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9 **Geochemical modelling of arsenic adsorption to oxide surfaces**

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16 **Abstract**

17 In natural environments, arsenic chemistry is dominated by the reactions of its two
18 predominant soluble forms arsenate and arsenite. To predict the fate of arsenic in the
19 environment, it is necessary to consider processes that act to restrict its mobility. The
20 mobility of arsenic is strongly influenced by adsorption reactions to particle surfaces.
21 Arsenate and arsenite may form surface complexes with a number of different oxides,
22 including Fe, Al, Mn and Ti oxides. The focus of this chapter is on the adsorption of
23 As(III) and As(V) to the surfaces of oxide surfaces, in particular Fe oxides. We have
24 analysed the existing data for arsenite and arsenate adsorption to ferrihydrite and
25 goethite. Spectroscopic results show that arsenate form bidentate binuclear complexes
26 under all conditions; for arsenite, evidence has been found both for a bidentate
27 binuclear complex and for a weaker outer-sphere complex, which may be of some

1 importance at low ionic strength. We optimized As adsorption parameters for two
2 surface complexation models, Diffuse Layer Model (DLM) and Three-Plane CD-
3 MUSIC Model (TPCD) taking into account these spectroscopic evidence. For arsenate
4 adsorption to ferrihydrite, the new DLM constants imply stronger binding than the
5 previous compilation by Dzombak & Morel (1990), whereas for arsenite the revised
6 DLM constants are in reasonable agreement. The surface complexation models could
7 not be optimized satisfactorily for data sets in which the dissolved arsenite
8 concentration at equilibrium was larger than 10 μM ; the reason for this are discussed.
9 Simulations of competition effects show that *o*-phosphate competes strongly with
10 arsenate over the whole pH range. Silicic acid and carbonate are important
11 competitors in the circumneutral pH range, while sulphate may have a small
12 competitive effect at low pH. Humic substances are important competitors when a
13 large part of the Fe oxides is covered with humic substances. By contrast, calcium
14 promotes arsenate adsorption at alkaline pH because of surface charge effects.

15

16 **Key words:** Geochemical modelling, arsenate, arsenite, Fe-oxides, Al-oxides, surface
17 complexation models, Humic substances.

18

1. Introduction

Arsenic chemistry is dominated by the reactions of its two redox states As(III) and As(V). Under most conditions, the predominant inorganic forms of these are: for As(III), arsenite or arsenious acid (H_3AsO_3); for As(V), arsenate ($\text{H}_2\text{AsO}_4^- / \text{HAsO}_4^{2-}$). Under anoxic conditions, various As-sulphide complexes can dominate the speciation (Nordstrom and Archer, 2002; Wilkin et al., 2003). In addition, methylated As species such as MMA and DMA are present, but generally in rather low concentrations (Cullens and Reimer, 1989.)

To predict the fate of arsenic in the environment, it is necessary to consider processes that act to restrict its mobility. Two groups of processes can be distinguished, precipitation and adsorption. As for the first of these, it is generally acknowledged that most arsenites and arsenates are quite soluble and not likely to form under ambient conditions. For example, a frequently mentioned arsenate phase in the literature is scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ (see, e.g. Dove and Rimstidt, 1985). Numerous characterisations of As-rich environments have shown that this and other arsenate phases are absent or at least nearly so (e.g. Rancourt et al., 2001; Carlson et al., 2002; Inskeep et al., 2004). The As(III) oxide phases claudetite and arsenolite, both with the structural formula As_2O_3 , may be stable in environments with extremely high As(III) concentrations (Nordstrom and Archer, 2002). Under reducing conditions, As-S phases may sometimes control As solubility; two examples are orpiment and realgar.

1 The mobility of arsenic is strongly influenced by adsorption reactions to particle
2 surfaces. Arsenate and arsenate may form surface complexes with a number of
3 different oxides, including Fe, Al, Mn and Ti oxides. In addition, Al silicates with
4 exposed Al octahedra form As surface complexes in much the same way. Recently it
5 has also been shown that considerable As adsorption occur on the surfaces of metal
6 sulphides (Bostick et al., 2002)

7
8 This chapter will focus on the adsorption of As(III) and As(V) to the surfaces of
9 oxide surfaces, in particular Fe oxides. Due to the common occurrence of these
10 oxides, and thanks to their high point-of-zero charge (PZC) and high affinity for As,
11 the sorption onto these oxides is often the dominating feature in the biogeochemical
12 cycling of As. Much effort has been devoted to understanding the As adsorption
13 mechanisms onto these oxides, and to the modelling of this interaction. Predictive
14 modelling of As behaviour in natural systems is clearly at an early stage; however,
15 reviews and experiments both identify surface complexation to oxide surfaces as the
16 main process of interest to describe correctly in such models (Lumsdon et al., 2001;
17 Sracek et al., 2004).

18
19 In their book *Surface complexation modeling*, Dzombak and Morel (1990) reviewed
20 the then existing data for arsenite and arsenate adsorption to “hydrous ferric oxide”,
21 the poorly crystalline Fe oxide now known as 2-line ferrihydrite. Since then many
22 new quantitative data have been published. In addition, spectroscopic research has
23 highlighted the mechanisms by which As(III) and As(V) adsorb; this information
24 should be used to constrain geochemical models. Here we attempt to arrive at
25 improved model descriptions of As(III) and As(V) adsorption, valid for 2-line

ferrihydrite and goethite. Because of their large surface areas and common occurrence, ferrihydrite and goethite are likely to be an important sorbent in many different environments. We will then briefly discuss the modelling of As(III) and As(V) to other important oxide minerals, such as gibbsite.

In addition, we will discuss competition effects and how they can be considered in modelling. As major soil constituents such as phosphate, silicic acid, sulphate and natural organic matter strongly affect As adsorption (e.g., Gustafsson, 2001), it may be necessary to consider competition in a realistic way to have any practical use of surface complexation models for describing As adsorption in soils and sediments.

2. Arsenic adsorption mechanisms

It is now widely recognized that arsenate and arsenite predominantly form strong inner-sphere complexes on Fe and Al oxides, but it is still not clear what structural arrangement that predominates. In pioneering EXAFS and WAXS work on arsenate adsorption to ferrihydrite, Waychunas et al. (1993, 1995, 1996) concluded that arsenate predominantly forms a bidentate binuclear complex under all conditions, in which arsenate was attached to edge-sharing pairs of Fe oxyhydroxyl octahedra. In another EXAFS study, Fendorf and coworkers (1997) found evidence both for monodentate complexes as well as bidentate mononuclear and bidentate binuclear complexes for goethite (see Fig. 1). According to these authors, the binding of arsenate as a monodentate complex is important especially at low surface coverages, whereas the bidentate complexes become more important at higher coverages. According to a recent study (Inskeep et al., 2004), arsenate forms both bidentate

mononuclear and bidentate binuclear complexes to ferrihydrite at high surface coverage. For lepidocrocite, Randall et al. (2001) found that arsenate was bound predominantly as a corner-sharing (binuclear) bidentate complex, using EXAFS. Sherman and Randall (2003) argued that this type of complex was energetically favoured over other arrangements also for hematite, goethite and ferrihydrite, for which similar EXAFS spectra were recorded. Furthermore, they attributed the bidentate mononuclear complexes found by Fendorf et al. (1997) to multiple scattering within the AsO_4 tetrahedron.

Take in Fig. 1 here

In the case of arsenite, limited spectroscopic results are available. In an EXAFS study, Manning et al. (1998) found evidence for the formation of bidentate binuclear complexes to goethite, confirming the IR and XANES spectroscopic results of Sun and Doner (1998).

Arai et al. (2001) investigated arsenate and arsenite binding onto aluminium oxide using EXAFS. They concluded that arsenate formed bidentate binuclear complexes under all conditions; for arsenite, evidence was found both for a bidentate binuclear complex and for a weaker outer-sphere complex, which gained some importance at low ionic strength. Goldberg and Johnston (2001) also obtained evidence for the existence of outer-sphere complexes for arsenite on amorphous aluminium oxide.

In conclusion, most spectroscopic evidence suggests that arsenate predominantly forms bidentate binuclear surface complexes on Fe and Al oxide surfaces. In the case

1 of arsenate, bidentate mononuclear complexes may possibly be of some additional
2 importance at high surface coverage, whereas monodentate complexes may occur to
3 some extent at low surface coverage. This is, however, a controversial matter and
4 needs further study. For arsenite, it seems that weak outer-sphere complexes may be
5 of some additional importance on Al oxide minerals, particularly at low ionic
6 strength.

7
8 Arsenate and arsenite may also be adsorbed to other solid surfaces. Titanium
9 oxides, which have points of zero charge reasonably close to Fe and Al oxides, are
10 probably strong As scavengers. Under reducing conditions and where sulphides are
11 stable, As may be adsorbed also to sulphides such as galena and sphalerite (Bostick et
12 al., 2003). The understanding of these and other As-S interactions is still, however, at
13 an early stage (Wilkin et al., 2003) and any geochemical modelling of these processes
14 would therefore be quite uncertain.

15
16 Apart from arsenite and arsenate, methylated As compounds such as MMA and
17 DMA may be adsorbed to oxides. Few data exist, but available evidence shows that
18 the methylated compounds are adsorbed more weakly than arsenate, but perhaps more
19 strongly than arsenite (Xu et al., 1991; Jing et al., 2004).

20 21 **3. Surface complexation modelling of arsenate and arsenite to ferrihydrite and** 22 **goethite**

23 *3.1. Surface complexation models*

24
25 A number of surface complexation models have been developed, which differ in
26 complexity (for a review of the theory and many previous applications, see Goldberg,

1992, and Venema et al., 1996). In this chapter we will test the applicability of two of these models that represent two extremes in terms of complexity, the 2-pK Diffuse Double-Layer Model (DLM) as used by Dzombak and Morel (1990) and the 1-pK Three Plane Model with the CD-MUSIC option (TPCD), as developed by Hiemstra and van Riemsdijk (1996).

In the DLM, the surface charging of the oxide surface is described with two reactions, shown in the table of species (Table 1), where SOH is a component entity representing a proton-active site to which protons and ions may be adsorbed or desorbed. The acid-base constants $K_{H,1}$ and $K_{H,2}$ include the electrostatic correction term $\exp(-F\Psi_o/RT)$, where F is the Faraday constant, Ψ_o is the electrostatic potential in the o -plane, R is the gas constant and T is the absolute temperature. The electrostatic potential is calculated from the surface charge directly by the Gouy-Chapman equation. Thus, the DLM contains only one plane in which protons and ions may adsorb (the o -plane or surface plane). Furthermore, the description of the potential gradient is simplistic in that no Stern layer is included in the model. On the other hand, the model contains few fixed and adjustable parameters and is therefore simple to set up and run.

Take in Table 1 here

In their compilation of sorption data to 2-line ferrihydrite, Dzombak and Morel (1990) (henceforth referred to as D&M) used the DLM primarily because of the absence of reliable information on the nature of the surface species. The DLM version

of D&M is still widely used despite the fact that structural information now exist that invalidate the model on the process-oriented level. Inadequacies include:

- The inability to distinguish between inner- and outer-sphere complexes
- The inability to account for the different effects of non-complex-forming electrolyte anions on surface charge (Rietra et al., 2000).
- The improper way of the 2-pK model formulation to account for proton binding
- The inability to describe correctly the near-linear dependence of proton surface charge on pH for crystalline oxides

Despite these deficiencies, the DLM may be used as a data-fitting algorithm that may be preferred to some of the isotherm models, as it explicitly tries to take account for coulombic effects on adsorption. The D&M database of complexation constants is frequently used; however, is now outdated and in great need for revision taking into account recent macroscopic data.

In the TPCD model, two Stern layers are included between the diffuse layer and the surface, each with its own capacitance. In the TPCD it is possible to distinguish between, i.e. singly and triply coordinated surface sites. Moreover, the acid-base characteristics of one surface site are described with only one reaction (see Table 2). In the TPCD it is also possible to position adsorbing ions on any of the three different surface planes, and also (as is done in the CD-MUSIC option) to allow the adsorbing ion to spread its valence over two adjacent planes. The TPCD has been shown to provide excellent fits to proton titration data for goethite (Hiemstra et al., 1996) and

also to be able to provide good descriptions of anion adsorption when the reactions have been constrained from spectroscopic information (Hiemstra et al., 1999; Rietra et al., 1999).

Take in Table 2 here

3.2. Strategy for model optimisation

To optimise equilibrium constants for DLM and for TPCD, we used FITEQL 4.0 (Herbelin and Westall, 1999), which was modified to include TPCD (Tadanier and Eick, 2002; Gustafsson, 2003). FITEQL is a non-linear least optimisation program that is based on the Gauss method for unconstrained problems. The main indicator of the goodness-of-fit is given by the overall variance, V_Y , which is defined as:

$$V_Y = \frac{\sum [Y_R(m) / S_R(m)]^2}{n_p n_R - n_u} \quad (1)$$

, where $Y_R(m)$ is the mass balance equation residuals for each data point m and for component R, $S_R(m)$ is the error calculated for $Y_R(m)$ from the experimental error estimates, n_p is the number of data points, n_R the number of R components, and n_u the number of adjustable parameters. The value of V_Y is heavily dependent on the experimental error estimates. To be consistent with the work of D&M, we applied a relative error $S_{\text{rel}} = 0.05$ for $[\text{H}^+]$, $[\text{AsO}_4^{3-}]$ and for $[\text{H}_3\text{AsO}_3]$, and an absolute error $S_{\text{abs}} = 1 \%$ of the total concentration of the sorbing ion.

1 Obtained equilibrium constants were averaged using the weighting method of
 2 D&M, in which the weighting factor w_i is defined as

$$w_i = \frac{(1/\sigma_{\log K})_i}{\sum (1/\sigma_{\log K})_i} \quad (2)$$

4
 5 where $(\sigma_{\log K})_i$ is the standard deviation of $\log K$ calculated by FITEQL for the i^{th}
 6 data set. The best estimate for $\log K$ is then calculated as:

$$\overline{\log K} = \sum w_i (\log K)_i \quad (3)$$

8
 9 In this work we used previously optimised proton-binding parameters for 2-line
 10 ferrihydrite. For the DLM, we used the site density and surface area recommended by
 11 D&M, *i.e.* 2.31 sites nm⁻² and 600 m² g⁻¹. This results in a total site concentration of
 12 0.205 mol mol⁻¹ Fe. The acid-base constants were also taken from D&M, and these
 13 are shown in Table 3.

14 In the case of TPCD, we used the parameters suggested by Gustafsson (2001), *i.e.* a
 15 site density of 4 sites nm⁻² and a surface area of 750 m² g⁻¹, resulting in a total site
 16 concentration of 0.443 mol mol⁻¹ Fe. Only singly coordinated oxygens were assumed
 17 to be proton-reactive. The inner Stern layer capacitance was set at 1.3 C m⁻², and the
 18 outer capacitance was 5 C m⁻², yielding an overall Stern layer capacitance of 1.03 C
 19 m⁻². The acid-base constant and ion-pairing constants for electrolyte anions are shown
 20 in Table 3.

1 For goethite, we used the TPCD model only, because of the known inability of
2 DLM to accurately reproduce acid-base titration data for this mineral (Lumsdon and
3 Evans, 1994). We chose to use the goethite parameters suggested by Hiemstra and
4 Van Riemsdijk (1996), as modified (in the case of the Cl^- and ClO_4^- ion-pairing
5 constants) of Rietra et al. (2000), see Table 3. This means that the site density of
6 singly coordinated FeOH groups was set to $3.45 \text{ sites nm}^{-2}$, whereas the density of
7 triply coordinated Fe_3O groups was $2.7 \text{ sites nm}^{-2}$. The Stern layer capacitances were
8 1.1 and 5 C m^{-2} for the inner and outer layer, respectively. In the modelling, we used
9 the same specific surface areas as determined analytically in the different studies
10 using the $\text{BET}(\text{N}_2)$ method.

11

12 **Take in Table 3 here**

13

14 It should be noted that the surface structure of 2-line ferrihydrite is still not well
15 known, and therefore the proton-binding parameters have been determined by
16 analysing proton titration data only. Unfortunately, similar fits are obtained using
17 different combinations of parameters. For example, Waite et al. (1994) used a site
18 density for the DLM of about 10 sites nm^{-2} , in combination with a much larger site
19 concentration, and obtained a similar fit to the data analysed by D&M. This allowed a
20 better description of U(VI) adsorption at high surface coverage. Until sufficient
21 structural information is available that constrains the values of proton-binding
22 parameters in different models, the choice of “correct” proton-binding parameters is a
23 difficult task. Although we feel that the DLM site density of D&M is probably
24 underestimated, we have chosen to use it here to be consistent with most other
25 previous DLM applications.

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In this work we used the recently reviewed arsenate protonation constants of Nordstrom and Archer (2002, see Table 4), and we used the Davies equation with a 0.3I term for activity corrections. However, for the 0.7 M data sets of Gao and Mucci (2001), we used a 0.2I term in agreement with the method used in their paper. Na-AsO₄ ion pairs were not considered, as relevant constants are not known (Gao and Mucci, 2001).

Take in Table 4 here

An important first step in the model optimisation was to identify the data sets that were suitable for the purpose. We used the following criteria:

1. The method of Schwertmann and Cornell (2000), or an equivalent method, should be used to synthesize 2-line ferrihydrite. The use of iron(III) sulphate salts in the synthesis is not acceptable, due to the strong competition between sulphate and arsenic species at low pH.
2. For ferrihydrite, the adsorbent should be used within a few days after synthesis to prevent further crystallization. Data sets were excluded that involved drying of the ferrihydrite prior to equilibration, as this alters the surface properties (Hofmann et al., 2004).

- 1 3. The equilibration time should be at least 2 h for ferrihydrite and 4 h for
2 goethite. The solid-solution separation should be adequate, using some kind of
3 filter.
- 4
- 5 4. Data sets were excluded where $\Gamma_{\max}$, the largest amount sorbed, exceeded the
6 theoretical adsorption maximum as predicted by the model used.
- 7
- 8 5. In the case of arsenite, data sets with equilibrium As(III) concentrations > 10
9 $\mu\text{mol L}^{-1}$ were excluded because of suspicions of As(III) polymerization at
10 high surface coverage (Stanforth, 1999; Jain and Loeppert, 1999b), c.f. the text
11 below.

12

13 In addition, for the arsenite systems we have assumed that the oxidation to arsenate
14 was negligible. In most studies, the possibility of arsenite oxidation was not checked,
15 but it is known that arsenite is oxidized slowly to arsenate in Fe oxide suspensions.
16 Sun and Doner (1998) reported that after 20 days of reaction, more than 20 % of the
17 adsorbed arsenite had been oxidized to arsenate. As the equilibration times employed
18 in the adsorption studies treated here were much smaller, we believe that the
19 assumption is acceptable.

20

21 3.3. *Modelling arsenate adsorption to ferrihydrite*

22

23 There were 18 data sets that fulfilled the above criteria for TPCD, and for DLM the
24 number of data sets was 16 (Table 5). Among the data sets that were excluded were
25 the ones of Pierce and Moore (1982), in which ferric sulphate was used to synthesize

ferrihydrite. The data sets of Goldberg and Johnston (2001), Goldberg (2002), and Grafe et al. (2002) were not considered because the ferrihydrite samples were dried prior to equilibration. Preliminary investigations on As affinity with FITEQL confirmed that the surface reactivity of the ferrihydrites used in these studies were much lower and therefore incompatible with the present selection. The data set of Holm (2002) was excluded, partly because most experiments were performed using HEPES buffer, and partly because the ferrihydrite synthesis method is not presented in the paper.

Take in Table 5 here

In case of the DLM, only monodentate complexes were considered in the model, despite the fact that spectroscopic evidence clearly indicates that bidentate complexes predominate. However, as was argued above, the total site concentration of the DLM is probably considerably underestimated. In fact, the 2-pK model is partly responsible for this as it involves the transfer of 2 protons to/from a single site across the pH scale, whereas the true figure is likely to be 1, according to the present structural information on Fe oxide surface structures (see, e.g., Hiemstra and van Riemsdijk, 1996). Therefore, a monodentate complex in the DLM may in reality well correspond to a bidentate complex in the TPCD, as a DLM site would encompass two proton-binding sites. Additional reasons for choosing monodentate complexes in the DLM were (i) to be consistent with the complexes chosen by D&M, and (ii) that the use of bidentate complexes instead of monodentate complexes led to poorer fits.

1 In Table 6, we summarize the results from the model optimizations with DLM.
2 Optimised arsenate complexation constants were obtained for most data sets, except
3 the ones of Wilkie and Hering (1996). The weighted log K values are larger than the
4 ones obtained by D&M. The reason is that D&M relied to a considerable extent on the
5 data set of Pierce and Moore (1982), for which the complexation constants were much
6 smaller than for any of the data sets analysed in the present study.

7

8 **Take in Table 6 here**

9

10 As for the TPCD model, we initially tested the use of the bidentate binuclear
11 complexes only (*i.e.* the complexes $\text{S}_2\text{O}_2\text{AsOOH}^-$ and $\text{S}_2\text{O}_2\text{AsO}_2^{-2}$ of Table 2).
12 However, at low pH and high surface coverage, conditions that were encountered in
13 the data sets Fh-AsV-10, Fh-AsV-13 and Fh-AsV-18, this description gave poor fits.
14 Therefore a diprotonated monodentate complex $\text{SOAsO}_3\text{H}_2^{-0.5}$ was introduced (as
15 suggested by Gustafsson, 2001), which provided acceptable descriptions of arsenate
16 sorption under these conditions (Table 7). Clearly this is at odds with spectroscopic
17 results, and we can offer no credible explanation at this point. One possibility is that
18 ferrihydrite is increasingly dispersed at low pH, thus exposing more surface sites to
19 which As can adsorb as bidentate complexes. If so, the error of the model may be
20 connected to the fact that the surface area is assumed to be constant over the whole
21 pH range. However, in the absence of facts, we prefer to include the $\text{SOAsO}_3\text{H}_2^{-0.5}$
22 complex, in order to provide acceptable fits. This illustrates that it is not always easy
23 to constrain surface complexation models with structural information.

24

The weighted log K 's can be seen as generic arsenate binding parameters. Examples of fits are shown in Fig. 2 and Fig. 3, which show the fits to the eight data sets of Jain and Loeppert (2000) and Dixit and Hering (2004). The best fit is to the data sets of Dixit and Hering (2004), for which the generic parameters were very close to the individually optimized log K values. As is clear from the figures, the DLM and TPCD models produced very similar fits to the data. To further test the performance of the models, we applied them to the proton coadsorption stoichiometries recorded by Jain et al. (1999a) for the Fh-AsV-05 and Fh-AsV-06 data sets. The proton coadsorption stoichiometry was defined as the molar amount of H^+ that was co-adsorbed for every mol AsO_4^{3-} adsorbed. When applying the models we used the individually optimized log K values shown in Table 6 and Table 7. It was found that the simulated proton coadsorption stoichiometry was considerably underestimated with DLM at pH 4.6. For the TPCD however, the simulated stoichiometry was reasonably close to observations at both pH 4.6 and pH 9.2 (Table 8). These results show that TPCD is likely to be the better model of the two; this was not unexpected due to the more sophisticated nature of the TPCD model.

Take in Tables 7 and 8 here

Take in Fig. 2 here

3.4. Modelling arsenite adsorption to ferrihydrite

For arsenite, the models were unable to describe arsenite sorption for the whole range of arsenite concentrations used in the different studies. The most dramatic example is one data set by Raven et al. (1998), in which the molar amount of adsorbed As exceeded the total site concentration in both models. In this case, a very

1 large concentration of As(III) (26.7 mM) had been added. However, also at lower
2 surface coverages there were problems, particularly so for the TPCD model.

3
4 To set up the TPCD model we relied on the spectroscopic data obtained by
5 Manning et al. (1998) for arsenite adsorption to goethite, which showed that arsenite
6 adsorbed as binuclear bidentate complexes. Therefore we used a combination of the
7 two bidentate complexes $\text{S}_2\text{O}_2\text{AsOH}^-$ and $\text{S}_2\text{O}_2\text{AsO}^{2-}$ (Table 2). The CD (charge
8 distribution) value for both complexes was fixed at 0.67, in line with that suggested
9 by Rietra et al. (1999), resulting in the stoichiometries shown in Table 2. Although a
10 somewhat larger CD value has been suggested for the $\text{S}_2\text{O}_2\text{AsOH}^-$ complex (Rietra,
11 2001), we found that this led to poorer fits for the majority of data sets.

12
13 However, the TPCD model only produced consistent results when the equilibrium
14 concentration of As(III) was lower than 10 μM . This was seen most clearly for the
15 data sets of Jain and Loeppert (2000). Figure 3 shows the relationship between the
16 modeled and observed As(III) concentration, when using optimized TPCD constants
17 for data set Fh-AsIII-05. At an As(III) concentration above about 10 μM , the model
18 performed poorly and overestimated the equilibrium As(III) concentration
19 considerably. Because this effect was seen also for the other data sets, we decided to
20 use only the data sets for which As(III) < 10 μM throughout for the optimization of
21 generic binding parameters. The optimized TPCD constants are shown in Table 9.
22 The fits of the resulting generic parameters to the data sets of Wilkie and Hering
23 (1996) and Jain and Loeppert (2000) are shown in Fig. 4.

To optimize constants for the DLM, we used a combination of two monodentate complexes (in line with the argument above for arsenate). In this case, we found that the model produced reasonably consistent fits up to an equilibrium concentration of about 1 mM As(III). However, to be consistent with the TPCD modeling, we decided to use the same seven data sets for optimization. The optimized constants are shown in Table 10, and compared to the result of Dzombak and Morel (1990), who only optimized $\log K$ for the most protonated surface complex. For arsenite, there is a reasonable agreement between the D&M constant and the ones obtained here. The V_Y values were, however, rather large (> 20), indicating a poor fit to most of the data sets. It should be noted that the modeling strategy in our work differs from that of Dixit and Hering (2004), who applied DLM to their data, finding optimum values of $\log K_{As5}$ and $\log K_{As6}$ of 4.02 and -2.87 , respectively, whereas we found much larger values for the same data sets (Fh-AsIII-06 and Fh-AsIII-07, see Table 10). The reason is that Dixit and Hering (2004) applied a separate site density for arsenite, amounting to 1.5 times that of the proton site density.

Take in Figs. 3 and 4 here

Take in Tables 9 and 10 here

Although the TPCD model could be used only for equilibrium concentrations lower than 10 μM As(III), the TPCD nevertheless performed much better than the DLM as regards the proton co-adsorption stoichiometry recorded by Jain et al. (1999a), see Table 8. Both models correctly predicted a net proton release (*i.e.* the proton coadsorption stoichiometry was negative), but the simulated TPCD model values were much closer to the observed values. Thus it appears that TPCD was the most realistic

model of the two. If so, it has to be asked: why does the model fail at large equilibrium As(III) concentrations? We can imagine only three different reasons:

1. Arsenite is precipitated as a ferric arsenite surface phase at large As(III) concentrations (Stanforth, 1999). However, this hypothesis is not compatible with the spectroscopic results of Manning et al. (1998) for goethite. Also Jain et al. (1999b) claimed that they could not identify a ferric arsenite phase in their suspensions. Consequently, this hypothesis is probably the least likely of the three presented here.
2. Surface polymerization of arsenious acid occurs. In solution however, arsenious acid polymerizes only at extremely large concentrations (Jain et al., 1999b; Nordstrom and Archer, 2002). Therefore, this hypothesis requires that surface polymerization is enabled considerably by the locally large concentrations of arsenious acid near the oxide surface (Jain et al., 1999b).
3. Arsenite adsorption does not necessarily involve two proton-binding sites, but may involve also, *i.e.* doubly or triply coordinated sites at the oxide surface, or monodentate complex formation. This hypothesis is, however, not easily compatible with Manning's spectroscopic results.

As is clear from the above, all three hypotheses are problematic, and further spectroscopic work is required to elucidate the odd behaviour of arsenite at large equilibrium concentrations. Fortunately, however, as the As(III) concentration in nature is nearly always lower than $10\text{ }\mu\text{M}$ ($= 0.7\text{ mg L}^{-1}$), model applications may not need to reflect this.

3.5. Modelling arsenate adsorption to goethite

Fourteen data sets fulfilled the criteria for optimisation (Table 11). A data set of Hingston (1970) (0.534 mM As added to goethite “C”) was not used because $\Gamma_{\max}$ exceeded the theoretical adsorption maximum with the model used. Three surface complexes were required to fit the data accurately; these are the same as previously suggested by Hiemstra and van Riemsdijk (1999), *i.e.* the two bidentate complexes $\text{S}_2\text{O}_2\text{AsOOH}^-$ and $\text{S}_2\text{O}_2\text{AsO}_2^{-2}$, and a monodentate complex $\text{SOAsO}_3^{-2.5}$, which becomes important at high pH and low surface coverage.

As Table 12 shows, the variation between different data sets in terms of optimised $\log K$'s was larger than for ferrihydrite. This was indicated also by the larger 95 % confidence interval. The smallest $\log K$ values were found for goethites from the Manning and Goldberg group (Manning and Goldberg, 1996; Manning et al., 1998), whereas the goethite used by Gao and Mucci (2001) at low pH exhibited a much stronger affinity for arsenate than the generic parameters would suggest (Fig. 5). Again, as seen in Fig. 5 and in Table 12, the observed arsenate adsorption in the data sets of Dixit and Hering (2004) was very close to that modelled using the generic arsenate binding parameters.

There may be many reasons for the wide variation in the optimized surface complexation constants for goethite. Probably, an important reason is the different equilibration times used. As Fig. 6 shows, there appears to be a relationship between the optimised $\log K_2$ and the equilibration times for individual data sets. Several previous authors (Willett et al., 1988, Strauss et al., 1997; Zhao and Stanforth, 2001;

Gao and Mucci, 2001) showed that at least a couple of days of shaking is required to attain equilibration for phosphate or arsenate adsorption to goethite. Most researchers attribute this to slow diffusion of the adsorbing anion into aggregates. Therefore, a majority of studies have employed insufficient equilibration times, which is mirrored in the lower $\log K_2$. Hence our above mentioned criterium of at least 4 hours equilibration time may not be strict enough, and this would mean that the ‘true’ $\log K$ ’s are likely to be larger than the generic parameters determined here would suggest. On the other hand, as Strauss et al. (1997) showed, prolonged equilibration times leads to anion diffusion into micropore surfaces, which are not measured by the conventional BET(N₂) technique; this would lead to an overestimation of $\log K$ with the optimization method used here. One example of the latter phenomenon could possibly be the large $\log K_2$ determined for the Go-AsV-10 data set, for which the equilibration time was 80 h. Despite the uncertainties, we feel that the arsenate binding parameters presented here are more realistic than earlier estimates.

Take in Figs. 5 and 6 here

Take in Table 11 here

3.6. Modelling arsenite adsorption to goethite

For arsenite adsorption, we used only five data sets for the optimisation of generic surface complexation constants, valid for the TPCD model. Three of these were from the study of Dixit and Hering (2004). Again, data sets with equilibrium As(III) concentrations of $> 10 \mu\text{M}$ were not used. For goethite, however, the mismatch between the model and the observations was less severe at larger concentrations,

1 compared to the case for ferrihydrite. Examples of this are shown in Fig. 7 for the data
2 sets of Manning et al. (1998) and Dixit and Hering (2004), where the data sets with >
3 10 μM dissolved As(III) have been greyed.

4
5 Because of the limited number of data sets analysed, the value of $\log K_{\text{As6}}$ was not
6 constrained sufficiently. This was evidenced from the 95 % confidence interval,
7 which spanned more than an order of magnitude.

8
9 **Take in Fig. 7 here**

10 11 **4. Arsenate and arsenite adsorption to Al oxides**

12
13 Although Al oxides are also potentially important As scavengers, much less work
14 has been made to obtain macroscopic As adsorption data for Al oxides that can be
15 used for modelling. In addition, for crystalline Al oxides such as gibbsite, modelling
16 is complicated due to the existence of different faces with different proton- and anion-
17 binding characteristics (see, e.g., Hiemstra et al., 1999). In an earlier study, we
18 showed the applicability of the TPCD model to the gibbsite data of Hingston et al.
19 (1972) and Manning and Goldberg (1996) in an effort to estimate arsenate-binding
20 parameters for allophane (Gustafsson, 2001). Moreover, in two recent studies,
21 Weerasoriya et al. (2003, 2004) have used the TPCD model to estimate arsenite and
22 arsenate binding to a crystalline gibbsite sample. However, due to the relative lack of
23 macroscopic data and microscopic understanding of the surface structure of Al oxide
24 surfaces, we feel that at present it is premature to suggest generic surface
25 complexation constants for arsenite and arsenate to Al oxides. In our earlier work we
26 showed that allophane may be an important arsenate adsorbent mineral in soils that

1 contain this constituent, but that ferrihydrite and goethite are likely to be more
2 important due to their greater affinity for As (Gustafsson, 2001).

3 4 5 **5. Interactions with other anions and cations**

6 7 *5.1 Interactions with inorganic ions on Fe oxide surfaces – literature evidence*

8 Many previous studies have reported strong effects of other anions and cations on
9 the arsenic binding to Fe oxides. For a long time, phosphate, which adsorbs in a very
10 similar way as arsenate does, has been shown to be a strong competitor with arsenate
11 and arsenite for available sorption sites (Hingston et al., 1971; Manning and
12 Goldberg, 1996; Jain and Loeppert, 2000; Smith et al., 2002). Hiemstra and Van
13 Riemsdijk (1999) showed that it was possible to simulate the competition between
14 arsenate and phosphate using the TPCD model. On the other hand, some authors
15 found it difficult to describe the phosphate-arsenate competition with the surface
16 complexation concept (Manning and Goldberg, 1996; Zhao and Stanforth, 2001); the
17 latter authors attributed this to surface precipitation of Fe-PO₄ and Fe-AsO₄ phases. At
18 present, however, there is no spectroscopic evidence that supports surface
19 precipitation in the concentration ranges employed in these studies.

20
21 In addition, silicic acid has been shown to compete with both arsenate and arsenite
22 for adsorption sites on oxide surfaces (Swedlund and Webster, 1999; Roberts et al.,
23 2004). This competition could be simulated with both the DLM and the TPCD model
24 (Swedlund and Webster, 1999; Gustafsson, 2001).

Carbonate also competes with arsenate for available adsorption sites; this has been shown for ferrihydrite (Appelo et al., 2002) as well as for hematite (Arai et al., 2004). Again these authors showed that surface complexation models could quantitatively account for this competition.

Furthermore, it is also probable that sulphate competes with arsenate and arsenite for adsorption sites (Gustafsson, 2001), although an in-depth study of this interaction has not been published, to our knowledge.

Finally, calcium also affects arsenate adsorption; however, in this case the effect of calcium is to promote arsenate adsorption (Smith et al., 2002). Rietra et al. (2001) showed that the interaction of calcium and phosphate could be explained as a result of the increased positive charge resulting from calcium adsorption, and that no ternary surface complexation or precipitation was probably involved. The interaction could be described with the Basic Stern version of the CD-MUSIC model. As phosphate and arsenate behaves similarly, we expect similar arguments to be valid for the calcium-arsenate interaction.

5.2 Interactions with inorganic ions on ferrihydrite – scenarios using generic parameters

Because so many common ions interact with arsenate on ferrihydrite, it is important to understand, and to be able to predict, the effect of competing ions on arsenic adsorption. This is particularly the case when surface complexation models are used to simulate arsenic behaviour in natural systems. To illustrate the potential importance of the interactions with other inorganic ions, we apply the TPCD model to simulate

1 arsenic adsorption in difficult binary systems, *i.e.* in systems that contain two
2 adsorbing components simultaneously. Of course, in reality many more ions are
3 present at the same time and need to be considered. We have chosen to simulate the
4 adsorption of a constant total amount of As in the presence of a constant dissolved
5 concentration of a competing component, at different pH. This provides a picture of
6 how As adsorption may be affected by competition in soils or sediments with different
7 equilibrium pH values. It should be noted that the graphs presented in Figures 8-12 do
8 not describe As adsorption for *an individual* soil, for which the pH is varied with
9 different acid or base additions, as is the case in a conventional batch experiment. The
10 latter type of simulation, which is equally possible with the parameters used, requires
11 that the total system concentration (*i.e.*, dissolved + adsorbed) of a competing
12 component is constant across the pH range, whereas in our simulation, it is *only the*
13 *dissolved concentration* that is kept constant. To produce the simulations, we have
14 used the surface complexation reactions for competing components described in Table
15 14. These and other simulations of the same type are possible to perform using the
16 Visual MINTEQ software, which is freely available on the web (Gustafsson, 2004).

17
18 The upper black line in the graphs of Fig. 8 shows the expected K_d value for
19 arsenate and arsenite as a function of pH, using the assumption that 10 μM As (as
20 arsenate or arsenite) is added to 1 g L^{-1} of 2-line ferrihydrite in a 5 mM NaCl
21 background electrolyte. The K_d value is dimensionless and defined as mol L^{-1}
22 adsorbed As divided by mol L^{-1} dissolved As. The graphs also show the expected K_d
23 value in the presence of three different *o*-phosphate equilibrium concentrations that
24 span the range expected in most natural environments, *i.e.* from 0.01 to 1 μM .
25 According to our surface complexation approach, it is evident that the adsorption of

1 arsenate and arsenite is very much affected by *o*-phosphate across the whole pH
2 range. For arsenite the effect is particularly dramatic in low-pH environments, where
3 arsenite is expected to adsorb rather weakly because of *o*-phosphate competition.

4
5 The presence of silicic acid also decreases As adsorption. In Fig. 9 we show that a
6 low equilibrium Si concentration (5 μM) only causes a minor effect on arsenate or
7 arsenite adsorption, but in Si-rich environments (Si = 500 μM) the effect can be quite
8 large. The competitive effect is most clearly seen in environments with circumneutral
9 pH (*i.e.*, around 7).

10
11 The graphs for carbonate are very similar to the silicic acid graphs (Fig. 10). Here
12 we have applied different partial CO_2 pressures in the simulation, ranging from $1.8 \times$
13 10^{-4} to 1.8×10^{-2} atm, *i.e.* from about 0.5 to 50 times the ambient atmospheric CO_2
14 pressure. Substantial carbonate competition is expected in circumneutral pH
15 environments that have high partial CO_2 pressures.

16
17 **Take in Figs. 8, 9 and 10 here**

18
19 Sulphate may compete with arsenate and arsenite, but only at low pH (Fig. 11). The
20 effect is rather small except in the lowermost pH range. When other more strongly
21 competing ions such as *o*-phosphate are also present, the sulphate effect becomes very
22 small and is practically negligible at pH > 5 (graphs not shown).

23
24 Calcium clearly differs from the other competing ions considered in that it
25 promotes As adsorption (Fig. 12). In our simulation, the effect is negligible at pH < 7,

1 but it is substantial in the alkaline pH range. The reason why calcium promotes As
2 adsorption is that adsorbing calcium suppresses the development of negative charge
3 on the oxide surface at high pH. Qualitatively, the simulations are very similar to the
4 observations by Rietra et al. (2001) for a Ca-PO₄-goethite system. In systems with
5 more competing anions (i.e., *o*-phosphate), Ca may promote As adsorption even at
6 lower pH values than in Fig. 12; in some systems the effect is visible even at pH 5
7 (graphs not shown).

8
9 **Take in Figs. 11 and 12 here**

10 11 *5.3 Interactions with organic acids*

12
13 Numerous studies have shown that organic acids, for example humic substances,
14 also compete with arsenic for adsorption sites on oxide surfaces (Xu et al., 1988; Xu
15 et al., 1991; Bowell, 1994; Gustafsson and Jacks, 1995; Simeoni et al., 2001; Redman
16 et al., 2002). This is natural given the anionic nature of organic acids and the strong
17 affinity of their carboxylic and phenolic functional groups for oxide surfaces (c.f.
18 Filius et al., 2000). The results are not always consistent; for example, Grafe et al.
19 (2001) showed that As adsorption to goethite was decreased in the presence of peat
20 humic acid and Suwannee River Fulvic Acid, but in a later paper they could not find
21 such an effect in the case of ferrihydrite. The latter results are difficult to explain,
22 although in our view it cannot be excluded that the pre-treatment procedure Grafe et
23 al. (2002) employed (drying), and the short equilibration time they used (2 h), could
24 have affected these results.

1 Because many environments contain large concentrations of humic substances (see,
2 e.g., Gustafsson and Jacks, 1995) the competition between As and humic substances
3 should be potentially important to describe in a model, as was done for the ‘inorganic’
4 competitors in section 5.2. However, it is difficult to describe the sorption of humic
5 substances to oxide surfaces in a simple way, both because of the large number of
6 possible surface configurations and because of the entropic contributions to sorption
7 (Filius et al., 2003). Additional difficulties arise from the fractionation of humic
8 substances that occurs because of the preferential sorption of high-molecular-weight
9 organic acids with many functional groups (Vermeer and Koopal, 1998). Therefore,
10 once adsorbed to the oxide surface, humic substances are difficult to desorb unless the
11 pH is increased considerably (this leads to increased polarity of the humic and at the
12 same time an increased negative charge on the oxide surface) (Avena and Koopal,
13 1998).

14
15 A mechanistically correct model for the adsorption of humic substances to oxide
16 surfaces needs to be fairly involved (see, e.g., Filius et al., 2003). To avoid this, we
17 here suggest a simplified model description, which does not aim to describe correctly
18 the partitioning of humic substances between solution and the adsorbed phase. We
19 argue that this is not strictly needed when our primary interest is to simulate the
20 competitive effect that the humic substances have on other ions such as arsenate and
21 arsenite. Because competition is governed by the occupancy of sites and the surface
22 charge adjustment brought about by the humic substances, we do not really need to
23 take into account the concentration of dissolved humic substances, as long as the
24 amount of adsorbed humic substances is not significantly changed by
25 adsorption/desorption in the system under study. Thus we emphasize the effect the

1 *already adsorbed* humic substances have on site availability and surface charge of the
2 oxide, and we assume that the desorption of these humic substances is insignificant.

3

4 In the model we describe the adsorption of a humic functional group, R-COO^- in
5 Table 13, to the oxide surface in terms of a monodentate complex in a single reaction.
6 The TPCD model formulation follows that of the most significant complex according
7 to Filius et al. (2003), except that the $\log K$ is set to a very large value (25) to ensure
8 near 100 % sorption under all conditions (Table 14). We also neglect any possible
9 surface charge effects caused by unbound dissociated organic acid groups in the outer
10 Stern layer.

11

12 To illustrate the use of our simplified model, we have applied it to the ferrihydrite
13 system defined in section 5.2, to illustrate the effect different surface coverages of
14 humic substances may have on arsenate and arsenite adsorption. The surface coverage
15 is in this case defined as the ratio of the concentration of adsorbed humic functional
16 groups R-COO^- to the concentration of singly coordinated surface sites (the $[\text{R-COO}^-]$
17 $/[=\text{FeOH}]$ ratio). We suggest that the ratio may vary between 0 and 0.5, depending on
18 the concentration of humic substances in the system under study. In Fig. 13 we
19 simulate As adsorption in systems with $[\text{R-COO}^-]/[=\text{FeOH}]$ ratios varying from 0.05
20 to 0.4. According to the model, humic substances have a rather small competitive
21 effect when only a small part of the oxide surface is covered, but at large surface
22 coverage the effect is important.

23

1 **Take in Fig. 13 here**

2 **Take in Tables 13 and 14 here**

3

4 Further laboratory work is needed to verify the applicability of this model to
5 describe competition effects. We are currently testing the model approach for
6 previously unpublished arsenate adsorption data for soils (Gustafsson, in preparation).

7

8 **Conclusions**

9

10 For two surface complexation models, the Diffuse Layer Model (DLM) and the
11 Three-Plane CD-MUSIC Model (TPCD), generic parameters for arsenate and arsenite
12 adsorption to ferrihydrite and goethite have been calculated. For arsenate adsorption
13 to ferrihydrite, the new DLM constants imply stronger binding than the previous
14 compilation by Dzombak & Morel (1990), whereas for arsenite the revised DLM
15 constants are in reasonable agreement. The surface complexation models could not be
16 optimized satisfactorily for data sets in which the dissolved arsenite concentration at
17 equilibrium was more than 10 μM ; the reason for this is not clearly understood.
18 Simulations of competition effects show that *o*-phosphate competes strongly with
19 arsenate over the whole pH range. Silicic acid and carbonate may be important
20 competitors in the circumneutral pH range, while sulphate may have a small
21 competitive effect at low pH. Humic substances are important competitors when a
22 large part of the Fe oxides is covered with humic substances. By contrast, calcium
23 promotes arsenate adsorption because of surface charge effects.

24

25

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25

FIGURE CAPTIONS

Fig. 1. Three possible surface complex configurations for arsenate on iron oxide; a) bidentate binuclear; b) bidentate mononuclear; c) monodentate (from Sherman and Randall, 2003).

Fig. 2. Percent adsorption of AsO_4 on ferrihydrite as a function of pH. The lines are fits with the generic surface complexation parameters shown in Table 6 (DLM, as solid lines) and Table 7 (TPCD, as dotted lines) as weighted averages. Upper panel: The systems of Jain and Loeppert (2000); lower panel: Dixit and Hering (2004).

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2 are fits with the generic surface complexation parameters shown in Table 11 as
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4 (1998); lower panel: Dixit and Hering (2004). Data sets not used for the
5 optimization of generic parameters are greyed.

6 **Fig. 8.** The dimensionless $\log K_d$ value (adsorbed As/dissolved As) for As adsorption
7 on ferrihydrite as a function of pH, in the absence and presence of different
8 equilibrium concentrations of *o*-phosphate, as simulated by the TPCD model.
9 Upper panel: AsO_4 ; lower panel: AsO_3 .

10 **Fig. 9.** The dimensionless $\log K_d$ value (adsorbed As/dissolved As) for As adsorption
11 on ferrihydrite as a function of pH, in the absence and presence of different
12 equilibrium concentrations of silicic acid, as simulated by the TPCD model. Upper
13 panel: AsO_4 ; lower panel: AsO_3 .

14 **Fig. 10.** The dimensionless $\log K_d$ value (adsorbed As/dissolved As) for As adsorption
15 on ferrihydrite as a function of pH, in the absence and presence of different
16 equilibrium concentrations of carbonate concentrations (expressed as partial
17 pressures of CO_2), as simulated by the TPCD model. Upper panel: AsO_4 ; lower
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19 **Fig. 11.** The dimensionless $\log K_d$ value (adsorbed As/dissolved As) for As adsorption
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21 equilibrium concentrations of sulphate, as simulated by the TPCD model. Upper
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1 equilibrium concentrations of calcium, as simulated by the TPCD model. Upper
2 panel: AsO_4 ; lower panel: AsO_3 .

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TABLE CAPTIONS

Table 1 Table of species for adsorption reactions in the DLM.

Table 2 Table of species for adsorption reactions in the TPCD model; singly coordinated sites.

Table 3 Values used for proton binding and electrolyte anion affinity in DLM and TPCD.

Table 4 Arsenate and arsenite protonation constants used in this work.

Table 5 Data sets used for optimisation of arsenic adsorption constants for ferrihydrite.

Table 6 Intrinsic DLM adsorption constants for arsenate adsorption on ferrihydrite (standard deviations in parentheses). Weighted average equilibrium constants are shown, with the 95 % confidence interval (*italics in parentheses*).

Table 7 Intrinsic TPCD adsorption constants for arsenate adsorption on ferrihydrite (standard deviations in parentheses). Weighted average equilibrium constants are shown, with the 95 % confidence interval (*italics in parentheses*).

Table 8 Proton co-adsorption stoichiometry in the data sets of Raven et al. (1998)

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Table 14 Table of species for adsorption reactions in the TPCD model; interacting ions on ferrihydrite.

Table 1

Table of species for adsorption reactions in the DLM^a

Species	P_o^b	SOH	H ⁺	AsO ₄ ³⁻	H ₃ AsO ₃	log K
SOH ₂ ⁺	1	1	1	0	0	log $K_{H,1}$
SO ⁻	-1	1	-1	0	0	log $K_{H,2}$
SH ₂ AsO ₄ ⁰	0	1	3	1	0	log K_{As1}
SHAsO ₄ ⁻	-1	1	2	1	0	log K_{As2}
SAsO ₄ ²⁻	-2	1	1	1	0	log K_{As3}
SOHAsO ₄ ³⁻	-3	1	0	1	0	log K_{As4}
SH ₂ AsO ₃	0	1	0	0	1	log K_{As5}
SHAsO ₃ ⁻	-1	1	-1	0	1	log K_{As6}

^aWater molecules are not included in the table of species^b $P_o = \exp(-F\Psi_o/RT)$, where F is the Faraday constant, Ψ_o is the electrostatic potential in the o -plane, R is the gas constant and T is the absolute temperature

Table 2

Table of species for adsorption reactions in the TPCD model; singly coordinated sites^a.

Species	P_o^b	P_b^b	P_d^b	SOH	H ⁺	Na ⁺	Cl ⁻	NO ₃ ⁻	ClO ₄ ⁻	AsO ₄ ³⁻	H ₃ AsO ₃	log K
SOH ₂ ^{+0.5}	1	0	0	1	1	0	0	0	0	0	0	log K_H
SOHNa ^{+0.5}	0	0	1	1	0	1	0	0	0	0	0	log K_{Na}
SOH ₂ ^{+0.5} -NO ₃ ⁻	1	0	-1	1	1	0	0	1	0	0	0	log $K_{NO3} + \log K_H$
SOH ₂ ^{+0.5} -Cl ⁻	1	0	-1	1	1	0	1	0	0	0	0	log $K_{Cl} + \log K_H$
SOH ₂ ^{+0.5} -ClO ₄ ⁻	1	0	-1	1	1	0	0	0	1	0	0	log $K_{ClO4} + \log K_H$
SOAsO ₃ H ₂ ^{-0.5}	0.5	-0.5	0	1	3	0	0	0	0	1	0	log K_{As1}
S ₂ O ₂ AsOOH ⁻	1	-1	0	2	3	0	0	0	0	1	0	log $K_{As2} - \log(\rho A N_{s,1})^c$
S ₂ O ₂ AsO ₂ ⁻²	0.5	-1.5	0	2	2	0	0	0	0	1	0	log $K_{As3} - \log(\rho A N_{s,1})$
SOAsO ₃ ^{-2.5}	0.25	-2.25	0	2	1	0	0	0	0	1	0	log K_{As4}
S ₂ O ₂ AsOH ⁻	0	0	0	2	0	0	0	0	0	0	1	log $K_{As5} - \log(\rho A N_{s,1})$
S ₂ O ₂ AsO ⁻²	0	-1	0	2	-1	0	0	0	0	0	1	log $K_{As6} - \log(\rho A N_{s,1})$

^aWater molecules are not included in the table of species^b $P_o = \exp(-F\Psi_o/RT)$, $P_b = \exp(-F\Psi_b/RT)$, and $P_d = \exp(-F\Psi_d/RT)$, where F is the Faraday constant, Ψ_o , Ψ_b and Ψ_d are electrostatic potentials in the o -, b - and d -planes, R is the gas constant and T is the absolute temperature^c ρ is the particle density of the suspension (g l⁻¹), A is the specific surface area (m² g⁻¹), and $N_{s,1}$ is the site density of singly coordinated SOH groups (here in mol m⁻²).

Table 3

Values used for proton binding and electrolyte anion affinity in DLM and TPCD

Equilibrium constant	2-line ferrihydrite	Goethite
<i>DLM</i>		
$\log K_{H,1}$	7.29	-
$\log K_{H,2}$	-8.93	-
<i>TPCD</i>		
$\log K_H$	8.1	9.2
$\log K_{Na}$	-0.4	-1.0
$\log K_{Cl}$	-0.4	-0.5
$\log K_{NO_3}$	-0.9	-1.0
$\log K_{ClO_4}$	-1.6	-1.7

Table 4

Arsenate and arsenite protonation constants used in this work^a

Reaction	$\log \beta$ at 25°C, I = 0	ΔH_r (kJ mol ⁻¹)
$\text{AsO}_4^{3-} + \text{H}^+ \leftrightarrow \text{HAsO}_4^{2-}$	11.80	-18.2
$\text{AsO}_4^{3-} + 2\text{H}^+ \leftrightarrow \text{H}_2\text{AsO}_4^-$	18.79	-21.2
$\text{AsO}_4^{3-} + 3\text{H}^+ \leftrightarrow \text{H}_3\text{AsO}_4$	21.09	-13.2
$\text{H}_3\text{AsO}_3 \leftrightarrow \text{H}_2\text{AsO}_3^- + \text{H}^+$	-9.17	27.6
$\text{H}_3\text{AsO}_3 \leftrightarrow \text{HAsO}_3^{2-} + 2\text{H}^+$	-23.27	59.4

^aAll constants are from Nordstrom and Archer (2002), except for ΔH_r for HAsO_3^{2-} , which is from Allison et al. (1991)

Table 5

Data sets used for optimisation of arsenic adsorption constants for ferrihydrite

ID number	Source	Total As (M)	Ferrihydrite concentration (g l ⁻¹)	Equilibration time (h)	Background electrolyte
<i>Arsenate</i>					
Fh-AsV-01	Leckie et al. (1980)	5×10^{-7}	0.089	4	0.1 M NaNO ₃
Fh-AsV-02	”	5×10^{-6}	”	”	”
Fh-AsV-03 ^a	Wilkie and Hering (1996)	1.33×10^{-7}	0.00445	2	0.01 M NaNO ₃
Fh-AsV-04 ^a	”	1.33×10^{-6}	”	”	”
Fh-AsV-05	Raven et al. (1998)	5.34×10^{-4}	2	24	0.1 M NaCl
Fh-AsV-06	”	1.6×10^{-3}	”	”	“
Fh-AsV-07 ^b	”	26.7×10^{-3}	”	”	“
Fh-AsV-08	Swedlund and Webster (1999)	5.3×10^{-5}	0.089	24	0.1 M NaNO ₃
Fh-AsV-09	”	1.07×10^{-4}	”	”	“
Fh-AsV-10	”	2.14×10^{-4}	”	”	“
Fh-AsV-11	Jain and Loeppert (2000)	1×10^{-3}	2	24	0.1 M NaCl
Fh-AsV-12	”	2.08×10^{-3}	”	”	“
Fh-AsV-13	”	4.16×10^{-3}	“	”	“
Fh-AsV-14 ^b	”	6.94×10^{-3}	“	”	“
Fh-AsV-15	Dixit and Hering (2004)	1×10^{-5}	0.03	4	0.01 M NaClO ₄
Fh-AsV-16		3.5×10^{-5}	“	”	“
Fh-AsV-17		5×10^{-5}	“	”	“
Fh-AsV-18		1×10^{-4}	“	”	“
<i>Arsenite</i>					
Fh-AsIII-01	Wilkie and Hering (1996)	1.33×10^{-7}	0.00445	2	0.01 M NaNO ₃
Fh-AsIII-02	“	1.33×10^{-6}	”	”	”
Fh-AsIII-03	Raven et al. (1998)	5.34×10^{-4}	2	24	0.1 M NaCl
Fh-AsIII-04	Swedlund and Webster (1999)	5.3×10^{-5}	0.089	24	0.1 M NaNO ₃
Fh-AsIII-05	Jain and Loeppert (2000)	1×10^{-3}	2	24	0.1 M NaCl
Fh-AsIII-06	Dixit and Hering (2004)	1×10^{-5}	0.03	4	0.01 M NaClO ₄
Fh-AsIII-07		2.5×10^{-5}	“	”	“

^aFor DLM, convergence could not be obtained with the surface species chosen^bData set not used for DLM optimisation, because observed $\Gamma_{\max}$ exceeded the total number of sites in the model

Table 6

Intrinsic DLM adsorption constants for arsenate adsorption on ferrihydrite (standard deviations in parentheses). Weighted average equilibrium constants are shown, with the 95 % confidence interval (*italics in parentheses*).

Data set	$\log K_{\text{As1}}$	$\log K_{\text{As2}}$	$\log K_{\text{As3}}$	$\log K_{\text{As4}}$	V_Y^a
Fh-AsV-01	-	-	-	11.58 (0.018)	3.0
Fh-AsV-02	-	-	-	11.59 (0.021)	0.2
Fh-AsV-05	-	-	19.14 (0.15 ^b)	12.34 (0.020)	0.2
Fh-AsV-06	-	25.26 (0.14)	19.64 (0.024)	12.11 (0.054)	8.8
Fh-AsV-08	-	-	19.52 (0.047)	11.73 (0.025)	18.4
Fh-AsV-09	-	26.58 (0.043)	20.29 (0.026)	11.40 (0.054)	1.6
Fh-AsV-10	32.46 (0.021)	26.98 (0.037)	19.86 (0.055)	11.71 (0.030)	3.0
Fh-AsV-11	-	-	18.86 (0.058)	12.30 (0.040)	0.8
Fh-AsV-12	30.69 (0.031)	25.27 (0.053)	19.18 (0.040)	11.61 (0.15 ^b)	5.4
Fh-AsV-13	30.16 (0.019)	25.00 (0.041)	18.40 (0.045)	10.86 (0.15 ^b)	2.6
Fh-AsV-15	-	-	-	12.81 (0.033)	90.9
Fh-AsV-16	-	26.10 (0.025)	19.98 (0.041)	12.71 (0.084)	12.5
Fh-AsV-17	30.88 (0.021)	25.69 (0.027)	19.58 (0.035)	11.79 (0.11)	4.0
Fh-AsV-18	30.74 (0.019)	25.28 (0.033)	17.79 (0.15 ^b)	11.91 (0.047)	4.6
Weighted averages	30.98 (<i>30.49, 31.47</i>)	25.84 (<i>25.64, 26.05</i>)	19.50 (<i>19.37, 19.63</i>)	11.92 (<i>11.85, 11.99</i>)	
Dzombak and Morel (1990)	29.31 (28.29, 30.34)	23.51 (23.33, 23.70)	-	10.58 (<i>10.01, 11.15</i>)	

^aWeighted sum of squares, calculated according to Dzombak and Morel (1990)

^bFixed at this value by convention (Dzombak and Morel, 1990).

Table 7

Intrinsic TPCD adsorption constants for arsenate adsorption on ferrihydrite (standard deviations in parantheses). Weighted average equilibrium constants are shown, with the 95 % confidence interval (*italics in parantheses*).

Data set	$\log K_{As1}$	$\log K_{As2}$	$\log K_{As3}$	V_Y^a
Fh-AsV-01	-	-	27.84 (0.018)	6.7
Fh-AsV-02	-	-	27.84 (0.020)	2.0
Fh-AsV-03	-	-	26.96 (0.039)	100.6
Fh-AsV-04	-	-	26.83 (0.054)	34.4
Fh-AsV-05	-	-	28.26 (0.016)	27.6
Fh-AsV-06	-	-	27.80 (0.020)	27.5
Fh-AsV-07	30.81 (0.013)	35.22 (0.025)	28.54 (0.052)	18.3
Fh-AsV-08	-	-	27.84 (0.022)	34.4
Fh-AsV-09	32.22 (0.12)	35.06 (0.050)	28.36 (0.025)	3.6
Fh-AsV-10	32.06 (0.022)	35.56 (0.030)	28.29 (0.029)	6.5
Fh-AsV-11	-	-	27.29 (0.020)	5.8
Fh-AsV-12	30.79 (0.045)	33.41 (0.032)	27.36 (0.045)	4.4
Fh-AsV-13	29.86 (0.017)	33.30 (0.022)	26.58 (0.044)	1.1
Fh-AsV-14	30.02 (0.018)	33.75 (0.024)	27.05 (0.059)	6.9
Fh-AsV-15	-	-	28.14 (0.024)	92.0
Fh-AsV-16	31.31 (0.080)	34.17 (0.054)	28.22 (0.036)	7.4
Fh-AsV-17	30.80 (0.023)	34.04 (0.026)	27.70 (0.029)	4.0
Fh-AsV-18	30.67 (0.019)	33.82 (0.027)	27.08 (0.042)	11.1
Weighted averages	30.72 (<i>30.53, 30.91</i>)	34.20 (<i>33.98, 34.41</i>)	27.77 (<i>27.70, 27.83</i>)	

^aWeighted sum of squares, calculated according to Dzombak and Morel (1990)

Table 8

Proton co-adsorption stoichiometry in the data sets of Raven et al. (1998)

Data set	pH	Measured P_{cs} ^a (Jain et al. 1999)	Modelled P_{cs} (TPCD)	Modelled P_{cs} (DLM)
Fh-AsV-05	4.6	2.08	2.06	1.17
	9.2	1.95	2.13	2.11
Fh-AsV-06	4.6	2.15	2.05	1.53
	9.2	1.80	1.98	1.92
Fh-AsIII-03	4.6	-0.14	-0.26	-0.57
	9.2	-0.41	-0.47	-0.20

^a P_{cs} is defined as: adsorbed $[H^+]$ /adsorbed $[A]$ (mol mol^{-1}), where A is AsO_4^{3-} or H_3AsO_3 .

Table 9

Intrinsic TPCD adsorption constants for arsenite adsorption on ferrihydrite (standard deviations in parantheses). Weighted average equilibrium constants are shown, with the 95 % confidence interval (*italics* in parantheses).

Data set	$\log K_{\text{As5}}$	$\log K_{\text{As6}}$	V_Y^a
Fh-AsIII-01	6.14 (0.012)	-2.22 (0.043)	61.4
Fh-AsIII-02	5.64 (0.015)	-2.33 (0.049)	25.8
Fh-AsIII-03	6.06 (0.005)	-1.91 (0.011)	27.5
Fh-AsIII-04	6.15 (0.008)	-2.31 (0.018)	33.2
Fh-AsIII-05	6.25 (0.008)	-1.77 (0.043)	20.2
Fh-AsIII-06	5.46 (0.013)	-1.87 (0.017)	2.2
Fh-AsIII-07	5.82 (0.007)	-1.84 (0.042)	3.0
Weighted averages	5.98 (<i>5.89, 6.07</i>)	-2.01 (<i>-2.09, -1.94</i>)	

^aWeighted sum of squares, calculated according to Dzombak and Morel (1990)

Table 10

Intrinsic DLM adsorption constants for arsenite adsorption on ferrihydrite (standard deviations in parantheses). Weighted average equilibrium constants are shown, with the 95 % confidence interval (*italics* in parantheses).

Data set	$\log K_{\text{As5}}$	$\log K_{\text{As6}}$	V_Y^a
Fh-AsIII-01	5.60 (0.024)	-2.09 (0.019)	34.1
Fh-AsIII-02	5.16 (0.026)	-2.66 (0.032)	25.8
Fh-AsIII-03	5.49 (0.008)	-2.01 (0.008)	134
Fh-AsIII-04	5.30 (0.010)	-2.15 (0.010)	95.9
Fh-AsIII-05	5.32 (0.011)	-2.10 (0.014)	26.3
Fh-AsIII-06	4.33 (0.074)	-2.28 (0.011)	51.3
Fh-AsIII-07	4.83 (0.015)	-2.51 (0.022)	19.4
Weighted averages	5.27 (<i>5.16, 5.37</i>)	-2.19 (<i>-2.26, -2.12</i>)	
Dzombak and Morel (1990)	5.41 (<i>5.26, 5.56</i>)	-	

^aWeighted sum of squares, calculated according to Dzombak and Morel (1990)

Table 11

Data sets used for optimisation of arsenic adsorption constants for goethite.

ID number	Source	Total As (M)	Goethite conc. (g l ⁻¹)	Equilibration time (h)	Specific surface area (m ² g ⁻¹)	Background electrolyte
<i>Arsenate</i>						
Go-AsV-01	Hingston et al. (1971)	1.07×10^{-3}	3.72	24	60	0.1 M NaCl
Go-AsV-02	Manning and Goldberg (1996)	1.33×10^{-4}	2.5	4	43.7	”
Go-AsV-03	”	2.66×10^{-4}	”	”	”	”
Go-AsV-04	Manning et al. (1998)	2.67×10^{-4}	”	16	45	”
Go-AsV-05	Eick et al. (1999)	1×10^{-3}	10	30	55.5	0.01 M NaNO ₃
Go-AsV-06	”	”	”	”	”	0.1 M NaNO ₃
Go-AsV-07	Rietra (2001)	1.53×10^{-4}	1.62	24	96.4	0.01 M NaNO ₃
Go-AsV-08	Gao and Mucci (2001)	8.8×10^{-6}	0.234	80	27.7	0.7 M NaCl
Go-AsV-09	”	2.29×10^{-5}	”	”	”	”
Go-AsV-10	”	3.42×10^{-5}	”	”	”	”
Go-AsV-11	Dixit and Hering (2004)	1×10^{-5}	0.5	24	54	0.01 M NaClO ₄
Go-AsV-12	”	2.5×10^{-5}	”	”	”	”
Go-AsV-13	”	5×10^{-5}	”	”	”	”
Go-AsV-14	”	1×10^{-4}	”	”	”	”
<i>Arsenite</i>						
Go-AsIII-01	Manning et al. (1998)	1.33×10^{-4}	2.5	16	45	0.1 M NaCl
Go-AsIII-02	Rietra (2001)	1.87×10^{-4}	1.62	24	96.4	0.01 M NaNO ₃
Go-AsIII-03	Dixit and Hering (2004)	1×10^{-5}	0.5	24	54	0.01 M NaClO ₄
Go-AsIII-04	”	2.5×10^{-5}	”	”	”	”
Go-AsIII-05	”	5×10^{-5}	”	”	”	”

Table 12

Intrinsic TPCD adsorption constants for arsenate adsorption on goethite (standard deviations in parantheses). Weighted average equilibrium constants are shown, with the 95 % confidence interval (*italics in parantheses*).

Data set	$\log K_{As2}$	$\log K_{As3}$	$\log K_{As4}$	V_Y^a
Go-AsV-01	34.79 (0.016)	27.87 (0.042)	-	50.5
Go-AsV-02	-	26.64 (0.064)	19.52 (0.015)	5.1
Go-AsV-03	33.91 (0.016)	27.30 (0.040)	20.00 (0.016)	2.9
Go-AsV-04	33.74 (0.020)	26.94 (0.034)	18.81 (0.019)	19.3
Go-AsV-05	34.47 (0.056)	28.76 (0.039)	21.67 (0.030)	0.6
Go-AsV-06	34.02 (0.046)	28.20 (0.038)	20.49 (0.028)	2.0
Go-AsV-07	-	29.25 (0.018)	20.88 (0.070)	2.0
Go-AsV-08	35.53 (0.039)	28.13 (0.034)	18.45 (0.014)	2.9
Go-AsV-09	36.51 (0.006)	29.19 (0.016)	-	28.8
Go-AsV-10	37.04 (0.015)	28.67 (0.073)	-	81.3
Go-AsV-11	-	-	19.70 (0.059)	143
Go-AsV-12	-	-	21.01 (0.030)	66.1
Go-AsV-13	35.39 (0.024)	28.15 (0.073)	20.74 (0.042)	4.0
Go-AsV-14	35.79 (0.017)	28.62 (0.067)	21.28 (0.048)	38.6
Weighted averages	35.48 (<i>35.21, 35.75</i>)	28.36 (<i>28.20, 28.52</i>)	20.14 (<i>19.95, 20.33</i>)	

^aWeighted sum of squares, calculated according to Dzombak and Morel (1990)

Table 13

Intrinsic TPCD adsorption constants for arsenite adsorption on goethite (standard deviations in parentheses). Weighted average equilibrium constants are shown, with the 95 % confidence interval (*italics* in parentheses).

Data set	$\log K_{\text{As5}}$	$\log K_{\text{As6}}$	V_Y^a
Go-AsIII-01	6.27 (0.008)	-1.78 (0.020)	22.1
Go-AsIII-02	6.44 (0.024)	-0.40 (0.029)	7.1
Go-AsIII-03	5.96 (0.011)	-2.13 (0.013)	28.6
Go-AsIII-04	6.39 (0.012)	-1.13 (0.028)	7.3
Go-AsIII-05	6.76 (0.006)	-	20.7
Weighted averages	6.40 (<i>6.23, 6.58</i>)	-1.56 (<i>-2.14, -0.97</i>)	

^aWeighted sum of squares, calculated according to Dzombak and Morel (1990).

Table 14

Table of species for adsorption reactions in the TPCD model; interacting ions on ferrihydrite

Species	P_o^b	P_b^b	P_d^b	SOH	H ⁺	PO ₄ ³⁻	H ₄ SiO ₄	CO ₃ ²⁻	SO ₄ ²⁻	Ca ²⁺	R-COO ⁻	log K^c
SOPO ₃ H ₂ ^{-0.5}	0.5	-0.5	0	1	3	1	0	0	0	0	0	32.51
S ₂ O ₂ POOH ⁻	1	-1	0	2	3	1	0	0	0	0	0	34.28 – log($\rho A N_{s,1}$) ^d
S ₂ O ₂ PO ₂ ⁻²	0.5	-1.5	0	2	2	1	0	0	0	0	0	28.29 – log($\rho A N_{s,1}$)
SOSi(OH) ₃ ^{-0.5}	0.6	-0.6	0	1	0	0	1	0	0	0	0	4.65
S ₂ O ₂ CO ⁻	0.67	-0.67	0	2	2	0	0	1	0	0	0	21.4 – log($\rho A N_{s,1}$)
SOSO ₃ ^{-1.5}	0.65	-1.65	0	1	1	0	0	0	1	0	0	9.6
SOH ^{-0.5} -Ca ²⁺	0.2	1.8	0	1	0	0	0	0	0	1	0	3.55
SOOC-R ^{-0.5}	0.5	-0.5	0	1	1	0	0	0	0	0	1	25 ^d

^aWater molecules are not included in the table of species^b $P_o = \exp(-F\Psi_o/RT)$, $P_b = \exp(-F\Psi_b/RT)$, and $P_d = \exp(-F\Psi_d/RT)$, where F is the Faraday constant, Ψ_o , Ψ_b and Ψ_d are electrostatic potentials in the o -, b - and d -planes, R is the gas constant and T is the absolute temperature^cThe phosphate constants were refitted from the data of Gustafsson (2003) using the methodology described in this chapter; for SOSi(OH)₃^{-0.5}, see Gustafsson (2001); the S₂O₂CO⁻ reaction was taken from Hiemstra et al. (2004), and fitted to the CO₃ data in Appelo et al. (2002); the SOSO₃^{-1.5} reaction was suggested by Rietra (2001) and here it was fitted to the data in Dzombak and Morel (1990); the SOH^{-0.5}-Ca²⁺ reaction was taken from Rietra et al. (2001) and fitted to the data in Dzombak and Morel (1990).^dThe constant for the humic complex SOOC-R^{-0.5} is set to 25 to ensure near 100 % sorption under all conditions.^e ρ is the particle density of the suspension (g l⁻¹), A is the specific surface area (m² g⁻¹), and $N_{s,1}$ is the site density of singly coordinated SOH groups (here in mol m⁻²).