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1 Redistribution of Electron Equivalents between Magnetite and Aqueous Fe^{2+}

2 Induced by a Model Quinone Compound AQDS

3

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28 **ABSTRACT:**

29 The complex interactions between magnetite and aqueous Fe^{2+} ($\text{Fe}^{2+}_{(\text{aq})}$)
30 pertain to many
31 biogeochemical redox processes in anoxic subsurface environments. The effect
32 of natural organic
33 matter, abundant in these same environments, on $\text{Fe}^{2+}_{(\text{aq})}$ -magnetite
34 interactions is an additional
35 complex that remains poorly understood. We investigated the influence of a
36 model quinone
37 molecule anthraquinone-2,6-disulfonate (AQDS) on
38 $\text{Fe}^{2+}_{(\text{aq})}$ -magnetite interactions by
39 systematically studying equilibrium $\text{Fe}^{2+}_{(\text{aq})}$ concentrations, rates and extents
40 of AQDS reduction,
41 and structural versus surface-localized Fe(II)/Fe(III) ratios in magnetite under
42 different controlled
43 experimental conditions. The equilibrium concentration of $\text{Fe}^{2+}_{(\text{aq})}$ in Fe^{2+} -
44 amended magnetite
45 suspensions with AQDS proportionally changes with solution pH or initial AQDS
46 concentration,
47 but independent of magnetite loadings through the solids concentrations that
were studied here.

39 The rates and extents of AQDS reduction by Fe^{2+} -amended magnetite
40 proportionally increased
41 with solution pH, magnetite loading, and initial $\text{Fe}^{2+}_{(\text{aq})}$ concentration, which
42 correlates with the
43 corresponding change of reduction potentials for the Fe^{2+} -magnetite system.
44 AQDS reduction by
45 surface-associated Fe(II) in the Fe^{2+} - magnetite suspensions induces solid-state
46 migration of
47 electron equivalents from particle interiors to the near-surface region and the
48 production of
49 non-magnetic Fe(II)-containing species, which inhibits $\text{Fe}^{2+}_{(\text{aq})}$ incorporation or
50 electron injection
51 into magnetite structure. This study demonstrates the significant influence of
52 quinones on
53 reductive activity of the Fe^{2+} -magnetite system.

48 INTRODUCTION

49 Magnetite (Fe_3O_4), one of the most common iron oxides, plays an
important role in
50 contaminant transformation, microbial extracellular respiration, and
biogeochemical cycling of
51 elements.¹⁻⁴ In addition, the growing use of magnetite for environmental and
industrial
52 applications may increase the release of synthetic magnetite into the
environment.⁵⁻⁷ In anoxic
53 subsurface environments magnetite can be formed from various
biogeochemical processes, such
54 as microbial or abiotic Fe(III) reduction and the weathering of Fe(II)-bearing
minerals.^{8, 9} Its
55 inverse spinel structure and mixed valent characteristics lead to a dynamic
exchange of ferrous
56 iron between the solid state and solution by topotactic oxidation/reduction
processes.¹⁰ This
57 exchange enables magnetite to encompass a range of stable stoichiometries
that reflect a variable
58 total oxidation state along a binary solid-solution with oxidized end-member
maghemite, as
59 described by the equation below:¹¹

61 Thus, the complex equilibria between $\text{Fe}^{2+}_{(\text{aq})}$ and magnetite can result in
variable properties and
62 redox reactivities of magnetite in natural environments.^{2, 3, 11-18} Although some
efforts have been
63 made to understand $\text{Fe}^{2+}_{(\text{aq})}$ -magnetite interactions under environmentally
relevant conditions,^{12-15,}
64 ¹⁸most of them have focused on sorption behavior of $\text{Fe}^{2+}_{(\text{aq})}$ onto magnetite
of different
65 stoichiometries¹⁴ or rates/extents of contaminant reduction by $\text{Fe}^{2+}_{(\text{aq})}$
associated with magnetite
66 nanoparticles.^{12, 13} Recent studies revealed that stable mineral recrystallization
can happen when
67 magnetite nanoparticles are exposed to $\text{Fe}^{2+}_{(\text{aq})}$ in low-temperature (<100 °C)
aqueous systems.^{15,}
68 ¹⁹⁻²¹ However, few studies have addressed electron transfer processes between
magnetite and

69 $\text{Fe}^{2+}_{(\text{aq})}$ under more complex environmental conditions. We recently examined the flow of electron

70 equivalents in the form of Fe(II) across the magnetite-solution interface and
 found that the
 71 equilibrium between $\text{Fe}^{2+}_{(\text{aq})}$ and magnetite can be easily and reversibly
 influenced by fluctuations
 72 in solution pH and $\text{Fe}^{2+}_{(\text{aq})}$ concentration.¹⁸ But the extent to which this applies
 to the less pristine
 73 settings expected in more complex environmental systems has not yet been
 addressed.
 74 For example, natural organic matter (NOM) may also affect $\text{Fe}^{2+}_{(\text{aq})}$ -
 magnetite interactions
 75 via their redox-accessible functional groups, such as quinones,²²⁻²⁴ Moreover,
 many
 76 microorganisms can use endogenous or exogenous quinone-like compounds as
 electron shuttles to
 77 facilitate extracellular electron transfer with iron oxides at a distance.²⁵⁻²⁷ Both
 $\text{Fe}^{2+}_{(\text{aq})}$ and
 78 magnetite can be formed from or participate in this process, so
 understanding the influence of
 79 redox-active organics on $\text{Fe}^{2+}_{(\text{aq})}$ -magnetite interaction is important for
 mimicking the
 80 biogeochemical complexity in more realistic anoxic subsurface environments.
 Previous studies
 81 mainly focus on redox reaction between iron oxide and reduced quinones.^{22,}
^{23, 28} To the best of
 82 our knowledge, no studies have been reported about the influence of redox-
 active quinones on the
 83 interaction between $\text{Fe}^{2+}_{(\text{aq})}$ and mixed-valent iron oxide. This
 furthermore applies to the
 84 development of magnetite-based remediation strategies designed to exploit its
 high reduction
 85 reactivity and simple magnetic separation.^{23, 29, 30} A magnetite coating often
 develops on the
 86 surface of nanoscale zero-valent iron (nZVI), one of the most studied
 nanomaterials for the
 87 remediation of subsurface contaminants.³¹⁻³³ The influence of ubiquitous redox-
 active organic
 88 compounds on the effectiveness of these remediation strategies is not well
 known.
 89 The objective of this study is to quantitatively assess the effects of redox-
 active organics on
 90 the equilibrium distribution of electron equivalents, in the form of Fe(II),
 between $\text{Fe}^{2+}_{(\text{aq})}$ and

91 magnetite at pH 6-8. We selected anthraquinone-2,6-disulfonate (AQDS) as a model

92 quinone-containing, redox-active compound, which has been well studied and understood in the

93 context as a biogeochemical electron shuttle. In the buffered aqueous solution at pH 6-8, the

94 relevant redox equilibrium of AQDS (E_{AQDS}) is the pH-dependent two electron mass balance

95 between AQDS and AH_2DS given as:²³

96

$$E_{\text{AQDS}} = E_{\text{AQDS}}^0 + \frac{RT}{2F} \ln \left(\frac{[\text{H}^+]^2 + K_{\text{a1}}^{\text{red}} [\text{H}^+]}{K_{\text{a2}}^{\text{red}}} \right) + \frac{RT}{2F} \ln \left(\frac{[\text{AQDS}_{\text{red}}]}{[\text{AQDS}]}\right) \quad (2)$$

98 where $[\text{AQDS}_{\text{red}}]$ is total activity of the reduced AQDS species, including AH_2DS , AHDS^- , and

99 AQDS^{2-} ; $K_{\text{a1}}^{\text{red}}$ and $K_{\text{a2}}^{\text{red}}$ are the corresponding acid dissociation constants of the reduced forms of

100 AQDS. Based on the relationship between E_{AQDS} and equilibrium AQDS speciation, AQDS has

101 been used as a non-sorbing chemical redox probe (CRP) to estimate reduction potentials of

102 heterogeneous iron systems, consisting of $\text{Fe}^{2+}_{(\text{aq})}$ and iron (oxyhydr)oxide.^{23, 24} However, it

103 remains unclear whether or not this method can be applied to mixed-valent iron oxides such as

104 magnetite, because the extent that CRPs are true spectator species that do not influence the

105 distribution of electron equivalents across the magnetite-solution interface and thus its reduction

106 potential is yet unknown.^{14, 34} Our results fill a knowledge gap in fundamental understanding of

107 the effects of quinones on redox processes between $\text{Fe}^{2+}_{(\text{aq})}$ and mixed-valent iron oxides, which

108 has not been systematically studied.

109 In this study, equilibrium concentrations of $\text{Fe}^{2+}_{(\text{aq})}$ were measured as a function of: (i)

110 solution pH; (ii) initial $\text{Fe}^{2+}_{(\text{aq})}$ concentrations ($[\text{Fe}^{2+}_{(\text{aq})}]_{\text{int.}}$); (iii) magnetite loading; and (iv) initial

111 AQDS concentration ($[\text{AQDS}]_{\text{int.}}$).³⁵ In addition, reduction kinetics and equilibrium speciation of

112 AQDS with Fe^{2+} -amended magnetite under the corresponding experimental conditions were also

113 studied using UV-visible (UV-vis) absorption spectroscopy. Moreover, the changes of structural

114 Fe(II)/Fe(III) ratios in magnetite interiors and at particle surface after reaction
with $\text{Fe}^{2+}_{(\text{aq})}$ and
115 AQDS were quantified using micro X-ray diffraction (μXRD) and synchrotron-
based Fe L -edge
116 X-ray absorption (XA) and X-ray magnetic circular dichroism (XMCD)
spectroscopies,
117 respectively.^{2, 11, 16, 18} The systematic quantification of compositional changes
in both magnetite
118 particles and the aqueous solution revealed a significant influence of AQDS
on the equilibrium
119 distribution of electron equivalents in the form of Fe(II) under various
environmentally relevant
120 conditions, which may help us understand the reactivity of $\text{Fe}^{2+}_{(\text{aq})}$ -magnetite
systems in
121 subsurface environments.

122

123 MATERIALS AND METHODS

124 Magnetite synthesis and all wet chemical experiments were conducted
inside an anoxic
125 glovebox. All syringe filters, glassware, and plastic were deoxygenated for at
least 24 h inside the
126 glovebox prior to use. The details of the glovebox, degassed and deionized
water (DDW), and all
127 chemicals for magnetite synthesis and wet chemical experiments were
described in the Supporting
128 Information (SI Section 1).

129 **Magnetite synthesis and characterization.** Magnetite was synthesized
using the
130 co-precipitation method that was previously reported.^{11, 18} The resulting
particles were
131 magnetically separated from the aqueous phase and washed with DDW for
three times to remove
132 residual metal chlorides. After the washing processes, the particles were re-
suspended in DDW (~
133 300 mL) and stored in a sealed bottle covered with aluminum foil and
inside the glovebox.

134 Particle density of the stock suspension, in terms of equivalent Fe(II)
concentration, was measured
135 using an acid digestion method.^{2, 18} The crystal phase, size, morphology, and
specific surface area

of the synthetic particles were characterized by micro X-ray diffraction (μ XRD), transmission electron microscope (TEM), and Brunauer-Emmer-Teller (BET) method, respectively. More details about magnetite synthesis and characterization are provided in SI Section 2.

Quantification of equilibrium concentrations. Batch experiments were conducted to measure final concentrations of $\text{Fe}^{2+}_{(\text{aq})}$ in the magnetite suspensions (69 - 695 mg L^{-1} , the equivalent Fe(II) concentration of 300 - 3000 μM) after equilibration with 0 - 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$ and 0 - 500 μM AQDS at pH 6 - 8 were measured. The buffer solution at pH 7 or 8 was 30 mM HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid, 99.5%) solution, and that at pH 6 was 30 mM MES (2-(N-Morpholino) ethanesulfonic acid, 99%) solution. The buffers were selected, because they have a low capability to complex with metal ions or adsorb onto iron oxide surface.^{36, 37} All experiments were conducted in sealed containers with continuous shaking at 10 rpm using a rotating mixer in the glovebox. Batches with desired magnetite loading and FeSO_4 concentration at a given pH were continuously shaken for 24 h in order to allow the $\text{Fe}^{2+}_{(\text{aq})}$ -magnetite system to reach equilibrium.¹⁴ Then, a certain volume of AQDS stock solution was spiked into the suspension that was shaken for another 24 h, until a new equilibrium state was established. Finally, the suspensions were filtered using 0.2 μm Nylon syringe filters (Whatman), and the first ~ 1 mL filtrate was discarded as a rinse. $\text{Fe}^{2+}_{(\text{aq})}$ concentration and AQDS speciation in the filtrates were measured, respectively, using the ferrozine assay³⁵ and the UV–VIS absorption spectra that were recorded using a Shimadzu UV-2501 PC spectrophotometer inside the glovebox. Within the pH range (pH 6-8) of this study, the interference of Fe^{3+} on the measurements of $\text{Fe}^{2+}_{(\text{aq})}$ by the ferrozine assay is negligible. The initial volume in all experiments was 10 mL, and

157 all experiments were performed at least in triplicate.

AQDS reduction kinetics. Reduction kinetics of 100 μM AQDS by magnetite (300 - 3000 μM [Fe(II)] equivalents) amended with 0 - 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$ at pH 7 - 8 were measured by monitoring the change of AQDS absorbance at 328 nm as a function of time.^{22-24, 38} No experiments were conducted at pH 6, because no measurable AQDS was reduced by 300-3000 μM magnetite amended with 0-1000 μM $\text{Fe}^{2+}_{(\text{aq})}$ at this pH. At pH 7, reduction experiments were initiated by spiking a given volume of AQDS stock solution to a suspension of magnetite equilibrated with a certain concentration of $\text{Fe}^{2+}_{(\text{aq})}$. Sample aliquots (2 mL) were taken using 10 mL syringes at desired time intervals and immediately filtered using 0.2 μm syringe filters. The absorbance spectra of the filtrates were recorded using the Shimadzu UV-2501 PC spectrophotometer inside the glovebox. At pH 8, AQDS reduction by Fe^{2+} -amended magnetite finished within several minutes, so the absorbance at 328 nm,^{22, 23, 38} instead of the whole spectrum, was recorded over time using the UV-VIS spectrophotometer at an interval of 0.2 seconds. The reduction experiments were initiated by spiking a certain volume of AQDS into Fe^{2+} -amended magnetite suspensions in a 3.5 mL screw-cap quartz cuvette that was capped and placed in a Peltier cell holder with a stirring system. Dilute particle suspensions were used in all experiments, so there was no detectable interference from light scattering by magnetite particles. The concentration of reduced AQDS (C_t) at time t (min) was calculated using the difference in absorbance at 328 nm (oxidized form of AQDS).^{22, 23, 38} The first-order rate constant (κ , min^{-1}) during the initial reaction stage of AQDS reduction by $\text{Fe}^{2+}_{(\text{aq})}$ -amended magnetite under different experimental conditions was calculated using the following equation:

$$\ln((C_0 - C_t)/C_0) = \kappa \cdot t \quad (3)$$

179 Where C_0 is the initial concentration of oxidized AQDS. All experiments were carried out at least

180 in triplicate. Because the reduction potentials of pure or Fe²⁺-amended
magnetite are lower than

181 that of reduced AQDS at the conditions present in our experiments (as
discussed below), no

182 experiments with pre-reduced AQDS in the Fe²⁺-magnetite systems were
conducted.

183 **Measurements of Fe(II)/Fe(III) ratios in magnetite.** The crystalline
phase and cell

184 parameters of magnetite in suspensions before and after reaction with Fe²⁺
(_{aq}) and AQDS were

185 measured by μ XRD. According to the linear correlation between the cubic unit
cell parameter (*a*)

186 and the structural Fe(II)/Fe(III) ratio (x_{stru}) in magnetite,¹¹ the change in x_{stru} of
magnetite after

187 reaction with Fe²⁺(_{aq}) and AQDS was determined from the refined unit-cell
parameters. Details

188 about μ XRD measurements and cell parameter refinement were described in SI
Section 2 and our

189 previous studies.^{2, 11, 18}

190 X-ray Magnetic Circular Dichroism (XMCD) was conducted to characterize
the oxidation

191 state and local structure of magnetically ordered iron cations at magnetite
surface (in the

192 outermost few Ångströms of particle surface). The synchrotron XMCD spectra
of magnetite were

193 collected at room temperature on beamline 6.3.1 at the Advanced Light
Source (ALS), Berkeley,

194 CA, using the eight-pole resistive magnet end-station. A nonlinear least-squares
analysis of

195 XMCD spectra was conducted to quantify surface-localized Fe(II)/Fe(III) ratios
(x_{surf}) of

196 magnetite as described in previous studies.^{2, 11, 18}

198 RESULTS AND DISCUSSION

199 TEM images (Figure S1) showed that the synthetic nanoparticles were
nearly spherical with a

200 diameter of 12 ± 2 nm. The BET specific surface area of the nanoparticles
was 55.7 m²/g. The

201 XRD pattern (Figure S2) indicated that magnetite was the only phase
present in the synthetic

nanoparticles.

Effects of AQDS on the equilibrium between magnetite and $\text{Fe}^{2+}_{(\text{aq})}$. Our previous study

shows that, in the absence of AQDS, $\text{Fe}^{2+}_{(\text{aq})}$ release from magnetite is more favorable at pH 6 - 7

due to proton-promoted dissolution of magnetite, while $\text{Fe}^{2+}_{(\text{aq})}$ uptake by magnetite is more

feasible at pH 8.¹⁸ In addition to solution pH, addition of $\text{Fe}^{2+}_{(\text{aq})}$ can also evidently affect the

reactions at the magnetite-solution interface, resulting in the inhibited dissolution at pH 6 - 7 but

the increased $\text{Fe}^{2+}_{(\text{aq})}$ uptake at more basic conditions. Increasing magnetite loading enhanced the

extent of $\text{Fe}^{2+}_{(\text{aq})}$ -magnetite interaction by providing more available surface sites.¹⁸

Correspondingly, the structural and surface-localized Fe(II)/Fe(III) ratios of magnetite changed as

a result of the dynamic $\text{Fe}^{2+}_{(\text{aq})}$ -magnetite interaction. These findings revealed the reversible flow

of Fe(II) across the magnetite-solution interface under different conditions.¹⁸

To study the effect of AQDS on the equilibrium distribution of electron equivalents in the

$\text{Fe}^{2+}_{(\text{aq})}$ -magnetite system, equilibrium concentrations of $\text{Fe}^{2+}_{(\text{aq})}$ ($[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$) in the magnetite

suspensions (69 - 695 mg L⁻¹) amended with 0 - 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$ before and after the addition of

100 μM AQDS at pH 6 - 8 were measured (Figure S3). Figure 1 shows the difference between

equilibrium ($[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$) and initial $\text{Fe}^{2+}_{(\text{aq})}$ ($[\text{Fe}^{2+}_{(\text{aq})}]_{\text{int.}}$) concentrations (i.e., $\Delta[\text{Fe}^{2+}_{(\text{aq})}] =$

$[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}} - [\text{Fe}^{2+}_{(\text{aq})}]_{\text{int.}}$) as a function of magnetite loading under various experimental conditions.

At pH 6, the addition of 100 μM AQDS barely changes $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$ or $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ under the

conditions of the present study. The dominant interfacial reaction at pH 6 is proton-promoted

dissolution of magnetite, which leads to the release of 80.7-575.3 μM Fe^{2+} from 300-3000 μM

magnetite (Figure 1). Correspondingly, the structural Fe(II)/Fe(III) ratio and reduction reactivity

of magnetite decrease after the release of Fe^{2+} . As mentioned above, no

detectable AQDS is

reduced by Fe^{2+} -amended magnetite (300-3000 μM magnetite, 0-1000 μM $\text{Fe}^{2+}_{(\text{aq})}$) at pH 6. Thus,

AQDS is unlikely to be reduced by the partially dissolved magnetite, even with the released Fe^{2+}

at pH 6 under the conditions of this study. As a non-sorbing redox molecule for iron oxide

minerals,²³ AQDS shows no significant impacts on the equilibrium of the non-redox dissolution

reaction.

At pH 7 without added $\text{Fe}^{2+}_{(\text{aq})}$, addition of 100 μM AQDS does not significantly change the

amount of released Fe^{2+} ($\Delta[\text{Fe}^{2+}_{(\text{aq})}]$) (Figure 1A). Only a very small amount (0.6-6.7 μM) of

AQDS was reduced at the end of the experiments at pH 7 (Figure S4). Proton-promoted

dissolution of magnetite is still the dominant interfacial reaction in this case, and the presence of

100 μM AQDS did not obviously affect the extent of magnetite dissolution at pH 7. However,

addition of 100 μM AQDS significantly decreased the value of $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$ in Fe^{2+} -amended

magnetite (Figure S3). Because AQDS cannot be reduced by dissolved Fe^{2+} at pH 7,²⁴ the

observed decrease in $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$ cannot simply be attributed to $\text{Fe}^{2+}_{(\text{aq})}$ oxidation by AQDS. The

production of reduced AQDS (Figure S4) and the corresponding change of the structural

Fe(II)/Fe(III) ratio (x_{stru}) in magnetite (Figure 2) after the addition of AQDS suggest that the

decrease of $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$ is probably related to the redistribution of electron equivalents in the

Fe^{2+} -magnetite system induced by AQDS, which will be discussed further below. In particular,

$\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ changes from positive to negative values (when $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{int}} = 250 - 750 \mu\text{M}$) after

adding AQDS, suggesting that the flow direction of electron equivalents across the

magnetite-solution interface changed from magnetite $\rightarrow$ solution to solution $\rightarrow$ magnetite.

Although adding 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$ to 300-3000 μM magnetite suspensions without AQDS at pH 7

245 can also result in the similar reversal of flow direction,¹⁸ the presence of 100 μM AQDS obviously

decreases the threshold concentration of $\text{Fe}^{2+}_{(\text{aq})}$ for the occurrence of this phenomenon from 1000

μM to 250 μM or less. Thus, the presence of AQDS facilitates the flow of electron equivalents

from the solution phase to the solid phase (i.e. magnetite).

At pH 8, no measurable Fe^{2+} was released from magnetite without added $\text{Fe}^{2+}_{(\text{aq})}$, no matter

whether AQDS was present. In the Fe^{2+} -magnetite system, AQDS is mainly reduced by

surface-associated Fe^{2+} (Fe(II)-Mt), because the reduction rate by Fe(II)-Mt ($[\text{Fe}^{2+}_{(\text{aq})}]_{\text{int}} =$

500-1000 μM , 300 - 3000 μM magnetite is 3 - 5 orders of magnitude faster than that of $\text{Fe}^{2+}_{(\text{aq})}$ or

Fe(II)_{stru} in magnetite under similar conditions (Table S1). Figure 1 shows that addition of 100 μM

AQDS generally results in more negative values of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ (i.e. a greater decrease in $\text{Fe}^{2+}_{(\text{aq})}$

concentration) at pH 8 in $\text{Fe}^{2+}_{(\text{aq})}$ -amended magnetite. Moreover, much more AQDS is reduced by

$\text{Fe}^{2+}_{(\text{aq})}$ -amended magnetite at pH 8 than at pH 7. The fast reduction of AQDS by Fe(II)-Mt at pH

8 drive the flow of electron equivalents from solution to magnetite and change the speciation of

AQDS, which will be discussed further with the XMCD and μXRD results below.

The presence of AQDS also changes the influence of magnetite loading on $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ at pH 7

and 8. In the absence of AQDS, the absolute value of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ increases linearly with the

increase of magnetite loading from 300 to 3000 μM at pH 6 - 8 (Figure 1), probably due to more

surface sites available for $\text{Fe}^{2+}_{(\text{aq})}$ -magnetite interaction with the increase of magnetite loading.¹⁸

However, in the presence of 100 μM AQDS, the absolute values of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ only slightly

increases or fluctuates around a fixed value as magnetite loading increases, when $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{int.}}$ was

0 - 1000 μM at pH 7 or less than 750 μM at pH 8 (Figure 1). As shown in Figure S4, the increase

of mineral loading results in more reduced AQDS, which probably offsets the effect of increasing

mineral loading on $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$.

At the same magnetite loading and initial $\text{Fe}^{2+}_{(\text{aq})}$ concentration, changing initial AQDS concentration ($[\text{AQDS}]_{\text{int.}}$) can also affect the equilibrium between magnetite and $\text{Fe}^{2+}_{(\text{aq})}$. For example, in the suspensions of 3000 μM magnetite with 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$, increasing $[\text{AQDS}]_{\text{int.}}$ from 100 to 500 μM significantly increases the absolute values of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ (i.e. more Fe^{2+} ions transfer from solution to solid) and the equilibrium concentrations of reduced AQDS ($[\text{AQDS}_{\text{red}}]_{\text{eq}}$) (Figure 3). Moreover, the change of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ and $[\text{AQDS}_{\text{red}}]_{\text{eq}}$ with the increase of $[\text{AQDS}]_{\text{int.}}$ is more significant in the suspensions amended with $\text{Fe}^{2+}_{(\text{aq})}$ at the elevated pH (Figure 3). These results show that the presence of AQDS generally decreases equilibrium concentrations of $\text{Fe}^{2+}_{(\text{aq})}$ ($[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$) in the Fe^{2+} -magnetite system at pH 7-8. The extent of this impact depends on solution pH and initial AQDS concentration. However, the decrease of $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$ after addition of AQDS can be related to electron injection from $\text{Fe}^{2+}_{(\text{aq})}$ to magnetite, or electron transfer from $\text{Fe}^{2+}_{(\text{aq})}$ to AQDS, or the change of $\text{Fe}^{2+}_{(\text{aq})}$ to surface-associated Fe^{2+} . The rate and extend of AQDS reduction and the change of Fe(II)/Fe(III) ratios in magnetite are needed to illustrate the flow of electrons in the Fe^{2+} -magnetite system with AQDS.

AQDS reduction by Fe^{2+} -amended magnetite. Kinetic profiles of AQDS reduction by

Fe^{2+} -amended magnetite (300-3000 μM magnetite, 0-1000 μM added $\text{Fe}^{2+}_{(\text{aq})}$) at pH 7 and 8 are shown in Figure S5 and S6, respectively. In 3000 μM magnetite suspension without added $\text{Fe}^{2+}_{(\text{aq})}$, the initial rate of AQDS reduction at pH 8 is one order of magnitude greater than that at pH 7 (Table S1). Reduction potentials of both $\text{AQDS}_{\text{ox}}/\text{AQDS}_{\text{red}}$ and magnetite/ Fe^{2+} couples decrease with increasing pH (Figure S7), but the magnetite/ Fe^{2+} couple has a steeper negative slope (-236 mV/pH)³⁰ than that of $\text{AQDS}_{\text{ox}}/\text{AQDS}_{\text{red}}$ (-59 mV/pH),^{23, 28, 39} resulting in the enhanced reduction

289 rates of AQDS at high pH. Our previous study shows that the bulk structural
Fe(II)/Fe(III) (x_{stru})

in magnetite in the absence of AQDS is higher at pH 8 than that at pH 7, when other experimental

conditions are same.¹⁸ Because reduction potential of magnetite is inversely proportional to x_{stru} in

magnetite,²⁹ magnetite exhibits a higher reactivity for AQDS reduction at pH 8 than at pH 7.

Recent studies of contaminant reduction by Fe^{2+} in the presence of Fe(III)-(oxyhydr)oxide

reported a linear relationship between the logarithms of the surface-area-normalized reduction rate

constants and reduction potentials for oxide-bound Fe^{2+} species, when electron transfer at the

solid/solution interface occurs during or before the rate-limiting step of the reactions.^{24, 40} This

linear free energy relationship (LFER) is also observed in our study. In Figure S8, the

surface-normalized rate constants ($\log k_{SA}$, data shown in Table S2) for AQDS reduction were

plotted versus the reduction potential (E_H) of magnetite suspension (300 to 3000 μM magnetite)

equilibrated with 0 to 1000 μM added $Fe^{2+}_{(aq)}$ at pH 7 and 8. The E_H value of magnetite suspension

was calculated from the measured $[Fe^{2+}_{(aq)}]_{eq}$ using the Nernst equation for the following

half-reaction (for more details about E_H calculation, refer to SI section 3):^{18, 40, 41}

A good linear correlation is observed between $\log k_{SA}$ and E_H for Fe^{2+} -amended magnetite at pH 7

and 8 (Figure S8), suggesting that the rates of AQDS reduction by Fe^{2+} -amended magnetite are

limited by electron transfer across the magnetite-solution interface. On the other hand, the rates of

AQDS reduction significantly increase with the increase of solution pH, magnetite loading, or

$[Fe^{2+}_{(aq)}]_{int.}$ (Table S1). For example, as magnetite loading increases from 300 to 3000 μM , the

reduction rate of AQDS by magnetite amended with 1000 μM $Fe^{2+}_{(aq)}$ increases two orders of

magnitude. The observed faster reduction rates of AQDS reflect the decrease of E_H for

Fe^{2+} -amended magnetite with the change of these experimental conditions.

312 The absorbance spectra of AQDS after reaction with Fe^{2+} -amended
 magnetite at pH 7 - 8
 313 (Figure S9) confirmed that AQDS reduction under these conditions is a two-
 electron transfer
 314 reaction. As shown in Equation 2, AQDS reduction is a pH-dependent reaction.
 When $\text{pH} < \text{pK}_{\text{a1}}^{\text{red}}$
 315 (the acidity constant for the reaction from AQDSH_2 to AQDSH^-), AQDS
 reduction involves
 316 two-electron transfer.⁴² Although the $\text{pK}_{\text{a1}}^{\text{red}}$ value varies (pH 7.2-8.7) in literature, the
 value of 8.1
 317 has been widely used for $\text{pK}_{\text{a1}}^{\text{red}}$.^{22-24, 43} The observed spectra in Figure S9 are
 consistent with the
 318 previous studies.^{23, 38, 44} To study electron balance of the reactions, the change
 of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ ($\delta =$
 319 $\Delta[\text{Fe}^{2+}_{(\text{aq})}]_{\text{without AQDS}} - \Delta[\text{Fe}^{2+}_{(\text{aq})}]_{\text{with AQDS}}$) in Fe^{2+} -amended magnetite before and
 after reaction
 320 with AQDS ($[\text{AQDS}]_{\text{int.}} = 100 \mu\text{M}$) was compared to the amount of electrons
 transferred to AQDS
 321 ($2 \cdot [\text{AQDS}_{\text{red}}]_{\text{eq}}$) (Figure S10). At pH 7, the values of δ are generally greater
 than the
 322 corresponding values of $2 \cdot [\text{AQDS}_{\text{red}}]_{\text{eq}}$, whereas at pH 8 the latter is greater in
 the suspensions
 323 amended with 0 - 500 μM $\text{Fe}^{2+}_{(\text{aq})}$. In all of these experiments, the values of δ
 and $2 \cdot [\text{AQDS}_{\text{red}}]_{\text{eq}}$
 324 are generally different, (Figure S10) suggesting that the change of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$
 after adding AQDS
 325 cannot simply be attributed to AQDS reduction by $\text{Fe}^{2+}_{(\text{aq})}$. Redistribution of
 electron equivalents
 326 between magnetite and aqueous phase may be induced by the addition of
 AQDS, which will be
 327 discussed together with the changes in the Fe(II)/Fe(III) ratios of magnetite.
 328 **Changes of Fe(II)/Fe(III) ratios in magnetite.** The μXRD patterns of
 all post-reaction
 329 samples show that no secondary crystalline phases were produced under all
 experimental
 330 conditions, but the unit-cell parameter of magnetite changed after
 reaction. The values of
 331 structural Fe(II)/Fe(III) ratio in magnetite (x_{stru}) derived from the μXRD patterns
 of magnetite (69
 332 - 695 mg L^{-1}) after reaction with 0 - 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$ and 100 μM AQDS at
 pH 7 and 8 are

333 compared in Figure 3 (data shown in Table S3). The results indicate that
 x_{stru} systematically

334 increases with solution pH, magnetite loading, and $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{int.}}$. Due to the
 negative linear
 335 relationship between reduction potential and x_{stru} value for the magnetite-
 maghemite (Fe_3O_4 -
 336 $\text{Fe}_{8/3}\text{O}_4$) system,⁴⁵ the higher x_{stru} values at the increased solution pH, magnetite
 loading, or
 337 $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{int.}}$ imply the lower reduction potential for magnetite as these
 conditions change. It is
 338 worth mentioning that the decrease of x_{stru} value upon addition of magnetite
 into the buffer
 339 solutions at pH 7 or 8 is due to the pH difference between the stock suspension
 of magnetite (~ 8.5)
 340 and the buffer solutions.^{11, 18} Spiking an aliquot of the stock suspension into
 the buffer solution
 341 can result in a sudden pH decrease, which can induce Fe^{2+} release or solid-
 state migration of
 342 electrons from the interior to the near-surface region. The changes of x_{stru}
 values with solution pH,
 343 magnetite loading, and $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{int.}}$ in the suspensions without AQDS were
 reported and discussed
 344 in our previous study.¹⁸
 345 Because the electrochemical determination of redox potential for Fe^{2+} -iron
 oxide redox
 346 couple in aqueous suspension is still quite challenging, due to the influences of
 many factors, such
 347 as particle aggregation, mass transport, lack of redox equilibria, and formation
 of secondary
 348 phases,^{24, 46} recent studies proposed a method for the estimation of reduction
 potential for
 349 Fe^{2+} -iron oxide redox couples using CRPs, like AQDS.^{23, 24, 47} According to this
 method, reduction
 350 potentials for Fe^{2+} -amended magnetite ($E_{\text{Fe(II)} - \text{Mt}}$) under different conditions
 can be calculated
 351 from $[\text{AQDS}_{\text{red}}]_{\text{eq}}$ and $[\text{AQDS}]_{\text{int.}}$, as shown in Figure S11 (for more details
 about $E_{\text{Fe(II)} - \text{Mt}}$
 352 calculation, see SI Section 4). The results indicate that the values of $E_{\text{Fe(II)} - \text{Mt}}$ became
 more
 353 negative with the increase of magnetite loading, $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{int.}}$, or pH (Figure S11),
 which is
 354 consistent with the trend in x_{stru} values for magnetite (Figure 3). It is worth
 mentioning that, at the

355 same experimental condition, the $E_{\text{Fe(II)}} - E_{\text{Mt}}$ is systematically higher than the calculated

356 calculated value of E_H (Figure S12). Because E_H was calculated mainly based on
 pH and
 357 $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$, the difference between $E_{\text{Fe(II)} - \text{Mt}}$ and E_H can be attributed to the changes of
 magnetite
 358 and the reduction of AQDS in the system (Figure 2 and 3).
 359 As shown in Figure 2 and 3, different $[\text{AQDS}]_{\text{int.}}$ values result in different
 values of x_{stru} ,
 360 $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$, and $[\text{AQDS}_{\text{red}}]_{\text{eq}}$ in the suspensions of $\text{Fe}^{2+}_{(\text{aq})}$ -amended magnetite,
 so the
 361 correspond ing $E_{\text{Fe(II)} - \text{Mt}}$ values for Fe^{2+} -amended magnetite can be different with
 the increase of
 362 $[\text{AQDS}]_{\text{int.}}$ (Figure S11). For example, as $[\text{AQDS}]_{\text{int.}}$ increases from 100 to 500
 μM in the 3000
 363 μM magnetite suspension amended with 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$ at pH 8, $[\text{AQDS}_{\text{red}}]_{\text{eq}}$
 changes from 95.8
 364 to 368.7 μM (Figure 3), and correspondingly $E_{\text{Fe(II)} - \text{Mt}}$ increases from -277.8 to -250.8
 mV
 365 (Figure S11). On the other hand, $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ changes from -682 to -988 μM
 (Figure 3), indicating
 366 that the change of $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$ is less than the change of $2 \cdot [\text{AQDS}_{\text{red}}]_{\text{eq}}$
 (546 μM). Thus, the
 367 decrease of x_{stru} in magnetite (Table S3) with the increase of $[\text{AQDS}]_{\text{int.}}$ may be
 related to AQDS
 368 reduction by structural Fe(II) in magnetite. The results suggest that increasing
 the initial
 369 concentration of AQDS can increase the flow of $\text{Fe}^{2+}_{(\text{aq})}$ from solution to solid,
 promote oxidation
 370 of structural Fe(II) (i.e. the decrease x_{stru}) in magnetite, and increase the
 reduction potential of the
 371 Fe^{2+} -magnetite system ($E_{\text{Fe(II)} - \text{Mt}}$). Thus, $E_{\text{Mt} - \text{Fe(II)}}$ calculated from equilibrium
 AQDS
 372 speciation represents the reduction potential for the Fe^{2+} -magnetite system
 after equilibration with
 373 AQDS, which can be different from the value of the system before AQDS
 addition. Caution must
 374 be taken when comparing $E_{\text{Mt} - \text{Fe(II)}}$ values calculated from equilibrium
 speciation of CRPs with
 375 different initial concentrations. In addition, reduction potentials of mixed-valent
 iron oxides, such
 376 as magnetite and green rust, depend on the structural Fe(II)/Fe(III) ratio

(x_{stru}) .²⁹ Even in the

377 reactions with other common CRPs, like carbon tetrachloride, 4-chloronitrobenzene (4-CINB),

378 and 2-chloroacetophenone, x_{stru} in the mixed-valent iron oxides may also
 change as the reactions
 379 proceed. For example, the reduction of 4-CINB by green rust was found to be
 increasingly slower
 380 over time, and correspondingly the reduction potential of the suspension
 gradually increased.⁴⁸
 381 X-ray absorption spectra indicate the increasing Fe(III) contents in green rust
 during reaction,
 382 suggesting that x_{stru} in green rust decreased during the reaction with 4-CINB.
 Different types of
 383 CRPs may with mixed-valent iron oxides to different extents, and
 correspondingly the measured
 384 reduction potentials from equilibrium speciation of CRPs may be different.
 385 In addition to structural Fe(II)/Fe(III) ratio (x_{stru}) of magnetite, the oxidation
 state and local
 386 structure of magnetically ordered iron cations at the magnetite surface
 (x_{surf}), before and after
 387 reaction with $Fe^{2+}_{(aq)}$ and AQDS, were also analyzed using Fe L_{2,3}-edge XMCD.
 Addition of 100
 388 μ M AQDS to magnetite suspensions ([Fe(II)] equivalents = 3000 μ M) without
 added $Fe^{2+}_{(aq)}$
 389 increases x_{surf} at both pH 7 and pH 8 (Figure 4 and Table 1). The
 corresponding structural
 390 Fe(II)/Fe(III) ratio decreases after adding AQDS (Table 1), suggesting that
 AQDS induces the
 391 solid-state migration of electrons from the interior to the near-surface region
 in magnetite under
 392 these conditions. However, in the magnetite suspensions amended with 1000
 μ M $Fe^{2+}_{(aq)}$, addition
 393 of 100 μ M AQDS obviously decreased x_{surf} at pH 7 and 8. The different
 changes of x_{surf} values
 394 after addition of AQDS in magnetite and Fe^{2+} -amended magnetite
 suspensions suggest different
 395 flow directions of electron equivalents in the system under different
 conditions, as discussed
 396 below.
 397 **Redistribution of electron equivalents induced by AQDS.** To study
 the effect of AQDS on
 398 mass and electron balance in $Fe^{2+}_{(aq)}$ -magnetite interactions under different
 experimental
 399 conditions, $\Delta[Fe^{2+}_{(aq)}]$ and $[AQDS_{red}]_{eq}$, as well as x_{stru} and x_{surf} in magnetite,

before and after

400 addition of 100 μM AQDS are compared in Table 1. Because of the limited beam
 time for XMCD
 401 measurements, only some representative samples were analyzed using
 XMCD. The x_{stru} value
 402 (0.498) of 3000 μM magnetite in the pH 7 buffer solution without added $\text{Fe}^{2+}_{(\text{aq})}$
 was smaller than
 403 that (0.544) of magnetite in the stock suspension (pH = ~ 8.5), due to the
 release of 250.5 μM
 404 $\text{Fe}^{2+}_{(\text{aq})}$ from magnetite after transferring magnetite from the stock solution to
 the buffer solution.
 405 The value of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ (250.5 μM) measured from chemical analysis is
 consistent with the
 406 decrease (251 μM) of structural Fe(II) in magnetite ($[\text{Fe(II)}_{\text{stru}}]$) that is calculated
 from the μXRD
 407 results (for details of $[\text{Fe(II)}_{\text{stru}}]$ calculation, see SI section S5). Thus, in the
 suspension without
 408 added $\text{Fe}^{2+}_{(\text{aq})}$ at pH 7, the increase of $[\text{Fe}^{2+}_{(\text{aq})}]$ is mainly attributed to Fe(II)
 release from
 409 magnetite structure as a result of proton-promoted dissolution.¹⁸
 410 Addition of 100 μM AQDS to the suspension under the same condition (pH
 = 7, 3000 μM
 411 magnetite) decreases the value of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ from 250.5 to 206.7 μM , and the
 corresponding value
 412 of $[\text{AQDS}_{\text{red}}]_{\text{eq}}$ is 6.7 μM (Table 1). There are 220.1 μM electron equivalents
 transferred from
 413 magnetite to the solution ($\Delta[\text{Fe}^{2+}_{(\text{aq})}] + 2*[\text{AQDS}_{\text{red}}]_{\text{eq}}$ in Table 1). The
 calculated decrease of
 414 $[\text{Fe(II)}_{\text{stru}}]$ in magnetite after reaction with AQDS is ~ 287 μM (for details of Δ
 $[\text{Fe(II)}_{\text{stru}}]$
 415 calculation, see SI Section S5.2), which is greater than the amount of electron
 equivalents
 416 transferred from magnetite to the solution ($\Delta[\text{Fe}^{2+}_{(\text{aq})}] + 2*[\text{AQDS}_{\text{red}}]_{\text{eq}}$). The
 decrease of x_{stru} and
 417 the increase of x_{surf} in magnetite after addition of AQDS (Table 1) suggest solid-
 state migration of
 418 electrons from the particle interior to the near surface region induced by
 AQDS reduction on
 419 magnetite surface. This similar outward migration of electron equivalents in
 magnetite structure
 420 was observed in the reduction of pertechnetate anions ($[\text{TcO}_4^-]$) and a bacterial
 enzyme MtoA by

421 magnetite.¹⁶ The calculated $[\text{Fe(II)}_{\text{stru}}]$ in the near-surface region is 319.4 μM
higher than the value

422 before reaction with AQDS (SI section S5.2). Thus, the difference between
 the calculated Δ
 423 $[\text{Fe(II)}]_{\text{stru}}$ from μXRD and the amount of $(\Delta[\text{Fe}^{2+}_{(\text{aq})}] + 2*[\text{AQDS}_{\text{red}}]_{\text{eq}})$ can be
 attributed to the
 424 solid-state migration of electrons from the particle interior to the near surface
 region. Although the
 425 amount (250.5 μM) of Fe^{2+} released from 3000 μM magnetite at pH 7 is
 theoretically sufficient for
 426 complete reduction of AQDS (100 μM), only a limited amount (6.7%) of AQDS is
 reduced in the
 427 system (Table 1). It is possible that accessibility to structural and surface-
 associated Fe(II) , and the
 428 coupled diffusion of the electrons to maintain charge balance in the solid,
 control the extent of
 429 AQDS reduction. Thus, in magnetite suspensions without added $\text{Fe}^{2+}_{(\text{aq})}$ at pH 7,
 the slight
 430 reduction of AQDS by Fe(II) in magnetite structure inhibits magnetite
 dissolution but induces
 431 solid-state migration of electrons from the interior to the near-surface region of
 magnetite.
 432 The amendment of 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$ to magnetite suspensions (3000 μM)
 at pH 7 results in
 433 the decrease of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ (Table 1), due to inhibition of magnetite dissolution
 by added $\text{Fe}^{2+}_{(\text{aq})}$.¹⁸
 434 Addition of 100 μM AQDS changes $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ from positive to negative values,
 and
 435 correspondingly 98% AQDS is reduced by the Fe^{2+} -magnetite system. The
 decrease of $[\text{Fe}^{2+}_{(\text{aq})}]_{\text{eq}}$
 436 is much more than the value of $2*[\text{AQDS}_{\text{red}}]_{\text{eq}}$, so not all electrons are
 transferred from $\text{Fe}^{2+}_{(\text{aq})}$ to
 437 AQDS. Both x_{stru} and x_{surf} in magnetite decreased after addition of AQDS to the
 Fe^{2+} -magnetite
 438 system (Table 1). The observed decrease of x_{stru} is probably attributed to solid-
 state migration of
 439 electrons from the interior to the near-surface region of magnetite due to
 AQDS reduction by
 440 surface-associated Fe^{2+} , which is similar to the phenomenon in magnetite
 suspensions without
 441 added $\text{Fe}^{2+}_{(\text{aq})}$. However, different from the case without added $\text{Fe}^{2+}_{(\text{aq})}$, x_{surf} of
 magnetite amended
 442 with 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$ obviously decreases after AQDS addition, which might
 be related to a

443 change of Fe(II) speciation on magnetite surface. XMCD is only sensitive to magnetically ordered

444 Fe(II) in the near-surface region of magnetite, but the XAS signal corresponds
 to both magnetic
 445 and non-magnetic Fe in the system. The intensity of Fe(II) peak in the XAS
 signal did not
 446 obviously decrease after addition of AQDS (Figure S13), suggesting the
 formation of
 447 non-magnetic Fe(II)(OH)₂-like species on magnetite surface in this case. This is
 different from the
 448 results of the Fe²⁺-magnetite system without AQDS, in which no stable Fe(II)
 surface complexes
 449 or secondary Fe²⁺ precipitates are formed.¹⁴ Further studies are needed to
 investigate the effect of
 450 AQDS on the complexation of Fe²⁺ on magnetite surface. There are no peaks of
 secondary phases
 451 in the μ XRD patterns of all post-reaction samples, indicating that the non-
 magnetic
 452 Fe(II)(OH)₂-like species is probably amorphous or at a quantity below the
 detection limit of
 453 μ XRD. The formation of Fe(II)(OH)₂-like species also makes it difficult to get a
 closed
 454 mass/charge balance from the changes of aqueous solution and magnetite. The
 results suggest that,
 455 in Fe²⁺-amended magnetite suspension at pH 7, AQDS promotes the transfer
 of electron
 456 equivalents from aqueous solution to magnetite, inhibits incorporation of Fe²⁺ or
 electron injection
 457 into magnetite structure, and also induces the production of non-magnetic Fe(II)
 (OH)₂-like species
 458 on magnetite surface.
 459 In magnetite suspension (3000 μ M) without added Fe²⁺_(aq) at pH 8, no
 measurable Fe²⁺_(aq) is
 460 released from magnetite ([Fe²⁺_(aq)] = 0 μ M), no matter whether AQDS is
 present (Table 1).
 461 Addition of 100 μ M AQDS results in 80.8 μ M reduced AQDS ($2*[AQDS_{red}]_{eq} =$
 161.6 μ M), and
 462 correspondingly decreases x_{stru} in magnetite from 0.526 to 0.501. The
 decrease of [Fe(II)]_{stru} in
 463 magnetite after reaction with AQDS is ~ 159 μ M (for details of $\Delta [Fe(II)]_{stru}$
 calculation, see SI
 464 Section S5.3) that is close to the value of $2*[AQDS_{red}]_{eq}$ (161.6 μ M). Thus,
 AQDS is reduced

465 mainly by structural Fe(II) of magnetite in this case. The value of x_{surf} slightly increases from

466 0.584 to 0.590 after AQDS addition (Table 1), implying the similar solid-
 phase migration of
 467 electron equivalents in magnetite that is mentioned above.
 468 The amendment of 1000 $\mu\text{M Fe}^{2+}_{(\text{aq})}$ to the 3000 μM magnetite suspension
 at pH 8 induces
 469 the uptake of 555 $\mu\text{M Fe}^{2+}_{(\text{aq})}$ by magnetite, coupled to an increase of x_{stru}
 from 0.526 to 0.538.
 470 The increase of x_{stru} is attributed to the incorporation of Fe^{2+} into magnetite
 structure or electron
 471 transfer from sorbed Fe(II) to structural Fe(III) in the underlying magnetite.
 After addition of 100
 472 μM AQDS to Fe^{2+} -amended magnetite at pH 8, AQDS is completely reduced,
 and $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$
 473 changes from -555 to -750 μM (Table 1). Correspondingly, the value of x_{stru}
 (0.525) for magnetite
 474 in this case is similar to that (0.526) of magnetite in the pH 8 buffer solution
 without added $\text{Fe}^{2+}_{(\text{aq})}$
 475 or AQDS. The increase in the absolute values of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ (195 μM) is close
 to the value of
 476 $2*[\text{AQDS}_{\text{red}}]_{\text{eq}}$ (200 μM), so electron equivalents mainly flows from $\text{Fe}^{2+}_{(\text{aq})}$ to
 AQDS, probably
 477 via the steps involving Fe^{2+} adsorption onto magnetite surface and subsequent
 AQDS reduction by
 478 Fe(II)-Mt. No further $\text{Fe}^{2+}_{(\text{aq})}$ incorporation or electron injection into magnetite
 structure occurred
 479 after AQDS addition under this condition, even though there are excess $\text{Fe}^{2+}_{(\text{aq})}$
 ions in the system.
 480 Compared to the Fe^{2+} -amended magnetite without AQDS, addition of AQDS
 results in the
 481 decrease of both x_{stru} and x_{surf} , which is similar to the trend observed at pH 7
 (Table 1). The XAS
 482 signal (Figure S13) shows the similar intensity of Fe(II) peak before and after
 reaction with AQDS
 483 in the Fe^{2+} -amended magnetite at pH 8, suggesting the presence of non-
 magnetic Fe(II) species on
 484 magnetite surface. The Fe(II) enrichment into surface structure and the
 formation of non-magnetic
 485 Fe(II)(OH)₂-like species after AQDS addition might inhibit $\text{Fe}^{2+}_{(\text{aq})}$ incorporation or
 electron
 486 injection into magnetite structure at pH 8.
 487

488 Environmental Implications

489 The findings in this study reveal that the model quinone molecule AQDS
can significantly
490 impact the interaction between magnetite and dissolved Fe^{2+} , causing changes
in: (i) redox
491 potentials for the Fe^{2+} -magnetite system; (ii) the equilibrium distribution of
 Fe(II) in the
492 magnetite-solution system; and (iii) the change of the structural Fe(II)/Fe(III)
versus
493 surface-localized Fe(II)/Fe(III) in magnetite, under environmentally relevant
conditions. The
494 findings show that the dynamic redistribution of electron equivalents between
 $\text{Fe}^{2+}_{(\text{aq})}$ and
495 mixed-valent iron oxide minerals, such as magnetite, can be significantly
impacted by the
496 presence of quinones, resulting in modified reduction reactivity of minerals.
The inhibition of
497 $\text{Fe}^{2+}_{(\text{aq})}$ incorporation or electron injection into magnetite structure by AQDS in
the Fe^{2+} -amended
498 magnetite suspension at pH 7-8 is consistent with our previous results that
humic acid-coated
499 magnetite transfers electrons between microbial cells of different species
mainly via humic acid
500 on magnetite surface.⁴⁹ Moreover, understanding the effect of quinones on
the flow of electron
501 equivalents in $\text{Fe}^{2+}_{(\text{aq})}$ -magnetite systems can aid understanding of the role of
magnetite in
502 biogeochemical processes and help develop applications of magnetite/zero
valent iron
503 nanoparticles for environmental remediation.

504 At the same time, the equilibrium speciation of AQDS can also be
changed, to different
505 extents, by magnetite in the absence or presence of $\text{Fe}^{2+}_{(\text{aq})}$. AQDS is usually
used as an electron
506 shuttle to promote dissimilatory microbial reduction of Fe(III) oxides.
Because magnetite and
507 $\text{Fe}^{2+}_{(\text{aq})}$ are common products of microbial Fe(III) reduction, the presence of
quinones may not
508 only facilitate electron transfer between microorganisms and iron oxides, but
also influence
509 reduction reactivity of biogenic magnetite. In addition, redox-active quinones

can act as recyclable

510 electron acceptors for anaerobic microbial respiration and become re-oxidized
during aeration of

511 temporarily anoxic systems.⁵⁰ Moreover, natural organic matters contain diverse
quinone moieties,

512 so the effect of other model quinones on Fe²⁺-magnetite interaction deserve
further exploration for

513 understanding the cycling and impacts of natural organic matters in
environmentally relevant

514 redox transition zones.

515

516 **ASSOCIATED CONTENT**

517 Supporting Information. Additional figures and details for Materials and Methods
and Results and

518 Discussion are presented. This material is available free of charge via the
Internet at

519 <http://pubs.acs.org>.

520

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528

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540 Table 1. Charge balance in the 3000 μM magnetite suspensions amended with 0
 - 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$
 541 and 0 - 100 μM AQDS at pH 7-8

Experimental conditions			$\text{Fe}^{2+}_{(\text{aq})}$	AQDS	Electron equivalents [‡]	Changes in magnetite	
$\text{Fe(II)}_{\text{added}}$ (μM)	pH	[AQDS] i nt (μM)	$\Delta[\text{Fe}^{2+}_{(\text{aq})}]^{\dagger}$ (μM)	$2*[\text{AQDS}]_{\text{red}}$ (μM)	$\Delta[\text{Fe}^{2+}_{(\text{aq})}] + 2*[\text{AQDS}]_{\text{red}}$ (μM)	$x_{\text{stru}}^{\perp}$	$x_{\text{surf}}^{\top}$
0	Stoc k	0	0	0	0	0.544	0.538
0	7	0	250.5	0	250.5	0.498	0.604
0	7	100	206.7	13.4	220.1	0.486	0.667
1000	7	0	19.2	0	19.2	0.511	0.714
1000	7	100	-380.0	196.0	-184	0.492	0.643
0	8	0	0	0	0	0.526	0.584
0	8	100	0	161.6	161.6	0.501	0.590
1000	8	0	-555	0	-555	0.538	0.618
1000	8	100	-750	200.0	-550	0.525	0.574

542 [†]The positive values of $\Delta[\text{Fe}^{2+}_{(\text{aq})}]$ represent the increase of $\text{Fe}^{2+}_{(\text{aq})}$, and the
 543 negative values denote

543 the decrease of $\text{Fe}^{2+}_{(\text{aq})}$

544 [‡]The positive values represent the flow of electron equivalents from aqueous
 545 solution to solid, and

545 the negative values denote the opposite direction.

546 [⊥] x_{stru} : structural Fe(II)/Fe(III) ratio deduced from μXRD results

547 [⊤] x_{surf} : surface-localized Fe(II)/Fe(III) ratio deduced from XMCD results

548

Figure 1. Comparison
with 0 (A), 250 (B)
500 (C), 750 (D),
750 (D), 1000 (E)
without (solid sym

icles equilibrated
t pH 6 (black),
).

553
 554 Figure 2. Structural Fe(II)/Fe(III) ratios of magnetite (300 - 3000 μM) in the
 suspensions amended
 555 with 0-1000 μM $\text{Fe}^{2+}_{(\text{aq})}$ at pH 7 (A) and 8 (B) with 100 μM AQDS. (C) Effects of
 initial AQDS
 556 concentration (0-500 μM) on structural Fe(II)/Fe(III) ratios of magnetite (3000
 μM) in the
 557 suspensions without $\text{Fe}^{2+}_{(\text{aq})}$ and with 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$, respectively, at pH 8.

558
 559 Figure 3 Effects of initial AQDS concentrations on (A) the change of $[\text{Fe}^{2+}]$ and (B) the
 560 equilibrium concentrations of reduced AQDS in the 3000 μM magnetite
 561 suspensions without
 562 added $\text{Fe}^{2+}_{(\text{aq})}$ (solid dots) or amended with 1000 μM $\text{Fe}^{2+}_{(\text{aq})}$ (open dots).

565

566 Figure 4 Comparison of XMCD spectra of 3000 μM magnetite NPs before (black)
 567 and after (red)

567 reaction with 100 μM AQDS in the pH 7 buffer solution without (A) or with (B)
 1000 μM added

568 $\text{Fe}^{2+}_{(\text{aq})}$, and in the pH 8 buffer solution without (C) or with (D) 1000 μM added
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