound</sub> is maximal and constant (see Fig. 1c; e.g. pH > 8 for M0.50, pH > 6.5 for  
255 M0.40). As shown in Figure 1a (NA) and Figure S6 (FLU), a relatively good fit to the  
256 adsorption data versus pH was found (unsuccessful extrapolations at lower pH are shown as  
257 dotted lines in Fig. 1a and S6). When plotting log <sup>S</sup>K for NA versus (Fe(II)/Fe(III))<sub>bound</sub> (Fig.

258 3), a linear relationship was found ( $R^2=0.99$ ). Data for FLU are also included and show a  
259 comparable behavior. Values of  $\log {}^S K$  increased by almost 8 orders of magnitude with  
260 increasing  $(\text{Fe(II)/Fe(III)})_{\text{bound}}$  from 0.40 to 0.50, suggesting that stoichiometric magnetite  
261 (Fe(II)-enriched) may have a much stronger affinity for NA or FLU than partially oxidized  
262 magnetite (Fe(II)-depleted). Such large variation in  $\log {}^S K$  cannot be attributed to potential  
263 modification in surface site density that was neglected by using the same site density for all  
264 magnetites. As more amount of Fe(II) at the magnetite surface is expected upon Fe(II)  
265 recharge, we may suppose that  $\equiv\text{Fe}^{\text{II}}\text{O}(\text{H})$  sites are more reactive than  $\equiv\text{Fe}^{\text{III}}\text{O}(\text{H})$  for NA or  
266 FLU binding.

267 To test the binding capacity of magnetite with lower stoichiometries, we prepared  
268 M0.33 and M0.24 (similar to magnetites found in some natural samples<sup>40,41</sup>), by exposing the  
269 M0.50 during 24h to (i) a known amount of  $\text{H}_2\text{O}_2$  (following the procedure of Gorski et al.<sup>6</sup>)  
270 and (ii) ambient air, respectively. Both oxidized magnetites exhibited similar NA adsorption,  
271 whereas  $[\text{Fe(II)}]_{\text{aq}}$  were found very low (Fig. 1b). For  $\text{pH} \leq 7$ , more pronounced NA  
272 adsorption was observed on M0.33 and M0.24 as compared to M0.40, a result that can be  
273 attributed to the complete suppression of dissolved Fe(II) at low pH. Consistently, the best  
274 fitting values of  ${}^S K$  were found very close for M0.24, M0.33 ( $\log {}^S K = 17.7$ ) and M0.40 ( $\log$   
275  ${}^S K = 17.5$ ). It is worth noting that the calculated surface complexation constant  ${}^S K$  remains  
276 constant for  $0.23 < \text{Fe(II)/Fe(III)}_{\text{bound}} < 0.40$ , and then sharply increased after 0.40 (Fig. 2).  
277 The existence of a threshold may be related to the surface amount of magnetite bound-Fe(II)  
278 required to trigger the enhancement of NA binding with magnetite surfaces.

279 Because non-stoichiometric magnetites may have oxidized magnetite/maghemite-like  
280 structure at the outermost surface (oxidation of magnetite particles is supposed to take place  
281 from the surface to the core<sup>25</sup>), NA adsorption to magnetites with  $\text{Fe(II)/Fe(III)} \leq 0.42$  was  
282 also evaluated using the surface complexation model developed for maghemite (i.e. fully

283 oxidized magnetite). Because of the little variation in site density, surface area and acid-base  
284 properties,  $\log K$  (for NA and FLU) determined using magnetite model or maghemite model  
285 were found very similar (Fig. 4).

286 This modification in binding properties is not specifically limited to NA or FLU  
287 molecule, since the adsorption of naturally occurring ligands such as salicylate (1-  
288 hydroxybenzoic acid, SA), humic acid (HA) and silicates (Si) was also considerably enhanced  
289 by the addition of dissolved Fe(II) to a non-stoichiometric magnetite M0.40 (See Figures S9-  
290 S11). Consequently, the stoichiometry of magnetite is not only a key parameter for Fe(II)  
291 uptake<sup>5</sup> and contaminant reduction<sup>6,10,11</sup> but also for the binding of emerging organic  
292 contaminants and naturally occurring ligands. Because emerging contaminants binding to  
293 magnetite might be affected by naturally occurring ligands, competitive experiments between  
294 NA and HA or Si were conducted. The presence of 100  $\mu\text{M}$  Si decreased NA binding to  
295 magnetite due to ligand competition, though the effect of Si on NA adsorption to M0.40 is  
296 insignificant (Fig. 4a). However, the impact of 10  $\text{mg L}^{-1}$  HA on NA binding implies both  
297 competitive (i.e. antagonistic effect) and cooperative (i.e. synergetic effect) mechanisms (Fig.  
298 4b). Indeed, at high Fe(II)/Fe(III), HA effectively decreases NA binding whereas, at low  
299 Fe(II)/Fe(III), NA binding is enhanced in presence of HA. The latter may arise from  
300 intermolecular interactions between HA and NA, as previously observed between NA and  
301 other organic compounds at goethite surfaces,<sup>38,39</sup> and supported by a quinolone-HA binding  
302 study.<sup>42</sup> While further investigations are required to understand the different competitive and  
303 cooperative effects, this data further supports that (i) binding properties of magnetite is  
304 affected upon Fe(II)-recharge, and (ii) this change towards adsorption of emerging  
305 contaminants is still observed in presence of naturally occurring ligands.

306 **Environmental implications.** Magnetites of differential composition and  
307 stoichiometry may exist in natural systems depending on the local redox and chemical

308 conditions, particularly in Fe-rich subsurface environments or temporary flooded soils (e.g.  
309 wetlands experiencing redox potential fluctuation).<sup>1,2,38,39</sup> Given its higher solubility and  
310 surface area-to-volume ratio, Fe(II) release and/or surface oxidation may occur for the  
311 nanosized magnetite, commonly found in environmental systems<sup>1</sup>. On the other hand,  
312 different kinds of magnetite can be obtained depending on the synthesis method, as reported  
313 in water remediation studies using magnetite as sorbent.<sup>27,31,32</sup> Consequently, the  
314 stoichiometry of magnetite and its potential Fe(II)-enrichment or Fe(II)-depletion in reaction  
315 medium should be appropriately considered in sorption and reactive transport studies. It is  
316 worth noting that the changes in binding properties of magnetite upon Fe(II)-recharge are still  
317 observed in presence of natural ligands, emphasizing the importance of the presently  
318 evidenced mechanisms in environmentally relevant conditions. Therefore, these findings call  
319 for refinements in current day modeling approaches used in the prediction of fate of organic  
320 contaminants in Fe-rich subsurface environments or magnetite-based remediation processes.

321

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325

326 **Supporting Information Available.** Characterization data of magnetite particles, NA and  
327 FLU aqueous speciation versus pH, surface complexation model parameters, additional  
328 results for adsorption kinetics and isotherms, impacts of cationic metals, Si and HA on  
329 adsorption behavior. This information is available free of charge via the Internet at  
330 <http://pubs.acs.org/>.

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- 442

443 **Figure captions**

444 **Figure 1.** (a) NA adsorption data versus pH for 50 m<sup>2</sup> L<sup>-1</sup> suspensions of M0.24, M0.33,  
445 M0.40, M0.42, M0.44, M0.5 and Fe(II)-amended M0.40 and M0.42 versus pH in a 10 mM  
446 NaCl + 20 μM NA solution, after 24h reaction time. Lines correspond to surface  
447 complexation modeling results (see text for more details). (b) Final Fe(II) aqueous  
448 concentration ([Fe(II)]<sub>aq</sub>) and (c) calculated (Fe(II)/Fe(III))<sub>bound</sub> in the corresponding  
449 experiments. The same legend is used in (a), (b) and (c). The same color is used for  
450 experiments conducted with the same total Fe(II)/Fe(III) ratio.

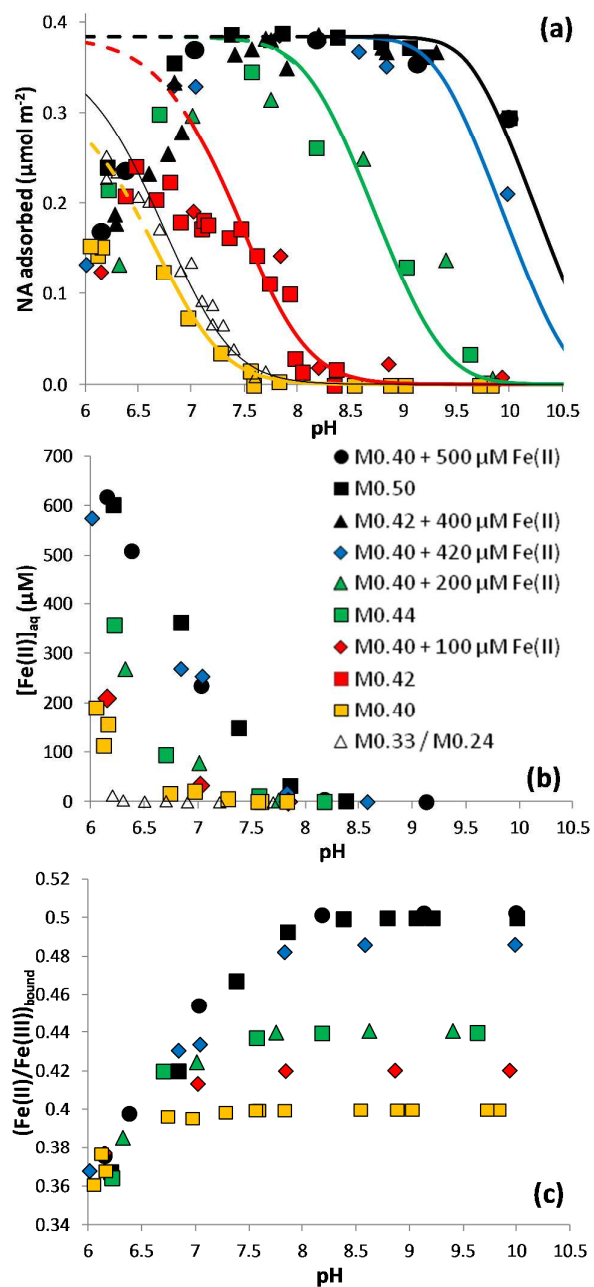
451 **Figure 2.** (a) Uptake data of 200μM Mn(II), Fe(II) or Ni(II) on M0.40 and (b) corresponding  
452 NA adsorption data versus pH. Experimental conditions: 50 m<sup>2</sup> L<sup>-1</sup> suspensions of magnetite,  
453 10 mM NaCl, 20 μM NA, 200μM Mn(II), Fe(II) or Ni(II), 24h reaction time. Negative values  
454 for Fe(II) uptake at low pH are due to magnetite dissolution.

455 **Figure 3.** Logarithm of surface complexation constant (log <sup>S</sup>K, for NA or FLU) versus  
456 (Fe(II)/Fe(III))<sub>bound</sub> determined at pH ≥ 8 (where (Fe(II)/Fe(III))<sub>bound</sub> is constant). This  
457 modeling data was obtained using either a magnetite model (for all data) or maghemite (for  
458 Fe(II)/Fe(III) ≤ 0.42).<sup>25</sup>

459 **Figure 4.** NA adsorption data versus pH for 50 m<sup>2</sup> L<sup>-1</sup> suspensions of M0.40 and Fe(II)-  
460 amended M0.40 in a 10 mM NaCl + 20 μM NA solution, after 24h reaction time, in presence  
461 of (a) silicates (100 μM) or (b) HA (10 mg L<sup>-1</sup>). Empty symbols represent the NA adsorption  
462 data without Si or HA.

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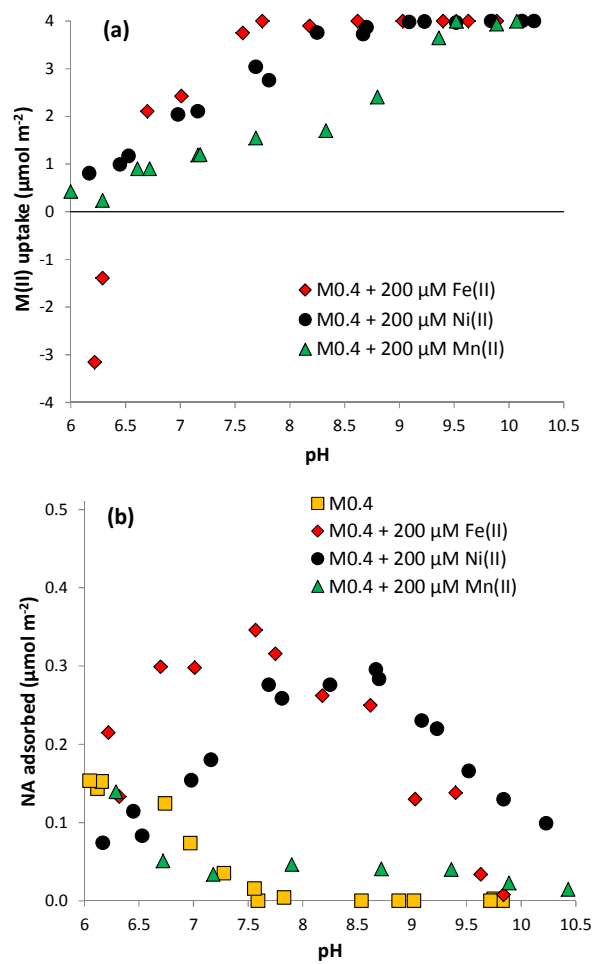
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Figure 1



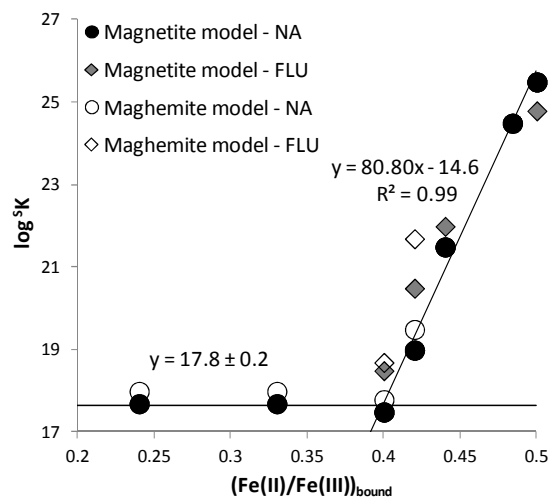
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**Figure 2**

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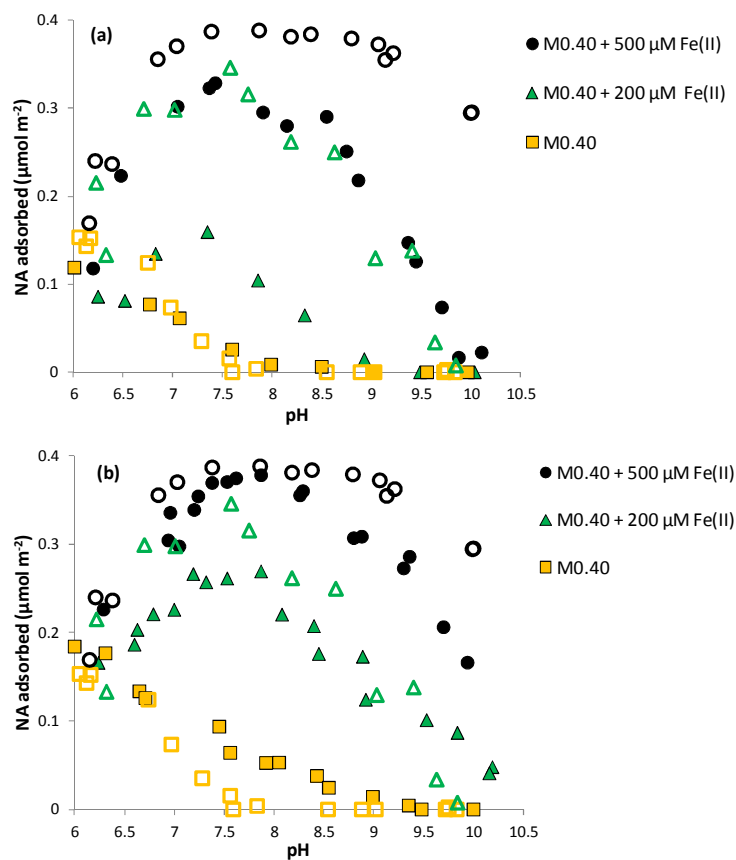
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**Figure 3**

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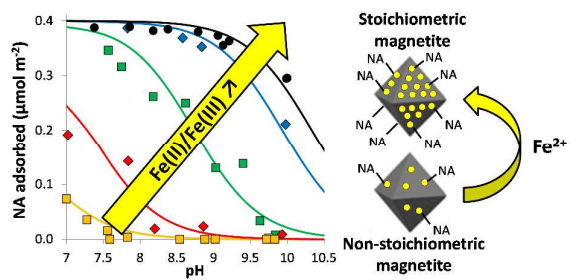
**Figure 4**

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## TOC



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