Nanoparticles in natural systems II: The natural oxide fraction at interaction with natural organic matter and phosphate

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Abstract

Information on the particle size and reactive surface area of natural samples and its interaction with natural organic matter (NOM) is essential for the understanding bioavailability, toxicity, and transport of elements in the natural environment. In part I of this series (Hiemstra et al., 2010), a method is presented that allows the determination of the effective reactive surface area (A, m^2/g soil) of the oxide particles of natural samples which uses a native probe ion (phosphate) and a model oxide (goethite) as proxy. In soils, the natural oxide particles are generally embedded in a matrix of natural organic matter (NOM) and this will affect the ion binding properties of the oxide fraction. A remarkably high variation in the natural phosphate loading of the oxide surfaces (Γ, μmol/m^2) is observed in our soils and the present paper shows that it is due to surface complexation of NOM, acting as a competitor via site competition and electrostatic interaction. The competitive interaction of NOM can be described with the charge distribution (CD) model by defining a $\equiv$NOM surface species. The interfacial charge distribution of this $\equiv$NOM surface species can be rationalized based on calculations done with an evolved surface complexation model, known as the ligand and charge distribution (LCD) model. An adequate choice is the presence of a charge of -1 v.u. at the 1-plane and -0.5 v.u. at the 2-plane of the electrical double layer used (Extended Stern layer model).

The effective interfacial NOM adsorption can be quantified by comparing the experimental phosphate concentration, measured under standardized field conditions (e.g. 0.01 M CaCl$_2$), with a prediction that uses the experimentally derived surface area (A) and the reversibly bound phosphate loading (Γ, μmol/m^2) of the sample (part I) as input in the CD model. Ignoring the competitive action of adsorbed NOM leads to a severe under-prediction of the phosphate concentration by a factor $\sim$10 to 1000. The calculated effective loading of NOM is low at a high phosphate loading (Γ) and vice versa, showing the mutual competition of both constituents. Both constituents in combination usually dominate the surface loading of natural oxide fraction of samples and form the backbone in modeling the fate of other (minor) ions in the natural environment.

Empirically, the effective NOM adsorption is found to correlate well to the organic carbon content (OC) of the samples. The effective NOM adsorption can also be linked to DOC. For this, a Non-Ideal Competitive adsorption (NICA) model is used. DOC is found to be a major explaining factor for the interfacial loading of NOM as well as phosphate. The empirical NOM–OC relation or the parameterized NICA model can be used as an alternative for estimating the effective NOM adsorption to be implemented in the CD model for calculation of the surface complexation of field samples. The biogeochemical impact of the NOM–PO$_4$ interaction is discussed.

1. INTRODUCTION

The bioavailability, toxicity, and mobility of ions in the environment are largely determined by the interaction with organic matter and mineral particles. The interaction is a

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complex process, involving factors such as the pH, ionic strength, the presence of competing or promoting ions as well as the nature and the amount of substrates, all affecting the distribution of cations and anions over the solid and solution phase.

Development of in-situ surface spectroscopy and surface complexation models (SCM) have largely increased our insight in the adsorption processes of ions, in particular for well-defined systems. Surface complexation models have been widely applied to these systems. Ideally, SCM may predict changes in situations where experimental data are not available or difficult to collect. This is highly relevant for understanding the fate of elements at the field scale.

The application of SCM to natural systems like soils, sediments, and other aquatic media is quite complicated. Natural systems usually contain many different elements that may interact with a range of particles. In part I of this series (Hiemstra et al., 2010), we have discussed how to derive the effective reactive surface area of the oxide particles. We proposed to use a naturally present probe ion and a model oxide with known binding properties as proxy to derive the effective reactive oxide surface area of natural samples. In this way, the adsorption behavior of the natural oxide fraction is represented by the behavior of the model oxide with a database of adsorption parameters. The rational is that in a first order approach the collective mutual behavior is strongly regulated by general electrostatic properties of a charged interface. In the method to determine the effective reactive surface area (A), a field sample is equilibrated with 0.5 M NaHCO$_3$ solutions at different solid solution rations (SSR) and the phosphate concentration is measured. The competitive phosphate–carbonate adsorption/desorption process in the sample is interpreted with the charge distribution model (Hiemstra and Van Riemsdijk, 1996). The CD model has been calibrated for the model oxide, i.e. goethite (Rahnemaie et al., 2007). Application of the CD model yields an effective surface area (A) and the amount of reversibly bound phosphate (R_{ev}). The particles of the natural oxide fraction are nano-sized (Hiemstra et al., 2010).

Even if an effective surface area is known and a database with parameters for ion binding to the model oxide is available, a remaining complication for applying SCM to natural systems is the presence of natural organic matter (NOM). It has been shown that the surfaces of the natural oxide particles are loaded with humic materials (Hiemstra et al., 2010; Kaiser and Guggenberger, 2000). This will strongly affect the binding of inorganic anions (Gerke, 1993; Karltun, 1998; Grafe et al., 2002; Bauer and Blodau, 2006; Gustafsson, 2006; Weng et al., 2008). Therefore, this organo–mineral interaction requires attention if the aim is to apply SCM to natural samples under field conditions.

The interaction of NOM and metal oxide particles has been studied by many authors (Tipping, 1981; Davis, 1982; Gu et al., 1996, 1994; Evanko and Dzombak, 1999; Filius et al., 2000; Weng et al., 2007). The interaction is complicated, even without the presence of other adsorbing ions that may interact, such as phosphate and calcium. At present, a mechanistic framework is in development to describe such interactions in model systems (Filius et al., 2003;

Weng et al., 2006, 2007). In the model, the NOM adsorption is calculated based on a ligand and charge distribution (LCD) approach. In a recent contribution (Weng et al., 2008), the competition between phosphate and humic and fulvic acids (HA and FA) has been studied for goethite. HA binds stronger than FA to goethite, but remarkably the study also showed that FA is a much stronger competitor for phosphate. This difference can be explained by a difference in the size of the molecules. HA molecules are more strongly bound than the FA molecules because the charge per molecule is much higher for large-sized molecules (Weng et al., 2007). On the other hand, the FA molecules are smaller and can approach the surface more closely. Adsorbed FA is mainly present in the compact part of the double layer, where it acts as a good competitor for phosphate. The LCD model (Weng et al., 2008) is potentially a powerful approach to model these interactions. However, for application to natural systems, it requires detailed information with respect to the mass distribution of natural organic acids in these systems. Therefore, we will formulate in the present paper a combined experimental and theoretical methodology that enables the incorporation of the interfacial NOM in the standard CD model.

In the new approach, the impact of adsorbed natural organic matter (NOM) on the binding of anions will be evaluated leading to an effective NOM density that is apparently active in the natural samples under standardized field conditions represented by 0.01 M CaCl$_2$ (van Erp et al., 1998). Phosphate is used as naturally present probe anion in the CaCl$_2$ solution and information of the phosphate loading, obtained with the 0.5 M HCO$_3$ equilibration (Hiemstra et al., 2010) will be included in the methodology. The phosphate loading is used as input in the CD model to evaluate the experimental phosphate concentration measured in the CaCl$_2$ systems. This leads to the calculation of the effective amount of NOM that is apparently active in the interface.

For a large set of samples, the variation of the NOM density will be studied, identifying factors that explain the calculated effective NOM density, such as the solution concentrations of PO$_4$ and DOC. This part of the data analysis will be done with a non-electrostatic version of the non-ideal competitive adsorption (NICA) model (Kinniburgh et al., 1999). Empirically, the relative NOM adsorption will be evaluated by considering general soil characteristics. If other information is absent, empirical relationships can be used to estimate the effective NOM adsorption to be implemented in the CD model for modeling the surface complexation of field samples.

The development of a consistent methodology to determine for natural samples the effective reactive oxide surface area as well as the effective NOM density enables, for the first time, a realistic scaling of SCM to field conditions.

2. MATERIALS AND METHODS

2.1. Soils samples

Representative agricultural top soils of the Netherlands (van Erp et al., 1998) have been used. The soil samples of

the Copernicus soil series cover a wide range of organic carbon contents (~1 to 15% OC) and clay contents (~3 to 30%). The amount of reactive oxides has been characterized by extracting the soil with ammonium oxalate (pH 3) and dithionite citrate bicarbonate (DCB). The effective surface area and reversibly bound fraction of phosphate have been determined with equilibration of the soils in 0.5 M NaHCO$_3$ (pH 8.5) at a variable solid–solution ratios (Hiemstra et al., 2010). The details of the methods and main relevant soil characteristics have been presented in Hiemstra et al. (2010).

2.2. Equilibration at standardized field conditions

A 10-mM CaCl$_2$ solution has been used to standardize the conditions at equilibration. This background electrolyte solution approximately simulates the relevant average field conditions of fertilized top soils. Native soils may have a lower ionic strength and for these, the use of 2.5 mM CaCl$_2$ has been suggested (Schroder et al., 2005). Our samples have been equilibrated using a high solid–solution ratio (SSR = 0.1 kg/L). The equilibrium state is reached relatively fast (2 h) since not much desorption is needed in this procedure (van Erp et al., 1998). The pH has been measured in the 0.01 M CaCl$_2$ suspension and after phase separation by centrifugation (20 min, 6000 rpm), the filtered supernatant has been analyzed for the major cations. In the extract, orthophosphate has also been measured. A molybdenum-blue method is used that has been adapted to measure relatively low PO$_4$ concentrations with a segmented flow analysis (SFA) device. These data are given in part I (Hiemstra et al., 2010).

For a limited number of samples, the speciation of DOC in the 0.01 M CaCl$_2$ solution has been measured. Hydrophilic acids (Hy), fulvic acids (FA), and humic acids (HA) have been separated using the method of Van Zomeren and Comans (2007). The concentration of dissolved C was measured with a TOC analyzer.

2.3. Surface complexation modeling

Surface complexation modeling will be done using the CD model (Hiemstra and Van Riemsdijk, 1996). The surface reactions, corresponding charge distribution, and affinity constants have been given in Hiemstra et al. (2010). The surface complexation modeling has been done with the ECOSAT software (Keizer and Van Riemsdijk, 1998) in combination with FIT (Kinniburgh, 1993).

3. RESULTS AND DISCUSSION

For clarity, the next sections treat two main issues. The first three sections (Sections 3.1–3.3) discuss the application of the probe ion method to soils at standardized field conditions (0.01 M CaCl$_2$). It shows that the PO$_4$ equilibrium concentration is strongly under predicted if the presence of NOM is ignored (Section 3.1). Therefore, an interfacial NOM loading is theoretically defined (Section 3.2) and application in SCM shows that the phosphate loading in natural soils is suppressed by competition of adsorbed

NOM that correlates with DOC (Section 3.3). In the next two sections, a thermodynamic model is formulated (Section 3.4) and applied (Section 3.5) to gain insight in the overall relationships between adsorbed and dissolved orthophosphate and NOM/DOC of natural soils. Finally (Section 3.6), a road map is added that describes the procedure to apply the effective NOM loading in surface complexation models.

3.1. P-loading and solution composition

The probe ion procedure to determine the reactive surface area of natural materials (Hiemstra et al., 2010) has been developed for the application to natural systems where ion adsorption is to be predicted. Its applicability can be tested for the soil samples under standardized field conditions (0.01 M CaCl$_2$). Starting point is the phosphate loading Γ (μmol PO$_4$/m^2) in the samples resulting from the 0.5 M NaHCO$_3$ equilibration extraction and subsequent modeling.

The variation in the phosphate loading, derived with the probe ion method (Hiemstra et al., 2010), is relatively high (Γ ~1 to 3 μmol/m^2). For natural soils, the observed loading is imposed by the average conditions experienced by the oxide fraction in the field, such as the pH and phosphate concentration (C_{PO4}). Surprisingly, the relationship between log Γ and log C_{PO4} measured in the 0.01 M CaCl$_2$ solution ($n = 19$ data points) shows a large scattering ($R^2 = 0.31$), whereas the correlation between log Γ and log DOC is much better ($R^2 = 0.66$). It is important to notice that without a scaling to surface area no relationship between the phosphate loading and the dissolved phosphate concentration is found ($R^2 = 0.06$). On a mass basis, one is blind in this respect.

This statistical result suggests that DOC is a major explaining factor for the variation in the adsorption of PO$_4$. The observed correlation might be due to a DOC–PO$_4$ competition at the oxide surface. According to the typical shape of a high-affinity adsorption isotherm, the adsorption of phosphate will only slightly change in the high concentration range, where the loading becomes increasingly independent of phosphate concentration (Fig. 1). If adsorbed NOM determines the phosphate
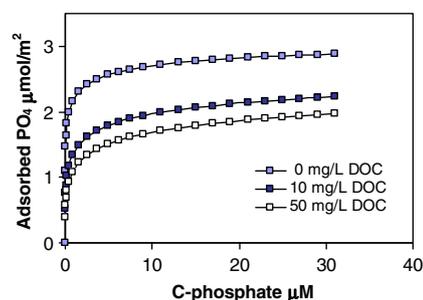

Fig. 1. Conceptual picture of the phosphate adsorption isotherms in 0.01 M CaCl$_2$ (pH 5.5) at a DOC concentration of 0, 10, and 50 mg/L. The variation in the DOC concentration has a large effect on the PO$_4$ adsorption. The lines have been calculated using the NICA model, which was fitted to the experimental data (see text).

surface saturation, one may observe a correlation with DOC that can be stronger than the contribution of the phosphate concentration.
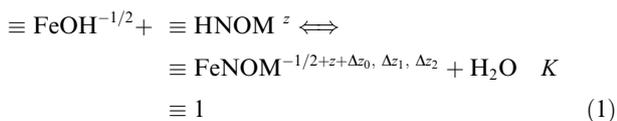
The experimental phosphate concentration in 0.01 M $CaCl_2$ can be evaluated using the reversible phosphate loading Γ as input in the CD model. The loading can be derived with the 0.5 M $NaHCO_3$ equilibration procedure (Hiemstra et al., 2010). In case of the presence of adsorbed NOM, it may be expected that the model will predict a lower phosphate concentration in 0.01 M $CaCl_2$ if the competition of adsorbed NOM is not included in the modeling. In the bicarbonate equilibrium extraction, adsorbed NOM is probably largely removed by the combination of a high pH, a very low Ca concentration, and the addition of active carbon in excess that all stimulate the removal of carbon from the soil matrix. In contrast, one may expect that the soil material in a 0.01 M $CaCl_2$ solution will have a nano-particle association of NOM and oxides such as depicted in Part I (Hiemstra et al., 2010).

The orthophosphate equilibrium concentrations in the 0.01 M $CaCl_2$ solutions, predicted with the above approach, are indeed much too low (10–1000 times) when compared to the experimental data. The deviations are very large and variable. The average concentration differs by $\Delta \log C = 1.6 \pm 0.7$.

The effective NOM density present in the interface can be quantified by comparing the predicted and the experimental phosphate concentration in the 0.01 M $CaCl_2$ solution. The possible influence of adsorbed NOM on the anion competition can be calculated by defining a NOM surface species that can be used in the standard CD approach. The NOM adsorption involves competition for surface sites as well as an electrostatic competition due to the introduction of negative charge in the EDL. This is discussed next.

3.2. NOM surface species

To implement the effect of the adsorption of NOM in the CD model, we may define a NOM surface species, $\equiv FeNOM$, that is formed from a surface component $\equiv HNOM^z$. The sole use of surface components is mathematically elegant. Others (Gustafsson, 2006) have used a solution component in combination with a hypothetical affinity constant ($\log K$) to create interfacial NOM. In the traditional calculation scheme of columns and rows as presented in Table 2 of part I (Hiemstra et al., 2010), adsorbed NOM can be created by combining the surface components $\equiv FeOH^{-1/2}$ and $\equiv HNOM^z$, visualized schematically as:

$$\equiv FeOH^{-1/2} + \equiv HNOM^z \Longleftrightarrow$$
$$\equiv FeNOM^{-1/2+z+\Delta z_0, \, \Delta z_1, \, \Delta z_2} + H_2O \quad K$$
$$\equiv 1 \tag{1}$$

In the calculation scheme (Table 2, part I, Hiemstra et al., 2010), $\equiv HNOM^z$ is a virtual component. NOM is only present as $\equiv FeNOM$ species. The total surface charge of the created $\equiv FeNOM$ species ($-1/2 + z$) is redistributed as defined by the three charge distribution coefficients Δz_i shown in Eq. (1). This charge can be redistributed over three electrostatic planes ($i = 0,1,2$). The sum of the charge

distribution coefficients is zero, i.e. $\Delta z_0 + \Delta z_1 + \Delta z_2 = 0$, since no additional charge from any solution component is entering the interface.

3.2.1. Classical use of CD

As suggested above, the interaction of adsorbed NOM with adsorbed PO_4 can be due to site competition as well as an electrostatic competition. Therefore, the charge (z) per reacted surface group and its location (Δz_i) are relevant. These have been chosen based on the results of surface speciation calculations done for fulvic acid that is adsorbed by goethite (Filius et al., 2000, 2003; Weng et al., 2005, 2008).

A typical small FA molecule may have on average about four –COOH groups and one –COH group (Filius et al., 2000). The works of Filius et al. (2000, 2003) suggest that upon adsorption one of the carboxylate groups ($RCOO^-$) will form an innersphere complex according to the ligand exchange reaction:

$$\equiv FeOH^{-1/2} + H^+(aq) + RCOO^{-1}(aq) \Longleftrightarrow$$
$$\equiv FeO^0 - CO^{-0.5} - R + H_2O(l) \tag{2}$$
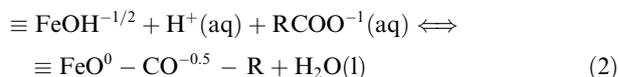
In this classical formulation, the charge of the proton is added to the surface plane and as result of ligand exchange releasing a H_2O. The charge of $RCOO^-$ is distributed equally over the 0- and 1-plane. The corresponding CD is $\Delta z_0 = +1 - 0.5 = +0.5$ valence units (v.u.) and $\Delta z_1 = -0.5$ v.u. (Filius et al., 1997). Overall, the reaction will neutralize the surface oxygen charge (changing from $-1/2$ to 0 v.u.) and adds a charge of -0.5 v.u. to the 1-plane.

The other functional groups of the adsorbed FA molecule are present outside the surface in the Stern layer. Surface complexation modeling suggests that this ensemble of functional groups attributes on average a net charge of about $\Delta z_1 = -1$ v.u. per $\equiv FeOH^{-1/2}$ to the 1-plane (Filius et al., 2000, 2003) in the relevant pH range. Therefore, the combination of inner- and outersphere complexation results in a total charge attribution to the 1-plane of $\Delta z_1 = -0.5 + -1 = -1.5$ v.u. In the presence of Ca^{2+}, the surface speciation suggested by the LCD model (Weng et al., 2005) is similar.

The above modeling results have been obtained with a SCM model that uses the Basic Stern approach. FA molecules are relatively large compared to inorganic anions and an Extended Stern layer model can be considered as more suitable. In that approach, the outer sphere ligands can be present in the 1- and 2-plane. If the corresponding charge of the outer sphere ligands (-1 v.u.) is equally distributed over both planes, the overall charge distribution, including innersphere complexation, results in $\Delta z_0 = +0.5$ v.u., $\Delta z_1 = -1.0$ v.u., and $\Delta z_2 = -0.5$ v.u. The FA surface species can be represented as $\equiv FeO^0 - CO^{-1} - R^{-0.5}$.

3.2.2. Effective CD using surface components only

The proposed coefficients in Section 3.2.1 are valid if the adsorption of FA is modeled using the combination of a solution component (FA, aq) and a surface component ($\equiv FeOH^{-1/2}$). However, in the reaction scheme (Hiemstra et al., 2010), the $\equiv FeNOM$ species is formed directly from

surface components only, i.e. from the combination of 1 $\equiv FeOH^{-1/2}$ and 1 $\equiv HNOM^z$ (Eq. (1)) with $z = -1$ v.u.. The total charge of these two surface components in the reference state is -1.5 v.u. When defined, the surface component charge is conventionally attributed to the surface plane but will be neutralized upon formation of the surface species $\equiv FeNOM$ (Eq. (1)). This is done by redistribution of the charge in the interface. A charge of $+1.5$ v.u. charge is transformed from the Stern planes to the surface plane, i.e. $\Delta z_0 = +1.5$ v.u., $\Delta z_1 + \Delta z_2 = -1.5$ v.u., and $\Delta z_0 + \Delta z_1 + \Delta z_2 = 0$ v.u. The charge in the Stern layers is distributed such that one gets the above suggested values for adsorbed FA, i.e. $\Delta z_1 = -1.0$ v.u. and $\Delta z_2 = -0.5$ v.u. In summary, the charge distribution coefficients in the present model for the formation of $\equiv FeNOM^{0-1-0.5}$ from 1 $\equiv FeOH^{-1/2}$ and 1 $\equiv HNOM^{-1}$ (Eq. (1)) will be $\Delta z_0 = +1.5$ v.u., $\Delta z_1 = -1.0$ v.u., and $\Delta z_2 = -0.5$ v.u. (Table 2 in part I).

Recently, the ligand and charge distribution (LCD) approach has been adapted (Weng et al., 2006, 2008). In the newest approach, half of the functional groups of FA is attributed to the 2-plane, while the other half is present in the 0- or 1-plane. The distribution of the ligands between the 0- and 1-plane depends on the degree of innersphere complexation, which is obtained by modeling. The new LCD approach confirms that on average approximately one ligand per adsorbed FA molecule will interact with the surface by ligand exchange forming an innersphere complex leading to $\Delta z_0 = +0.5$ v.u. and $\Delta z_1 = -0.5$ v.u. However, according to the new model approach, the other –COOH groups will dissociate protons more strongly than previously suggested, i.e. -2 v.u. instead of -1 v.u. per FA. This is found for simple oxide systems with only FA, but the situation changes if phosphate is present too. In that case, the interface becomes more negatively charged and this will suppress the dissociation of the –COOH groups. As a result, the charge present on the functional groups in the 1-plane is on average more close to -1 v.u. and therefore, the above chosen coefficients (Table 2 in part I) are consistent with this recent picture (Weng et al., 2008), if adsorbed phosphate is present.

It should be noted that the present approach (Eq. (1)) is a strong simplification. Actually, the charge and ligand distribution is variable and depends on factors such as pH, phosphate, and NOM loading. Moreover, large NOM molecules like HA may attribute charge to the DDL (Weng et al., 2007). Calculation of these effects requires an adequate theoretical framework such as the recent LCD model (Weng et al., 2007, 2008). In principle, such an approach allows quantification of the relationship between dissolved and adsorbed NOM, which is absent in the above model formulation (Eq. (1)).

3.3. Effective NOM adsorption density

3.3.1. Phosphate NOM competition

By defining a NOM surface species (Eq. (1)), the CD model can calculate an effective NOM adsorption density ($\equiv FeNOM$). In the calculation, we search for the apparently required NOM adsorption density that explains the

10–1000 times higher phosphate concentration in 0.01 M $CaCl_2$ in the various samples using as constraint the phosphate loading and surface area that we derived with equilibration in 0.5 M $NaHCO_3$ (part I, probe ion method). For the calculation of $\equiv FeNOM$, we used the experimental pH value in 0.01 M $CaCl_2$ as well as the measured Na^+, K^+, Ca^{2+}, and Mg^{2+} concentrations as given in Hiemstra et al. (2010). We note that it turned out that the latter is not essential. The use of only 0.01 M Ca^{2+} and 0.02 M Cl^- as ion concentrations is sufficient.

The phosphate loading Γ ($\mu mol/m^2$) of a soil is an essential factor in the calculation of $\equiv FeNOM$. The loading Γ is the combination of the amount of reversibly adsorbed phosphate content R_{ev} and the effective reactive surface area A, which are both used as input parameters in the CD model. It is important to notice that the uncertainty in the determination of the absolute value of A as well as R_{ev} is usually relatively high, on average about 10% (Hiemstra et al., 2010). However, the uncertainty in the phosphate loading Γ is generally much smaller, i.e. about 2%, even though Γ is a combination of the surface area A and the content R_{ev} ($\Gamma = R_{ev}/A$), The reason is that the values of A and R_{ev} are strongly correlated. A small uncertainty in the phosphate loading Γ is important because a small variation in Γ will already lead to a rather large variation in the phosphate concentration in solution, as follows from the shape of the isotherm in Fig. 1. Correspondingly, this leads to a relatively large uncertainty in the calculated effective NOM adsorption. Practically, it implies that the calculation of the effective NOM adsorption density should only be based on that combination of A and R_{ev} that correctly represents the value of Γ found at evaluation of the $NaHCO_3$ equilibration data with the probe ion method.

In Fig. 2, the error bar for the phosphate loading Γ refers to the difference in loading at evaluation of the
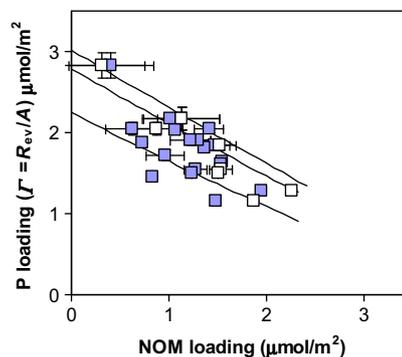

Fig. 2. The PO_4 loading (Γ) derived from the interpretation of the $NaHCO_3$ equilibrium extraction data as a function of the effective NOM adsorption ($\equiv FeNOM$ in $\mu mol/m^2$) that explains the PO_4 concentration in the $CaCl_2$ extracts. The closed symbols refer to the soils presented in Table 1 of part I (Hiemstra et al., 2010). The open symbols are from additional measurements of the PO_4 concentration and pH in 0.01 M $CaCl_2$ after sample storage for 10 years (see text). The lines have been calculated with the CD model described for an average pH of pH $= 5.5$ and from bottom-up for respectively c-PO_4 $= 1$, 10, and 30 μM. The parameters are given in Table 2 of part I (Hiemstra et al., 2010).

NaHCO$_3$ extract using the linear or the logarithmic scale for the phosphate concentration, as described in part I. The uncertainty in Γ leads to a variation in the predicted equilibrium concentration of phosphate in the 0.01 CaCl$_2$ solution, which is rather high due to the high-affinity shape of the adsorption isotherm (Fig. 1), and correspondingly, this leads to an uncertainty in the calculated effective NOM adsorption.

As follows from Fig. 2, the calculated effective NOM adsorption density ($\equiv$FeNOM) clearly varies amongst the soils studied. Our analysis shows that soils with a high PO$_4$ loading (Γ in µmol/m^2) have a low effective NOM adsorption density ($\equiv$FeNOM µmol/m^2) and vice versa (Fig. 2). The behavior observed is typical for a competitive adsorption process.

Our calculations immediately make clear why the selected soils have a relatively large variation in the P-loading (Γ ~1 to 3 µmol/m^2) while this is not expected from the variation of the experimental PO$_4$ concentration in the CaCl$_2$ extract if the PO$_4$ adsorption is based on only PO$_4$, H$^+$, and Ca^{2+} interaction (Fig. 1, upper curve). What causes this difference? It is most likely the presence of DOC that leads to adsorbed NOM.

3.3.2. Interfacial NOM and DOC

The CaCl$_2$ data set used (Hiemstra et al., 2010) refers to the original measurements done shortly after sampling. Ten years later, a number of samples have been reanalyzed and these CaCl$_2$ data are in Table 1 as part of this study. Meanwhile, the PO$_4$ concentrations in the 0.01 M CaCl$_2$ extract have increased. The DOC concentrations have increased too, probably due to some slow NOM disintegration. The simultaneous increase of the phosphate as well as the DOC concentration is consistent with the concept of a NOM–PO$_4$ competition. The increase of the amount of relatively small DOC molecules will lead to some more adsorption of NOM in the compact part of the EDL, resulting in more competition with PO$_4$. The corresponding amount of adsorbed NOM has been calculated and is given in Figs. 2 and 3 as open symbols.

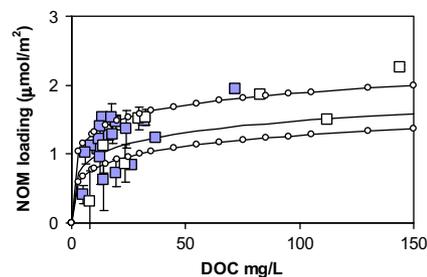In Fig. 3, the calculated NOM adsorption of the soils is given as a function of the DOC concentration (mg/L) mea-

Fig. 3. The effective NOM adsorption density (µmol/m^2) acting as competitor for phosphate plotted versus the DOC concentration present in 0.01 M CaCl$_2$ extract of the Copernicus soil series. The data points (symbols defined in Fig. 2) have been found by analyzing the experimental phosphate concentrations of the 0.01 M CaCl$_2$ solutions using the PO$_4$ loading Γ derived from the NaHCO$_3$ equilibrium extractions. The lines in Fig. 3 are calculated with the NICA model (Table 2) for three phosphate concentrations that cover the experimental range (top-down for, respectively, 1, 10, and 30 µM) using the average pH (pH 5.5).

sured in a 0.01 M CaCl$_2$. Soils with a low effective NOM adsorption also have a low DOC concentration in solution. As illustrated in Fig. 3, increase of the DOC concentration leads to an increase of the NOM adsorption, and according to Fig. 2, to a decrease of the PO$_4$ loading. At high DOC concentrations, the loading of NOM apparently approaches a maximum.

3.3.3. Interfacial carbon loading

With the present approach, it is impossible to link the calculated effective NOM adsorption (Fig. 2) directly to an actual carbon density. This can be seen as a limitation. The effective NOM adsorption density has been derived by fit, evaluating the competition of NOM with PO$_4$. The same level of competition, i.e. the same effective NOM adsorption, can be due to a very different amount of adsorbed carbon because the competition of NOM with PO$_4$ depends largely on the molecular size of the NOM molecules involved. This distribution is difficult to quantify. From a practical perspective of surface complexation modeling, the use of an effective loading may be seen as an advantage. Our approach does not require particular knowledge about the amount of interfacial carbon bound and its detailed speciation.

Despite the above, quantifying the carbon density that might be involved in the effective NOM adsorption may gain insight in the amount of carbon that is active in the Stern layer region near the oxide surface. To calculate the apparent amount of carbon that is involved in the effective NOM adsorption, an arbitrary choice is used for the molar mass of 750 g/mol. Such a molar mass leads to a particle size that fits to the total Stern layer.

This molar mass can be combined with the range of observed effective NOM adsorption, being 0–1.5 µmol/m^2 (Fig. 3), leading to 0–0.5 mg OC/m^2 or 0–0.8 mg NOM/m^2. These numbers are substantially lower than the total carbon and NOM adsorption on natural oxide surfaces, which is ~1.4 mg OC/m^2 or ~2.5 mg NOM/m^2 as shown in part I (Hiemstra et al., 2010). The apparent amount of

Table 1
The pH and phosphate concentration in 0.01 M CaCl$_2$ solution, and the corresponding speciation of DOC with hydrophilic acids (Hy), fulvic acids (FA), and humic acids (HA) using the method of Van Zomeren and Comans (2007). The data were collected 10 years after sampling of the Copernicus soil series. For comparison to the original data, see Table 1 part I.

Soil	pH	P–PO$_4$	DOC (mg C/L)			
		µM	Total	Hy	FA	HA
2	5.16	24.6	29	23	6	0
3	5.64	3.5	32	24	8	0
7	5.77	16.3	14	11	3	0
9	4.45	7.7	112	89	20	2
10	5.02	1.9	83	65	18	0
11	5.45	10.4	144	107	37	0
13	7.24	4.5	24	19	5	0
14	6.75	20.9	8	4	4	0

carbon in the interface is only about 30%. Nevertheless, the estimated effective carbon loading may agree conceptually with the structure of an association of NOM and oxide nanoparticles as depicted in part I. Only a part of the total amount of adsorbed organic matter is directly involved in the competition with phosphate in the compact part of the double layer. A large fraction of the adsorbed organic matter is further away from the surface. Based on the total thickness of the Stern layer of 0.7 nm (Hiemstra and Van Riemsdijk, 2006) and the corresponding volume, the maximum NOM adsorption in the inner Stern layer can be calculated at a given a mass density of 1250 kg/m^3, leading to about 0.8 mg NOM/m^2. This maximum loading is rather close to the highest effective loading in our soils in case of a molar mass of 750 g/mol.

3.4. NICA model: linking DOC and ≡NOM

Thermodynamics are the basis of surface complexation modeling. A thermodynamic approach implies that it may not reflect necessarily the processes at the molecular level. We will discuss here a simplified non-electrostatic version of the non-ideal competitive adsorption (NICA) model to describe the interaction between DOC and phosphate in relation to adsorbed NOM and phosphate. It will be used to gain insight in overall relationships between adsorbed and dissolved phosphate and NOM/DOC.

The NICA model has been developed to describe the adsorption of the ions by organic matter (Kinniburgh et al., 1999). The model combines chemical heterogeneity with a local non-ideal adsorption isotherm. In case of a homogeneous surface, the NICA equation for the adsorption of ion i with a binding constant K_i reduces to:

$$\Gamma_i = \Gamma_{\max} \frac{n_i}{n_{\mathrm{REF}}} \frac{(K_i C_i)^{n_i}}{1 + \sum (K_j C_j)^{n_j}} \qquad (3)$$

in which $\Gamma_{\max}$ (μmol/m^2) is the maximum adsorption density and n_i represents the non-ideality parameter of ion with index i. The index j in the denominator refers to the various types of ions that may adsorb. In our case, this may be protons, phosphate, and DOM molecules. Thermodynamic consistency requires that the adsorption is scaled to a chosen reference ion (Kinniburgh et al., 1999). In the modeling, the non-ideal coefficients of DOC and PO$_4$ were set equal and therefore, both can be used as reference. Implicitly, this choice means that both species can reach the same adsorption maximum if all sites are occupied and both species have the same reaction stoichiometry with respect to the surface sites used. We note that the NICA model has been used previously to model the binding of phosphate (Abou Nohra et al., 2007; Jiao et al., 2008). A major difference is that we use a scaling per unit surface area, which reveals the influence of DOC/NOM, which has not been considered previously. We note that the NICA equation will reduce to the competitive Langmuir equation for $n_i = 1$.

The challenge is to describe simultaneously the PO$_4$ adsorption with and without the presence of DOC as a function of phosphate concentration and pH. Therefore, we have generated with the CD model 36 data points for the PO$_4$ adsorption in 0.01 M CaCl$_2$ in the absence of

DOC for a wide range of phosphate concentrations (0.1–30 μM) and covering the range pH 4–7. These synthetic adsorption data could be described very well ($R^2 = 0.97$) with the fitted parameters of Table 2. In the approach, the site density was set at $\Gamma_{\max} = 3.5$ μmol/m^2. With this chosen number, a reasonable description can be obtained for the adsorption density of phosphate as well as NOM in soil without further scaling. The binding constant for DOC was derived by trial and error, evaluating simultaneously the phosphate and NOM adsorption for the soils studied. The standard deviation for the description of the phosphate adsorption of the soils (27 data points) is 0.25 μmol/m^2 and $R^2 = 0.66$. For NOM, the standard deviation is 0.25 μmol/m^2 and $R^2 = 0.32$.

In this thermodynamic model, total dissolved orthophosphate (C_{PO4}) was used. Moreover, the DOC is represented by one type of molecule whereas it has been shown that natural DOC fraction is a mixture of different types of organic molecules such as fulvic (FA), humic (HA), and hydrophilic acids (Hy), which all have variable charge. For a limited set of eight samples, we have fractionated the DOC in the three above-mentioned fractions using the method of Van Zomeren and Comans (2007). As follows from Table 1, most carbon in the solution was present as hydrophilic acids, $76 \pm 8\%$. A small fraction was present as FA and very little or no humic acid was found in the 0.01 M CaCl$_2$ extracts. The data show that the DOC has a low molecular mass and for these organic molecules in particular, it may be expected that they have a relatively strong interaction with phosphate (Weng et al., 2008). Moreover, small natural organic acids are more weakly bound by (hydr)oxide surfaces compared to molecules with a high molecular mass and corresponding charge such as HA (Weng et al., 2007). Therefore, DOC can be considered as labile and reactive for oxyanion competition.

Table 2
The parameters of the non-ideal competitive adsorption model describing which is used to construct the lines of Figs. 1, 3, and 4.

Parameter	Value
$n_{\mathrm{REF}} \equiv n\text{-PO}_4 \equiv n\text{-DOM}$[a]	0.29 ± 0.01
$\log K_{\mathrm{PO4}}$	8.5 ± 0.1
$\log K_{\mathrm{DOM}}$[b]	6.9 ± 0.1
$n\text{-H}$[c]	0.09 ± 0.01
$\log K_{\mathrm{H}}$	$\equiv 9$
$\Gamma_{\max}$[c] μmol/m^2	$\equiv 3.5$

[a] Equal numbers implies that PO$_4$ and DOC can reach the same adsorption maximum. Both n values can serve as reference in Eq. (3) (n_{REF}). Note ≡ chosen.

[b] The value of $\log K_{\mathrm{DOM}}$ is valid assuming a molar mass of $M = 750$ g/mol for DOM ($= CH_2O)_x$, $x = 25$).

[c] The low value of n-H illustrates the weak pH dependency of the overall adsorption of PO$_4$ in the multi-component systems. The value of n-H is low compared to the value found for humics (Milne et al., 2003), and might be related to the much stronger feedback of electrostatics on the change of the relative proton loading of sites θ_{H} on oxide surfaces. For H$^+$, the highest adsorption will be much lower, i.e. $\Gamma_{\mathrm{H}} = \Gamma_{\max} n_{\mathrm{H}}/n_{\mathrm{REF}} \sim 1.1$ μmol/m^2 which is ~ 100 mC/m^2. This number can be considered in a first order approach as representative for sesquioxides in the pH range considered.

For modeling, the DOC (mg/L) concentration is to be expressed as a DOM particle concentration (C_{DOM} in mol/L). An arbitrary assumption was made for the molar mass and carbon content. We assume that DOM can be represented by $(CH_2O)_x$ with a molar mass of $M = 750$ g/mol (i.e. $x = 25$ mol C/mol DOM). The resulting molar DOM concentration (mol/L) has been used to parameterize the NICA model in combination with the total molar orthophosphate concentration of the solution (C_{PO4}) and the H^+ activity. It is important to note that any other choice of a value for the molar mass M will lead in the fitting to the same description of the data, but another fitted value of K_{DOM}. In the fitting, the product $K_{DOM} \cdot C_{DOM}$ is independent of the choice of the molar mass M. A higher M leads to a lower C_{DOM} and *vice versa* but a correspondingly higher K_{DOM}.

3.5. NICA application

The parameter set of Table 2 has been used to construct the phosphate isotherms for a number of DOC concentrations, as given in Fig. 1. The results of the thermodynamic model (Fig. 1), as well as the previous multi-linear regression of the data (Section 3.2), show the relative significance of the variation in DOC for the phosphate loading. In nature, many biogeochemical factors may influence the actual DOC concentration in ecosystems. DOC can be produced as a byproduct of microbial degradation of organic matter but can also be released from oxide surfaces due to changes in the phosphate status of a soil. DOC itself can also be decomposed or absorbed in NOM supra-molecules. The complex nature of these interactions and processes makes it very difficult to do predictions of the DOC concentrations in the field. Therefore, like pH, the DOC concentration is most effectively used as input in, rather than as output from, modeling.

The undemanding non-electrostatic NICA approach has been used to relate the NOM adsorption to the DOC concentration in solution. The lines in Fig. 3 have been calculated for three phosphate concentrations that cover the experimental range (1, 10, and 30 μM) using the average pH value (pH 5.5). As is clear from Fig. 3, the quality of prediction of the density of ≡FeNOM is only reasonable. The standard error is 0.25 μmol/m^2. As discussed above, the amount of adsorbed NOM is based on the interaction with PO_4, and therefore it will refer particularly to small organic acids, because these are most effective in the competition as discussed above.

The NICA model can be used to generate the expected relationship between dissolved phosphate and the DOC concentration at a given pH and P loading (Fig. 4). The range of conditions corresponds to those previously used to calibrate the NICA model, i.e. pH ~4 to 7, c-PO_4 ~0.1 to 30 μmol/L, and DOC ~0 to 100 mg/L, all in 0.01 M $CaCl_2$ solution. The calculations have been done for a SSR, representative for soils in the field (10 kg/L) and refer to an average effective surface area of $A = 15$ m^2/g soil. Fig. 4 shows that one may expect for a given phosphate loading a rather strong increase of phosphate concentration in case of an increase of the DOC concentration. The large
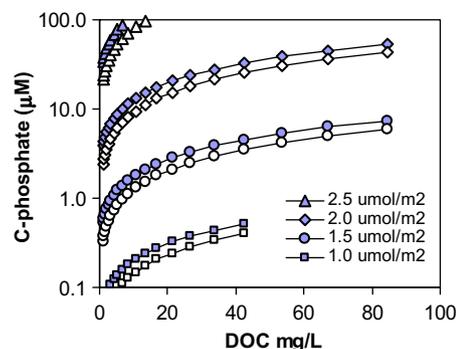

Fig. 4. The effect of DOC on the phosphate concentration (note the logarithmic scale) in 0.01 M $CaCl_2$ for a soil with a P loading of 1.0, 1.5, 2.0, and 2.5 μmol/m^2 at pH 5 and 7 (closed and open symbols respectively), SSR = 10 kg/L, and an average $A = 15$ m^2/g soil. The lines have been calculated with the NICA model (Table 2).

variation in the c-PO_4 and DOC relationship (Fig. 4) implies that if a series of soils with a variable PO_4 loading is considered, no simple relationship between dissolve phosphate and DOC will be found. A third point is that the calculated phosphate concentration decreases with an increase of the pH from 5 to 7 in a 0.01 M $CaCl_2$ extract. Calcium ions will promote the adsorption of phosphate at high pH (Rietra et al., 2001) and this effect is large in 0.01 M $CaCl_2$. In nature, the situation may be different. The pH dependency can be smaller, absent, or even opposite depending on the Ca^{2+} and Mg^{2+} concentrations in the pore water under field conditions. Moreover, the solubility of DOC may change with pH, which will effect the competition with phosphate at the oxide surfaces and the corresponding phosphate concentration in solution.

3.6. Epilogue

Above, we have shown how CD modeling can be implemented when it comes to application in field samples. It can be summarized as follows:

(A) The $NaHCO_3$ equilibrium extraction method (Hiemstra et al., 2010) will provide a straightforward measure for the oxidic surface area of a sample. The surface area is to be considered as an effective surface area that has the advantage that it is able to mimic the observed adsorption behavior using the most important oxyanion bound by natural oxide surfaces as calibrating ion (PO_4).

(B) The $NaHCO_3$ equilibrium extraction method will also reveal the fraction of reversibly bound ions (PO_4). The combination of this fraction and the effective surface area can be introduced in the CD model for an environmental application, if one accounts for the impact of the presence of adsorbed humic material. The impact of organic matter can be incorporated in the CD model in a first order approach by defining with only surface components a hypothetical surface species (≡FeNOM) that mimics the site and electrostatic competition. The effective NOM density (≡FeNOM) can only be applied in the CD model as long as the effective NOM adsorption is not significantly changed by the competition with other ions.

(C) There are several approaches to derive or estimate the effective adsorption density of NOM ($\equiv$FeNOM). Above, we have described how one may derive the effective adsorption density of NOM using as input the pH and phosphate concentration determined in a 0.01 M CaCl$_2$ extract for a given amount of reversibly bound phosphate (R_{ev}) and a known effective surface area A.

If a change of DOC is to be considered for a prediction, we suggest to estimate the effective adsorption density of NOM using the parameterized NICA model (Table 2). For this approach, data have to be available for the PO$_4$ and DOC concentrations and the pH value, preferably measured in a 0.01 M CaCl$_2$ extract at SSR of 0.1 kg/L. The actual calculation of $\equiv$FeNOM is straightforward, simply introducing the experimental concentrations in the NICA model (Eq. (3)), yielding Γ_{DOC} (mol/m^2), which can be recalculated to $\equiv$FeNOM in nm^{-2} (1 nm^{-2} = 1.66 μmol/m^2).

A third approach to estimate the effective NOM site density is based on an empirical relationship and can be deployed if other data are not available. We have found for our agricultural top soils (27 data points) that the relative NOM densities, defined as $\Gamma_{NOM}/(\Gamma_{NOM} + \Gamma_{PO4})$, are strongly related ($R^2 = 0.79$) by the total organic carbon content of the sampled material (Fig. 5). The advantage of the use of this relationship is that the organic carbon percentage is often measured as a general characteristic of samples. The measured carbon content in combination with the phosphate loading Γ_{PO4} determined experimentally with the probe ion method leads to an estimation of the Γ_{NOM}, which then can be applied in the CD model for application to field samples. This increase of surface coverage of NOM with the organic carbon content is in line with recent results found by studying the energetics of N$_2$ gas adsorption in soils (Wagai et al., 2009).

(D) Once the effective adsorption density of NOM ($\equiv$FeNOM) has been derived or estimated, it can be implemented in the SCM calculation scheme given in part I (Hiemstra et al., 2010).

In natural systems, the interfacial properties of the oxides will be determined by the dominant binding of only a few inorganic ions and additionally interfacial $\equiv$NOM. The proton is generally the potential determining ion of the surface and this ion will indirectly also determine the pristine Stern potentials (ψ_1 and ψ_2). However, the Stern potentials are strongly changed by electrostatic charge entering the interface via adsorption of other species (Δz_1 and Δz_2). Modeling shows that in non-acid soils, NOM, PO$_4^{3-}$, and Ca^{2+} are generally the most important components in determining these electrostatic potentials. For this reason, these components (H$^+$, Ca^{2+}, PO$_4^{3-}$, and NOM) can not be ignored in any realistic study or description of the adsorption of these ions and those present in minor amounts in the interface, in particular oxyanions such as As(OH)$_3$, AsO$_4^{3-}$, CrO$_4^{2-}$, SeO$_3^{2-}$, etceteras. Some species may have an intermediate position, being present in higher concentrations, such as SO$_4^{2-}$ and H$_4$SiO$_4$. The latter one can be important at neutral and alkaline pH conditions (ground and surface waters) and the first one is bound in acid soils (e.g. forest soils), together with Al^{3+}. Our calculations suggest that these ions may adsorb, but the amounts are often relatively low in comparison to PO$_4$ and NOM. In such case, these species are not primary potential determining ions strongly affecting the adsorption of the major species of the interface.

4. CONCLUSIONS

For the agricultural top soils studied, the variation in the reversible phosphate loading is unusually large ($\Gamma = \sim$1 to 3 μmol/m^2). This natural variation is strongly related to the amount of adsorbed NOM and vice versa. The effective amount of adsorbed NOM (0–2 μmol/m^2) is found by interpreting the phosphate concentration in 0.01 M CaCl$_2$ using the phosphate loading derived in the 0.5 M NaHCO$_3$ equilibration experiment as input in CD model. The competition is based on a defined $\equiv$FeNOM surface species that competes with phosphate. This interaction is due to site and electrostatic competition. The charge attribution to the 1-plane of the EDL is important for the electrostatic competition. The attribution of -1 v.u. per reacted group to the 1-plane is adequate to describe the competition and this choice can be rationalized by the surface speciation calculated with the various LCD model approaches. At a given pH and phosphate concentration in solution, the calculated PO$_4$–NOM competition shows an approximately 1:1 exchange.

At a given P loading, the PO$_4$ concentration in natural aqueous solutions is largely driven by the presence of DOC and adsorbed NOM. The actual PO$_4$ loading in field samples, measured with NaHCO$_3$ equilibration, is generally much lower than predicted from the phosphate concentration in the natural aqueous solutes or 0.01 M CaCl$_2$. Conversely, the PO$_4$ concentration predicted with the CD model without considering the presence of adsorbed $\equiv$NOM is about 10–1000 (or more) times too low.

The effective NOM density (0–2 μmol/m^2) as well as phosphate density (1–3 μmol/m^2) are correlated to the experimental phosphate and DOC concentration. The effective NOM adsorption can be linked to these solution parameters using a simplified NICA model that is parameterized on the available data. The model calculations show how DOC may affect the apparent phosphate loading and
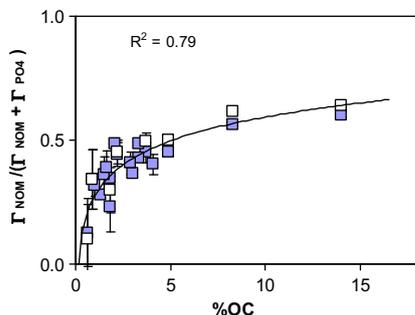

Fig. 5. The relative adsorption of effective NOM $\equiv \Gamma_{NOM}/(\Gamma_{NOM} + \Gamma_{PO4})$ can be correlated (line) with the logarithm of organic carbon percentage in the agricultural soil samples studied, i.e. $y = 0.32 \log x + 0.27$. Symbols as defined in Fig. 2.

its relation with the phosphate concentration. The model also shows that the NOM adsorption density is predominantly determined by the DOC concentration with only a minor effect of the phosphate concentration.

The DOC fraction of agricultural soils in 0.01 M CaCl$_2$ extracts consists of small organic acids with a prominent fraction of hydrophilic acids. These small and labile organic acids are expected to be most competitive for anion binding.

The parameterized NICA model can be used to estimate the change in effective NOM adsorption if a change of DOC is to be considered.

The effective NOM adsorption of agricultural top soils can be estimated using an empirical correlation between the relative NOM adsorption and the logarithm of the total organic carbon content of the samples. This approach is useful if other relevant information is lacking.

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