Use of iron oxide nanoparticles for immobilizing phosphorus in-situ: Increase in soil reactive surface area and effect on soluble phosphorus

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Highlights
- The recently developed probe ion method for assessing the iron oxide surface area was simplified.
- Siliceous Fh with a primary particle size of 2 nm is the major oxide in iron oxide sludge.
- Surface area is lost by aggregation of siliceous Fh to a size of 6–8 nm.
- Field-application of iron oxide sludge increases the soil reactive surface area from 5 to 13 m² g⁻¹.
- Iron oxide sludge application strongly reduces readily available phosphate in a noncalcareous sandy soil.

Abstract
Phosphorus (P) immobilization has potential for reducing diffuse P losses from legacy P soils to surface waters and for regenerating low-nutrient ecosystems with a high plant species richness. Here, P immobilization with iron oxide sludge application was investigated in a field trial on a noncalcareous sandy soil. The sludge applied is a water treatment residual produced from raw groundwater by Fe(II) oxidation. Siliceous ferrihydrite (Fh) is the major Fe oxide type in the sludge. The reactive surface area assessed with an adapted probe ion method is 211–304 m² g⁻¹ for the Fe oxides in the sludge, equivalent to a spherical particle diameter of ~6–8 nm. This size is much larger than the primary Fh particle size (~2 nm) observed with transmission electron microscopy. This can be attributed to aggregation initiated by silicate adsorption. The surface area of the indigenous metal oxide particles in the field trial soils is much higher (~1100 m² g⁻¹), pointing to the presence of ultra-small oxide particles (2.3 ± 0.4 nm). The initial soil surface area was 5.4 m² g⁻¹ and increased linearly with sludge application up to a maximum of 12.9 m² g⁻¹ when 27 g Fe oxides per kg soil was added. In case of a lower addition (~10–15 g Fe oxides per kg soil), a 10-fold reduction in the phosphate (P-PO₄) concentration in 0.01 M CaCl₂ soil extracts to 0.3 mM was possible. The adapted probe ion method is a valuable tool for quantifying changes in the soil surface area when amending soil with Fe oxide-containing materials. This information is important for mechanistically predicting the reduction in the P-PO₄ solubility when such materials are used for immobilizing P in legacy P soils with a low P-PO₄ adsorption capacity but with a high surface loading.

Abbreviations: A, effective reactive surface area; AAO, acid ammonium oxalate; c, equilibrium P-PO₄ concentration in solution; CD model, charge distribution model; Fh, ferrihydrite; M, molar mass; PSI, phosphorus saturation index; Rₑ, reversibly adsorbed P-PO₄; SSA, specific surface area; SSR, solution-to-solid ratio; TEM, transmission electron microscopy; WTR, water treatment residual; XRD, X-ray diffraction.

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1. Introduction

Agricultural soils with a legacy of elevated soil phosphorus (P) contents from historic P applications represent a chronic source of dissolved P losses to surface waters, contributing to eutrophication (Kleinman et al., 2011; Schoumans and Chardon, 2015). Although halting P applications to these so-called “legacy P soils” can prevent a further increase in dissolved P losses (Kleinman et al., 2011; Koopmans et al., 2004; Van der Salm et al., 2009), current P emissions to surface waters can be significant and long-lasting, requiring additional measures to solve this environmental problem (Buda et al., 2012; Groenenberg et al., 2013; Schoumans et al., 2014).

One strategy for reducing environmental P losses is to immobilize P in situ in legacy P soils with a low P adsorption capacity by mixing P-adsorbing materials through the P-rich topsoil. To achieve this goal, numerous studies have proposed the use of Fe oxide-containing materials (Agyin-Birikorang et al., 2007; Callery et al., 2015; Elliott et al., 2002; Fenton et al., 2011; Schärer et al., 2007; Stoner et al., 2012). Such materials have been used as well for reducing the level of bioavailable P in lake sediments (Fuchs et al., 2018) as for immobilizing trace metals in contaminated soils (Lin et al., 2019; Nielsen et al., 2014; Rajapaksha et al., 2015).

Rln various studies (Agyin-Birikorang et al., 2007; Callery et al., 2015; Elliott et al., 2002), water treatment residuals (WTRs) have been used for increasing P adsorption to the solid phase, causing a corresponding decrease in the equilibrium P concentration in the soil solution. These WTRs were obtained from drinking water production facilities using Fe or Al salts as coagulant to remove the soil solution. These WTRs were obtained from drinking water (Chardon et al., 2012). In our field trial, soil samples were taken shortly before and 3 and 14 months after sludge application. The field trial soils were used for measuring their SSA and the equilibrium P-PO4 concentration in 0.01 M CaCl2 soil extracts to mimic soil solution conditions (McDowell and Sharpley, 2001). Our main goal was to quantify how the change in the solubility of P-PO4 could be mechanistically interpreted from the increase in the SSA of the field trial soils after sludge application. Since the reactivity of the field trial soils amended with sludge results from the SSA of the indigenous natural metal oxides initially present and the SSA of the Fe oxides added with the sludge, the challenge was to disentangle the contribution of both sources to the overall SSA. Although the SSA of WTRs has been assessed before (Chardon et al., 2012; Makris et al., 2005), the change in the soil surface area after application of WTRs has received no attention yet in P immobilization trials.

To realize the above goal, we identified and characterized the Fe oxides in the initial iron oxide sludge used in the field trial. For this purpose, a suite of physico-chemical methods was used, comprising transmission electron microscopy (TEM), X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), and BET-N2 gas adsorption. For assessing the contributions of the indigenous oxides initially present and the Fe oxides added with the sludge to the overall SSA of the field trial soils, we used the so-called “probe ion” method from Hiemstra et al. (2010a). Since the experimental approach corresponding to this method is rather laborious, we adapted it to make it more convenient for a large series of soil samples.

With our work, we want to demonstrate how the contribution of the Fe oxides added with the iron oxide sludge to the overall SSA of the field trial soils can be resolved by measuring the soil surface area with the adapted probe ion method. The surface areas of the indigenous oxides initially present and the added Fe oxides were compared for disclosing any differences in SSA and corresponding particle diameter. For this comparison, we included the information collected during our physico-chemical characterization of the Fe oxides in the sludge.

In the last part of our work, we want to demonstrate how the P-PO4 concentration in the 0.01 M CaCl2 soil extracts is related to the SSA of the field trial soils for providing a mechanistic understanding of the reduction in P-PO4 solubility after iron oxide sludge application. To put our results in a more practical context, we determined the effect of sludge application on the P saturation index (PSI) of the field trial soils, defined as the molar ratio x between the amount of reversibly adsorbed P-PO4 and the summed amounts of amorphous Fe and Al oxides (Van der Zee and Van Riemsdijk, 1988). Based on the PSI (Elliott et al., 2002) and how it relates to the P-PO4 concentration in soil solution, the application rate of Fe oxide-containing materials required to reduce the P-PO4 solubility to the desired level can be determined when considering a P immobilization scenario for legacy P soils.

2. Materials and methods

2.1. Field trial and sampling

The field trial was conducted in the nature reserve area “Grote Heide” on a noncalcareous sandy soil near Heeze in the south of The Netherlands. In the past, the field trial site was used as an agri-
cultural grassland. After abandonment, a semi-natural grassland vegetation developed due to repeated mowing as a management practice for removing nutrients (Timmermans and Van Eekeren, 2016). Two blocks with 8 plots each were established. The plots had a size of 6 by 6 m and were separated by an intermediate distance of 1.5 m. For one block, the upper 5 cm-soil layer of each plot was removed whereas the topsoil remained present in the other block. For both blocks, 3 plots were amended with iron oxide sludge (25 June 2013).

The iron oxide sludge used is an industrial by-product from the production of drinking water in a water treatment facility of Brabant Water Ltd. A description of the process of iron oxide sludge production at this facility (Chardon et al., 2012) can be found in Section S1 of the Supplementary data. The raw groundwater has a pH of 6.1 ± 0.1 and contains 23.5 ± 2.2 mg Ca L⁻¹, 10.7 ± 1.3 mg Fe L⁻¹, 8.9 mg Si L⁻¹, and 0.07 mg P L⁻¹. The values for pH, Ca, and Fe represent the average and standard deviation of 13 samples analyzed by Brabant Water Ltd between 2009 and 2012. The values for Si and P are from a single sample collected in 2012 and analyzed at Eawag. Liquid iron oxide sludge was collected from a sedimentation basin at the water treatment facility (Fig. S1) and transported to the field trial site with a tank truck.

The iron oxide sludge was injected from a slurry tank into the soil using a trailing-foot system by cutting a shallow slit in the soil into which the sludge was injected (Fig. S1). Next, the sludge was mixed with the soil by mechanical mixing of the upper 20 cm-soil layer with a cultivator. In the field, a grab sample of the iron oxide sludge was taken from the slurry tank. From each plot receiving sludge, composite soil samples were taken shortly before sludge application. The soil sampling depth was 25 cm for the block where the topsoil remained present whereas it was 20 cm for the block where the upper 5 cm soil layer was removed. For each composite soil sample, 20 subsamples were combined. Soil sampling was repeated 3 months (25 September 2013) and 14 months (8 September 2014) after sludge application.

The sludge and soil samples were dried at 40 °C and sieved (2 mm). Before sieving, the sludge sample was crushed.

2.2. Chemical analysis of the iron oxide sludge

2.2.1. General chemical properties

The pH was measured in a settling suspension of the sludge in 0.01 M CaCl₂, prepared at a solution-to-solid ratio (SSR) of 10 L kg⁻¹ and shaken for 2 h on a linear shaker at 180 strokes (S) min⁻¹ (Houba et al., 2000). The sludge was digested with Aqua Regia (AR) (Houba et al., 1997) for total element analysis in combination with a fully automated segmented flow spectrophotometer (Varian Vista Pro, Varian Australia, Mulgrave, Australia) for As, Cd, Ni, and Pb. Total Al, Ca, and Si contents were analyzed using a desktop-energy-dispersive X-ray fluorescence spectrometer (XPEOS, SPECTRO Analytical Instruments GmbH, Kleve, Germany). The BET-SSA was determined with the BET-N₂ gas adsorption method (Quantachrome Nova; duplicate 6-point analysis). Data for the organic and inorganic carbon (C) contents were taken from Chardon et al. (2012) who determined these properties for another batch of sludge from the same water treatment facility.

2.2.2. Acid ammonium oxalate extraction

Since the standard 0.2 M acid ammonium oxalate extraction (AAO) method used for extracting amorphous Fe oxides from soil (Schuhamms, 2000; Schwertmann, 1964) may be inadequate for Fe-rich WTRs, we adapted this method for iron oxide sludge searching for the optimal SSR and extraction time. The dried sludge was extracted with 0.2 M AAO (pH 3.0 ± 0.1) at an SSR of 20, 100, 200, 300, and 400 L kg⁻¹. Duplicate samples of 1.5 g dried sludge were suspended in × mL 0.2 M AAO solution in polyethylene bottles with × = 30 mL (20 L kg⁻¹), 150 mL (100 L kg⁻¹), 300 mL (200 L kg⁻¹), 450 mL (300 L kg⁻¹), and 600 mL (400 L kg⁻¹) and shaken at 180 S min⁻¹ on a linear shaker in the dark. For the SSRs of 20, 100, and 200 L kg⁻¹, a subsample (5 mL) was taken from the suspensions after 2, 4, and 24 h of shaking. The subsamples were centrifuged for 10 min at 3000 revolutions min⁻¹ (~2100 × g) and filtered over a 0.45 μm-filter membrane (Aqua 30/0.45 CA Whatman) with removal of the first ~2 mL of the filtrate. Subsequently, Fe (Feox), Al (Alox), and P (Pox) were measured by ICP-OES. The pellets precipitated at the bottom of the centrifuge tubes from the subsamples taken after 2 and 4 h were re-suspended in 5 mL 0.2 M AAO and back-donated to the suspensions to maintain a constant SSR during shaking in the remaining extraction period. The amounts of Fe, Al, and P removed from the suspensions with the 5 mL subsamples taken after 2 and 4 h were added up to the amounts of these elements extracted at 24 h, respectively. For the SSRs of 300 and 400 L kg⁻¹, subsamples were taken after 4 h of shaking and analyzed as described above. In a parallel experiment with the same setup, the pH was measured in the settling suspensions.

2.2.3. Bicarbonate extraction

The iron oxide sludge was equilibrated with 0.5 M NaHCO₃ according to Liemstra et al. (2010a) to measure the P-PO₄ concentration in solution. For this extraction, an SSR of 50 L kg⁻¹ was used, prepared by suspending a sample of 1 g dried iron oxide sludge in 50 mL 0.5 M NaHCO₃. To facilitate removal of OM, 0.4 g powdered activated carbon was added. The activated carbon was pre-cleaned by extraction with 0.2 M AA (in the dark using an SSR of 50 L kg⁻¹ and 180 S min⁻¹ for 12 h, followed by rinsing the material with demineralized water and drying at 70 °C. The suspension was shaken on a linear shaker for ~255 h at 30 S min⁻¹ to achieve equilibrium. After pH measurement in a settling suspension, it was centrifuged for 10 min at 3000 revolutions min⁻¹ (~2100 × g) and filtered over a 0.45 μm-filter membrane. The filtrate was acidified with 5 M HCl to pH 2 before measuring P-PO₄ as dissolved reactive P (DRP) using the molybdenum-blue method (Murphy and Riley, 1962) and a fully automated segmented flow analyzer (SFA; San²⁺, Skalar, Breda, The Netherlands).

2.2.4. Structural characterization

For the identification of crystalline compounds, the dried and sieved iron oxide sludge was analyzed by X-ray diffraction (X'Pert Powder diffractometer, Malvern Panalytical; Co Kα X-ray source with Kβ (Fe) filter), 40 mV, 45 kV; fixed divergence slits; continuous scan from 15° to 95° 20 with 0.017° step size and 2 h total counting time; X'Celerator detector). For characterizing the atomic structure of the Fe(III)-precipitates, the sludge was analyzed with XAS at the SUL beamline at ANKA at the Karlsruhe Institute of Technology (KIT), Germany. About 15 mg of the sludge were mixed with about 150 mg of cellulose and pressed into a 13-mm diameter pellet for analysis in transmission mode at room temperature. Data extraction and analysis was performed in analogy to previous work (Senn et al., 2015) using the software code Athena (Ravel and Newville, 2005). The spectra were evaluated by comparison to reference spectra from previous work concerned with the atomic structure of Fe(III)-precipitates formed by Fe(II) oxidation (Senn et al., 2015; Voegelin et al., 2010).

For the analysis of the iron oxide sludge by TEM, 35 mg of the material were suspended in 100 mL doubly deionized (DDI) water and ultra-sonicated for 10 min (bath sonication) to disperse particle aggregates. The iron oxide sludge suspension was diluted 100-fold in DDI water and ultra-sonicated for 10 s with a VialTweeter.
(Hielscher Ultrasonics GmbH, Germany). One mL of this suspension was centrifuged for 1 h at 14,000 revolutions min\(^{-1}\) (\(\sim 26000 \times g\)) onto poly-L-lysine-functionalized TEM grids (C-coated Cu grids; EM Resolutions; UK). Scanning transmission electron microscope (STEM) analyses were performed on a STEM (HD2700Cs, Hitachi, Japan) operated at 200 kV. Electron microscopy images were collected using a secondary electron (SE) detector and a high-angle annular dark field (HAADF) detector. Signal processing was done using DigitalMicrograph (Gatan Inc., Pleasanton, US).

2.3. Chemical analysis of the field trial soils

Soil organic matter (SOM) content was determined by loss-on-ignition in a muffle furnace (550 °C). The soil samples were extracted with 0.01 M CaCl\(_2\) at an SSR of 10 L kg\(^{-1}\) for 2 h on a linear shaker at 180 S min\(^{-1}\) (Houba et al., 2000). A subsample was taken for measuring the pH. The remaining suspension was centrifuged for 10 min at 3000 revolutions min\(^{-1}\) (\(\sim 2100 \times g\)). After 0.45 \(\mu\)m-filtration, P-PO\(_4\) was measured as DRP using a novel system in which our SFA instrument was equipped with a 50-cm liquid waveguide capillary cell (LWCC; World Precision Instruments) and a LED lamp operating at 880 nm. This instrumental setup leads to an increase in the sensitivity and a 10-fold lower detection limit (\(\sim 0.06 \mu\)M P-PO\(_4\)) compared to a conventional cell with 5-cm path length (Gimbert et al., 2007). Dissolved organic carbon (DOC) was calculated as the difference between total carbon and inorganic carbon, both measured by using an SFA. Total dissolved P (TDP) was measured using HR-ICP-MS. Dissolved unreactive P (DUP) was calculated as the difference between TDP and DRP. Total dissolved As, Cd, Cu, Ni, and Pb in the 0.01 M CaCl\(_2\) extracts from the soil samples taken at the first and third sampling time were measured using HR-ICP-MS.

To determine Fe\(_{ox}\), Al\(_{ox}\), and P\(_{ox}\), the soil samples were extracted with 0.2 M AAO according to the standard method including an SSR of 20 L kg\(^{-1}\) and a shaking time of 2 h (Schoumans, 2000; Schwertmann, 1964). Other analytical details can be found in Section 2.2.2. Based on the amounts of Fe\(_{ox}\), Al\(_{ox}\), and P\(_{ox}\), the molar PSI was calculated according to:

\[
a = \frac{P_{ox}}{Fe + Al_{ox}}
\]

where P\(_{ox}\) and [Fe + Al]\(_{ox}\) are expressed in mmol kg\(^{-1}\) (Van der Zee and Van Rijmsdijk, 1988).

The Olsen P extraction method with 0.5 M NaHCO\(_3\) at an SSR of 50 L kg\(^{-1}\) (see Section 2.2.3.) was applied to measure the P-PO\(_4\) concentration in solution after equilibration for \(\sim 255\) h. For the soil samples taken at the first and third sampling time, the size of the reactive As, Cd, Cu, Pb, Ni, and Zn pools was determined by extracting soil with 0.43 M HNO\(_3\) (Groenenberg et al., 2017). The soil samples were extracted at an SSR of 10 L kg\(^{-1}\) on an end-over-end shaker for 4 h with 30 rotations min\(^{-1}\). Next, the soil extracts were centrifuged for 10 min at 3000 revolutions min\(^{-1}\) (\(\sim 2100 \times g\)). After 0.45 \(\mu\)m-filtration, As, Cd, Cu, and Ni were measured by using HR-ICP-MS whereas Zn was measured with ICP-OES.

2.4. Data analysis

2.4.1. Surface complexation modelling

The charge distribution (CD) model (Hiemstra and Van Rijmsdijk, 1996) was used to calculate the P-PO\(_4\) loading of the iron oxide sludge and field trial soils from the experimental P-PO\(_4\) concentration and pH in the 0.5 M NaHCO\(_3\) extracts (see Section 2.2.3.). A detailed CD modelling description can be found in Hiemstra et al. (2010a). We used a consistent set of binding parameters (log K and CD values) available for goethite. In the CD model calculations for the data of the 0.5 M NaHCO\(_3\) extracts, only competition between P-PO\(_4\) and bicarbonate for binding to sites at the Fe oxide surface was considered. Any additional competition with OM was not included, because excess activated carbon was added to remove OM to suppress this interaction.

2.4.2. Statistical analysis

A two-way analysis of variance (ANOVA) was used to test the significance of the effects imposed by the treatments toposoil removal and iron oxide sludge reaction time on the different response variables of the field trial (\(P < 0.05\)). For the treatment toposoil removal, the upper 5 cm-soil layer was either removed or remained present whereas the treatment iron oxide sludge reaction time encompassed three soil sampling times, i.e., shortly before and 3 and 14 months after sludge application (see Section 2.1.1.). The data was transformed prior to analysis to agree with the assumption of data normality when necessary. For the DRP and DUP concentrations in the 0.01 M CaCl\(_2\) soil extracts, Fe\(_{ox}\), and the effective reactive surface area of the field trial soils, a log transformation of the data was used, whereas a double log transformation was used for the reactive Pb pool. The Bonferroni post-hoc test was used to test the significance of the differences between the means of the two treatments. All statistical analyses were performed using GenStat 19th edition (VSN International, 2017).

3. Results and discussion

3.1. Characterization of the iron oxide sludge

3.1.1. Composition

Selected chemical properties of the iron oxide sludge used in this study are presented in Table 1. The sludge contains some OM which may originate from the presence of dissolved organic matter (DOM) in the raw groundwater (Postma et al., 1991). Deposition of organic residues in the sedimentation basin may have

| Property | Unit | Value |
|----------|------|-------|
| pH\(^1\) |      | 7.2   |
| OM\(^2\) | g kg\(^{-1}\) | 33 |
| Inorganic C\(^2\) | g kg\(^{-1}\) | 24 |
| Al\(^3\) | g kg\(^{-1}\) | 2.5 |
| Ca\(^3\) | g kg\(^{-1}\) | 63 |
| Fe\(^4\) | g kg\(^{-1}\) | 328 |
| Mn\(^4\) | g kg\(^{-1}\) | 9.1 |
| P\(^4\) | g kg\(^{-1}\) | 2.8 |
| P/Fe | mol/mol | 0.016 |
| Si\(^3\) | g kg\(^{-1}\) | 29 |
| Si/Fe | mol/mol | 0.17 |
| Cd\(^5\) | mg kg\(^{-1}\) | 5.2 |
| Cu\(^5\) | mg kg\(^{-1}\) | 0.29 |
| Ni\(^5\) | mg kg\(^{-1}\) | 10 |
| Pb\(^5\) | mg kg\(^{-1}\) | 9.8 |
| Zn | mg kg\(^{-1}\) | 2.4 |
| Olsen P| µM | 28 |
| BET-SSA | m\(^2\) g\(^{-1}\) | 136 |

\(^1\) Measured in a 1:10 (w/v) 0.01 M CaCl\(_2\) extract.
\(^2\) Data from Chardon et al. (2012) for a different batch of iron oxide sludge from the same water treatment facility.
\(^3\) XRF analysis.
\(^4\) Aqua Regia digestion.
\(^5\) DRP concentration measured in 0.5 M NaHCO\(_3\) at an SSR of 50 L kg\(^{-1}\), based on a modified Olsen P extraction method (Hiemstra et al., 2010a).
contributed to the presence of OM in the sludge as well (Chardon et al.,
2012).

Iron is the dominant macro-element in the iron oxide sludge,
with 33% of its total weight. This is larger than in various other
industrial by-products including WTRs used for removing P from
solution (Cucarella and Renman, 2009; Ippolito et al., 2011). Cal-
cium (6.3%) is the second most important macro-element and is
accompanied by a high inorganic C content of 2.4% (determined
for another batch of iron oxide sludge), pointing to the presence
of ~16% CaCO3 if all Ca would be present as CaCO3. Calcite was
indeed identified as a dominant crystalline component of the
sludge by XRD (Fig. S2). For Fe(II) removal, the raw groundwater
mixed with ample fresh air is led over a filter bed filled with mar-
ble grains (Chardon et al., 2012), which explains the presence of
calcite in the sludge as well as its slightly alkaline pH.

Silicon (2.9%) is the third most important macro-element in our
iron oxide sludge. This can be explained by co-precipitation of sil-
lcite with the Fe oxide particles formed during groundwater treat-
ment (Hiemstra, 2018a), leading to a molar Si/Fe ratio of 0.17
(Table 1). This ratio is intermediate to the range encountered for
natural siliceous Fe oxides of 0.06 to 0.37 (Childs, 1992; Cismasu
et al., 2011; Jambor and Dutrizac, 1998; Parfitt et al., 1992). The
molar Siwater/Fewater ratio in the raw groundwater is 1.7 whereas
the SiFh/FeFh ratio in the sludge is 0.17. Hence, the Siwater/Fewater
ratio is 10-fold higher than the SiFh/FeFh ratio. This points to an excess of 1.5 mol Si per mol Fe in the raw groundwater
(Siexcess/Fewater), which follows from Siexcess/Fewater = Siwater/Fewater
– SiFh/FeFh if all Fe would precipitate in the sludge (Fewater =
FeFh). The result of this calculation illustrates the abundance of
dissolved Si in the raw groundwater (see Section 2.1.).

3.1.2. Mineralogy

The XRD pattern of the iron oxide sludge revealed the presence of
two Fe oxide phases: 2-line ferrhydrite (Fh) and poorly crys-
talline goethite (Fig. S2). Based on Fe K-edge extended X-ray
absorption fine structure spectroscopy, ~94% of the Fe was present
as Fh, with a small fraction of ~6% occurring as goethite (Fig. 1). The
Fe(III) in our Fh was less polymerized than synthetic 2-line Fh
formed by neutralization of Fe(III) according to standard protocols.
This may indicate the formation of smaller Fh particles with a rel-
atively high surface contribution leading to more octahedral edge
sharing and less polyhedral corner sharing (Hiemstra, 2018b),
which is in line with a smaller coherent scattering domain as
observed for co-precipitated siliceous Fh (Cismasu et al., 2014). These
findings are in agreement with the well-documented formation
of poorly-polymerized siliceous Fh during Fe(II) oxidation in
aqueous solutions with silicate (Schwertmann et al., 1984; Senn
et al., 2015) and water treatment systems (Nielsen et al., 2014;
Van Genuchten et al., 2014; Voegelin et al., 2014).

The presence of some goethite in our sludge may be due to Fe
(II)-catalyzed Fh transformation in the filter bed with marble grains
used for Fe(II) removal from the raw groundwater (Boland
et al., 2014; Carlson and Schwertmann, 1990). When all Fe in the
sludge would be present as Fh, the total Fe content of 33% corre-
sponds to 48 to 63% of Fh, depending on the molar mass (M) of
Fh used. This may range from ~82 g mol$^{-1}$ for FeO$\cdot$1.4(OH)$\cdot$0.2
(Hiemstra, 2013) to ~107 g mol$^{-1}$ in the case of Fe(OH)$_3$ as the
chemical composition (Jambor and Dutrizac, 1998).

3.1.3. Particle size and surface area

In Fig. 2, TEM images of our iron oxide sludge are presented. The
primary Fe oxide particles remained highly aggregated despite
intensive physical dispersion. This may be due to the presence of
adsorbed Si polymers (Hiemstra, 2018a) or OM (Hiemstra et al.,
2010a; Kaiser et al., 2012). Structures visible in the Z-contrast and
SE images point to a primary particle size of ~2 nm. This is
in accordance with the results of Cismasu et al. (2011) and
Parfitt et al. (1992) who found a primary particle size of ~1.5 to
4 nm for natural siliceous Fh. Ultra-fast formation of Fe oxides
(~minutes) may lead to particles with a size of about 1.7 nm
(Hiemstra et al., 2019; Hiemstra and Zhao, 2016; Mao et al.,
2012). Silicate adsorption may inhibit the growth of Fh crystallites
(Childs, 1992; Cismasu et al., 2011; Hiemstra, 2018a; Parfitt et
al., 1992) and preserve the initial small size of the Fh particles. As long
as these particles remain small (<~8 nm), Fe is thermodynamically
the most stable nano-sized Fe(III) oxide phase (Hiemstra, 2015).
Hence, co-precipitation of Si and Fe leads to a relatively small par-
ticle size and inhibits growth, explaining why crystalline Fe oxides
are nearly absent in our iron oxide sludge (Fig. S2).

The SSA of the Fe oxide particles can be calculated from the sur-
face area of a spherical particle and its volume and mass density
according to:

$$SSA = \frac{6}{\rho_{nano} \times d}$$ (2)

where SSA is the specific surface area ($m^2$ kg$^{-1}$), $\rho_{nano}$ the mass
density ($kg$ m$^{-3}$), and d the average diameter of a non-porous spherical
particle (m). For primary Fe oxide nanoparticles with a size of 2 nm and
a mass density of ~3500 kg m$^{-3}$ (Hiemstra and Van Riemsdijk,
2009), the SSA equals ~850 m$^2$ g$^{-1}$. The result of this calculation can be compared with the BET-SSA. Scaling the BET-SSA of 136 m$^2$ g$^{-1}$
for our iron oxide sludge (Table 1) to the total Fe content leads to
217 m$^2$ g$^{-1}$ when $M = 107$ g mol$^{-1}$ for Fe(OH)$_3$ or 284 m$^2$ g$^{-1}$
when $M = 82$ g mol$^{-1}$ for FeO$_2$ (OH)$_2$. Hence, the BET-SSA of the Fe oxide
particles in our sludge is about 3- to 4-fold lower than calculated
above for the primary Fe oxide particle diameter. This difference
can be explained by the observed dense particle aggregation
(Fig. 2) under the influence of adsorbed Si polymers (Hiemstra,
2018a), the presence of Ca (Keagi et al., 2010), or blocking of micro-
pores by OM preventing N₂ gas molecules to occupy the internal surface of the aggregates (Eusterhues et al., 2008; Kaiser and Guggenberger, 2003).

3.1.4. Molar P/Fe ratio
The molar P_{sludge}/Fe_{sludge} ratio of 0.016 of our iron oxide sludge is markedly close to the P_{water}/Fe_{water} ratio of 0.012 of the raw groundwater. This illustrates the high affinity of P for Fe (Geelhoed et al., 1997), the latter effectively scavenging P from solution via adsorption to the Fe oxide particles formed by Fe(II) oxidation during groundwater treatment. Combining the SSA of ~850 m² g⁻¹ for the 2 nm-sized Fe oxide particles (see Section 3.1.3.) with an Fe concentration of 10.7 mg L⁻¹ in the raw groundwater (see Section 2.1.) yields a reactive surface area of 17 m² L⁻¹ when a size-dependent molar mass of 101 g mol⁻¹ is used for Fh (Hiemstra, 2018b). Implementing these numbers as input for the CD model in combination with recent binding parameters of P-PO₄ and Si for Fh (Hiemstra, 2018a), more than 95% of all P in the raw groundwater is removed from solution by adsorption to Fh at neutral pH whereas this is only ~10% for Si (Fig. S3). The difference in P and Si removal can be explained by the abundance of dissolved Si in the raw groundwater, making it impossible to bind it all. In contrast, nearly all P-PO₄ is bound due to its very high affinity for Fh (Geelhoed et al., 1997) and its 140-fold lower concentration in the raw groundwater.

The apparently high total P content of our iron oxide sludge (0.28%) needs some discussion in light of its potential use for P immobilization to regenerate low-nutrient ecosystems with a high plant species richness on former agricultural land. The total P content of 2.8 g kg⁻¹ is quite similar to the average value of 2.2 g P kg⁻¹ reported for Al-based WTRs (Ippolito et al., 2011). Such total P contents are typical for agricultural soils having received excessive P applications over a prolonged period of time (Koopmans et al., 2007; Lehmann et al., 2005). However, WTRs have a much higher metal oxide content than agricultural soils (Ippolito et al., 2011; Koopmans et al., 2006). Consequently, the molar P/Fe ratio of WTRs will be much lower than for excessively fertilized agricultural soils (Koopmans et al., 2007). Therefore, our iron oxide sludge will be very capable to bind large quantities of P and to reduce the solubility of P when it is applied to legacy P soils. Since the molar P_{sludge}/Fe_{sludge} ratio of 0.016 in our sludge is very low (Table 1), the P will be hardly available for release to solution (Baken et al., 2016).

3.1.5. Acid ammonium oxalate extraction
For the iron oxide sludge, the effectiveness of Fe extraction by 0.2 M AAO was tested. The recovery of Fe extraction depends on the SSR employed in the extraction (Fig. 3A and Table S1). At the lowest SSR of 20 L kg⁻¹, only 14% of the total Fe content was recovered as Fe_{ox} within an extraction time of 2 h. Prolonging the extraction time to 4 and 24 h had only a small effect on Fe extraction, as the recovery increased to 17 and 21% of the total Fe content, respectively. However, when the SSR was increased to 100 L kg⁻¹, Fe extraction became nearly complete within 2 h. All Fe was extracted for the SSRs of 200 L kg⁻¹ and higher.

The effectiveness of P extraction at the lowest SSR (20 L kg⁻¹) was even lower than for Fe as <2% of the total P content was recovered as P_{ox} (Fig. 3B). At an SSR of 100 L kg⁻¹, the recovery increased to 71 to 79% (Fig. 3B). At these SSRs, P remains at least partly effectively bound, probably by re-adsorption of released P to yet undisolved Fe oxide particles. For the SSRs of 200 L kg⁻¹ and higher P extraction was virtually complete, with a P recovery of 94 to 100%. For Alox, however, the extraction effectiveness was far from complete (Fig. 3C). Hence, only a small fraction of the Al in the sludge is present as nano-sized Al (hydr)oxides. Part of the Al may be present in crystalline forms such as Al silicates (e.g., clay minerals). The pH measured in the AAO extracts decreased with an increase in SSR, from 7.0 at an SSR of 20 L kg⁻¹ to 3.1 at an SSR of 400 L kg⁻¹ (Table S1). However, this is not the main reason for the low Fe recovery for the lowest SSR, as found by our chemical speciation calculations.

Chemical speciation modelling was done to gain insight in the performance of AAO extraction of the iron oxide sludge. The solubility product used in the modelling was calculated for 2 nm-sized Fe particles by applying the Ostwald equation using a surface Gibbs free energy of $\gamma = 0.186$ J m⁻² for Fh (Hiemstra, 2015), an SSA of ~850 m² g⁻¹ oxide (see Section 3.1.3.), and a size-dependent molar mass of 101 g mol⁻¹ (Hiemstra, 2018b). This calculation leads to a solubility product of $Q_{eq} = (Fe^{3+}) (OH^-)^3 = 10^{-37.8}$. According to our speciation calculations, the solubility of Fe...

![Fig. 2. Transmission electron microscopy (TEM) images of the aggregated particles in the iron oxide sludge. The Z-contrast image (ZCM) indicates the sample density (A) and the secondary electron image (SE) the surface morphology (B). The white sphere next to the scale bar indicates the size of a spherical particle with a diameter of 2 nm.](image-url)
3.2. Reactive surface area of the iron oxide sludge

The effective reactive surface area of the Fe oxides in the iron oxide sludge was assessed with ion surface probing. Since the original probe ion method of Hiemstra et al. (2010a) is rather laborious, a more simple and rapid method is desired. Here, we will introduce a modification to the experimental approach used in the probe ion method through which it can be applied more conveniently to a large series of soil samples. The adapted method will be used first to assess the surface area of the grab sample of the sludge and later it will be applied to the field trial soils. Before describing this modification, first the principle of the probe ion method will be discussed.

For ion surface probing, P-PO$_4$ is used because this ion is omnipresent in soils and adsorbs predominantly to metal oxides. In the original method of Hiemstra et al. (2010a), soil samples were equilibrated in 0.5 M NaHCO$_3$ at a series of different SSRs for ~10 days before measurement of the P-PO$_4$ concentration in solution. This chemical matrix fixes the pH, ionic strength, and carbonate concentration, suppresses the influence of Ca and Mg ions on P-PO$_4$ adsorption to metal oxides via their precipitation as carbonates, and desorbed and dissolved OM is largely removed due to the excess activated carbon addition (see Section 2.2.3.). In combination, this leads to the dominance of the interaction of P-PO$_4$ and bicarbonate with Fe and Al oxides allowing an interpretation of the measured equilibrium P-PO$_4$ concentration in the 0.5 M NaHCO$_3$ solution with the CD model, yielding the effective reactive surface area ($A$) of the soil sample as well as the amount of reversibly adsorbed P-PO$_4$ ($R_{ev}$).

During soil equilibration in 0.5 M NaHCO$_3$, the total amount of reversibly adsorbed P-PO$_4$ will be redistributed over the solution and solid phase according to the following mass balance:

\[ R_{ev} = A \times \Gamma \times \text{SSR} \times c \]  

where $R_{ev}$ represents the total amount of reversibly adsorbed P-PO$_4$ (mol kg$^{-1}$) initially present in the soil sample when collected in the field, $A$ the effective reactive surface area of the soil sample (m$^2$ kg$^{-1}$), $\Gamma$ the P-PO$_4$ surface loading (mol m$^{-2}$), SSR the solution-to-solid ratio employed (L kg$^{-1}$), and $c$ the equilibrium P-PO$_4$ concentration in the solid phase (mol L$^{-1}$).

As mentioned, in the original probe ion method of Hiemstra et al. (2010a) a series of different SSRs was used for equilibrating soil in 0.5 M NaHCO$_3$ to calculate $R_{ev}$ and $A$. A less laborious approach is the use of Pox as a proxy for the reversibly adsorbed P-PO$_4$ pool ($R_{ev}$) in combination with a single 0.5 M NaHCO$_3$ extraction to yield the equilibrium P-PO$_4$ concentration ($c$). The latter can then be directly translated to the corresponding P-PO$_4$ surface loading ($\Gamma$) using the CD model. Details on the single NaHCO$_3$ extraction and the surface complexation modelling with the CD model can be found in Sections 2.2.3. and 2.4.1., respectively. Combining $\Gamma$ in Eq. (3) with the experimental value of Pox for the reversibly adsorbed P-PO$_4$ pool ($R_{ev}$), the effective reactive surface area ($A$) can be derived. The use of Pox as a proxy for $R_{ev}$ seems justified, because $R_{ev}$ agreed reasonably well with Pox for a series of Dutch agricultural topsoils used to develop the probe ion method (Hiemstra et al., 2010a). Furthermore, the use of Pox is in line with findings from a long-term P desorption experiment with a P sink where all Pox could be desorbed (Lookman et al., 1995).

Our modified approach was applied to all field trial soils as well as the grab sample of the iron oxide sludge taken from the slurry tank during sludge application in the field. For the sludge, Pox measured at an SSR of 200 L kg$^{-1}$ and an extraction time of 4 h (see Section 2.2.2.) was taken as $R_{ev}$ in Eq. (3). For the value of $c$, we used the DRP concentration measured in the 0.5 M NaHCO$_3$ extract of the sludge at an SSR of 50 L kg$^{-1}$ (Table 1). This SSR is intermediate to the series of different SSRs employed by Hiemstra et al. (2010a) for the 0.5 M NaHCO$_3$ extraction method.

With the approach used, a value of 113 m$^2$ g$^{-1}$ was calculated for the effective reactive surface area of the iron oxide sludge. When scaled to the amount of Feox$_{ev}$ extracted at an SSR of 200 L kg$^{-1}$ for 4 h (Fig. 3A), the surface area of the Fe oxide particles in the sludge is 211 m$^2$ g$^{-1}$ when $M = 89$ g mol$^{-1}$ (FeOOH). The corresponding equivalent spherical particle diameter is ~8 nm accord-
slurry tank before the application (Fig. S1). Clearly, it is not a trivial task to apply suspended materials homogeneously to soil in a deviation of 3 plots, either with topsoil removed (0–5 cm) or present. Different letters in Table 2. Removal of the upper 5 cm soil layer before iron oxide sludge application caused a significant decrease in SOM. The difference in size can be explained by the aggregation of the primary particles, as discussed in Section 3.1.3. The aggregation of these particles is rather irreversible when assessing the surface area with the probe iron oxide sludge application. This will be further discussed in relation to the surface area of the metal oxide particles in the field trial soils.

3.3. Characterization of the field trial soils

Selected chemical properties of the field trial soils are presented in Table 2. Removal of the upper 5 cm soil layer before iron oxide sludge application caused a significant decrease in SOM. The difference in SOM between the plots without and with topsoil remained statistically significant at the third sampling time. Sludge application in SOM between the plots without and with topsoil remained statistically significant at the third sampling time. Sludge application caused a significant decrease in SOM. The difference in size can be explained by the aggregation of the primary particles, as discussed in Section 3.1.3. The aggregation of these particles is rather irreversible when assessing the surface area with the probe iron oxide sludge application. This will be further discussed in relation to the surface area of the metal oxide particles in the field trial soils.

3.4. Effects of iron oxide sludge on P solubility in the field trial soils

Before iron oxide sludge application, DUP contributed on average 62 ± 1% and 79 ± 5% to the TDP concentration in the 0.01 M CaCl₂ soil extracts of the plots without and with topsoil, respectively (Fig. 4D). Hence, the TDP concentration is dominated by DUP, which is typical for extensively managed soils such as our field trial soils (Lehmann et al., 2005). This DUP can consist of organic P compounds and P-PO₄ associated with mineral colloids including clay, metal oxides, and metal ion clusters bound by humic substances (Hens and Merckx, 2002; Jiang et al., 2017; Regelink et al., 2013). The application of sludge caused a statistically significant decrease in the DUP concentration in the 0.01 M CaCl₂ soil extracts of the plots without topsoil. For the plots with topsoil, DUP decreased only significantly 14 months after sludge application. The reduction in the DUP concentration can be explained by binding of specific soluble organic compounds to oxides added with the sludge (Celi et al., 2003; Lu et al., 2017).

Iron oxide sludge application caused a statistically significant decrease in the DRP concentration in the 0.01 M CaCl₂ soil extracts of the plots with topsoil (Fig. 4E). For the plots without topsoil, this effect was only significant three months after sludge application. Since the spatial heterogeneity in the Feox content is high (see Section 3.3.), it is better to assess the effect of sludge application on P-PO₄ solubility from the relationship between the DRP concentration in the 0.01 M CaCl₂ soil extracts and the increase in the oxide content for the individual field trial plots (Fig. 4F). The reduction in the DRP concentration becomes high at an intermediate and high oxide addition. At our field trial site, a reduction in the DRP concentration to 0.3 µM was possible with an addition of ~10 to 15 g Fe oxides per kg soil. A further increase in the amount of added oxides is much less effective for further reducing the DRP concentration.

3.5. Reactive surface area of the field trial soils

Our modified probe iron method was used to determine the effective reactive surface area of the field trial soils. Similar to the iron oxide sludge, the DRP concentrations measured in 0.5 M NaHCO₃ at an SSR of 50 L kg⁻¹ (Table S3) were used as the values for c in Eq. (3) and J was calculated with the CD model. For Rₑᵥ, the values of the Pox contents were used (Fig. 4C), as measured by the standard AAO method (Schoumans, 2000; Schwertmann, 1964).

The application of iron oxide sludge caused a statistically significant increase in the effective reactive surface area of the soil samples collected from the plots with topsoil after 3 months whereas no significant effect was found for the soil samples collected after 14 months (Fig. S9). For the plots without topsoil, sludge application did not lead to a significant change in the effective reactive surface area. One of the main reasons why the application of the sludge did not result in a consistent increase in the soil surface area for the plots without and with topsoil is most likely related to the high spatial heterogeneity in the Feox content (see Section 3.3.). The relation between iron oxide sludge application and the effective reactive surface area of the soil samples from the individual plots becomes more evident when plotting the reactive surface against the increase in the oxide content (Fig. S5). The data points fit well to a linear relationship (Rₑᵥ = 93% and P < 0.001). The intercept equals the surface area of the initial soil before sludge application. For the initial soil, the surface area is 5.4 ± 0.3 m² g⁻¹. Increasing

| Sampling time | Topsoil | SOM(%) | pH | DOC(mg C L⁻¹) |
|---------------|--------|--------|----|--------------|
| Before        | Removed | 2.0±(0.4) | 4.6±(0.1) | 11.8±(1.8) |
|               | Present | 3.1±(0.4) | 4.7±(0.1) | 19.0±(1.6) |
| 3 months      | Removed | 2.2±(0.2) | 6.0±(0.3) | 11.0±(0.4) |
|               | Present | 3.7±(0.5) | 7.0±(0.4) | 22.6±(2.1) |
| 14 months     | Removed | 2.1±(0.1) | 6.0±(0.5) | 10.0±(0.6) |
|               | Present | 3.1±(0.3) | 6.5±(0.4) | 15.2±(1.0) |
up to a maximum of 12.9 m\(^2\) g\(^{-1}\) after sludge amendment. The slope of the relationship reveals the surface area per unit mass oxides added. The thus calculated surface area of the added Fe oxide particles is 304 ± 24 m\(^2\) g\(^{-1}\) when \(M = \) 89 g mol\(^{-1}\) for FeOOH and 78 g mol\(^{-1}\) for Al(OH)\(_3\). Since the surface area of the Fe oxide particles in the grab sample of the iron oxide sludge taken from the slurry tank in the field is 211 m\(^2\) g\(^{-1}\) (see Section 3.2.), the surface area can be said to range between 211 and 304 m\(^2\) g\(^{-1}\) with an intermediate value of ~260 m\(^2\) g\(^{-1}\). This value can be compared to the BET-SSA of the sludge after scaling it to the oxide content, resulting in a surface area of 217 to 284 m\(^2\) g\(^{-1}\) with an intermediate value of ~250 m\(^2\) g\(^{-1}\) (see Section 3.1.3.). Hence, the results of the BET-SSA and our adapted probe ion method are rather similar.

All data points in Fig. 5 align well to the same linear relationship. Consequently, no transformation of the Fe oxides added with the iron oxide sludge into more crystalline oxides with a larger particle size seems to have occurred after a residence time in soil of 3 to 14 months. The relative stability of the added Fe oxide particles may be due to the adsorption of P-PO\(_4\) (Borch et al., 2007; Makris et al., 2005) and OM (Hiemstra et al., 2019) as well as the presence of Si in the sludge, as discussed in Section 3.1.3. However, transformation of Fe oxides into more crystalline oxides in cannot be excluded as Fh may reform in topsoils as part of the biogeochemical recycling of Fe (Jambor and Dutrizac, 1998). One other factor which needs to be taken into account when discussing the relative stability of the added Fe oxide particles is the length of our field trial, because it may not have been long enough to observe a measurable aging effect. The apparent lack of such an aging effect is in line with the results of Nielsen et al. (2014) who found a half-life of circa 4 years for the in-situ transformation of a Si-containing Fh buried in soil into more crystalline Fe phases whereas Schwertmann et al. (2004) determined a half-life of circa 7 years for Fh transformation into goethite and hematite in an in-vitro experiment at 4 °C and pH 6.

It is interesting to compare the surface areas of the Fe oxide particles added with the iron oxide sludge and the indigenous metal oxide particles initially present in the field trial soils. The initial soil surface area at zero oxide addition is 5.4 ± 0.3 m\(^2\) g\(^{-1}\) (Fig. 5). This surface area has been derived using the molar mass of crystalline oxide materials whereas oxide nanoparticles have a higher molar mass resulting from a larger contribution of surface groups (Hiemstra, 2018b). To estimate these molar masses in a consistent manner, we treated the indigenous metal oxides either as nano-Fh or as nano-gibbsite using a set of equations from Hiemstra (2018b). This leads to a molar mass of nano-Fh and nano-gibbsite of 105 and 90 g mol\(^{-1}\), respectively.
Combining these masses with the amounts of Feox and Alox, we calculate a corresponding surface area of $1117 \pm 216 \text{ m}^2 \text{ g}^{-1}$. This can be translated to a particle size using the appropriate mass densities, which are very different for both nano-materials, i.e., $\sim 3400 \text{ kg m}^{-3}$ for nano-Fh and $\sim 2300 \text{ kg m}^{-3}$ for nano-gibbsite (Hiemstra, 2018b). This results in an equivalent particle size of $2.3 \pm 0.4 \text{ nm}$. This is very close to the TEM-based size of $\sim 2 \text{ nm}$ for the primary Fe oxide particles in the sludge (Fig. 2). However, the primary particles in the sludge are highly aggregated due to the presence of adsorbed Si (see Section 3.1.3.), leading to a loss in surface area as opposed to the indigenous metal oxide particles initially present in the field trial soils. The indigenous metal oxide particles are likely embedded in a matrix of OM. In this matrix, the OM molecules are soft and penetrable for ions, keeping the internal surface area accessible for P-PO$_4$ and the particles separated from aggregation (Hiemstra et al., 2010a).

3.6. The relation between P-PO$_4$ surface loading and P-PO$_4$ solubility in the field trial soils

In Fig. 6A, the adsorption isotherm of P-PO$_4$ is given using $P_{ox}$ as a measure of the reversibly adsorbed P-PO$_4$ pool and the DRP concentration in the 0.01 M CaCl$_2$ soil extracts before and after iron oxide sludge application. When $P_{ox}$ is presented on a soil mass basis ($\mu$mol g$^{-1}$), the data points are highly scattered. This is caused by spatial heterogeneity, especially for the Feox content (see Section 3.3.). By scaling $P_{ox}$ to the surface area of the soil samples, a large part of the scattering disappears (Fig. 6B), revealing the P-PO$_4$ adsorption isotherm. Some variation remains because the soil samples differ for example in pH and DOC concentration (Table 2), which may affect P-PO$_4$ adsorption density (Hiemstra et al., 2010b; Regelink et al., 2015). The L-shape of the isotherm is typical for a high affinity ion adsorption (Hiemstra et al., 2010a). The ion adsorption behavior can be described very well with the Langmuir equation ($R_{adj}^2 = 84\%$ and $P < 0.001$) having a $Q_{max}$ of $2.6 \pm 0.1 \mu$mol m$^{-2}$. This value can be compared to the maximum P-PO$_4$ adsorption density of different Fe oxide types. In the case of goethite, the P-PO$_4$ adsorption density is usually limited to about 2.5 to 3.5 $\mu$mol m$^{-2}$, depending on its crystallinity (Hiemstra and Van Riemsdijk, 1996). For Fh, a higher maximum P-PO$_4$ adsorption density can be found. Under acid conditions (pH 4 or 4.5), the value ranges from 3.9 to 4.6 $\mu$mol m$^{-2}$ (Celi et al., 2003; Hiemstra and Zhao, 2016; Wang et al., 2013) whereas it is about 2 $\mu$mol m$^{-2}$ at a pH of 7 (Hiemstra, 2013; Hiemstra and Zhao, 2016). The sludge-amended field trial soils had a pH between 5.7 and 7.3 (Fig. S8).

From a practical perspective, one can scale $P_{ox}$ to the sum of the molar Feox and Alox contents present in the field trial soils. The data collection requires only a single 0.2 M AAO extraction. This concept of scaling is known as the PSI as defined in Eq. (1) by $x$ (Van der Zee et al., 2010).

![Fig. 5.](image-url) The effective reactive surface area of the field trial soils ($A_{soil}$) plotted against the increase in the oxide content for the individual field trial plots. The intercept of the linear relationship equals the surface area of the initial soils before iron oxide sludge amendment whereas the slope reveals the surface area per unit mass oxides added (** significant at the $P < 0.001$ level).

![Fig. 6.](image-url) Results of $P_{ox}$ (A) and $P_{ox}$ scaled to the effective reactive surface area $A_{soil}$ (B) plotted against the dissolved reactive P (DRP) concentration in the 0.01 M CaCl$_2$ extracts for the field trial soils sampled before (25 June 2013) and 3 months (25 September 2013) and 14 months (8 September 2014) after iron oxide sludge application. Based on Fig. 5, $A_{soil}$ was calculated. The white and grey symbols represent the plots without and with topsoil, respectively. In Fig. 6B, the solid line represents the fitted Langmuir equation (** significant at the $P < 0.001$ level).
and Van Riemstijik, 1988). For our field trial soils, this scaling method leads to an excellent description of the data using the Langmuir equation ($Q_{\text{max}} = 96\%$ and $P < 0.001$) (Fig. S10). Conceptually, the underlying assumption of the PSI is a constant surface area per mole Feox + Alox present in soil. In our case, this assumption is incorrect because the overall surface area of our field trial soils originates from two distinct sources, i.e., the indigenous metal oxides initially present and the Fe oxides added with the iron oxide sludge. The difference in surface area between both sources (see Section 3.5.) initially present and the Fe oxides added with the iron oxide sludge. This is in contrast with the indigenous metal oxide particles diameter. This size is much larger than the TEM-based primary Fe particle size. Hence, these particles are strongly aggregated due to linkage by adsorbed Si polymers, causing a loss in surface area. This is in contrast with the indigenous metal oxide particles initially present in the field trial soils, which have a size of 2.3 ± 0.4 nm. This is very similar to the primary Fe particle size in the sludge. However, the surface area of the indigenous metal oxide particles is much higher (~1100 m$^2$ g$^{-1}$) due to little aggregation. Sludge application increased the surface area of the field trial soils from 5.4 up to a maximum of 12.9 m$^2$ g$^{-1}$ and strongly reduced the P-PO$_4$ concentration in the 0.01 M CaCl$_2$ soil extracts. A reduction in the P-PO$_4$ concentration to 0.3 μM was possible at an addition of ~10 to 15 g oxides per kg soil. A higher addition is much less effective in further reducing the P-PO$_4$ concentration. The adapted probe ion method is a useful tool for assessing the surface area of metal oxides in Fe-rich WTRs as well as soils amended with such materials. Information on the surface area of Fe oxides is crucially important to understand how Fe oxide-containing materials can reduce the P-PO$_4$ solubility when such materials are used for immobilizing P in legacy P soils with a low P-PO$_4$ adsorption capacity but with a high surface loading.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.135220.

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Supplementary data

Use of iron oxide nanoparticles for immobilizing phosphorus in-situ: Increase in soil reactive surface area and effect on soluble phosphorus

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S1. Iron oxide sludge production process

The iron oxide sludge used in this study is an industrial by-product from the production of drinking water from groundwater by a water treatment facility (Brabant Water Ltd), located near Vessem in the south of The Netherlands. The process of iron oxide sludge production at this water treatment facility has previously been described by Chardon et al. (2012). In short, anaerobic groundwater is pumped up from an aquifer at a depth between 21 and 54 m. The Fe(II) is removed from the raw water by mixing it with ample fresh air, leading to the oxidation of Fe(II) and precipitation of Fe oxides with a concomitant release of protons. The acid is neutralized by filtering the water over marble grains. With ample air added and slow filtering, a sludge of Fe oxides forms in the filter. The sludge is regularly removed from the filter by backwashing. The backwash water with the sludge is collected in a sedimentation basin. The sludge particles gradually settle at the bottom of the basin, forming a wet sediment which continues to build up until the basin needs to be cleared. Next, the sediment is transferred into a drying bed for dewatering. Since the sludge from the drying bed gets a structure with large solid clods, it is difficult to mix this material with the soil. Therefore, liquid iron oxide sludge from the sedimentation basin was used in the field trial. The sludge was collected from the basin by pumping the wet sediment into a tank truck (Fig. S1).

S2. Structural characterization of the iron oxide sludge with EXAFS

The EXAFS spectrum of the iron oxide sludge sample taken directly from the slurry tank in the field (Fig. S1) presented in Figure 1 in the main text could perfectly be reproduced as a mixture of the spectra of three reference compounds: 71% Si-containing ferrihydrite (Si-Fh*), 23% two-line ferrihydrite (2L-Fh) and 6% goethite (Goe) (effective sum of fitted fractions 102%; r-factor 1.2×10^{-3}). Although the first two reference spectra are relatively similar and the fitted fraction of goethite was low, each spectrum significantly improved the quality of the fit compared to the respective two-component fit. In addition, the presence of a small fraction of goethite was supported by the XRD pattern of the iron oxide sludge (Fig. S2).
The reference Si-Fh* corresponds to a siliceous Fh formed by the oxidation of 0.5 mM dissolved Fe(II) in a bicarbonate-buffered solution at pH 7.0 containing 0.5 mM silicate (molar Si/Fe ratio of 1), i.e., under conditions comparable to those under which the iron oxide sludge used in our field trial is formed. The reference material 2L-Fh is formed by forced hydrolysis of a concentrated Fe(III) solution through base addition. The small variations in the two spectra can be attributed to a lower degree of distortion of Fe(III)-octahedra and a lower degree of 3-dimensional Fe polymerization in Si-Fh* than 2L-Fh (Senn et al., 2015). The seemingly higher degree of polymerization of Fh in the iron oxide sludge than of Si-Fh* formed under similar chemical conditions (oxidation of Fe(II) in the presence of bicarbonate and silicate) may be due to the lower Si concentration in the raw groundwater from the water treatment facility of Brabant Water Ltd (8.9 mg L\(^{-1}\)) than in the synthetic groundwater (14 mg L\(^{-1}\)) from which the Si-Fh* was derived. In addition, aging of Fh in the iron oxide sludge over time may have contributed to the difference between Fh in the sludge and the Si-Fh* derived from the synthetic groundwater, although Si is known to significantly inhibit Fh transformation kinetics. The minor fraction of goethite in the iron oxide sludge may have formed during Fe(II) oxidation in the filtration bed with marble grains, promoted by the presence of calcite or it may indicate some moderate aging of the Si-stabilized Fh.

**S3. Chemical speciation calculations for acid ammonium oxalate extraction of the iron oxide sludge**

Chemical speciation calculations were done to calculate the solubility of Fh present in the iron oxide sludge in 0.2 M acid ammonium oxalate (AAO) at different values for the the solution-to-solid ratio (SSR). At a given pH, the solubility of Fh will depend on its particle size. For 2 nm-sized primary Fh particles with a theoretical SSA of \(\sim 850 \text{ m}^2 \text{ g}^{-1}\) oxide (see Section 3.1.3. in the main text) and a size-dependent molar mass of 101 g mol\(^{-1}\) (Hiemstra, 2018b), one can calculate a solubility product of \(Q_{so} = (\text{Fe}^{3+} \cdot \text{(OH)}^3)^{3} \approx 10^{-37.8}\) by applying the Ostwald equation in case of a surface Gibbs free energy of \(\gamma = 0.186 \text{ J m}^{-2}\) (Hiemstra, 2015). In this calculation, a solubility product of \(Q_{so} = 10^{-40.6}\) was used for the related Fh
bulk material (Hiemstra, 2018b). For Al oxides (gibbsite), the solubility product of $Q_{so} = (\text{Al}^{3+}) \cdot (\text{OH}^-)^3 = 10^{-33.3}$ was taken from (Keizer and Van Riemdijk, 2005). The main Ca source in the iron oxide sludge is calcite (see Section 3.1.1. in the main text). For the latter, a solubility product of $Q_{so} = (\text{Ca}^{2+}) \cdot (\text{CO}_3^{2-}) = 10^{-8.41}$ was used (Lindsay, 1979). Calcite will dissolve in 0.2 M AAO and Ca will precipitate with oxalate as solid Ca-oxalate. The solubility product of Ca-oxalate (s) was set at $Q_{so} = (\text{Ca}^{2+}) \cdot (\text{Ox}^2-) = 10^{-8.56}$ (Ulmgren and Radestrom, 1999). Complexation constants for the binding of Fe, Al, and Ca by oxalate and inorganic ligands in solution were taken from Keizer and Van Riemdijk (2005). For Fe and Ca, their total contents in the iron oxide sludge were used as input in the speciation calculations (Table 1). Since only a small fraction of the total Al content in the sludge is present in the form of amorphous Al oxides, the results of 0.2 M AAO extraction of the sludge for 24 h were used as input as input for Alox (Table S1). A CO$_2$ pressure of 0.03 bar was used in the speciation calculations.

In Figure S4, the pH-dependent presence of Fh and Ca-oxalate (s) in a 0.2 M AAO extract of the iron oxide sludge with an SSR of 20 L kg$^{-1}$ is presented. Although the calculated solubility product of Fh is very high, i.e., $Q_{so} = 10^{-37.8}$, only a small fraction of the Fe oxides dissolves at this SSR during AAO extraction of the iron oxide sludge in the pH range from 3 to 7. In the experiment with AAO extraction of the iron oxide sludge, the pH measured in the AAO extract at this specific SSR was 7.1 ± 0.1 (Table S1). In addition, calcite dissolves in 0.2 M AAO with an SSR of 20 L kg$^{-1}$ and Ca precipitates with oxalate as solid Ca-oxalate (Fig. S4). Only a small fraction of the Ca is soluble at low pH due to the formation of CaHOx$^+$ (aq) and CaOx$^0$ (aq) species (Fig. S5). Hence, the amounts of Fe and Ca dissolved in 0.2 M AAO at an SSR of 20 L kg$^{-1}$ are limited by the solubility of the Fh and Ca-oxalate (s). Figure S5 shows the calculated total dissolved concentrations of Fe, Al, and Ca in a 0.2 M AAO extract with an SSR of 20 L kg$^{-1}$ at equilibrium with Fh and Ca-oxalate (s) as a function of pH. The solubility of Fe is rather independent of the pH in the range from 3 to 7 at this SSR. The composition of the the total dissolved Fe concentration in solution is dominated by the presence of aqueous Fe-oxalate complexes. At a very low pH
(pH < 3), inorganic Fe-OH complexes contribute to the total dissolved Fe concentration as well. In the iron oxide sludge, a relatively small amount of Al oxides is present (Table S1). All Al is strongly complexed in solution with oxalate and, therefore, it is not present as Al(OH)$_3$ (s).

The solubility of Fh present in the iron oxide sludge is rather limited when an SSR of 20 L kg$^{-1}$ is used in the 0.2 M AAO extraction method, as follows from the above speciation calculations. The use of a higher SSR will lead to more Fh dissolution, as demonstrated in Figure S6. The use of an SSR of 200 L kg$^{-1}$ suffices to dissolve all Fh from the iron oxide sludge by extraction with 0.2 M AAO.

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Acid ammonium oxalate-extractable amounts of $\text{Fe}_{\text{ox}}$, $\text{Al}_{\text{ox}}$, and $\text{P}_{\text{ox}}$ and $\alpha$ for the iron oxide sludge at a different solid-to-solution ratio (SSR) and an extraction time of 2, 4, and 24 h. For the SSRs of 300 and 400 L kg$^{-1}$, an extraction time of 4 h was used. Furthermore, the pH measured in the acid ammonium oxalate extracts of the iron oxide sludge at the different SSRs and extraction times is given. All values represent average ± standard deviation of duplicate samples.

| SSR  (L kg$^{-1}$) | Time (h) | $\text{Fe}_{\text{ox}}$ (mmol kg$^{-1}$) | $\text{Al}_{\text{ox}}$ (mmol kg$^{-1}$) | $\text{P}_{\text{ox}}$ (mmol kg$^{-1}$) | $\alpha^1$ | pH |
|---------------------|----------|----------------------------------------|----------------------------------------|----------------------------------------|--------|----|
| 20                  | 2        | 831 (± 5)                              | 3.4 (± 0.0)                            | 0.65 (± 0.00)                          | 0.001 ± 0.000 | 6.9 ± 0.0 |
| 100                 | 2        | 5434 (± 63)                            | 8.5 (± 1.0)                            | 64.7 (± 3.4)                           | 0.012 ± 0.001 | 5.2 ± 0.1 |
| 200                 | 2        | 6016 (± 51)                            | 8.9 (± 4.2)                            | 91.0 (± 0.0)                           | 0.015 ± 0.000 | 3.4 ± 0.0 |
| 300                 | 2        |                                        |                                        |                                        |        | 3.2 ± 0.0 |
| 400                 | 2        |                                        |                                        |                                        |        | 3.1 ± 0.0 |
| 20                  | 4        | 978 (± 3)                              | 4.3 (± 0.1)                            | 0.72 (± 0.05)                          | 0.001 ± 0.000 | 7.0 ± 0.0 |
| 100                 | 4        | 5607 (± 2)                             | 11.0 (± 0.0)                           | 69.1 (± 3.1)                           | 0.012 ± 0.001 | 6.0 ± 0.0 |
| 200                 | 4        | 6027 (± 26)                            | 10.5 (± 0.1)                           | 90.9 (± 1.4)                           | 0.015 ± 0.000 | 3.4 ± 0.0 |
| 300                 | 4        | 5881 (± 38)                            | 12.8 (± 0.8)                           | 86.7 (± 0.7)                           | 0.015 ± 0.000 | 3.2 ± 0.0 |
| 400                 | 4        | 5885 (± 10)                            | 14.1 (± 3.1)                           | 85.9 (± 0.9)                           | 0.015 ± 0.000 | 3.2 ± 0.0 |
| 20                  | 24       | 1220 (± 6)                             | 4.6 (± 0.1)                            | 1.4 (± 0.2)                            | 0.001 ± 0.000 | 7.1 ± 0.0 |
| 100                 | 24       | 5770 (± 2)                             | 10.8 (± 2.4)                           | 72.7 (± 2.3)                           | 0.013 ± 0.000 | 6.4 ± 0.0 |
| 200                 | 24       | 6001 (± 52)                            | 15.1 (± 2.0)                           | 91.8 (± 0.5)                           | 0.015 ± 0.000 | 3.4 ± 0.0 |
| 300                 | 24       |                                        |                                        |                                        |        | 3.2 ± 0.0 |
| 400                 | 24       |                                        |                                        |                                        |        | 3.1 ± 0.0 |

$^1$Calculated according to Eq. (1) in the main text.
Table S2

Total dissolved trace metal concentrations and reactive trace metals pools for the field trial soils. Values represent average ± standard deviation of 3 plots, either with topsoil removed (0-5 cm) or present. Different letters denote a significant difference ($P < 0.05$).

| Sampling time | Topsoil   | Total dissolved trace metal concentration | Reactive trace metal pool |
|---------------|----------|-------------------------------------------|--------------------------|
|               |          | As ($\mu g$ L$^{-1}$) | Cd ($\mu g$ L$^{-1}$) | Cu ($\mu g$ L$^{-1}$) | Ni ($\mu g$ L$^{-1}$) | Pb ($\mu g$ L$^{-1}$) | Zn (mg L$^{-1}$) | As (mg kg$^{-1}$) | Cd (mg kg$^{-1}$) | Cu (mg kg$^{-1}$) | Ni (mg kg$^{-1}$) | Pb (mg kg$^{-1}$) | Zn (mg kg$^{-1}$) |
| Before        | Removed  | 2.0a (±0.2) | 19.3a (±4.1) | 2.4a (±0.8) | 6.0a (±1.1) | 3.6a (±0.25) | 0.77a (±0.1) | 1.1a (±0.14) | 0.42a (±0.4) | 1.3a (±0.4) | 0.26a (±0.05) | 11.5a (±2.9) | 19.2a (±7.4) |
|               | Present  | 1.6ab (±0.4) | 16.5ab (±3.1) | 2.4a (±0.3) | 4.8ab (±0.7) | 3.3ab (±0.04) | 0.51ab (±0.1) | 1.2a (±0.05) | 0.41a (±0.3) | 1.5a (±0.3) | 0.30ab (±0.14) | 11.7a (±0.30) | 16.6a (±0.3) |
| 14 months     | Removed  | 0.87bc (±0.47) | 6.6bc (±5.0) | 1.7bc (±0.3) | 2.6bc (±1.3) | 0.60bc (±0.95) | 0.23bc (±0.21) | 1.1bc (±0.12) | 0.46bc (±0.3) | 1.6bc (±0.3) | 0.33bc (±0.05) | 14.8bc (±0.02) | 17.1bc (±0.6) |
|               | Present  | 0.83bc (±0.49) | 4.8bc (±5.7) | 1.7bc (±0.3) | 2.2bc (±1.5) | 0.57bc (±0.98) | 0.15bc (±0.24) | 0.71bc (±0.22) | 0.45bc (±0.03) | 1.6bc (±0.1) | 0.41bc (±0.07) | 11.4bc (±0.12) | 11.5bc (±1.8) |

$^1$Total dissolved trace metal concentrations were measured in 0.01 M CaCl$_2$ soil extracts (Houba et al., 2000).

$^2$Reactive trace metal pools were determined by soil extraction with 0.43 M HNO$_3$ (Groenenberg et al., 2017).

$^3$Total dissolved trace metal concentrations and reactive trace metal pools were determined for the field trial soils sampled before (25 June, 2013) and 14 months (8 September, 2014) after iron oxide sludge application.
Table S3

The DRP concentration measured in 0.5 M NaHCO₃ extracts from the field trial soils at an SSR of 50 L kg⁻¹, based on a modified Olsen P method (Hiemstra et al., 2010). Values represent average ± standard deviation of three plots, either with topsoil (0-5 cm) removed or topsoil present.

| Sampling time¹ | Topsoil | Olsen P² (µM) |
|----------------|---------|---------------|
| Before         | Removed | 150ᵃ (± 26)   |
|                | Present | 96ᵇ (± 28)    |
| 3 months       | Removed | 145ᵃ (± 21)   |
|                | Present | 56ᵇ (± 13)    |
| 14 months      | Removed | 137ᵃ (± 37)   |
|                | Present | 58ᵇ (± 16)    |

¹Field trial soils were sampled before (25 June, 2013) and 3 months (25 September, 2013) and 14 months (8 September, 2014) after iron oxide sludge application.

²Different letters denote a significant difference (P < 0.05).
Fig. S1. Liquid iron oxide sludge was collected from a sedimentation basin of a water treatment facility of Brabant Water Ltd near Vessem, The Netherlands (left). The field trial was conducted in the nature reserve area “Groote Heide” on a noncalcareous sandy soil near Heeze, The Netherlands. In the field trial, the iron oxide sludge was injected from a slurry tank into the soil using a trailing-foot system by cutting a shallow slit in the soil into which the iron oxide sludge was injected (right). The iron oxide sludge was mixed with the soil by intense mechanical mixing of the upper 20 cm-soil layer with a cultivator.
**Fig. S2.** X-ray diffraction (XRD) pattern of the iron oxide sludge sample taken directly from the slurry tank in the field. Sharp peaks in lower panel are from calcite (C), which is the dominant crystalline component of the sludge. The upper panel shows a minor contribution from quartz (Qz; two sharp peaks) and some poorly-crystalline goethite (Gt; small broad peaks). The two marked areas with an elevation of the background correspond to the very broad peaks of synthetic two-line ferrhydrite (Fh).
**Fig. S3.** The pH-dependent adsorption of P as P-PO$_4$ and S as silicic acid (H$_4$SiO$_4$) to ferrihydrite (Fh) expressed at a relative scale (A) and as an adsorption density (C) with the corresponding equilibrium P and Si concentrations (B) and the molar Si/Fe and P/Fe ratio of Fh (D) formed during treatment of the raw groundwater from the water treatment facility of Brabant Water Ltd. The CD model calculations were done for 2 nm-sized primary Fh particles with a theoretical SSA of ~850 m$^2$ g$^{-1}$. The latter corresponds to 17 m$^2$ L$^{-1}$ in the groundwater, calculated from the measured Fe concentration of 10.7 mg L$^{-1}$ and a size-dependent molar mass of 101 g mol$^{-1}$ for Fh (Hiemstra, 2018b). In the calculations, the adsorption parameters of Hiemstra (2018a) were used. The ionic strength was set at 0.01 M and the initial P and Si concentrations measured in the raw groundwater were 2.3 μM P and 0.32 mM Si.
Fig. S4. The pH-dependent presence of Fh and Ca-oxalate (s) in a 0.2 M acid ammonium oxalate (AAO) extract of the iron oxide sludge at a solution-to-solid ratio of 20 L kg⁻¹. For a description of the modelling setup, see Section S3 of the Supplementary data.
Fig. S5. The logarithm of the total dissolved Fe, Al, and Ca concentrations in a 0.2 M acid ammonium oxalate (AAO) extract of the iron oxide sludge at a solution-to-solid ratio of 20 L kg⁻¹ as a function of the pH. For a description of the modelling setup, see Section S3 of the Supplementary data.
Fig. S6. Calculated solubility of Fh from the iron oxide sludge in 0.2 M acid ammonium oxalate (AAO) expressed at a relative scale as a function of the solution-to-solid ratio (SSR). The symbols refer to the experimental values for the extraction time of 24 h. For the SSRs of 20, 100, and 200 L kg\(^{-1}\), the pH was set at a value of 7.1, 6.4, and 3.4, respectively (Table S2). The line represents the calculated solubility of Fh. For a description of the modelling setup, see Section S3 of the Supplementary data.
**Fig. S7.** The DOC concentration in the 0.01 M CaCl₂ soil extracts plotted against the SOM content for the individual field trial plots. The white and grey symbols represent the plots without and with topsoil, respectively (*** significant at the $P < 0.001$ level).
Fig. S8. The pH in the 0.01 M CaCl$_2$ soil extracts plotted against the increase in the oxide content for the individual field trial plots. The amount of added oxides was calculated from the difference in the $Fe_{ox}$ and $Al_{ox}$ contents before and after sludge amendment using a molar mass of 89 g mol$^{-1}$ (FeOOH) and 78 g mol$^{-1}$ (Al(OH)$_3$), respectively. The white and grey symbols represent the plots without and with topsoil, respectively. To guide the eye, an exponential curve was added (** significant at the $P < 0.001$ level).
**Fig. S9.** The effective reactive surface $A$ soil for the field trial soils sampled before (25 June, 2013) and 3 months (25 September, 2013) and 14 months (8 September, 2014) after iron oxide sludge application. Values represent average ± standard deviation of 3 plots, either with topsoil removed (0-5 cm) or present. Different letters denote a significant difference ($P < 0.05$).
Fig. S10. The P saturation index $\alpha$ defined in Eq. (1) in the main text plotted against the dissolved reactive P (DRP) concentration in the 0.01 M CaCl$_2$ soil extracts for the field trial soils sampled before (25 June, 2013; diamonds) and 3 months (25 September, 2013; circles) and 14 months (8 September, 2014; squares) after iron oxide sludge application. The white and grey symbols represent the plots without and with topsoil, respectively. The solid line represents the fitted Langmuir equation (*** significant at the $P < 0.001$ level).