

# Removal of sewage phosphorus by adsorption and mineral precipitation, with recovery as a fertilizing soil amendment

Craig Jowett, Irina Solntseva, Lingling Wu, Chris James and Susan Glasauer

## ABSTRACT

Clear sand adsorbs 15–35% total phosphorus (P) from septic tank effluent, but P is mobilized when low-P effluent is applied. Amorphous P compounds formed by alkali aluminate chemical addition may also be subject to leaching. Crystalline mineralization is the desired end effect that isolates P thoroughly from the water resource. Using new low-energy iron electrochemistry (EC-P process), dissolved ferrous iron reacts with sewage phosphate ions ( $\text{PO}_4$ ) and precipitates onto filtration medium as vivianite [ $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ], as identified by scanning electron microscopy and X-ray diffraction and predicted from Eh–pH– $\text{aHPO}_4^{2-}$  phase relations. Removal rates of 90–99% in sand, soil and synthetic foam filters are obtained. The precipitation of vivianite demonstrates that P can be immobilized quickly and without intermediary adsorption phases, as with Fe-rich soils. Vitreous silicate material (VSM) or rockwool that traps and precipitates mineral P after EC-P treatment was investigated as a means of P reuse as a fertilizing soil amendment. Comparative soil leaching and growth studies using corn plants demonstrate that the VSM alone reduces P losses from soils, and that VSM which has received EC-P effluent is equivalent to or better than commercial superphosphate fertilizer.

**Key words** | fertilizer, phosphorus, recovery, sewage, soil amendment, vivianite

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## INTRODUCTION

Removal of phosphorus (P) from sewage systems is vital when residences are near freshwater rivers or lakes, or where fractured bedrock can channel nutrients quickly to groundwater and surface water. Soil is the receiving body for on-site system dispersal. Successful treatment and acceptance into the soil is critical to minimize surface breakouts of septic tank effluent (STE), which enhances the nutrient content of stormwater runoff to lakes. This is especially important in clay soil where raised beds are prone to surface breakout. Even when subsurface dispersal is successful, however, certain soils, for example those low in aluminum and iron oxides, typically remove only a small fraction of the P introduced.

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The precipitation of relatively insoluble P-bearing minerals will sequester P in the soil (e.g., [Robertson 1995](#)) or other filtration medium. In this paper, we present updated field and laboratory results from investigations of the *Waterloo EC-P*<sup>TM</sup> technology, an iron dissolution + filtration system. The results show that P is removed from septic discharge to very low values before entering groundwater. The iron-phosphate mineral vivianite [ $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ] precipitates in the filter medium receiving effluent from the EC-P system, thereby sequestering P as a relatively insoluble mineral phase above the water table. By this means, a high rate of P removal is achieved with the EC-P despite the low adsorption capacity of the filter medium for P. The spent EC-P material may be recycled for use in soil to stimulate plant growth.

To provide context to the EC-P process, this paper begins with a review of earlier work to remove P at

individual residences. This includes removal via the formation of Fe-Al-rich 'B-horizon' soil, a discussion of historical data on P adsorptive removal by clear septic sand (without fines or iron oxides), and evidence showing that P previously adsorbed on septic sand is subsequently leached into groundwater, using results from multi-year field studies. This is followed by a presentation of the results from the EC-P system. The paper concludes with a study in which the filtration medium from the EC-P process, a waste product, is shown to be an effective fertilizing soil amendment for corn in a greenhouse trial.

## PHOSPHORUS REMOVAL USING INDIVIDUAL SEPTIC SYSTEMS

### Removal of P by Fe and Al

Conventional sewage phosphorus removal processes using Al- or Fe-based chemical addition purposely generate a P-rich sludge. The sludge is separated to remove the phosphorus physically for off-site treatment (Brandes 1976), although high-P sludge is accepted at fewer municipal treatment plants. An Al- or Fe-based reactive submerged medium can be used for P adsorption (Hutchinson & Jowett 1997; Heufelder & Mroczka 2006), even for individual residential septic systems. The resulting effluent pH is typically highly alkaline. When depleted, the P-rich medium is again taken off-site for disposal; treatment is challenging due to its chemical composition. Mineralizing the P in the soil leach field is an option without disposal issues.

### Role of natural 'B-horizon' soil in removing P

B-horizon soil is formed when degraded iron silicates in the upper A-horizon release  $\text{Fe}^{2+}$  ions into solution, aided by decomposing organic matter. The dissolved iron percolates downwards and precipitates, primarily as oxidized ferric iron oxides and hydroxides, where it becomes part of the underlying B-horizon mineral matrix. Reactive phosphorus dissolved in water passing through the B-horizon soil binds chemically to iron oxides to ultimately form iron-phosphate minerals, and these reactions can be very quick (e.g., Schulte & Kelling 1996; Barber 2002). Because Fe-P minerals have very low solubility under both aerobic and anoxic conditions (Hansen & Poulsen 1999; Barber 2002), phosphorus that exists below septic system leach fields is thus removed from the hydrologic cycle and kept out of groundwater and adjacent surface water bodies (e.g., Robertson 1995).

Soil organic matter in A-horizon soil degrades to form  $\text{CO}_2$  and carbonic acid ( $\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$ ), whose protons ( $\text{H}^+$ ) help break down Fe-rich silicate minerals, releasing ferrous ions ( $\text{Fe}^{2+}$ ) into solution. The organic matter also fosters the activity of microorganisms that can reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , mobilizing Fe until it encounters a suitable counterion for precipitation. In the oxidizing B-horizon soil, ferrous iron converts to ferric iron ( $\text{Fe}^{3+}$ ), which readily precipitates as the characteristically coloured yellow, red, and brown hydroxides.

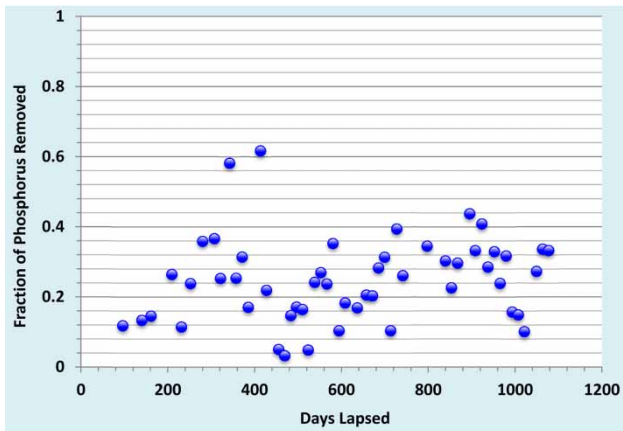
Stable, insoluble Fe-P minerals form in both oxic and anoxic conditions, e.g., as strengite [ $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ] in oxidizing, ferric ( $\text{Fe}^{3+}$ ) conditions, and as vivianite in reducing, ferrous ( $\text{Fe}^{2+}$ ) conditions. Strengite has a solubility product constant  $K_{\text{sp}} = 10^{-22}$  and vivianite has a  $K_{\text{sp}} = 10^{-36}$ . These  $K_{\text{sp}}$  values are very low (compared to, for example, calcium carbonate, with a  $K_{\text{sp}} = 10^{-9}$ ), indicating that these minerals are highly stable in typical soil environments (see Schulte & Kelling 1996; Barber 2002). Fostering the conditions for the formation of these low-solubility minerals is desirable to sequester P in soil or other solid filter media.

Al- or Fe-rich hydroxides in natural B-horizon soils adsorb reactive P when placed below a standard leach field. In this case, the P is left *in situ*, where it is available to crystallize as minerals of low solubility (Robertson 1995, 2003, 2008). The P may, however, be released when oxygen and pH conditions change (e.g., Patrick & Khalid 1974). While this latter soil-based method has low maintenance and no disposal or re-treatment issues, there is no assurance that preferential flow paths do not develop which by-pass the reactive soil. In addition, little research has been conducted to assess whether insoluble P-based minerals actually do form and impede the movement of P to discharge water (Wilfert et al. 2015; Wilfert et al. 2016).

## LEACHING OF ADSORBED PHOSPHORUS

### Adsorption by clear sand

Conventional leach fields composed of clear sand that receive STE remove 15–35% of phosphorus (e.g., Figure 1). If the association of P with mineral surfaces is weak, it is susceptible to subsequent leaching (Robertson 1995, 2003). Results from a 3-year sand filter study (1999–2002) in the Environmental Technology Initiative (ETI) program in Massachusetts (MASSTC 2003) demonstrate this removal rate, though no leaching studies were carried out.



**Figure 1** | Phosphorus removed in Massachusetts single-pass sand filter between TP of STE and  $\text{PO}_4\text{-P}$  of sand filter effluent ( $\text{TP}_{\text{inf}} - \text{PO}_4\text{-P}_{\text{eff}}/\text{TP}_{\text{inf}}$  in 24' (7.3 m) depth pan lysimeter (from MASSTC 2003).

Following the standard for groundwater studies (e.g., Robertson 1995), only soluble  $\text{PO}_4\text{-P}$  was analyzed in the effluent from buried pan lysimeters, because total phosphorus (TP), including soluble and solid-bound P, can be contaminated by soil particles. Total P was analyzed in STE, however, averaging 4.84 mg/L TP entering the F2 sand filter ( $N=63$ ). A calculated P removal rate is thus a maximum, as the ratio of  $\text{PO}_4\text{-P}:\text{TP}$  entering the sand filter was about 0.79 ( $N=4-8$ ). The F2 sand filter removed a maximum of 26.4% P between the F2 STE (4.84 mg/L TP;  $N=63$ ) and the 600 mm deep pan lysimeter (3.56 mg/L  $\text{PO}_4\text{-P}$ ;  $N=62$ ).

A similar multi-year study by Chowdhry (1974) on a variety of 750 mm deep sand filters demonstrated rates of TP removal of 14–29% from STE. Although the published data are presented in terms of percentile values only, the overall removal rate is estimated at 18.4% TP, from an overall 7.6 mg/L TP in STE, to overall 6.2 mg/L in effluent of all five sand filters (Chowdhry 1974). During the trickle flow-dosing test period, the two finer sands averaged 30.8% TP removal, and the three coarser sands averaged 15.8% TP removal. The percent removal declined to different extents when large doses of wastewater were pumped to the sand filters, especially in the coarsest sand filter.

### Leaching of adsorbed phosphorus

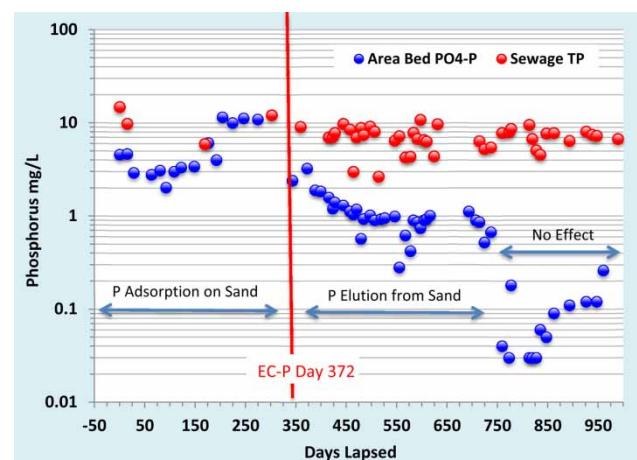
The potentially ephemeral nature of adsorbed P is illustrated by long-term sampling at School BB in Ontario, Canada, conducted by Waterloo Biofilter staff. A pan lysimeter was

placed below the 250-mm layer of fine sand in the disposal bed receiving filtered sewage without phosphorus removal (carbonaceous biological oxygen demand and total suspended solids <5 mg/L;  $\text{PO}_4\text{-P} = 7-8$  mg/L). For 2 years, the disposal bed sand layer removed about 30% of  $\text{PO}_4\text{-P}$ . After an EC-P unit was installed to remove P from the wastewater to a discharge concentration of about 0.5 mg/L  $\text{PO}_4\text{-P}$ , the same sand then began to actually contribute phosphorus to the treated water, resulting in a concentration around 1.0 mg/L (Figure 2). The formation of vivianite in the open-cell polyurethane foam biological filter upstream of the sand layer is discussed below.

After a year of leaching phosphorus from the sand layer, the low-P influent passed through the sand with little change in concentration, and about 0.1 mg/L  $\text{PO}_4\text{-P}$  from the EC-P + Biofilter entered the groundwater. The clear sand had adsorbed phosphorus when P-rich effluent passed through it, but only temporarily. The retained phosphorus was then eluted from the sand when the P-poor effluent flowed through, until the absorbed phosphorus was eluted completely. The phosphorus was still retained in the Biofilter medium as a more stable compound.

We have observed that there is little overall effect on water pH after installing the EC-P unit (Table 1).

These studies illustrate the challenging nature of removal and long-term sequestration of P from septic system effluent. The key issue for permanent P sequestration is to precipitate relatively insoluble forms of P. In the following, we present the results of our studies to treat effluent P using the EC-P system with a rockwool filter to trap P and foster mineral precipitation.



**Figure 2** | Dissolved phosphorus ( $\text{PO}_4\text{-P}$ ) below clear sand layer demonstrates P adsorption until Day 372, followed by elution of adsorbed phosphorus until removal is complete by Day 750.

**Table 1** | Changes in pH due to installation of the EC-P on Day 372 are not substantial, and possibly due to changes in the chemical composition of the raw sewage

	Raw sewage Pre EC-P	Septic tank Post EC-P	Final biofilter Post EC-P	Area bed 250 mm Post EC-P
Before Day 372	7.08 <i>N</i> = 6	—	7.17 <i>N</i> = 11	7.13 <i>N</i> = 7
After Day 372	7.34 <i>N</i> = 32	7.19 <i>N</i> = 30	7.25 <i>N</i> = 33	7.16 <i>N</i> = 36

## PHOSPHORUS REMOVAL BY THE EC-P PROCESS: FIELD STUDIES

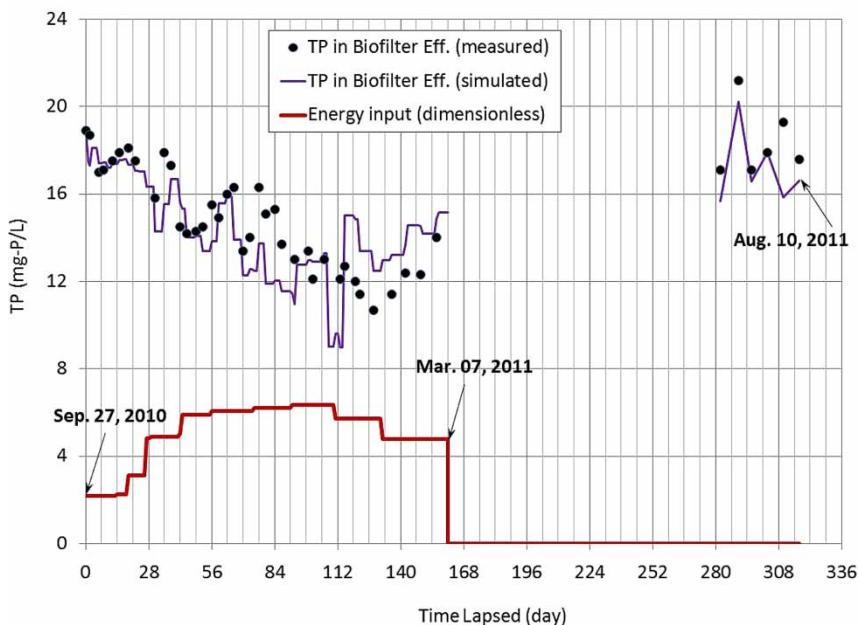
### Mimicking B-horizon processes in soil

High P-removal rates are achieved in septic systems using sacrificial anode electrochemistry followed by filtration (Waterloo EC-P). In the EC-P electrochemical system, natural iron electrodes are dissolved into the sewage stream as ferrous ions, where they react with phosphorus to form insoluble P-based minerals downstream of the electrodes. The EC-P method differs from the standard ‘electrocoagulation’ method (e.g., Holt *et al.* 2005) that purposely produces a P-rich sludge that can then be physically separated. This process is akin to natural processes in soil that are catalyzed by microorganisms, but without the intervening hydroxide-adsorption stage (Xu 2010; Jowett *et al.* 2013, 2014). Filtration media used to date includes polyurethane foam, coarse sand,

and sandy-loam soil. The technology is abiotic and thus relatively independent of temperature, consumes about 0.5 kWh per day per residence, is largely independent of water salinity as it produces its own electrolyte for current between electrodes (Xu 2010), has no sludge or reactive medium issues, and the EC-P process has no adverse effect on pH (Table 1).

### Predicting TP removal with EC-P

During early testing at an Ontario truck stop, the EC-P treated several cubic metres of Waterloo Biofilter effluent each day, returning the Fe-P-rich effluent back to the septic tank to be passed again through the Waterloo system. As Fe and P accumulated in the filtration medium over time, the concentrations of P in the Waterloo effluent decreased, from the initial TP  $\approx$  19 mg/L to TP  $\approx$  12 mg/L near the end of the testing (Figure 3), even though only a small percentage of the total flow was treated.

**Figure 3** | Predictability of TP removal applied in bench-scale testing (from Jowett *et al.* 2013).

Knowing the intimate sewage details at this facility provided an opportunity to test another hypothesis: predicting TP removal as outlined in Xu (2010). If the test analytical data conform to standard physics and chemistry theory, the technology gains greater confidence and more general acceptance. The simulation uses actual hydraulic flow rates of influent sewage, of reused water (this facility uses Waterloo effluent for toilets and urinals), and of water passing through the experimental systems. These data are combined with the concentrations of TP in the three water types. By using physical relationships of Fe-P chemical bonding, the TP concentration in the Waterloo effluent is calculated and compared to actual laboratory analyses (Xu 2010).

In Figure 3, the energy input (lower rectilinear line) increases from the starting date of September 27, 2010, to Day 112, and TP in Waterloo effluent (black dots) is thereby depleted at a rate conforming to that predicted by theory (upper solid line). This outcome confirms that known physical-chemical theory does apply, that the technology is designed and operated appropriately, and that the mass of TP removed can be predicted.

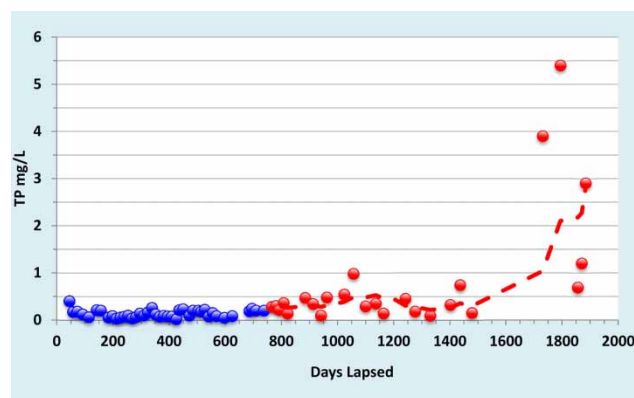
After Day 112, the energy input (lower rectilinear line) is decreased and the predicted concentration of TP (upper solid line) increases as expected along with the actual concentration of TP (black dots) until termination at March 7, 2011. The fluctuations observed in the predicted line around Day 112 are due to anomalously low flows followed by a seven-fold increase in sewage volume from the facility.

After the experiments were discontinued and energy to the system shut off on March 7, 2011, the TP in the Waterloo effluent had returned to normal values of 18–20 mg/L by July–August 2011. The simulated theory predicted these concentrations as well, based on the flow rates and zero energy input to the TP removal system.

It should be noted that the volume of mineral precipitate accumulating in the upper 0.5 m of soil is small, calculated at <2% of pore space in soils over 20 years of operation at peak design flow. The effective plugging volume will be less if larger discrete mineral concretions are formed, as expected, rather than widely distributed fine-grained crystals.

### EC-P + soil field results

An on-going 3-year study at Massachusetts Alternative Septic System Test Center facility using the EC-P technology retrofitted into a conventional septic tank + soil leach field demonstrated that the EC-P + 300 mm of soil removed



**Figure 4** | Pan lysimeter TP results at 300 mm soil depth below STE with EC-P to soil leach field. Results of 600 and 900 mm pan are removed for clarity. The EC-P system (circles) was removed on Day 743 to determine the removal of background P in soil, shown in squares.

98% TP (Figure 4). The amount removed increases to >99% when 600 and 900 mm depths are included. The soil was a mixture of 60% coarse sand used in the ETI sand filter study (Figure 1) and 40% silt. The fraction of P removal in the EC-P + soil averaged 99.2% TP removal after passage through 600 mm of soil, compared to 26.2% P in 600 mm clear sand filter (Figure 1). The EC-P was removed at Day 743 to determine the background P-attenuation potential of the soil, and is reflected in the increasing values for P over time after removal. The residual adsorption–mineralization capacity from the EC-P in the 300 mm soil column was such that it took about 3 years after Day 743 to break through to near-background values (Figure 4). The 600 mm and 900 mm soils are still removing all P that passes through the first 300 mm from the septic tank.

### PRECIPITATION OF P MINERALS DURING THE EC-P PROCESS

We conducted studies to identify new minerals formed in the EC-P filter to assess the capacity of the EC-P system to sequester P during operation at two schools (School MV and School BB).

### Sampling procedures and analytical methods

The Waterloo Biofilter foam filter medium was sampled at two schools in Ontario using BD GasPak EZ anaerobic collection pouches to prevent oxidation of minerals. Both samples were taken at 300 mm depth in the filter medium. School MV uses an alkali-aluminum chemical to remove

phosphorus, while School BB uses the iron-based EC-P unit. Samples collected from the schools were freeze-dried and analyzed for physical structures and chemical elements by scanning electron microscopy (SEM). Following different attempts at sample preparation, the dried Al-based sediment-sludge from School MV was physically knocked out of the foam, whereas School BB foam samples were sectioned into thin slices for examination.

SEM and X-ray diffraction (XRD) studies of accumulated solids in Waterloo Biofilter filtration medium were conducted at the University of Waterloo. For XRD analyses, powder was scanned with an EMPYREAN diffractometer with Co-K $\alpha$  radiation and a PIXcel3D fixed slit scintillation detector (40 mA, 45 kV). The XRD profile was recorded at a scan speed of 0.026°/s under a continuous scanning mode. Data were collected and treated by Data Collector and HighScore Plus software produced by PANalytical B.V., Almelo, The Netherlands. For SEM-EDS (SEM coupled to energy dispersive X-ray spectroscopy) imaging and element analysis, the SEM (Hitachi TM-3000) was operated under high vacuum conditions using secondary electron (SE) and back-scattered electron detectors at accelerating voltages of 15 kV. EDS (Bruker QUANTAX 70) spectra were collected at selected locations at 15 kV under high vacuum conditions.

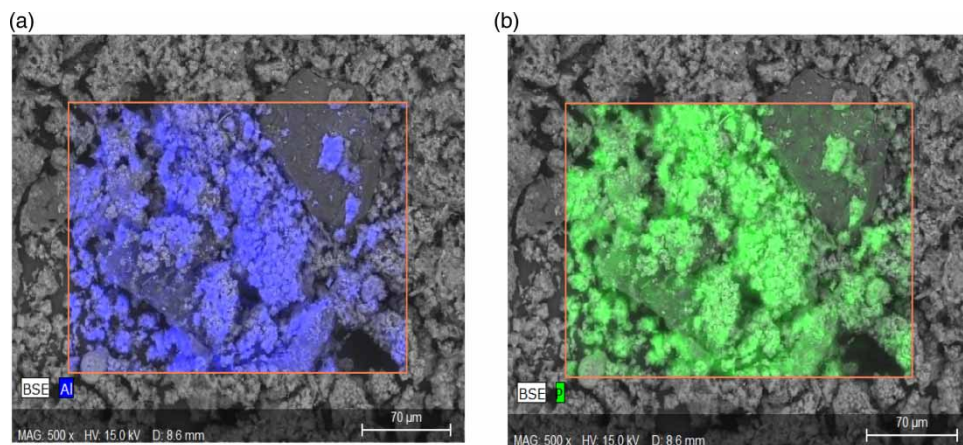
## Results and discussion of mineral formation during EC-P treatment

At School MV, P was observed to be co-associated with Al, using SEM-EDS (Figure 5). However, no crystalline Al-P mineral fraction could be identified by XRD, although

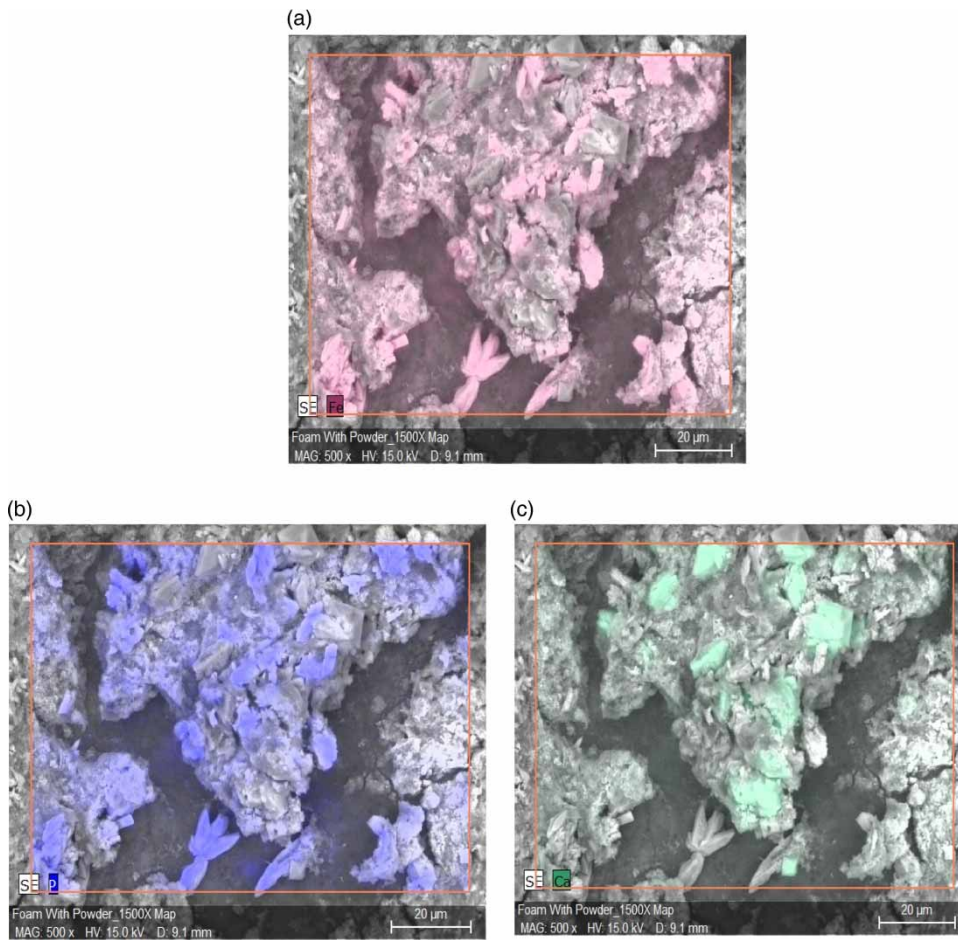
the treatment system had operated for several years. At School BB, where the iron-based EC-P is used, we identified Fe-P compounds using SEM-EDS (Figures 6 and 7), which formed within 18 months of system initiation. For XRD analysis, smears of accumulated solids from School BB were prepared from freeze-dried samples and assessed for crystallinity and to identify precipitated minerals. Due to the small quantities of material, a series of 1-hour scans over 24 hours was carried out to remove background interference and accentuate distinguishing peaks. XRD analysis indicated crystalline minerals of the calcium oxalate weddellite [CaC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O] and the iron (II) phosphate vivianite. Vivianite is diagnostic for Fe-reducing conditions.

We observed bladed crystals of vivianite, as anticipated in Xu (2010) and Jowett *et al.* (2013). No calcite or dolomite crystals were detected, but we did observe crystals of weddellite, which has a tetragonal crystal habit with the common morphology shown in Figure 7(b). It is found in urinary tracts as 'kidney stones', in sea floor mud, and in peat sediments. Both minerals are hydrated and both form in oxygen-poor environments. The results from the XRD scans are shown in Table 2 and Figure 8.

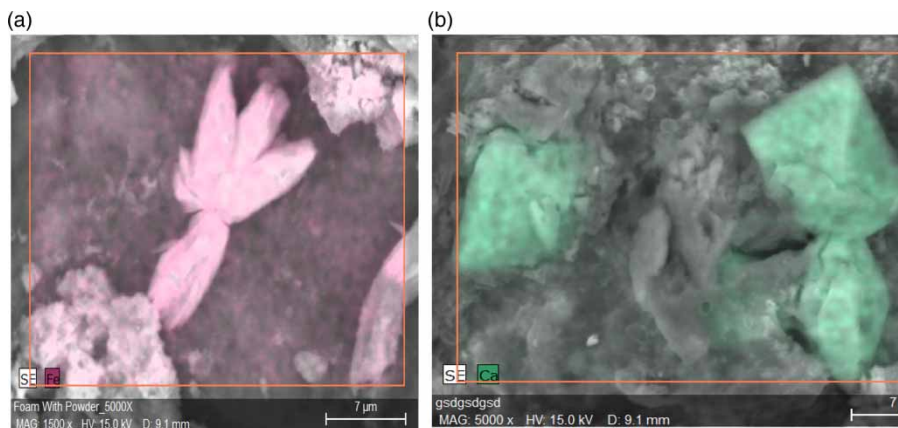
Masood & Recht (1971) identified vivianite in settleable sludge produced by adding ferrous iron to phosphate solution in an anaerobic environment. In their batch experiments, the pH ranged from 6 to 9, with optimum removal by precipitation (and flocculation) at initial pH = 8 (their Experiment 8). Iron-phosphate precipitates on 100  $\mu$ m screens were amorphous to XRD after 15 minutes of mixing, but crystalline after 5 hours. Using secondary effluent at pH = 8 (their Experiment 15), ferrous iron precipitated as vivianite after 1 hour of mixing, identified based on colour change from light green to blue upon exposure



**Figure 5** | Element maps (SEM-EDS) of School MV foam medium showing the co-association of Al and P in a poorly crystalline mass. (a) Aluminum. (b) Phosphorus.



**Figure 6** | SEM-EDS element maps of School BB foam medium show close co-association of Fe and P in bladed prismatic crystals of vivianite, with Ca located separately in double-tetrahedral crystals of weddellite. (a) Iron. (b) Phosphorus. (c) Calcium.



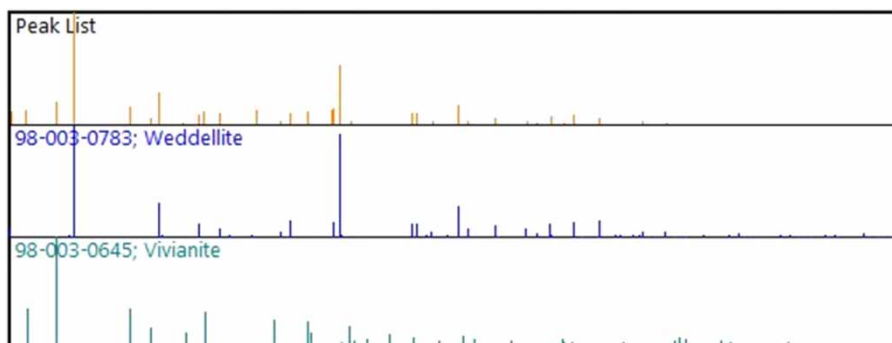
**Figure 7** | Close-up views from Figure 6 of SEM-EDS element maps showing Fe-P in vivianite (a) and calcium in weddellite (b) as identified by XRD scans in Table 2. (a) Iron in vivianite. (b) Calcium in weddellite.

to air. In their review, Wilfert *et al.* (2015) emphasize the importance of understanding iron–phosphorus chemistry when adding iron to sewage, as it controls the ultimate

compound, including vivianite. Azam & Finneran (2014) identified microbially associated vivianite when ferric iron salts were introduced to the reducing environment of the

**Table 2** | Pattern list of XRD scan of Brisbane filtered solids identified the calcium oxalate weddellite and Fe-PO<sub>4</sub> mineral vivianite

Visible	Ref. code	Score	Compound name	Displacement [°2Th.]	Scale factor	Chemical formula
*	98-003-0783	59	Weddellite	0.000	0.648	C <sub>2</sub> H <sub>4.75</sub> Ca <sub>1</sub> O <sub>6.375</sub>
*	98-003-0645	22	Vivianite	0.000	0.248	H <sub>16</sub> Fe <sub>3</sub> O <sub>16</sub> P <sub>2</sub>

**Figure 8** | XRD peak scans compared to the mineral database indicate weddellite (hydrated calcium oxalate) and vivianite (hydrated ferrous phosphate) minerals.

septic tank. Similarly, Wilfert *et al.* (2016) identified vivianite in sewage sludge when ferric salts were added and subsequently reduced to the ferrous state. These results confirm that vivianite can form under similar conditions to those found in the EC-P system.

The presence of crystalline minerals confirms that new minerals formed during water treatment using the EC-P technology. The crystallization of vivianite is particularly important because it stabilizes P within a highly insoluble mineral structure under O<sub>2</sub>-free conditions; the K<sub>sp</sub> for vivianite is ~10<sup>-29</sup> M. This important finding indicates that the precipitation of Fe-P minerals occurs within 18 months.

## SUITABILITY OF EC-P PHOSPHORUS AS FERTILIZING SOIL AMENDMENT

### Leaching of phosphorus from amended soil

The P sequestered from wastewater has potential for recovery and reuse, if the P trapped in the filter material during EC-P treatment can be remobilized under plant growth conditions. Studies were conducted at the University of Guelph using the rockwool filter (vitreous silicate material, VSM) from an EC-P system to investigate (1) the solubility of recovered P in soils and (2) the use of VSM treated with sewage effluent as a fertilizing soil agent. The VSM, used in Europe as a soil amendment, is the filter medium that

receives STE after the EC-P process at School BB. As a comparative benchmark, VSM with STE from School ER with no EC-P was also used.

### Agronomic study on corn plants

The plant response of corn, an important Ontario crop, was studied in soil amended with different VSM and EC-P treated materials and compared to soil amended with conventional mineral fertilizers. Low phosphorus sandy-loam soil was used from Ontario croplands where corn is cultivated and where mineral fertilizer is required. Soil phosphorus deficiency suppresses root development especially during the early stages. Corn is a fast-growing species and was chosen to provide quality results within the short time frame of the project. Although the focus was on P, the VSM filters would have trapped other nutrient ions that may also stimulate plant growth. Sulfate and calcium are likely not important in this regard, because both are sufficient in the soils we used, as is typical for Ontario soils used for agriculture. Nitrate probably did contribute to plant growth. Its high solubility means that it would have been subject to more leaching than P.

### Analysis of VSM for pathogenic bacteria

The VSM materials treated with septic discharge were analyzed for the presence of human pathogens, i.e.,



*Escherichia coli* and fecal coliform bacteria. Each cube of treated silicate material was cut into layers (10 cm from top and from bottom) and 10 g of randomized samples were collected for analysis from both layers. An amount of 10 g of wet samples was placed in 90 mL of phosphate-buffered saline (PBS) solution with glass beads (diameter 2 mm) and shaken for 20 min at room temperature on a laboratory shaker at 200 rpm.

Serial dilutions ranging from  $10^1$  to  $10^5$  were prepared in PBS solution for plating on 3M™ Petrifilm™ Coliform Count Plates, which were inoculated in triplicate with 1 mL from each dilution, following manufacturer instructions. Plates were incubated at 35 °C for 24 hours for enumeration of coliforms and for 48 h for *E. coli* (AOAC Official Method 991.14). According to the Petrifilm kit instructions, an intensive blue colour for colonies associated with gas bubbles should be identified as *E. coli*. Our results showed no evidence of *E. coli* for all tested samples; coliform and enterobacteria were, however, present in all four samples in top and bottom layers, at abundances up to 1,500 cfu/g of dry material. As a result, we sterilized all VSM material prior to handling and to performing all subsequent tests and experiments. Materials were sterilized in an autoclave at 121 °C for 30 min.

### Leaching of P from VSM applied to soil

To determine the retention of P in the different types of VSM treatment, leaching experiments were performed using two soils that have different texture characteristics (sand-loam and silt-loam) to investigate the impact of texture on P mobility. Shredded VSM material was mixed with sandy-loam and silty-loam soils in pots, and water was added periodically in an amount to displace one pore volume for each dosing period. Effluent leachates were analyzed for water-soluble orthophosphates ( $H_xPO_4-P$ ;  $x = 0-2$ ) using an Astoria flow-cell analyzer. After 2 weeks, the soil in the pots was analyzed for water-extractable and total phosphates (reverse aqua regia method) by inductively coupled plasma mass spectrometry.

### Use of VSM as a fertilizing soil amendment

Five different soil treatments using the sandy-loam soil in 4 kg pots were prepared for the plant growth study in a greenhouse at the University of Guelph. The treatments consisted of: (a) natural soil with no added materials, (b) soil with only shredded virgin VSM added, and (c) soil with only P fertilizer added. These controls were compared to (d) soil with shredded VSM which received STE for 4 months at School

ER with no EC-P, and (e) soil with shredded VSM having received EC-P STE for 4 months at School BB. The materials were added on the basis of equivalency to  $P_2O_5$  fertilizer applied at a conventional rate of 80 kg P per hectare.

Clean VSM was included to eliminate any effect of the material itself, which tends to keep P from leaching with water, and better compare with other treatments. The VSM material is very porous and its presence in the pots affects critical physical properties of the soil such as aeration and bulk density, which in turn might affect chemical processes in the soil, as well as plant responses.

Five replicates of each of the five soil treatments were used, and each planted with six pretreated corn seeds of cultivar Pioneer P9675 AMXT. The soil was packed to equal bulk density of  $1.2 \text{ g/cm}^3$  prior to planting. Six seeds were sown per pot at a uniform 1-cm soil depth, and after 10 days were thinned to three evenly spaced seedlings per pot. The pots were maintained under greenhouse conditions and were watered automatically each day according to crop requirements.

After 2 months, the plants were harvested and analyzed for height, dry biomass and phosphorus content in plant tissues. The leaves and stems of each corn plant were dried in an oven at 65 °C and ground into a homogeneous powder. For phosphorus analyses, samples were then dry-ashed in a muffle furnace at 500 °C and the residue dissolved in 0.1 N HCL. The phosphorus content of the acid extract was measured using an automated Astoria-2 Flow Cell colorimeter.

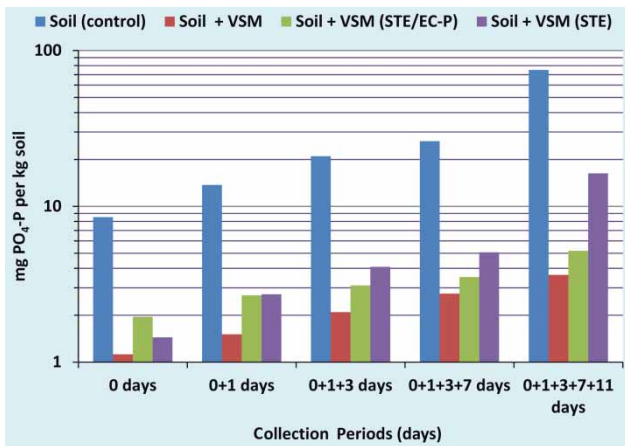
### Leaching P from VSM in soil

The values of  $H_xPO_4-P$  in collected leachates were calculated based on the total amount of orthophosphate removed from each pot per gram of added material (Figure 9).

Over a 2-week period, the control soil with no additives leached out much more P than did the soil with barren medium or with EC-P medium (School BB), indicating that the presence of the VSM itself retains P in the soil. Water extracted substantially more P from the STE-soil than from the STE-EC-P soil, suggesting that P associated with the VSM (STE) is more soluble than with the VSM (STE-EC-P), indicating a more insoluble form of P in the EC-P treatments. Alternatively, the VSM material may have adsorbed soluble P, retarding P removal through leaching.

### Performance as fertilizing soil amendment

Corn plant heights showed visible differences in growth within 2 weeks as a function of treatment, and this relationship was consistent to the end of the 2-month study



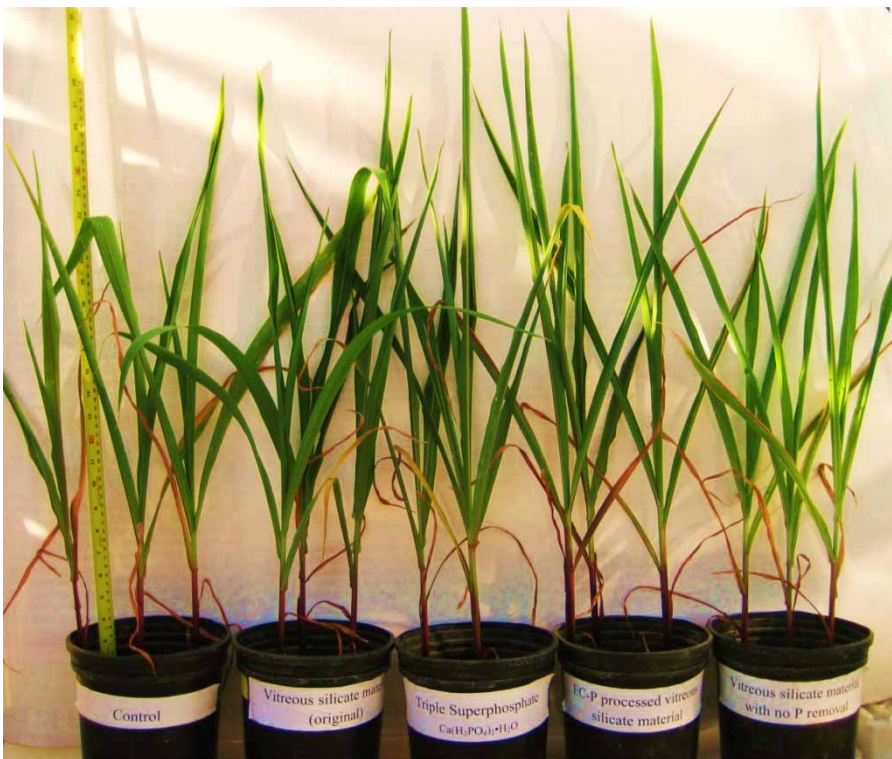
**Figure 9** | Cumulative mass of  $\text{PO}_4\text{-P}$  leached from silt-loam soil over 11 days, shows that addition of the VSM treatment alone and VSM + EC-P retards phosphorus leaching into the groundwater. Results are similar for leaching trials using the sandy-loam soil.

(Figure 10). The heights of the plants grown in soil that received mineral fertilizer (c) or the STE-EC-P VSM material (e) were comparable and were the tallest overall. Plants grown in soil with virgin VSM (b) or VSM (STE) (d) were shorter, and the control soil (a), which received

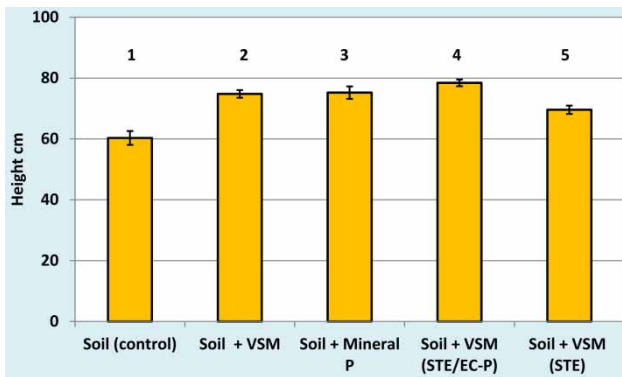
no amendment, was the shortest. These differences demonstrate that P available from the EC-P process stimulated plant growth similar to conventional fertilizer. It also indicates that the virgin VSM material in itself enhanced plant growth, perhaps connected to its ability to retain phosphorus during leaching (Figure 9).

Tukey's multiple-comparison test was used to determine which means of the five populations (columns 1 to 5 in Figure 11) differ significantly from any of the other four means. At a probability of  $P < 0.001$ , the mean plant height of the soil control (column 1) after 2 months' growth differs from the soil + VSM (column 2), the soil + mineral fertilizer (3), and the soil + VSM (STE/EC-P) (4) populations. At  $P < 0.01$ , the control soil (1) and the soil + VSM (STE/EC-P) (4) populations differ from soil + VSM (STE) (5). All other differences are not significant at  $P < 0.05$ .

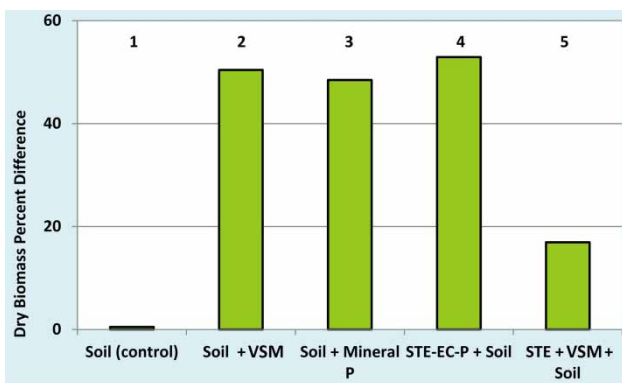
Identical Tukey relationships were found with the dry biomass populations depicted in Figure 12, except that the soil control (column 1) and the soil + VSM (STE) (5) were not significantly different at  $P < 0.05$ . For the relative mass of phosphorus taken up by the plants (not shown), there was no difference between populations 2, 3, and 4 at  $P < 0.001$ .



**Figure 10** | Corn plant growth study indicates that the VSM alone and the VSM (STE/EC-P) acted as positive 'fertilizer' soil amendments compared to the control soil. Left to right: control soil (no amendments added to sand-loam soil); soil + VSM (virgin medium); soil + triple superphosphate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ; soil + VSM (STE/EC-P); soil + VSM (STE).



**Figure 11** | Height of corn plants after 2 months (mean of  $N = 15$  for each of the five treatments; error bars represent standard error of the mean).

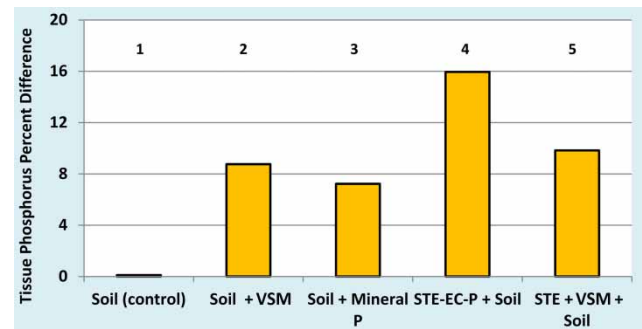


**Figure 12** | Percent difference of dry biomass in comparison to control treatment after 2 months (average of  $N = 15$  for each of the five treatments).

Based on plant height, biomass, and phosphorus uptake in plant tissue, the data demonstrate that corn plants responded well to the VSM-based treatments, including untreated VSM, compared to the soil control (Figures 11–13). The mass of the dry plants for the treatments was about 50% greater than the soil control as depicted in Figure 13.

The total uptake of phosphorus by plants in each pot was calculated by multiplying the phosphorus content per gram of dried biomass by dry biomass weight. The results reveal the plant response to the various treatments. The phosphorus uptake of the plants was about 8–16% greater than the soil control as depicted in Figure 13.

It is not known why the VSM itself, with no P added, was equivalent to the other treatments in terms of dry biomass. A possible explanation is that it helps retain soil P against leaching (Figure 9) and thus provides a readily available supply of P to the plant roots. The VSM itself may foster plant growth by helping soil retain moisture. The greater plant tissue concentration of P in the STE/EC-P treatment



**Figure 13** | Percent difference of plant tissue phosphorus in comparison to control treatment after 2 months (average of  $N = 15$  for each of the five treatments).

supports that P associated with the VSM was available to the plants. Fodoué *et al.* (2015) carried out similar plant studies using quarried mineral vivianite as fertilizer and found that soil chemistry was adequate to enable its use as a well-performing natural fertilizer.

Further study is required to distinguish the contribution of other nutrients to plant growth, particularly nitrogen compounds, which are also present in the VSM material after exposure to the septic effluent, as well as organic compounds used as binders. Studies using a broader range of plants are currently in progress. The results in this study support that phosphorus leaching can be minimized, and that P may be retained in the soil for plant growth.

## CONCLUSIONS

Conventional leach fields with clear sand or soil (no fines or Fe-rich material) can expect to remove 15–30% TP from STE. In general, the finer the soil is, the higher the removal. Soils will remove nutrient constituents adequately from watersheds when sewage does not break out to the surface. Clear sand, however, bonds sewage TP loosely; the sequestered P can be subsequently leached out when geochemical conditions change.

A 3-year study using iron-based EC-P technology in a conventional septic tank + soil leach field demonstrated that high phosphorus removals can be attained. More than 98% of the total phosphorus was removed at a depth of 300 mm and >99% at 600 mm and 900 mm depths. Gradual removal with depth suggests phosphorus is distributed throughout the soil profile rather than concentrated at the soil-trench surface.

When aluminum-based chemicals are used to remove TP in foam filtration medium, there is evidence that amorphous

or poorly crystalline Al-P compounds are formed. After EC-P treatment, well crystallized forms of Fe-P minerals as weddellite and vivianite were precipitated in the filtration medium after EC-P treatment, or were filtered from the effluent solution, indicating that a more sustainable removal of phosphorus from the hydrologic cycle is attained.

Soil leaching studies showed that VSM-based amendments retain soil P during leaching experiments, and that P accumulated on the EC-P VSM material may promote growth of higher and more robust corn plants compared to the control soil alone, and was equivalent to superphosphate fertilizer amendment.

The EC-P technology and filtration effectively removes P from sewage water before discharge to the natural environment, and shows promise of reuse as a fertilizing soil amendment. The Waterloo Biofilter coupled with the EC-P system is a decentralized septic tank system that is suited for single-family homes or small businesses, and it requires little maintenance. Coupling the water treatment system to reuse of the EC-P filter as a fertilizing soil amendment provides a more sustainable alternative to landfilling.

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