Sorption of phosphorus released through agricultural runoff and productive recycling using reactive filter materials

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Abstract

This project aimed to use reactive bed filter materials, based on experience in small-scale wastewater treatment, to treat agricultural drainage water to prevent phosphorus (P) loss from tile-drained and ditch-drained land. Short- and long-term bench-scale laboratory and pilot-scale field experiments were performed to evaluate the removal efficiency of filter media under dynamic conditions with simulated and real agricultural runoff respectively. It is concluded that the filter materials Polonite® and Sorbulite® are promising filter media for efficient removal of P from agricultural runoff. In this study total P runoff concentrations varied from about 30 to 1000 μg/L. The average PO_4-P removal efficiency ranged from 11% to 86% depending on the filter runtime. Analyses using XANES showed that the P removed by the filter media was bound Ca phosphate mineral phases. The dominating phase for Sorbulite was apatite (65-70%) but also notable amounts of ACP, OCP and monetite were found. More laboratory testing followed by field experiments are needed to completely evaluate their feasibility for widespread use and the spent material´s suitability for recycling in agriculture. The studied filter materials have good potential for P reduction although their applications in well-designed filter traps should target agriculture runoff with low turbidity and high P concentration.

Introduction

Bed filters filled with phosphorus sorbing materials (PSMs) have become a new option to reduce the load of phosphorus (P) from agricultural land and farm activities (Buda *et al*.,

These PSMs include calcium and aluminum silicate minerals from natural origin and calcium and iron oxides from steelmaking slags, i.e. by-products. We performed short- and long-term bench-scale laboratory and pilot-scale field experiments to evaluate the removal efficiency of certain filter media under dynamic conditions with simulated and real agricultural runoff respectively. The commercial products Polonite® and Sorbulite® aimed for P recovery and recycling were tested in dual filter systems. The light-weight aggregate, Absol, made of aerated concrete, was also used for testing P removal in ditch water.

The low concentrations of P and the occasionally events of peak flow in drainage water is of concern for treatment with reactive filter media. Clogging of filters is a phenomenon that often occurs so the combination of high P sorption and large treatment volumes is a challenge for development of a long-lasting filter. The specific aims of the project were to estimate the P

sorption capacities of selected filter materials and to understand the mechanisms responsible for P removal under the conditions prevailing in agricultural drainage waters.

Materials and methods

The filter materials used in this research were Polonite® and Sorbulite®, both innovated at KTH by Gunno Renman. These are basically calcium-silicate materials. In Sorbulite, a strong crystal structure of tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot H_2O$) appear. The first experiment that took place in Nybble, Jönåker, also included crushed aerated concrete (Yxhult/Svesten AB).

A bench-scale laboratory experiment with a box divided into two chambers and filled with 3 L Sorbulite and 3 L Polonite was fed with phosphate solution (about 0.5 mg/L PO_4-P, from KH_2PO_4 dissolved in tap water)(Fig. 1). Two experiments was performed: 1. Only solution 2. Solution mixed with kaolin clay to a turbidity of 150 NTU. The latter test aimed to simulate the presence and effect of clay minerals in drainage water. The first experiment was also used for testing the P removal capacity during increased flow.

Figure 1. Dual filter test with media Sorbulite (right) and Polonite (left). P-solution was pumped to the system with a loading rate of 3 L/hr.

The field tests took place in Kårsta, Vallentuna and Nybble, Jönåker. Two box experiments were applied in agricultural ditches (Fig. 2) to test Polonite (6 L) during *in situ* conditions at Kårsta. One large-scale, horizontal saturated continuous flow system, filled with Polonite (2-6 mm, 1 m³) and crushed autoclaved aerated concrete (CAAC, 10-70 mm, 4 m³) was tested at Nybble (Fig. 3). CAAC was used in the first purification step because of its suggested ability to remove particles and organic matter, hence improving the conditions for sustained P removal by Polonite. The design water flow through the systems at Kårsta and Nybble was 0.1 and 20 L/min respectively. The retention time (HRT) was for the Kårsta filters 27 minutes and for Nybble filter 2 hours 18 minutes.
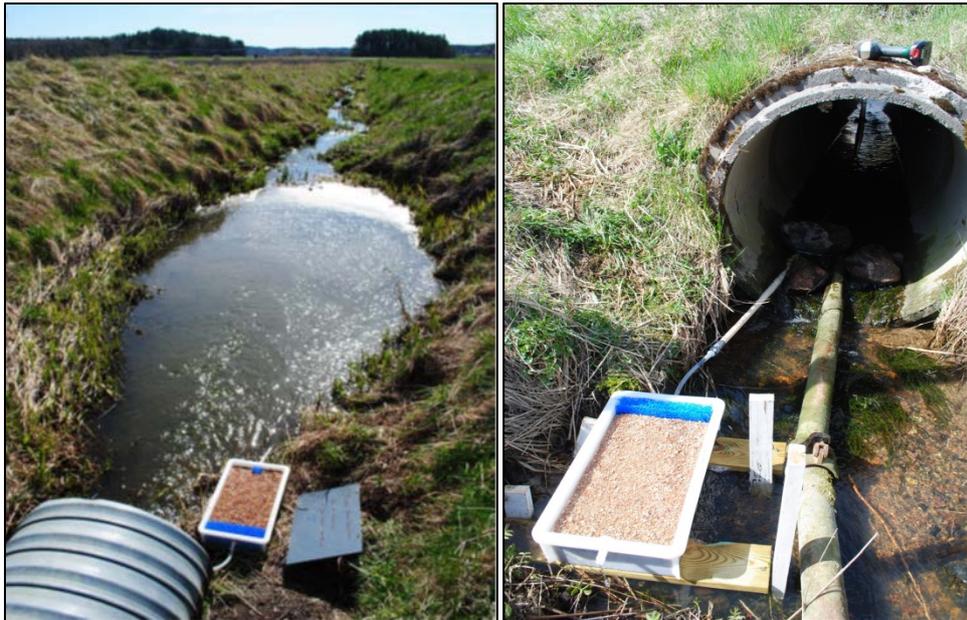
Figure 2. Box experiments applied in two agricultural ditches (Kårsta, Vallentuna municipality) to study P removal capacity of filter materials.

Samples of the filter material were taken after termination of the field experiment at Nybble. The aerated concrete was of particular interest as this material was the dominating media in the P filter and had a visible change in character due to the loading of particulate matter. The samples were ground in a mineral grinder and mounted on Kapton tape and then analysed using P K-edge XANES spectroscopy on beamline BL8 of the Synchrotron Light Research Institute, Thailand (Klysubun *et al*., 2012). The beamline were operated in fluorescence mode and Figure 1. the fluorescence signal was measured using a solid state 13-channel Ge detector. The beam current ranged from 80 to 150 mA. We used an InSb(111) double crystal monochromator with an energy resolution ($\Delta E/E$) of 3×10^{-4} and a dwell time of 3 s. To minimize X-ray absorption by air, the sample compartment was filled with helium gas.
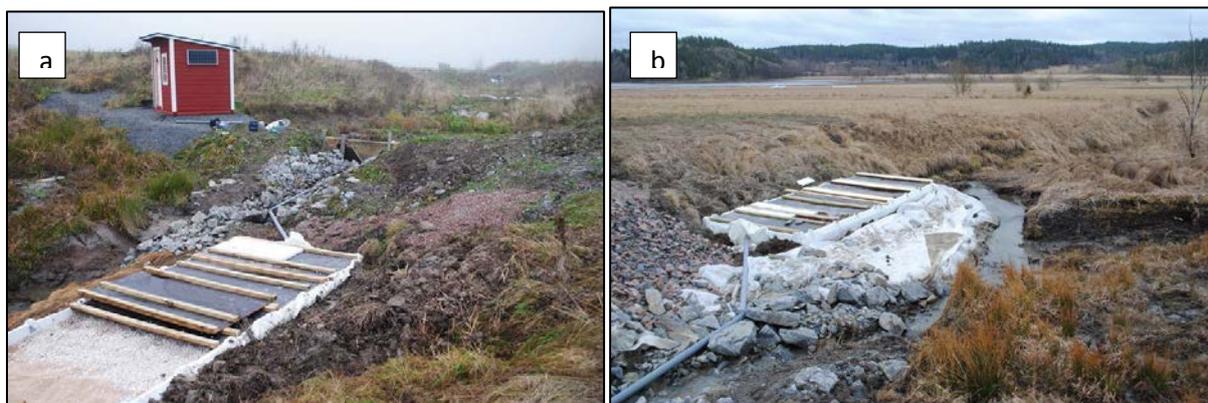

Figure 3. Field experiment at Nybble, Jönåker. Ditch water after treatment in a wetland pond is discharged to the filter through a pipe (a). Water treated in the filter is discharged back to the natural ditch.

The scans ranged from 2100 to 2320 eV with a smaller energy step near the absorption edge (down to 0.2 eV between 2144-2153 eV). Between 3 and 7 scans per each sample were collected depending on the level of noise in the data, and subsequently merged.

The XANES data processing was performed by means of the Athena program in the Demeter Software Package (v 0.9.20) (Ravel & Newville, 2005). The energy was by setting the maximum of the first derivative of the spectrum of elemental P powder to 2146 eV ($\pm$0.11 eV). Correction of any shifts on energy scale caused by monochromator drift could be performed since validation data for variscite (E_0 = 2154.2 eV) periodically were collected. Merged spectra were normalized using a consistent procedure. A linear baseline function was subtracted from the spectral region below the edge (between -30 to -10 eV relative to E_0), and spectra were normalized to unit edge step and quadrature removed across the post-white-line region (between 30 and 50 eV relative to E_0) to obtain normalized XANES spectra.

By means of a linear combination fitting (LCF) approach (Tannazi & Bunker, 2005) a set of spectra of known standards were combined and fitted to the sample spectra. All standards used in the evaluation were characterized by, and XANES data were collected at the same beamline as the samples. The standard compounds included amorphous calcium phosphate (ACP), octacalcium phosphate (OCP), natural apatite, brushite, monetite, amorphous aluminium phosphate, phosphate adsorbed to aluminium hydroxide, phosphate adsorbed to gibbsite, variscite, amorphous iron phosphate, phosphate adsorbed to ferrihydrite, phosphate adsorbed to goethite, strengite, struvite, lecithin and phytate. In the fitting procedure no energy shifts were permitted and the sum of the weighting factors was not forced to one. At most three standards were accepted in each fit and the fitting range was constrained to between -10 to 30 eV relative to E_0.

Results and discussion

Bench-scale laboratory experiment

A total volume of 14 000 liter of tap water spiked with an average concentration of 0.5 mg PO_4-P /L was pumped to the dual filter. The rate of removal vs. pumped volume is shown in figure 4. The average P removal was 52%. In the second experiment, tap water was spiked with the same concentration of PO_4-P but also with kaolin. This turbid water was discharged to the dual filter (fresh material) at a hydraulic loading rate of the same as the previous experiment. The result is presented in figure 5.

The ability of the dual filter to resist peak flows of drainage water in terms of clogging tendencies and P removal was tested. The result is shown in figure 6 a and b.

This experiment showed that a dual filter operated with Polonite and Sorbulite can significantly reduce P at short hydraulic retention time. A filter with only the first-mentioned media would probably reduce more P for the same volume of treated water because of the kinetics with faster release of Ca^{2+}. Turbid water with clay particles will affect the P removal

and lifetime of the filter. Ditch filters without preceding ponds for sedimentation will therefore have much shorter lifetime and the risk for clogging should be noticed.
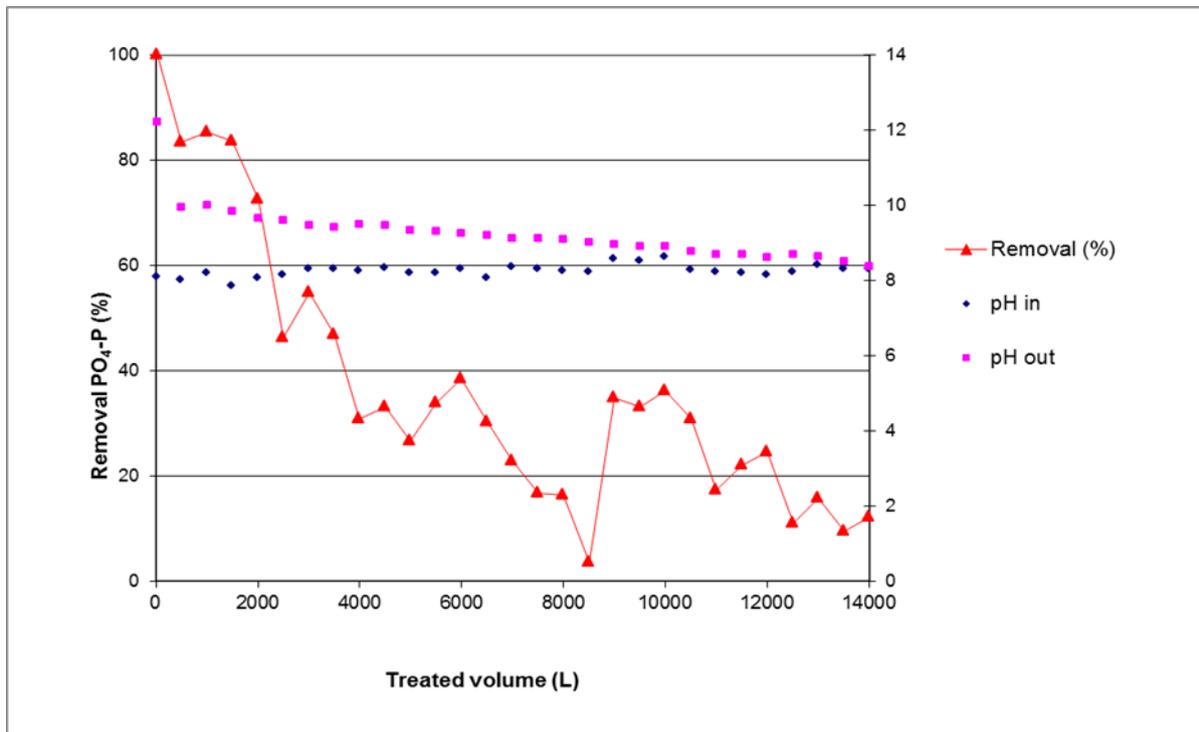

**Figure 4**. Removal of PO_4-P in dual filter and pH of the influent and effluent water.
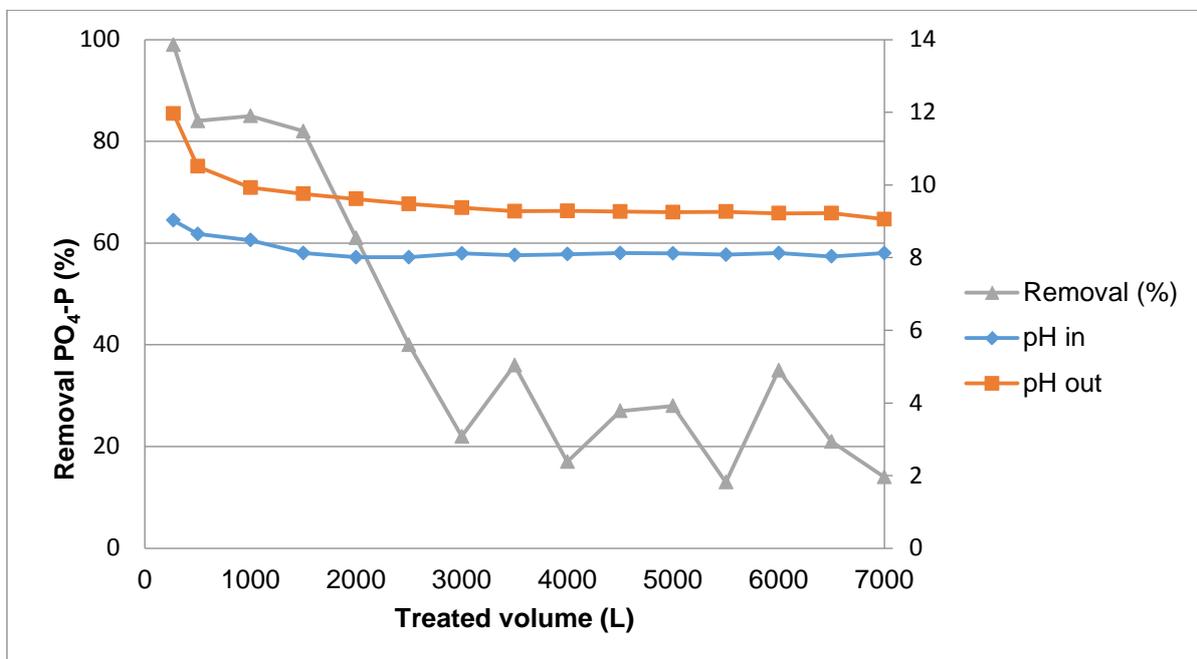
Figure 5. Removal of PO_4-P in dual filter and pH of the influent and effluent water. The water was here spiked with kaolin to simulate the normal turbidity of drainage water (150 NTU).
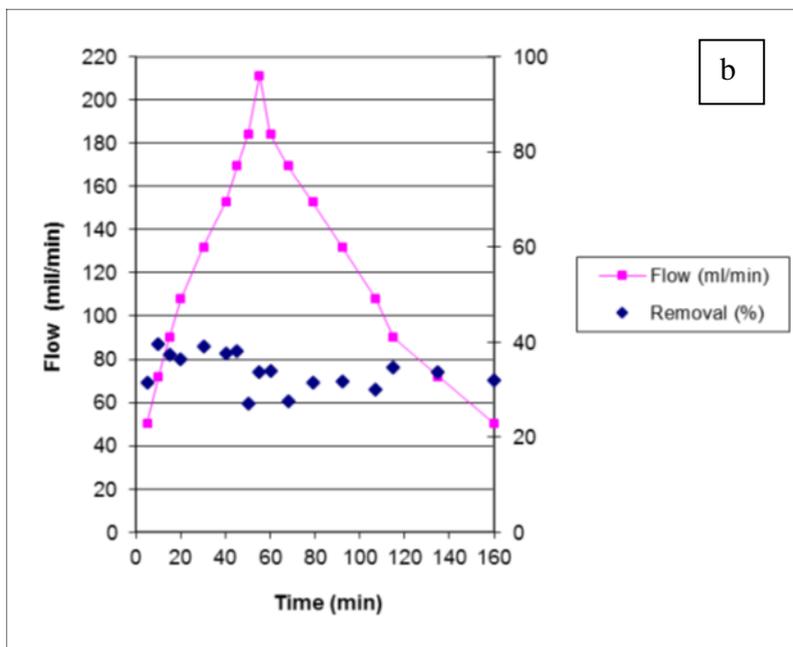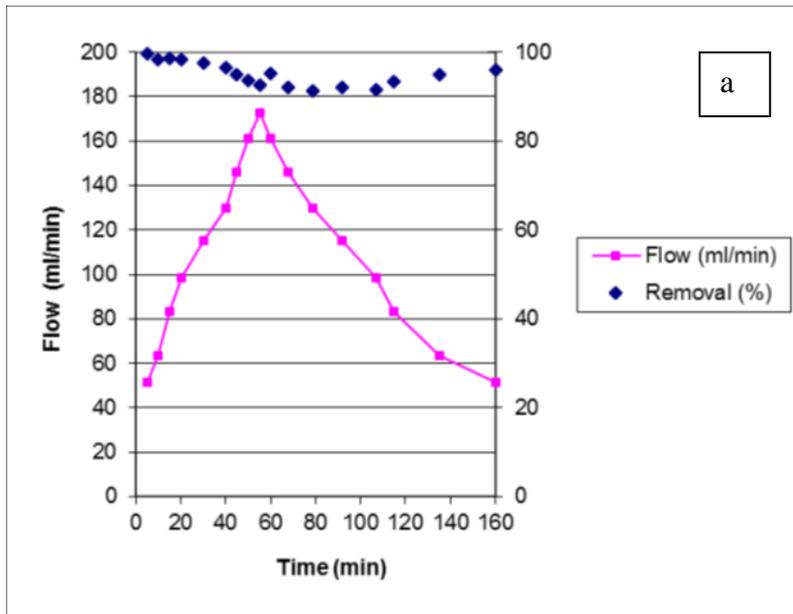
Figure 6. Test of the impact of increasing flow on the P removal efficiency. In fig. 6a the dual filter media is new while in fig. 6b the filter has already treated 4000 L of water.

Ditch filters can be designed according to different criteria. Beside the turbidity of the water, the discharge to the filter is of concern. The results shown in figure 6 indicate that temporary peak flows do not affect the P removal significantly in both scenarios with virgin and exhausted filter materials respectively.

This box experiment was constructed as a serpentine flow system with two compartments of different filter materials. In full-scale application such system could be installed in a ditch as a passive flow system, able to by-pass water during runoff events with extremely high flow.

Experimental ditch filters

The two box experiments (filled with Polonite only) in agricultural ditches at the farm Backa gård, Kårsta, showed promising results. The period of measurement was 2012-05-02 – 2012-10-17. A ditch water volume of about 23 000 L passed through each of the filters (some few days the systems were out of operation due to clogging in the inlet pipes). The influent PO_4-P concentrations in the two ditches were 60.8 ±126 µg/L and 44.9 ±20.1 µg/L respectively. The PO_4-P removal was 86% and 68% respectively. For total-P the corresponding values were 36% and 43%.

The Nybble site where a large-scale, plug-flow system with CAAC was constructed, was operated during four periods from 2011-11-01 to 2013-12-11. In total 8 870 m^3 of ditch water was treated during 308 days. Here the average PO_4-P and total-P concentrations were 65.7 µg/L and 275 µg/L respectively. The average PO_4-P and total-P removal was 11% and 24% respectively.

The small box experiments treated two times more ditch water per unit filter material than the experiment at Nybble. The difference in efficiency can be explained from the fact that the small boxes contained the high P-sorbing Polonite while Nybble was mainly loaded with a very coarse CAAC. There were no big differences in turbidity (about 40 NTU) between the sites which could explain the different P sorption. A higher removal capacity would have been expected if the CAAC was prepared to a particle size similar to that of Polonite.

XANES speciation of P in samples

The mechanisms for P removal and P speciation for Polonite has been investigated in previous research. We analysed one sample of CAAC from the Nybble site which was taken in the inlet zone of the engineered filter. This zone was filled with brown clay particles that were trapped onto the surfaces of the CAAC. One sample was taken from this clay surrounding the filter material (denoted ANy1 in table 1, figure 7). The other sample was prepared from the filter material itself (denoted ANy2).

All samples were dominated by Ca phosphate mineral phases; this is clear both from visual inspection of the stacked spectra (not shown) and from the linear combination fitting results (Table 1 and Fig. 7).

Both ANy1 and ANy2 had post-edge features similar to those of apatite although the post-white line peaks were less intense; this is probably due to the presence of other minor phases. According to the LCF results, which showed close agreement with the data (Table 1 and Fig. 7), ANy1 contained roughly 70 % apatite and 19 % OCP. The dominance of apatite and OCP was consistent among the best fits, and in the best fit, ACP was also present at 11 %. In the case of the ANy2 sample, the secondary phase was not OCP but instead monetite (23 % in the best fit).

Table 1. Phosphorus speciation as evidenced from linear combination fitting of XANES spectra. The five best fits are numbered from 1 to 5 in italics.

Sample		Apatite	OCP	Monetite	ACP	R-factor[a]
ANy1	weight (%)	70±1%	19±2%		11±2%	0.002
	presence	*1,2,3,4,5*	*1,3,4,5*	*2*	*1,2*	
ANy2	weight (%)	65±1%		23±1%	11±1%	0.001
	presence	*1,2,3,4,5*	*2,4,5*	*1,3,4*	*1*	

[a]R-factor calculated according to (Ravel, 2009).
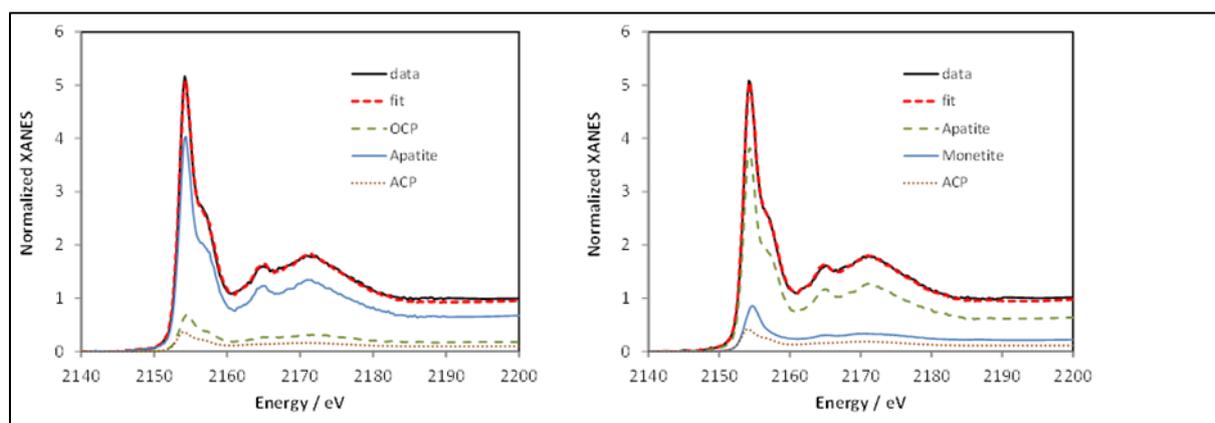
Figure 7. Linear combinations and normalized sample data for ANy1 (upper panel) and ANy2 (lower panel).

Other information and summing-up

The laboratory box experiment with P-solution and the Nybble experiment had temporary breaks. It was observed that the filters during periods of no water flow had ability to rejuvenate. In figure 4 this is demonstrated as a rapid change in removal capacity after treatment of 8000 L of P-spiked water.

Several papers will be published in international journals from the research results that have been briefly presented here.

Further research, including additional laboratory experiments, field pilot tests, economic analysis, is needed to determine if any of the filter materials evaluated in this study have feasibility alone or in combination for widespread use in removing phosphorus from surface and subsurface drainage waters within both small- and large-scale settings.

Acknowledgements

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