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Phosphorus in soil treatment systems:

accumulation and mobility

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Abstract

Septic tanks with subsequent soil treatment systems (STS) are a common treatment technique for domestic wastewater in rural areas. Phosphorus (P) leakage from such systems may pose a risk to water quality (especially if they are located relatively close to surface waters). In this study, six STS in Sweden (11 to 28 years old) were examined. Samples taken from the unsaturated subsoil beneath the distribution pipes were investigated by means of batch and column experiments, and accumulated phosphorus were characterized through X-ray absorption near edge structure (XANES) analysis. At all sites the wastewater had clearly influenced the soil. This was observed through decreased pH, increased amounts of oxalate extractable metals and at some sites altered P sorption properties. The amount of accumulated P in the STS were found to be between 0.32 and 0.87 kg m^{-3}, which in most cases was just a fraction of the estimated P load ($< 30\%$). Column studies revealed that high P concentrations (up to 6 mg L^{-1}) were leached from the material when deionized water was applied. However, the response to deionized water varied between the sites. As evidenced by XANES analysis, aluminium phosphates or P adsorbed to aluminium (hydr)oxides, as well as organically bound P, were important sinks for P. Generally soils with a high content of oxalate-extractable Al were also less vulnerable to P leakage.

1   Introduction

Phosphorus (P) discharge from anthropogenic sources is a crucial factor for eutrophication of many inland aquatic systems worldwide (Smith, 2003). In most areas, agricultural activities are believed to account for the majority of the P discharge on an annual basis (e. g. Smith et al., 2005; Brandt et al., 2009) . The contribution from onsite wastewater treatment systems

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40 (OWTs) is smaller but they can still be a relevant P source, especially in areas such as the

41 Baltic sea region where the reduction of P loads is of high priority (Boesch et al., 2006; Wulff

42 et al., 2007)

43 Among OWTs, the use of septic tanks with subsequent soil treatment systems (STS) is the

44 most predominant treatment technique for domestic wastewater. The use of STS is extensive

45 in rural parts of Australia, North America, Canada and parts of Europe in rural areas (Butler

46 & Payne, 1995; USEPA, 2002; Beal et al., 2005; Weiss et al., 2008; Gill, 2011; Motz et al.,

47 2012). In STS, the unsaturated subsoil beneath the soil trench and above the water table can

48 be defined as the overall treatment system (Gill et al., 2009). In clay soils (which are not

49 suitable for infiltration) the STS can be constructed using imported sand. The wastewater then

50 has to be drained out at the bottom of the system and piped to a surface recipient.

51 Phosphorus removal in STS is attributed to chemical precipitation and sorption processes in

52 the soil matrix. Formation of Al(III) and Fe(III) (hydr)oxide surface complexes or

53 precipitation of Al(III), Fe(III) and/or Ca phosphates are all possible attenuation mechanisms

54 (Robertson, 2003; Eveborn et al., 2012). In addition Fe(II) precipitates may form at low redox

55 potential (Zanini et al., 1998).

56 From a recipient perspective it has been shown that OWT systems can be a significant factor

57 for the P status of freshwaters under certain conditions (Macintosh et al., 2011; Withers et al.,

58 2011); these authors suggested that the observed impacts are attributed to poor design or

59 insufficient maintenance of the treatment systems rather than general leakage. However, in

60 the scientific literature there has been observations of both high, variable and low P removal

61 (e.g. Carroll et al., 2006; Lowe & Siegrist, 2008; Robertson, 2008; Eveborn et al., 2012;

62 Robertson, 2012).

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As support within management of decentralized wastewater sources, knowledge regarding

long term P removal in STS and the P immobilization/mobilization mechanisms involved is

important. Eveborn et al. (2012) used a mass balance approach to assess the P removal

capacity of the unsaturated subsoil in a Swedish STS. The study gave evidence for a very poor

P removal (~12%), but was limited to four sites with comparably high P loads. The aim of this

study was to explore the validity of the results by performing additional (simplified) mass

balance calculations and investigate both accumulation and mobility of P in the unsaturated

subsoil of old STS. Specific aims were to:

1. Investigate the overall removal capacity in the unsaturated subsoil of the systems by
   calculating the amount of accumulated P.

2. Study the P leaching and P removal potential of soil materials from STS through pilot
   scale column experiments with reconstructed bed profiles.

3. Investigate the mechanisms behind the observed P retention and P release by
   evaluation of data from batch experiments and physical/chemical characterization
   (including X-ray absorption near edge structure (XANES) measurements).

2 Materials and Methods

2.1 Investigated sites

Six STS located in various parts of Sweden were investigated: Tullingsås (Tu) near Östersund

N 63° 49.17', E 15° 31.09', Biverud/Glanshammar (Gl) near Örebro N 59° 19.95', E 15°

27.90', Knivingaryd (Kn) near Nybro N 56° 54.45', E 15° 57.44', Luvehult (Lu) near Nybro N

56° 52.59', E 16° 6.95', Ringamåla (Ri) near Karlshamn N 56° 21.94', E 14° 44.26' and

Halahult (Ha) near Karlshamn N 56° 14.05', E 14° 58.06'. Among these sites Lu and Gl were

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85 traditional single-household systems whereas the other ones served between 40 and about 200

86 persons each (Table 1). The age of the sites varied between 11 and 28 years, the hydraulic

87 load was between 0.9 and 33 cm d^{-1} and the estimated P load was between 30 and 540 g m^{-2}

88 yr^{-1} (Table 1). At the Kn site a lined pond (open to the air) was used as a pre-treatment step

89 for particle removal while at all other sites septic tanks or similar sludge removal devices

90 were used. The Tu, Ri and Ha sites were all constructed using parallel beds, which were

91 loaded periodically. The areas of the beds were between 30 and 196 m^2 (Table 1) and the soils

92 used were imported from local gravel pits. The pre-treated wastewater was distributed to the

93 soil through conventional drainage distribution pipes. However, the Tu and Ha sites were

94 constructed with infiltration surfaces open to the air (framed by an embankment). At these

95 sites the wastewater was applied over the soil from a centred (Tu) or mobile (Ha) inflow

96 device. The sites Tu, Gl and Lu were gravity-fed systems whereas the wastewater at the sites

97 Kn, Ri and Ha was distributed through pumping. The wastewater was finally discharged to

98 the groundwater (Gl, Kn and Lu sites) or to a nearby stream through a drainage collection and

99 distribution system (Tu, Ri and Ha sites). None of the latter systems had any liners, and

100 therefore the proportion of wastewater that is discharged through the drainage system is

101 unclear.

102 **2.2 Soil sampling**

103 The STS were sampled at five different depths (where the filter bed was sufficiently deep) by

104 collection of samples from the 0-5, 5-15, 15 – 30, 30 - 60 and 60 –100 cm layers by use of a

105 spade (in total about 350 kg soil). Sample locations were selected as close to the wastewater

106 source as possible. However, at the sites Ri and Lu limited accessibility prevented us to

107 collect samples immediately adjacent to the inlet. Reference samples were also collected at

108 each site, which represented filter bed material that had not been exposed to P-containing

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109   wastewater. At sites where imported sand was used (Ha, Kn, Tu, Ri) one single reference

110   sample from unused sand was used. However at the other sites, 2 (Lu) or 5 (Gl) reference

111   samples were selected to be able to consider vertical heterogeneity in soil properties.

112   Reference samples were collected above the distribution level. Where this was not possible

113   (Lu 60-100, Gl 0-30, and Gl 30-100) offset samples were collected (offset >2 m). The dry

114   bulk density was determined by collection of undisturbed soil cores (by use of metal

115   cylinders) in four replicates. The cores were dried at 105°C before weighing. At all STS soil

116   sampling was performed at one single location. After collection, all soil samples were placed

117   in plastic bags and stored in an isolated room protected from freezing (T <12 °C) prior to

118   further use.

119   **2.3 Soil analyses**

120   Samples larger than 15 kg (all samples excluding reference samples) were homogenized in a

121   concrete mixer (for at least 15 minutes) before collection of subsamples of volumes relevant

122   for soil analyses. The subsamples were then stored at 4°C. Field-moist samples from the 0-5

123   and 5-15 cm depths as well as the reference samples were analyzed for pH in deionized water

124   (using a liquid to solid ratio of 2) with a combination electrode and a PHM93 Reference pH

125   Meter (Radiometer A/S, Brønshøj, Denmark). Total C was determined for all samples (dried

126   at 105°C) using a LECO CNS-2000 Analyzer. Samples for total P analysis were delivered to

127   the laboratory at ALS Scandinavia AB in Luleå, Sweden, and analysed according to EPA

128   methods (modified) 200.7 (ICP-AES) and 200.8 (ICP-QMS). This method was also used for

129   elemental analysis of reference samples and included the elements Al, Fe, Ca, Mg, Mn, K and

130   Si. Briefly, the soil samples were dried at 105°C and subsequently 0.1 g dried sample was

131   melted with 0.375 g $LiBO_2$ and dissolved in HNO_3. The loss of ignition was determined at

132   1000 °C.

133   Reactive aluminium and iron (hydr)oxides, as well as phosphorus associated with these

134   fractions, were determined by extraction with ammonium oxalate (0.2 M oxalate buffer, pH 3)

135   (van Reeuwijk, 1995). However, apart from P associated with aluminium and iron

136   (hydr)oxides, other P species that are unstable at low pH will also be dissolved by this extract

137   (e.g. calcium phosphates). Field-moist samples (in duplicates) from the six sites were

138   extracted using a liquid to solid ratio of 100:1, shaken for 4 hours in the dark in an end-over-

139   end shaker. Oxalate-extracted Fe, Al and P were determined with inductively coupled plasma

140   emission spectrometry (ICP-OES) using a Perkin-Elmer Optima 3000 DV instrument.

141   **2.4   Batch experiments**

142   For the reference samples and for the 0-15 and 5-15 cm samples from the sites Lu, Kn, Ri and

143   Tu, further analysis were made through batch experiments. These sites varied in terms of

144   loading history as well as in basic chemical and physical properties and were selected also for

145   the column experiment. Sorption properties were studied through equilibration (5 days

146   shaking time at 21°C) of 4 g soil in 30 ml phosphate solutions (NaH_2PO_4) of the following

147   initial P concentrations: 0, 0.02, 0.05, 0.1, 0.15, 0.2, 0.3 and 0.5 mM. 10 mM $NaNO_3$ was

148   used as a background electrolyte. Another batch experiment was performed to study the pH

149   dependence of P desorption. This experiment was set up in an identical manner but with

150   additions of NaOH (0.5 mM) or HNO_3 (0.5, 1, 2, and 3 mM) instead of P.

151   In both experiments the equilibrations were set up in duplicate. After the equilibration the

152   samples were centrifuged and the pH value was determined on the unfiltered supernatant

153   immediately after centrifugation. Subsequently the supernatant was filtered through a 0.2 μm

154   Acrodisc® PF filter and the inorganic PO_4–P concentration was determined colorimetrically

155 with the acid molybdate method using flow injection analysis (Aquatec-Tecator autoanalyser,

156 Foss Analytical, Copenhagen).

2.5   Column experiments

158 To investigate the P discharge from old or decommissioned STS (at 1 m depth) a column

159 experiment was set up with reconstructed bed profiles. In the experiments, columns were

160 loaded either with a reference material (silica sand, SiO_2 content 99,8 %) or with wastewater-

161 loaded soils from four sites (Tu, Lu, Kn and Ri). The columns were 0.3 m in diameter, the

162 experiment was reproduced in duplicate and soil columns prepared so that they reached a final

163 depth of the subsoil equivalent to 1 m (Fig. 1). For the Ri columns where the depth of the real

164 STS was less than 1 m, additional soil sampled from the bottom layer was added to reach a

165 depth of 1 m soil in the column. Distribution and draining layers (height ~0.15 m) of

166 macadam (16-32 mm) were put at the top and at the bottom of the columns, and a piece of

167 geotextile was used to separate the subsoil from the drainage layer (Fig. 1 (a)). The leachate

168 was collected in polyethylene containers (40 L) which were arranged so that they could be

169 weighed *in situ*.

170 During the first 12 weeks of the experiment, the columns were fed with domestic wastewater

171 (from a community with about 2500 inhabitants). A mechanical treatment (2 mm drum

172 screen) was applied before transfer to a 1 m^3 buffer tank. The columns were fed from the

173 buffer tank (Fig. 1 (b)), which was completely refilled with fresh wastewater once a week.

174 The hydraulic loading rate was adapted to the design hydraulic loading rates given in the

175 Swedish guidelines (Swedish EPA, 2003), which implies a value between 3 and 6 cm d^{-1}

176 depending on the grain size distribution of the soil (Fig. 1 (b)). The columns were fed

177 intermittently with 3 hours interval. Detailed characterisation of the influent wastewater

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178   quality was performed at weeks 1, 5 and 9 through spot-checks directly from the buffer tank.

179   The samples were analysed at the laboratory at Uppsala Vatten och Avfall AB, Uppsala,

180   Sweden, according to standardised methods (Table S1, supporting information). In short, the

181   concentration of BOD, NH4-N and alkalinity varied between 120 and 160, 42 and 50 and 517

182   and 569 mgL^{-1} respectively (Table S1). Effluent water from each sample container (including

183   untreated wastewater, see Fig. 1 (b)) was weighed (in order to follow mass flows) and

184   sampled regularly (typically once a week) for analysis of pH and total P. At week 5 and 9 (24

185   hours after characterization of the influent wastewater) also BOD_7, PO_4-P, NH_4-N, NO_3+NO_2-

186   N and NO_2-N were determined in the leachate. The pH value was determined instantly after

187   collection with a combination electrode and a PHM93 Reference pH Meter (Radiometer A/S,

188   Brønshøj, Denmark). Samples for BOD_7 analysis were instantly delivered and analysed at the

189   laboratory at Uppsala Vatten och Avfall AB according to international standards (ISO

190   5815:1989). An additional sample volume was frozen (-18°C) for later analysis of remaining

191   parameters. Inorganic forms of nitrogen were analysed using flow injection analysis (FIA,

192   Aquatec-Tecator autoanalyser, Foss Analytical, Copenhagen, Denmark). PO_4-P was

193   determined as for the batch experiments and for total P unfiltered samples were first digested

194   in acid potassium persulfate solution before subsequent analysis.

195   After the end of the first column experiment, the buffer tank was cleaned and filled with

196   deionized water. An identical column experiment (but with deionized water instead of

197   wastewater) was then started. This experiment was carried out for a period of 9 weeks. The

198   buffer tank was recharged with fresh deionized water every third week. The hydraulic loading

199   scheme, as well as the sampling scheme, was identical to that of the first experiment with

200   wastewater (Fig. 1 (b)). However, characterization of effluent water was performed at week 5

201   and 9 and included (in addition to total P and pH) only PO_4-P. Analyses were conducted as

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202   above. As a consequence of hydraulic failure (clogging) in the reference columns at the

203   beginning of the deionized water experiment, the ref 1 and ref 2 columns had to be run with a

204   decreased loading rate. The ref 2 column even had to be closed for most part of the

205   experiment. However there was always sufficient leachate available for sampling.

206   **2.6   XANES analysis**

207   Soil samples from the 5-15 cm layer of the Lu, Ha and Tu site (dried at 105°C and ground in a

208   mineral grinder) were mounted on caption tape and analysed using P *K*-edge XANES

209   spectroscopy on beamline BL8 of the Synchrotron Light Research Institute, Thailand

210   (Klysubun et al., 2012). The beamline were operated in fluorescence mode and the

211   fluorescence signal was measured using an solid state Ge detector. The scans ranged from

212   2100 to 2320 eV with a smaller energy step near the absorption edge (down to 0.2 eV

213   between 2144-2153eV). The counting time was constantly 3 s. Between 3 and 9 scans per

214   each sample were collected depending on the level of noise in the data, and subsequently

215   merged.

216   The XANES data processing was performed by means of the Athena program in the Demeter

217   Software Package (v 0.9.18) (Ravel & Newville, 2005). All samples and standards were

218   calibrated to a common energy scale by setting the maximum of the first derivative of the

219   spectrum of variscite to 2149.0 eV. Correction of any shifts on energy scale caused by

220   monochromator drift could be performed since validation data for variscite periodically were

221   collected. Merged spectra were normalized using a consistent procedure. In brief, a linear

222   baseline function was subtracted from the spectral region below the edge (typically between -

223   45 to -6 eV relative to E_0), and spectra were normalized to unit edge step and quadrature

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224   removed across the post-white-line region (typically between 26 to 170 eV relative to E_0) to

225   obtain normalized XANES spectra.

226   By means of a linear combination fitting (LCF) approach (Tannazi & Bunker, 2005) a set of

227   spectra of known standards were combined and fitted to the sample spectra. All standards

228   used in the evaluation have been characterized by XRD (Eriksson et.al., manuscript in

229   preparation), and XANES data were collected at the same beamline as the samples. The

230   standard compounds included amorphous calcium phosphate, octacalcium phosphate,

231   hydroxyapatite, brushite, monetite, amorphous aluminium phosphate, phosphorus adsorbed to

232   aluminium hydroxide, variscite, amorphous iron phosphate, phosphorus adsorbed to

233   ferrihydrite, strengite, struvite, potassium tarankite, lecithin and phytate. In the fitting

234   procedure no energy shifts were permitted and the sum of the weighting factors were not

235   forced to one. With support from earlier studies (Eveborn et al., 2009), the first derivative was

236   chosen as the fitting space. At most three standards were accepted in each fit and the fitting

237   range was constrained to between -5 to 30 eV relative to E_0.

238   **3   Results**

239   **3.1   Characterization of reference soils**

240   According to element analyses there were no dramatic differences in the elemental

241   composition of the soil between the six sites (Table S2). The somewhat higher Ca content at

242   the sites Ri and Ha (17 and 30 mg g^{-1} dw^{-1} compared to around 10 mg g^{-1} for the other sites)

243   coincides with a higher pH value (around 8.9 for Ri and Ha compared to between 5.9 and 6.8

244   for the other sites). This may be caused by the presence of calcite ($CaCO_3$) at the Ri and Ha

245   sites. The initial P content ranged from 0.15 to 0.31 mg g^{-1}. Between 6 and 100 % of the total

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246 P was oxalate-extractable (Table S2). According to the grain size distribution analysis the

247 GD_{50} values for the soils ranged from 0.21 to 3.93 mm.

3.2 Phosphorus accumulation and correlation to soil properties

249 The amount of accumulated P (calculated as the difference between total P in a sample and

250 total P in the corresponding reference sample) typically varied between 0.15 and 0.6 mg g^{-1}

251 (Fig. 2 and Fig. S1). However, the Lu site showed evidence for stronger (up to 1.2 mg g^{-1}) P

252 accumulation (Fig. 2). An even stronger P accumulation (2.28 mg g^{-1}) was observed for the

253 Tu 0-5 sample. However, this result was associated with an extreme (and abnormal) amount

254 of organic content (Fig. S1) and this particular layer visually resembled sewage sludge.

255 A distinct relationship between oxalate-extractable P and oxalate-extractable Al was observed

256 for wastewater loaded samples ($r^2 = 0.92$, $p < 0.001$), whereas the correlation between

257 oxalate-extractable P and oxalate-extractable Fe was much weaker ($r^2 = 0.6$).

258 As evidenced by the pH-dependence experiment, the solubility of the bound P was generally

259 lowest at pH values ranging from 4 to 6 (for the Kn, Lu, Ri and Tu soils, see Fig. S2). All

260 sites showed an increasing P solubility when the pH value was decreased further (pH < 4).

261 Except for the Tu site (for which no high-pH data were available), an increased P solubility

262 was observed at higher pH starting at pH 5.5 for Lu and at around 6 for the sites Kn and Ri.

263 If the layer thickness and the density of the soil are considered, the total P accumulation on a

264 volume basis in each bed can be summed up to 0.32, 0.32, 0.46, 0.66, 0.73 and 0.87 kg m^{-3} for

265 the Gl, Ri, Ha, Kn, Tu and Lu sites respectively (Fig. 3). Among the studied sites no

266 relationship could be established between the estimated P load and the amount of accumulated

267 P (Fig. 3).

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3.3 XANES Analysis

Of the 15 standard compounds included in the evaluation, 8 standards (Fig. 4 (a)) were represented in any of the ten best fits at weights above 10 % (Table 2). In both the Ha, Lu and Tu samples the XANES analysis indicated significant amounts of P bound as amorphous aluminium phosphates or as P adsorbed onto aluminium (hydr)oxide surfaces. The best fits resulted in weights between 24 and 62% of these phases (Table 2, Fig. 4 (b)). Organically bound phosphates were also well represented in all analyses (weights between 35 and 43%). Evidence for the importance of calcium phosphates was found only in the Ha sample where calcium phosphates predominated with 43% weight in the best fit (Table 2, Fig. 4 (b)).

For the best fits (Fig. 4 (b)) the Athena software reported R factors between 0.022 and 0.045. In general the distribution of P between Al, Ca and organically bound P was stable among the 10 best fits (Table 2). The differences between the fitting results from the Lu site was caused by a small amount (weight less than 10%) of a third component, the identity of which differed in the fits. The weight of iron phosphates never exceeded 16% at any site.

3.4 Soil properties as affected by wastewater

When comparing reference samples and wastewater-loaded samples, several differences in soil properties were observed. In the wastewater-loaded samples, the pH of the top layer was typically between 1 and 2 pH units lower than in the reference samples. Further, oxalate-extractable metals had increased considerably in the deeper layers at many sites (Fig. 2, Fig. S1). However, there were no distinct patterns in the depth distributions of oxalate extractable-metals (Fig. S1). The sorption experiment revealed that for the Lu site, the sorption capacity was higher in reference samples than in wastewater loaded samples (Fig. S3). In fact, the opposite was true for the Tu site while no significant differences were observed at the Kn and

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291   Ri sites. According to the sorption data of the reference samples, the soils at the Tu and Lu

292   sites were superior to the Kn and Ri sites in terms of the P removal capacity (Fig. S3). At an

293   equilibrium concentration of 1 mg P L^{-1} the Lu and Tu reference samples both removed more

294   than 50 mg P kg^{-1} whereas the Kn and Ri sites removed less than 30 mg kg^{-1}. However, as

295   evidenced from the mass balance calculations, the Tu, Lu, Kn and Ri sites had removed

296   between 213 and 680 mg P kg^{-1}. Thus, the laboratory-established P removal capacities were

297   about an order of magnitude lower than those obtained through mass balances.

298   **3.5   Phosphorus leaching in the column experiment with wastewater**

299   After five weeks of wastewater load biological processes in the columns were active and

300   performed well in terms of nitrification and organic degradation. More than 97 % of the N

301   (NO_3-N+ NO_2+NH_4-N) was present as NO_3 and the BOD concentrations were below the

302   detection limit of 3 mg L^{-1} (data not shown). In week 9 the results indicated 100% nitrification

303   and the reduction of BOD was still complete. The fraction of total P that was inorganic PO_4-P

304   (as evidenced by the acid molybdate method), varied between 13 and 80 % with a mean value

305   of 50 % (data not shown).

306   The total P concentrations were generally low in the effluent waters during wastewater load

307   (Fig. 5). The Kn and Ri sites had relatively weak P removal (the effluent P concentrations

308   ranged from 0.8 to 3 mg L^{-1}, which corresponded to between 74 and 85 % P removal on mass

309   basis). By contrast the Lu and Tu sites had very strong P removal, with effluent P

310   concentrations always being <0.3 mg L^{-1}, corresponding to 97 % P removal (Fig. 5). For the

311   silica reference a small and relatively constant P removal (18 % on mass basis) was observed

312   and the effluent concentrations varied between 3 and 5 mg L^{-1} (Fig. 5). The amount of P

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313　accumulated during the loading period was around 8.3 mg P kg^{-1} for the Lu and Ri sites and

314　around 9.6 mg P kg^{-1} for the Kn and Tu sites.

315　The pH value in the effluent was variable (Fig. S4). The Ri and Silica reference columns were

316　following the pH of the influent wastewater closely (around pH 8), whereas the other sites

317　generally had a lower and more variable pH (5.7- 7.7). The Kn site had a rising pH trend

318　(from about pH 7 to pH 7.7) during the experiment and was approaching the pH value of the

319　influent wastewater. However, the Lu and Tu sites did not follow any distinct pattern and the

320　pH varied between 5.7 and 7.7.

321　**3.6　Phosphorus leaching in the column experiment with deionized water**

322　When the influent to the columns was shifted from wastewater to deionized water a dramatic

323　colour shift occurred in the effluent, i.e. from transparent and clear to yellowish or brownish

324　with high turbidity. However, this observation did not bring about a consistently different PO_4

325　: total P ratio. The concentration of dissolved PO_4-P in the effluent was in the range from 20

326　to 80 % of the total P with a mean value of around 50 %, i.e. similar as in the first column

327　experiment with wastewater. The P concentration in the effluent varied between the different

328　sites, but effluent P concentrations were consistently higher than during wastewater load (Fig.

329　5). The Kn columns generally had the highest effluent P concentrations which were initially

330　up to 6 mg L^{-1} (Fig. 4). After week 4 the Kn column effluent concentrations stabilized at

331　around 3 mg L^{-1}. The silica reference columns and the Ri site columns followed a similar

332　pattern with initially high effluent P concentrations (up to 4 and 3 mg L^{-1} respectively) and

333　then the P concentrations decreased to about 2 mg L^{-1} at the end of the experiment (Fig. 4).

334　The P leaching patterns for the Ri and Lu site columns were different and the P discharge

335　from these columns were significantly lower. In the latter two columns the dissolved P

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336   concentration was quite stable from week 6 onwards, with dissolved P ranging from about 1

337   to 1.5 mg L^{-1} (Fig. 4).

338   The shift from wastewater to deionized water generally resulted in a pH increase in the

339   effluent waters except for the Ri site columns and the silica reference columns, for which pH

340   value decreased a little (Fig. S5). At the end of the experiment the pH value in all columns

341   ranged from 6.7 to 7.7.

4   Discussion

343   The decrease in soil pH and the increase in oxalate-extractable metals that we observed (Fig.

344   2, Fig. S1) is consistent with other studies (Robertson, 2003; Eveborn et al., 2012). In most

345   cases (neutral to strongly acid soils) a pH decrease will probably favour the P removal, as

346   sorption and precipitation processes that involve iron and aluminium (hydr)oxides are usually

347   more efficient at low pH. According to the pH-dependence results (Fig. S2), the lower pH

348   limit (below which P solubility rapidly increases) are between pH 3.5 and 4. In calcareous

349   soils the pH decrease might prevent the formation of calcium phosphates as these

350   precipitation processes is most effective at pH >9 (Eveborn et al., 2009).

351   The increasing levels of oxalate extractable aluminium and iron over time (Fig. 2, Fig. S1)

352   may enhance the P removal. It is likely that both precipitation of aluminium phosphates and

353   surface complexation reactions occur. As concluded earlier (Eveborn et al., 2012), the P to Al

354   ratio in the oxalate extract is larger (0.73 according to linear regression of oxalate-P vs.

355   oxalate-Al) than would be expected if surface complexation reactions alone would be

356   responsible for the P removal. The XANES analysis confirms the importance of aluminium

357   chemistry (Table 2) but the spectral differences between amorphous aluminium phosphates

358   and phosphorus adsorbed to aluminium (hydr)oxides is small (Fig. 4 (a)). Thus, it is not

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359   evident that any of these two mechanisms predominates at any of the sites. Aluminium-rich P

360   phases have been identified as important sinks for P in similar environments (Zanini et al.,

361   1998; Arai & Livi, 2013). According to the XANES analysis (Table 2), even organic P may

362   play an important role in the P accumulation. However, the long term stability of this P pool is

363   unclear. Degradation of the organic substances will result in the release of mineralized P.

364   Several mechanisms have been proposed that may cause the transfer of surface-bound P into

365   stable P pools (Robertson, 2008), which may in the long run increase the P sorption capacity

366   of soils. In this study we observed clear discrepancies (up to over tenfold) between laboratory

367   sorption data on reference samples and the long term P accumulation in the field (based on

368   mass balances). Changes in pH and in oxalate-extractable metals during the wastewater load

369   can partly explain these discrepancies and therefore the results do not necessarily imply that

370   any P will be immobilized into inactive, "insoluble" forms. In fact Lookman et al. (1995)

371   found that all oxalate- extractable P was reversibly fixed in a selection of acid sandy soils

372     $(3.9 < pH_{KCL} < 5.7)$.

373   It is clear from our P load estimates and P accumulation calculations that the P removal

374   capacity in the subsoil can be easily exceeded. From this we can conclude that the long term

375   performance of STS are much dependent on the wastewater load. Let us assume that the

376   phosphate concentration in a septic tank effluent is on average 10 mg L^{-1}, that the long term

377   hydraulic loading rate is 0.6 cm d^{-1} and that the available soil volume for treatment in the

378   unsaturated subsoil is 1 m^3 per meter of drainage tube. In such a scenario (close to that of

379   Robertson (2012)), the STS studied here will theoretically (as estimated from mass balance)

380   be able to accumulate P during 15 to 40 years of wastewater load, the exact value depending

381   on the soil properties (Fig. 3). However, if the hydraulic loading rate is increased to 3 cm d^{-1}

382   (close to the maximum load according to USEPA guidelines, but still common with Swedish

17

383   design specifications) the time it takes to saturate the system will decrease to between 3 and 8

384   years. Accordingly, the hydraulic loading rate is crucial for the P mass balance calculations.

385   We expected poor P removal when the already overloaded soil (according to P mass

386   balances) was subject to further wastewater application but the results were contradictory

387   (Fig. 5). The P discharge during the experiment was even lower than that reported from

388   several short-term field studies (Nilsson & Stuanes, 1987; Aaltonen & Andersson, 1996;

389   Nilsson et al., 1998). Accordingly, the results obtained do not seem to reflect the actual P

390   leakage from old and heavily loaded STS. One possible explanation to the contradictory

391   behavior could be that the collected soil layers were mixed (separately) during the setup of

392   column replicates. This homogenization procedure may eventually expose new or hidden

393   sorption or precipitation agents in the soil and eliminate macro pore pathways that might be

394   present in an undisturbed soil profile.

395   The release pattern observed during the deionized water load is not fully understood. It is

396   surprising that much higher concentrations of P were found in the leachate during deionized

397   water load than during wastewater load (Fig. 5). Zurawsky et al. (2004) partly explained

398   similar observations (leachate concentrations up to 9 mg L^{-1}) from subsoils of STS by

399   reductive dissolution of Fe-P phases. However, according to the XANES analysis, iron

400   phosphates were not present to any considerable extent in the studied soils and the Fe

401   concentrations in the leachate during wastewater load were usually very low (< 0.25 mg L^{-1};

402   data not shown). The evidence for substantial amounts of aluminium phosphates in the soil

403   (Table 2) indicates that dissolution of these compounds is a possible P release mechanism.

404   However, the P concentrations in the leachate were unreasonably high to be explained only

405   through this mechanism. We hypothesize that the dramatic shift in ionic strength might

406   destabilize particulate material and increase the mobilization of non-reactive P. A substantial

18

407   part of the P is organically bound (Table 2) and may be a source for such mobile forms of P.

408   Destabilization mechanisms has been proved to be important elsewhere (Laegdsmand et al.,

409   2005). Although no significant changes in the ratio of PO_4-P:total P could be observed in the

410   experiments (when comparing data from the periods of deionized water load and wastewater

411   load) this hypothesis might still be possible.

412   The result from the column study using deionized water load, indicates that certain STS bed

413   material cause substantial wash-out of P. The P wash-out could be caused by e.g. ground

414   water inflow, diluted wastewater application or long-term drainage after decommissioning.

415   However, the sites Lu and Tu, which had the highest oxalate extractable aluminium contents

416   (Fig. 2 and Fig. S1), showed much less P discharge during both wastewater application and

417   deionized water application (Fig. 4) in comparison to the other sites. These observations

418   emphasize the role of aluminium chemistry for efficient P removal and are supported by other

419   desorption studies on acid sandy soils (Lookman et al., 1995). The findings also show that

420   despite favourable conditions for strong P fixation, significant amounts of P can be released.

421   In terms of groundwater quality even a discharge of 1 mg P L^{-1} is substantial. Hinsby et al.

422   (2008) suggested 0.08 mg P L^{-1} as threshold value for P in Danish ground water systems (for

423   the protection of dependent ecosystems).

424 **5   Conclusion**

425   •   Phosphorus removal in the unsaturated subsoil of STS is limited, and the risk for P

426   leakage will be dependent on the long term magnitude of the P load. Thus, STS in

427   close proximity to water bodies will pose a risk for significant P leakage.

428   • It is not safe to assume that P accumulated in STS is immobilized irreversibly. The

429   vulnerability to wash-out of P through groundwater through-flow or atmospheric

430   precipitation could be high.

431   • In the investigated sandy soils both the P accumulation and the vulnerability to wash-

432   out are correlated to the amount of oxalate-extractable Al. In the most P-retaining STS

433   P is accumulated mainly as aluminium phosphates or as P associated with aluminium

434   oxyhydroxide surfaces, although organically bound P was also an important phase

435   according to the XANES analysis.

Acknowledgements

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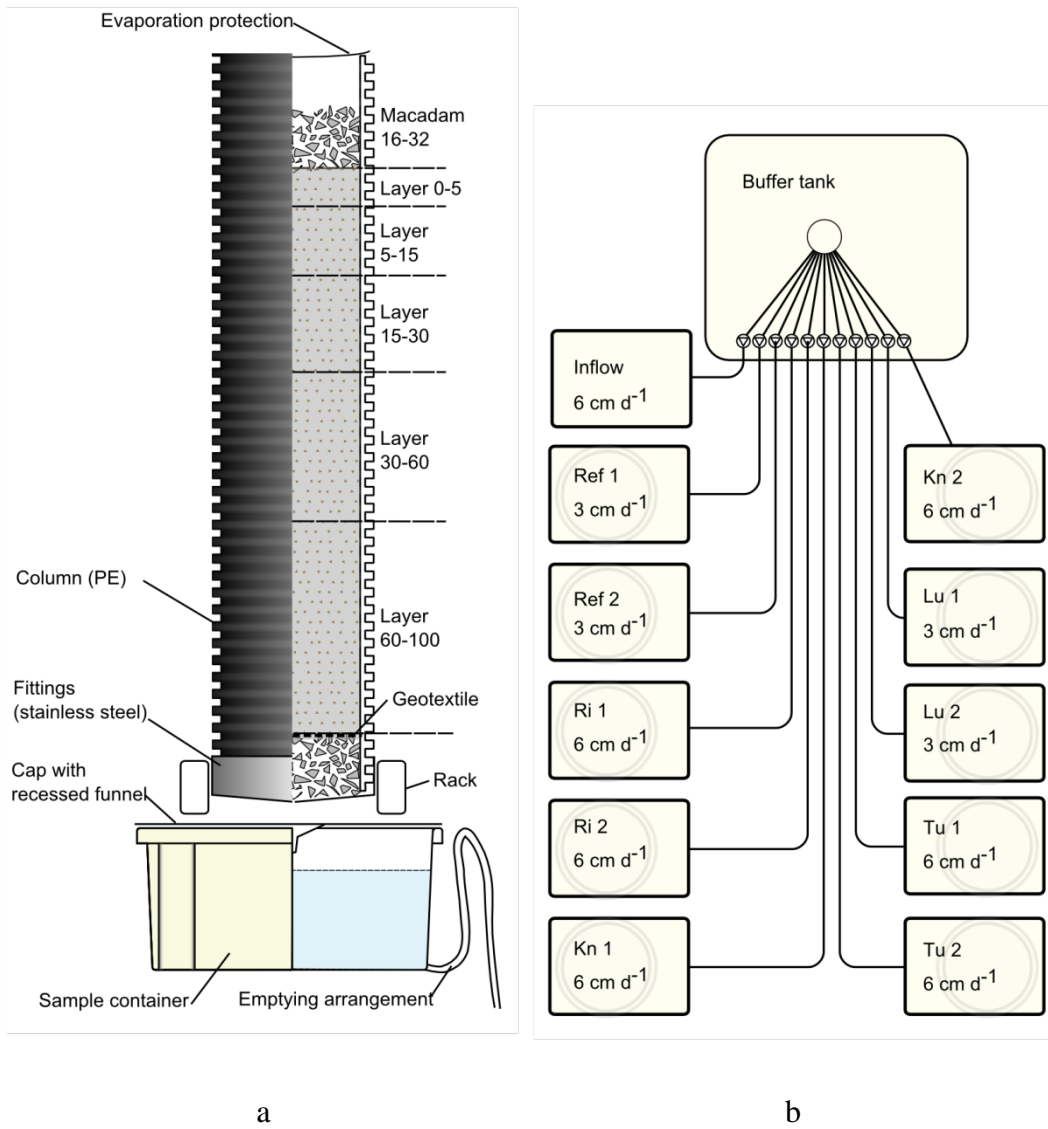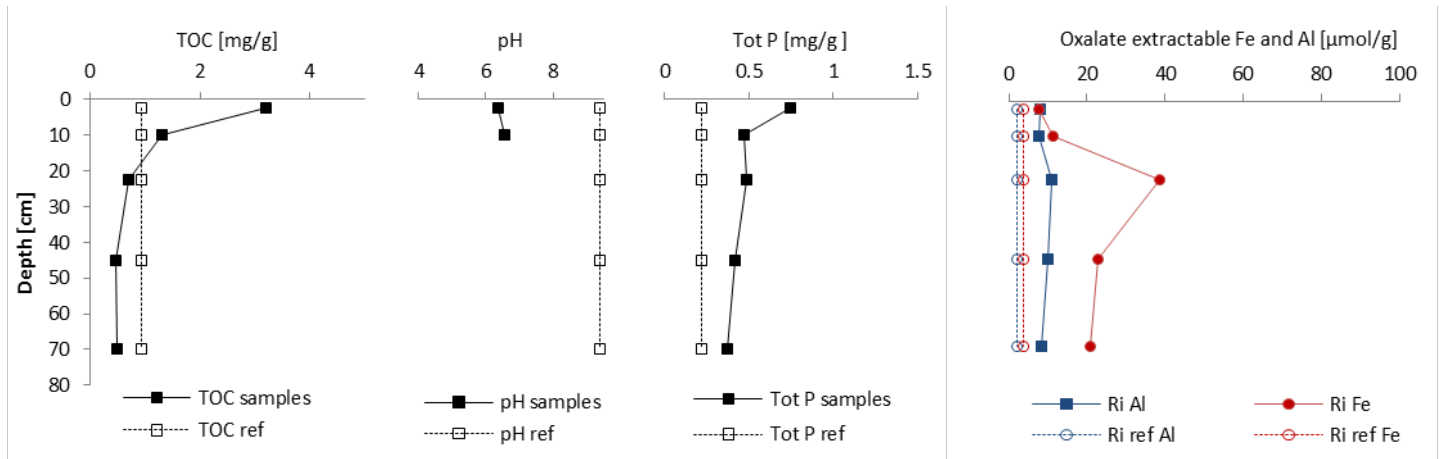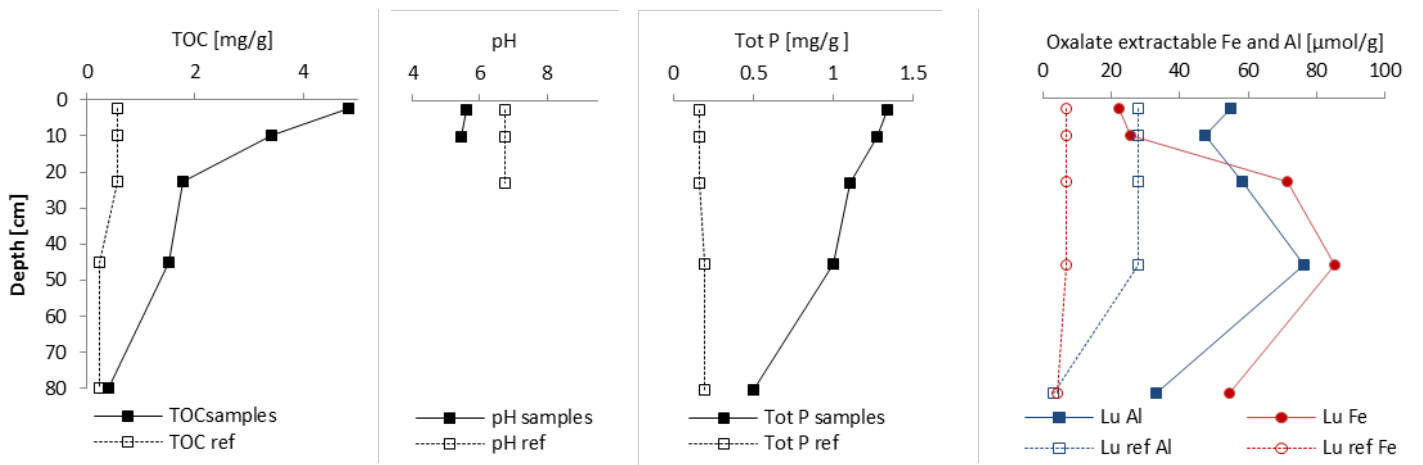a   b

Figure 1. Layout of columns and sample containers (a) and schematic view over the column experiment including soils and loading rates (b).
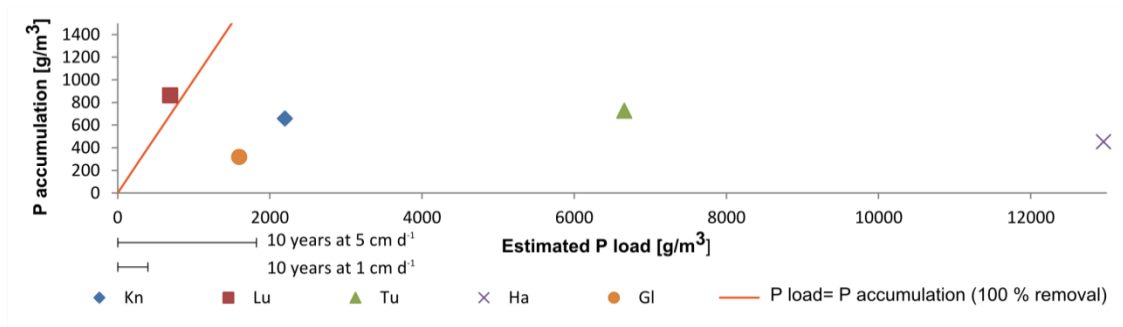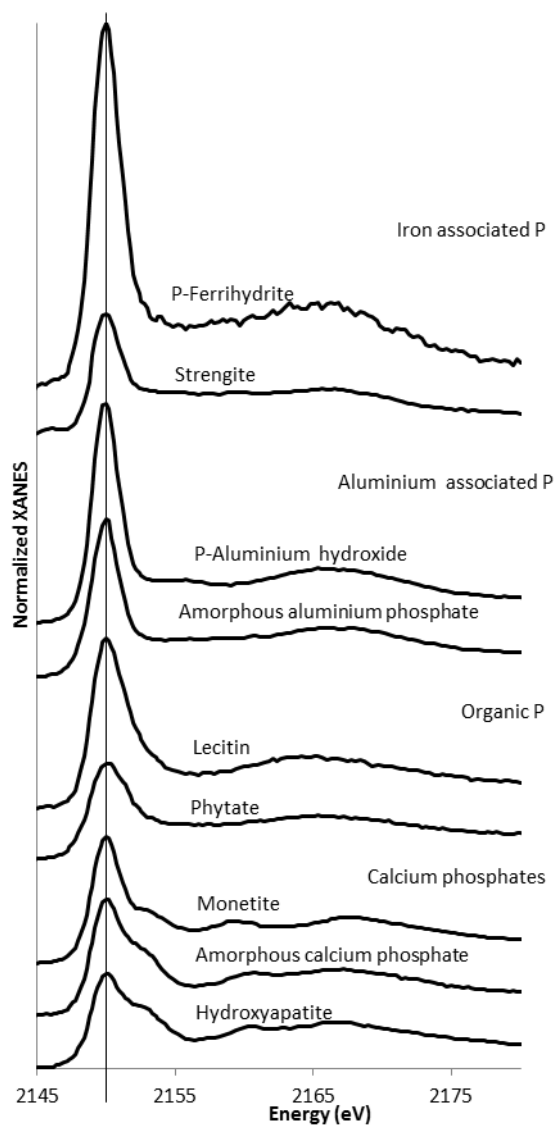
a)   Ri site

b)   Lu site

Figure 2. Depth distribution of different soil properties for samples and reference samples at a) site Ri and b) site Lu.
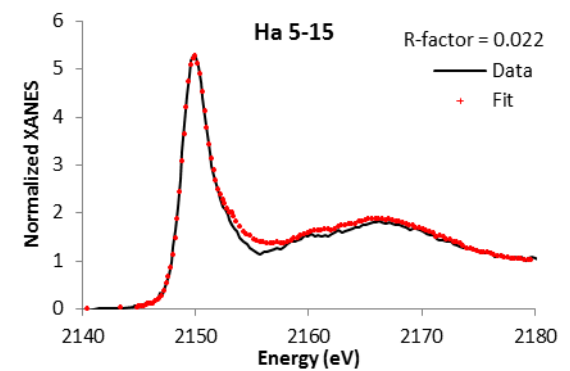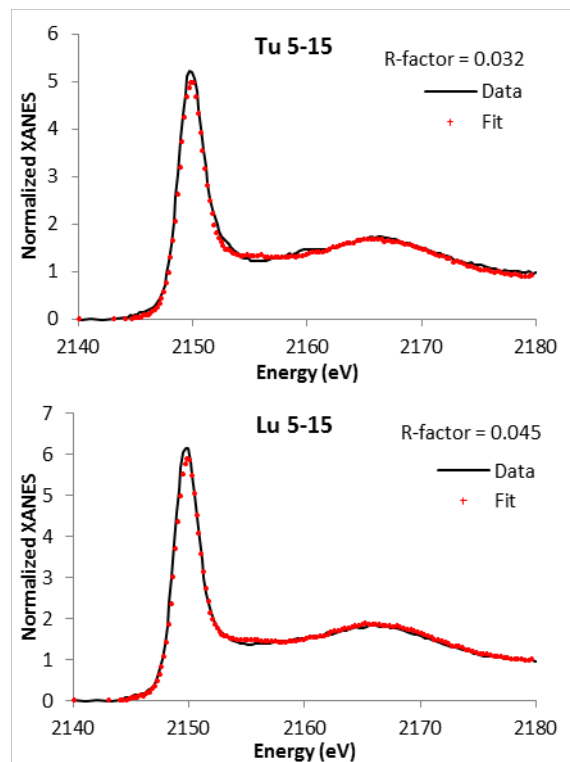
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Figure 3. P accumulation at the studied sites in relation to the estimated P load. P load estimations and the basis for these are given in Table 1.
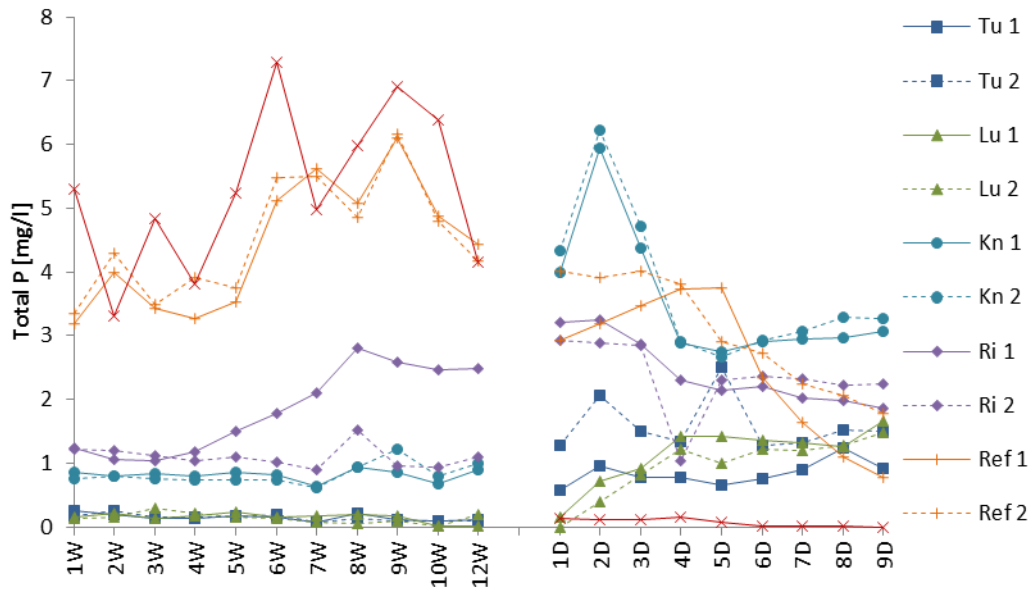
560   Figure 4. Spectra for standards represented (with weights>10%) in the 10 best linear

561   combination fits for the samples (a) and overlaid plots of sample data and the best (lowest R-

562   factor) linear combination fits (b).

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565 Figure 5. Total P concentrations in inflowing water and leachates from the Tu site column

566 replicates (Tu 1, Tu 2), Lu sites column replicates (Lu 1, Lu 2), Kn site column replicates (Kn

567 1, Kn 2), Ri sites column replicates (Ri 1, Ri 2) and silica reference replicates (Ref 1, Ref 2)

568 during 12 weeks of wastewater water load (W1-W12) and 9 weeks of deionized water load

569 (D1-D9).

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Table 1. Description of studied soil treatment systems

	Tu	Gl	Lu	Kn	Ri	Ha
Design base (pe)	225	5	5	75	150	100
Connected (pe)	n.a.	6	4	40	n.a.	n.a.
Surface area(s) (m^2)	2x196	30	50	80	2x160	2x50
Hydraulic load[a] (cm d^{-1})	33	2.2	0.9	25	n.a.	30
P load (g m^{-2} yr^{-1})	370[c]	80[b]	30[b]	200[b]	n.a.	540[c]
Age (year)	18	20	23	11	28	24
Pre treatment	Septic tank	Septic tank	Septic tank	Lined pond	Septic tank	Septic tank
Wastewater distribution	Gravity fed, open surface distribution	Gravity fed, drain field	Gravity fed, drain field	Pump fed, drain field	Pump fed, drain field	Pump fed, open surface distribution
Thickness of soil bed (m)	>1	>1	>1	0.9	0.8	0.9
Discharge	Drained to surface water	Ground-water	Ground-water	Ground-water	Drained to surface water	Drained to surface water

[a] Based on annual mean flows and active infiltration areas (where several beds are shifted). Mean flows for the sites Gl, Lu and Kn have been calculated based on a water usage equivalent to 180 L person^{-1} d^{-1} and 60 % home attendance. Mean flows at other sites taken from Bylund (2003).

[b] An estimation based on mean flows (as described above), total infiltration area and a 10 mg L^{-1} P concentration in the wastewater (Jönsson et al., 2005).

[c] Calculated from a dataset of ~50 inflow and P concentration measurements (Bylund, 2003) and total infiltration area.

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Table 2. Fitting results for linear combination fit performed in first derivative space with an energy range between -5 and 30 eV. Standards represented with weights<10% not reported.

Category	Standard component	Weight, best fit				Presence in 10 best fits							Mean weight
						Ha 5-15							
Al-P	Amorphous aluminium phosphate				x	x	x	x					0.29
	P adsorbed to Al(OH)$_3$	0.24	x	x						x	x	x	0.21
Ca-P	Apatite			x		x			x				0.41
	Amorphous calcium phosphate	0.43	x		x		x	x	x		x	x	0.47
Organic P	Phytic Na	0.35	x	x				x	x				0.32
	Lecithin				x	x			x		x		0.27
Fe-P	P adsorbed to ferrihydrite					x		x		x			0.13
						Lu 5-15							
Al-P	Amorphous aluminium phosphate	0.3	x										0.3
	P adsorbed to Al(OH)$_3$	0.32	x	x	x	x	x	x	x	x	x	x	0.45
Organic P	Phytic Na	0.36	x	x	x	x	x	x	x	x	x	x	0.4
Ca-P	Monetite				x								0.11
						Tu 5-15							
Al-P	Amorphous aluminium phosphate	0.28	x	x	x	x			x		x		0.37
	P adsorbed to Al(OH)3	0.2	x				x	x		x		x	0.27
Ca-P	Monetite									x	x		0.23
	Amorphous calcium phosphate					x		x	x				0.19
Organic P	Phytic Na	0.43	x	x	x		x	x	x	x	x	x	0.4
Fe-P	P adsorbed to ferrihydrite				x		x	x					0.11
	Strengite				x							x	0.26

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Supplementary Material

Manuscript title: Phosphorus in soil treatment systems: accumulation and mobility

Authors: David Eveborn*, Jon Petter Gustafsson, Elin Elmefors, Lin Yu, Ann-Kristin Eriksson, Emelie Ljung, Gunno Renman

Pages: 8

Number of Tables: 2

Number of Figures: 5

Table S1. Characteristics of wastewater used in the column study and analytical methods utilized. All values in mg L^{-1}(except pH).

|	Week 1	Week 5	Week 9	Analytical method
BOD7	120	140	160	ISO 5815:1989
CODCr	280	280	370	Kuvette test (Dr Lange LCK814)
SS	110	90	140	EN 872:2005
Tot-N	56.1	59.5	75.3	ex- SS 028131-1 oxidation with peroxodisulphate
NH4-N	41.8	40.5	49.8	ISO 11732, flow analysis and spectrometric detection
NO2-N	0.25	0.22	0.47	ISO 6777:1984, molecular absorption spectrometric method.
NO3-N+ NO2-N	0.70	0.62	0.35	SS 028133-2 appendix A, reduction of nitrate with copperized cadmium followed by spectrophotometric detection
Tot-P	6.2	5.9	7.8	SS-EN 15681-2:2005
PO4-P	4.1	4.4	4.9	SS-EN 15681-2:2005
Fe	0.14	0.28	0.19	ISO 17294-2, ICP-MS
Al	0.62	0.60	0.72	ISO 17294-2, ICP-MS
Ca	81	89.4	132	ISO 17294-2, ICP-MS
Alk	537	517	569	ISO 9963-1:1994, acidimetric titration
TOC	85.4	61.3	84.6	SS-EN 1484 ed. 1. High temperature catalytic oxidation
pH	8.3	8.1	8.1	SS 028122-2

Table S2. Characteristics of unused soils (reference samples) at the studied sites

|		Gl 0-30	Gl 30-100	Lu 0-60	Lu 60-100	Ri	Ha	Kn	Tu
Elementanalys (mg/g dw^{-1})	Si	418	425	378	364	395	383	367	371
	Al	57	60	78	77	55	61	81	73
	Ca	10	9	8	11	17	30	10	10
	Fe	31	37	26	43	23	24	29	44
	K	22	31	41	37	30	37	41	37
	Mg	4	3	4	5	2	3	5	7
	Mn	0.44	0.49	0.50	0.67	0.35	0.37	0.57	0.65
	P	0.20	0.15	0.16	0.19	0.22	0.16	0.19	0.31
pH (in H$_2$0)		5.89	-	6.25	-	8.89	8.94	6.84	6.45
[d]P$_{ox}$ (mg/g dw^{-1})		0.20	-	0.07	-	0.06	0.01	0.05	0.15
GD50 (mm)		0.044[a]	0.21[b]	0.26[a]	1.64[b]	1.50	3.93	1.45	1.02
[c]K sat (m/d)		0.21		24.53		20.93	90.23	25.30	7.44
Dry bulk density (kg/m^3)		1700		1300		1500	1400	1500	1600

a) Fine grained layers in the bed
b) Coarse grained layers in the bed
c) Measured at 55 cm depth
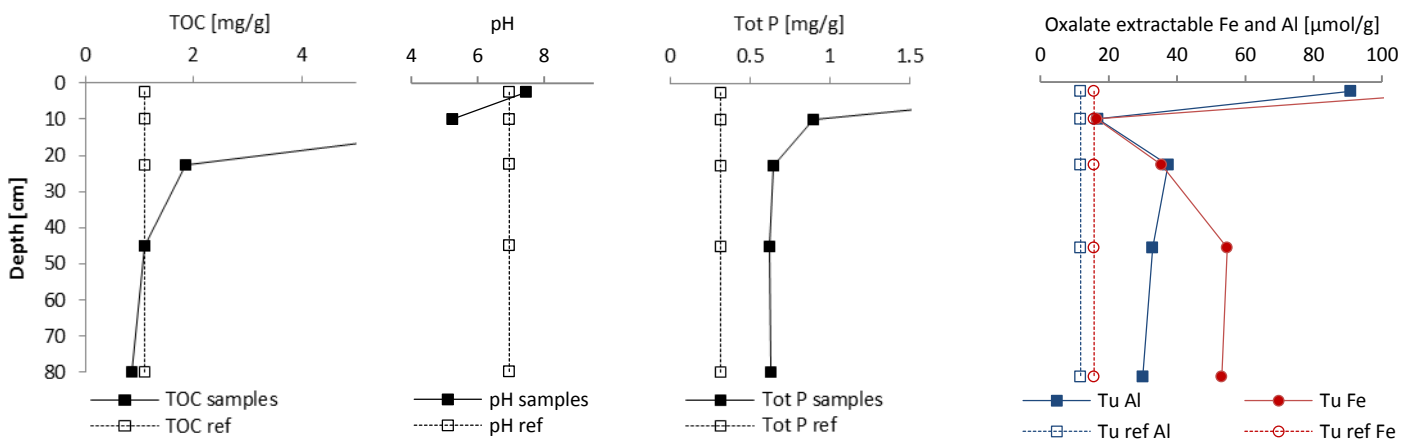d) P$_{ox}$ = Oxalate extractable P
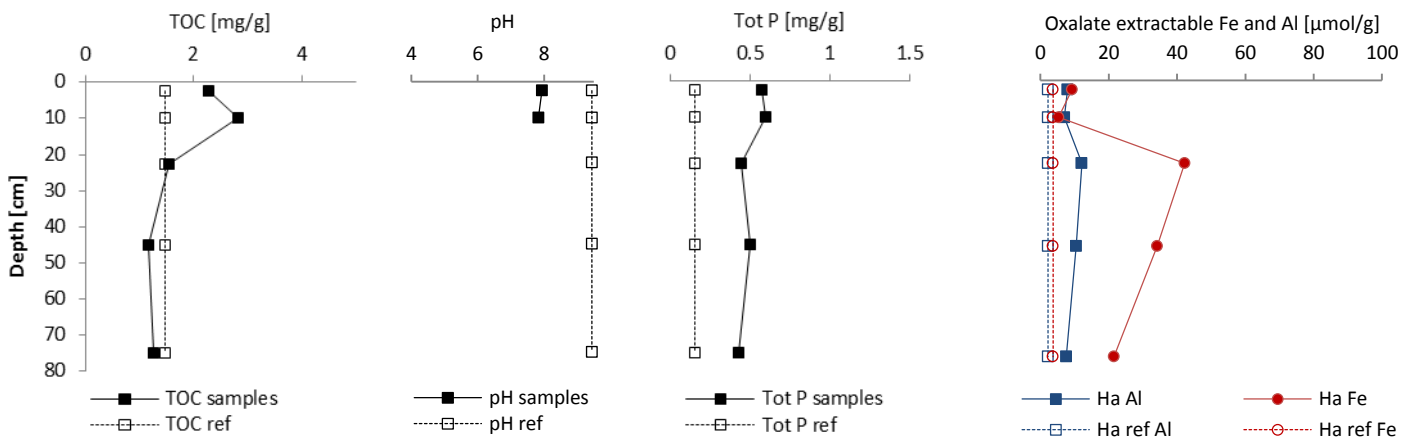
a) site Ha
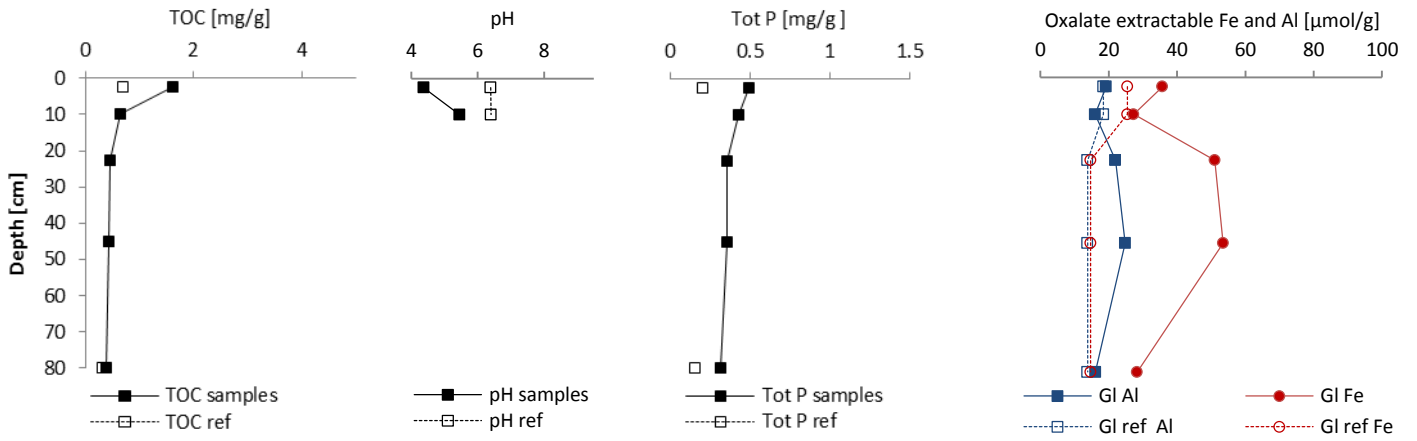
b) site Gl
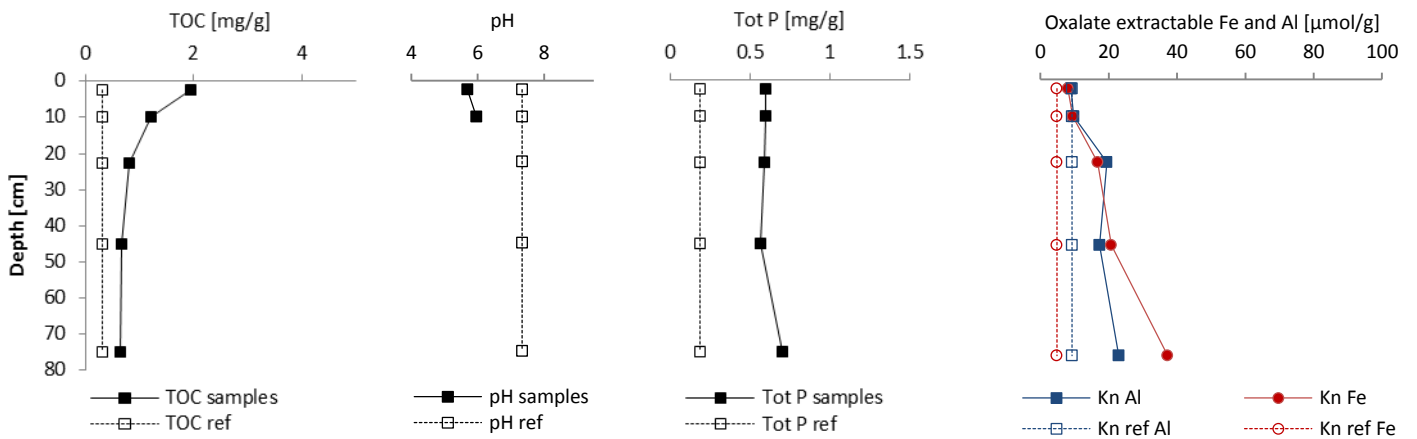
c) site Kn

d) site Tu

Figure S1. Depth distribution of different soil properties for samples and reference samples at *a* site Ri , *b* site Gl, *c* site Kn and *d* site Tu.
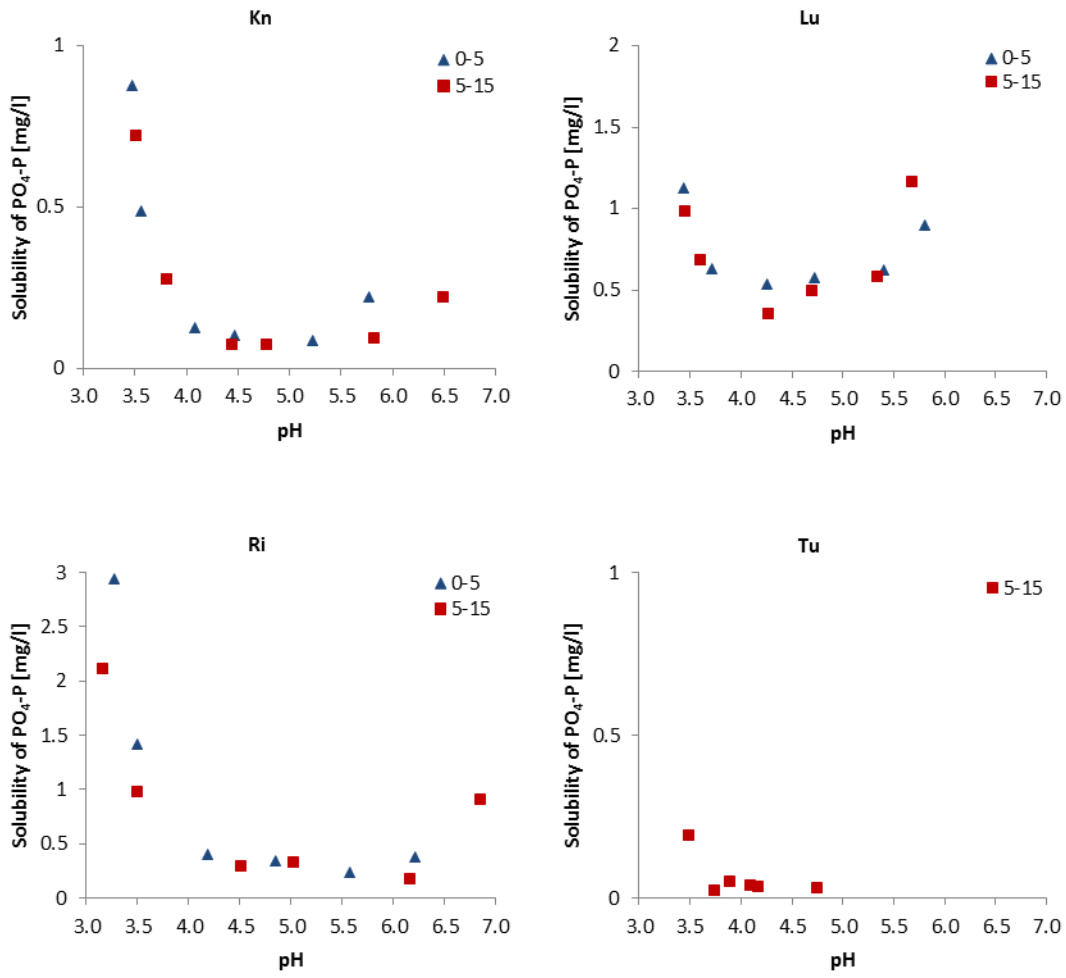
Figure S2. Solubility of PO$_4$-P as a function of the pH obtained in solution after equilibration with acid (HNO$_3$) and base (NaOH) additions.

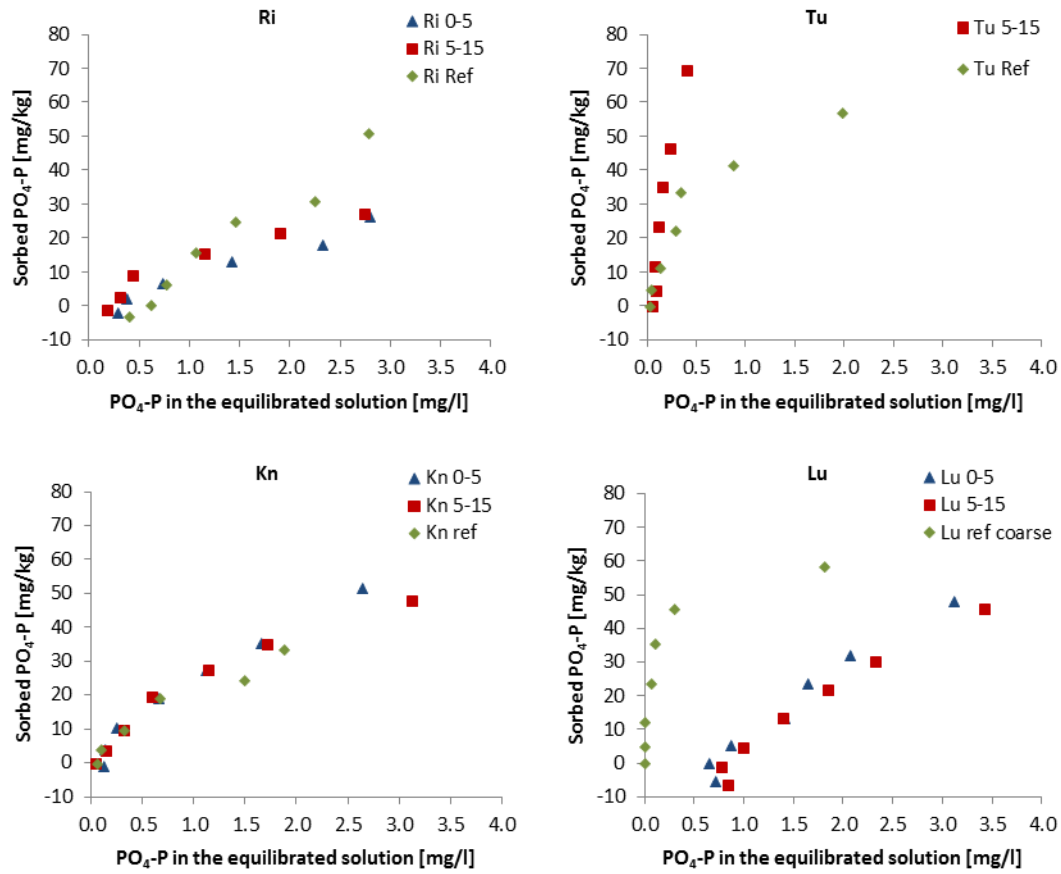Figure S3. Sorbed (removed) P (mg P /kg soil) as a function of the equilibrium concentration of PO$_4$-P (mg PO$_4$-P/l) for layers 0-5, 5-15 and reference samples at the sites Ri, Tu, Kn and Lu. Values for the layer 0-5 at the Tu site are excluded because of its extremely large concentration of organic matter.
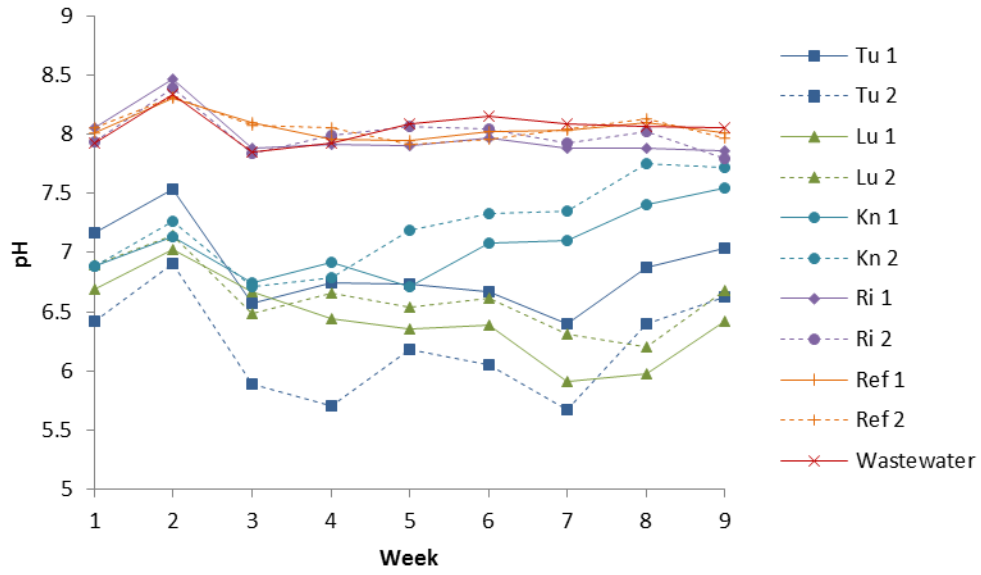
Figure S4. pH in influent wastewater and leachates from the Tu site column replicates (Tu 1, Tu 2), Lu sites column replicates (Lu 1, Lu 2), Kn site column replicates (Kn 1, Kn 2), Ri sites column replicates (Ri 1, Ri 2) and silica reference replicates (Ref 1, Ref 2) during 9 of 12 weeks of wastewater load.
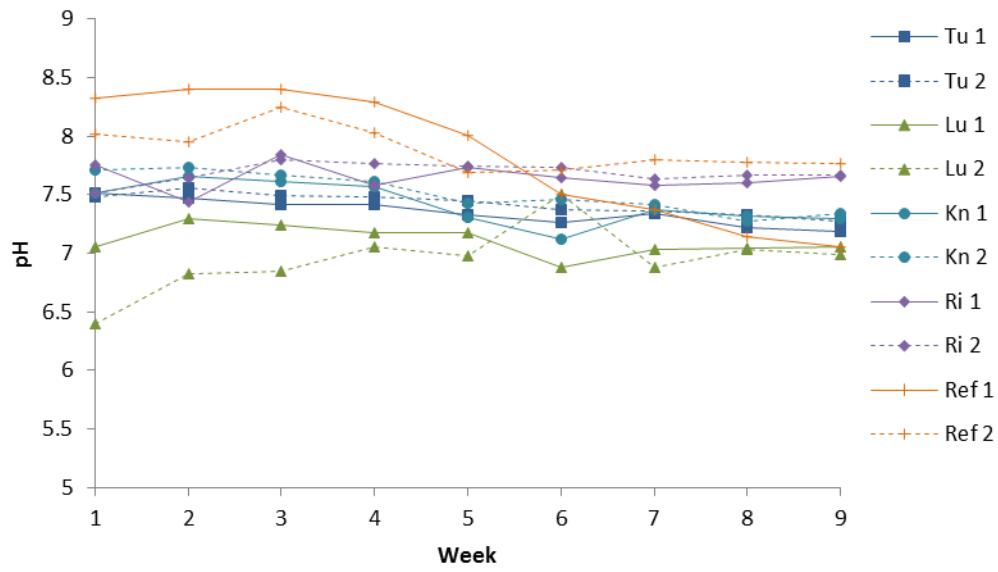
Figure S5. pH in leachates from the Tu site column replicates (Tu 1, Tu 2), Lu sites column replicates (Lu 1, Lu 2), Kn site column replicates (Kn 1, Kn2), Ri sites column replicates (Ri 1, Ri 2) and silica reference replicates (Ref 1, Ref 2) during 9 weeks of deionized water load.