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Journal of Environmental Quality SPECIAL SUBMISSIONS

Use of Reactive Materials to Bind Phosphorus

Wim J. Chardon,* Jan E. Groenenberg, Erwin J. M. Temminghoff, and Gerwin F. Koopmans

Phosphorus (P) losses from agricultural soils have caused surface water quality impairment in many regions of the world, including The Netherlands. Due to the large amounts of P accumulated in Dutch soils, the generic fertilizer and manure policy will not be sufficient to reach in time the surface water quality standards of the European Water Framework Directive. Additional measures must be considered to further reduce P enrichment of surface waters. One option is to immobilize P in soils or manure or to trap P when it moves through the landscape by using reactive materials with a large capacity to retain P. We characterized and tested two byproducts of the process of purification of deep groundwater for drinking water that could be used as reactive materials: iron sludge and iron-coated sand. Both materials contain low amounts of inorganic contaminants, which also have a low (bio) availability, and bound a large amount of P. We could describe sorption of P to the iron sludge in batch experiments well with the kinetic Freundlich equation ($Q = a \times t^m \times C^n$). Kinetics had a large influence on P sorption in batch and column experiments and should be taken into account when iron-containing materials are tested for their capability to immobilize or trap P. A negative aspect of the iron sludge is its low hydraulic conductivity; even when mixed with pure sand to a mixture containing 20% sludge, the conductivity was very low, and only 10% sludge may be needed before application is possible in filters or barriers for removing P from groundwater. Due to its much higher hydraulic conductivity, iron-coated sand has greater potential for use under field conditions. Immobilizing P could be an option for using iron sludge as a reactive material.

As in many countries, phosphorus (P) losses from heavy fertilized agricultural soils have caused surface water quality impairment in The Netherlands. This is especially the case in the western part of the country, where soils have a low sorption capacity for P and where seepage through decomposing peat layers in the subsoil occurs (Chardon and Schoumans, 2007). The generic Dutch fertilizer and manure policy, which strives toward equilibrium fertilization in 2015, will not be sufficient to reach the surface water quality standards of the European Water Framework Directive in 2015 due to the large amounts of P accumulated in Dutch soils (Reijneveld et al., 2010). Additional measures must be considered to further reduce the enrichment of surface waters with P (Sharpley et al., 1994; Chardon et al., 1996; Withers and Jarvis, 1998; Kronvang et al., 2005). Phytomining soils enriched in P by crop harvesting without P application can be an effective measure to reduce transport of P from agricultural land to surface waters. However, phytomining is a time-consuming process and removes P primarily from the topsoil (McCollum, 1991; Koopmans et al., 2004b; van der Salm et al., 2009). Particulate P in drainage water can be removed in constructed wetlands (Braskerud et al., 2005). Yet, the size required for a constructed wetland to be effective can be problematic in regions where the price of agricultural land is high, as in the western part of The Netherlands. Hence, there is a need for measures that can become effective shortly after implementation and that occupy little space.

Alternative options are immobilizing P in soils or trapping P when it moves through the landscape by using reactive materials. For both options, many different materials have been proposed, which can be categorized as (i) natural materials or their synthetic analogs (e.g., ironhydroxides, allophane, and wollastonite), (ii) industrial waste materials or byproducts (e.g., steel slag and blast furnace slag), and (iii) man-made products (e.g., expanded clay aggregates or lanthanum modified clays) (Douglas et al., 2004). Examples of the application of reactive materials are mixing with land-applied P sources, such as animal manure or litter, to reduce P solubility (Moore and Edwards, 2005) or mixing with P-rich topsoil to decrease P release from the soil solid phase to the soil solution (Elliott

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Abbreviations: BTC, breakthrough curve; C_i, initial concentration in batch experiment; CI, confidence interval; IC, inorganic carbon; ICP–AES, inductively coupled plasma–atomic emission spectrometry; K_{sat}, saturated hydraulic conductivity; OM, organic matter; PBC, phosphorus binding characteristics; SFA, segmented flow analyzer; TC, total carbon; WTR, water treatment residuals.

et al., 2002; Dayton and Basta, 2005b; Agyin-Birikorang et al., 2007; Ippolito et al., 2011). Reactive materials can also be used in a barrier placed along ditches for removal of P from subsurface runoff (Kronvang et al., 2005). Such a barrier is permeable for water and is made by filling a vertical trench with a reactive material that removes or converts contaminants from groundwater flowing horizontally. Permeable reactive barriers were previously proposed for various contaminants, such as As (Lindberg et al., 1997), NO_3 (Robertson and Cherry, 1995), and chlorinated compounds (Zolla et al., 2009). For P loss to lowland streams, tile drains can be an important pathway (Sims et al., 1998). In this case, a possible remediation practice is adding reactive materials to backfill material around tile drains (Saulys and Bastiene, 2007; McDowell et al., 2008). Another example of using reactive materials is retention filters that have been tested for filtering pond effluent (Shilton et al., 2006), for small-scale wastewater treatment (Gustafsson et al., 2008; Dobbie et al., 2009), and for use at the end of tile drains (McDowell et al., 2008).

Before field application, the phosphorus binding characteristics (PBC) of reactive materials should be known, which are strongly related to their physicochemical properties such as grain size, pH, and Fe, Al, or Ca content. The PBC are a criterion for material selection and are needed for estimating the amount of material needed to control P solubility in the treated soil water at the desired level (Douglas et al., 2004; Cucarella and Renman, 2009). In addition to good PBC, the reactive material should have good hydraulic conductivity to minimize the risk of system clogging or the occurrence of preferential flow when applied in barriers or filters. Also, their concentration and bioavailability of inorganic contaminants must be evaluated because some materials may contain elevated levels of trace metals (e.g., industrial byproducts like slags) (McDowell et al., 2008) but occasionally also natural precipitates like ochre (Fenton et al., 2009).

A reactive material that has received much attention in the United States is water treatment residuals (WTR), formed by adding $Al_2(SO_4)_3$, $FeCl_3$, or $Fe_2(SO_4)_3$ to raw surface water. The aim of the addition of WTR is to coagulate suspended solids and natural organic matter, followed by filtering, during the production of drinking water (Ippolito et al., 2011). In The Netherlands, approximately 60% of the drinking water is produced from groundwater. When the groundwater is anaerobic, it can contain dissolved iron in the reduced Fe^{2+} form (Postma et al., 1991); this must be removed before human consumption to prevent colored or bad-tasting drinking water. After the oxidation of Fe^{2+} in the raw water, amorphous $Fe(OH)_3$ forms as a sludge or as a coating on filter sand. After processing, the iron sludge is comparable to Fe-WTR. In contrast to Fe-WTR, the Fe in the sludge and coated sand is of natural origin and was not added during raw water treatment. Compared with WTR, P binding by reactive materials obtained from Fe^{2+} that is naturally present in groundwater has received much less attention. The aim of our study was to test the potential usefulness of iron sludge and iron-coated sand for P binding in barriers or around tile drains by determining (i) their elemental composition, (ii) the content of contaminants (total and available), (iii) their saturated hydraulic conductivity (K_{sat}), and (iv) PBC in batch and column studies.

Materials and Methods

Materials

The iron sludge and iron-coated sand are byproducts of the production of drinking water from groundwater by water treatment plants near Vessem and Someren, respectively. Both plants are located in the Province Noord-Brabant in the south of The Netherlands and are run by Brabant Water Ltd. At the Vessem location, anaerobic groundwater is pumped up from an acquifer at a depth between 21 and 54 m, whereas in Someren the depth is 153 to 266 m. The Fe^{2+} in the raw water is removed via mixing of the raw water with fresh air. After the oxidation of Fe^{2+}, amorphous $Fe(OH)_3$ and protons are produced. At the Vessem location, the protons are neutralized via filtration of the raw water over marble grains. With ample air added and slow filtering, a sludge of $Fe(OH)_3$ forms and is removed regularly from the filter by backwashing. The sludge and the washing liquid are led into a sedimentation pond, from which the sediment is transferred to a drying bed for dewatering. The sludge is sold as a byproduct (e.g., for capturing H_2S during biofuel production or for use in the brick industry). By contrast, at the Someren location the aerated water is led relatively fast over a coarse sand filter, so that less contact is possible with O_2. Here, the Fe^{2+} adsorbs onto surface hydroxyl groups on the sand, after which Fe^{2+} oxidizes on the surface, leading to an increase of the thickness of the iron oxide coating of the sand (Tamura et al., 1980). This process is called heterogeneous oxidation of iron (Wolthoorn et al., 2004). In nature, coating of silica sand with iron oxides is a widespread phenomenon (Scheidegger et al., 1993). The top layer of the filter with iron-coated sand is removed regularly to optimize the microbial properties of the filter material, which is also sold as a byproduct.

After dewatering in the drying bed, the iron sludge has a clay-like structure with large clumps and can still contain a considerable amount of water. At arrival in our laboratory, the iron sludge had a water content of approximately 550 g kg^{-1}, whereas the iron-coated sand had a water content of approximately 150 g kg^{-1}. Both materials were dried before being used for experiments. To avoid the risk of phase transformation of the iron oxides during drying at elevated temperature, the iron sludge and iron-coated sand were freeze-dried (Schwertmann and Cornell, 1991; Redding et al., 2008). For the determination of the general characteristics and the batch and column experiments, both materials were sieved over 2 mm.

General Characteristics

For the iron sludge and iron-coated sand, particle size distribution, moisture, organic matter (OM), calcium carbonate ($CaCO_3$), and total extractable macroelements and trace metals were determined using standard analytical procedures (Houba et al., 1997). Particle size distribution over texture classes 0 to 2 μm (clay), 2 to 50 μm (silt), and 50 to 2000 μm (sand) was determined by the pipette method after removal of organic matter and $CaCO_3$. Moisture content was determined by oven-drying at 105°C. Organic matter content was calculated from C, determined by spectrophotometric measurement after a $K_2Cr_2O_7$ destruction, assuming a C content of OM of 58%. The amount of $CaCO_3$ was determined by measuring the volume of CO_2 produced after the addition of HCl. Total contents of macroelements (Al, Ca, Fe, Mg, Mn, P, and S) were determined with inductively coupled plasma–atomic emission spectrometry (ICP–AES) (Iris-3300 DV; Thermo, Franklin, MA) after digestion with Aqua Regia. As a measure of the readily available amounts of ortho-P and total P and trace metals (As, Cd, Cu, Ni, Pb, and Zn), an extraction with 1:10 (w:v) 0.01 mol L^{-1} $CaCl_2$ was executed (Houba et al., 2000). In addition, pH and dissolved organic carbon (DOC) were measured. Ortho-P and DOC were determined with a fully automated segmented flow analyzer (SFA) (Skalar, Breda, The Netherlands), whereas total P and trace metals were measured with ICP–AES. The specific surface area of the materials was determined using BET-N_2 adsorption (BET-specific surface area [BET-SSA]). The content of pure sand in iron-coated sand was determined by digestion with Aqua Regia followed by washing with demineralized water and weighing of the residual sand fraction. Except for the particle size distribution, OM, and $CaCO_3$, all other characteristics were determined in duplicate.

Batch Sorption Study

The iron sludge (30 mg) was shaken horizontally (57 strokes min^{-1}) in 40-mL tubes in a solid/solution ratio of 1:1000 (w/v) with a 2.5 mmol L^{-1} $Ca(NO_3)_2$ solution as a background electrolyte and containing different initial concentrations (C_i) of ortho-P (0, 2, 4, 8, 16, 32, 64, and 130 mg ortho-P L^{-1}) prepared with KH_2PO_4. Experiments were executed in duplicate, and blank tubes with P but without sludge were included for checking all C_i. We selected the 1:1000 solid-to-solution ratio because it enabled us to obtain a reliable estimate of the equlibrium concentration of ortho-P even with high P sorption to the iron sludge. Shaking time was 1, 3, 8, or 21 d, after which the solution was centrifuged at 10,000 rpm and passed through a 0.45-µm filter (Aqua 30; Schleicher & Schuell, Dassel, Germany), and ortho-P was measured with a SFA. Sorption of ortho-P was calculated from the difference between C_i and ortho-P at equilibrium. In addition, pH, inorganic carbon (IC), total carbon (TC), and total concentrations of Al, Ca, Fe, K, Mg, and Mn were measured with ICP–AES in the solutions collected after 8 d equilibration time. Total C and IC were measured with a TOC analyzer (TC5000; Shimadzu, Kyoto, Japan), and DOC was calculated from the difference.

For each equilibration time, sorption data from the batch experiments were fitted to the linearized version of the Freundlich equation:

$$\log(Q) = \log(K) + n\log(C) \quad [1]$$

where Q is the amount of ortho-P sorbed by the iron sludge (mg g^{-1}), K is the sorption constant (mg^{1-n} g^{-1} L^n), C is the concentration in solution (mg L^{-1}), and n is the Freundlich coefficient (–). Because Q and log(K) increased with time, the data were fitted to the kinetic Freundlich equation in which K is replaced with a t^m (Barrow and Shaw, 1975; Chardon and Blaauw, 1998):

$$Q_t = a\,t^m\,C_t^n \quad [2]$$

where t is time (d), and a and m are empirical constants (–).

Equation [2] can be linearized as

$$\log(Q_t) - n\log(C_t) = \log(a) + m\log(t) \quad [3]$$

The coefficients a and m were obtained by linear regression of the left hand side of Eq. [3] with log(t). Because the value of the coefficient n is not a priori known, we simultaneously optimized n using the solver routine in Excel. This procedure has been shown to be successful in a previous study to optimize Freundlich-based partition relations for trace metals (Groenenberg et al., 2010b).

For iron-coated sand, it was not possible to perform a batch sorption study because the iron oxide coating came off the sand during shaking. In batch P sorption experiments, shaking can break adsorbent particles, increasing the specific surface area (Drizo et al., 2002). Therefore, we tested the P binding behavior of iron-coated sand only in the column study.

Column Study

For selecting the set-up of the column experiment, the K_{sat} (cm d^{-1}) was determined for different mixtures of iron sludge and acid-washed (nonreactive) quartz sand: 5, 10, 20, or 50% (by weight) sludge and 95, 90, 80, or 50% acid-washed sand. The K_{sat} of unsieved iron-coated sand was also determined. For each sample, a ring with a volume of 2865 mL was filled. The samples were saturated with water from the bottom to avoid the inclusion of air bubbles. After 24 h of equilibration, the K_{sat} was determined in triplicate.

The set-up of the column experiment was based on the results of the K_{sat} determination. One column was filled with iron-coated sand, and three other columns were filled with mixtures containing 1, 5, or 10% iron sludge and 99, 95, or 90% acid-washed quartz sand. Perspex columns were used with a length of 10 cm and an inner diameter of 4.6 cm. The columns had a glass frit at the bottom and a paper filter on the frit, with a pore diameter of 12 to 25 µm (Whatman Grade 589/1, black ribbon). Then a layer of 8 cm thickness was filled with iron-coated sand or with a mixture of iron sludge and acid-washed sand. To prevent separation of the iron sludge and acid-washed sand during filling, the mixtures were pre-wetted with the electrolyte that was used later for percolation. On top of the 8 cm layer, another Whatman 589/1 paper filter was placed, and the rest of the column was filled with acid-washed glass pearls. Using a peristaltic pump, the columns were percolated from the bottom for removing entrapped air bubbles and to avoid preferential flow paths at a rate of 1 L d^{-1} on average. This rate equals a water column height of approximately 60 cm d^{-1} and gives an average hydraulic pore volume retention time of 1.0 h. Percolation was done with a 2.5 mmol L^{-1} $Ca(NO_3)_2$ electrolyte containing on average 3.95 mg ortho-P L^{-1} (SD, 0.06). The relatively high ortho-P concentration was chosen because it is a common concentration in tile drainage water in the flower bulb growing region in the west of The Netherlands where problems with P losses and surface water quality are large (Chardon and Schoumans, 2007). Column effluents were collected and weighed daily for the calculation of the P load of each column. For the column with 1% iron sludge, ortho-P in the effluent samples was measured by SFA daily during the first week and two times a week until Day 167. Subsequently, this column was percolated with the 2.5 mmol L^{-1} $Ca(NO_3)_2$ electrolyte but without P to determine the desorption kinetics of ortho-P. On Days 168 to 209, ortho-P in effluent samples was measured on weekdays and weekly from Day 210 until the end of the experiment (Day 238). For the other columns, ortho-P in effluent samples was measured twice a week until Day 167 and weekly until the end of the experiment.

Biweekly, pH and concentrations of total Al, Ca, Fe, K, Mg, and Mn (ICP–AES) as well as TC and IC (Shimadzu TC5000) were measured; DOC was calculated as the difference between TC and IC. At the end of the column experiment, the column material was removed intact from the columns and divided into layers of 1 cm thickness. Total Fe and P contents of the material from each layer were determined with ICP–AES after Aqua Regia digestion.

Saturation Indices

To evaluate the possibility of the formation of Ca-, Al-, and Fe-P precipitates, the saturation indices were calculated for a number of minerals for all measurements in solutions of the batch and column experiments. Solubility products were taken from Lindsay (1979). For calculations, the chemical speciation model ORCHESTRA was used (Meeussen, 2003), which includes the NICA-Donnan model for cation binding to dissolved organic matter (DOM) (Kinniburgh et al., 1999). We used generic model parameters for the NICA-Donnan model as provided by Milne et al. (2003). For the calculations, we used measured pH and concentrations of ortho-P, DOC, and total Al, Ca, Fe, K, Mg, and Mn as input. The concentration of NO_3 was set to the concentration of the electrolyte used in the batch sorption and column studies (5 mmol L^{-1}). Because total concentrations of Al and Fe were below the detection limit of the ICP–AES (i.e., 0.03 mg Al L^{-1} and 0.09 mg Fe L^{-1}), Al^{3+} and Fe^{3+} activities were used as input variables that were calculated with the solubility products of $Al(OH)_3$ (log $K_{so,25}$ = 8.5) and $Fe(OH)_3$ (log $K_{so,25}$ = 2.5), which is representative for soil solutions (Groenenberg et al., 2010a). The DOM concentrations were calculated from DOC assuming a carbon content of 50%, and we modeled DOM as being 50% fulvic acids (Groenenberg et al., 2010a).

Results and Discussion

General Characteristics

The general characteristics of the iron sludge and the iron-coated sand are given in Table 1. Both materials have a neutral to slightly alkaline pH and contain $CaCO_3$. The high $CaCO_3$ content in the iron sludge is due to eroded marble particles from the filter, which are removed from the filter by regular backwashing, together with the iron sludge formed during groundwater treatment. Both $CaCO_3$ and iron sludge settle in the sedimentation pond where the washing liquid is collected. The $CaCO_3$ content in the iron-coated sand is much lower than in the iron sludge. At the water treatment plant where the iron-coated sand was produced, no marble grains are used in the filter; only coarse sand is used. Iron sludge largely consists of silt- and clay-sized particles and contains a small (19%) fraction of sand-sized particles. This is much less than the sand-sized fraction reported in a review paper on WTR by Ippolito et al. (2011), who reported 69 ± 8% for Al-WTR and 85 ± 2% for Fe-WTR. The difference might be due to a larger fraction of soil separates in the treated raw water or by a stronger aggregation of the oxides in WTR due to the use of polymers for dewatering biosolids. As expected, the iron-coated sand consists of 97% sand-sized particles. The remainder probably consists of clay- and silt-sized oxides abraded during handling of the material. Iron sludge and iron-coated sand contain solid OM and DOM. The presence of OM in both materials could originate from DOM in the raw groundwater (Postma et al., 1991), which is sorbed by the iron oxides formed during water treatment. The higher OM content in iron sludge as compared with iron-coated sand could result from deposition of organic residues in the sedimentation pond. The pure sand content of the iron-coated sand was about 533 g kg^{-1} (Supplemental Table S1).

The total contents of macroelements in the iron sludge and iron-coated sand are shown in Table 2. As expected, Fe was the dominant macroelement in both materials, with 33 and 20% of the total weight, respectively. During oxidation, the Fe^{2+} probably precipitated as amorphous $Fe(OH)_3$ (Schwertmann and Cornell, 1991). When Fe is recalculated as $Fe(OH)_3$, this corresponds with 63% by weight of the iron sludge and with 38% of the iron-coated sand (Supplemental Table S1). Calcium is the second most important macroelement in both materials, as part of $CaCO_3$. The Ca content can be explained almost completely from the $CaCO_3$ content of the materials (Table 1). Nearly 100% of the composition of the materials can be explained by $Fe(OH)_3$, $CaCO_3$, OM, and moisture, plus pure sand for iron-coated sand (Supplemental Table S1). The remainder in the iron sludge and iron-coated sand can probably be ascribed to compounds of Al, Mg, Mn, P, and S.

Table 1. General characteristics of the iron sludge and iron-coated sand.†

Material	pH‡	Texture class			$CaCO_3$	OM	DOC‡	Moisture	BET-SSA
		0–2 μm	2–50 μm	50–2000 μm					
		%			g kg^{-1}		mg C kg^{-1}	g kg^{-1}	m^2 g^{-1}
Iron sludge	7.6 ± 0.0	35	46	19	200	33	195 ± 1	84 ± 1	113
Coated sand	7.2 ± 0.0	2	1	97	18	7.3	19 ± 1	48 ± 0.1	71

† Texture, $CaCO_3$, organic matter (OM), and BET-specific surface area (BET-SSA) were determined on one sample. The pH, dissolved organic carbon (DOC), and moisture content were determined in duplicate (average ± SD).

‡ Measured in 1:10 (w/v) 0.01 mol L^{-1} $CaCl_2$ extract.

Table 2. Total contents of macroelements (Aqua Regia). The contents were determined in duplicate.

Material	Al	Ca	Fe	Mg	Mn	P	S	P/Fe†
	g kg^{-1}							
Iron sludge	2.1 ± 0.0‡ (0.21)§	73 ± 1 (7.3)	329 ± 4 (33)	0.97 ± 0.01 (0.10)	7.8 ± 0.1 (0.78)	2.6 ± 0.1 (0.26)	0.65 ± 0.02 (0.07)	0.014
Coated sand	0.62 ± 0.12 (0.06)	6.1 ± 0.2 (0.61)	198 ± 1 (20)	0.36 ± 0.05 (0.04)	2.9 ± 0.9 (0.29)	3.4 ± 0.0 (0.34)	0.23 ± 0.01 (0.02)	0.031

† Molar ratio.

‡ Average ± SD.

§ Values in parentheses are percentage by weight.

The values of BET-SSA are in line with values reported for WTR by Makris et al. (2005b) but are relatively low when compared with values that are reported for pure amorphous $Fe(OH)_3$. This can partly be explained by the presence of $CaCO_3$, sand, and OM in the materials because these compounds usually have a much smaller BET-SSA than pure $Fe(OH)_3$ (Endo et al., 2009; Guo et al., 2009). Based on the measured BET-SSA, values reported in literature for the BET-SSA of $CaCO_3$, sand, and organic matter, and the composition of iron sludge and iron-coated sand, BET-SSA values of 167 and 176 $m^2\ g^{-1}$ were calculated for the amorphous $Fe(OH)_3$ in both materials. This order of magnitude corresponds reasonably well with usually measured BET values for pure $Fe(OH)_3$ (200–300 $m^2\ g^{-1}$) (Dzombak and Morel, 1990).

Iron sludge and iron-coated sand contain considerable amounts of P, probably captured by the $Fe(OH)_3$ from the raw groundwater. Ippolito et al. (2011) reported an average P content of Al-WTR of 2.2 g kg^{-1}, comparable to the P content of our iron sludge (2.6 g kg^{-1}). Only agricultural soils highly enriched by a large P surplus have such high total P contents (Koopmans et al., 2007). However, because the P/Fe ratio of both materials is rather low (Table 2), the readily available amount of P is expected to be low. Indeed, no ortho-P could be detected in $CaCl_2$ extracts of both materials (Supplemental Table S2).

The total Cd content of both materials exceeds the median value of Cd content in Dutch topsoils (0–10 cm) (Supplemental Table S3), as given for agricultural soils and soils in natural areas by Lamé et al. (2004). Total contents of other trace metals were lower than the median values in Dutch topsoils. Besides the total contents of trace metals, their readily available amounts in the iron sludge and iron-coated sand as extracted with 0.01 mol L^{-1} $CaCl_2$ were determined (Supplemental Table S2). No Cd, Cu, and Ni could be detected by ICP–AES in the $CaCl_2$ extracts, whereas for Pb and Zn very small amounts were present. Ortho-P could not be detected in the $CaCl_2$ extracts (Table 2); however, there was some total P present, which was probably associated with colloidal Fe.

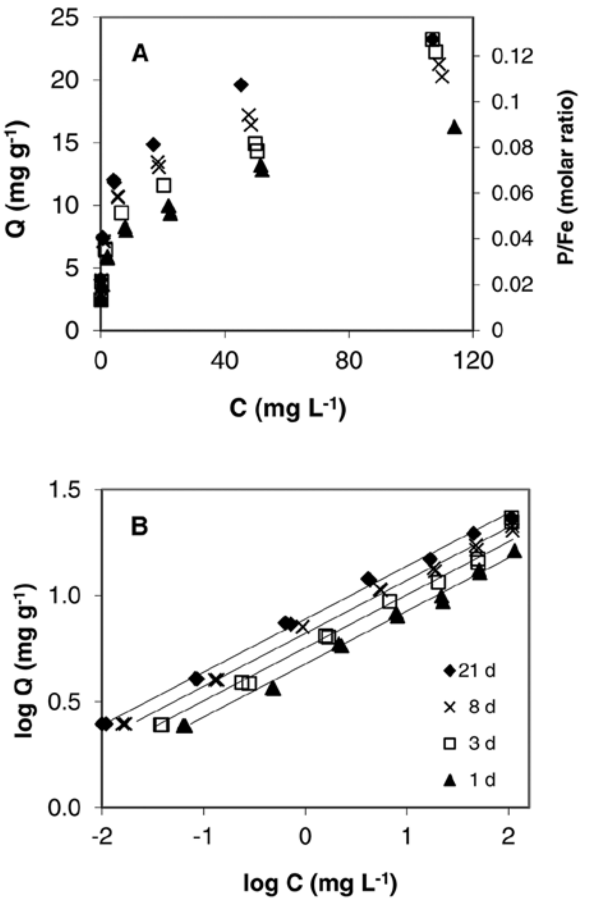

Fig. 1. Sorption data of ortho-P by iron sludge with equilibration times of 1, 3, 8, and 21 d, with calculated molar P/Fe ratio (A) and the same data plotted on a log-log scale (B). Lines in (B) show the fitted kinetic Freundlich equation $Q = 4.76\ t^{0.16}\ C^{0.25}$, with t = time (d) (Eq. [2], with parameters of Table 4).

Batch Sorption Study

Figure 1A shows, for the various equilibration times, the relation between the amount of ortho-P sorbed by iron sludge (Q) and the ortho-P concentration measured in solution (C). A nonlinear increase of Q with C is found for all equilibration times, meaning that the increase in Q decreases with increasing C.

For each equilibration time, the sorption data for ortho-P on iron sludge were fitted after log transformation to the linearized version of the Freundlich equation (Eq. [1]); the parameters found are presented in Table 3. The value of log(K) clearly increases with time: A plot of log(K) against log(time) yields a straight line (R^2 = 0.999; not shown). The derived parameter n is more or less constant (average value, 0.25; SD, 0.01). Fitting the linearized kinetic Freundlich equation (Eq. [3]) to all sorption data resulted in a good fit of the data (Table 4) with a high explained variance (R^2), low standard deviations of the parameters, and the same value for n as the average value obtained for n with the individual fits of the Freundlich equation for the different equilibration times.

The sorption data for all equilibration times (1, 3, 8, and 21 d) are presented in Fig. 1B, with the lines showing the predictions from the kinetic Freundlich equation using the parameters of Table 4. The data and model predictions correspond very well. The value of parameter m (0.16) of the kinetic Freundlich equation falls within the range found for m (0.1–0.3) in a number of studies in which the equation was applied on various soil types (see references in Chardon and Blaauw, 1998). The kinetic Freundlich equation was previously shown to be applicable for a number of soil amendments by Cheung and Venkitachalam (2006). From their data for ortho-P sorption experiments, which lasted up to 16 d, we estimated a value for parameter m varying between 0.18 and 0.35. Although the value of m that we found for iron sludge falls in the lower range of the values found in other studies, the consequence is clear: The sorption capacity of iron sludge for ortho-P will be underestimated strongly when only sorption within 24 h is taken into account. Kinetic effects for sorption to soils are ascribed to

Table 3. Optimized parameter values of the Freundlich equation (Eq. [1]) for sorption of ortho-P by iron sludge for equilibrium times of 1, 3, 8, and 21 d.

Time	log K	n	R^2
d			
1	0.671	0.255	0.995
3	0.751	0.266	0.988
8	0.830	0.241	0.997
21	0.887	0.244	0.996

Table 4. Optimized parameter values for the kinetic Freundlich equation (Eq. [2]).

log(*a*)	*a*	*m*	*n*	R^2	se-y‡
0.68 (0.01)†	4.76	0.16 (0.01)	0.25 (0.01)	0.89	0.028

† Values in parentheses are SD.

‡ Standard error of the prediction

diffusion of P into particles, where more sorption sites become available (Barrow and Shaw, 1975; van Riemsdijk et al., 1984; Chardon and Blaauw, 1998; Koopmans et al., 2004a). For WTR, diffusion-controlled sorption was shown to be applicable (Makris et al., 2004; Dayton and Basta, 2005a).

Sorption Mechanism

For the three lowest additions of ortho-P ($C_i \leq 8$ mg L^{-1}), the pH in solution as measured after an equilibration time of 8 d increased with the level of added P but decreased at higher levels ($C_i \geq 16$ mg L^{-1}) (Fig. 2A). Ligand exchange can explain the rise in pH at the lower addition levels whereby OH^- is exchanged against $H_2PO_4^-$ (van Riemsdijk and Lyklema, 1980). A decrease in pH with increasing level of P addition was previously found, but not explained, by Cheung et al. (1994) for sorption of ortho-P by solid wastes like red mud, fly ash, and bottom ash. The pH decrease at higher C_i might be caused by an acidifying effect of the KH_2PO_4 solution that we used or by a reaction of P with the solid phase whereby protons are released to the solution. Possible reactions are (i) surface precipitation reactions of Ca-P compounds at higher surface coverage (Dzombak and Morel, 1990), (ii) formation of precipitates inside iron-hydroxide particles after diffusion of P into the particles (van Riemsdijk et al., 1984), and (iii) precipitation of a new mineral phase. The saturation indices calculated for various Ca-, Al-, and Fe-P minerals indicate oversaturation for hydroxyapatite at all levels of C_i and for other Ca-P minerals at higher levels of C_i (see Supplemental Table S4). However, the saturation indices continue to increase with an increasing level of ortho-P addition. Equilibrium with a new mineral phase was thus not attained. Also, the continuous increase in the ortho-P concentration in solution with the addition level conflicts with precipitation of a new mineral phase. Therefore, a combination of surface complexation and surface precipitation reactions is the most likely mechanism for P sorption by this iron sludge. However, evidence for a surface precipitation reaction can only be obtained with mineralogical techniques (Shenker and Bloom, 2005).

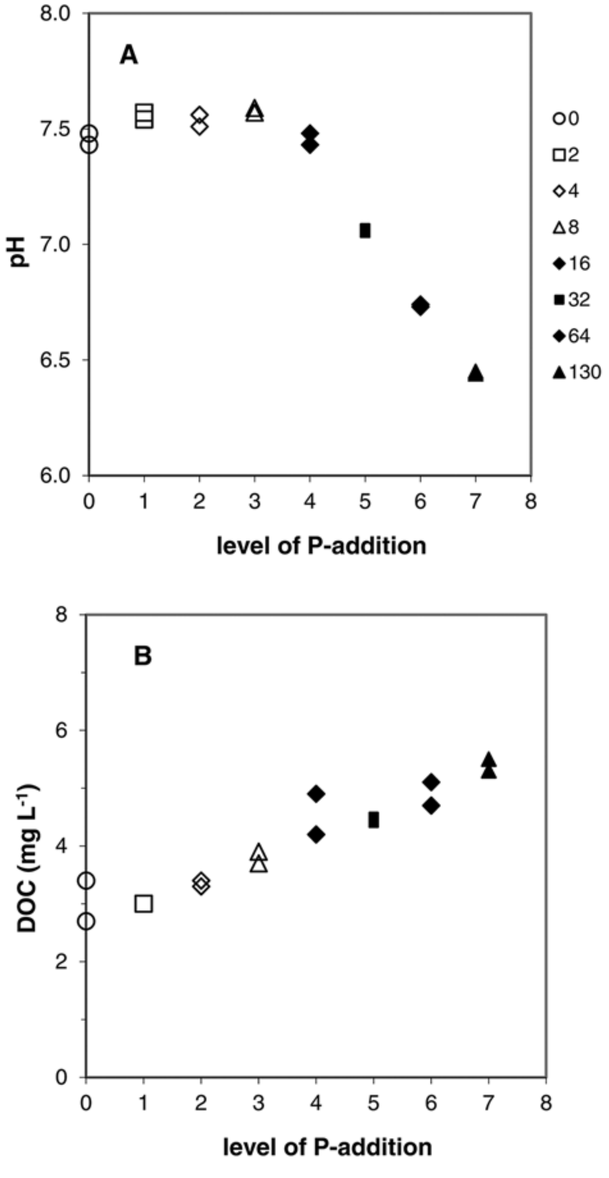

Fig. 2. The pH (A) and dissolved organic carbon (DOC) concentration (B) in the solutions of the batch study for the different levels of P addition (ranging from 0 to 130 mg ortho-P L^{-1}) after an equilibration period of 8 d. Duplicate values are shown in the figure.

Figure 2B shows an increase of the concentration of DOC with increasing P addition for the equilibration time of 8 d. The increase is likely due to a release of organic matter from the iron oxide surface, due to competition between ortho-P and DOC for sorption sites as shown for goethite (α-FeOOH) by Weng et al. (2008).

Column Study

The K_{sat} of iron-coated sand and four mixtures of iron sludge and acid-washed sand are plotted in Fig. 3, showing that K_{sat} decreased strongly when the fraction iron sludge increased. With 20% sludge, the mixture had a K_{sat} of 29 cm d^{-1}, which is lower than the value of 53 cm d^{-1} found for coarse sandy soils low in OM in The Netherlands (Wösten et al., 2001). The K_{sat} of iron-coated sand was 384 cm d^{-1}, which is much higher than the value for coarse sand. In The Netherlands, problems with P leaching mainly occur on coarse sandy soils. Very low values of K_{sat} (<30 cm d^{-1}) were also found by Cheung et al. (1994) for pure fly ash and bottom ash when tested as potential soil amendment. Our results suggest that when a mixture of iron sludge and sand is used in a P-reactive barrier, or when used as backfill material with tile drains, water transport in the soil could be hampered. Therefore, within the column experiment, only mixtures of 1, 5, or 10% iron sludge were used.

Breakthrough curves (BTCs) of ortho-P in the effluents of the columns are shown in Fig. 4A. For the columns filled with mixtures of iron sludge and acid-washed sand, the ortho-P concentration in the effluent increased rapidly with time from the beginning of the percolation. This in contrast to a symmetrical S-shaped BTC, which starts with a time period with very low effluent concentrations before the concentration starts to rise. Symmetrical S-shaped curves are typically found for systems

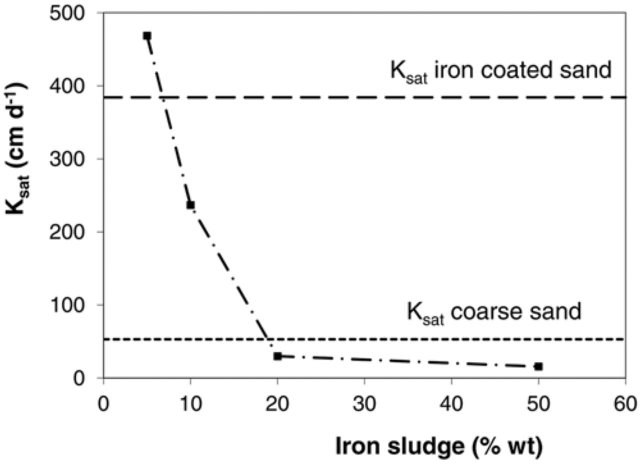

Fig. 3. Saturated hydraulic conductivity (*K*$_{sat}$) measured for different mixtures containing 5, 10, 20, and 50% iron sludge and 95, 90, 80, or 50% acid-washed sand and for iron-coated sand. For comparison, *K*$_{sat}$ is added, as calculated for coarse sandy soils in The Netherlands (Wösten et al., 2001).

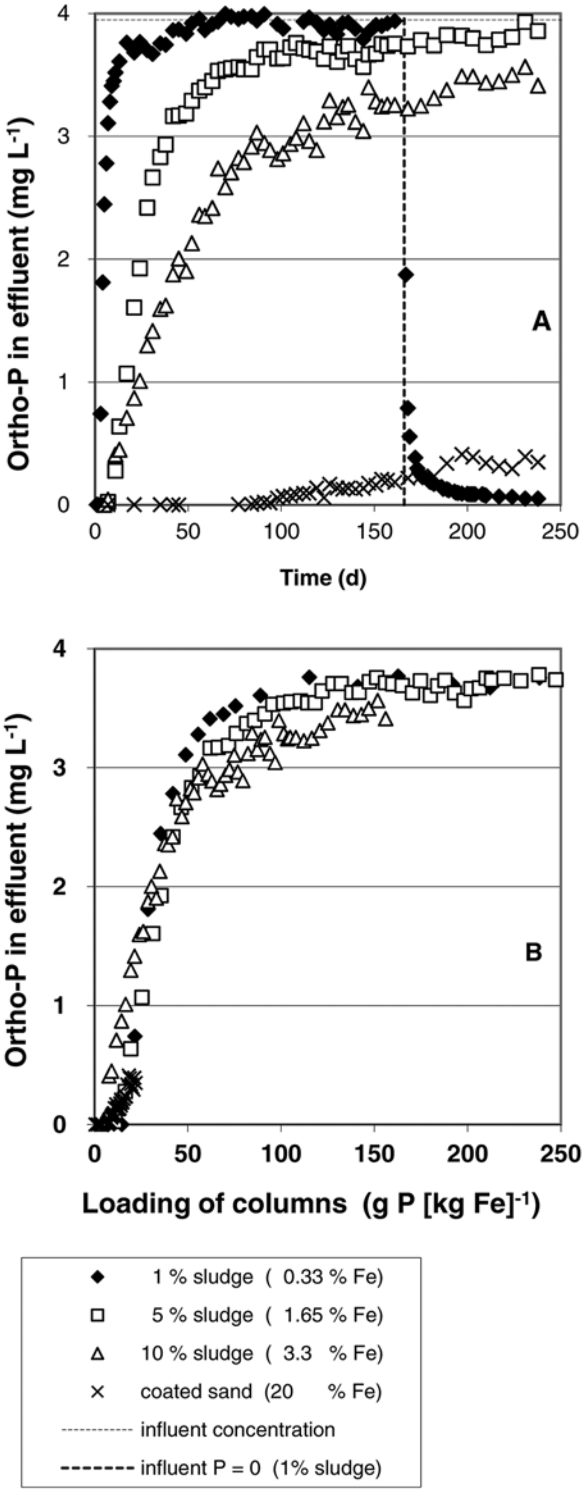

Fig. 4. Ortho-P concentrations measured in the effluent samples of columns filled with mixtures of iron sludge and acid-washed sand or with iron-coated sand (A). Ortho-P concentration in the influent was 3.95 mg L^{-1} (SD, 0.06). After 166 d, the column with 1% iron sludge received no more ortho-P in the influent during the final 72 d. (B) Ortho-P concentration in the effluent samples plotted against the loading of the columns with ortho-P per unit Fe in the column.

with fast reaction kinetics. Examples are the S-shaped BTCs found by Agyei et al. (2002) for fly ash, slag, and Portland cement, which showed a reaction time with P of less than 7 h in batch experiments. The lack of such an initial phase with low effluent concentrations for the BTCs of P in our iron sludge columns indicates slow sorption. Sperlich et al. (2005, 2008) found similar BTCs as in our study for As, ortho-P, salicylate, and DOC in columns filled with granulated ferric hydroxide; they attributed the asymmetry to slow intraparticle diffusion. We found a fast increase in the effluent concentrations up to approximately 70 to 90% of the influent concentration of 3.95 ± 0.06 mg L^{-1}, after which the increase leveled off. The point where the effluent concentration levels off tends to decrease to a lower effluent concentration with increasing amounts of iron sludge (to 3.8, 3.4, and 3.0 mg ortho-P L^{-1} for the columns with 1, 5, and 10% iron sludge, respectively).

For the column filled with iron-coated sand, the ortho-P concentration in the effluent increased gradually, and at the end of the experiment it reached only 10% (0.39 mg L^{-1}) of the influent concentration, probably caused by the much larger amount of Fe in the column as compared with the columns with 1, 5, and 10% iron sludge. The four columns contain 0.3, 1.7, 3.3, and 20% Fe (by weight) in total for the iron sludge–filled and iron-coated sand–filled columns, respectively. Figure 4A shows that the higher the total amount of Fe in the column, the slower the ortho-P concentration in the effluent increases with time. When we plotted the effluent data against the amount of P applied per unit Fe in the column, a more or less uniform BTC was found (Fig. 4B), indicating that a comparable, rate-limited sorption mechanism for P could be applicable for the iron sludge and iron-coated sand.

The pH of the effluent for all columns, including the iron-coated sand column, decreased with time (Supplemental Table S5). This could indicate surface complexation reactions at higher surface coverage, similar to the batch study. Also, the calculated saturation indices indicate oversaturation, especially for hydroxyapatite (Supplemental Table S5). However, the saturation indices were calculated for the effluent and thus refer to processes near the outlet of the column and may not be valid for the whole column. The DOC concentrations in the effluent of all columns decreased with time to levels below the detection limit, which can be ascribed to depletion of the sorbed DOC pool.

After 161 d of percolation, the column with 1% iron sludge seemed to be saturated with ortho-P because the concentration in the effluent was equal to the influent concentration for some period (Fig. 4A). By continuing percolation for another 72 d, but without ortho-P in the influent, we tested if P would desorb from the column. Figure 5 shows the ortho-P concentration in the effluent during the sorption and desorption periods plotted against the calculated amount of P bound by the iron sludge. The concentration in the effluent decreased sharply during the initial period of desorption and more gradually thereafter. The ortho-P concentration finally decreased by 99%, whereas the calculated sorbed amount of ortho-P decreased only by 37%. Hence, sorption of ortho-P to the iron sludge shows strong hysteresis because part of the sorbed P was not released. Previously, Makris et al. (2005a) found evidence for the long-term stability of P sorbed by Fe- and Al-WTR. Slow dissolution of Ca-P precipitates, if formed, may also contribute to the observed hysteresis in Fig. 5.

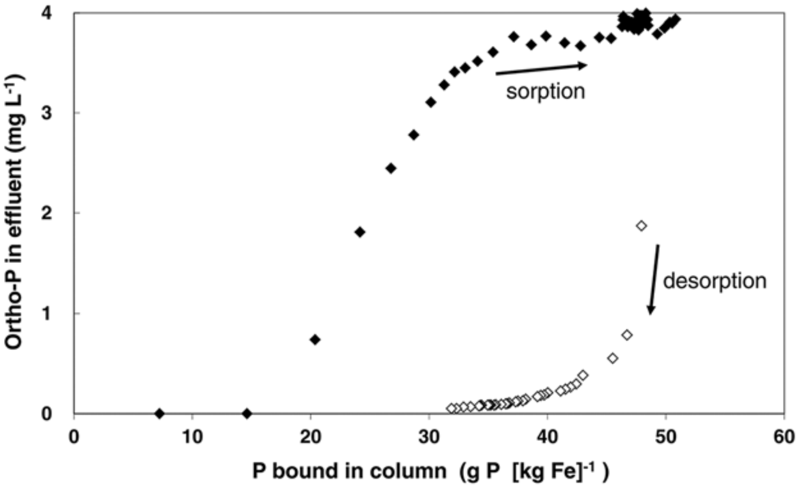

Fig. 5. Concentrations of ortho-P measured in the effluent samples of the column filled with a mixture of 1% iron sludge and 99% acid-washed sand plotted against the calculated amount of ortho-P bound in the column. The picture shows hysteresis during the desorption phase when the column received no more P in the influent. The effluent ortho-P concentration decreased with 99%, while P bound in the column decreased with 37%.

Distribution of Iron and Phosphorus within the Soil Columns

At the end of the column study, the material of each column was divided into layers of 1 cm to determine the total Fe and P contents in each layer. When comparing the Fe content of the layers within the columns with iron sludge, the Fe content increased toward the top of the columns. This is demonstrated in Fig. 6A, which shows for each layer the Fe content divided by the Fe content of the bottom layer. For the columns containing iron sludge, the ratio increases up to approximately 2 toward the top of the column but is rather constant (1.02 ± 0.03) for the column filled with iron-coated sand. Because the columns were percolated upward, Fe from the iron sludge must have been transported upward within the columns with iron sludge. However, the total Fe concentrations in all effluent samples were below the detection limit of the ICP–AES (i.e., 0.09 mg L^{-1}). Hence, transport within the column probably took place in colloidal forms that must have been retained by the filter paper at the top of the column. In a column study with fly ash, Ugurlu and Salman (1998) found high amounts of fly ash lost from their columns during the first 2 d of percolation. Thus, the stability of a filter or barrier filled with fine reactive materials should receive attention in practice. Within the column filled with iron-coated sand, no indication for transport was found, so the iron coating was strongly fixed on the sand grains.

The total P content in the columns with 1 or 5% iron sludge increased toward the top of the columns (Fig. 6B). For the column with 10% iron sludge, this was true for the lower five layers. Because the columns were percolated upward, one would expect a higher P content in the bottom layers, but this was clearly not the case. Therefore, we checked if the increase of the P content toward the top could have been related to the transport of Fe within the columns. A plot of the molar ratio P/Fe (Fig. 7) shows that transport is plausible: The column with 5% iron sludge has a constant ratio (0.121 ± 0.002) throughout the column and was saturated with P (Fig. 4A). The column with 10% iron sludge has a comparable P/Fe ratio below 3 cm (0.123 ± 0.005), but the ratio decreases further toward the top of the column because the column was not fully saturated with P (Fig. 4A). In the column with 1% iron sludge, the P/Fe ratio in the upper four layers was constant (0.089 ± 0.000), and the ratio decreased below to 0.078 in the bottom layer. For the 1% column, the influent contained no P during the last 72 d of the experiment, so one may expect that the ratio will be lowest at the bottom of the column. In the column with iron-coated sand, a steady decrease of the P/Fe ratio was found toward the top of the column, which can be expected because at the end of the experiment the column was still in the stage of loading with ortho-P from the bottom.

Kinetics of Phosphorus Sorption in the Column Study

We used the derived kinetic Freundlich equation (Eq. [2] and Table 4) to estimate the amount of P that accumulated at the inlet of the columns with iron sludge. When assuming that the ortho-P concentration in the bottom layers was constant during the whole experiment (238 d) at the level of the influent concentration (3.95 mg L^{-1}), a value for Q of 16.1 mg P g^{-1} iron sludge was calculated. Taking into account the uncertainty of the model, a 95% confidence interval (CI) was calculated based on the standard error of the prediction (Table 4) of $14.1 \le Q \le 18.2$ mg P g^{-1}. However, when the initial total P content of the iron sludge (2.6 g kg^{-1}) (Table 2) is added, the value for Q becomes 18.7 mg g^{-1} (95% CI, $16.7 \le Q \le 20.8$ mg P g^{-1}). Using the total Fe content of the iron sludge (329 g kg^{-1}) (Table 2), this Q value corresponds with a molar P/Fe ratio of 0.102 (95% CI, 0.092–0.114), which is only slightly lower than the ratio found experimentally for the iron sludge columns, which varied between 0.121 and 0.123. The calculated P/Fe ratio of 0.102 (95% CI, 0.092–0.114) also corresponds very well with the ratio of 0.098 found for the bottom layer of the column with iron-coated sand (Fig. 7). The kinetic Freundlich equation can thus be used to estimate the amount of P that can be bound by iron sludge when exposed during a long period to a constant concentration

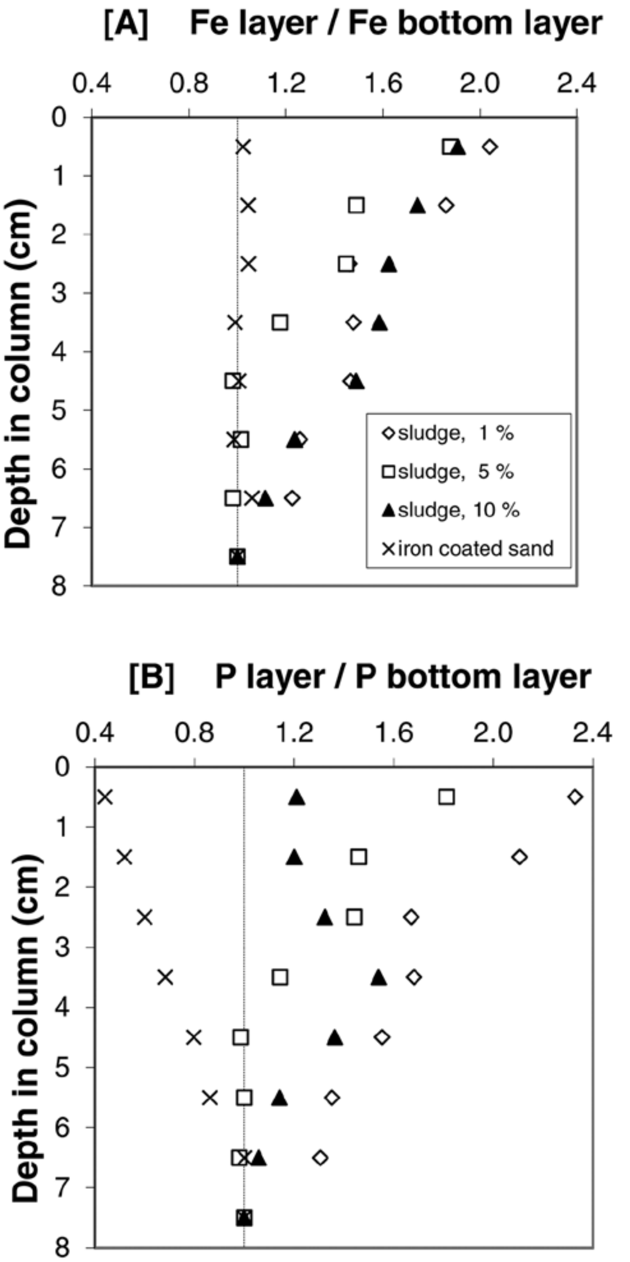

Fig. 6. Ratio of the total Fe content of different layers of the soil columns and the content in the bottom layer of the column at the end of the column experiment (A) and ratio of the total P content (B) as before for the total Fe content. The columns were percolated in an upward direction, meaning the layer between 7 and 8 cm is located at the inlet of the column and the layer between 0 and 1 cm is at the top of the column.

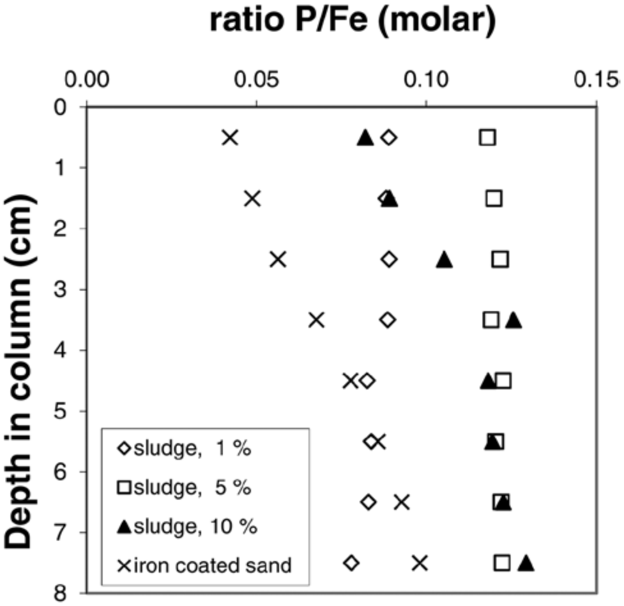

Fig. 7. Molar ratio of total P/total Fe for different layers of the soil columns at the end of the column experiment. The columns were percolated in an upward direction, meaning the layer between 7 and 8 cm is located at the inlet of the column and the layer between 0 and 1 cm is at the top of the column.

of ortho-P, even for much longer time periods (238 d) than for the batch experiments (21 d) on which the kinetic Freundlich equation was parameterized. It also stresses the need to take into account the sorption kinetics for ortho-P. Using Eq. [2] with m = 0.16 (Table 4), one can calculate that after 1 d only 42% is sorbed of the amount sorbed after 238 d (Q_1/Q_{238} = $[1/238]^{0.16}$ = 0.42) and that it takes 60 d to get 80% of the amount sorbed after 238 d. The kinetic Freundlich equation cannot be used to calculate ortho-P concentrations in the effluent of the columns (Fig. 4) because both the time of exposure and the concentration levels of ortho-P are not known for the various layers in the columns. This also limits the use of the kinetic Freundlich equation in practical applications, such as the design of filters and reactive barriers. For that specific purpose, a kinetic model is needed that can deal with a changing exposure concentration of ortho-P in solution, such as the kinetic model discussed by Koopmans et al. (2004a), which describes the kinetics of the diffusion of P from the surface to the inside of spherical aggregates. For the type of iron-rich material that we studied, sorption kinetics can thus play an important role in estimating the life-time of barriers and filters for ortho-P, and studies of the kinetics should preferably include long equilibration periods. Even though P sorption kinetics has been known to be important for soils since around 1935 (Wild, 1950 and references therein), kinetics often receives little attention when studying the P-binding behavior of reactive materials. For example, Cucarella and Renman (2009) reviewed 13 studies on methods for studying the P sorption capacity of reactive materials, but only two studies used a (single) equilibration time longer than 25 h. Unfortunately, studies on P sorption kinetics often cover only short periods (e.g., 30 min [Ugurlu and Salman, 1998], 4 h [Sibrell et al., 2009], or 8.3 h [Kostura et al., 2005]). Yet, Makris et al. (2004) studied P sorption on Al- and Fe-WTR up to 80 d, and Dayton and Basta (2005a) studied P sorption on Al-WTR during 19 d and recommended an equilibration time of 6 d for further studies.

Practical Aspects of Results

Iron sludge and iron-coated sand can bind large amounts of P when exposed to high concentrations of ortho-P for a prolonged period. Iron-coated sand has the advantage of a high total Fe content and thus has a large sorptive capacity per unit volume. Its high K_{sat} makes it possible to use it in barriers or filters in coarse sandy soils. Currently, we are testing iron-coated sand in a barrier along a ditch and around a tile drain in the west of The Netherlands. Water flowing from a field to a ditch will occur concentrated through the wall between field and ditch, through the surface of drain pipes, or at the end of the pipes. On these places, flow velocity will be much higher than elsewhere in the soil profile. The velocity used in our column experiment (60 cm d^{-1}) equals the velocity that can be expected under field conditions in sandy soils. The slow reaction kinetics of the P binding to iron sludge, therefore, limits its use in practice. The column experiments with iron sludge showed that concentrations of ortho-P in the effluents increased sharply to environmentally unwanted levels, although there was still a large capacity to bind P. Only at high Fe contents in the column can the effluent concentration be kept sufficiently low, as demonstrated with the iron-coated sand. The low value of K_{sat} of iron sludge (17 cm d^{-1}), even when mixed with 50% sand (Fig. 3), necessitates further reducing the sludge/sand ratio before the mixture is applicable in a filter or barrier for P retention. Thus, when used in pure form in a filter, iron sludge can only be used at a very low hydraulic loading rate. Although a low to medium value of K_{sat} has the advantage of a longer contact time between water and the adsorbent (Cheung et al., 1994), this also has the risk of creating a preferential flow path that reduces functioning of filter systems (Dobbie et al., 2009; Kirkkala et al., 2011). Displacement of the adsorbent within the filter, as found for iron sludge in our column study, may contribute to the creation of preferential flow paths and should receive attention in practice. In our study, freeze-dried sludge was used, so mixing was not a problem for the column study. However, when the dewatered iron sludge was delivered, it still had a water content of 550 g kg^{-1} and a clay-like structure with large clumps, which would severely hamper mixing in practice. When the aspect of mixing iron sludge is solved, it could be used for immobilizing P in enriched topsoils or in animal manure, applications frequently studied for WTR (Ippolito et al., 2011).

Granulation or pelletizing the iron sludge could increase its low hydraulic conductivity, making application in filters or barriers possible. Examples of materials used for granulation are ferric hydroxide (Genz et al., 2004; Sperlich et al., 2008) and acid mine drainage sludge (Dobbie et al., 2009; Sibrell et al., 2009). However, drying and further processing of sludges can be expensive, which makes the end product costly.

Acknowledgments

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References

Agyei, N.M., C.A. Strydom, and J.H. Potgieter. 2002. The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends. Cement Concr. Res. 32:1889–1897. doi:10.1016/S0008-8846(02)00888-8

Agyin-Birikorang, S., G.A. O'Connor, L.W. Jacobs, K.C. Makris, and S.R. Brinton. 2007. Long-term phosphorus immobilization by a drinking water treatment residual. J. Environ. Qual. 36:316–323. doi:10.2134/jeq2006.0162

Barrow, N.J., and T.C. Shaw. 1975. The slow reactions between soil and anions: 2. Effect of time and temperature on the decrease in phosphate concentration in the soil solution. Soil Sci. 119:167–177. doi:10.1097/00010694-197502000-00010

Braskerud, B.C., K.S. Tonderski, B. Wedding, R. Bakke, A.-G.B. Blankenberg, B. Ulén, and J. Koskiaho. 2005. Can constructed wetlands reduce the diffuse phosphorus loads to eutrophic water in cold temperate regions? J. Environ. Qual. 34:2145–2155. doi:10.2134/jeq2004.0466

Chardon, W.J., and D. Blaauw. 1998. Kinetic Freundlich equation applied to soils with a high residual phosphorus content. Soil Sci. 163:30–35. doi:10.1097/00010694-199801000-00005

Chardon, W.J., and O.F. Schoumans. 2007. Soil texture effects on the transport of phosphorus from agricultural land in river deltas of Northern Belgium, The Netherlands and North-West Germany. Soil Use Manage. 23(suppl. 1):16–24. doi:10.1111/j.1475-2743.2007.00108.x

Chardon, W.J., O. Oenema, O.F. Schoumans, P.C.M. Boers, B. Fraters, and Y.C.W.M. Geelen. 1996. Survey of possibilities for management and recovery of phosphorus leaking soils (In Dutch.) Rep. 8. Dutch Integrated Soil Research Program, Wageningen, the Netherlands.

Cheung, K.C., and T.H. Venkitachalam. 2006. Kinetic studies on phosphorus sorption by selected soil amendments for septic tank effluent renovation. Environ. Geochem. Health 28:121–131. doi:10.1007/s10653-005-9021-1

Cheung, K.C., T.H. Venkitachalam, and W.D. Scott. 1994. Selecting soil amendment materials for removal of phosphorus. Water Sci. Technol. 30(6):247–256.

Cucarella, V., and G. Renman. 2009. Phosphorus sorption capacity of filter materials used for on-site wastewater treatment determined in batch experiments: A comparative study. J. Environ. Qual. 38:381–392. doi:10.2134/jeq2008.0192

Dayton, E.A., and N.T. Basta. 2005a. A method for determining the phosphorus sorption capacity and amorphous aluminum of aluminum-based water treatment residuals. J. Environ. Qual. 34:1112–1118. doi:10.2134/jeq2004.0230

Dayton, E.A., and N.T. Basta. 2005b. Use of drinking water treatment residuals as a potential best management practice to reduce phosphorus risk index scores. J. Environ. Qual. 34:2112–2117. doi:10.2134/jeq2005.0083

Dobbie, K.E., K.V. Heal, J. Aumonier, K.A. Smith, A. Johnston, and P.L. Younger. 2009. Evaluation of iron ochre from mine drainage treatment for removal of phosphorus from wastewater. Chemosphere 75:795–800. doi:10.1016/j.chemosphere.2008.12.049

Douglas, G.B., M.S. Robb, D.N. Coad, and P.W. Ford. 2004. A review of solid phase adsorbents for the removal of phosphorus from natural and waste waters. p. 291–320. *In* E. Valsami-Jones (ed.) Phosphorus in environmental technologies: Principles and applications. IWA Publishing, London.

Drizo, A., Y. Comeau, C. Forget, and R.P. Chapuis. 2002. Phosphorus saturation potential: A parameter for estimating the longevity of constructed wetland systems. Environ. Sci. Technol. 36:4642–4648. doi:10.1021/es011502v

Dzombak, D.A., and F.M.M. Morel. 1990. Surface complexation modeling: Hydrous ferric oxide. John Wiley & Sons, New York.

Elliott, H.A., G.A. O'Connor, P. Lu, and S. Brinton. 2002. Influence of water treatment residuals on phosphorus solubility and leaching. J. Environ. Qual. 31:1362–1369. doi:10.2134/jeq2002.1362

Endo, S., P. Grathwohl, S.B. Haderlein, and T.C. Schmidt. 2009. Characterization of sorbent properties of soil organic matter and carbonaceous geosorbents using n-alkanes and cycloalkanes as molecular probes. Environ. Sci. Technol. 43:393–400. doi:10.1021/es802277n

Fenton, O., M.G. Healy, M. Rodgers, and D.O. Huallachain. 2009. Site-specific P absorbency of ochre from acid mine-drainage near an abandoned Cu-S mine in the Avoca-Avonmore catchment, Ireland. Clay Miner. 44:113–123. doi:10.1180/claymin.2009.044.1.113

Genz, A., A. Kornmuller, and M. Jekel. 2004. Advanced phosphorus removal from membrane filtrates by adsorption on activated aluminium oxide and granulated ferric hydroxide. Water Res. 38:3523–3530. doi:10.1016/j.watres.2004.06.006

Groenenberg, J.E., G.F. Koopmans, and R.N.J. Comans. 2010a. Uncertainty analyses of the Nonideal Competitive Adsorption-Donnan Model: Effects of dissolved organic matter variability on predicted metal speciation in soil solution. Environ. Sci. Technol. 44:1340–1346. doi:10.1021/es902615w

Groenenberg, J.E., P.F.A.M. Römkens, R.N.J. Comans, J. Luster, T. Pampura, L. Shotbolt, E. Tipping, and W. de Vries. 2010b. Transfer functions for solid solution partitioning of cadmium, copper, nickel, lead and zinc in soils: Derivation of relations for free metal ion activities and validation on independent data. Eur. J. Soil Sci. 61:58–73. doi:10.1111/j.1365-2389.2009.01201.x

Guo, H., D. Stüben, Z. Berner, and Q. Yu. 2009. Characteristics of arsenic adsorption from aqueous solution: Effect of arsenic species and natural adsorbents. Appl. Geochem. 24:657–663. doi:10.1016/j.apgeochem.2008.12.017

Gustafsson, J.P., A. Renman, G. Renman, and P. Poll. 2008. Phosphate removal by mineral-based sorbents used in filters for small-scale wastewater treatment. Water Res. 42:189–197. doi:10.1016/j.watres.2007.06.058

Houba, V.J.G., E.J.M. Temminghoff, G.A. Gaikhorst, and W. van Vark.

2000. Soil analysis procedures using 0.01 *M* calcium chloride as extraction reagent. Commun. Soil Sci. Plant Anal. 31:1299–1396. doi:10.1080/00103620009370514

Houba, V.J.G., J.J.G. van der Lee, and I. Novozamsky. 1997. Soil and plant analysis. Part 1: Soil analysis procedures. Wageningen Univ., Wageningen, the Netherlands.

Ippolito, J.A., K.A. Barbarick, and H.A. Elliott. 2011. Drinking water treatment residuals: A review of recent uses. J. Environ. Qual. 40:1–12. doi:10.2134/jeq2010.0242

Kinniburgh, D.G., W.H. van Riemsdijk, L.K. Koopal, M. Borkovec, M.F. Benedetti, and M.J. Avena. 1999. Ion binding to natural organic matter: Competition, heterogeneity, stoichiometry and thermodynamic consistency. Colloids Surf. A 151:147–166. doi:10.1016/S0927-7757(98)00637-2

Kirkkala, T., A.-M. Ventelä, and M. Tarvainen. 2011. Long-term field-scale experiment on using lime filters in an agricultural catchment. J. Environ. Qual. (in press). doi:10.2134/jeq2010.0429.

Koopmans, G.F., W.J. Chardon, P. de Willigen, and W.H. van Riemsdijk. 2004a. Phosphorus desorption dynamics in soil and the link to a dynamic concept of bioavailability. J. Environ. Qual. 33:1393–1402. doi:10.2134/jeq2004.1393

Koopmans, G.F., W.J. Chardon, P.A.I. Ehlert, J. Dolfing, R.A.A. Suurs, O. Oenema, and W.H. van Riemsdijk. 2004b. Phosphorus availability for plant uptake in a phosphorus-enriched noncalcareous sandy soil. J. Environ. Qual. 33:965–975. doi:10.2134/jeq2004.0965

Koopmans, G.F., W.J. Chardon, and R.W. McDowell. 2007. Phosphorus movement and speciation in a sandy soil profile after long-term animal manure applications. J. Environ. Qual. 36:305–315. doi:10.2134/jeq2006.0131

Kostura, B., H. Kulveitova, and J. Lesko. 2005. Blast furnace slags as sorbents of phosphate from water solutions. Water Res. 39:1795–1802. doi:10.1016/j.watres.2005.03.010

Kronvang, B., M. Bechmann, H. Lundekvam, H. Behrendt, G.H. Rubæk, O.F. Schoumans, N. Syversen, H.E. Andersen, and C.C. Hoffmann. 2005. Phosphorus losses from agricultural areas in river basins: Effects and uncertainties of targeted mitigation measures. J. Environ. Qual. 34:2129–2144. doi:10.2134/jeq2004.0439

Lamé, F.P.J., D.J. Brus, R.H. Nieuwenhuis, G.B. Derksen, and M.E. van Vliet. 2004. Background values 2000. (In Dutch.) Report NITG 04-242-A. TNO, Utrecht, the Netherlands.

Lindberg, J., J. Sterneland, P.O. Johansson, and J.P. Gustafsson. 1997. Spodic material for in situ treatment of arsenic in ground water. Ground Water Monit. Rem. 17:125–130. doi:10.1111/j.1745-6592.1997.tb01272.x

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

Makris, K.C., W.G. Harris, G.A. O'Connor, and T.A. Obreza. 2004. Phosphorus immobilization in micropores of drinking-water treatment residuals: Implications for long-term stability. Environ. Sci. Technol. 38:6590–6596. doi:10.1021/es049161j

Makris, K.C., W.G. Harris, G.A. O'Connor, and T.A. Obreza. 2005a. Long-term phosphorus effects on evolving physicochemical properties of iron and aluminum hydroxides. J. Colloid Interface Sci. 287:552–560. doi:10.1016/j.jcis.2005.02.011

Makris, K.C., W.G. Harris, G.A. O'Connor, T.A. Obreza, and H.A. Elliott. 2005b. Physicochemical properties related to long-term phosphorus retention by drinking-water treatment residuals. Environ. Sci. Technol. 39:4280–4289. doi:10.1021/es0480769

McCollum, R.E. 1991. Buildup and decline in soil phosphorus: 30-year trends on a Typic Umprabuult. Agron. J. 83:77–85. doi:10.2134/agronj1991.00021962008300010019x

McDowell, R.W., A.N. Sharpley, and W. Bourke. 2008. Treatment of drainage water with industrial by-products to prevent phosphorus loss from tile-drained land. J. Environ. Qual. 37:1575–1582. doi:10.2134/jeq2007.0454

Meeussen, J.C.L. 2003. ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models. Environ. Sci. Technol. 37:1175–1182. doi:10.1021/es025597s

Milne, C.J., D.G. Kinniburgh, W.H. van Riemsdijk, and E. Tipping. 2003. Generic NICA-Donnan model parameters for metal-ion binding by humic substances. Environ. Sci. Technol. 37:958–971. doi:10.1021/es0258879

Moore, P.A., Jr., and D.R. Edwards. 2005. Long-term effects of poultry litter, alum-treated litter, and ammonium nitrate on aluminum availability in soils. J. Environ. Qual. 34:2104–2111. doi:10.2134/jeq2004.0472

Postma, D., C. Boesen, H. Kristiansen, and F. Larsen. 1991. Nitrate reduction in an unconfined sandy aquifer: Water chemistry, reduction processes, and geochemical modeling. Water Resour. Res. 27:2027–2045. doi:10.1029/91WR00989

Redding, M.R., B. Welten, and M. Kear. 2008. Enhancing the P trapping of pasture filter strips: Successes and pitfalls in the use of water supply residue and polyacrylamide. Eur. J. Soil Sci. 59:257–264. doi:10.1111/j.1365-2389.2007.00990.x

Reijneveld, J.A., P.A.I. Ehlert, A.J. Termorshuizen, and O. Oenema. 2010. Changes in the soil phosphorus status of agricultural land in the Netherlands during the 20th century. Soil Use Manage. 26:399–411. doi:10.1111/j.1475-2743.2010.00290.x

Robertson, W.D., and J.A. Cherry. 1995. In-situ denitrification of septic-system nitrate using reactive porous-media barriers: Field trials. Ground Water 33:99–111. doi:10.1111/j.1745-6584.1995.tb00266.x

Saulys, V., and N. Bastiene. 2007. The impact of lime admixture into trench backfill on the variation of phosphorus in drainage outflow. Irrig. Drain. 56:99–105. doi:10.1002/ird.288

Scheidegger, A., M. Borkovec, and H. Sticher. 1993. Coating of silica sand with goethite: Preparation and analytical identification. Geoderma 58:43–65. doi:10.1016/0016-7061(93)90084-X

Schwertmann, U., and R.M. Cornell. 1991. Iron oxides in the laboratory. VCH, Weinheim, Germany.

Sharpley, A.N., S.C. Chapra, R. Wedepohl, J.T. Sims, T.C. Daniel, and K.R. Reddy. 1994. Managing agricultural phosphorus for protection of surface waters: Issues and options. J. Environ. Qual. 23:437–451. doi:10.2134/jeq1994.00472425002300030006x

Shenker, M., and P.M. Bloom. 2005. Comments on "Amounts, forms, and solubility of phosphorus in soils receiving manure." Soil Sci. Soc. Am. J. 69:1353–1354. doi:10.2136/sssaj2005.0077

Shilton, A.N., I. Elmetri, A. Drizo, S. Pratt, R.G. Haverkamp, and S.C. Bilby. 2006. Phosphorus removal by an 'active' slag filter: A decade of full scale experience. Water Res. 40:113–118. doi:10.1016/j.watres.2005.11.002

Sibrell, P.L., G.A. Montgomery, K.L. Ritenour, and T.W. Tucker. 2009. Removal of phosphorus from agricultural wastewaters using adsorption media prepared from acid mine drainage sludge. Water Res. 43:2240–2250. doi:10.1016/j.watres.2009.02.010

Sims, J.T., R.R. Simard, and B.C. Joern. 1998. Phosphorus loss in agricultural drainage: Historical perspective and current research. J. Environ. Qual. 27:277–293. doi:10.2134/jeq1998.00472425002700020006x

Sperlich, A., S. Schimmelpfennig, B. Baumgarten, A. Genz, G. Amy, E. Worch, and M. Jekel. 2008. Predicting anion breakthrough in granular ferric hydroxide (GFH) adsorption filters. Water Res. 42:2073–2082. doi:10.1016/j.watres.2007.12.019

Sperlich, A., A. Werner, A. Genz, G. Amy, E. Worch, and M. Jekel. 2005. Breakthrough behavior of granular ferric hydroxide (GFH) fixed-bed adsorption filters: Modeling and experimental approaches. Water Res. 39:1190–1198. doi:10.1016/j.watres.2004.12.032

Tamura, H., S. Kawamura, and M. Hagayama. 1980. Acceleration of the oxidation of Fe^{2+} ions by Fe(III)-oxyhydroxides. Corros. Sci. 20:963–971. doi:10.1016/0010-938X(80)90077-3

Ugurlu, A., and B. Salman. 1998. Phosphorus removal by fly ash. Environ. Int. 24:911–918. doi:10.1016/S0160-4120(98)00079-8

van der Salm, C., W.J. Chardon, P.A.I. Ehlert, G.F. Koopmans, and J.C. van Middelkoop. 2009. Phyto-extraction of phosphorus-enriched grassland soils. J. Environ. Qual. 38:751–761. doi:10.2134/jeq2008.0068

van Riemsdijk, W.H., L.J.M. Boumans, and F.A.M. de Haan. 1984. Phosphate sorption by soils: I. A model for phosphate reaction with metal-oxides in soil. Soil Sci. Soc. Am. J. 48:537–541. doi:10.2136/sssaj1984.03615995004800030013x

van Riemsdijk, W.H., and J. Lyklema. 1980. The reaction of phosphate with aluminumhydroxide in relation with phosphate bonding in soils. Colloids Surf. 1:33–44. doi:10.1016/0166-6622(80)80036-9

Weng, L.P., W.H. van Riemsdijk, and T. Hiemstra. 2008. Humic nanoparticles at the oxide-water interface: Interactions with phosphate ion adsorption. Environ. Sci. Technol. 42:8747–8752. doi:10.1021/es801631d

Wild, A. 1950. The retention of phosphate by soil: A review. J. Soil Sci. 1:221–238. doi:10.1111/j.1365-2389.1950.tb00734.x

Withers, P.J.A., and S.C. Jarvis. 1998. Mitigation options for diffuse phosphorus loss to water. Soil Use Manage. 14:186–192. doi:10.1111/j.1475-2743.1998.tb00638.x

Wolthoorn, A., E.J.M. Temminghoff, and W.H. van Riemsdijk. 2004. Colloid formation in groundwater by subsurface aeration: Characterisation of the geo-colloids and their counterparts. Appl. Geochem. 19:1391–1402. doi:10.1016/j.apgeochem.2004.01.023

Wösten, J.H.M., G.J. Veerman, W.J.M. de Groot, and J. Stolte. 2001. Water retention and hydraulic conductivity characteristics of topsoils and subsoils in the Netherlands: The Staringreeks. (In Dutch.) Rep. 153. Alterra, Wageningen, the Netherlands.

Zolla, V., F.S. Freyria, R. Sethi, and A. Di Molfetta. 2009. Hydrogeochemical and biological processes affecting the long-term performance of an iron-based permeable reactive barrier. J. Environ. Qual. 38:897–908. doi:10.2134/jeq2007.0622