Assessing the Reactive Surface Area of Soils and the Association of Soil Organic Carbon with Natural Oxide Nanoparticles Using Ferrihydrite as Proxy

Juan C. Mendez,* Tjisse Hiemstra, and Gerwin F. Koopmans

ABSTRACT: Assessment of the surface reactivity of natural metal-(hydr)oxide nanoparticles is necessary for predicting ion adsorption phenomena in soils using surface complexation modeling. Here, we describe how the equilibrium concentrations of PO₄ obtained with 0.5 M NaHCO₃ extractions at different solution-to-soil ratios, can be interpreted with a state-of-the-art ion adsorption model for ferrihydrite to assess the reactive surface area (RSA) of agricultural top soils. Simultaneously, the method reveals the fraction of reversibly adsorbed soil PO₄ (R-PO₄). The applied ion-probing methodology shows that ferrihydrite is a better proxy than goethite for consistently assessing RSA and R-PO₄. The R-PO₄ pool agrees well with ammonium oxalate (AO)-extractable phosphorus, but only if measured as orthophosphate. The RSA varied between ~2 and 20 m²/g soil. The corresponding specific surface area (SSA) of the natural metal-(hydr)oxide fraction is ~350–1400 m²/g, illustrating that this property is highly variable and cannot be represented by a single value based on the AO-extractable oxide content. The soil organic carbon (SOC) content of our top soils increases linearly not only with the increase in RSA but remarkably also with the increase in mean particle size (1.5–5 nm). To explain these observations, we present a structural model for organo-mineral associations based on the coordination of SOC particles to metal-(hydr)oxide cores.

1. INTRODUCTION

The chemical behavior of many nutrients and pollutants in the environment is largely controlled by sorption phenomena occurring at the surfaces of metal-(hydr)oxides. These surfaces are also crucial for the formation of organo-mineral complexes, contributing to ion adsorption competition and to the long-term stabilization of organic carbon in soils and sediments. Particularly, nanocrystalline Fe- and Al-(hydr)-oxides may dominate the reactive metal-(hydr)oxide fraction in, for instance, podzols and agricultural top soils. Surface complexation models (SCMs) are powerful tools for describing ion adsorption to metal-(hydr)oxides. Presently, the charge distribution (CD) model, combined with a multisite ion complexation (MUSIC) model, is one of the most advanced SCMs. This approach was originally developed using the surface structure of well-crystallized metal-(hydr)-oxides. Recently, it has been extended for modeling ion adsorption to metal-(hydr)oxide nanoparticles, particularly ferrihydrite (Fh). Incorporating recent insights from the mineral and surface structure of this nanomaterial, the CD-MUSIC framework can also be used for describing the solid-solution partitioning of oxyanions in soils. However, for a realistic modeling of ion adsorption in soils, information about the reactive surface area (RSA) of the natural metal-(hydr)oxide fraction is an indispensable prerequisite, and therefore, this constitutes the main topic of the present contribution.

An accurate and consistent assessment of the RSA in soil samples is challenging. The use of traditional gas adsorption methods (i.e., Brunauer–Emmett–Teller (BET)) is not suitable because the drying process during sample preparation leads to irreversible aggregation of the metal-(hydr)oxide nanoparticles, resulting in underestimation of the RSA. Alternatively, polar compounds (e.g., ethylene glycol monoethyl ether) have been used as probe molecules, but this approach typically provides an estimation of the surface area of clays. Humic acids have also been used as probe molecules to determine the relative surface area abundance of goethite and kaolinite in sediments, but this approach has been developed for systems composed of only two mineral phases. For SCM applications to soils, the RSA of the metal-(hydr)oxide fraction is often estimated based on selective extractions of Fe and Al. In this approach, the nanocrystalline fraction of...
metal-(hydr)oxides is assessed using a traditional acid ammonium oxalate (AO) extraction \(^{33,34}\) and next converted to the RSA (m\(^2\)/g soil) using, for the extracted metal-(hydr)oxides, a standard value for the specific surface area (SSA) and a fixed value for the molar mass (\(M_{nano}\)). However, this may lead to inconsistent results because both properties are particle size-dependent \(^{35,36}\) and can greatly vary among soil samples.\(^{37-39}\)

Hiemstra et al.\(^7\) have developed a probe-ion method for assessing the effective RSA of soils in which soil samples are equilibrated with 0.5 M NaHCO\(_3\) (pH 8.5) at different solution-to-soil ratios (SSRs), followed by analysis of the equilibrium PO\(_4\) concentration. These data are then interpreted with the CD model to retrieve the RSA, using a chosen metal-(hydr)oxide as a reference to represent the natural metal-(hydr)oxide fraction of soils. At the time of development, well-crystallized goethite was chosen as a proxy because the PO\(_4\)−CO\(_3\) interaction had only been studied extensively for this material.\(^{40}\) However, the application of this proxy\(^7,41\) revealed for the metal-(hydr)oxide fraction of the studied soils SSA values that are typical for nanosized particles with diameters of ~2–8 nm, which is in conflict with the use of well-crystallized goethite as a proxy. Recently, the interaction of PO\(_4\)−CO\(_3\) has been measured and modeled for Fh nanoparticles,\(^{42}\) and we have shown that both oxanions have rather different competitive adsorption in Fh and goethite systems.\(^{42}\) This implies that using Fh as a proxy will inevitably affect the RSA of the soil estimated by modeling probe-ion data, and therefore, this will be studied here.

Besides the effective RSA, the above ion-probing methodology also simultaneously reveals the pool of reversibly bound PO\(_4\) (R-PO\(_4\)) that is associated with the metal-(hydr)oxides. This calculated R-PO\(_4\) pool can be compared with the pool of orthophosphate extracted with, e.g., ammonium oxalate (AO-PO\(_4\)). We consider the agreement between R-PO\(_4\) and AO-PO\(_4\) as a keystone in making the ion-probing methodology a valid and valuable instrument for consistently assessing the RSA of soils. In the earlier approach,\(^7\) it was overlooked that in the data collection total soluble phosphorus (P\(_{tot}\)) rather than orthophosphate was measured in the AO extracts, while the samples may contain a variable amount of organic P.\(^{43-45}\) Therefore, in this study, new AO-PO\(_4\) data have been collected for the same soils as those used by Hiemstra et al.\(^7\)

The aforementioned ion adsorption framework for Fh includes a systematic implementation of the size dependency of the fundamental properties of this nano-oxide material, including molar mass (\(M_{nano}\)) and mass density (\(\rho_{nano}\)), which are both crucial for a consistent interpretation of the ion adsorption data.\(^{46,47}\) However, in our application of SCM to soils, a complicating factor is that not only Fe but also Al contributes to the composition of the natural metal-(hydr)-oxides. This will affect, among other things, the \(M_{nano}\) and particularly the \(\rho_{nano}\) of the natural metal-(hydr)oxide fraction. The latter is essential for translating the SSA of the nano-oxide fraction into a corresponding mean particle diameter, which in turn may affect the SCM calculations.\(^7\) In this study, our goal is to develop a systematic and consistent approach for modeling ion adsorption data in soils when this process is governed by Fe- and Al-(hydr)oxide nanoparticles.

Another objective of our study is to gain insights into the close relationship between the calculated RSA and the content of soil organic carbon (SOC) in our top soils. For this purpose, we develop a novel view on how SOC and metal-(hydr)oxide nanoparticles are structurally associated. This is important as these organo-mineral associations are considered as a key factor in determining the long-term stability of SOC.\(^{5,26,48}\) We show that the variation in the SOC content of our top soils can be largely understood by analyzing the effective RSA of the soil and the SSA of the metal-(hydr)oxide fraction.

2. METHODOLOGY

2.1. Soil Samples. We used the data set of Hiemstra et al.\(^7,49\) of 19 soil samples, which were selected from a larger collection of representative Dutch agricultural top soils.\(^{50}\) The selected samples (Table S1) cover a wide range of pH values (~4.0–7.0), SOC (~1–15%), clay content (~3–30%), 0.01 M CaCl\(_2\)-soluble PO\(_4\) (~1–30 μM), and Fe- and Al-(hydr)oxides extractable with AO ([Fe + Al]\(_{AO}\), 14–361 mmol/kg) and with dithionite–citrate–bicarbonate (DCB) ([Fe + Al]\(_{DCB}\), 22–879 mmol/kg).

The above data set\(^7,49\) has been complemented in this study with newly collected data for the orthophosphate concentration in the AO soil extracts (AO-PO\(_4\)), which was measured colorimetrically\(^{51}\) with a segmented flow analyzer (SFA) after dilution with demineralized water (x100) to eliminate the interference of oxide in the AO-PO\(_4\) measurements.\(^{52,53}\) The total soluble phosphorus was also measured in the AO extracts (AO-P\(_{tot}\)), showing an excellent agreement with previously reported data for the same soil series\(^7,49\) (Figure S1).

2.2. Phosphate Desorption Data. The PO\(_4\) desorption data are from Hiemstra et al.\(^7\) which were obtained by equilibrating soil samples (~10–15 days) with freshly prepared 0.5 M NaHCO\(_3\) solutions (pH 8.5) at six SSRs ranging between 5 and 300 L/kg. The equilibrium PO\(_4\) concentrations were measured colorimetrically,\(^{51}\) using an SFA instrument. To remove the dissolved organic matter released during the NaHCO\(_3\) extractions, powdered activated carbon (AC) was added (0.40 g/g soil) to the soil suspensions. The detailed experimental procedure is given in Hiemstra et al.\(^7\)

2.3. Surface Complexation Modeling. The competitive PO\(_4\)−CO\(_3\) interaction in the 0.5 M NaHCO\(_3\) soil extracts was interpreted with a modeling framework built from the combination of the CD model\(^1\) and a novel structural multisite surface complexation (MUSIC) model for Fh.\(^{11}\) The compact part of the electrical double layer (EDL) was described with the extended Stern layer approach for curved surfaces.\(^{52,53}\) The latter includes the complication of protons, electrolyte ions, PO\(_4\) and CO\(_3\).\(^{11,42}\) The pH, NaHCO\(_3\) concentration, SSR, and gas-to-solution volume ratio (L/L) were used as input data for the modeling. The effective RSA and R-PO\(_4\) were the only adjustable parameters, which were fitted simultaneously by iterative CD model calculations (Section 3.1). Model calculations were done with the software Ecosat\(^{44}\) (version 4.9) in combination with the FIT\(^{55}\) program for parameter optimization.

3. RESULTS AND DISCUSSION

3.1. Background. For a soil, a pool of reversibly bound orthophosphate (R-PO\(_4\), mol/kg) can be defined for which the value is fixed at the time of sampling and imposed by the field conditions. Depending on the SSR (L/kg), the R-PO\(_4\) pool is redistributed over the solid and solution phases in 0.5 M NaHCO\(_3\) extracts according to the mass balance.
Goethite and Fh systems, and this difference is PO₄-loading-dependent.

The competitive adsorption isotherm applied in eqs 1 and 2 to relate \( \Gamma \) and \( c_i \) will depend on the type of metal-(hydr)oxide. This implies that the calculation of both \( A \) and R-PO₄ by measuring the equilibrium concentrations \( c_i \) at various SSRs allows the calculation of the surface area \( A \) according to

\[
R\text{-PO}_4 = A \Gamma + SSR \ c
\]

where \( A \) is the effective RSA of the soil (m²/kg soil), \( \Gamma \) is the PO₄ surface density of the metal-(hydr)oxide fraction present in the soil (mol/m²), and \( c \) is the PO₄ concentration in solution (mol/L).

If equilibrium is attained, this mass balance can be used to iteratively derive the surface area \( A \) and R-PO₄ by measuring the equilibrium concentrations \( c_i \) at various SSRs. The measurement of \( c \) as a function of SSR results in a PO₄ desorption curve, as shown in Figure S2. Key in the methodology to derive \( A \) and R-PO₄ is the translation of the measured concentrations \( c_i \) into the PO₄ surface density \( \Gamma_i \). Actually, the relationship \( \Gamma_i - c_i \) is the competitive adsorption isotherm of PO₄ in the NaHCO₃ solution, whose interpretation will depend on the type of metal-(hydr)oxide used as reference in the CD model calculations. For a chosen reference oxide, a minimum set of two \( (i = 2) \) combinations of \( c_i \) and SSR allows the calculation of the surface area \( A \) according to

\[
A = \frac{\Delta(SSR \times c)}{\Delta \Gamma_i}
\]

with \( \Delta \) indicating the change in the values of the respective parameters with indices \( i = 1 \) and 2.

The calculation of the PO₄ surface density is sensitive to uncertainty in the experimental \( c \) value in the 0.5 M NaHCO₃ extracts. Therefore, six SSRs are used in the present study. These data reveal a part of the desorption isotherm that can be interpreted with the CD model to derive the values of \( A \) and R-PO₄ by iterative optimization.

### 3.2. PO₄ Adsorption in Model Systems: Ferrihydrite vs Goethite

The competitive adsorption isotherm applied in eqs 1 and 2 to relate \( \Gamma \) and \( c_i \) will depend on the type of metal-(hydr)oxide. This implies that the calculation of both \( A \) and R-PO₄ will be influenced by the choice of either Fh or goethite as reference oxide in the data interpretation of the probe-ion method. Recently, it has been shown that CO₃ competes more PO₄ than goethite and this is related to the higher protonation of the adsorbed PO₄ species on Fh.

In the absence of CO₃ as a competitor, the adsorption of PO₄ on Fh and goethite is rather similar at pH 8.5, as shown in Figure 1b. However, at lower pH values (e.g., pH 5), Fh adsorbs more PO₄ than goethite and this is related to the higher protonation of the adsorbed PO₄ species on Fh.

In 0.5 M NaHCO₃ systems (Figure 1a), the adsorption of PO₄ to both Fe-(hydr)oxides is lower than in systems with 0.5 M NaNO₃ (Figure 1b). This is due to the competition of CO₃ and PO₄ for the same binding sites at the mineral surfaces. In the presence of CO₃, the decrease of the PO₄ adsorption is most distinct for Fh, particularly at low PO₄ concentrations, illustrating that CO₃ suppresses PO₄ adsorption more efficiently on Fh than on goethite. Differences in the surface speciation of CO₃ might explain the different CO₃-PO₄ interactions for both oxides. Inner-sphere bidentate complexes dominate the CO₃ speciation in both oxides; however, the formation of a ternary complex by the interaction of a Na⁺ ion with an adsorbed bidentate CO₃ complex \( (\equiv FeO)CO_{\cdots Na^+}) \) is more favored by Fh than by goethite (Figure S3).

In 0.5 M NaHCO₃, Fh preserves less well the high-affinity character of PO₄ adsorption, which is visible in the form of a lower slope of the isotherm, particularly at low PO₄ concentrations. It implies that Fh has a lower capacity to buffer the PO₄ concentration in the NaHCO₃ solutions. This property will have implications for the probe-ion method in assessing the RSA of soils. Hence, a fundamental question arises: which Fe-(hydr)oxide most accurately represents the ion adsorption behavior of the natural metal-(hydr)oxide fraction of top soils? In other words, which Fe-(hydr)oxide, i.e., Fh or goethite, is a better proxy for the natural oxide fraction in our soils? This is answered in the following section.

### 3.3. Reversibly Adsorbed Phosphate: Experimental and Model Results

For testing which reference Fe-(hydr)oxide material, either Fh or goethite, is a better proxy for describing with SCM the reactivity of the natural metal-(hydr)oxide in top soils, one may collect experimental information regarding the size of the reversibly PO₄ pool in soils and compare the results with the calculated R-PO₄ pools.

Soil extractions with AO are often used for assessing the fraction of metal-(hydr)oxides present in soils as nanoparticles, because it has been shown that Fh is completely dissolved with that procedure, in contrast to well-crystallized metal-(hydr)-oxides. The AO extraction method is also used to assess
the degree of P saturation of soils\textsuperscript{58–60} by measuring with inductively coupled plasma atomic emission spectroscopy (ICP-OES) simultaneously the amount of P released in the AO extracts. Laboratory experiments using a P sink technique have shown that all P\textsubscript{tot} extractable from soils with AO is potentially desorbable.\textsuperscript{61} This P\textsubscript{tot} pool was also largely available for uptake by grass in a long-term P-mining experiment.\textsuperscript{62} However, part of the measured P\textsubscript{tot} in the AO extracts may not be present as orthophosphate\textsuperscript{63,64} whereas the probe-ion method is based on the measurement of the equilibrium PO\textsubscript{4} concentration in the NaHCO\textsubscript{3} extracts. Therefore, the molybdenum-blue method\textsuperscript{65} has been applied in this study to measure the orthophosphate pool in the AO extracts.\textsuperscript{44,45}

For our soils, the difference between the amounts of P\textsubscript{tot} (AO-P\textsubscript{tot}) and orthophosphate (AO-PO\textsubscript{4}) as extracted with AO is illustrated in Figure S4a. On average, AO-PO\textsubscript{4} contributed to 74 ± 9% to AO-P\textsubscript{tot}. The remainder is probably due to the presence of organic P species (P\textsubscript{org}).\textsuperscript{45} Indeed, a positive relationship ($R^2 = 0.65$) is found between P\textsubscript{org} (i.e., AO-P\textsubscript{tot} minus AO-PO\textsubscript{4}) and the SOC content of the soils (Figure S4b).

The presence of P\textsubscript{org} in the AO extracts implies that the validation of the probe-ion method cannot be based on the comparison of the calculated R-PO\textsubscript{4} and the amount of AO-P\textsubscript{tot} as it was done previously.\textsuperscript{44,45} In other SCM studies, the use of AO-P\textsubscript{tot} rather than AO-PO\textsubscript{4} as a measure for R-PO\textsubscript{4} has led to an overestimation of the PO\textsubscript{4} concentration in soil leachates\textsuperscript{64} and soil-solution extracts.\textsuperscript{25} Therefore, the authors proposed the use of isotopically exchangeable PO\textsubscript{4} (E-value) as a proxy for R-PO\textsubscript{4} in SCM. However, the results of this methodology are inherently associated with the kinetics of P exchange and are influenced by the chosen evaluation time.\textsuperscript{65}

In Figure 2a, the modeled R-PO\textsubscript{4} pools are compared with the experimental measurements of AO-PO\textsubscript{4}. When goethite is used as reference oxide material in the interpretation of the results of the probe-ion method, the calculated amounts of R-PO\textsubscript{4} are on average ~1.5 times larger than the measured amounts of AO-PO\textsubscript{4}. These model overestimations of the reversibly bound PO\textsubscript{4} pool clearly indicate that the PO\textsubscript{4} adsorption behavior of the metal-(hydr)oxide fraction of soils in 0.5 M NaHCO\textsubscript{3} cannot be well represented by goethite. However, when Fh is used as a reference oxide material, a better agreement is found between modeled and measured amounts of reversibly adsorbed PO\textsubscript{4}, identifying Fh as a better proxy for the natural metal-(hydr)oxide fraction of our top soils. This suggests that the overall PO\textsubscript{4} binding to the natural metal-(hydr)oxide fraction is more similar to the PO\textsubscript{4} binding behavior on Fh than to that on goethite. Nevertheless, for some soil samples, the Fh model underestimates the experimental AO-PO\textsubscript{4} values, which may be due to the presence of a small fraction of nondesorbable AO-PO\textsubscript{4} (e.g., present in an occluded form) or to the presence of more crystalline materials, e.g., nanosized goethite, that contribute to the overall PO\textsubscript{4} adsorption.

Additionally, a basic assumption in our approach is that soil organic matter (SOM) does not interfere with the interpretation of the CO\textsubscript{3}−PO\textsubscript{4} competition. Therefore, an excess of activated carbon (AC) is added to remove SOM.\textsuperscript{7} Organic P species such as inositol hexa-phosphate (IHP) form coprecipitates with Al, Fe, and Ca\textsuperscript{56} but may also strongly interact with the surfaces of metal-(hydr)oxides in soils, particularly at low pH.\textsuperscript{55,67} If the latter fraction is not removed effectively by the AC added to the alkaline NaHCO\textsubscript{3} soil extracts, these IHP species can compete with orthophosphate for the same reactive sites, thereby affecting the value of R-PO\textsubscript{4}.

### 3.4. Reactive Surface Area of Fe and Al-(Hydr)oxides.

Figure 2b shows the effective RSA of our top soils as a function of the amount of AO-extractable Fe and Al ([Fe + Al]\textsubscript{AO}). The RSA, calculated with the CD model using Fh as a proxy for the natural metal-(hydr)oxide fraction, varies by a factor of ~10 across the soil sample series, i.e., ~2–20 m\textsuperscript{2}/g. These RSA values, combined with the PO\textsubscript{4} surface density that is simultaneously found by CD modeling, explain the agreement between the experimental AO-PO\textsubscript{4} and the modeled R-PO\textsubscript{4} values (Figure 2a). This cannot be said when goethite is used as a proxy because in that case more R-PO\textsubscript{4} is predicted by modeling than measured in the AO extracts (Figure 2a). In other words, the RSA values found using Fh as a proxy are bona fide.

As expected, the effective RSA and the content of [Fe + Al]\textsubscript{AO} are positively correlated (Figure 2b). When using Fh as proxy, the slope of the (full) line that approximates the mean value of the specific surface area (SSA) of the soil metal-
(hydr)oxide fraction is \(\sim 65 \pm 12 \text{ m}^2/\text{mmol} \) of Fe and Al. In the erroneous case of using goethite, the mean value would be SSA = 1120 \(\pm 250 \text{ m}^2/\text{g} \) oxide. Using \([\text{Fe} + \text{Al}]_{\text{DCB}}\) in the scaling instead of \([\text{Fe} + \text{Al}]_{\text{AO}}\) (Figure S5), these SSA values will decrease because \([\text{Fe} + \text{Al}]_{\text{AO}}\) in our soil samples represents on average \(\sim 60 \pm 15\% \) of the total metal-(hydr)oxide content (Table S1). The difference \([\text{Fe} + \text{Al}]_{\text{DCB}}\) minus \([\text{Fe} + \text{Al}]_{\text{AO}}\) is due to the presence of well-crystallized metal-(hydr)oxides. However, the SSA of this fraction is likely much lower. Crystalline Fe-(hydr)oxides prepared in the laboratory usually have SSAs that are up to a factor of \(\sim 10\) smaller than the SSA of Fh.6,36 Hence, well-crystallized oxides in our top-soil samples may contribute more in terms of mass than in terms of surface reactivity. Indeed, exploratory calculations (Figure S6) suggest that the \([\text{Fe} + \text{Al}]_{\text{AO}}\) fraction represents \(\sim 90 \pm 10\% \) of the total metal-(hydr)oxide reactivity of our soils on a surface area basis.

The RSA values derived from the probe-ion method represent an “effective” reactive surface area, resulting from probing all surfaces in soil that bind PO4, for which the adsorption interactions are described using a well-characterized proxy, e.g., Fh in our case. The metal-(hydr)oxide fraction is thought to be the most important reactive material for the binding of PO4 in soils due to its much higher affinity for oxyanions and larger SSA in comparison with other reactive soil surfaces.24,43,68 For instance, calcium carbonate minerals (e.g., calcite) can also bind PO45,69 but due to their low binding affinity and SSA, the contribution of these minerals to the effective RSA would be relevant only in strongly calcareous soils with low metal-(hydr)oxide content. The oxides of clays can also contribute to the calculated RSA, particularly in fine-textured soils.70 The possible clay contribution to the RSA in our soils can be inferred from the regression analysis of the relationship between RSA and \([\text{Fe} + \text{Al}]_{\text{AO}}\) (Figure 2b), provided that the clay and metal-(hydr)oxide contents are not significantly correlated. A positive and significant intercept of the linear regression line in Figure 2b would then suggest a contribution of clay minerals to the RSA. However, such a contribution cannot be resolved statistically from our data, i.e., the intercept is not significantly different from zero (\(p < 0.001\)). Therefore, the RSA estimated for our top soils is likely dominated by metal-(hydr)oxides, particularly by the nanocrystalline fraction of Fe- and Al-(hydr)oxides.

The physicochemical properties of naturally formed metal-(hydr)oxide nanoparticles may differ from those of their synthetic counterparts.67,71 In nature, the nanocrystalline structure and particle size distribution of Fh are affected when it precipitates in the presence of organic matter2–75 or inorganic ions (e.g., Al3+, Si4+).76–78 This has raised concerns about the use of SCMs that are parameterized for synthetic oxides for describing ion adsorption to the metal-(hydr)oxide fraction of soils.74 However, despite molecular-scale differences found for the binding preferences of PO4 to Al/Fe coprecipitates, the macroscopic adsorption of PO4 was indistinguishable from that of pure Fh at Al/(Fe + Al) molar ratios <0.50,79 meaning that the adsorption isotherms were similar. Likewise, our results show that the overall macroscopic adsorption behavior of PO4 to metal-(hydr)oxides in soils can be well described using Fh as reference oxide material. From a practical perspective, this study is relevant as it supports the use of Fh as a single proxy for describing the interaction of oxyanions with the reactive fraction of metal-(hydr)oxides in top soils with SCM. Implications of using only Fh as a proxy in the assessment of the effective RSA are discussed in Section 3.5.

Despite the uncertainties associated with the calculation of RSA and R-PO4 with our probe-ion approach, these parameters can be well used in SCM to get for soils more mechanistic insights into the chemical processes affecting the soil-solution partitioning of PO4 in, for instance, equilibrium extractions that are routinely used for assessing the P-status of soils.

3.5. Size-Dependent Properties of Natural Metal-(Hydr)oxides. Translation of the SSA (m2/mol) to an equivalent mean particle size \(d\) (m) of natural metal-(hydr)oxide nanoparticles requires a consistent set of values for the molar mass \(M_{\text{nano}}\) (g/mol) and mass density \(\rho_{\text{nano}}\) (g/m3). These values can be assessed using a set of mathematical relationships, as given by Hiemstra.46 Since \(M_{\text{nano}}\) and \(\rho_{\text{nano}}\) are both particle size-dependent, they cannot be calculated directly, but their values are derived iteratively as explained in Section S6 of the Supporting Information (SI).

The \(M_{\text{nano}}\) and \(\rho_{\text{nano}}\) of Fe- and Al-(hydr)oxide nanoparticles depend on their chemical composition. For Fh, the chemical properties of Fe- and Al-(hydr)oxide nanoparticles may differ from those of their synthetic counterparts.67,71 In nature, the nanocrystalline structure and particle size distribution of Fh are affected when it precipitates in the presence of organic matter2–75 or inorganic ions (e.g., Al3+, Si4+).76–78 This has raised concerns about the use of SCMs that are parameterized for synthetic oxides for describing ion adsorption to the metal-(hydr)oxide fraction of soils.74 However, despite molecular-scale differences found for the binding preferences of PO4 to Al/Fe coprecipitates, the macroscopic adsorption of PO4 was indistinguishable from that of pure Fh at Al/(Fe + Al) molar ratios <0.50,79 meaning that the adsorption isotherms were similar. Likewise, our results show that the overall macroscopic adsorption behavior of PO4 to metal-(hydr)oxides in soils can be well described using Fh as reference oxide material. From a practical perspective, this study is relevant as it supports the use of Fh as a single proxy for describing the interaction of oxyanions with the reactive fraction of metal-(hydr)oxides in top soils with SCM. Implications of using only Fh as a proxy in the assessment of the effective RSA are discussed in Section 3.5.

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Despite the uncertainties associated with the calculation of RSA and R-PO4 with our probe-ion approach, these parameters can be well used in SCM to get for soils more mechanistic insights into the chemical processes affecting the soil-solution partitioning of PO4 in, for instance, equilibrium extractions that are routinely used for assessing the P-status of soils.

3.5. Size-Dependent Properties of Natural Metal-(Hydr)oxides. Translation of the SSA (m2/mol) to an equivalent mean particle size \(d\) (m) of natural metal-(hydr)oxide nanoparticles requires a consistent set of values for the molar mass \(M_{\text{nano}}\) (g/mol) and mass density \(\rho_{\text{nano}}\) (g/m3). These values can be assessed using a set of mathematical relationships, as given by Hiemstra.46 Since \(M_{\text{nano}}\) and \(\rho_{\text{nano}}\) are both particle size-dependent, they cannot be calculated directly, but their values are derived iteratively as explained in Section S6 of the Supporting Information (SI).

The \(M_{\text{nano}}\) and \(\rho_{\text{nano}}\) of Fe- and Al-(hydr)oxide nanoparticles depend on their chemical composition. For Fh, the chemical properties of Fe- and Al-(hydr)oxide nanoparticles may differ from those of their synthetic counterparts.67,71 In nature, the nanocrystalline structure and particle size distribution of Fh are affected when it precipitates in the presence of organic matter2–75 or inorganic ions (e.g., Al3+, Si4+).76–78 This has raised concerns about the use of SCMs that are parameterized for synthetic oxides for describing ion adsorption to the metal-(hydr)oxide fraction of soils.74 However, despite molecular-scale differences found for the binding preferences of PO4 to Al/Fe coprecipitates, the macroscopic adsorption of PO4 was indistinguishable from that of pure Fh at Al/(Fe + Al) molar ratios <0.50,79 meaning that the adsorption isotherms were similar. Likewise, our results show that the overall macroscopic adsorption behavior of PO4 to metal-(hydr)oxides in soils can be well described using Fh as reference oxide material. From a practical perspective, this study is relevant as it supports the use of Fh as a single proxy for describing the interaction of oxyanions with the reactive fraction of metal-(hydr)oxides in top soils with SCM. Implications of using only Fh as a proxy in the assessment of the effective RSA are discussed in Section 3.5.

Despite the uncertainties associated with the calculation of RSA and R-PO4 with our probe-ion approach, these parameters can be well used in SCM to get for soils more mechanistic insights into the chemical processes affecting the soil-solution partitioning of PO4 in, for instance, equilibrium extractions that are routinely used for assessing the P-status of soils.
composition can be given as $\text{FeO}_{1.4} (\text{OH})_{0.2} \cdot n \text{H}_2\text{O}$, where $\text{FeO}_{1.4} (\text{OH})_{0.2}$ is the composition of the bulk mineral and $n \text{H}_2\text{O}$ is the amount of chemisorbed water completing the coordination sphere of the Fe atoms present at the surface.\textsuperscript{18,36} Similarly, the composition of nanosized $\text{Al(OH)}_3$ particles may be written as $\text{Al(OH)}_3 \cdot n \text{H}_2\text{O}$. The fraction of metal ions forming surface groups increases when the particle size decreases, leading to an increase in $n \text{H}_2\text{O}$. Consequently, $M_{\text{nano}}$ increases when the particle size decreases, whereas $\rho_{\text{nano}}$ simultaneously decreases because the surface groups ($-\text{OH}$ and $-\text{OH}_2$) contribute more to the particle volume than to the mass.\textsuperscript{36}

In Figure 3a, the excess amount of chemisorbed water ($n \text{H}_2\text{O}$) is presented for $\text{Fh}$ and $\text{Al(OH)}_3$ nanoparticles as a function of the SSA. For $\text{Fh}$, the data are from Hiemstra.\textsuperscript{42} For comparison, experimental $\text{Fh}$ data of Michel et al.\textsuperscript{20} are also given. The data for $\text{Al(OH)}_3$ have been derived in the present study following a whole particle construction approach, as described previously.\textsuperscript{18,82} Briefly, near-spherical nanoparticles varying in size are constructed with the Crystalmaker software and the amount of coordinative water of these particles is calculated after completion of the coordination sphere of the metal ions at the surface by adding additional $-\text{OH}$ and $-\text{OH}_2$ groups.\textsuperscript{42} As follows from Figure 3a, the excess amount of water is less for $\text{Al(OH)}_3$ nanoparticles than for $\text{Fh}$. The reason is that for $\text{Al(OH)}_3$, part of the surface ligands is already present as $-\text{OH}$, while this is mainly $-\text{O}$ in the case of $\text{Fh}$. The slope of the linear relationships of Figure 3a represents the surface loading of excess chemisorbed water, with $N_n\text{H}_2\text{O}$ being $12.6 \text{ mol/m}^2$ for $\text{Fh}$ and $6.3 \text{ mol/m}^2$ for $\text{Al(OH)}_3$.

In Figure 3b, the theoretical relationship between SSA and the equivalent spherical particle diameter $d$, calculated with $\text{SSA} = 6/(\rho_{\text{nano}}d)$, is given for $\text{Fh}$ and $\text{Al(OH)}_3$ nanoparticles. For spherical particles with the same diameter, the SSA of $\text{Al(OH)}_3$ is higher than that of $\text{Fh}$. The reason is that $\text{Al(OH)}_3$ has a much lower $\rho_{\text{nano}}$ since the oxygen ions of the lattice are neutralized by light (Al) and very light (H) elements, in contrast to $\text{Fh}$ where most neutralizing cations are heavy (Fe).

Figure 3b also shows the equivalent particle diameter ($d$) of the natural metal-(hydr)oxide nanoparticles in the various soils of this study. The calculated $d$ varies between $\sim 1.5$ and $5$ nm. The smallest particles will contain typically $\sim 50$ metal ions and the largest ones $\sim 2000$. The calculated $d$ values are between those of $\text{Fh}$ and $\text{Al(OH)}_3$, because the natural metal-(hydr)oxides contain $\sim 5$–$50$ mol % Al as found in the AO extracts (Table S1). This Al can be partly present in the Fe-(hydr)oxides by Al-substitution.\textsuperscript{1} When $\text{Fh}$ is synthesized in the presence of increasing amounts of Al, a substitution of up to $\sim 20$–$30$ mol % Al has been reported before the precipitation of secondary $\text{Al(OH)}_3$ phases occurred.\textsuperscript{83,64}

The $d$ values of the natural metal-(hydr)oxide fraction (Figure 3b) have been calculated by scaling the effective RSA to the amount of $\text{Fe + Al \cdot AO}$. In the approach, the overall SSA of the metal-(hydr)oxide fraction is calculated assuming that the $M_{\text{nano}}$ and $\rho_{\text{nano}}$ are weighted values of two constituting nano-oxide phases, i.e., $\text{Fh}$ and nano-$\text{Al(OH)}_3$, that are treated as endmembers in the calculations. The overall $M_{\text{nano}}$ and $\rho_{\text{nano}}$ values of the natural metal-(hydr)oxides are, respectively, the mole-weighted $M_{\text{nano}}$ and the volume-weighted $\rho_{\text{nano}}$ of the two endmember nano-oxide phases, for which the corresponding $M_{\text{nano}}$ and $\rho_{\text{nano}}$ values are found with the set of equations given by Hiemstra.\textsuperscript{42} Details of the calculation procedure are given in Section S6 of the SI.

Table 1 summarizes the variation in $M_{\text{nano}}$ and $\rho_{\text{nano}}$ of the constituting nano-(hydr)oxide phases that contribute to the size-dependent properties of the natural metal-(hydr)oxide fraction of our top soils. The SSAs of the reactive metal-(hydr)oxides obtained for our soils (Tables 1 and S1) largely vary, as it ranges between $\sim 350$ and $1400 \text{ m}^2/\text{g}$. Hence, the use of a "standard" SSA value for AO-extractable Fe- and Al-(hydr)oxides, as often done in SCM studies (e.g., $600 \text{ m}^2/\text{g}$), may lead to a large deviation in the supposed availability of reactive sites in the soils. This, in turn, will affect the outcome of the ion adsorption modeling.

$M_{\text{nano}}$ values of the nano-oxide endmembers (Table 1) are larger than the molar masses of the bulk minerals, $\text{FeO}_{1.4} (\text{OH})_{0.2}$ ($81.65 \text{ g/mol}$) and $\text{Al(OH)}_3$ ($78 \text{ g/mol}$). Using these bulk mineral molar masses will lead to smaller values for $d$ and, correspondingly, to larger values for SSA. Following our consistent approach, the estimated $d$ in our top soils ranges between $\sim 1.5$ and $5.0$ nm, which is in agreement with previous studies stating that nanosized particles dominate the reactive metal-(hydr)oxide fraction in top soils.\textsuperscript{36,85} Direct measurements for the size of natural metal-(hydr)oxide nanoparticles in soils are scarce in the literature. Using asymmetric flow field-flow fractionation, a size range of $\sim 2$–$10$ nm was found for Fe-(hydr)oxide nanoparticles from a podzol soil dispersed with pyrophosphate, with maximum concentrations found at a particle size of $\sim 5$ nm.\textsuperscript{37} These results provided direct evidence for the presence of reactive nanosized particles in the metal-(hydr)oxide fraction of the soil studied.

The effective RSA values used in the above calculations were derived using only FeH as a proxy in the CD model. As mentioned, the macroscopic PO$_4$ adsorption behavior of the reactive metal-(hydr)oxides in our top soils is similar to that of $\text{Fh}$. However, if differences exist in PO$_4$ affinity between Fe-
and Al-(hydr)oxides, this will lead to a systematic bias in the RSA calculations. A larger PO₄ adsorption capacity, expressed in mol PO₄ per mol Al or Fe, has been reported for nanocrystalline Al-(hydr)oxide compared to that for Fe. This may suggest a difference in binding affinity. However, it cannot be excluded that the materials differ in particle size and SSA, rather than in affinity. As the SSA of Al(OH)₃ nanomaterials is currently unknown, no parameterized SCM exists to date that can be deployed. This underlines the relevance of the present approach that uses only Fe as proxy for the overall reactive metal-(hydr)oxide in soils. A future challenge will be the development of an SCM approach that distinguishes between nanocrystalline Fe- and Al-(hydr)oxides. This may be particularly relevant for describing the competitive adsorption of AsO₄⁻⁻PO₄ as these oxyanions may have different competitive behavior in mixed systems containing both Fe and Al-(hydr)oxides.

3.6. Organo-Mineral Interactions: Structural Arrangement. In the literature, the relationship between SOC and metal-(hydr)oxide content has been well recognized for various soil types. With our ion-probe methodology, the relationship between SOC and the calculated values of RSA can now be evaluated, which will help gain more insights into the interaction between natural metal-(hydr)oxide nanoparticles, as shown in the inset for SOC in Figure 4. The implemented approach for calculating the layer thickness L of SOM is given in Section S10 of the SI. This approach leads for our top soils to fitted L values between ∼1 and 3 nm (Figure 4b). These L values are thicker than the thickness of the compact part of the electrical double layer (EDL), i.e., ∼0.7 nm (dotted line, Figure 4b). As shown in Figure 4b, only the smallest metal-(hydr)oxide nanoparticles with a low layer thickness L can accommodate a significant fraction of the total SOM closely to the surface, in the compact part of the EDL.

Remarkably, the calculated layer thickness L increases linearly (R² = 0.98, p < 0.001) with an increase in the mean diameter of the metal-(hydr)oxide nanoparticles, as given in Figure 4b. If this is due to a physical and/or chemical protection of SOM against microbial decomposition, the relationship suggests a more efficient SOM protection when particles are relatively large. This picture might be understood from a more robust structural organization of the organo-mineral particles forming larger microaggregates.

The SOM–mineral interaction can also be interpreted with another structural picture in which the organo-mineral association is seen as a collection of more discrete particles of metal-(hydr)oxide and SOM. A significant relationship is found (R² = 0.96, p < 0.001) between the volume of both types of particles, yielding a volume ratio (Rᵥ) of ∼10. This Rᵥ is high in comparison to the value of ∼1 estimated from the maximum adsorption of SOM to synthetic Fe-(hydr)oxides. If the mean Rᵥ value from Figure 4c is interpreted as a particle coordination number (CN), the arrangement of SOM particles around a metal-(hydr)oxide core varies between cubic (CN = 8) and cub-octahedral (CN = 12). The latter arrangement is shown in the inset.
organomineral associations varies between a cubic (CN = 8) and a cuboctahedral (CN = 12) configuration. According to Pauling’s first rule, the CN can be related to the ratio of particle radii being 0.73 (CN = 8) and 1.0 (CN = 12). These radii ratios suggest that the particles in the organo-mineral entities are similar in size. An increase in the size of the mineral nanoparticles is accompanied by a corresponding increase in the mean size of the SOM particles, and this results in a constant $R_v$ (Figure 4c). Once formed, the organo-mineral entities may be organized at a higher structural level, forming aggregates that are more robust in encountering microbial degradation.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c02163.

Properties of the selected soil samples (Section S1), consistency of total P measurements in the ammonium oxalate extracts (Section S2), thermodynamic databases used in the modeling (Section S3), results of the probe-ion method (0.5 M NaHCO3 extractions) (Section S4), surface speciation of CO3 in competitive systems with PO4 (Section S5), calculation of size-dependent properties of metal-(hydr)oxide nanoparticles (Section S6), orthophosphate vs organic phosphorus in the ammonium oxalate soil extracts (Section S7), relationship of RSA vs DCB-extractable Fe- and Al-(hydr)oxides (Section S8), relative contribution of the nanocrystalline and crystalline metal-(hydr)oxides (Section S9), and calculation of SOM layer thickness (Section S10) (PDF)

**AUTHOR INFORMATION**

Corresponding Author

Juan C. Mendez – Soil Chemistry and Chemical Soil Quality Group, Wageningen University and Research, 6700 AA Wageningen, The Netherlands; orcid.org/0000-0002-1658-400X; Phone: +31 317 48 2342; Email: juan.mendezfernandez@wur.nl

Authors

Tjisse Hiemstra – Soil Chemistry and Chemical Soil Quality Group, Wageningen University and Research, 6700 AA Wageningen, The Netherlands

Gerwin F. Koopmans – Soil Chemistry and Chemical Soil Quality Group, Wageningen University and Research, 6700 AA Wageningen, The Netherlands

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.est.0c02163

Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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