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Ca–Fe oxide granules as potential phosphate barrier material for critical source areas: a laboratory study of P retention and release

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Phosphate barriers may mitigate dissolved P losses from critical source areas. We studied P retention of industrially produced Ca–Fe oxide as potential P barrier material. In batch tests with 1 mg l^{-1} P solution, P retention was 85% efficient in 5 min. In a flow-through system, the granules' phpsphate-retention capacity was 6–7 mg g^{-1}, being largely unaffected by pre-leaching. Phosphate release from P-saturated granules was pH-dependant and suggested P association with Fe oxides, and as Ca-phosphate precipitates. In a sequential extraction of P-saturated granules, about 25% of retained P was released, whereas a separate anaerobic incubation resulted in negligible release of P. Immersion of unleached, P-saturated granules for 16 days in a low-P–concentration lake resulted in more than 80% Ca loss, but no loss of metals, and about 25% loss of P accumulated earlier in granules. These granules are promising for P retention and merit a field-scale study.

Key words: Fe oxides, phosphorus, eutrophication, best technologies, permeable reactive barriers

Introduction

Of the Finnish coastal sea areas, the Archipelago Sea (SW Finland) is especially affected by nutrient losses from agriculture. From an outer Archipelago Sea monitoring station, Bonsdorff et al. (1997) reported an average annual 0.5 µg l^{-1} increase in wintertime total P concentration in the productive water layer during 1968–1993. They also referred to other studies that showed decreasing trends in N:P ratio, transparency, and oxygen concentrations, all indicating a decline in quality of the coastal waters of the northern Baltic Sea. However, according to a recent ecosystem modelling study by Pitkänen et al. (2007), a 30–40% reduction in N and P loads would significantly decrease the algal biomasses of the Archipelago Sea in 5 years. A break in the undesired trends, with a visible improvement in water quality of this agriculturally affected sea area, could thus be possible at a surprisingly rapid pace with effective nutrient loss abatement from agricultural sources. A 30–40% reduction in P losses in a few years, however, calls for novel, more effective measures to complement the water protection operations currently supported in the Finnish Agri-Environmental Programme.

Omitting unnecessary P inputs to agricultural soils is naturally required for developing sustainable ways to control P losses and for ensuring that P mitigation is most cost effective (e.g. McDowell and Nash 2012). However, if a soil already has a high P content, years may be required for the concentration to decrease so that P losses decline to acceptably low levels. Until the changes in nutrient management translate into lower nutrient losses additional methods are needed to intercept P along the pathway from the source to the watercourse. Efficient methods are also needed for coping with critical source areas (e.g. feedlots). Intercepting P outside field borders or in drainage trench backfills has the advantage of not complicating agricultural operations and not posing risks for adverse effects on plant growth or animal health.

Treatment of agricultural runoff water has been performed experimentally at a small scale in Finland; as an example, P-stripping chemicals, such as ferric sulphate, have been effective in decreasing soluble P losses from horse exercise yards (Närvänen et al. 2008). However, application of chemical precipitants to water requires regular care, e.g. filling up chemical storage, maintenance of the equipment, and possibly removal of precipitates/sludge. An alternative method, permeable reactive barriers, adopts a concept that is familiar from remediation of contaminated ground water. Such barriers would include solid P sorbing materials applied in relatively modest quantities, the quantity depending on the P sorption capacity of the material, size of the drainage area, and P loading of the barrier. The material used for P retention would then be, in intervals of a few years, replaced by a fresh propor-

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tion after the P retention capacity of the sorbent is exhausted. Reactive barriers for treating agricultural runoff are thus far largely untested in Finland (but see Kirkkala et al. 2012a, 2012b).

Phosphate retention materials have been studied since the 1960s (e.g. Yee 1966, Shiao and Akashi 1977), and field-scale experiments have been performed in several countries (see the review of Klimeski et al. 2012 in this issue). Most of the studies have been performed with wastewater but also increasingly on agricultural runoff and drainage waters in recent years. In New Zealand, McDowell et al. (2008) studied the effects of steel slag applied as backfill of subsurface drainage trenches and reported decreases as high as 70% in drainflow dissolved reactive P (DRP) concentrations on a site with P-enriched topsoil. Averages during their 2-year study were 0.33 mg l^{-1} for the flow from control drains with soil backfill and 0.09 mg l^{-1} for the flow from drains with slag backfill. In another study, McDowell et al. (2007) applied a steel slag mixture enclosed in a mesh tubing fabric (P-socks) to a section of a stream draining an agricultural catchment and calculated reductions in downstream transports of 44% for DRP and 10% for total P during a 6-month period. The authors suggested that the greatest benefit with these P-socks would be obtained in small and slow flows in proximity to critical source areas.

Penn et al. (2007) mitigated a distinct hotspot of P loss by a barrier made of Fe-rich mine drainage residual. Water to their barrier drained from an area with excessive soil test P levels, and in ditchwater, DRP concentrations exceeded several (up to 16) milligrams per litre. During a single 300-mm storm event, the P barrier retained 0.5 kg of P, removing virtually all of the dissolved P that passed through it. The structure, however, could take only a part of the flow, and the authors suspected that the P removal efficiency would realistically be less than 50% because all storm event runoffs could not be directed through the barrier. Even though all of the P cannot be retained, a 40–50% reduction in DRP loss is impressive when compared to any of the traditional water protection measures.

Also, several other types of materials have been studied as potential P sorbents (see, e.g. Drizo et al. 2006, Cucarella and Renman 2009, Ballantine and Tanner 2010). In addition to by-products of industrial processes and mining operations, products that are specifically tailored or modified for the purpose have also been presented (e.g. Ádám et al. 2007, McDowell et al. 2007). Waste materials provide a cheap alternative whereas the cost-efficiency of more expensive tailored products depends on their efficiency in P retention relative to that of other available materials, or alternative ways to reach the target for P load mitigation. A higher initial price may be justified by a longer effective life-time, higher P retention ability under fluctuating environmental conditions, lower maintenance costs, or the ease of recycling of the P collected by the material.

In the present laboratory test series, we examined the P binding ability of industrially produced Ca–Fe oxide granules. Phosphate retention was tested in flow-through columns, and the tests were done for fresh and pre-leached batches of the granules. The tests on the release of previously retained P were made on P-saturated granules containing 6–7 mg g^{-1} P and included extractions in water with variable pH, a sequential extraction that included a low-redox step, a 308-day anaerobic incubation, and an incubation in a lake with low P concentration (below 5 µg l^{-1}).

Material and methods

The Ca–Fe granules studied are co-products of titanium dioxide pigment and associated ferrous sulphate production at the plant of Sachtleben Pigments Oy in Pori, Western Finland. In brief, the granules are made by mixing acidic ferrous sulphate, calcium oxide, and water in a granulator. The end product is 70% gypsum (CaSO$_4$×2 H$_2$O) with about 10% Fe and has a pH$_w$ value of 9–11 (1:2.5 vol/vol), indicating the presence of Ca(OH)$_2$. Volume weight is about 1.5 kg dm^{-3}. The price at plant-gate is estimated to be about 100–150 € per Mg (metric tonne), and annual production of about 150 × 10^6 kg is possible.

The content of potentially harmful elements is below the guideline concentrations for soil amendment materials (including liming agents such as fly ash), as well as the permissible concentrations in fertilizer products, except for total Cr (Table 1). As for Cr, there is an alternative limit that takes into account the toxic water-soluble form, Cr(VI) (see footnotes of Table 1). Solubility of Cr was assessed in this work with findings presented in the results section.

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Table 1. Element concentrations in Ca–Fe oxide granules, given as the range of six replicates, and the permissible limits for soil amendments and fertilizer products (MMM 2009).

Element	Ca–Fe oxide granules	Highest permissible concentrations	
		Soil amendments	Fertilizer products
Ca, g kg^{-1}	140–198	NA[a]	NA
Fe, g kg^{-1}	74–86	NA	NA
Al, g kg^{-1}	4.2–5.0	NA	NA
Mn, g kg^{-1}	3.4–4.0	NA	NA
Cr, mg kg^{-1}	710–810	NA	300[b]
Zn, mg kg^{-1}	191–214	1500	1500
Ni, mg kg^{-1}	40–44	100	100
Pb, mg kg^{-1}	7.6–12.8	150	100
Cu, mg kg^{-1}	1.6–5.2	600	600
Cd, mg kg^{-1}	0.03–0.11	3.0	1.5
Hg, mg kg^{-1}	<0.5	2.0	1.0

[a] NA = not applicable
[b] For Cr, an alternative limit is less than 2 mg kg^{-1} for Cr(VI) (in soluble form).

Granule size varies, but usually 90% of the mass consists of particles greater than 1 mm. As an example, granule size distribution for a 30 Mg batch produced in January 2010 was as follows: 32% above 6 mm, 46% 2–6 mm, 12% 1–2 mm, 5% 0.6–1 mm, 3% 0.2–0.59 mm, and 2% below 0.2 mm. Water content of these granules was 22–28%. A sieve that can be used later in the production line allows selection of granule size distribution for different applications. Granules used in the laboratory tests were sieved to a 2–5-mm size fraction.

For P analyses in the test series, phosphate concentrations were measured using the molybdate blue method of Murphy and Riley (1962). The instruments used in measuring P were a LaChat (Wisconsin, MI, USA) flow injection analyser for all other tests except for the incubation of P-saturated granules in a reduced environment, which was done with a Shimadzu (Tokyo, Japan) UV-1601 spectrophotometer.

Phosphate retention tests

Batch test with variable contact time

Two grams of the granules were weighed into centrifuge tubes, 50 ml of stock P solutions (1 or 10 mg l^{-1}) was added, and the samples were shaken on an orbital shaker at 120 rpm. Single tubes were removed from the shaker after 5, 15, and 45 min, and 2, 4, 8, and 16 h, and the solution was passed through a 0.2 µm Nuclepore filter and analysed for molybdate-reactive P. Seven-point unreplicated retention curves were fitted for the two solution P concentrations.

Retention of P in flow-through columns

The P retention capacity was tested in conditions that resemble the physical settings of reactive barriers and using both unleached (out-of-the-pile) and pre-leached granules. Pre-leaching was motivated by the fact that when granules are in flowing water, soluble compounds (with e.g. Ca^{2+}) will gradually dissolve and leave the barrier, possibly affecting P retention. For pre-leaching, 300 g of granules was enclosed in a nylon netting bag with 300 µm openings and put in a 7-l bucket containing about 5 l of tap water. During the following 6 weeks, the water was changed every couple of days until no changes in electrical conductivity readings were measured after water change. At that point, the bag was lifted from the bucket and left to air-dry for about a week, the remaining mass was weighed, and the total (Aqua Regia-soluble) concentrations of Al, Fe, Ca, K, Cd, Cr, and Pb were determined (Thermo Jarrel Ash, Franklin, MA, USA, inductively coupled plasma–atomic emission spectrometer, ICP-AES).

The flow-through tests were done with a SampleTech (Science Hill, KY, USA) vacuum extractor. The extractor consists of two attached reservoirs and a collector syringe that generates suction on the reservoirs. The upper reservoir is for extractant or other feed solution, and the lower one contains the sample on a filter plate. As suction

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is generated, the feed solution from the upper reservoir drips onto the sample and through it to the collector syringe. It is possible to set the maximum speed of a 50 ml (max volume) pulse to 30 min, and a pre-test with 30, 60, 120, and 240 min pulse speeds showed that the shortest contact time would be enough to decrease P concentration by about 50% when the feed P solution contained 50 mg l^{-1}; this feed solution P concentration and the 30 min speed were also the settings used during the flow-through tests. A relatively high P concentration was used to obtain an estimate of the maximum retention capacity during a reasonable time span, whereas a 30-min runtime was considered to be a reasonable contact time for field applications.

Portions of 6 g of the unleached and pre-leached Ca-Fe oxide granules (with 6 replicates, the same mass for both unleached and pre-leached granule batches) were weighed into plastic sample columns of the extractor. A proper contact of a granule bed only 1–2 cm thick and feed solution was ensured by first pipetting 5 ml of the feed solution to the sample column with the granules without applying suction while the remaining 45 ml of the feed solution was measured to the upper reservoir. With application of suction to the sample column, feed solution from the upper reservoir gradually replaced small portions of the solution volume in contact with the granules. Once the 50-ml volume had been passed through the granule bed, another portion of P stock solution was applied (in 5 + 45 ml portions) to initiate a new feed cycle. In total, 40 feed cycles were needed to saturate the fresh (unleached) granules over about a month, whereas the pre-leached granules required 92 feed cycles over about two months.

In addition to (dissolved) P concentration that was measured from each collected eluent, pH and electrical conductivity (EC) were also monitored during all feed cycles. The concentrations of Ca^{2+} and total S in the eluent solutions were, for the unleached granules, determined after 1, 33, and 40 feed cycles. For the pre-leached granules, determinations were done for every fifth (the first 25 feed cycles) and later for every tenth feed cycle. In measuring Ca^{2+} and S concentrations, ICP-AES was used.

Phosphorus release from P-saturated granules

The granules for the experiments described below were obtained from the earlier saturation runs. The total P content of the unleached P-saturated granules was 6.8 mg g^{-1}, whereas for the pre-leached granules, the total P content was about 15 mg g^{-1}.

The effect of pH modification

To test how solution pH affects the release of P, 1 g of P-saturated granules were shaken in 100 ml of deionised water spiked with different amounts (0–800 µl) of 1 M HCl. The samples were allowed to equilibrate for 18 h on an orbital shaker at 70 rpm, after which the solution was filtered (0.2 µm) and analysed for DRP. This test was performed in triplicate on both unleached and pre-leached granules.

Sequential extraction

To assess the P present as Ca precipitates and as Fe oxide-adsorbed P, the P-saturated unleached granules were subsequently extracted by (i) two portions of water (0.5 g granules and 50 ml water), first for 10 min and then for 2 h, (ii) a mixture of anion exchange resin (AER) (1 g of Dowex 1 × 8 AER; Sigma-Aldrich, Inc., St. Louis, MO, USA) and cation exchange resin (CER) (1 g of Amberlite IR-120 CER; Dow Chemicals, Inc., Midland, MI, USA) (0.5 g granules and 40 ml water, for 18 h), and (iii) with pH-buffered dithionite solution (0.25 g granules and 40 ml water, for 15 min; see Uusitalo and Turtola 2003). Buffering of pH of the dithionite solution was done by adding 2 ml of 0.5 M $NaHCO_3$, which gave a post-extraction pH of 6.9.

The extractions with water and the AER/CER mixture were supposed to dissolve mainly Ca-associated P. Readily soluble Ca–P associations should be dissolved in water, and the less soluble ones in the AER/CER mixture because of removal of P and Ca from the solution phase. The P mass that dissolved in bicarbonate-buffered dithionite solution was assumed to result from Fe oxide dissolution – reduction of Fe(III)oxides to soluble Fe(II) – in low redox potential (Eh drop from about 600 mV to less than –300 mV).

Incubation of P-saturated granules in a reduced environment

To study the effects of long-term anoxia, 0.25 g of P-saturated, unleached granules were weighed (in 4 replicates) into 100 ml glass bottles equipped with thick, air-tight rubber caps. The bottles were filled with 80 ml of P-free synthetic brackish water, "Z8" nutrient medium (Kotai 1972, Ekholm et al. 2009), which is a solution containing Na^+, K^+, Mg^{2+}, Cl^-, SO_4^{2-}, and CO_3^{2-} corresponding to a brackish water with a salinity of 6 practical salinity units. To promote microbial reduction processes, an inoculum of sediment bacteria (10 µl brackish sediment suspension) was added together with 3 mg of labile C (as acetate) to the bottles. During the incubation, additional C was supplied at 141 and 196 days of incubation.

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As a control treatment, similar vessels were prepared with a 0.25-g soil sample. The soil was a silty clay obtained from an agricultural field with somewhat higher than average P status for the Finnish clay soils, with 15 mg P l^{-1} extractable in acidic (pH 4.65) ammonium acetate, 18 mg kg^{-1} water-extractable P (1:50 soil–water ratio), or 69 mg kg^{-1} Olsen-P. The total P concentration of the soil was about 1.3 mg g^{-1}. The soil contained 95 and 175 mmol kg^{-1} of (pH 3.0) oxalate-extractable Al and Fe, respectively, which is clearly more than was extracted from the unleached, intact granules: Al 4.5 and Fe 42.5 mmol kg^{-1}. The granules were extracted intact because they were used intact in the tests, and we wanted an estimate of the metals on the reactive surface, rather than in finely ground mass.

The anoxic incubation of the suspensions took place on a rotary table and lasted for 308 d. During that time, two 5 ml solution samples (on days 141 and 196) were retrieved with injection needles through the rubber caps and analysed for molybdate-reactive P and Ferrozine-reactive Fe (Stookey 1970). At the end of the incubation, the suspensions were also analysed for total Fe, NH_4^+, SO_4^{2-}, dissolved inorganic C, and pH. Filtering of the solution samples was not done because the solution phase (salty Z8 solution) was completely clear.

Element loss during immersion of P-saturated granules in a lake

This final test was conducted in an open system, i.e. with free element (solute) and water movement in the vicinity of the granules. Three 2-g portions of P-saturated unleached granules were enclosed in small bags (about 2 × 8 cm) of nylon filter fabric with 300 μm openings. The bags were immersed for 16 days in an oligotrophic lake (Lake Iso-Jurvo with a forested catchment located in central Finland), at about 20–30 cm depth and about 1 m above the bottom, after which they were brought back to the laboratory and weighed. Subsamples of finely ground granules (the ones that were incubated in the lake, as well as subsamples of the same P-saturation batch that were stored in the laboratory) were dissolved in 7 N HNO_3 in a microwave digester. Of the digests, Ca, Fe, Al, P, total S (presumably present as SO_4^{2-}), and the trace metals listed in Table 1 were determined, and mass loss of these elements was calculated as the difference between lake-immersed granules and granules that were stored in the laboratory.

Results
Phosphate retention
Effect of contact time on P retention by the granules in batch tests

The granules showed a high P retention efficiency and rapid P retention in P solution concentrations of 1 and 10 mg l^{-1} (Fig. 1). For the 1 mg l^{-1} bathing solution, 85% or more of the P was already withdrawn from the solution phase by the granules at the shortest, 5-min contact time. At the 10 mg l^{-1} P concentration, 50% withdrawal would, according to the fitted curve, be obtained in 17 min under batch test conditions. For both bathing solutions, all of the added P had disappeared from the solution in 45 min.
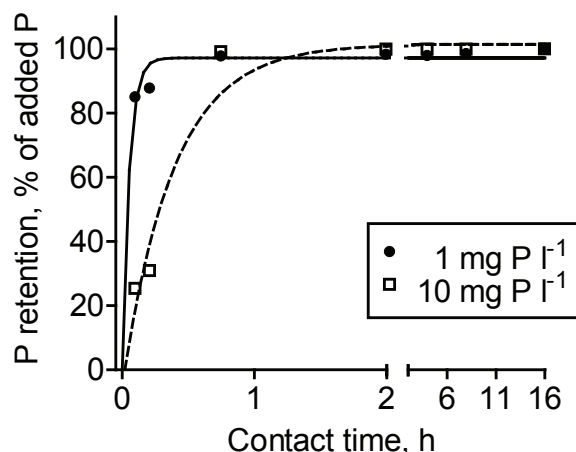

Fig. 1. Retention efficiency (as % of added P) plotted against contact time at initial bathing solution P concentrations of 1 mg l^{-1} (solid line) and 10 mg l^{-1} (dotted line). Test conditions: solid-to-solution ratio 1:25 (w vol^{-1}), T = 20 °C.

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Phosphate retention capacity estimated in a flow-through system

The capacity of P retention was assessed in a flow-through system that is (as compared to batch tests) less likely to overestimate retention in field conditions when dealing with a material that contains abundant soluble Ca and elevates the pH of the solution. In addition, this test was run on granules in the unleached and pre-leached states. Because dissolution of soluble elements decreased the weight of the material, the results of the pre-leached granules are in Fig. 2 recalculated to the original, fresh-weight equivalents.

The cumulative P mass retained by the unleached granules was 6.8 mg g^{-1}, corresponding to 40% of the cumulative amount of P fed during the whole test (Fig. 2). A similar percentage was also retained by the pre-leached granules, even though pre-leaching caused a 63% loss in the granule mass (associated with 74% loss of Ca, 92% loss of K, but less than 6% loss of Al, Fe, Cd, Cr, and Pb). In the actual test settings, when the pre-leached granules were used in the same 6-g mass as the unleached ones (and the weight loss was not taken into account), P retention was as high as 15.2 mg g^{-1}. After recalculating to fresh-weight equivalents (i.e. taking the mass loss during pre-leaching into account), the weight loss during pre-leaching seemed to have a small effect on the P retention capacity that equalled 5.6 mg g^{-1} (fresh-weight of the granules) after 92 feed cycles.

During the course of the flow-through test (with 50 mg l^{-1} P solution), the P retention efficiency of the unleached granules exceeded 60% of the P added during the first 10 feed cycles, and then gradually decreased. The test was terminated after the 40th feed cycle, and during the last runs, only 10–15% of the P applied was retained by the unleached granules. For the pre-leached granules, the efficiency of P retention was 60–70% during the first five P feed cycles and gradually decreased to 30–40% at the halfway point of the test, and finally to 20% at the end of the test. Retention efficiency at the point when the test was ended was thus still higher for the pre-leached granules than for the unleached ones, indicating less complete P saturation.
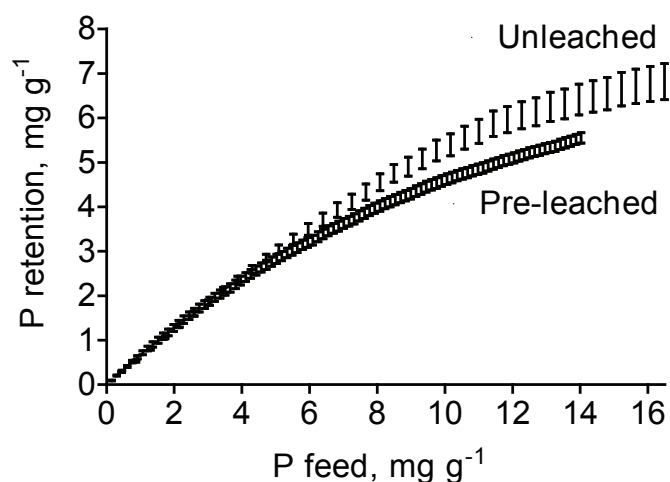

Fig. 2. Cumulative P retention by the unleached and pre-leached Ca–Fe oxide granules as a function of the cumulative P feed to the columns. Both x- and y-axis values are recalculated to the original (unleached) mass of the granule bed. Error bars show the 95% confidence intervals of 6 replicate columns.

A less complete P saturation was also indicated when calculating molar ratios of retained P to total Fe: In unleached granules, the P:Fe ratio was 0.16 as compared to 0.12 in the pre-leached granules at the end of the flow-through test. Here, total Fe rather that oxalate-extractable Fe was used because oxalate-extractable Fe (extraction of intact granules) did not seem to give comparable results for the unleached and pre-leached granules. For the unleached granules, the concentration of oxalate-extractable Fe was 42.5 mmol kg^{-1}, as compared to 1400 mmol kg^{-1} for the pre-leached granules. The increased extractability of Fe in oxalate probably indicates exposure of new Fe-oxide surfaces upon pre-leaching.

The feed solution (50 mg l^{-1} P solution) had a pH value of about 6.5 whereas the pH of the solution that had passed the bed of unleached granules was about 7 at the beginning of the test and declined to the level of the feed solution at the end of the test. For the first eluates of the unleached granules, the concentration of soluble Ca^{2+} was 300–320 mg l^{-1} but declined to 33–56 mg l^{-1} in the 33rd and 40th feed cycles. Pre-leaching effectively decreased soluble Ca such that we recorded 22 mg l^{-1} Ca^{2+} concentration in the first eluate and less than 10 mg l^{-1} from feed cycle 10 onwards. For some reason, the pH of the eluates of the pre-leached granules was higher than in the feed solution and remained within a range 7.4–7.8 throughout the test.

A G R I C U L T U R A L   A N D   F O O D   S C I E N C E

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By visual inspection, the granules were intact at the end of the test. However, for the unleached granule batch, we recovered only 83% of the granule mass added to the columns, the loss presumably being for the major part the result of leaching of Ca^{2+} (with counter ions SO_4^{2-} and OH^-). Regarding pre-leached granules, they were visually more porous than the unleached ones, presumably because of dissolution of $CaSO_4$ from the granule interiors during the pre-leaching step.

Phosphate release from P-saturated granules

The effect of pH modification

There was a clear pH effect on P release from P-saturated granules, but the unleached and pre-leached batches showed opposite trends (Fig. 3). For the unleached granules, increased solubility of P upon a pH decrease from almost 9 to neutral was an expected outcome for a Ca-phosphate system. For a pure Ca-P system, one would expect an exponential increase in solution P concentration when lowering pH below 7. Instead, P release at pH below neutral appeared to level out rather than increase at a greater pace, at least for the two replicates acidified to about pH 5.5. This second phase of P solubility regulation when moving down the pH scale from 7 to almost 5 might occur because Fe hydroxides retained P. The amount of P released from P-saturated granules, after a very marked (more than 3 units) decline in pH, corresponded to about a 10% loss of the initially retained mass of P.
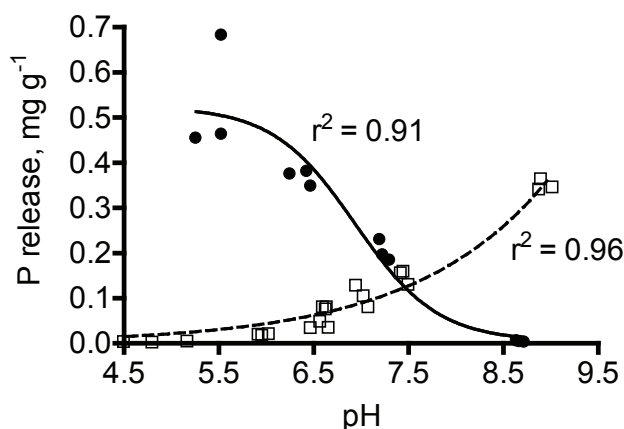

Fig. 3. Phosphate released from P-saturated unleached (black markers, solid line) and pre-leached (white markers, dotted line) granules as a function of pH of the solution after equilibration for 18 h. The actual P content (weight loss not taken into calculation) before pH manipulations was 6.8 mg g^{-1} for the unleached granules and 15.2 mg g^{-1} for the pre-leached ones.

As for the pre-leached batch, substantially more P was released at pH 9 than from the unleached granules at the high pH levels (Fig. 3). The release of P from the pre-leached granules then continuously decreased as pH declined. At pH 6.5, the pre-leached granules released only about a fifth of the P mass that was released at pH 9, which would agree with the fact that Fe oxides have a P sorption maximum at acidic environments. The lower relative share of P that was solubilised from the pre-leached granules (they contained twice the concentration of the unleached ones, but at pH 7.5 released about as much P) was probably the result of the absence of Ca-phosphates and also a less complete saturation than in the case of unleached granules (Fig. 2).

The effect of low redox potential

To study the effect of strongly reduced conditions on P release from P-saturated unleached granules, we performed a sequential extraction that involved two sequential extractions by water, followed by overnight equilibration with a mixture of AER and CER, and as the final step, the low-redox treatment by applying dithionite as a reducing agent in pH-buffered solution.

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The P pool extractable in the two portions of water was about similar in size (0.76 mg g^{-1}) to the amount of P solubilised when decreasing pH to less than 6 in a single extraction (*cf*. Figs. 3 and 4). In the subsequent extraction with AER and CER, a surprisingly small amount of P was released (0.14 mg g^{-1}), possibly because most of the newly formed Ca-P precipitates had already dissolved in the preceding water extractions. In the final step, about as much redox-labile P (0.75 mg g^{-1}, likely Fe oxide-associated P) was released from the P-saturated granules as was obtained by the water extractions. About 25% of the total amount of P initially retained by the granules (6.8 mg g^{-1}) was solubilised as the sum of this extraction sequence.
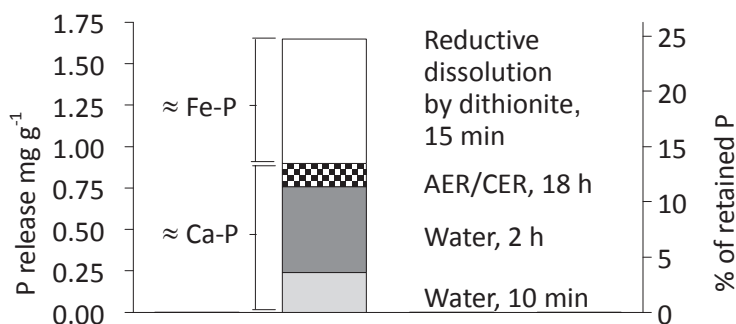

Fig. 4. Phosphate released from P-saturated granules in two sequential extractions by water, by a mixture of anion and cation exchange resins (AER/CER), and by pH-neutral dithionite solution. The three first fractions were assumed to be mainly Ca-associated P whereas the dithionite addition presumably released Fe-associated P.

A long incubation of P-saturated granules in an anaerobic environment

Another test on the fate of Fe-associated P included a 308-day anaerobic incubation in sediment bacteria–inoculated synthetic sea water. The concentrations of dissolved Fe and P after 141 and 196 days and at the end of the incubation suggested that only small amounts of these elements were liberated from the P-saturated Ca–Fe oxide granules (Fig. 5). The P concentration of the solution in contact with the granules was at the highest in the last sampling, corresponding to a P release of 0.052 mg g^{-1} (SEM 0.005 mg g^{-1}, $n = 4$) from the solid phase, or less than 1% of the total P content of the granules. This number is thus radically lower than those obtained in the extractions by water and dithionite solution (Fig. 4). On the other hand, for the soil sample included as a control, microbial activity appeared to lead to solubilisation of P from the soil in amounts that were appreciably higher than those of the Ca–Fe oxide granules despite the lower concentration of total P in the soil sample. The amount of P released from the soil sample in anoxic conditions (in the final sampling, 0.402 mg g^{-1}, SEM 0.006 mg g^{-1}, $n = 5$) agrees well with the estimates of "Fe-associated P" (viz. the NaOH-extraction step of Chang–Jackson fractionation) obtained in other studies of Finnish agricultural soils (e.g. Hartikainen 1979, Peltovuori et al. 2002).

The colour of the granules remained brown throughout the test whereas the soil matter turned from grey to almost black in the course of the incubation. This change was accompanied by a decrease in SO_4^{2-} concentration (from about 2 initially to 0.65–0.78 g l^{-1}) in the solution with a suspended soil sample, and a strong smell of H_2S, indicating SO_4^{2-} reduction. For the granules, after the incubation, the concentration of SO_4^{2-} was 1.8–1.9 g l^{-1}; thus, the sulphate concentration seemed to remain constant throughout the incubation. Of the added C (9 mg), about 10% (0.9–1.1 mg) was recovered in solution of soil or granule samples after the test.

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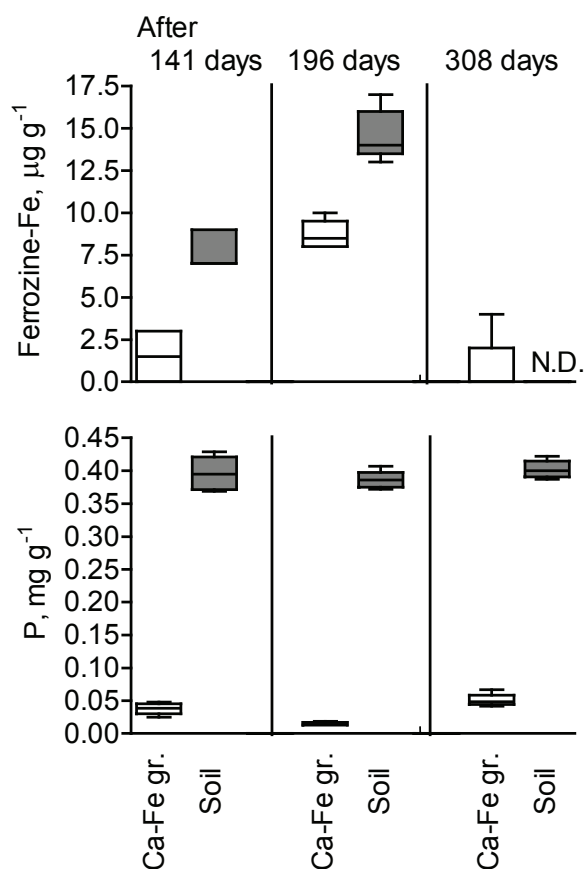
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Fig. 5. Ferrozine-reactive Fe and P solubilised from P-saturated Ca–Fe oxide granules and a soil sample during a 308-day anoxic incubation with added C, SO_4^{2-}, and sediment bacteria. N.D. = not detected.

Phosphate release in an infinitely P-depleted environment

The final test on P solubilisation from the P-saturated Ca–Fe oxide granules was made in an open system with free element exchange with the surrounding solution, i.e. the granules were immersed inside nylon netting bags in an oligotrophic lake.

After 16 days of immersion in the lake, 35–40% of the added granule mass was recovered from the bags. Hence, the mass loss was about the same as in the pre-leaching in laboratory. As for the element concentrations, 100% of the Fe and 76% of the P present in the P-saturated granule mass were recovered after the immersion (Table 2), with the molar ratio of P:Fe decreasing from 0.16 before lake immersion to 0.12 afterwards. On the other hand, only 18% of the Ca and 2% of the total S were recovered after 16 days in the lake. Of the other elements that were determined, recoveries were 60–70% for Cd and Pb (with low initial concentrations), 80–90% for Cu and Ni, and 90–100% for Al, Mn, Cr, and Zn. It thus seems that most of the P, Al, and heavy metals remained in the Fe oxide matrix whereas $CaSO_4$ and residual $Ca(OH)_2$ dissolved in water. The high recovery of Cr suggests that it was present in other valences than the soluble Cr(VI).

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Table 2. The total mass of elements Ca, Fe, P, Al, and S in nylon mesh bags that contained 2 g of granules before immersion in a lake, and the mass of the elements recovered in the bags after 16 days of immersion. After the immersion, the total mass of granules recovered was on average 0.74 g for a bag (35–40% of the original granule mass added to the bags). The results of all 3 replicate bags are shown.

Ca	Fe	P	Al	S
Element mass (mg) before immersion of granules in a lake, in 2 g of granule mass				
317	162	14.5	5.5	197
323	159	14.5	5.7	193
322	154	13.8	5.6	192
Average: 320	159	14.3	5.6	194
Element mass (mg) after 16 days of immersion, in 0.74 g of recovered granule mass				
56	170	9.8	5.6	2
53	169	12.2	5.3	4
60	157	10.7	5.0	7
Average: 56	166	10.9	5.3	4
Recovery-%: 18	105	76	94	2

Discussion

Phosphate retention

Batch tests with variable contact times suggested that P retention by the Ca–Fe oxide granules is rapid at relatively low P concentrations (1 mg l^{-1}) but that with increasing P concentration, a longer contact time between solution and the granules is required. Much of the P retention by the fresh granules likely occurs by means of precipitation of Ca-phosphates because of the presence of abundant soluble Ca^{2+} and high pH. Because precipitation strips Ca^{2+} from the solution, the time required to replenish the solution Ca^{2+} concentration may have affected P removal efficiency at the shortest contact time in our batch test. In addition, given that $CaSO_4$ and $Ca(OH)_2$ are incorporated into the granule matrix, replenishment of solution Ca^{2+} by dissolution logically slows down as soon as the stock on the surface of the granules has dissolved, and Ca^{2+} ions need to migrate from the granule interiors. In the field situation, where water flows quickly through a barrier, the kinetics of Ca-phosphate precipitation may thus differ from what is observed in batch tests, with the latter providing an optimistic estimate of the retention kinetics.

Bastin et al. (1999) had previously studied a material chemically very similar to the Ca–Fe oxide granules, named OX (synthesized of $Fe_2(SO_4)_3$ and $Ca(OH)_2$ in water and finely crushed after drying). These authors suggested that both precipitation as Ca-phosphates and sorption onto Fe hydroxides were responsible for P removal from solution, at a capacity of about 15 mg P g^{-1} OX in acidic solution and up to 30 mg P g^{-1} OX at pH >10. In our work, effective P retention by the pre-leached granules (with low soluble Ca content) made of the same ingredients showed that the gradual loss of soluble, pH elevating constituents ($Ca(OH)_2$) would have a minor effect on P retention by the granules. By contrast, it became evident that pre-leaching and loss of soluble constituents – mostly gypsum and Ca hydroxide – increased the P retention capacity of the granules when compared on an equal-mass basis. When the weight-loss–corrected P retention was incorporated, the pre-leached granules retained an amount of P similar to that of the unleached granules.

Because the Fe oxides were ultimately responsible for P retention by the granules, P retention capacity can be related to the Fe content in the material. As for total element contents, the molar ratios of P to Fe were 0.16 after P saturation, when 50 mg l^{-1} P solution was passed in pulses (non-continuously) through the columns over about a one-month period, and 0.12 after subsequent immersion of these granules in the lake. Also, the P:Fe ratio of the pre-leached, not fully P-saturated granules was 0.12 when P saturation was done in about a 2-month period with 50 mg l^{-1} P solution pulses. A recalculation of the results of the batch tests conducted by Bastin et al. (1999), who used a 24-h reaction time and 10 mg l^{-1} P solutions, shows that at acidic pH, the P:Fe molar ratio was approximately

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0.19 because P retention equalled 14.5–15 mg g^{-1} OX and the Fe content of their Fe oxide was about 14%. Chardon et al. (2012), after a 238-day flow-through column study on Fe hydroxide sludge continuously fed with about 4 mg l^{-1} P solution, reported P:Fe ratios of 0.12 in the most P-saturated inlet part of their flow-through columns. After they then fed (for 72 days) one of the columns that had reached P saturation with P-free solution, the P:Fe ratio decreased to about 0.08. It thus seems that Fe oxide–rich materials may in laboratory tests yield P:Fe ratios well above the molar ratio of 0.1 (up to about 0.3 for biogenic Fe hydroxide studied by Rentz et al. 2009) when fed with P solutions, but a P:Fe value of 0.1 would probably be close to the maximum P saturation that Fe hydroxide–rich materials can realistically achieve in field barriers where the material contacts water occasionally low in soluble P.

In addition to the capacity to retain P, reaction kinetics is of primary interest in the search for suitable materials for P barriers. Recently, Chardon et al. (2012) pointed out that in most studies on P retention materials, short contact times (mostly up to some hours) have been used, whereas slower reactions tend to be neglected. For P barriers in ditches or streams, the emphasis on fast reactions is understandable because the fast reactions (adsorption and precipitation) withdraw phosphate from the solution phase when water passes through the barrier. The slower reactions, such as diffusion inside the Fe oxide matrix, add to the retention capacity by "refreshing" the sorption sites on the material surface when P concentration of the Fe oxide matrix exterior and interior moves towards a new state of equilibrium; thus, the slower reactions affect the long-term performance of P retention materials. If a P retention material is used as a soil amendment, the relative importance of slow kinetics becomes more obvious because contact times are typically longer than in P barriers placed in streams.

Reversibility of P retention

The environmental conditions (such as pH, redox) in natural waters may fluctuate widely (see Baas Becking et al. 1960), and these fluctuations may promote changes in the retention efficiency and release of retained P (e.g. Pratt et al. 2007). Then, if the material used in a reactive barrier is left in contact with water for longer times, knowledge about the reversibility of P sorption is of importance. In case substantial release of P from P-saturated material occurs, the material needs to be continuously monitored for P saturation and removed as soon as the saturation state is being approached.

For the unleached Ca–Fe oxide granules, a decline in pH from the level of about 9 increased the release of previously retained P. In the first phase, P release increased rapidly when the solution was acidified to slightly acidic pH values, but the release of additional P rather levelled off than further accelerated when the solution was acidified to pH 5.0–5.5. As stated earlier, our hypothesis is that the first burst of P release resulted from dissolution of Ca-P precipitates, but thereafter P sorption by Fe oxides increased (by the newly exposed oxide surfaces when more Ca-associations dissolved at acidic pH), diminishing further release of previously retained P. For the pre-leached granules, P release systematically decreased upon acidification of the ambient solution, suggesting that P retention by Fe oxides became more effective as pH declined from the basic side of the scale down to pH 5. This pattern is familiar from studies on P solubility in non-calcareous soils and on pure metal oxide systems (e.g. Murrmann and Peech 1969, Violante and Pigna 2002). In the intended application of the studied material at edge-of-field barriers, especially in a non-calcareous environment, it is likely that pH and the concentrations of soluble Ca will decline before P saturation is achieved, and a barrier made of Ca–Fe oxide granules will behave like the pre-leached granules.

In addition to pH, anoxia and consequent microbial or chemical reductive dissolution also need to be considered because Fe is the most abundant metal in the granules. Phosphate associated with Fe oxides can be solubilised when Fe oxides serve as terminal electron acceptors in microbial Fe reduction, or during chemical reduction when Fe sulphides are formed after sulphate reduction (e.g. Roden and Edmonds 1997). The result of the purely chemical reduction in our test series, obtained by means of dithionite extraction, showed that about 10% of the P retained by the granules (at high P saturation) was released in the presence of sulphides. However, we were unable to obtain support for this result by performing an incubation test with sediment bacteria in a substrate rich in SO_4^{2-} and degradable C. In that incubation, no sign of a marked solubilisation of Fe or P from the granules to ambient solution was detected, even though the anoxic conditions were maintained for a period extending over 10 months. One possible explanation for the absence of soluble P and Fe could be formation of secondary minerals, such as vivianite ($Fe_3(PO_4)_2 \times 8 H_2O$), but this formation was not confirmed.

The outcome from the anoxic incubation of the soil sample (a positive control sample) showed that the test settings used would trigger microbial Fe and SO_4^{2-} reduction and the accompanying P solubilisation, so the bacteria added in the samples were active at the start of the incubation. From the additional data available, i.e. SO_4^{2-} and C concentrations, we found no solid evidence to establish whether the sediment bacteria remained active in con-

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tact with the granule samples. During the incubation, 90% of the added C disappeared from the solution phase of both soil and granule samples, but the dissolved C concentration may have decreased because of sorption onto Fe oxides. On the other hand, the observation that practically all of the SO_4^{2-} added to the granule samples (with the synthetic brackish water solution) was recovered at the end of the incubation period does not prove that sulphate reduction was totally absent because the granules contained gypsum, dissolution of which could have buffered the changes in SO_4^{2-} concentration. Gypsum has a solubility of about 2 g l^{-1} in water, which was the level found in the solution phase at the end of the incubation. Hence, the outcome of the bacterial incubation test remains uncertain.

Most of our desorption/dissolution tests involved a closed system that can result in an elevation of P and other soluble elements in the solution phase, and such changes in solution composition may depress further P solubilisation, regardless of the type of P associations and mechanisms involved. To complement the laboratory tests with a test that did not include uncertainty brought about by solute accumulation, we conducted a 16-day equilibration of the P-saturated granules in a lake. The results showed that about 25% of the P disappeared from the granules over about two weeks. This share of P released approximately equalled the results of our sequential extraction test, even though the mechanism of P release during the lake immersion was probably different from that active in the sequential extraction test; it is highly unlikely that redox potential in the near-surface lake water had wide fluctuations and would have dropped to negative values.

From the viewpoint of P loss abatement, materials that bind P in high-energy bonds can be considered the best candidates for P barrier applications in the field. However, the effectiveness of P retention conflicts with the aim of recycling P accumulated to a barrier material. After reaching P saturation, reuse of the P retained by high-energy bonds may turn out to be expensive if the material needs to be processed to increase plant availability of P before application to fields. Hence, the loss of the value from a recycling point of view needs to be evaluated against the efficiency in pollution abatement. For water bodies that suffer from severe eutrophication because of agricultural P loading, such as the Archipelago Sea, the loss in recycling value may be of secondary importance.

Conclusions

The studied Ca–Fe oxide granules have a P retention capacity that is an order of magnitude higher than Finnish soils typically have, and they can be regarded as efficient P sequesters. Our data on retention kinetics in the batch test conditions are likely to provide rather optimistic estimates because (unlike in field settings) the soluble compounds remained in the reaction vessel and may have affected the results. Under the test conditions of our study, a substantial part (up to 60%) of soluble P was retained in the 30-min contact time. This period can be regarded as a realistic contact time in a field barrier that takes up water from a relatively small drainage area. Retention of P appeared to predominantly occur through strong (high-energy) bonds, which means that once P has been retained by the granules, it will not leach out easily even if P concentration of the ambient solution decreases. The content of harmful elements is low, or – in case of Cr – in a form (oxidation state) that renders the element insoluble in water. From these perspectives, the granules appear to be a good candidate for edge-of-field P retention barriers. However, the granules have a relatively high cost (100–150 € Mg^{-1}), which means that the cost-effectiveness of their use depends on the site where they are applied. Estimates of cost-effectiveness of the use of these granules can be made first after sufficiently long field tests. If the performance in actual field settings were similar to that in these laboratory tests, they could provide an additional measure to be used in sites that produce high P concentration in runoff or drainage waters.

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