Treatment of fish farm sludge supernatant by aerated filter beds and steel slag filters – Effect of organic loading rate

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Abstract

The goal of our study was to develop an on-site cost-effective and extensive method for the treatment of supernatant of the sludge settling silo of fresh water fish farms. The main objectives of this study were 1) to determine the effect of the organic loading rate (OLR) on organic matter and nutrient removal efficiency of a pilot treatment system consisting of a series of aerated filter beds (AFBs) and electric arc furnace steel slag filters operated at different void hydraulic retention times (HRT_V), 2) to validate the P-Hydroslag model as a design tool for slag filters and 3) to propose preliminary design options for fish farm sludge treatment. The 11.5 month experiment was divided into two phases: Phase 1 (P1) of 8.5 months with a low OLR to the AFBs of 0.015 kg BOD_5 m^{-3} d^{-1}, and Phase 2 (P2) of 3 months with a high OLR of 0.5 kg BOD_5 m^{-3} d^{-1}. The results showed that the OLR affected the organic matter mineralization and nitrification efficiency of AFBs. With a low OLR and an influent COD concentration of 320 mg L^{-1}, an average COD removal efficiency of 95% was observed while with a high OLR and an influent COD of 5400 mg L^{-1}, an average COD reduction of 65% was achieved. Due to the high OLR during P2, no nitrification took place probably due to the low availability of oxygen in the AFBs. The TP removal efficiency of the AFBs was 50% during P1 (influent of 5.2 mg L^{-1}), and 88% during P2 (influent of 110 mg L^{-1}). All SCs showed a high o-PO_4 removal efficiency of >98% during P1 (average influent of 1.8 mg P L^{-1}, effluent of 0.04 mg P L^{-1}) and >85% during P2 (average influent of 8.7 mg P L^{-1}, effluent of 0.65 mg P L^{-1}) with a decrease in efficiency only observed over time in the SC that received the highest organic loading rate. It was concluded that with optimal loading rates, this compact biological and physicochemical semi-extensive treatment system offers a promising alternative to the high energy demand and maintenance treatment systems for organic matter and phosphorus removal, and that this treatment system could be applicable to other agro-environmental, municipal or residential effluents.

Keywords: aeration, calcium-rich, phosphorus, precipitation, reactive filter material, steel slag

1. Introduction

Fresh water trout farms discharge a significant amount of polluting nutrients, estimated to be for ammonium between 100-150 g N d^{-1} per ton of annual fish production and for orthophosphate (o-PO_4) between 20-60 g P d^{-1}per ton (Boaventura et al., 1997). The main source of P in trout farms is raw sludge that is composed of fish excreta, uneaten food and fish carcass debris, and contains 30–84% of the total P discharged from fish farms (Lefrançois et al., 2010). Fish farms in Quebec, Canada are required to limit their global P discharge to the environment to 4.2 kg P per ton of fish produced, according to the Sustainable Development Strategy for Freshwater Aquaculture in Quebec (i.e. STRADDAQ). The commonly used approach to reduce pollutants from the effluent of fish farms is by separating the solids from water through physical settling (Cripps and Bergheim, 2000). Once collected and settled, however, fish sludge still presents environmental problems mainly due to the management of the nutrient-rich sludge supernatant. Due to their remote location and relatively small volume of sludge supernatant (e.g. from 10 to 250 m^3 d^{-1} in the fish farm of this study) the use of conventional intensive treatment systems is not commonly used. Therefore, more ecological, economically beneficial and low maintenance treatment options have to be found with the main goal of reducing P discharge.

Several studies (Comeau et al., 2001; Drizo et al., 2006; Chazarenc et al., 2010; Pratt and Shilton, 2010; Puigagut et al., 2011) were conducted to find the best methods for organic matter and nutrient (especially P) removal from fish farm wastewater. One ecological option is to use treatment wetlands (TWs) with filter systems as has been done for various types of wastewater from mainly domestic but also industrial, mining, agricultural, landfill leachate origins (Kadlec and Wallace, 2009). Common TW technologies, however, require large land area that is not always available. Furthermore, there are several constraints that derive from using TWs in cold climate conditions. One key element for efficient organic matter and nitrogen removal in TWs is the supply of oxygen that is needed for aerobic microbial processes. To address this issue, several studies have been done with intensified (i.e. engineered) TWs that use forced aeration (Muñoz et al., 2006; Nivala et al., 2013; Ouellet-Plamondon et al., 2006; Vymazal, 2011).

In TWs, phosphorus is mainly precipitated in or sorbed onto filter media (Kadlec and Wallace, 2009). A sustainable solution could be to use reactive filter units containing replaceable material with a high P binding capacity (Brix et al., 2001; Drizo et al., 2006; Kõiv et al., 2010; Shilton et al., 2006). High P removal efficiency has been shown through calcium (Ca)-phosphate precipitation using reactive filtration in Ca-rich alkaline filter materials (Liira et al., 2009; Claveau-Mallet et al., 2012, 2014). Potential materials for P precipitation include high Ca content industrial by-products such as metallurgical slags and ashes, in which Ca occurs in CaO form (lime) and/or Ca-silicates (Vohla et al., 2011).

As determined by the toxicity characteristic leaching procedure TCLP (U.S. Environmental Protection Agency, 1992) only non-hazardous filter materials should be selected for wastewater applications. Slags from 58 mills in the U.S. were tested and it was shown that although the total concentration of some metals in slag may be elevated, they remained tightly bound to the slag matrix and were often not readily leachable (Proctor et al., 2000). In current study electric arc furnace steel slag from Quebec, Canada was used and it has been considered as safe material according to TCLP procedure.

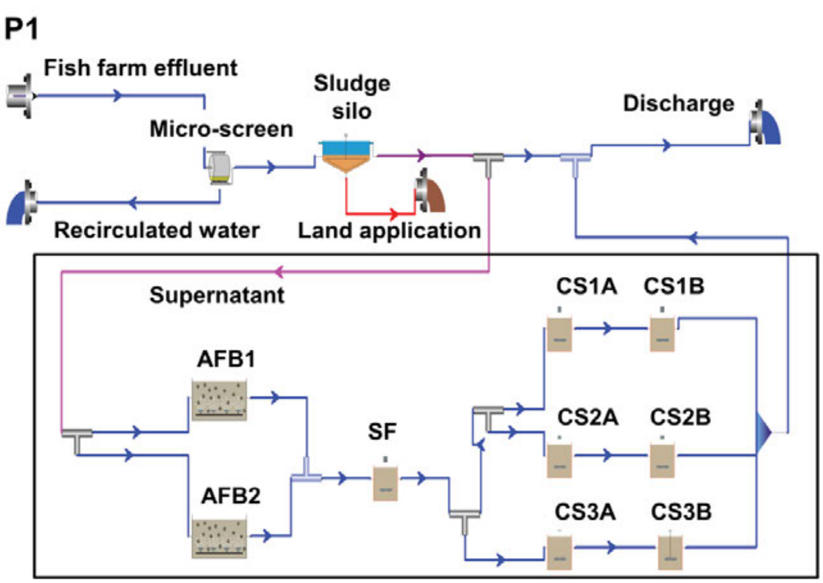
With reactive filter materials, appropriate biological pre-treatment for removing solids, organic matter and nutrients is crucial to provide a long lifetime of the reactive media by decreasing the risk of clogging and permitting the use of finer reactive filter media with higher P sorption capacity (Hedström, 2006). Phosphorus sorption sites may be blocked by organic matter or sorption may be reduced by competitive sorption of organic anions or by metal complexation (Nilsson et al., 2013). Supersaturation of pore water with respect to Ca and o-PO_4 is essential for the precipitation of stable Ca-phosphate phases (House et al., 1999; Liira et al., 2009).

The goal of our study was to develop an on-site compact, cost-effective and environmentally friendly method for the treatment of the supernatant of fish farm sludge settling silos. The main objectives of this study : a) to determine the organic matter and nutrients removal efficiency of a pilot treatment system consisting of a series of aerated gravel filter beds (AFBs, as a replacement for an aerated TW) and electric arc furnace steel slag filters; b) to determine the effect of loading rate on performance; c) to determine the effect of void hydraulic retention time (HRT_V) on o-PO_4 removal in slag filters; d) to validate the P-Hydroslag model as a design tool for slag filters; and e) to propose preliminary design options for fish farms.

2. Material and Methods

2.1. Site description

An on-site pilot experiment (Fig. 1) for the treatment of the supernatant from sludge settling silo (i.e. reservoir) was established in 2010 at the "Ferme Piscicole des Bobines", a fresh water trout farm in East Hereford, Quebec, Canada that ran for a total of 11.5 months. In the Bobines fish farm, there is a total 40 interior fish tanks. The water used (10 000 to 20 400 m^3 d^{-1}) originates from fresh groundwater (15%) and from microscreened recirculated water (85%).



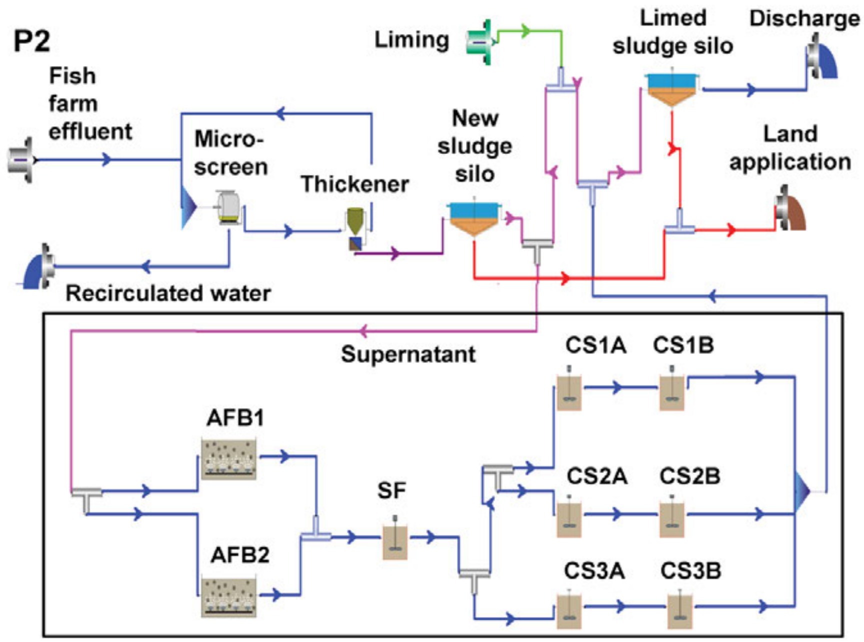


Figure 1. Schematic diagram of the fish farm treatment system and experimental system during Phase 1 (P1) and Phase 2 (P2) when the sludge supernatant contained a low (P1) or a high pollutant (P2) concentration. Abbreviations: AFB1 and AFB2 – two parallel aerated filter beds; SF – sacrificial slag filter; SC1A+SC1B, SC2A+SC2B, SC3A+SC3B – three parallel dual-stage steel slag columns with different void hydraulic retention times.

In 2010 and 2011 (during P1), about 250 m^3 d^{-1} of screenings were collected and stored in a settling silo of 250 m^3 with an HRT of about one day (Fig. 1). During the winter and spring of 2012 (just before P2), a sludge thickener, a new settling tank and a liming system for P removal were added. This new installation reduced the flowrate of concentrated sludge from 250 m^3 d^{-1} to about 10 m^3 d^{-1} and increased its pollutant concentration. The supernatant of the new sludge thickener (~240 m^3 d^{-1}) was returned to the microscreen and the thickened sludge (~10 m^3 d^{-1}) was sent to a newly built sludge silo with a volume of 370 m^3 providing an HRT of 37 days. After settling in the new sludge silo, the highly concentrated supernatant was limed for P removal and then stored in silo for limed sludge. Two times per year the thickened sludge from the new sludge silo and the limed sludge were spread on agricultural land for fertilization and land amendment (Fig. 1).

2.2. Experimental design

The experimental treatment system was composed of two parallel downflow saturated aerated filter beds (AFBs) followed by a sacrificial slag filter (SF) and three parallel dual-stage steel slag columns (SCs; Fig. 1). An insulated truck trailer was used to install the experimental system to avoid freezing during winter periods.

The main design parameters of the experimental filter units are summarized in Table 1.

Table 1. Summary of design parameters of the experimental filter units in Phase 1 (P1) and Phase 2 (P2). Abbreviations: AFB1 and AFB2 – two parallel aerated filter beds; SF – sacrificial slag filter; SC1, SC2, SC3 – three parallel dual-stage steel slag columns.

Design parameters	**Units**	**AFB1, AFB2**	**SF**	**SC1, SC2, SC3**
Water flow conditions		saturated downflow	saturated upflow	saturated upflow
Filter size (diameter × height or *length × width × height)	m×m or *m×m×m	*1.0×1.0×1.0 (each AFB)	0.45×0.8	0.3×1.3 (each stage)
Water level in filter units	m	1.0	0.8	1.3
Volume of filter material	m^3 $filter^{-1}$ (*or $stage^{-1}$)	0.90	0.13	*0.095
Filter material		gravel	EAF steel slag	EAF steel slag

Design parameters	Units	AFB1, AFB2	SF	SC1, SC2, SC3
Particle size of material	mm	10-25	P1 SF1 = 20-40 P2 SF2 = 10-30 P2 SF3 = 10-30	5-10
Density of material	kg L^{-1}	2.6	3.6	3.6
Porosity of filter (estimated)	%	38	45	40
Initial void volume	m^3	0.36	0.052	0.038
Void hydraulic retention time (HRT_V)	h	P1 = 48 P2 = 65	P1 = 3.5 P2 = 4.8	P1: 20, 12, 4.5 P2: 30, 15, 6.0 (per stage)
Organic loading rate (OLR)	kg BOD_5 m^{-3} d^{-1}	P1 = 0.015 P2 = 0.50	–	–
Air flow direction		counter-current	–	–

Even though the aerated filter beds (AFBs) are aerated saturated downflow biofilters, the lower design values of trickling filters (Metcalf and Eddy et al., 2014) were used to minimize maintenance of the AFBs. The design criterion chosen was based on a specific nitrogen removal rate per rock surface area (see also Table 3). The AFB effective volume was 0.36 m^3 each and they were periodically fed with sludge supernatant. The aeration system consisted of a porous diffuser that was connected to an air pump with a total air flow rate of 0.15 m^3 min^{-1}. The supernatant treated in both AFBs was combined and then gravity flowed to the airtight upflow sacrificial filter with coarse steel slag (SF; Fig. 1). The main functions of the SF were to capture some inorganic carbon and P to improve the efficiency of the subsequent SCs. During P1, the coarse steel slag in SF was changed after 184 days of utilization to smaller size slag material (see Table 1). For P2, a new and finer steel slag was used (Table 1). For the SF, three periods are used, SF1 (first 184 d) and SF2 (lasting 77 d) both during P1, and SF3 (lasting 77 d) during P2 (Table 1).

The effluent from the SF was pumped to three parallel dual-stage upflow EAF steel slag columns (SC1A+SC1B; SC2A+SC2B; SC3A+SC3B; Fig. 1) which main function was o-PO_4 precipitation. The dual-stage SCs had different HRT_V (Table 1) to determine the effect of hydraulic and pollutant loading rates on the efficiency of the EAF filters. All steel slag units were closed airtight to prevent atmospheric CO_2 dissolution into the high pH water that would result in bicarbonate formation and calcium carbonate precipitation. Gravity flow was favored in the slag columns by installing a venting system connected to a siphon filled with mineral oil to minimize atmospheric CO_2 dissolution while allowing liquid flow.

The onsite pilot experiment was divided into two phases. Phase 1 (P1) lasted from the end of November 2010 to the middle of August 2011 for a duration of 8.5 months. During P1, the sludge supernatant was relatively diluted and the OLR of 0.015 kg BOD_5 m^{-3} d^{-1} to the experimental system was low. Phase 2 (P2) lasted from the end of May 2012 to the end of August for total duration of 3.0 months. During P2 the sludge supernatant was highly concentrated and the OLR was high (0.5 kg BOD_5 m^{-3} d^{-1}). Between the two phases, during rebuilding of the fish farm sludge treatment system, the experimental system was at rest for 9 months with the filter units drained and all slag filters kept airtight.

2.3. Filter materials

Electric arc furnace (EAF) steel slag, a by-product of the steel industry, was used in the experimental filters and was produced by Arcelor Mittal of Contrecoeur, Quebec, Canada and obtained from "Minéraux Harsco", also of Contrecoeur. The tested steel slag has been used also in previous studies (Claveau-Mallet et al., 2012, 2014). Washed gravel (schist) used as a filter media in our aerated filter beds and as a bottom drainage layer in slag filters was obtained from a nearby quarry in East-Hereford, Quebec, Canada. The chemical composition of the EAF steel slag and gravel used in our experiment is presented as supplementary material in Supplementary Table S1.

2.4. Sampling and analytical methods

Samples from the influent and effluent of all filter units and from combined effluent of aerated filter beds (AFB_{cb}) were taken once a week during the whole period of the operation using standard procedures (APHA et al., 2012). Extra samples were taken from the middle of the first slag columns ($SC1A_{mid}$; $SC2A_{mid}$; $SC3A_{mid}$). The chemical oxygen demand (COD), carbonaceous biochemical oxygen demand ($CBOD_5$), total suspended solids, (TSS), volatile suspended solids (VSS), total Kjeldahl nitrogen (TKN), ammonium (NH_4), nitrate plus nitrite (NO_x), total phosphorus (TP), orthophosphate (o-PO_4), calcium (Ca^{2+}), alkalinity and pH were determined according to Standard Methods (APHA et al., 2012). The Statistica 7.0 software was used for data analyses for which a level of significance of α=0.05 was used in all cases. In the "Results and discussion" section, significant differences were outlined when $p < 0.05$ was obtained.

2.5. Numerical simulations

Slag column operation was simulated using the P-Hydroslag model written in the PHREEQC software, using slag exhaustion equations that were determined previously for the "Minéraux Harsco" EAF slag (Claveau-Mallet et al. 2014). The exhaustion equations were adapted to consider 40% porosity, resulting in the following equations (1) and (2):

$$log(k_{diss}) = -0.3688B - 5.46 \quad (1)$$

$$pH_{sat} = 1.71B^2 - 3.835B + 12.44 \quad (2)$$

where k_{diss} is the slag dissolution kinetic constant (M Ca s^{-1}), pH_{sat} is the slag saturation pH and B is the total leached CaO in the slag filter (mol L^{-1}).

Slag column influent solutions were reproduced using chemicals ($CaCl_2$, KH_2PO_4, K_2HPO_4, CaO, NH_4Cl, $NaHCO_3$ and KCl) in the REACTION datablock. Solutions were equilibrated with hydroxyapatite, monetite and calcite in the EQUILIBRIUM_PHASES datablock. Resulting solutions are shown in Table 2. Simulations were conducted for both phases P1 and P2, and for the first columns SC1A, SC2A and SC3A. Simulated and experimental results were compared. Additional simulations using the AFB effluent as column influent were conducted to assess the effect of removing the SF.

Table 2. Composition of simulated influent solutions of the slag columns (AFBs effluent feeding the SF and SF effluent feeding the SCs).

Phase	**pH**	**Ca^{2+}**	**TIC**	**o-PO_4**	**NH_4**	**Alkalinity**
	-	mg L^{-1}	mg C L^{-1}	mg P L^{-1}	mg N L^{-1}	mg $CaCO_3$ L^{-1}
AFB P1	7.19	24.6	13.4	2.42	-	51.6
SF P1	8.27	28.1	13.4	2.42	-	60.3
AFB P2	7.39	23.4	159.8	13.6	210	645.3
SF P2	8.07	30.7	145.2	13.6	210	663.4

3. Results and discussion

During P1, the supernatant from the sludge silo had a composition similar to typical low strength municipal wastewater while it was much more concentrated during P2 (Supplementary Table S2). Standard deviation (SD) values indicate that during both phases the influent concentration of most pollutants was quite variable over time (Supplementary Table S2). The variability was due to the varying amount of solids in the sludge silo with peak concentrations due to the silo being full of solids and in need of cleaning.

3.1. Removal of organic matter, solids and nitrogen

The main functions of the aerated filter beds were to remove solids and to oxidize organic matter and ammonium. During P1, the aerated filter beds (AFB_{cb} – shown as combined effluent) were very efficient in mineralizing organic matter and removing solids (Supplementary Table S2; Fig. 2). Average reductions obtained in the AFBs were 95.3% for COD, 97.3% for BOD_5, 95.8% for TSS and 94.9% for VSS resulting in effluent values of less than 3 mg TSS L^{-1} (Fig. 2). During P2, the degradation of organic matter in AFBs was quite good (Supplementary Table S2; Fig. 2), with an average removal of 65% for COD and 71% for BOD_5 (Fig. 2). However, the AFB effluent COD and BOD_5 values remained high at 1730 and 895 mg O_2 L^{-1}, respectively.

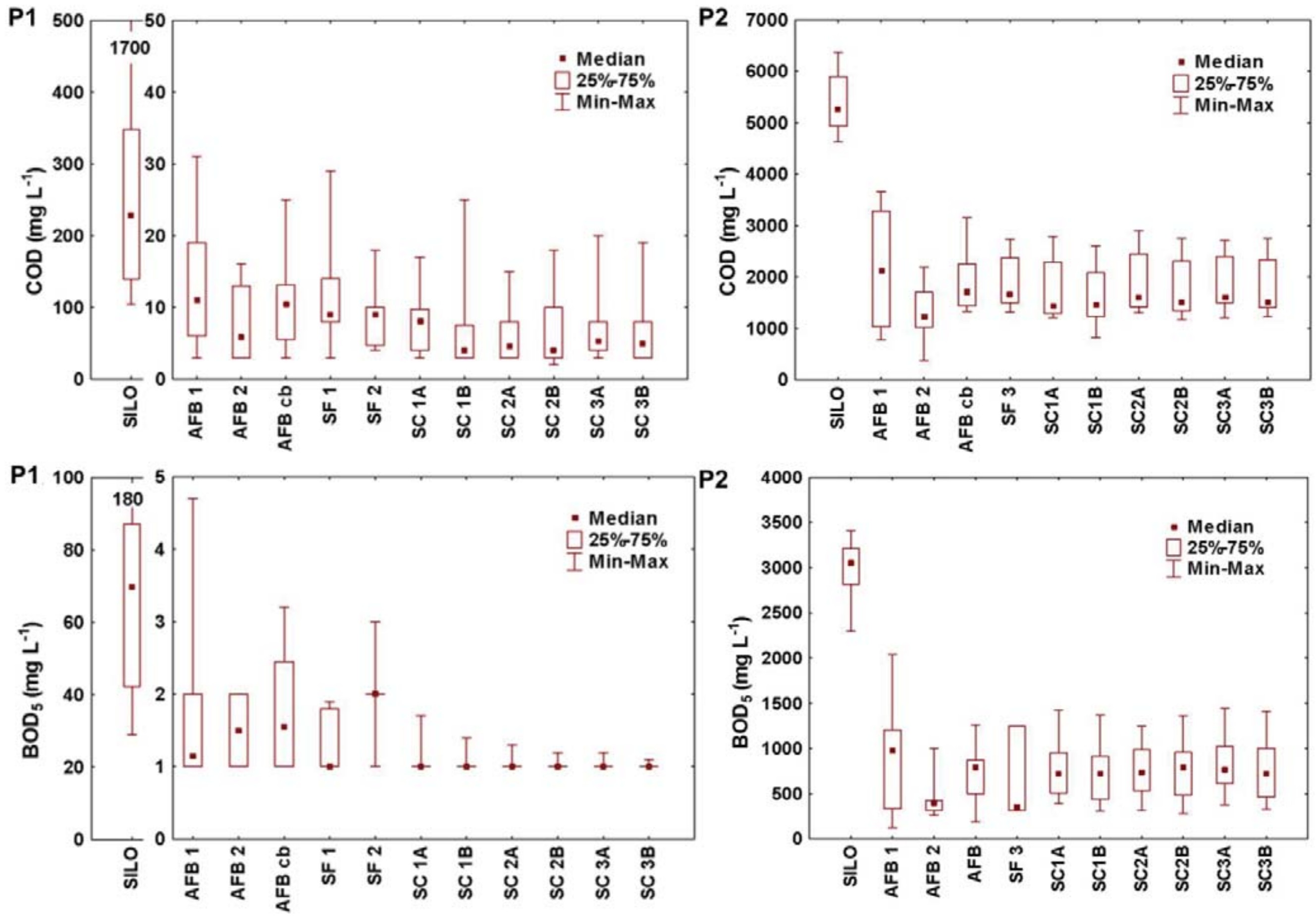


Figure 2. Organic matter removal by the various treatment units (presented as changes in BOD_5 and COD values) during Phases 1 and 2 (P1 and P2) of the experiment. Note: The two AFBs and the three sets of two columns in series of SCs were operated in parallel.

A rapid increase in TSS and VSS concentration from the sludge silo was observed after about 170 days of operation during P1 (Fig. 3) indicating that the sludge silo needed to be emptied. During P2, the effluent from the AFBs had a higher TSS and VSS concentration than the influent, indicating that the AFBs should have been backwashed to prevent excessive solids accumulation. Backwashing could be achieved by sending AFB treated water and air at the bottom of the AFB to clean the bed of excess biosolids, as is typically done for biofilters (Metcalf and Eddy et al., 2014). The recovered solids would then be sent to a settling tank for treatment. With low loaded AFBs, such an operation may have to be done once a month or less.

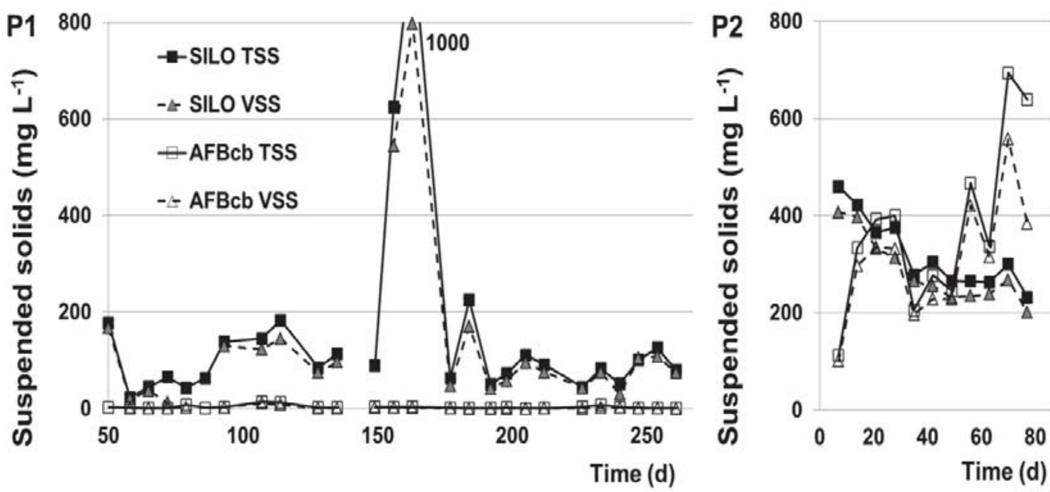


Figure 3. Evolution of total suspended solids (TSS) and volatile suspended solids (VSS) concentration in the combined effluents of the aerated filter beds (AFB_{cb}) effluent during P1 and P2.

Efficient ammonification of organic nitrogen (TKN minus NH_4) and nitrification were observed in the AFBs during P1 (average effluent TKN only 0.9 mg N L^{-1}) as confirmed by the increase of oxidized nitrogen concentration in the effluent (from 0.05 to 5.1 mg L^{-1}, Fig. 4).

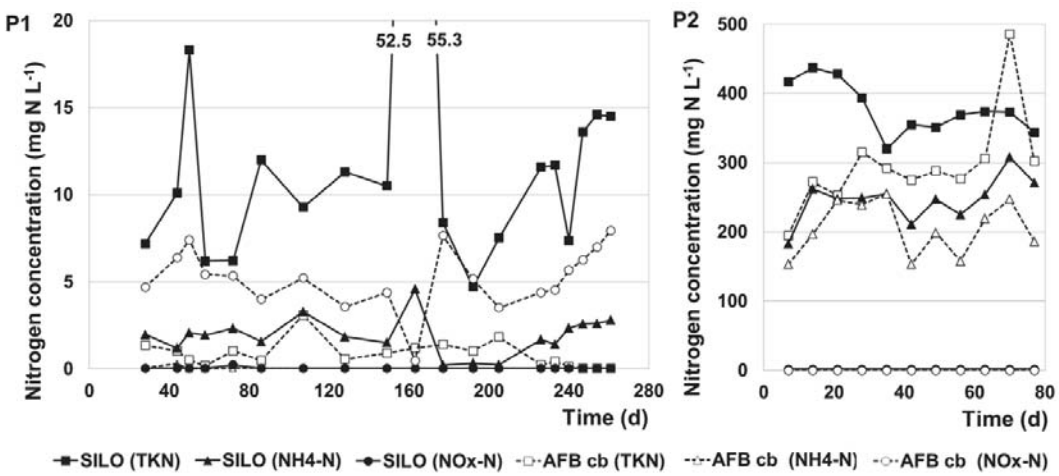


Figure 4. Nitrogen removal and transformation (presented as changes in TKN, NH_4-N and NO_x-N concentrations) in the combined effluent of the aerated filter beds (AFB_{cb}) during Phase 1 and 2 (P1; P2).

During P2, the overall efficiency of TKN removal by the system was 32% of which 20%, on average, was achieved by the AFBs ($p>0.03$; Fig. 4). The AFBs removed only 17% of ammonium and there was no increase in NO_x concentration. This can be explained by the BOD_5 concentration that was too high to allow efficient nitrification (Metcalf and Eddy et al., 2014). In summary, the AFB is suitable technology for sufficient pre-treatment of fish farm supernatant when appropriate loading rates are used (shown in details in Section 3.4).

3.2. Removal of total phosphorus and orthophosphate

The TP removal in the AFBs during P1 was on average 35% (effluent 2.6 mg TP L^{-1}) while the $o\text{-}PO_4$ concentration increased by about 10% due to hydrolysis (effluent concentration 2.4 mg L^{-1}).

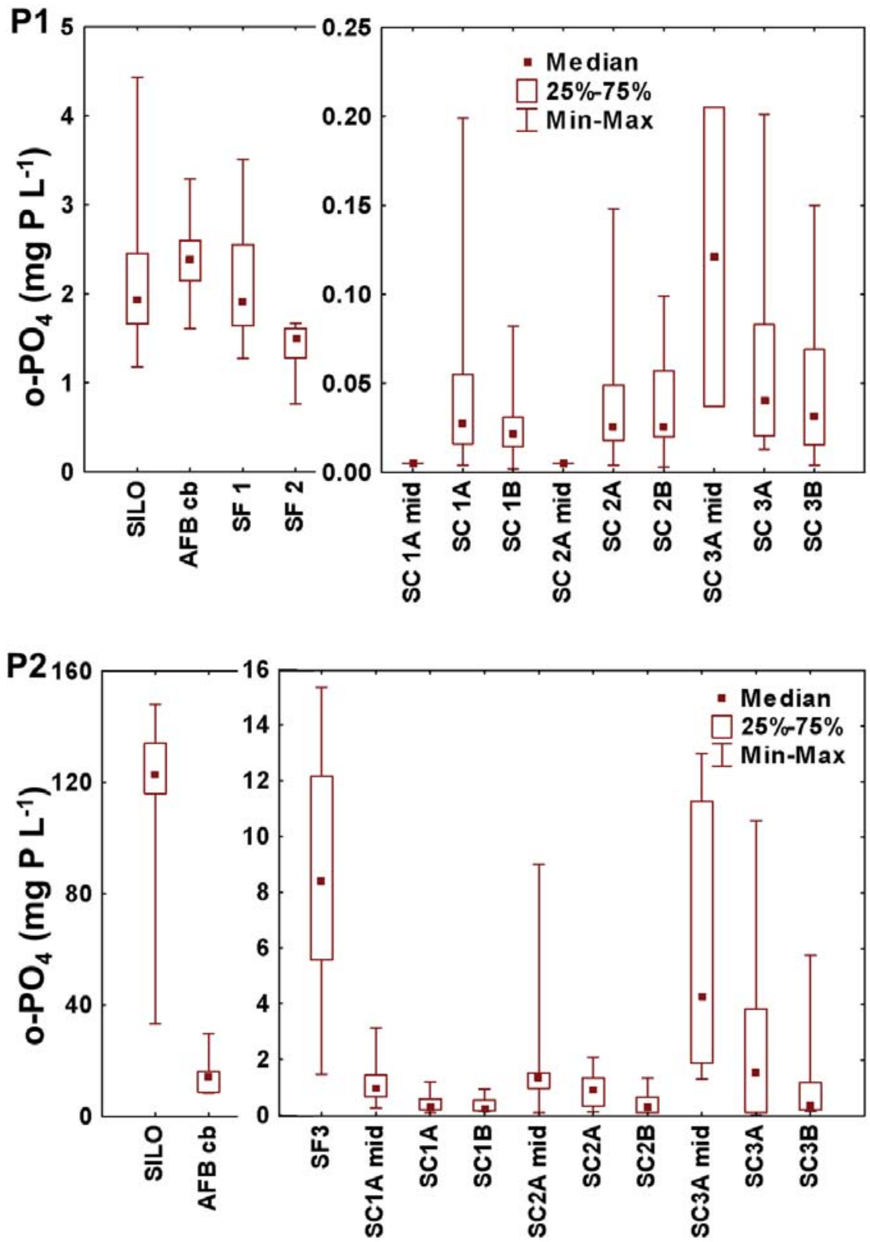


Figure 5. Evolution of orthophosphate ($o\text{-}PO_4$) during P1 and P2 in the filter units.

During P2, an average 78% of TP and 86% of o-PO_4 was removed in the AFBs (Fig. 5). This high efficiency was unexpected and could be attributed to phosphate precipitation with calcium, iron or aluminium ions present in the sludge supernatant. In P2, sludge supernatant had a sufficiently high calcium concentration (145 mg L^{-1} soluble) to induce precipitation. Calcium leaching of the AFBs was also observed in P1.

During P1, the sacrificial slag filter showed an average o-PO_4 removal of only 17% and 34% in SF1 and SF2, respectively (Fig. 5). During P2, the cumulative amount of TP removed and the removal efficiency in SF3 was higher than in SF1 and SF2 during P1 (Fig. 6), with an average o-PO_4 removal of 47%. During P2, the efficiency of SF3 was comparable with SC3A – the slag column that received the highest loading rates during the whole experiment. Similarly to the constant decrease in the TP removal efficiency there was concomitant decrease in the pH value of the effluent from pH 9.0 to pH 8.0. Thus, the SF increased somewhat the pH of the treated supernatant, but contributed only slightly to phosphorus removal.

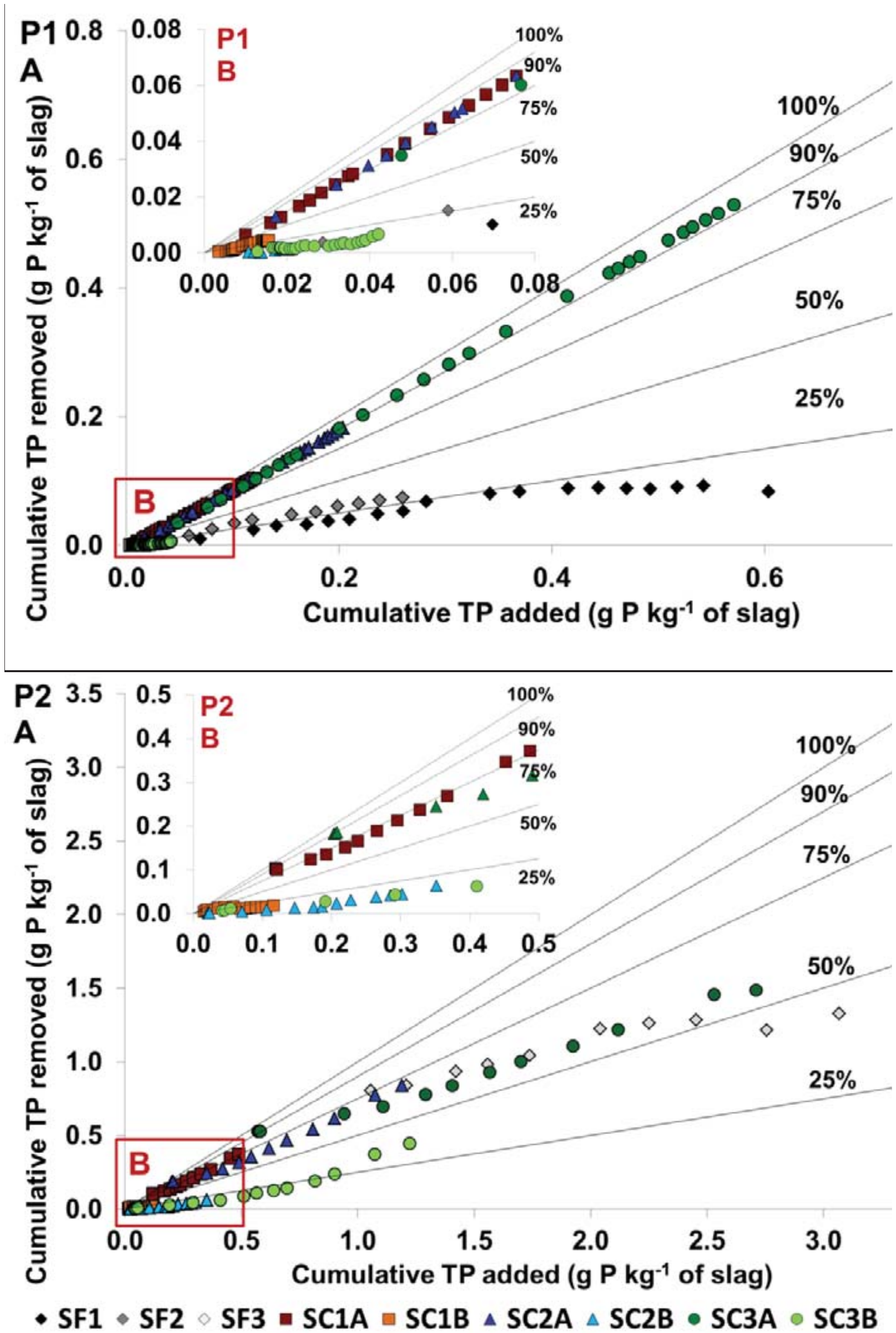


Figure 6. Ratio between cumulative total phosphorus (TP) added and removed in steel slag filters (SF and SCs) during Phase 1 and 2 (P1 and P2). All SCs used during P1 continued to be used during P2, which explains why the first data points at the beginning of P2 (graph B) are not located at the origin of the graph.

3.2.1. Phosphorus removal in dual-stage steel slag columns

All dual-stage slag columns (SCs) removed on average more than 96% of TP during P1 with a stable effluent concentration averaging from 0.10 to 0.17 mg P L^{-1}. During P2, a lower TP removal efficiency of 85-91% was observed. This resulted in an effluent TP of 5.4 to 7.4 mg L^{-1} but a relatively low o-PO_4 concentration of 0.3 to 1.1 mg P L^{-1} (Supplementary Table S2; Fig. 5). Slag columns removed o-PO_4 by Ca-phosphate precipitation (Claveau-Mallet et al., 2012) and particulate P mainly by physical filtration. Particulate P removal could be increased by increasing the HRT_V as this would slow down the water velocity inside the filter material and increase the solids filtration (Claveau-Mallet et al., 2012). As particulate matter can clog slag columns, sufficient pre-treatment is needed to prevent solids accumulation (Hedström, 2006).

During P1, almost all o-PO_4 was precipitated in the first stage of the SCs (e.g. in SC1A >97%), and the final effluent o-PO_4 concentration varied from 0.03 to 0.05 mg P L^{-1} (Fig. 4). There were only slight differences in the final TP and o-PO_4 concentration in between the SCs during P1 even though there was a tendency for the columns with longer HRT_V to remove phosphate a little more efficiently (Fig. 5). The SC3A+SC3B with the shortest HRT_V (4.5 h + 4.5 h) and highest P loading rate had the highest orthophosphate removal efficiency during P1 (96%). Furthermore, the SC3A started to show its first signs of saturation during the last month of operation when the effluent o-PO_4 concentration increased rapidly from 0.03 to as high as 10.6 mg P L^{-1} (see also Fig. 8). In the downstream SC3B the average o-PO_4 removal efficiency during P2 remained above 90% (TP removal 63%), but during last two weeks of operation, the o-PO_4 removal efficiency of this column decreased to 58%.

During P2, the effect of cumulative loading on the SCs efficiency was observed (Fig. 6). Over time, the SC3A+SC3B with higher TP loading removed less TP. During this phase, SC1A+SC1B removed up to 0.4 g P kg^{-1} and SC2A+SC2B a total of 0.9 g P kg^{-1} of slag. The first column SC3A of dual-stage slag filter which received the highest TP loading, removed a total of 1.4 g P kg^{-1} slag.

The effect of HRT_V on the average o-PO_4 removal efficiency in slag filters is shown on Figure 7. The SCs with longer HRT_V had high and relatively stable P removal efficiency during both phases, and an effluent o-PO_4 concentration over 2 mg L^{-1} in SC2A was only observed during the last week of operation. The only slag column that showed significantly lower o-PO_4 removal efficiency during P2 was SC3A. These results indicate that there is a clear effect of HRT_V on o-PO_4 removal especially when a high OLR is applied to the system. At a high OLR, the slag filters should be operated at a minimum HRT_V of 30 hours to ensure efficient o-PO_4 removal.

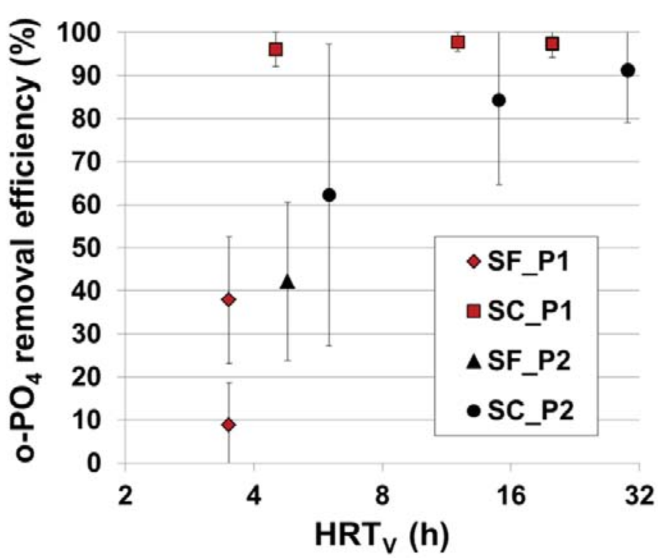


Figure 7. Effect of void hydraulic retention time (HRT_V) on average orthophosphate (o-PO_4) removal efficiency during P1 (red; low o-PO_4 load) and P2 (black; high o-PO_4

load) in sacrificial slag filters (SFs) and dual-stage slag columns (SCs). Error bars denote standard deviations.

The evolution of SCs effluents composition is compared to P-Hydroslag model simulation results on Figure 8. The experimental curves of pH were reasonably well reproduced by simulation, except for SC3A at the end of P2, where the observed pH drop was larger than that simulated. The o-PO_4 simulated curves generally reproduced experimental curves, but they were less accurate during P2. The HRT_V effect predicted by the model was observed in experimental results. The model properly predicted an o-PO_4 concentration over 1.0 mg P L^{-1} for SC3A during P2.

The model also predicted the effect of changing from P1 to P2, and showed that removing the SF did not significantly decrease the SCs performance (solid vs dotted lines on Fig. 8). This result constitutes the first calibration of the P-Hydroslag model with a field-scale application and validates the potential of this model as a design tool. The current version of the model is intended to simulate secondary effluent containing low suspended solids content, as it considers soluble influent only. The model still needs improvement concerning some model assumptions regarding the effect of particulate matter accumulation and the refinement of the methods to measure kinetic parameters. These aspects are included in a forthcoming version of the model (Claveau-Mallet et al., In preparation).

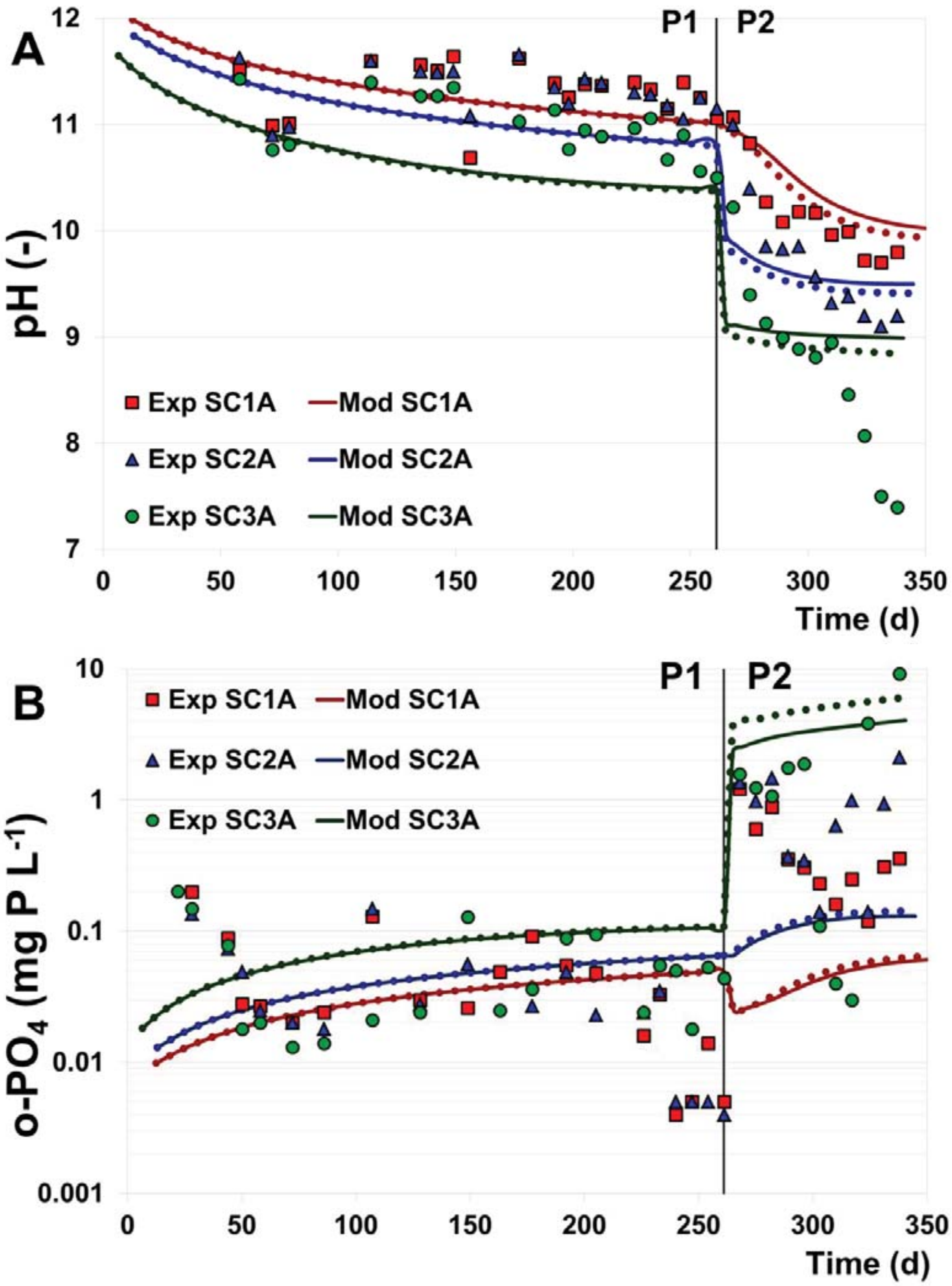


Figure 8. Simulation results of the P-Hydroslag model and comparison with experimental data for A) pH and B) o-PO_4. Simulated curves with sacrificial slag filter (SF; solid lines) and without SF (dotted lines) are shown.

A longer HRT_V should improve the contact between the substrate and the wastewater and increase P removal. Liira et al. (2009) using hydrated oil shale ash, a material with similar removal mechanisms to slag, showed that at a long HRT_V, a dense and tightly packed layer of acicular calcite crystallites forms that gradually covers the entire surface of the particles. As a result, the dissolution of Ca is inhibited, and the phosphate precipitation decreases.

From experimental results and according to numerical simulations, it was confirmed that the HRT_V plays a central role in the long-term operation of slag filters. Previous research (Shilton et al., 2006; Vohla et al., 2011) showed that slag filters are capable to precipitate much higher amounts of o-PO_4 than observed during this experiment (e.g. P retention capacity of EAF slag 6.4 g P kg^{-1} of slag; Claveau-Mallet et al., 2012). Such high capacity was achieved in batch and lab-scale experiments with a synthetic P containing feed and there are only few studies done with onsite and full-scale systems during extended periods of time. Shilton et al. (2006) presented results of full-scale treatment plant with reactive steel slag filters where an average TP removal efficiency of 77% and a maximum removal level of 1.2 g TP kg^{-1} (total of 20 tons of P removed) of slag were reported during the first 5 years of operation.

In full-scale systems, the HRT_V of the slag filter should be chosen to favour compact crystallization (crystal growth and not formation of new crystal seeds) of Ca-phosphate and to minimize the precipitation of Ca-carbonates (Claveau-Mallet et al., 2012). The minimum HRT_V required to support crystal growth and long-term operation is related to the hydroxyapatite crystal growth rate, which is related to the composition of the wastewater (Claveau-Mallet et al., 2012, 2014). Finding the optimal HRT_V according to the characteristics of wastewater is possible by using the P-Hydroslag model.

3.4. Preliminary design of the hybrid treatment system

Preliminary full-scale design options for the treatment of sludge settler supernatant based on the average composition of the supernatant from “Les Bobines” fish farm during P1 and P2, and experimental results of this study were proposed (see Table 3). For low strength supernatant (P1), the conditions were characterized by a relatively high flowrate (50 m^3 d^{-1}) but a low pollutant concentration that was similar to those of a typical low strength municipal wastewater. For high strength supernatant (P2), the conditions were for a lower flowrate (10 m^3 d^{-1}) but a higher pollutant concentration.

A low-rate AFB (version P1 in Table 3) with nitrification was chosen for supernatant similar to the one used during P1, while a high-rate AFB with recirculation was chosen for wastewater similar to P2. Aeration was provided for BOD_5 and ammonia oxidation for P1 and P2. AFB effluent recirculation was not tested during this experiment but such a mode of operation could improve the treatment efficiency when dealing with high strength wastewater.

A potential alternative for the AFBs when treating a low concentration supernatant could be more passive and low maintenance treatment wetlands (Kadlec and Wallace, 2009). The sacrificial filter with coarse slag used in the experiment was not incorporated in this full-scale design because the SF increased somewhat the pH of the treated supernatant, but contributed only slightly to bicarbonate and phosphorus removal. Furthermore, the simulation results showed that removing the SF did not significantly decrease the SCs performance (Fig. 8).

Table 3. Preliminary full-scale design parameters for the treatment of low (P1) and high strength (P2) supernatant of a freshwater fish farm sludge settling tank, consisting of a) an aerated filter bed (AFB) and b) a reactive slag filter.

Wastewater type		P1 (low strength)	P2 (high strength)
Aerated filter bed			
1) AFB influent data (see Supplementary Table S2)			
2) Objectives			
TKN removal efficiency	%	90	10
BOD removal efficiency	%	80	50
3) AFB design criteria (results from trickling filter design, Metcalf and Eddy et al., 2014)			
Type of AFB		low-rate	high-rate (with recirculation)
Specific surface area in the reactor	$m^2\ m^{-3}$	60	60
Hydraulic loading rate	$m\ d^{-1}$	3.6	1.04
Organic loading rate	$kg\ BOD_5\ m^{-3} d^{-1}$	0.13	1.57
Specific TKN removal rate per rock area	$g\ m^{-2}\ d^{-1}$	0.40	0.33
4) Design values			
Filter volume (empty bed)	m^3	28	19
Filter depth	m	2	2
Filter area	m^2	13.9	9.6
Particle size of material	mm	10-20	10-20
Aeration rate	$m^3\ min^{-1}$	0.83	2.92
Slag filter			
1) Slag filter influent data (see Supplementary Table S2)			
2) Objectives			
P removal efficiency	%	80	80
3) Slag filter design criteria (results from numerical simulations using the P-Hydroslag model)			
Void hydraulic retention time	h	8	30
Longevity	pore volumes	5400	315
	years	5	1
P retention capacity	$g\ P\ kg^{-1}$ slag	4.5	1.7
4) Design values			
Filter volume (empty bed)	m^3	42	31
Filter depth	m	2	2
Filter area	m^2	21	15.5
Particle size of material	mm	5-10	5-10

The reactive slag filter design was based on numerical simulations performed with the P-Hydroslag model. Using the information from this experiment and previous research (e.g. Barca et al., 2012; Claveau-Mallet et al., 2013, 2012; Drizo et al., 2002; Liira et al., 2009; Shilton et al., 2006) it was estimated that during P1, the optimal HRT_V for slag columns should be about 8 h (Table 3). For a more concentrated supernatant as during P2, a HRT_V of 30 h was proposed. The longevity and P retention capacity of slag filters were determined using numerical simulations as previously presented; considering that the filter longevity was reached when the effluent o-PO_4 concentration was above 1 mg P L^{-1}. A safety factor of 2 was used for longevity. The resulting longevity was 5400 pore volumes for P1 and much lower for P2 (315 pore volumes). Longevity expressed in pore volumes allows a more direct comparison of operating conditions of designs of P1 and P2, independently of the HRT_V. The longevity expressed in total time was 5 years for P1 and 1 year for P2. In the latter case, the designer could choose between frequent replacement of the media (every 1 or 2 years) or increasing the size of the slag filter.

For best performance and for preventing short-circuiting in the filter, a vertical upflow feeding mode with a uniform influent distribution system at the bottom of the slag filter is proposed. The slag filters should be built deeper than usual filter units and as airtight as possible to allow water to flow but to minimize gaseous CO_2 dissolution, thus reducing calcium carbonate precipitation and rapid pH lowering in the slag. At least two filters in series should be constructed to provide redundancy in the treatment system.

Bringing down the high effluent pH of the slag column is needed. At a fish farm, the slag filter effluent could simply be diluted in the main effluent by a ratio of at least 100:1 prior to discharge to the receiving stream, bringing the final pH value well below 9.5 which is the required pH limit in Quebec, Canada. If dilution into a larger stream is not an option, then it is possible to install a post treatment unit for pH adjustment. A peat filter installed downstream of an reactive hydrated ash filter was tested in lab-scale by Liira et al. (2009) for pH neutralization from > 10 to pH 7-8. An alternative option is pH neutralization with gaseous CO_2 (Sawyer et al., 2003).

Once the slag filter capacity is "exhausted", an extra TCLP test (U.S. Environmental Protection Agency, 1992) should be run to determine if saturated material should be disposed of as a hazardous waste, a municipal solid waste or can be valorised by land application as a soil amendment (Bird and Drizo, 2009). However, the direct use of non-soluble phosphate such as from hydroxyapatite would require an effective and economical means of solubilisation. This problem might be solved with the use of microorganisms (e.g. phosphate-solubilizing bacteria, Richardson, 2001) and phosphate-solubilizing fungi (Whitelaw, 1999). Other research demonstrated that plant root exudates produce organic acids that are strong enough to dissolve P even from hydroxyapatite and the P-saturated filter materials could be source of slow release P (Cucarella et al., 2007; Kõiv et al., 2012).

Highly concentrated influents would require a more intensive biological pre-treatment upstream of the reactive slag filters and the slag would saturate faster and would need to be changed at a higher frequency. Therefore, when considering that most of freshwater fish farms produce sludge supernatant that is more similar to the characteristics of P1 it was concluded that a hybrid treatment system consisting of an aerated filter bed or a treatment wetland followed by reactive slag filters would provide efficient pollutants removal from the supernatant.

Conclusions

The goal of our study was to develop an on-site compact, cost-effective and extensive system for the treatment of fish farm sludge supernatant. The conclusions of the project regarding initial objectives are the following:

a) The tested system composed of a downflow AFB followed by a SF and a series of two SCs achieved a mean effluent concentration (and mean % of removal) of

6.0 mg COD L^{-1} (98%), 3.0 mg TSS L^{-1} (98%), 0.5 mg TKN L^{-1} (96%), 0.13 mg NH_4-N L^{-1} (93%), 0.10 mg TP L^{-1} (98%) and 0.05 mg o-PO_4-P L^{-1} (98%) in a low concentration supernatant and a low OLR (0.015 kg BOD_5 m^{-3} d^{-1}; Phase 1); and 1490 mg COD L^{-1} (67%), 200 mg TSS L^{-1} (37%), 256 mg TKN L^{-1} (32%), 188 mg NH_4-N L^{-1} (24%), 5.9 mg TP L^{-1} (96%) and 0.5 mg o-PO_4-P L^{-1} (99.5%) in a high concentration supernatant and a high OLR (0.5 kg BOD_5 m^{-3} d^{-1}; Phase 2). The system was especially efficient in removing o-PO_4, achieving effluent concentration below 1.0 mg P L^{-1} consistently during the whole experimental period and according to P-Hydroslag model results could have continued to do so for 5 years (when average o-PO_4 loading similar to P1).

b) The OLR had a substantial effect on the organic matter mineralization and nitrification efficiency of aerated filter beds. At a low OLR, the AFBs were efficient at removing COD (95%) and nitrifying the effluent while at a high OLR, COD removal was reduced to 65% and no nitrification took place.

c) A high HRT_V (>12 h) of SC resulted in higher o-PO_4 removal efficiency for both phases compared to SC with HRT_V < 6 h.

d) The P-Hydroslag model was used to predict the slag filter behaviour. Experimental pH and o-PO_4 in the effluent were reasonably well reproduced by simulated results, confirming the potential of the model as a design tool. The general effect of HRT_V and phase change was correctly predicted by the model.

e) Preliminary design options for a fish farm supernatant treatment system were proposed for two types of supernatant (similar to Phases 1 or 2). The suggested design included one AFB followed by a steel slag filter, without a sacrificial slag filter. The design of the AFB was based on the OLR and the design of the slag filter was based on numerical simulations with the P-Hydroslag model. The proposed AFB HRT_V was 2.4 and 96 h for P1 and P2, respectively, while the HRT_V of slag filter was 8 and 30 h for P1 and P2. The expected longevity was at least 20 years for the AFB (both phases), 5 years for the slag filter in P1, and 1 year for the slag filter during P2.

It was concluded that with proper loading rates, this compact biological and physico-chemical treatment system offers a good alternative to the high energy demand and high maintenance treatment systems for organic matter and phosphorus removal, and that this treatment system could be applicable to other agro-environmental, municipal or residential effluents.

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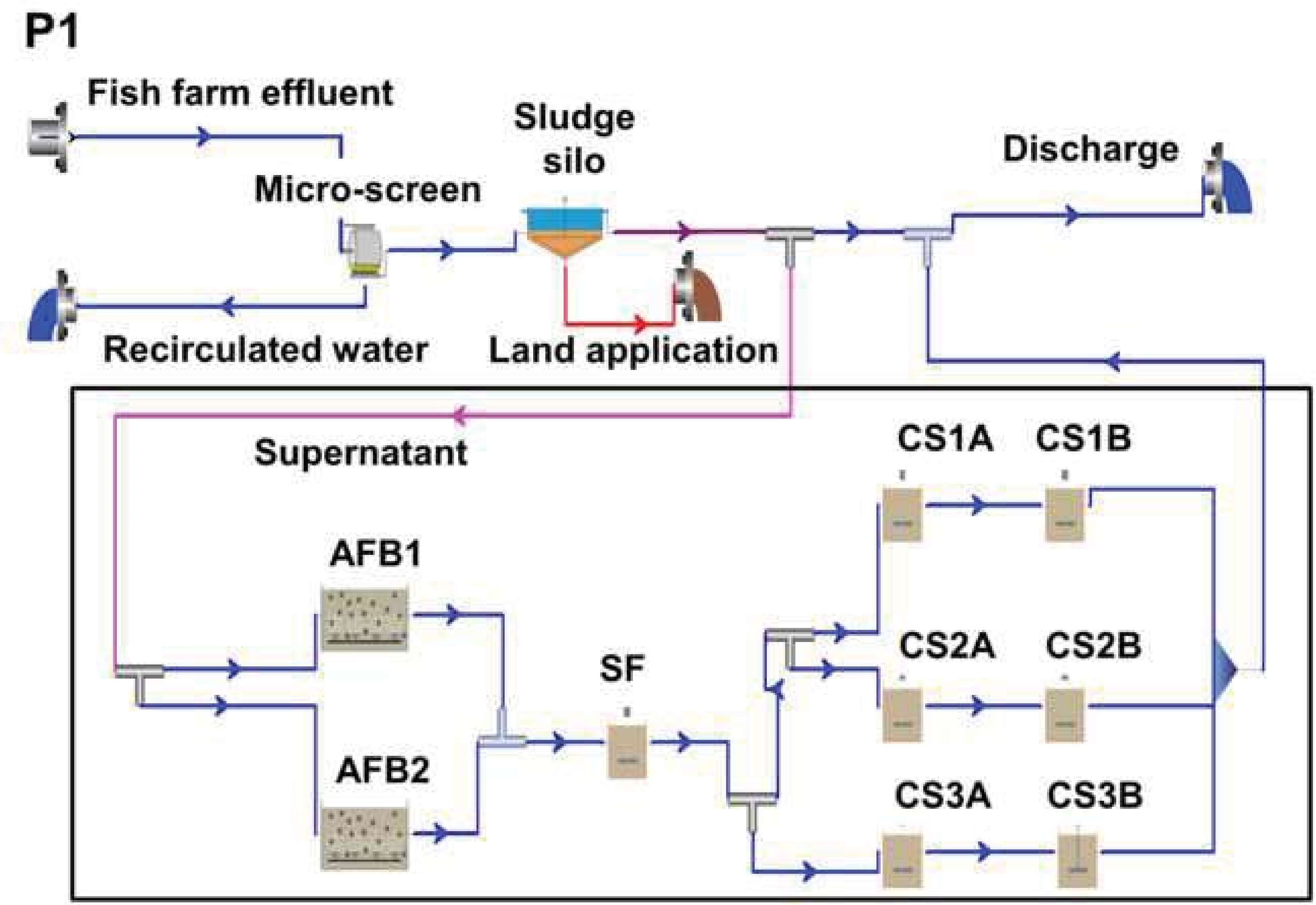
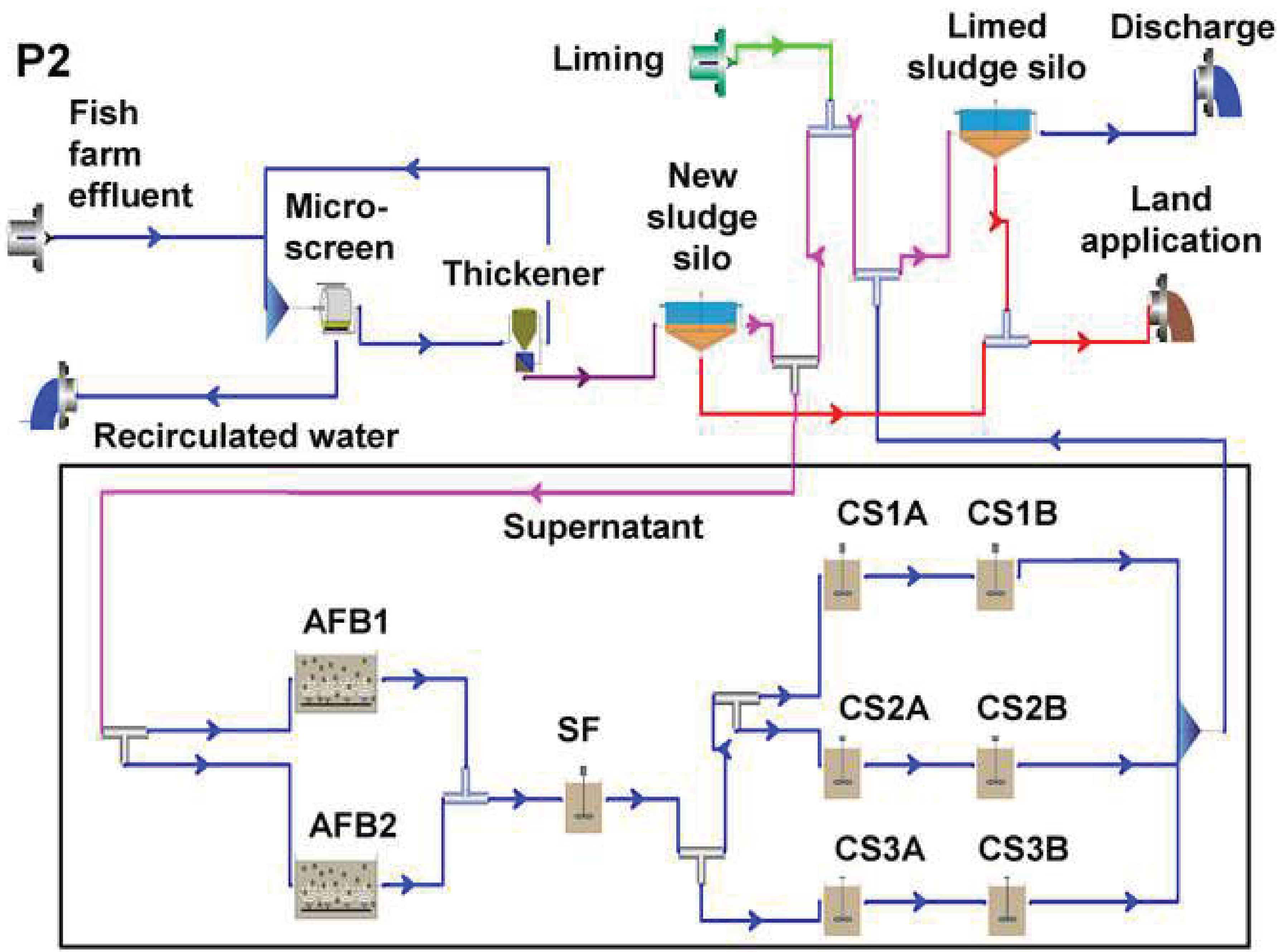
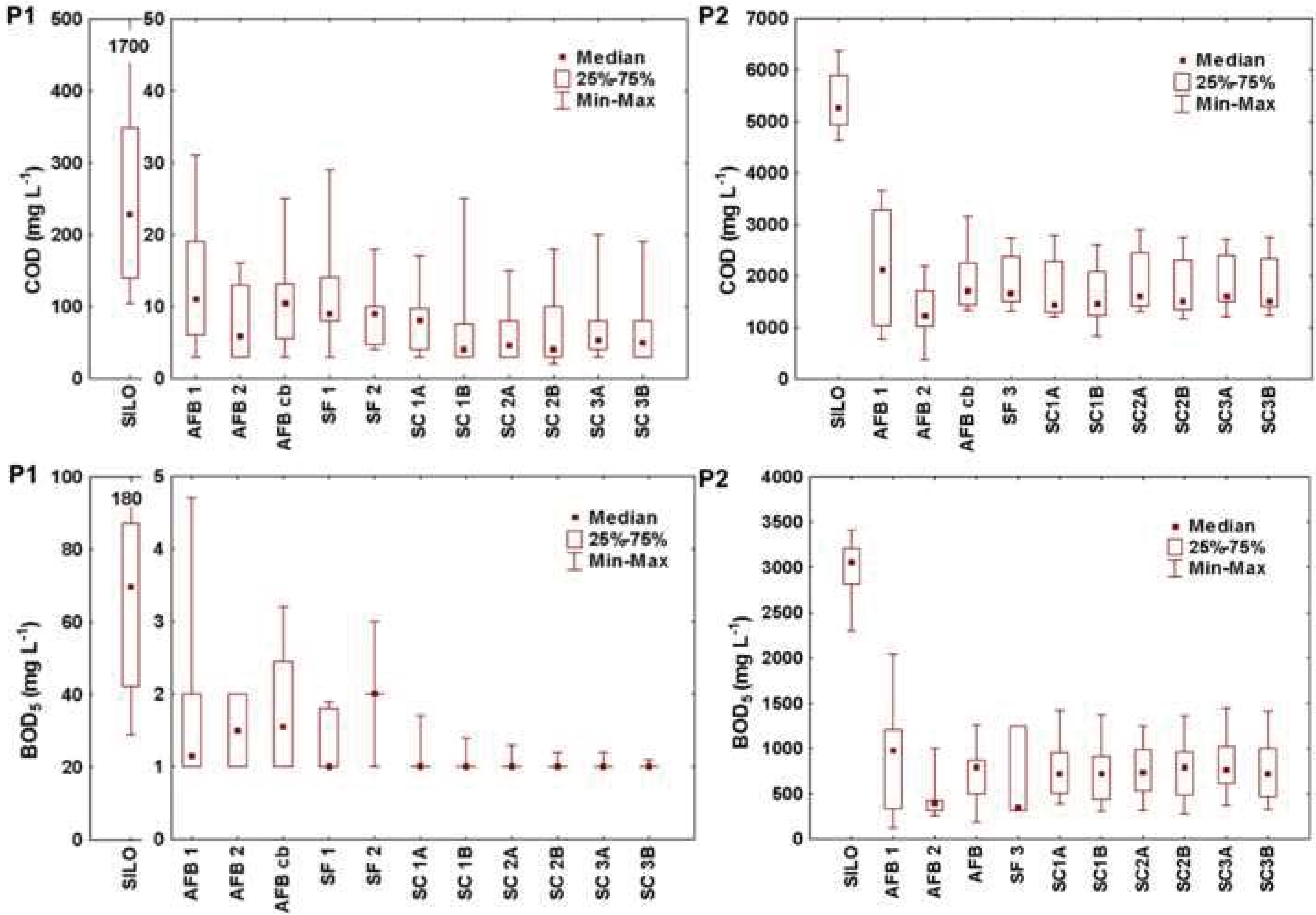

P1
Fish farm effluent
Micro-screen
Recirculated water
Sludge
silo
Land application
Discharge
Supernatant
AFB1
AFB2
SF
CS1A
CS1B
CS2A
CS2B
CS3A
CS3B

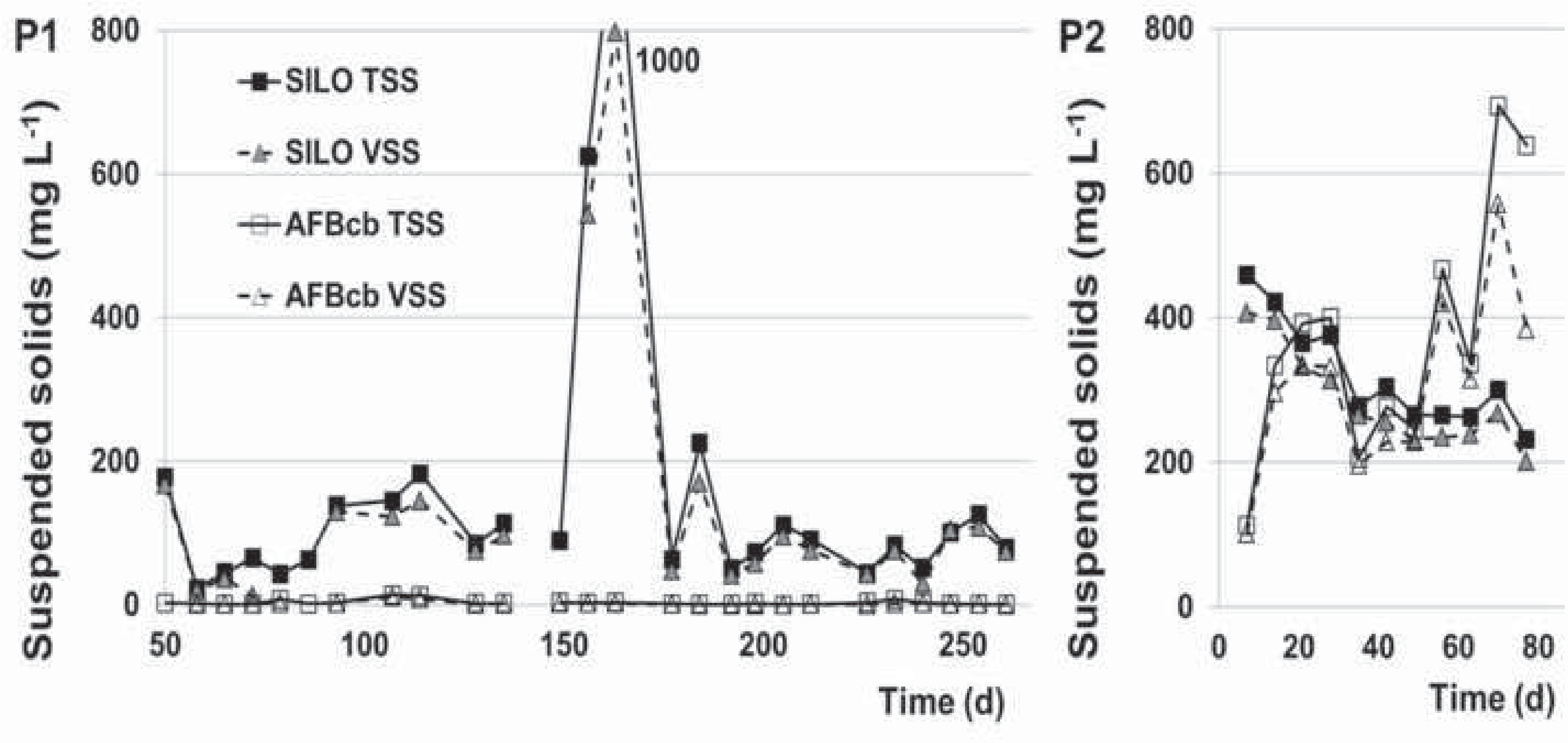
Figure


P2
Fish farm effluent
Micro-screen
Thickener
Recirculated water
Liming
New sludge silo
Limed sludge silo
Discharge
Land application
Supernatant
AFB1
AFB2
SF
CS1A
CS1B
CS2A
CS2B
CS3A
CS3B

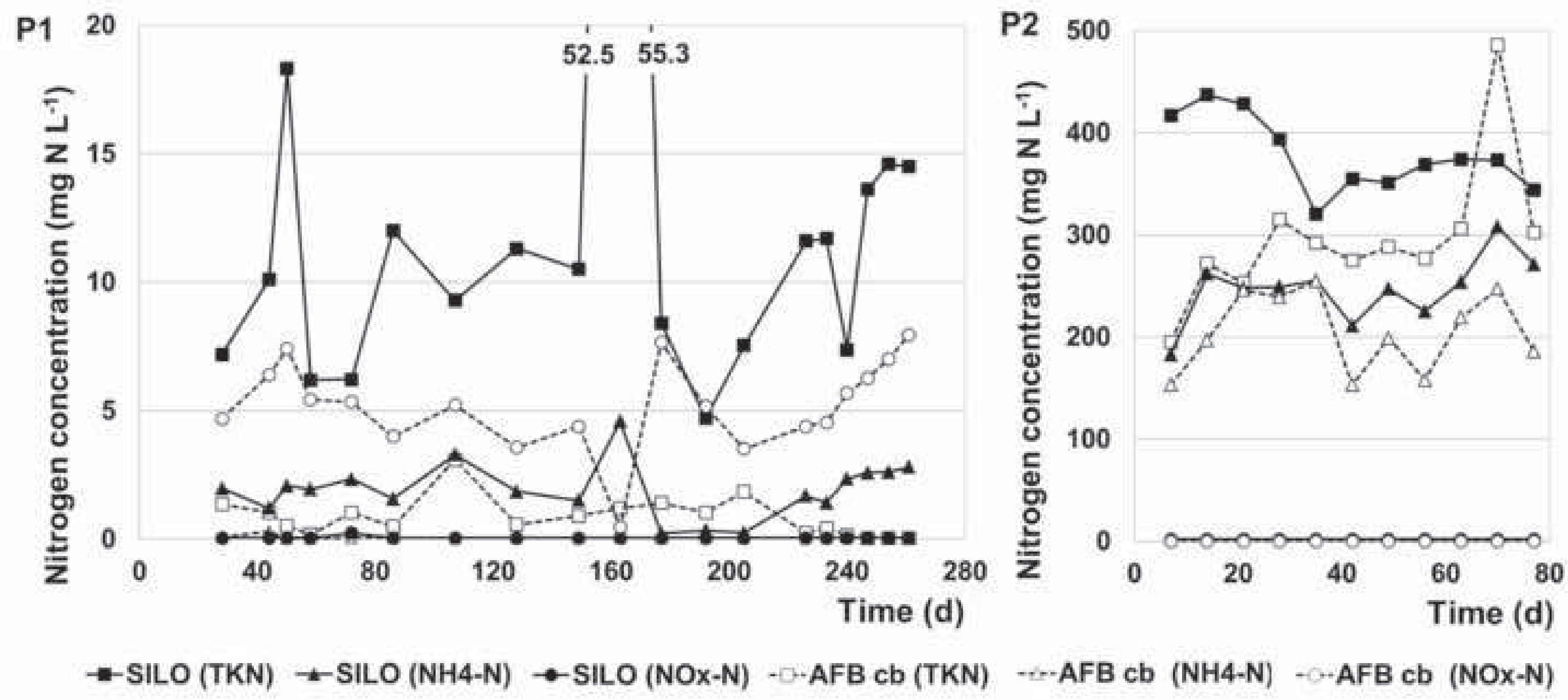
Figure


P1
COD (mg L-1)
1700
Median
25%-75%
Min-Max
SILO
AFB 1
AFB 2
AFB cb
SF 1
SF 2
SC 1A
SC 1B
SC 2A
SC 2B
SC 3A
SC 3B
P2
COD (mg L-1)
SILO
AFB 1
AFB 2
AFB cb
SF 3
SC1A
SC1B
SC2A
SC2B
SC3A
SC3B
P1
BOD5 (mg L-1)
180
P2
BOD5 (mg L-1)
AFB
SF 3

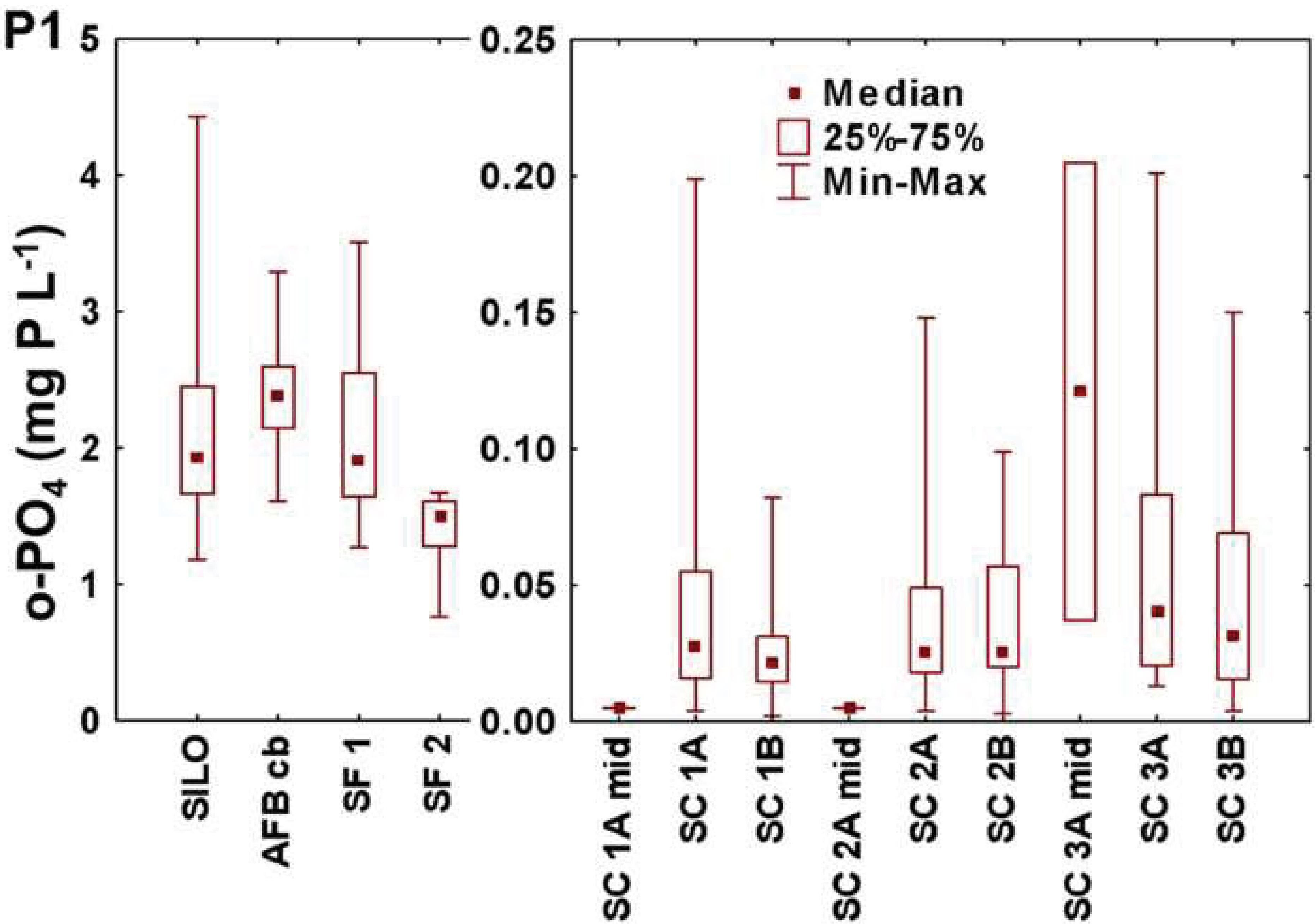
Figure


P1
Suspended solids (mg L-1)
800
600
400
200
0
SILO TSS
SILO VSS
AFBcb TSS
AFBcb VSS
1000
50
100
150
200
250
Time (d)
P2
Suspended solids (mg L-1)
800
600
400
200
0
0
20
40
60
80
Time (d)

Figure


P1
P2
Nitrogen concentration (mg N L-1)
20
15
10
5
0
0
40
80
120
160
200
240
280
Time (d)
52.5
55.3
500
400
300
200
100
0
20
60
80
SILO (TKN)
SILO (NH4-N)
SILO (NOx-N)
AFB cb (TKN)
AFB cb (NH4-N)
AFB cb (NOx-N)

Figure


P1
o-PO4 (mg P L-1)
0
1
2
3
4
5
SILO
AFB cb
SF 1
SF 2
0.00
0.05
0.10
0.15
0.20
0.25
Median
25%-75%
Min-Max
SC 1A mid
SC 1A
SC 1B
SC 2A mid
SC 2A
SC 2B
SC 3A mid
SC 3A
SC 3B

Figure

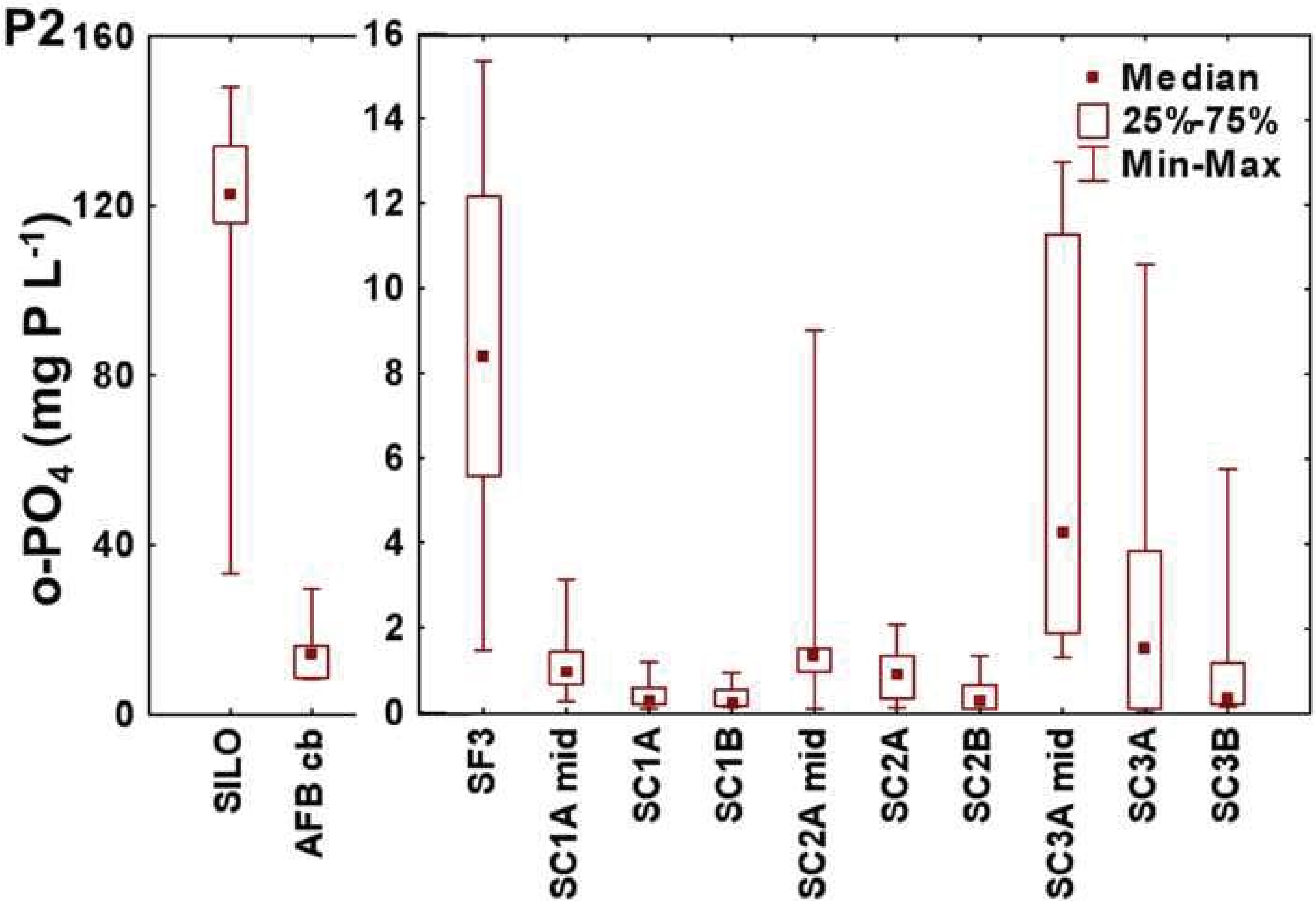
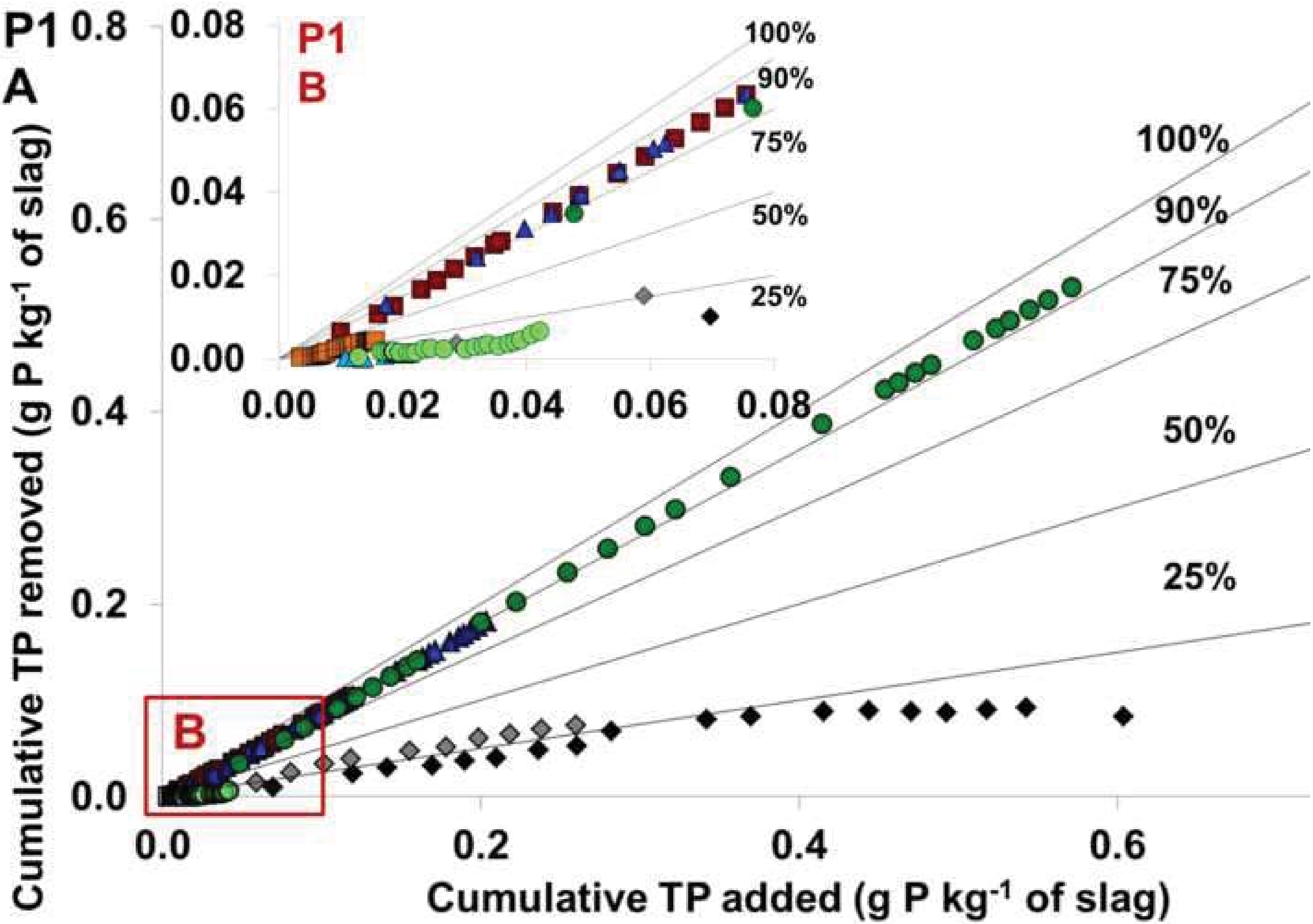
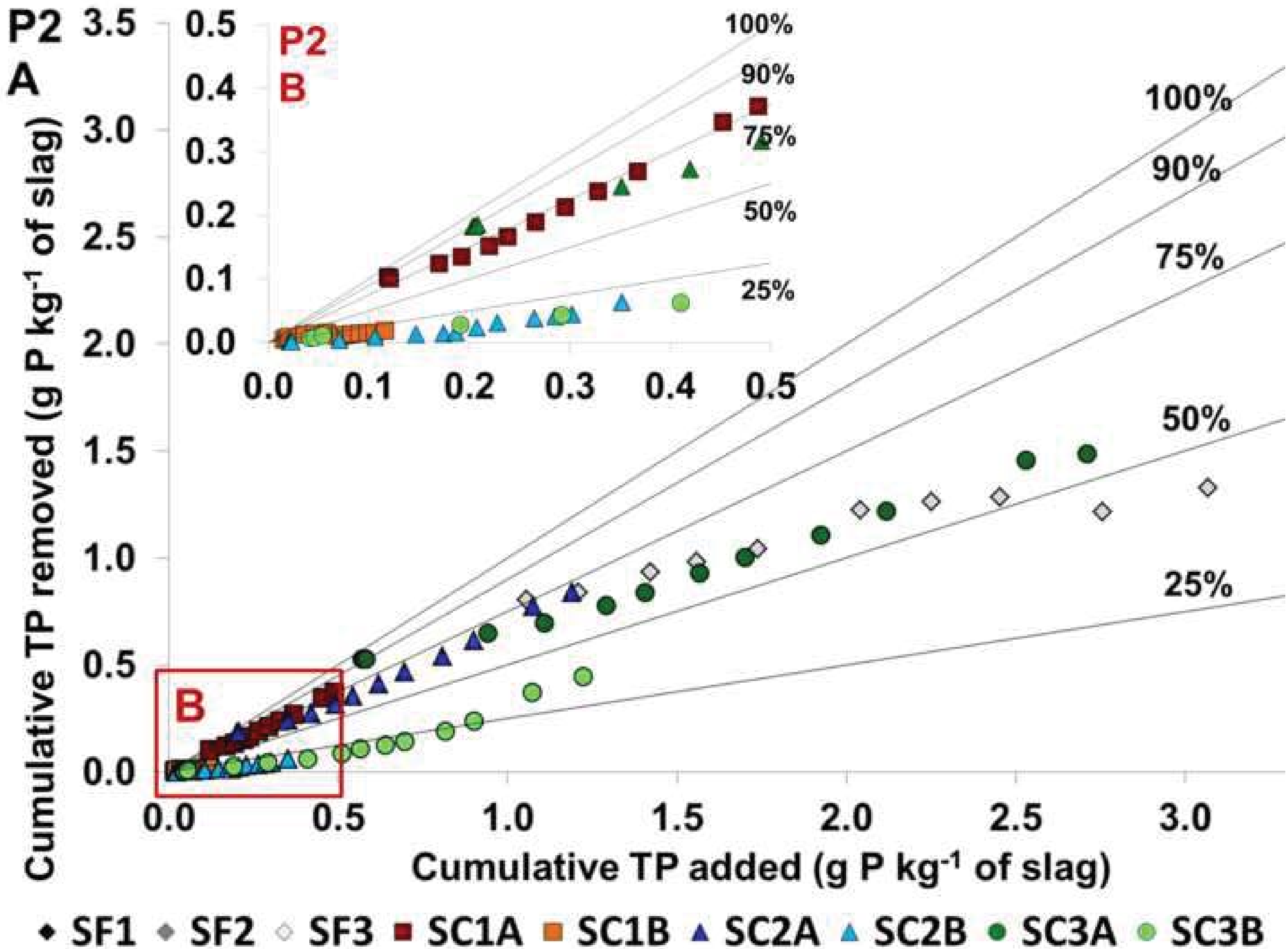

P2
o-PO4 (mg P L-1)
160
120
80
40
0
16
14
12
10
8
6
4
2
0
Median
25%-75%
Min-Max
SILO
AFB cb
SF3
SC1A mid
SC1A
SC1B
SC2A mid
SC2A
SC2B
SC3A mid
SC3A
SC3B

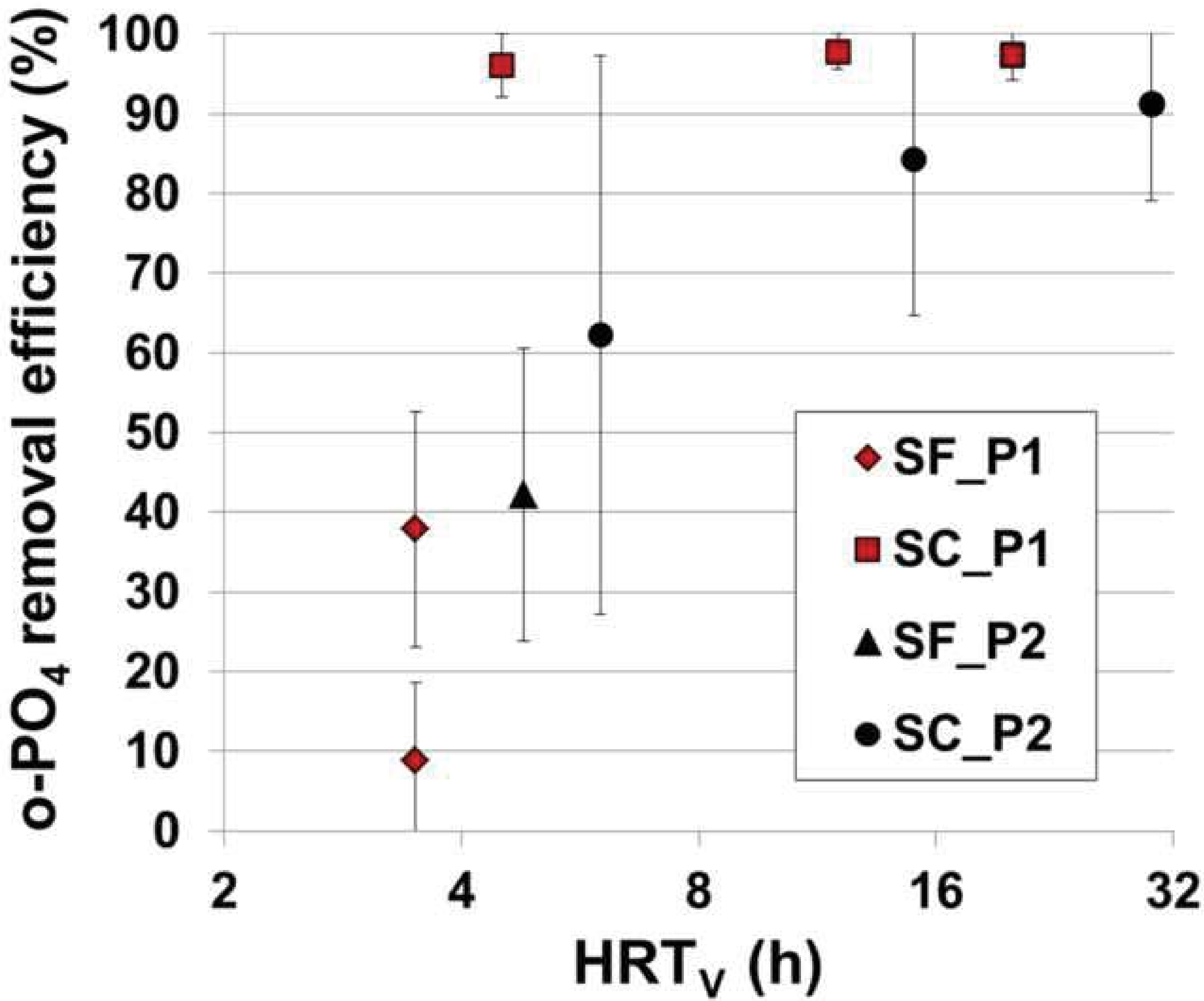
Figure
Click here to download high resolution image



Figure


P2
A
Cumulative TP removed (g P kg-1 of slag)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Cumulative TP added (g P kg-1 of slag)
100%
90%
75%
50%
25%
B
P2
B
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.1
0.2
0.3
0.4
0.5
100%
90%
75%
50%
25%
SF1
SF2
SF3
SC1A
SC1B
SC2A
SC2B
SC3A
SC3B

Figure


o-PO4 removal efficiency (%)
100
90
80
70
60
50
40
30
20
10
0
2
4
8
16
32
HRTV (h)
SF_P1
SC_P1
SF_P2
SC_P2

Figure
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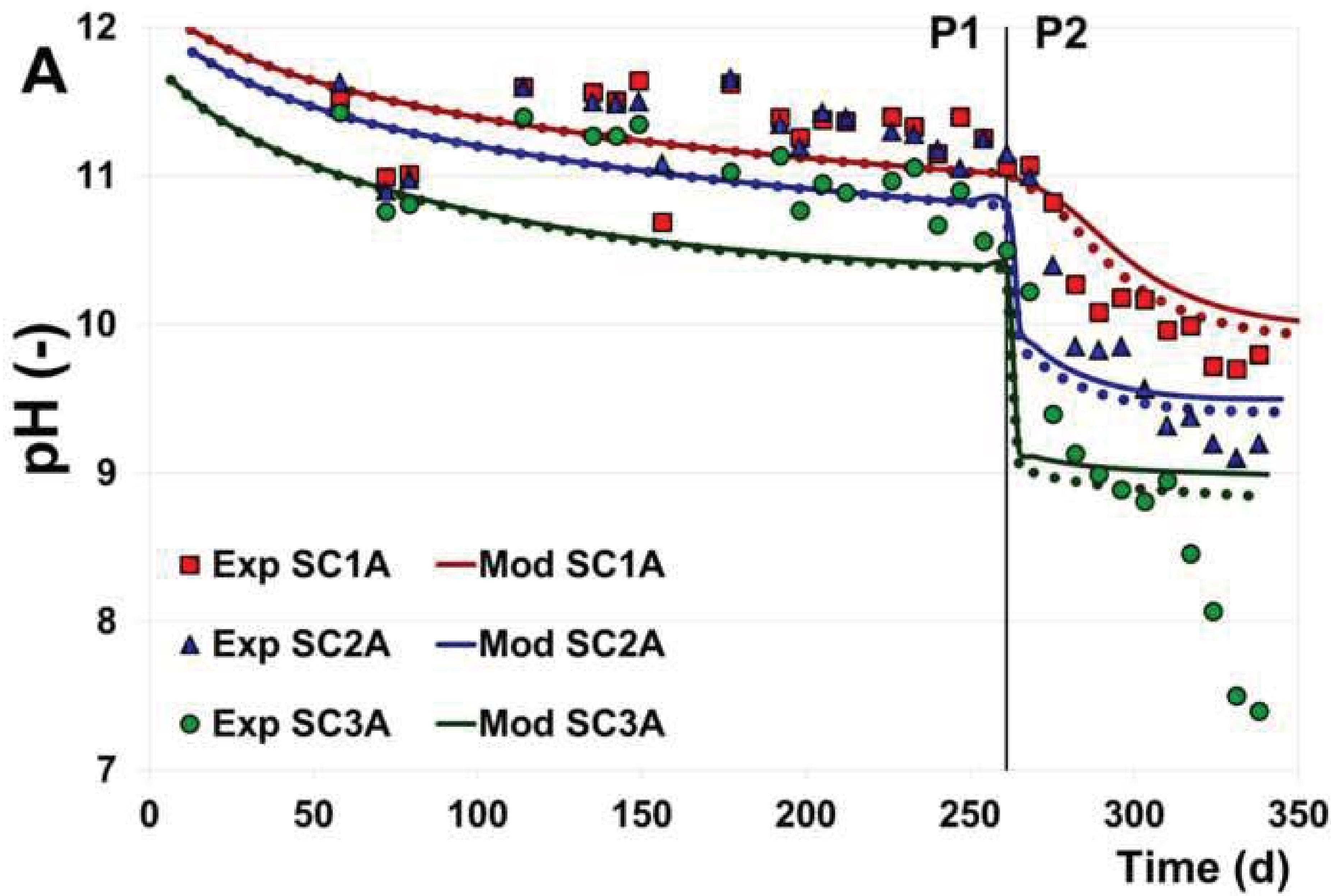
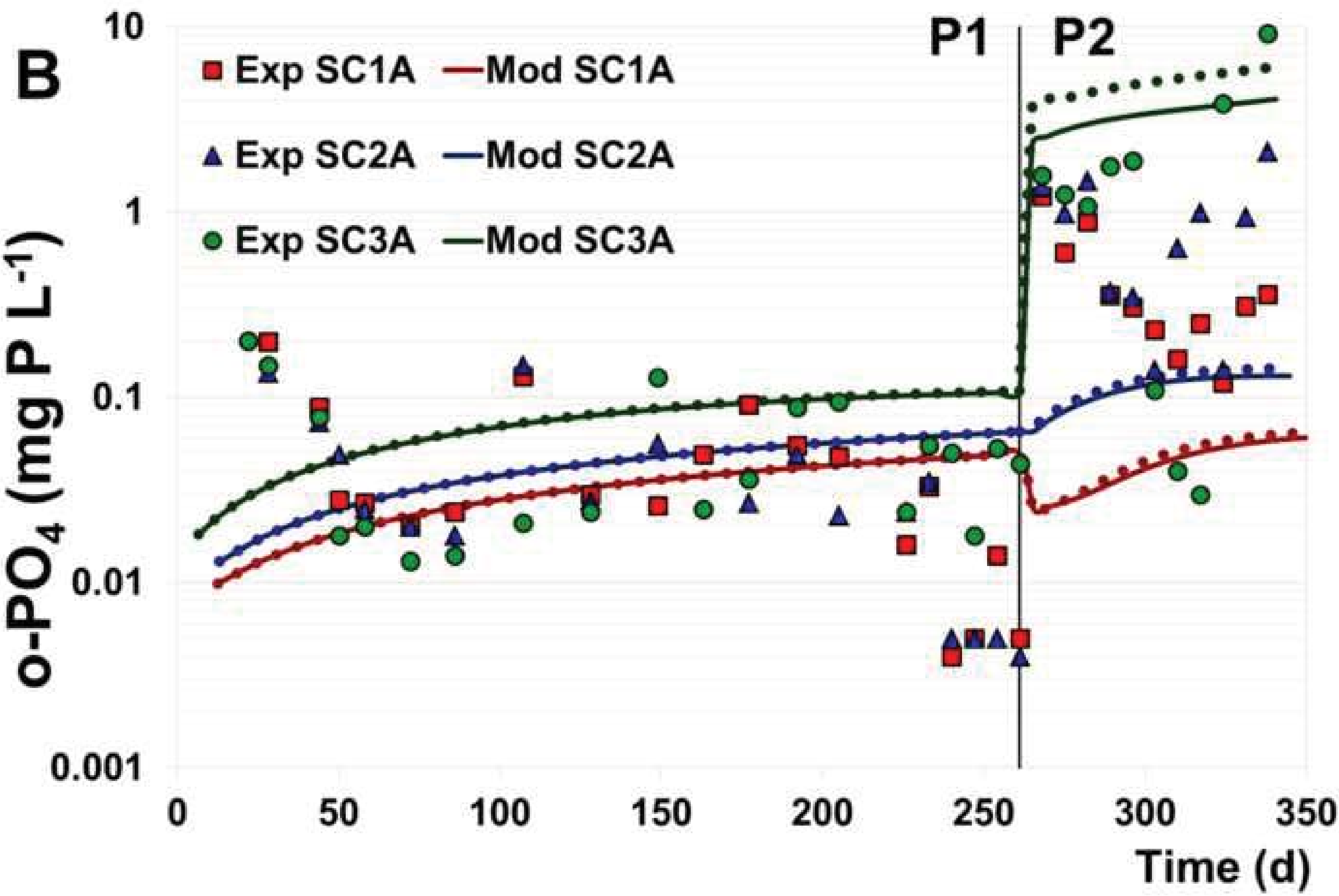


Figure


B
Exp SC1A
Mod SC1A
Exp SC2A
Mod SC2A
Exp SC3A
Mod SC3A
P1
P2
o-PO$_4$ (mg P L^{-1})
10
1
0.1
0.01
0.001
0
50
100
150
200
250
300
350
Time (d)

Koiv et al., TABLES

Table 1. Summary of design parameters of the experimental filter units in Phase 1 (P1) and Phase 2 (P2). Abbreviations: AFB1 and AFB2 – two parallel aerated filter beds; SF – sacrificial slag filter; SC1, SC2, SC3 – three parallel dual-stage steel slag columns.

Design parameters	**Units**	**AFB1, AFB2**	**SF**	**SC1, SC2, SC3**
Water flow conditions		saturated downflow	saturated upflow	saturated upflow
Filter size (diameter × height or *length × width × height)	m×m or *m×m×m	*1.0×1.0×1.0 (each AFB)	0.45×0.8	0.3×1.3 (each stage)
Water level in filter units	m	1.0	0.8	1.3
Volume of filter material	m^3 filter^{-1} (*or stage^{-1})	0.90	0.13	*0.095
Filter material		gravel	EAF steel slag	EAF steel slag
Particle size of material	mm	10-25	P1 SF1 = 20-40 P2 SF2 = 10-30 P2 SF3 = 10-30	5-10
Density of material	kg L^{-1}	2.6	3.6	3.6
Porosity of filter (estimated)	%	38	45	40
Initial void volume	m^3	0.36	0.052	0.038
Void hydraulic retention time (HRT_V)	h	P1 = 48 P2 = 65	P1 = 3.5 P2 = 4.8	P1: 20, 12, 4.5 P2: 30, 15, 6.0 (per stage)
Organic loading rate (OLR)	kg BOD_5 m^{-3} d^{-1}	P1 = 0.015 P2 = 0.50	–	–
Air flow direction		counter-	–	–

Design parameters	Units	AFB1, AFB2	SF	SC1, SC2, SC3
		current		

Table 2. Composition of simulated influent solutions of the slag columns (AFBs effluent feeding the SF and SF effluent feeding the SCs).

Phase	pH	Ca^{2+}	TIC	o-PO_4	NH_4	Alkalinity
	-	mg L^{-1}	mg C L^{-1}	mg P L^{-1}	mg N L^{-1}	mg $CaCO_3$ L^{-1}
AFB P1	7.19	24.6	13.4	2.42	-	51.6
SF P1	8.27	28.1	13.4	2.42	-	60.3
AFB P2	7.39	23.4	159.8	13.6	210	645.3
SF P2	8.07	30.7	145.2	13.6	210	663.4

Table 3. Preliminary full-scale design parameters for the treatment of low (P1) and high strength (P2) supernatant of a freshwater fish farm sludge settling tank, consisting of a) an aerated filter bed (AFB) and b) a reactive slag filter.

Wastewater type		**P1 (low strength)**	**P2 (high strength)**
Aerated filter bed			
1) AFB influent data (see Supplementary Table S2)			
2) Objectives			
TKN removal efficiency	%	90	10
BOD removal efficiency	%	80	50
3) AFB design criteria (results from trickling filter design, Metcalf and Eddy et al., 2014)			
Type of AFB		low-rate	high-rate (with recirculation)
Specific surface area in the reactor	m^2 m^{-3}	60	60
Hydraulic loading rate	m d^{-1}	3.6	1.04
Organic loading rate	kg BOD_5 $m^{-3}d^{-1}$	0.13	1.57
Specific TKN removal rate per rock area	g m^{-2} d^{-1}	0.40	0.33
4) Design values			
Filter volume (empty bed)	m^3	28	19
Filter depth	m	2	2

Filter area	m^2	13.9	9.6
Particle size of material	mm	10-20	10-20
Aeration rate	m^3 min^{-1}	0.83	2.92
Slag filter			
1) Slag filter influent data (see Supplementary Table S2)			
2) Objectives			
P removal efficiency	%	80	80
3) Slag filter design criteria (results from numerical simulations using the P-Hydroslag model)			
Void hydraulic retention time	h	8	30
Longevity	pore volumes	5400	315
	years	5	1
P retention capacity	g P kg^{-1} slag	4.5	1.7
4) Design values			
Filter volume (empty bed)	m^3	42	31
Filter depth	m	2	2
Filter area	m^2	21	15.5
Particle size of material	mm	5-10	5-10

Supplementary Material

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