

ADVANCES IN UNDERSTANDING PHOSPHORUS REMOVAL IN SEPTIC SYSTEMS

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Abstract

Removal of phosphorus in residential septic systems to over 95% is now being attained using electrochemistry (*Waterloo EC-PTM*, patents pending) to introduce iron or aluminum into sewage to react with phosphorus and form insoluble P-based mineral cements. Conventional leach fields made of clear sand remove perhaps 15 – 35% of phosphorus from septic tank effluent, but if it is only loosely adsorbed onto surfaces of other minerals and is susceptible to being leached out at a later date.

Loose surface adsorption is suspected in a school study where leaching bed sand first removed 30 – 35% of phosphorus from filtered high-P influent for two years. After phosphorus was removed from the wastewater with the *EC-P*, the sand began to contribute phosphorus to the low-P influent. After a year of leaching phosphorus, the low-P influent then passed through the sand with little effect. The clear sand had only temporarily retained the adsorbed phosphorus.

A two-year study using iron-based *EC-P* technology in a conventional septic tank + soil leach field demonstrates that high phosphorus removal rates can be attained even with retrofits. More than 98% of phosphorus is removed after a depth of 300 mm of soil, increasing to 99% at 900 mm.

Scanning electron microscopy (SEM) studies of accumulated solids in a filtration medium where aluminum-based chemicals are used indicate the presence of Al – P compounds, but no definite crystalline mineral fraction. However, actual crystalline forms of Fe – P minerals are frequently found where the iron-based *EC-P* is used.

Initial XRD analysis indicates that hydrated crystalline minerals of calcium oxalate weddellite and iron phosphate vivianite are being formed where the iron-based *EC-P* is in use. Precipitation of low-solubility crystals like vivianite provides a much higher confidence that removal of phosphorus from the hydrologic cycle is permanent and sustainable.

Introduction

Septic System Phosphorus Removal

Conventional phosphorus-removal processes by Al- or Fe-based chemical addition purposely generate a P-rich sludge, and separate this sludge to remove the phosphorus physically. Reactive media systems can also be designed for individual residences

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(Brandes 1976; Hutchinson & Jowett 1997; Heufelder & Mroczka 2006). The contained phosphorus is then taken off-site and treated elsewhere by removing the reactive medium when its capacity is depleted.

The *Waterloo EC-PTM* process electro-chemically dissolves metallic iron (or aluminum) directly into a septic tank or pump tank, and sends the P-rich effluent to a filtration medium where P is retained as Fe-P or Al-P compounds (Jowett et al. 2013; 2014). The benefit of this method is simplicity, ability to be retrofitted, no sludge or reactive medium disposal issues, low energy, and the phosphorus is contained in the filtration medium, as in natural soil processes, rather than having to be treated again.

In natural soil-forming processes, iron (and aluminum) ions are released from minerals in the uppermost A-horizon soil, migrate downwards, and precipitate, primarily as ferric iron oxides-hydroxides, in the underlying B-horizon soil. Reactive phosphorus passing through the B-horizon soil adsorbs and binds chemically to the oxides, and in some cases, ultimately mineralizes into iron-phosphate or aluminum-phosphate cements (Robertson 1995; 2003; Schulte & Kelling 1996; Barber 2002).

The *Waterloo EC-P* was developed to duplicate these natural processes of mineral precipitation, but without the intervening step of adsorption onto ferric oxides or other surfaces (Xu 2010; Jowett et al. 2013; 2014). Because Fe-P and Al-Fe-P minerals have very low solubility coefficients, reactive phosphorus below septic system leach fields is removed from the hydrologic cycle and kept out of groundwater and adjacent surface water bodies.

Present Research Objectives

This paper uses literature data on sand filters to show that, under normal circumstances, phosphorus adsorbed by clean septic sand (as opposed to forming tightly bonded mineral cements) can subsequently be leached out. An update is given to the multiple-year field studies of the limits and performance of the alternative *EC-P* process, primarily at a public school and a soil leach field at the MASSTC (Buzzards Bay) test facility. Additional sites studied are detailed in Jowett et al. (2013; 2014).

Also discussed is progress made in SEM and XRD identification of minerals formed in filtration media by sewage dosed with Al chemicals and with Fe ions by the *EC-P*, and that *EC-P*-generated minerals include insoluble Fe – P crystals for more permanent removal, rather than being adsorbed onto surfaces.

Phosphorus Adsorption in Septic Sand

In 1969 – 1973, the Ontario Ministry of Environment tested six types of 750-mm deep, single-pass sand filters of various grain sizes (Chowdhry 1974), which demonstrated a removal efficiency of ~18% between TP = 7.6 mg/L in septic tank effluent to TP = 6.2 mg/L in the sand filter effluent (Chowdhry Tables 32 – 37).

Testing of the single-pass Massachusetts sand filter was carried out between 1999 and 2002 at MASSTC in the EPA-sponsored Environmental Technology Initiative program, providing another comparative benchmark. Pan lysimeter samples at a 24” (600 mm) depth in the F2 filter bed, for 36 months (N = 62), revealed overall removal efficiencies of $\leq 24\%$ between TP = 4.8 mg/L in septic tank effluent and PO₄-P = 3.6 mg/L in sand filter effluent (Figure 1). Analyses for TP are not available for sand filter effluent, and therefore this percentage removal represents the correct value when effluent PO₄-P = TP, but the removal is overstated when PO₄-P < TP, as is usually the case.

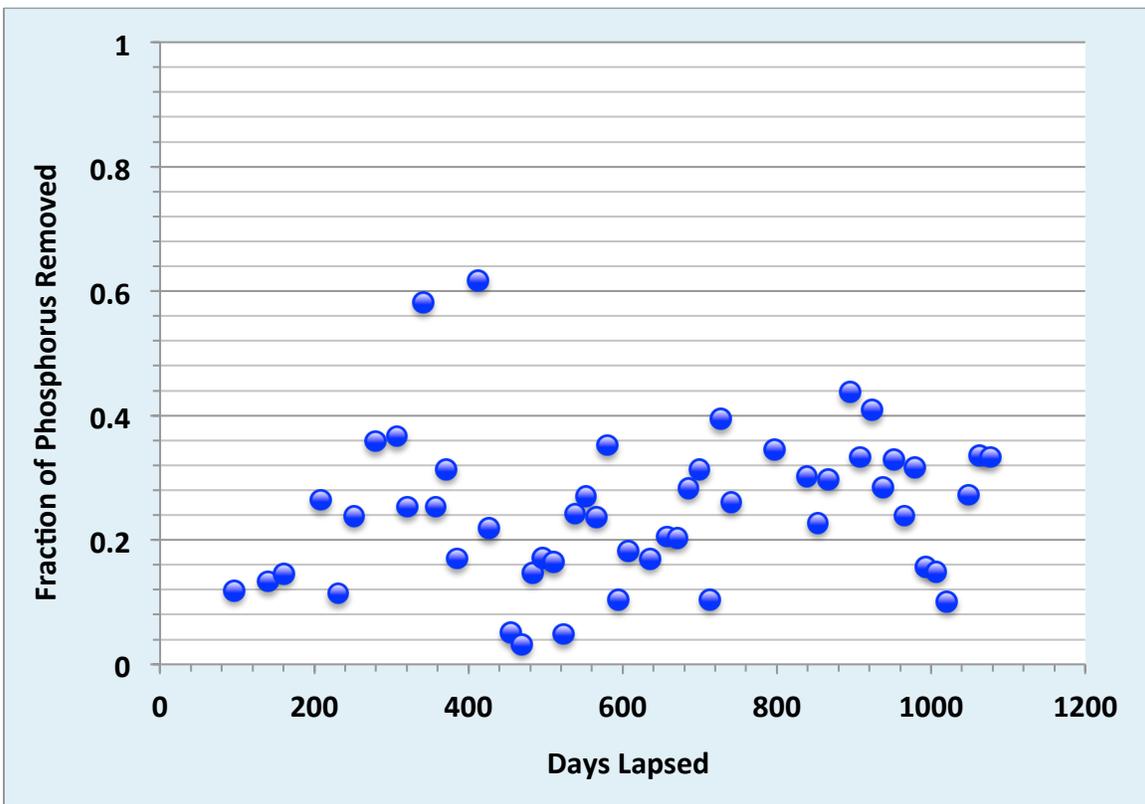


Figure 1. Phosphorus removed in Massachusetts single-pass sand filter between TP of septic tank effluent and PO₄-P of sand filter effluent $(TP_{inf} - PO_{4-P_{eff}})/TP_{inf}$ in 24” (600 mm) pan lysimeter.

No leaching tests were carried out in either of these studies to determine the strength of the adsorptive bonding.

Phosphorus Adsorption + Elution in Septic Sand

At an Ontario school, the overall sewage TP = 7.0 mg/L was lowered to 0.1 – 0.7 mg/L and Total PO₄-P = to 0.03 – 0.1 mg/L in Waterloo Biofilter effluent after the *EC-P* was installed. (Sewage PO₄-P analyses are available only since Day 472 and average 63% of the TP value.) An exception was during severe groundwater flooding through a hole in the concrete tank in which TP percent removal decreased to 70-75% until the tank was repaired.) Total iron averaged 0.4 mg/L in the effluent compared to 0.6 mg/L in the sewage, and effluent pH averaged 7.3, similar to the sewage average of 7.4.

A pan lysimeter was installed in the leach field below 10” of fine sand a year after start-up, and was sampled for a year before the *EC-P* was installed on Day 372 (Figure 2). Prior to the *EC-P*, the sand layer adsorbed phosphorus, decreasing the average value in filtered effluent from TP = 8.3 mg/L to PO₄-P = 5.4 mg/L, a removal level of ≤35% of the PO₄-P. (The use of TP to PO₄-P is consistent with that used at MASSTC above and by Robertson (2003; 2008) for groundwater-borne phosphorus. With pan lysimeters it is difficult to avoid contamination by soil particles, which gives anomalously high TP analyses.)

Following installation of the *EC-P* which removed phosphorus from the Biofilter effluent, this removal process reversed, and the sand layer added phosphorus, increasing the average values from PO₄-P = 0.82 mg/L in the Biofilter effluent to 1.03 mg/L as it passed down to the pan lysimeter, an increase of about 25%. This leaching out or eluting of P from the sand continued to Day 750. After Day 750, the PO₄-P in the sand effluent (0.09 mg/L) was the same as the Biofilter effluent (0.09 mg/L).

A reasonable interpretation is that the sand particles loosely adsorbed phosphorus from P-rich effluent during the two years prior to the *EC-P* being installed, whereupon the adsorbed P was then eluted from the sand by low-P effluent produced by the *EC-P*. After a year of elution (Day 750), there was apparently no more readily eluted phosphorus to remove and the low-P effluent simply passed through without reaction (Figure 2).

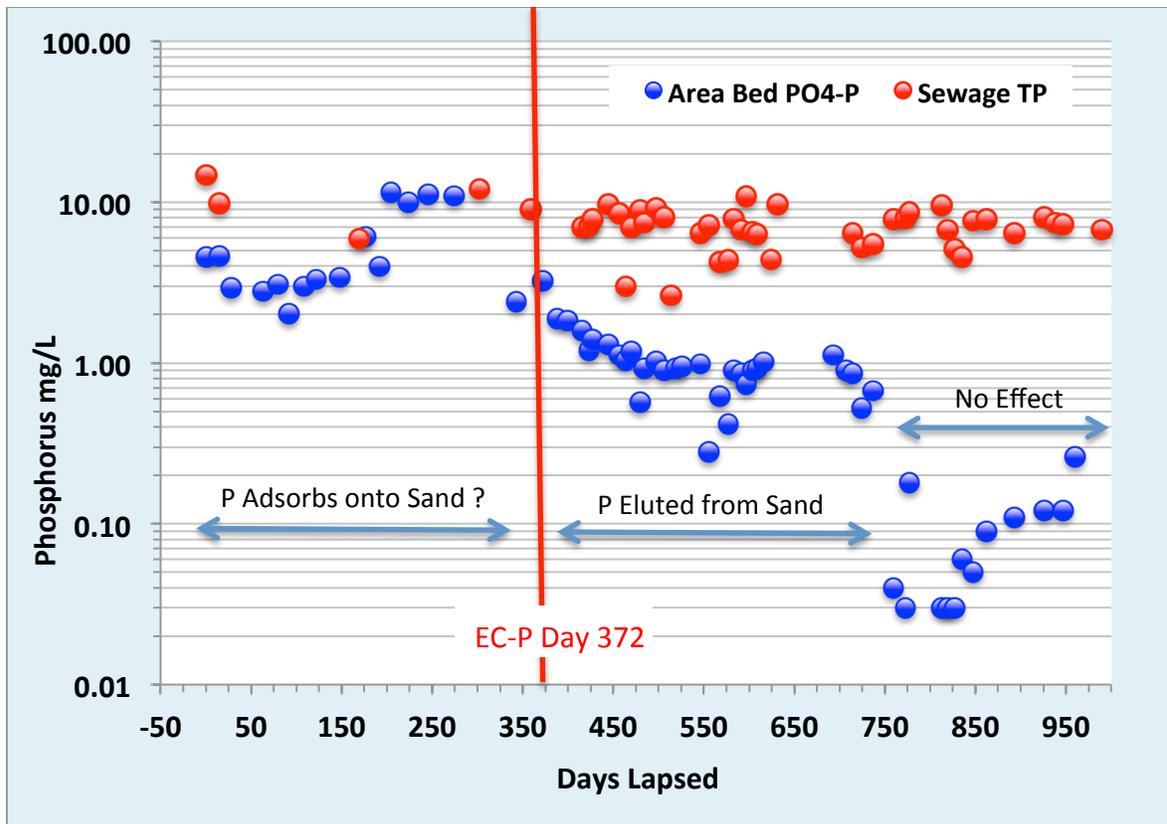


Figure 2. Dissolved phosphorus (PO₄-P) below Ontario School ‘Area Bed’ sand layer demonstrates evolution from adsorption to elution after Day 372 until adsorbed phosphorus is removed at Day 750 (on-going study).

Overall, the removal between sewage TP and groundwater PO₄-P below the leach field was 45-50% during normal operation before the *EC-P* (~25% in the Biofilter, possibly by ‘luxury uptake’ by microbes, and a further ~30% in the sand layer). This increased to 85-90% for the first year after the *EC-P* was installed, and once adsorbed phosphorus had been eluted from the sand layer, this rate increased further to over 95%.

Loosely adsorptive bonding of P onto clean sand would be expected, and this may be the norm for conventional septic systems (see discussion in Robertson 2008). However, chemical bonding would be far stronger had Fe-P or Fe-Al-P minerals actually been precipitated; phosphorus removal would be more permanent and lakefront development would be environmentally sustainable. There is no evidence of phosphorus leaching from the Biofilter when the *EC-P* is installed, and it had been anticipated that insoluble Fe-P minerals are formed, as discussed below.

Phosphorus Retention by Septic Soil + EC-P

To understand how a standard soil leach field would behave, the *EC-P* unit was retrofitted into an existing septic tank at MASSTC with pan lysimeters installed at 12" (300 mm), 24" (600 mm), and 36" (900 mm) depths within a sandy loam soil. Figure 3 shows the results of the on-going study. All pans show generally improving removals with time, with average TP = 7.04 mg/L in septic tank effluent lowered between Day 60 and Day 700 to averages of:

- 12" depth: TP = 0.2 mg/L to 0.1 mg/L (98.6%)
- 24" depth: TP = 0.1 mg/L to 0.03 mg/L (99.6%)
- 36" depth: TP = 0.03 mg/L to 0.02 mg/L (99.7%)

The apparent improvement with depth suggests that the P is removed gradually along its passage through the soil, and not just at the stone-soil interface. The logarithmic regression lines in Figure 3 show the 24" and 36" lysimeter values converging with each other, and diverging from the 12" lysimeter values. This pattern suggests that, with time, more of the TP is removed in the upper 24" and less in the 24 – 36" segment.

Sampling of the pan lysimeters were grab samples from the sump reservoirs a day or two after they were flushing out. All TP analyses were carried out at Barnstable County Health Laboratory using Method #SM 4500-P.

The *EC-P* was cleaned and re-installed on Day 370 and again on Day 680 due to resistance build-up in the electrodes. Although the electrodes looked like they could operate another year, the *EC-P* was taken out on Day 743 to allow background values of phosphorus removal without the *EC-P* to be determined.

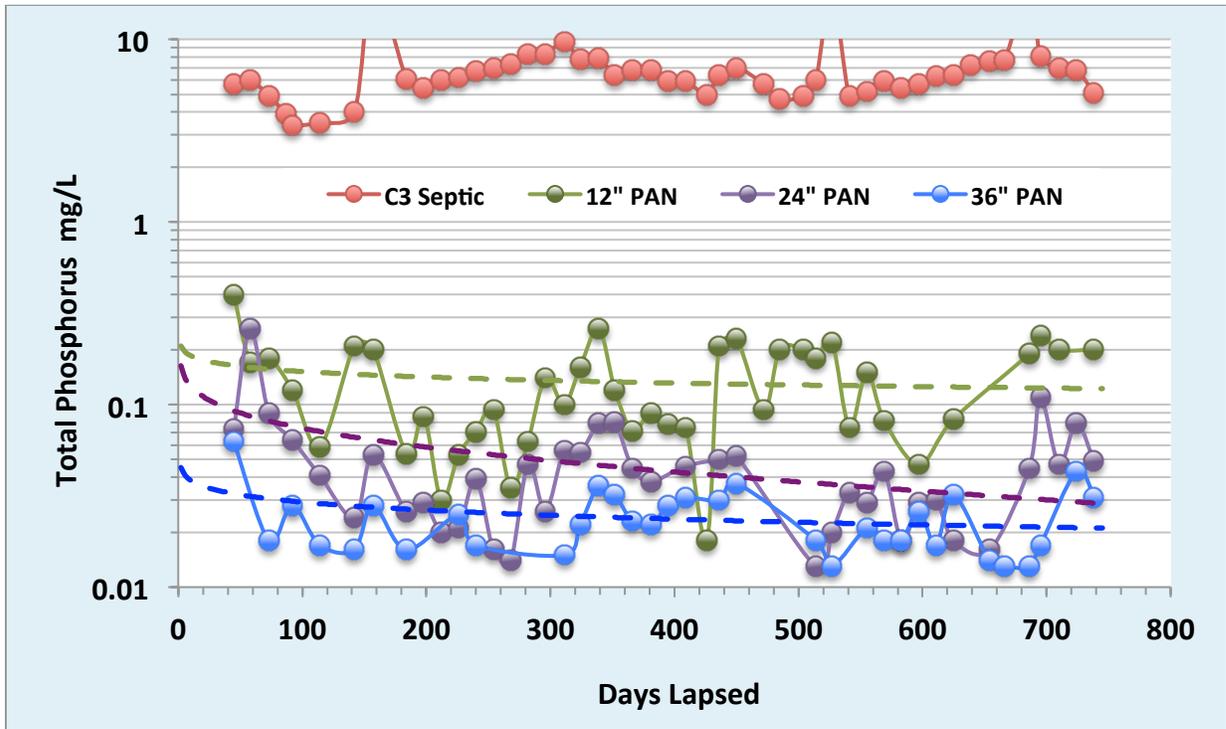


Figure 3. On-going study at Site C3 at MASSTC with *EC-P* in existing septic tank for removal of phosphorus in a soil leach field.

The *EC-P* unit can be retrofitted into existing conventional sand and soil leach fields with minimal disturbance. In Minnesota, two residences had the *EC-P* retrofitted into existing pump chambers leading to standard sand leach fields with pan lysimeters installed. A third house had a pan lysimeter installed as a control. Although septic tank effluent analyses indicate the *EC-P*s are functioning properly, the pan lysimeters have yielded insufficient effluent for analysis. As a back-up, sand samples have been hand-dug from below pipe orifices and are being analyzed at the University of Waterloo to identify minerals formed in the process, using SEM and XRD techniques.

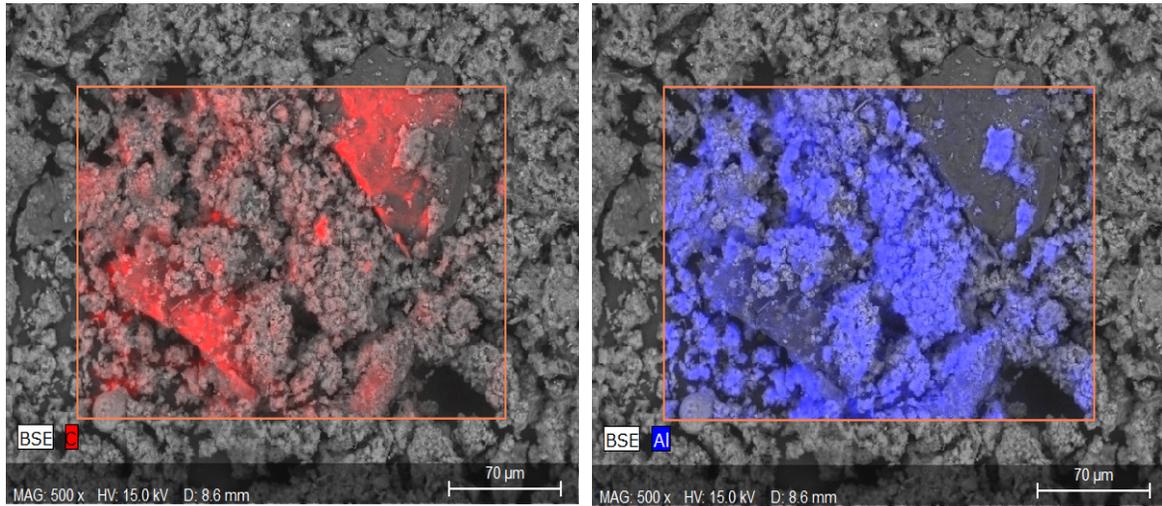
Mineral Identification by SEM Analysis

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 as prescribed in Wu (2014). Both samples were taken at 300 mm (12") depth in the filter medium. Macville School uses an alkali-aluminum chemical to remove phosphorus, while Brisbane School uses the iron-based *EC-P* unit.

The samples were freeze-dried under anaerobic conditions to remove water and prevent oxidation of iron, and analyzed by SEM. Following different attempts at sample preparation, the dried Macville Al-based sediment-sludge was physically knocked from the foam, and the Brisbane foam samples were sliced whole and used.

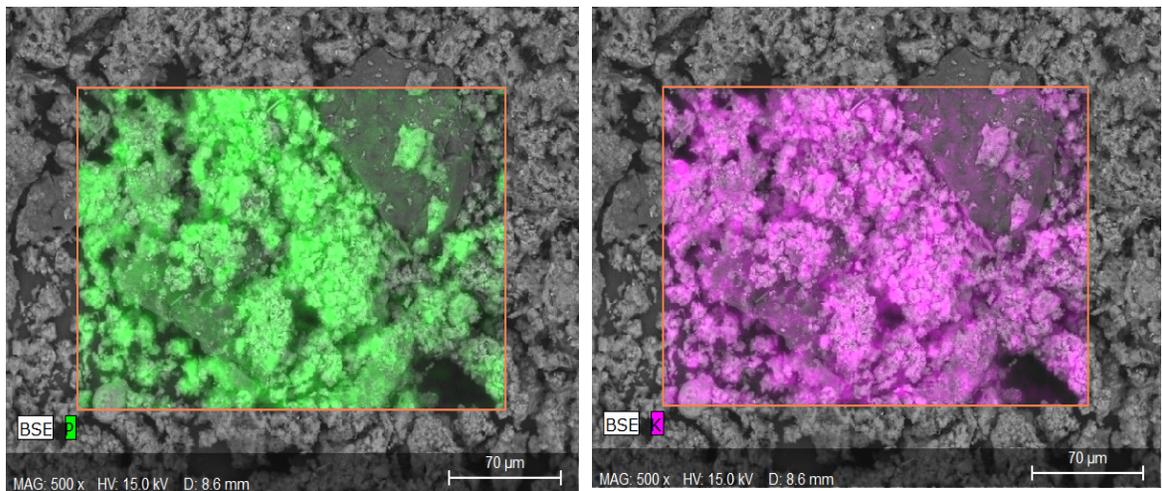
Macville School

SEM analysis shows that Al and P are closely associated with each other in the accumulated solids (Figure 4). Alkali elements and silica are also spatially associated, but C is separated from these other elements. Point scan analysis of a P-rich area in center-right area of Figure 4c (~25 μm diameter) shows Al:P ratio of 4.7, with substantial alkalis and silicon (Figure 5).



a. Carbon

b. Aluminum



d. Phosphorus

c. Potassium (also Na, Ca, Si)

Figure 4. SEM element maps of filtration solids show close association of Al and P, as well as K, Na, Ca, Si, indicating potential Al – P mineral formation. Colors are arbitrary.

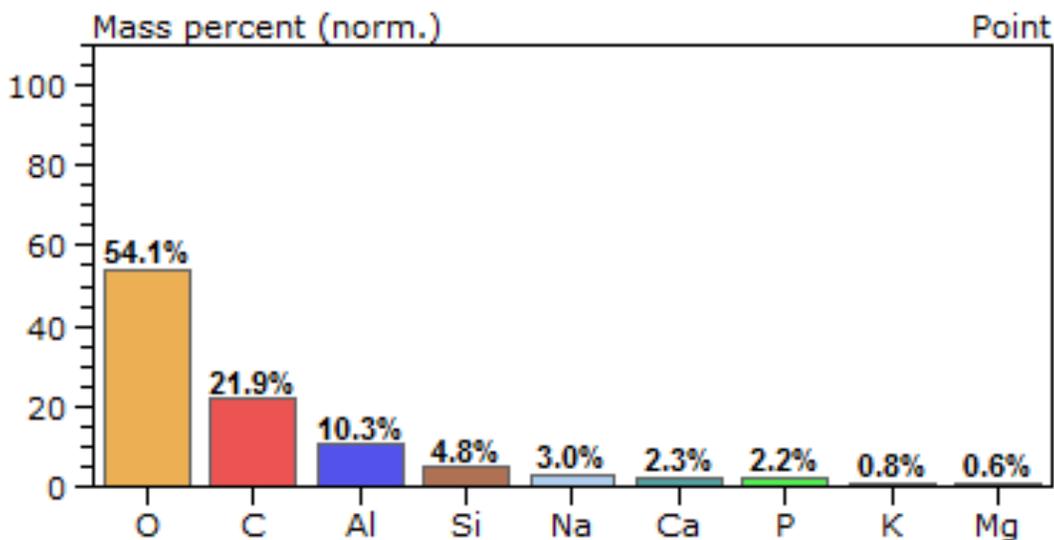


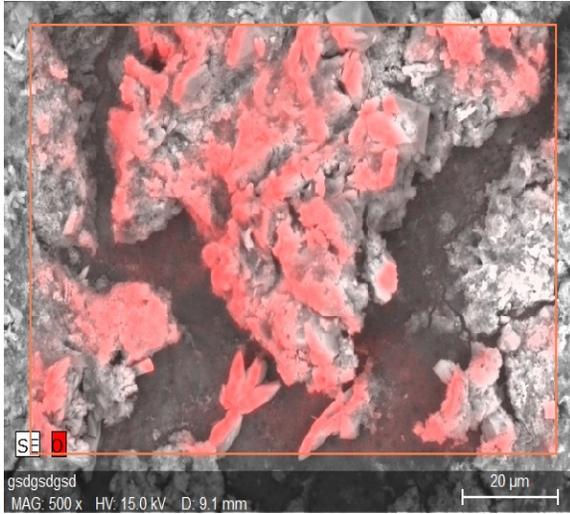
Figure 5. SEM analytical point scan (~25 μm) of P-rich zone in Figure 4 shows Al – P concentrations, along with associated alkalis.

Substantial carbon is present in the scan but most carbon is not associated with P (Figure 4a). The Macville sample showed no crystalline forms for Al – P although there may be unconfirmed small calcium-rich crystals.

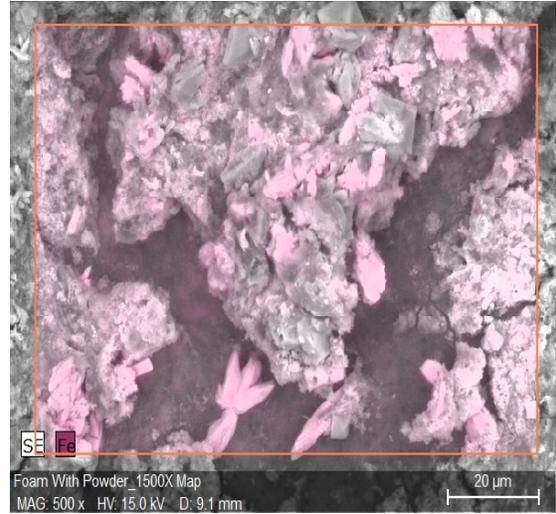
Brisbane School

In the Brisbane samples, Fe and P are closely associated with each other, while Ca is distributed separately from those two elements (Figure 6). Na is in the amorphous phase. The Fe:P molar ratio is always greater than 3:2, which supports the possibility that vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ formed during the *EC-P* Fe treatment.

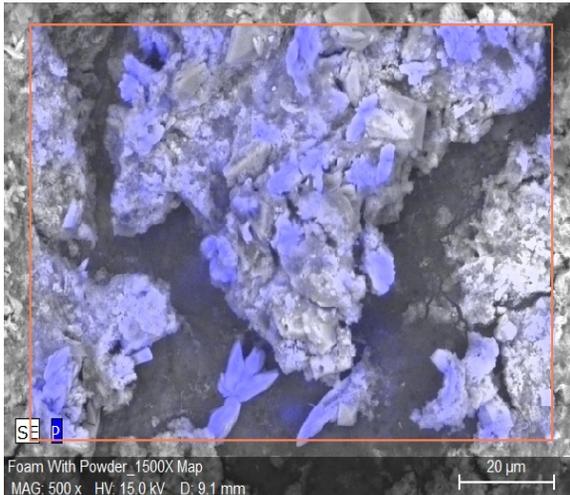
SEM scans found bladed crystals rich in Fe and P (Figures 7a, b) that share the vivianite prismatic crystallinity. It is noteworthy that Fe – P crystalline minerals are found in that it indicates a reasonable <18-month time line for mineralization. Equant tetrahedral crystal forms rich in Ca are also found (Figures 8a, b), and are likely the calcium oxalate weddelite precipitating in the foam. (XRD has now determined that vivianite and weddelite are present.)



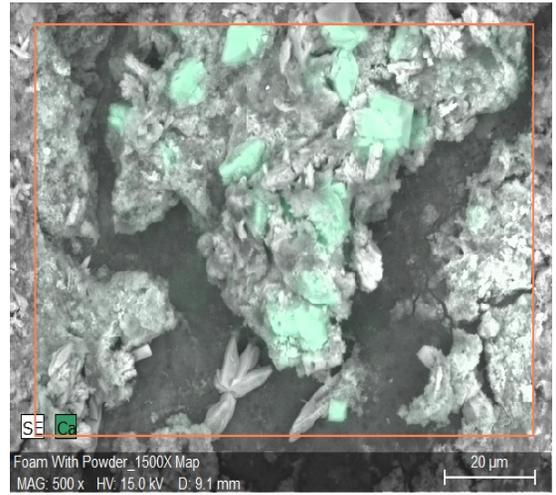
a. Oxygen



b. Iron

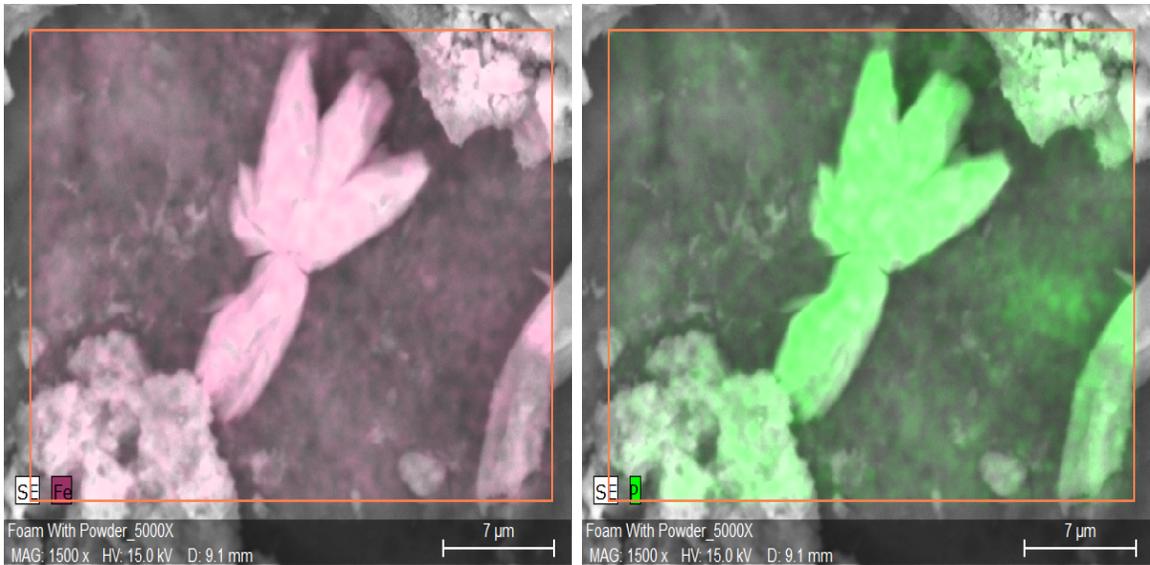


c. Phosphorus



d. Calcium

Figure 6. SEM element maps of Brisbane School medium showing close association of Fe and P, but not Ca, indicating potential Fe-P mineral formation. Oxygen is associated with Fe, P and Ca.



Iron

Phosphorus

Figure 7a. SEM element mapping of Fe-P rich crystals with bladed prismatic form (likely vivianite as identified in XRD analysis), visible in the lower middle of Figure 6.

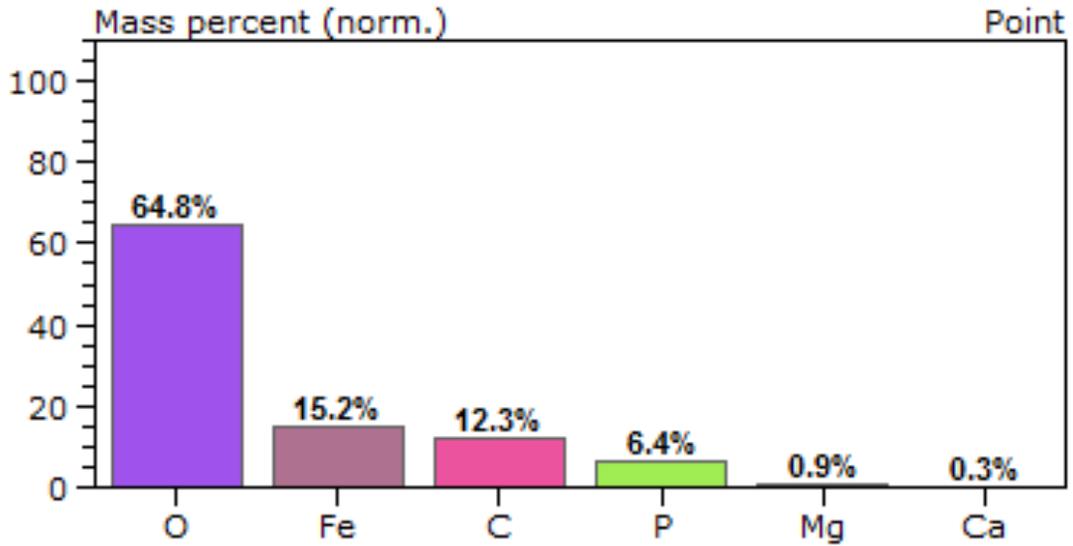


Figure 7b. SEM analytical point scan (~5 μm) of the Fe – P crystalline form in Figure 7a shows Fe – P concentrations, indicating Fe-PO₄ mineralization, potentially vivianite, but which has now been confirmed by XRD.

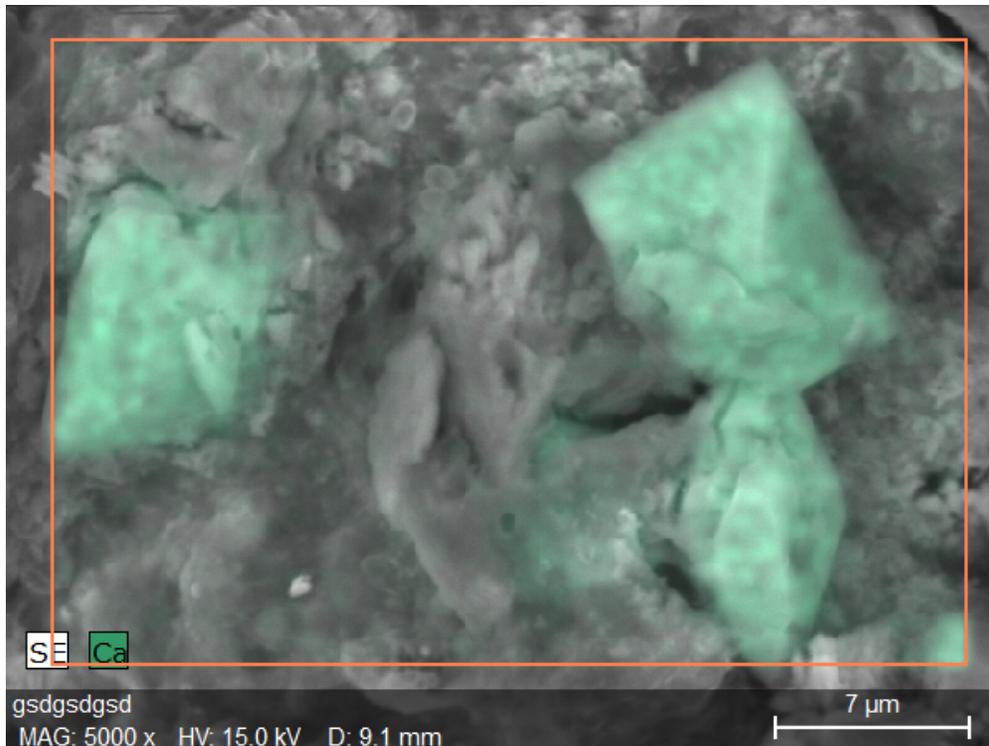


Figure 8a. SEM element mapping of the Ca-rich grains with apparent tetrahedral crystalline form, visible in the upper middle of Figure 6.

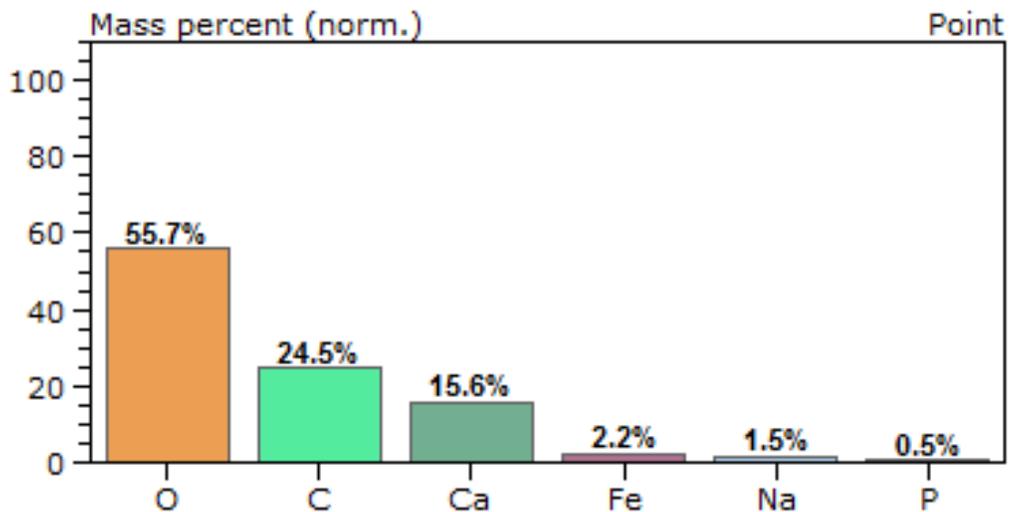


Figure 8b. SEM point analytical scan (~5 μm) of the Ca crystalline form in Figure 8a shows Ca – C – O concentrations, with low Fe & P, likely weddelite CaC_2O_4 mineralization, now confirmed by XRD (see below).

Mineral Identification by XRD Analysis

Brisbane School

Smears of accumulated solids from Brisbane were prepared by anaerobic freeze-drying and analyzed by x-ray diffraction (XRD) technique to determine crystallinity and identify precipitated minerals. Due to the small quantity of material, a series of 1-hour scans over 24 hours was carried out to remove background interference and accentuate distinguishing peaks.

Results indicate no calcite or dolomite crystals but do verify calcium oxalate crystals known as weddellite $\text{CaC}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$, which has a tetragonal crystal habit similar to the Ca-rich crystal in Figure 8a. It is found in urinary tracts as ‘kidney stones’, in sea floor mud, and in peat sediments. Also verified were bladed crystals of the ferrous Fe – P mineral vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, as anticipated in Xu (2010) and Jowett et al. (2013). Both minerals are hydrated and both form in oxygen-poor environments. These XRD scan output results are depicted in Table 1 and Figure 9.

Table 1. Pattern list of XRD scan of Brisbane filtered solids identifies the calcium oxalate weddellite and Fe- PO_4 mineral vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$.

Visible	Ref. Code	Score	Compound Name	Displacement [$^{\circ}2\text{Th.}$]	Scale Factor	Chemical Formula
*	98-003-0783	59	Weddellite	0.000	0.648	$\text{C}_2 \text{H}_{4.75} \text{Ca}_1 \text{O}_{6.375}$
*	98-003-0645	22	Vivianite	0.000	0.248	$\text{H}_{16} \text{Fe}_3 \text{O}_{16} \text{P}_2$

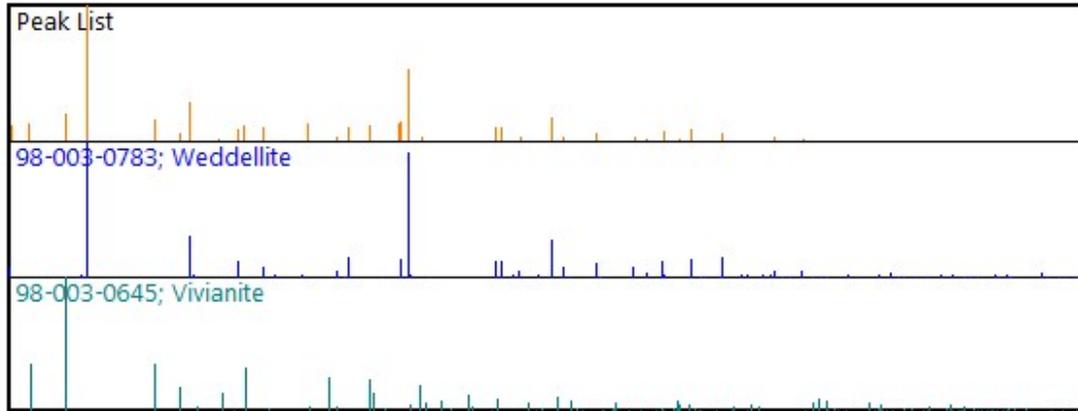


Figure 9. XRD peak scans compared to database scans indicate best estimate as weddellite (hydrated calcium oxalate) and vivianite (hydrated ferrous phosphate) minerals.

The presence of crystalline minerals confirms that there is actual mineral cementation occurring as a result of the *EC-P* technology, and that phosphorus is being tightly bonded within a crystalline structure such as vivianite, and not just loosely adsorbed onto the surface another mineral. Vivianite is very insoluble, with solubility constant in the order of 10^{-29} . This important finding indicates that precipitation of crystalline minerals happens quite quickly, at least within 18 months, and that the phosphorus removed by the *EC-P* process is successfully removed from the hydrologic cycle.

Conclusions

Conventional leach fields using clear sand with no Fe-rich soil can expect to remove about 15 – 30% TP from septic tank effluent. Additional studies are needed to clarify under what conditions the bonds and is susceptible to leaching out.

Phosphorus in filtered effluent was adsorbed onto clear sand in a disposal bed at a school for two years. When the effluent had phosphorus removed, phosphorus was then leached out from the sand and added to the groundwater. After a year of leaching, the low-P effluent passed through the sand without reaction. In this case, sewage phosphorus was loosely bonded onto the sand and was leached out when geochemical conditions changed.

A two-year study using iron-based *EC-P* technology in a conventional septic tank + a soil leach field demonstrates that high phosphorus removals can be attained. More than 98% of the total phosphorus was removed at a depth of 300 mm (12”), and >99% at 600 mm (24”) and 900 mm (36”) depths. Gradual removal with depth suggests phosphorus is being disseminated in the soil rather than being concentrated at the soil-trench surface.

SEM studies of accumulated solids in filtration medium samples indicate formation of Al – P compounds at a school where aluminum-based chemicals are used, but no crystalline forms were evident. Actual crystalline forms of Fe – P minerals were precipitated where the iron-based *EC-P* is used. Preliminary XRD analysis indicates that hydrated crystalline minerals of weddellite and low-solubility vivianite are being formed, indicating that a more sustainable removal of phosphorus from the hydrologic cycle is being attained.

Acknowledgements

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