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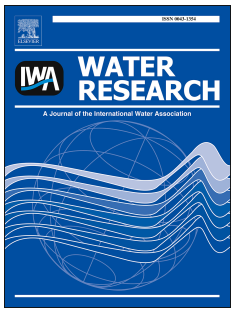

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Acidification and recovery of phosphorus from digested and non-digested sludge

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Abstract

Acidification was used to dissolve phosphorus from digested and non-digested sludge from five wastewater treatment plants in order to make phosphorus accessible for subsequent recovery. More phosphorus was dissolved from digested sludge (up to 80%), with respect to non-digested sludge (~25%) and the highest recovery was observed at pH 2. The acid consumption for digested sludge was higher than for non-digested sludge due to the presence of the bicarbonate buffer system, thus CO_2 stripping increased the acid consumption. In all the experiments, the sludge was exposed to acid for 1h. For the five tested sludge types, 60-100 mmol o-P was released per added mol H_2SO_4. It was mainly iron and calcium compounds that accounts for the phosphorus release at low pH. The release of heavy metals was in general low (<30%) for all the wastewater treatment plant, as Zn, Cd and Ni showed the most critical release after acidification of non-digested sludge.

Keywords: *Phosphorus, acidification, sludge, heavy metals*

Introduction

The human population will grow to 9.3 billion by 2050, meaning that food production needs to increase accordingly. A high production of agricultural products can only be achieved by the use of fertilizers of

which nitrogen, phosphorus and potassium are usually deficient in the soil. The P-fertilizers used today almost exclusively comes from mining of phosphate rocks, which are estimated to be depleted by the end of this century (Cordell et al., 2009; Shu et al., 2006). Consequently, it is necessary to recycle phosphorus to ensure food security for future generations. Recovery of phosphorus from wastewater is one method to overcome the possible phosphorus scarcity. Wastewater contains large amounts of phosphorus and the Danish Environmental Protection Agency has estimated that it eventually can cover around 20% of the total phosphorus import in Denmark (Miljøministeriet (The DanishEnvironmental Protection Agency), 2013). Moreover, Denmark is nexporting agricultural products (mainly meat and dairy products), thus phosphorus is also leaving the country–(Klinglmair et al., 2015). In Denmark, the ratio of out- to inflows of phosphorus is 0.66, which is higher compared to the EU (0.27) (Klinglmair et al., 2015). In 2013, the Danish government had an ambition to increase the phosphorus recycling from sewage sludge from 50-55% to 80% (The Danish Government, 2013). Therefore, new and improved methods for phosphorus recycling and recovery needs to be developed. In this study, we explore the potential to improve phosphorus recovery by sludge acidification of various sludge types from different wastewater treatment plants in Denmark.Today, phosphorus in wastewater is usually removed biologically or chemically to meet discharge criteria whereby the phosphorus ends up in sewage sludge. Sewage sludge can be used directly as a fertilizer, but in several countries in Europe (Tarayre et al., 2016), land spreading of sludge is banned as sludge may be contaminated by heavy metals, pathogens and toxic organic compounds (Vardanyan et al., 2018). If sludge is incinerated, phosphorus can to be recovered from the ash, but it is still an expensive method and it has been questioned, whether incineration and recovery of phosphorus from ash is a sustainable technology (Vaneeckhaute et al., 2017). An alternative method is to recover and recycle dissolved phosphorus through precipitation from the liquid phase after removal of the solid material. For instance, phosphorus can be precipitated from the centrate or filtrate after dewatering of digested sludge. Some wastewater treatment plants has implemented fluidized bed reactors to recover phosphorus from liquid phase by adding magnesium and precipitating struvite ($MgNH_4PO_4 \cdot 7H_2O$) (Cordell et al., 2011). However, Hermann et al. (Hermann, 2009) and Pinnekamp et al. (Pinnekamp et al., 2013) states that only 30-50 % of all the phosphorus present in the wastewater can be recovered by this technique depending on the efficiency of the biological phosphorus

53 removal process. A large fraction of phosphorus in sludge exists as particulate phosphorus including metal-
54 salts e.g. calcium phosphates and iron phosphates, and phosphorus accumulated in microorganisms (as
55 polyphosphate and in the cell wall) (Venkiteshwaran et al., 2018). Polyphosphate-accumulating organisms
56 are embedded in the sludge flocs and removed with solid fraction during dewatering (Larsen et al., 2006). A
57 part of the phosphorus stored in phosphate accumulation organism is released during digestion (Hu et al.,
58 2018). Metals salts are also expected to end up in the solid phase (Meulepas et al., 2015). Thus, most of the
59 phosphorus in the metal-salts and the microbial mass is expected to end up in the sludge and not in the liquid
60 phase and the phosphorus content in the sludge is thus not accessible for phosphate recovery.

61

62 The current study focusses on phosphorus recovery through acidification, separation and phosphorus
63 precipitation. Recent studies have shown that acidification of sludge increases the dissolved phosphorus
64 concentration due to dissolution of the metal-phosphate-complexes (Latif et al., 2015). Low pH anaerobic
65 digestion can be utilized, but it reduces the biogas production (Latif et al., 2015). Alternatively, sludge can
66 be acidified after digestion, which has previously been done by Antakyali et al. (Antakyali et al., 2013),
67 Shiba and Ntuli (Shiba and Ntuli, 2017) and SEG et al. (SEG - Stadtentwässerung Göppingen et al., 2014),
68 who acidified digested sewage sludge and precipitated struvite on a large-scale plant (The Stuttgart Process).
69 The results showed a dissolution of phosphorus by 75%, which enhances the recovery of the subsequent
70 struvite precipitation process to around 98%. The purity of the product has not been reported (Antakyali et
71 al., 2013). One of the potential negative consequence of acidification, is the simultaneously dissolution of
72 iron, aluminium, and heavy metals (Wozniak and Huang, 1982). The purity of the phosphorus product might
73 decrease and thereby lowering the value of the phosphorus product as a fertilizer. However, the requirements
74 of purity depends on if the phosphorus product is used directly or as a raw material for producing fertilizers.
75 To avoid precipitation of iron phosphate, citric acid has been added to bind iron, which increase the costs of
76 the process (SEG - Stadtentwässerung Göppingen et al., 2014). Alternatively, iron can be removed by ion
77 exchange (Shiba and Ntuli, 2017). In the Gifhorn process, sulfuric acid and Na_2S is used for acidification to
78 dissolve phosphorus and remove interfering ions such as iron by sulfidic precipitation (Amann et al., 2018;

Tarayre et al., 2016). Phosphorus is then precipitated as a mixture of struvite and calcium phosphate at pH 9 (Tarayre et al., 2016). In the Seaborn Process hydrogen sulfide from the digester tank is used to precipitate aluminium, iron and heavy metals (Müller et al., 2007). In the Budenheim process, sludge is aerated with CO_2 at 10 bars pressure to lower pH and dissolve phosphorus (Stössel, 2013). Phosphorus precipitate as calcium phosphate and most of the CO_2 is recycled during the process (Stössel, 2013). (Levlin and Hultman, 2007) suggested a two-step process. In the first step, acetic acid is added to reduce pH to 4, whereby part of the phosphorus is dissolved and ends up in the liquid after solid-liquid separation; iron- and aluminium phosphate is not dissolved and ends up in the solid materials. In the second step sodium hydroxide is added to the solid material from the first step, whereby phosphorus from iron- and aluminium phosphate is dissolved. Iron and aluminium is precipitated as iron- and aluminium hydroxide and removed with the solid material. Phosphorus is then precipitated as struvite and calcium phosphate (Levlin and Hultman, 2007). Thus, if sludge cannot be used directly as a fertilizer; three commercial alternatives exist: recovery from the liquid phase, recovery from the sludge and recovery from the ash. These methods vary in the amount of phosphorus that can be recovered and the need of chemicals that have to be added (Amann et al., 2018).

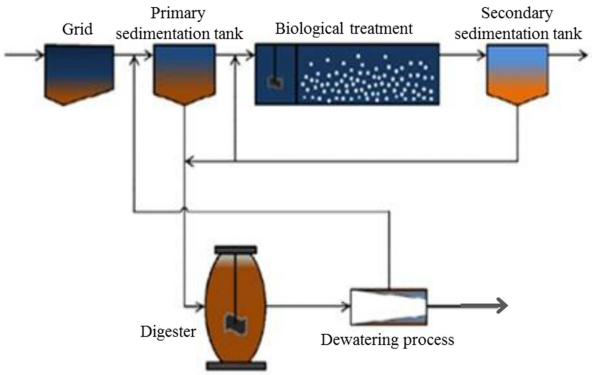
In this study, we explore the potential to improve phosphorus recovery by means of sludge acidification. Sludge from five different wastewater treatment plants in Denmark has been used - both digested (primary and secondary sludge) and non-digested sludge (secondary sludge) has been used. The aim is to maximize the phosphorus release after acidification and to study the rate of iron, aluminium and heavy metal dissolution.

Materials and methods

Description of the wastewater treatment plants

Wastewater sludge samples were collected from five wastewater treatment plants (WWTPs) located in different cities in Denmark i.e. Randers, Aaby, Skagen, Kolding and Haderslev. The WWTPs located in Randers and Skagen are characterized by digesting both primary and secondary sludge (Figure 1a), Aaby

WWTP (Figure 1b) digest secondary sludge, whereas Kolding WWTP (Figure 1c) digest only primary sludge and Haderslev WWTP (Figure 1d) does not apply a digester. Four of the plants use biological phosphorus removal combined with iron dosing, the exception being Kolding WWTP where iron is not added in the primary tanks (Table 1).



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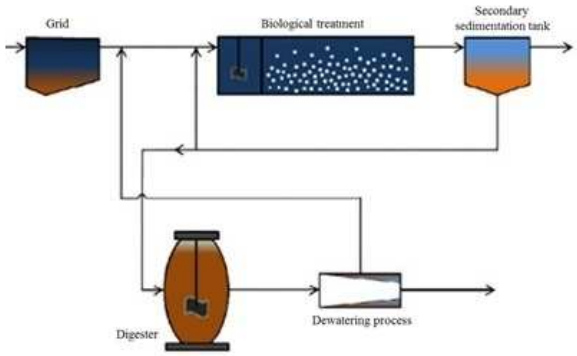

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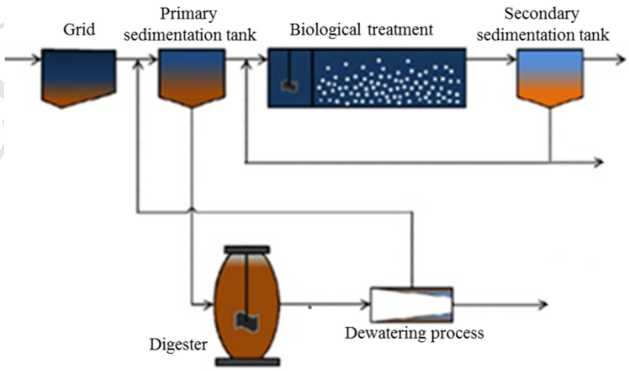

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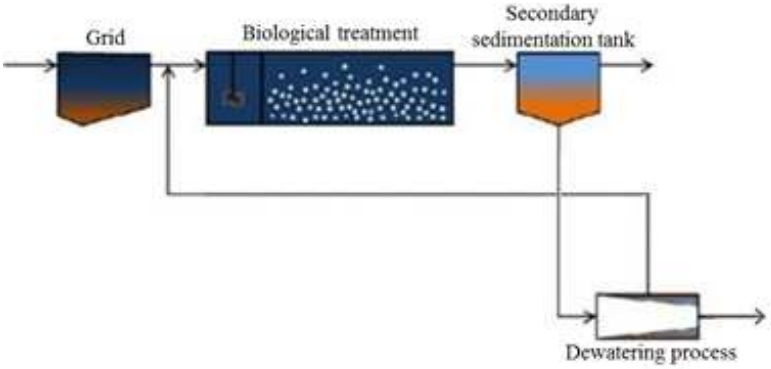

(d)

Figure 1: Flow sheet for the wastewater treatment plants, a) Randers and Skagen; b) Aaby; c) Kolding; d) Haderslev

Data for inlet flow and phosphorus concentration of the raw wastewater is shown in Table 1. The amount of phosphorus removed by the biological and chemical process varies between 80-95% for the different plants. These data are average values provide by the wastewater treatment plants and the details of the sludge analyzed in this study can be found in Table 2and Table 3.

Table 1: Characteristics of the wastewater treatment plants.

	Sludge type	Inlet flow [m^3/d] [a]	Inlet phosphorus concentration [mg/L] [a]	Outlet phosphorus concentration [mg/L] [a]
Randers WWTP	Digested (Primary + secondary)	23,150	6.78	0.42
Aaby	Digested (Secondary)	16,874	6.70	0.34
Skagen	Digested (Primary + secondary)	8,736	20	0.47
Kolding WWTP	Digested (Primary)	28,449	6.20	1.03
Haderslev WWTP	Non-digested (Primary + secondary)	10,953	7.75	0.45

[a] Average values provided by the wastewater treatment plants

Acidification of sludge

Sludge samples from each WWTP were collected after digestion but prior to dewatering except for Haderslev where excess sludge from the secondary treatment process was collected. A series of experiments were performed where 100 ml of sludge was acidified by 0.5 M H_2SO_4 to pH 4, 5, 6, 7 and 2 M H_2SO_4 to pH 2 and 3. The 2M H_2SO_4 solution was used at the lower pH in order to reduce dilution of the sludge samples. In addition, 100 ml of sludge was collected and pH increased to pH 11 by adding 2 M NaOH. All sludge samples (with sulfuric acid, sodium hydroxide or no treatment) was centrifuged at 2880 G for 3 minutes and filtered through a 0.45 µm filter. The concentration of ortho-phosphate (o-P), total phosphorus, metals and heavy metals were measured. One series of experiments (one for each type of sludge) were carried out in order to test the rate of phosphorus dissolution by reducing pH to 2.5, after which o-P was analyzed after 10 min and up to 5 h. The concentration of o-P was almost constant during the whole time period; thus for all samples reported in this paper, the samples where left for stirring for 1 h after addition of sulfuric acid or sodium hydroxide.

The o-P concentration was measured in the filtrate, whereas the total phosphorus concentration was measured before centrifugation and filtration. Both ortho-phosphate and total-phosphorus was measured as described in the Danish Standards (Danish Standard, 1985a, 1985b). The o-P release was estimated according to equation 1:

$$\text{o-P release } [\%] = \frac{[\text{o-P}]}{[\text{t-P}]} \cdot 100 \qquad \text{(eq. 1)}$$

where [o-P] is the concentration of o-P in the filtrate after sludge acidification and [t-P] is the concentration of total phosphorus in the sludge.

Concentration of metals and heavy metals was analyzed in the filtrate by inductively coupled plasma optical emission spectrometry (ICP-OES) and compared to the concentration of metals in the sludge before acidification. The ICP-OES was a Thermo Scientific iCap 6300 operated in axial view mode. The spectrometer was calibrated against matrix matched multi element standards. The dry matter content of the

149 samples was estimated by leaving around 15 g of raw sludge in a drying oven at 105 ºC for 24 hours.
150 Afterwards, the dry matter was incinerated at 550 ºC for 2 h to determine the organic/inorganic matter. The
151 weight loss was determined as the organic matter, whereas the inorganic part was determined as from the
152 weight that remains incineration at 550 ºC.

153 *Sludge analysis*

154 Potentiometric titrations were performed using Titralab™ 900 equipment from Radiometer Denmark, and a
155 SI Analytics Blue Line 17 pH glass electrode calibrated against standard buffer solution at pH 4 and 7.
156 Diluted samples were prepared dissolving 1 mL sludge samples in 19 mL 0.1 M $NaClO_4$. All experiments
157 were performed at 23 °C under a nitrogen atmosphere by stepwise adding 100 mM H_2SO_4 until pH reached
158 pH3, then the experiment was stopped. The buffer capacity was calculated according to eq. 2.

159 $$\beta = \frac{dn}{dpH} \quad \text{(eq. 2)}$$

160 where, β is the buffer capacity, *dn* denotes the changes of moles acid added to the sludge and *dpH* denotes
161 the equal changes in pH. It is assumed that the acid is completely dissociated. The second dissociation
162 constant for sulfuric acid is $1.2 \cdot 10^{-2}$ M; thus at pH 3 less than 10% of the sulfuric acid is present as HSO_4^-.
163 The alkalinity is equal to the amount of strong acid required to lower pH to 4.5 and can be calculated by
164 integrating the buffer capacity from pH 4.5 to the initial pH value. The alkalinity is often used as a measure
165 of the bicarbonate/carbonate concentration, but a more precise analysis is possible by plotting the buffer
166 capacity as function of pH.

167 Particle size distributions were analyzed using a laser diffraction particle size analyzer (Beckman & Coulter
168 LS 13320) with universal liquid module. The Frauenhofer theory was used for data treatment, and tap water
169 was used for background measurements. The experiments were replicated twice. Sludge before and after
170 acidification has been analyzed by light microscope (Zeiss Axioskop) connected to a computer in order to
171 identify the floc structure. The sludge has been spread on a glass plate and imaging through the microscope.

172 *Separation and precipitation of phosphorus*

Sludge samples from Randers and Kolding were acidified to pH 2. The solid material was removed by centrifugation at 2800 G for 3 minutes and the supernatant was filtered through a 0.45 µm filter. Phosphorus was precipitated from the liquid phase by adding 2M NaOH to pH 6, 7, 8, and 9, respectively. The precipitate was removed by centrifugation, weighed and analyzed by ICP-OES.

Results and discussion

Raw sludge analysis

Sludge from five different WWTPs was collected and analyzed (Table 2). At the WWTPs with a digester, sludge is thickened before digestion; hence the digested sludge has a higher dry matter content than un-digested sludge (Haderslev WWTP). Kolding WWTP, which only digests primary sludge, was found to have a slightly lower dry matter content than Randers, Aaby and Skagen WWTPs, where both primary and secondary sludge is digested. The highest fraction of organic matter was observed in the un-digested sludge from Haderslev as expected.

Table 2: Dry matter, organic and inorganic matter for the different sludge types

	pH	Dry matter [g/kg]	Organic matter [g/kg]	Inorganic matter [g/kg]
Randers WWTP	7.35	39.3	22.0 (56%)	17.3 (44%)
Aaby WWTP	7.1	42.1	28.4 (68%)	14.7 (32%)
Skagen WWTP	8.24	41.2	26.2 (64%)	15.0 (36%)
Kolding WWTP	7.31	31.4	19.1 (61%)	12.3 (39%)
Haderslev WWTP	6.60	15.4	11.1 (72%)	4.23 (28%)

The composition of sludge has been analyzed (Table 3). All concentrations were lower in the non-digested sludge as the dry matter content of the sludge was low. The concentration of iron varied between the different plants depending on the wastewater treatment process and how much iron that was added to reduce the amount of discharged phosphorus. The concentration of iron in Aaby WWTP was relatively low as

192 phosphorus was removed biologically in the secondary treatment process. The concentration of iron was also
193 low in Kolding WWTP, as no iron is added during the primary wastewater treatment (Table 1). The
194 concentrations of heavy metals was high at Kolding WWTP. The reason for this is not known.

195

196 *Table 3: Composition of the different sludge types.*

	total-P mg/gTS	Ca mg/gTS	Mg mg/gTS	Al mg/gTS	Fe mg/gTS	Cd mg/gTS	Cr mg/gTS	Cu mg/gTS	Ni mg/gTS	Pb mg/gTS	Zn mg/gTS
Randers WWTP	33.1	39.0	5.78	8.2	45.9	0.00168	0.0298	0.187	0.0442	0.0657	1.17
Aaby WWTP	33.6	28.2	7.68	6.7	22.2	0.00111	0.0172	0.217	0.0302	0.0542	0.627
Skagen WWTP	32.1	14.8	4.19	3.2	72.6	0.00196	0.0110	0.0622	0.0219	0.0125	0.354
Kolding WWTP	37.6	51.1	3.90	14.1	16.3	0.00483	0.0641	0.457	2.30	0.114	2.92
Haderslev WWTP	23.5	25.4	5.61	5.9	30.4	0.000970	0.0626	0.140	0.0408	0.0446	0.798

197

198 The floc size has been measured (Table 4) and images are shown for all sludges (Figure 2). Activated sludge
199 (Haderslev) had the largest floc structures (~80 µm). The floc size of digested sludge was slightly smaller
200 than non-digested sludge and contained more fines and irregular flocs. The smallest floc size was observed in
201 the digested primary sludge (Kolding). The floc structure was seemingly not fully broken down after
202 acidification for all the sludge types but more fluffy flocs was obtained and more particles and filament was
203 observed between the flocs (Figure 3).

204

205

206

207

208

209 *Table 4: Size of sludge*

	Mean [µm]	Median [µm]	S.D. [µm]
Randers WWTP	130	73	160
Aaby WWTP	110	64	160
Skagen WWTP	90	63	110
Kolding WWTP	110	37	172
Haderslev WWTP	110	80	126

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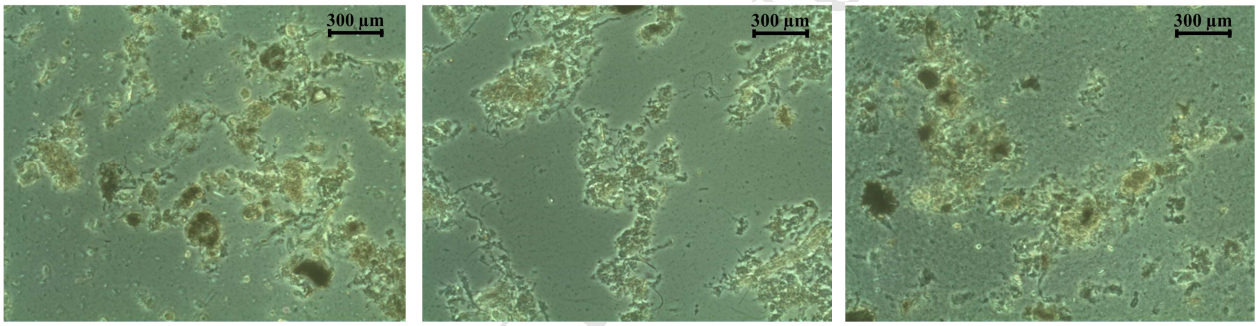

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214 *(a)* *(b)* *(c)*

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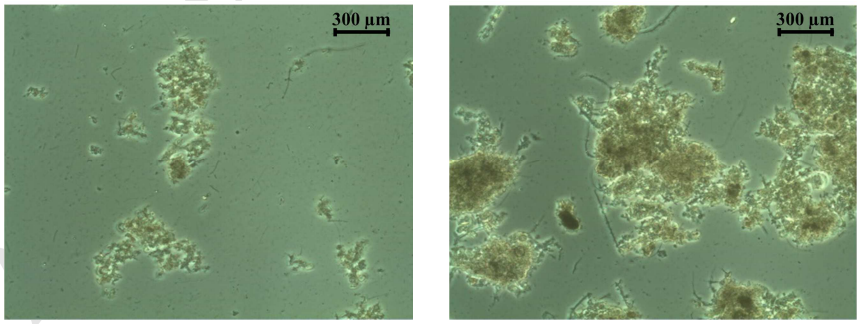

216

217 (d) (e)

218 *Figure 2: Floc structure in raw sludge (100x magnification) at (a) Randers; (b) Aaby; (c) Skagen; (d) Kolding; (e) Haderslev WWTP*

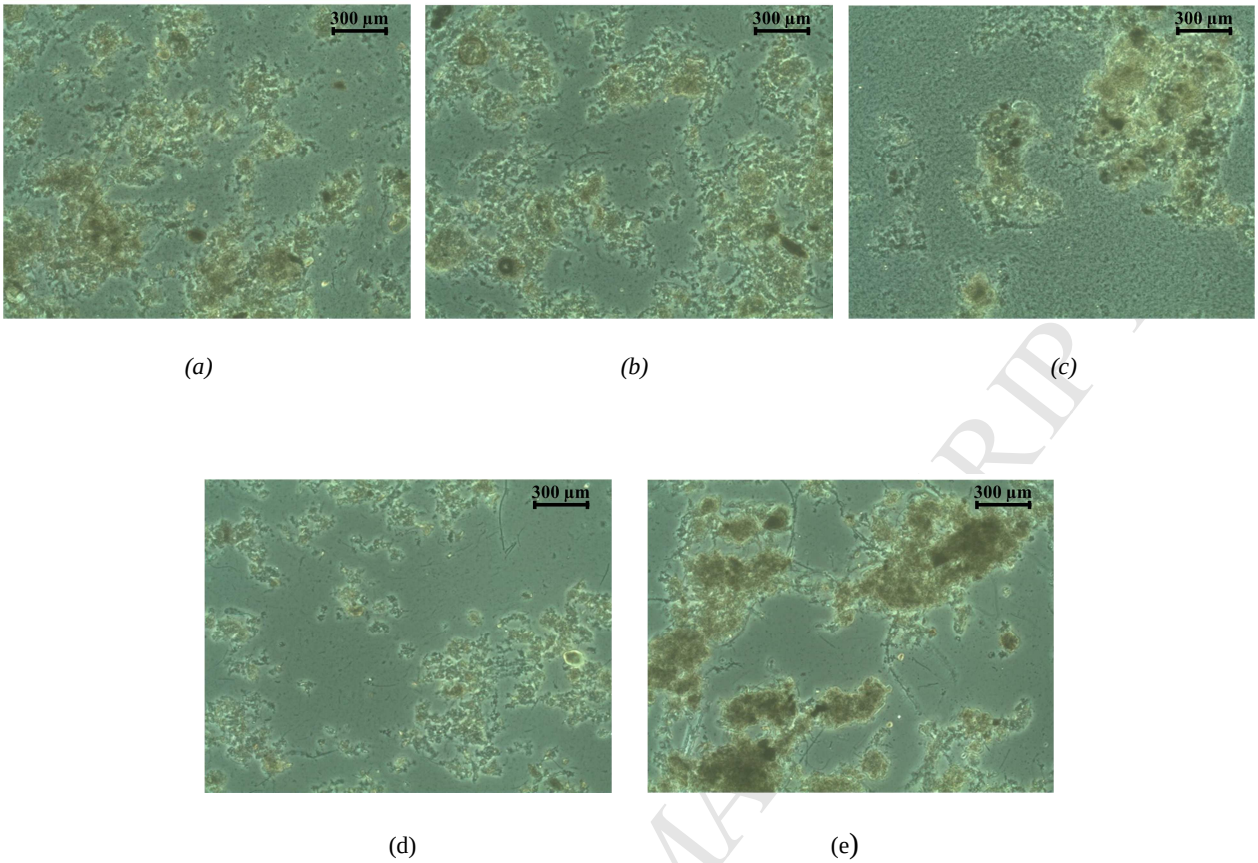

Figure 3: Floc structure at pH 3 (100x magnification) at (a) Randers; (b) Aaby; (c) Skagen; (d) Kolding; (e) Haderslev WWTP

Sludge acidification

The sludge samples were acidified with sulfuric acid (Figure 4). The required amount of acid was lowest for the undigested sludge (Haderslev). In the digested sludge, more acid were consumed due to CO_2 stripping as high amounts of carbonate were produced when the substrate were degraded to methane and carbonate (Chipasa, 2003). The removal of CO_2 is illustrated by a buffer capacity plot (Figure 5), which corresponds well with the H_2CO_3/HCO_3^- equilibrium that has a pKa value of 6.3.

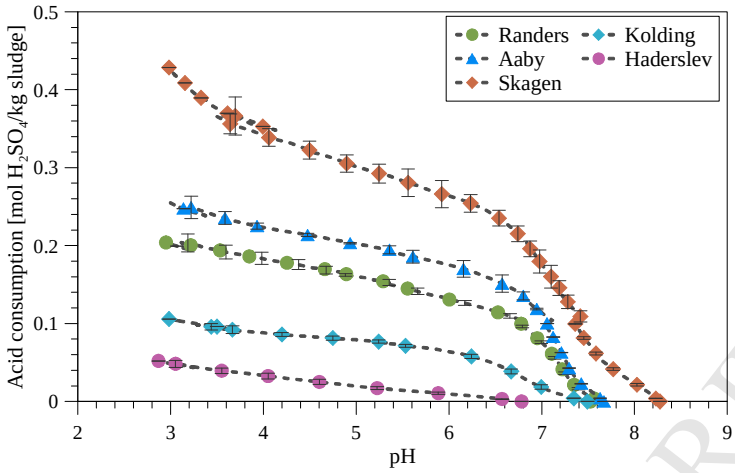

Figure 4: Acid consumptions for pH regulation of the different sludge types.

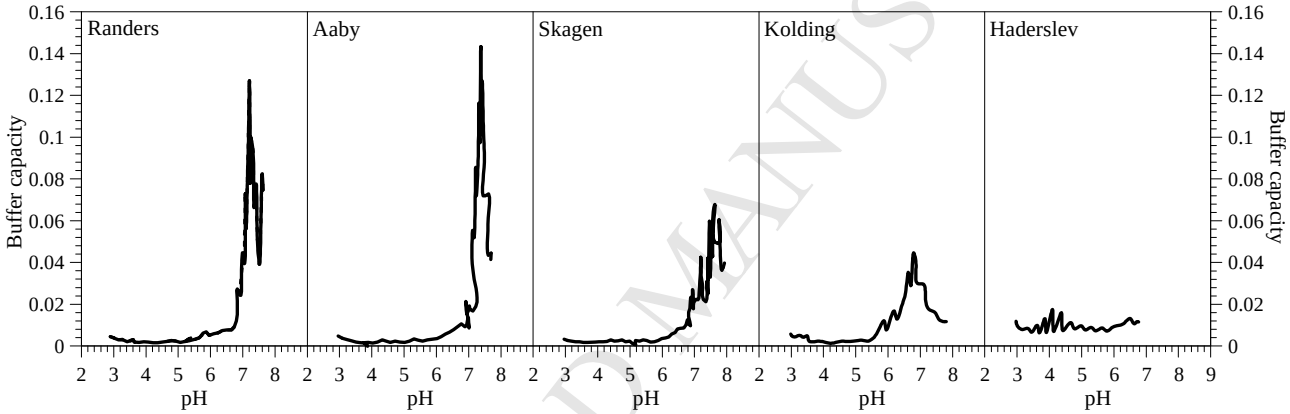

Figure 5: Buffer capacity for the different sludge types.

The released amount of dissolved ortho-phosphate (o-P) increased with decreasing pH (Figure 6) as observed in previous studies due to dissolving of mainly inorganic phosphorus (He et al., 2016; Xu et al., 2015)Digestion followed by acidification can release more than 80% of phosphorus, which corresponds with previous studies (Antakyali et al., 2013). Aaby WWTP has a higher amount of dissolved phosphorus at pH 7-8 (no acidification) compared to the other WWTPs. The Aaby plant is designed for biological P removal and has a fluidized bed reactor implemented to precipitate and extract struvite from the digester centrate. As already discussed, an optimized biological P removal during secondary treatment and P release during digestion can facilitate recovery of struvite or other P products, still the potential for phosphorus recovery

246 can be significantly improved by lowering pH to 3 prior to sludge dewatering. Contrary to the digested
247 sludge, the non-digested sludge (Haderslev WWTP) shows low o-P release during acidification. Moreover,
248 the inorganic matter (Table 2) from Haderslev WWTP is low, and thus the metal-phosphorus salt content
249 also limits the o-P release. A slight increase in dissolved phosphorus is observed for sludge from Randers
250 and Skagen when NaOH is added, but P release is low compared with the phosphorus release obtained by
251 acidification. To conclude, acidification improve P removal - i.e. around 85% of the phosphorus was
252 dissolved for WWTP handling mixed primary and secondary sludge that has been digested. For WWTPs
253 using chemical P removal, acidification is the only feassible way to release and harvest phosphorus.
254 Moreover, (Chen et al., 2001) found that acidification improves the dewaterability of activated sludge due to
255 exocellular polymer (ECP) leaves the activated sludge surface, which makes it easier to pack the sludge and
256 reduces the water content of the sludge. Therefore, acidification both increases phosphorus recovery and
257 improve dewaterability. On the contrary, acidification limits the later use on agricultural land, but since land
258 application is not allowed in many European countries and which is the reason for the acidification process
259 (Tarayre et al., 2016), incineration is a more feasible method that at the same time produces energy (Lundin
260 et al., 2004).

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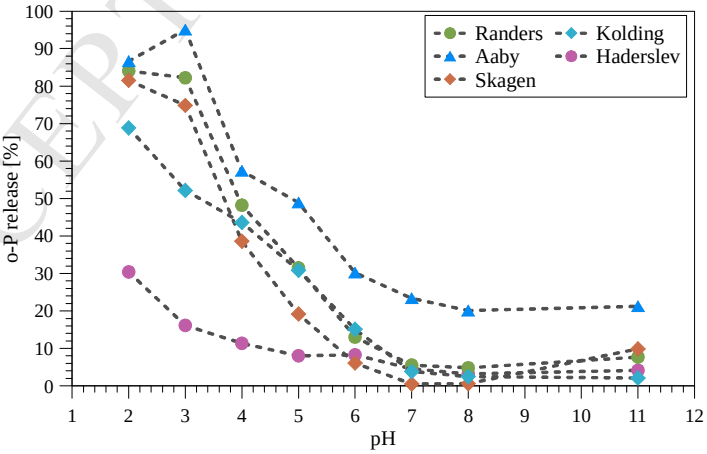

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263 *Figure 6: o-P concentration with respect to t-P concentration at different pH. Reaction time: 1h.*

264 The required amount of acid for dissolving phosphorus is shown in Figure 7. The release of phosphorus
265 increases almost linearly with the added amount of sulfuric acid. The regression line (dashed line) shows that

about 100 mmol o-P was released per added mol H_2SO_4, i.e. about 10 mole diprotic acid per mole o-P. The larger amount of acid used is due to CO_2 stripping. It should be noticed that for Aaby WWTP, 10 mM o-P was dissolved when no acid was added. Still the extra release of phosphorus was the same as for the other sludge types e.g. 100 mmol o-P was released per added mol H_2SO_4. The lowest release of phosphorus as function of sulfuric acid dosage was observed for Skagen and Kolding. The phosphorus release was 25% lower for Skagen and 40% lower for Kolding.

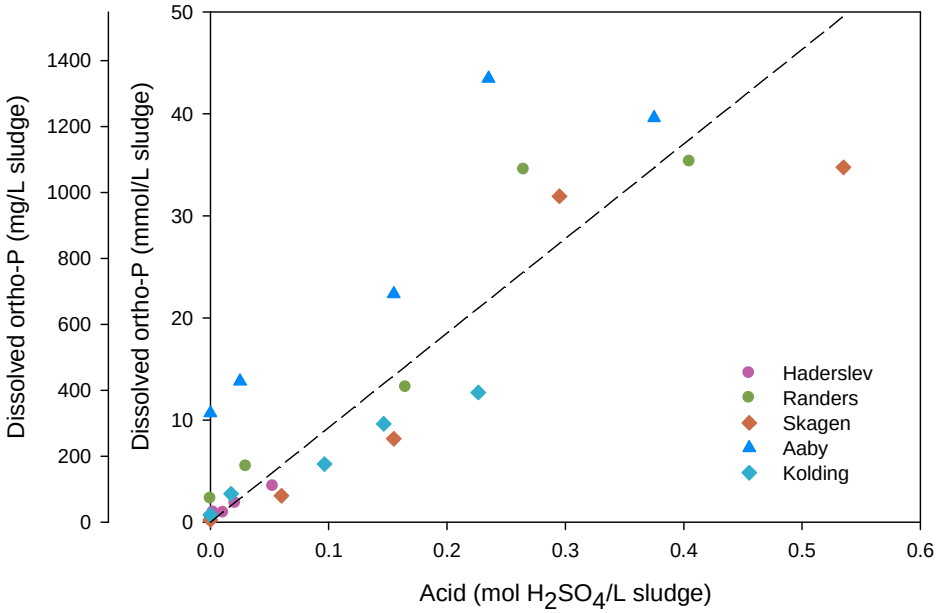


Figure 7: Acid consumption with respect to o-P release

Dissolution of metals during acidification

Most of the released phosphorus and carbonate originate from calcium, magnesium, aluminum and iron carbonates and phosphates. The metals in these compounds dissolve following the same trend as the phosphorus release at decreasing pH (Figure 8). Randers WWTP has a high total concentration of calcium and iron in the raw sludge and Kolding has a high concentration of calcium. The magnesium release is between 30% and 70% depending on the WWTP, but as magnesium is found in lower concentrations in the raw sludge (Table 3), it is not the main contributor to phosphorus release. Aluminum has in general a low

release and also a low concentration in raw sludge (Table 3), which is as expected as the WWTPs investigated are not adding aluminum during the wastewater treatment.

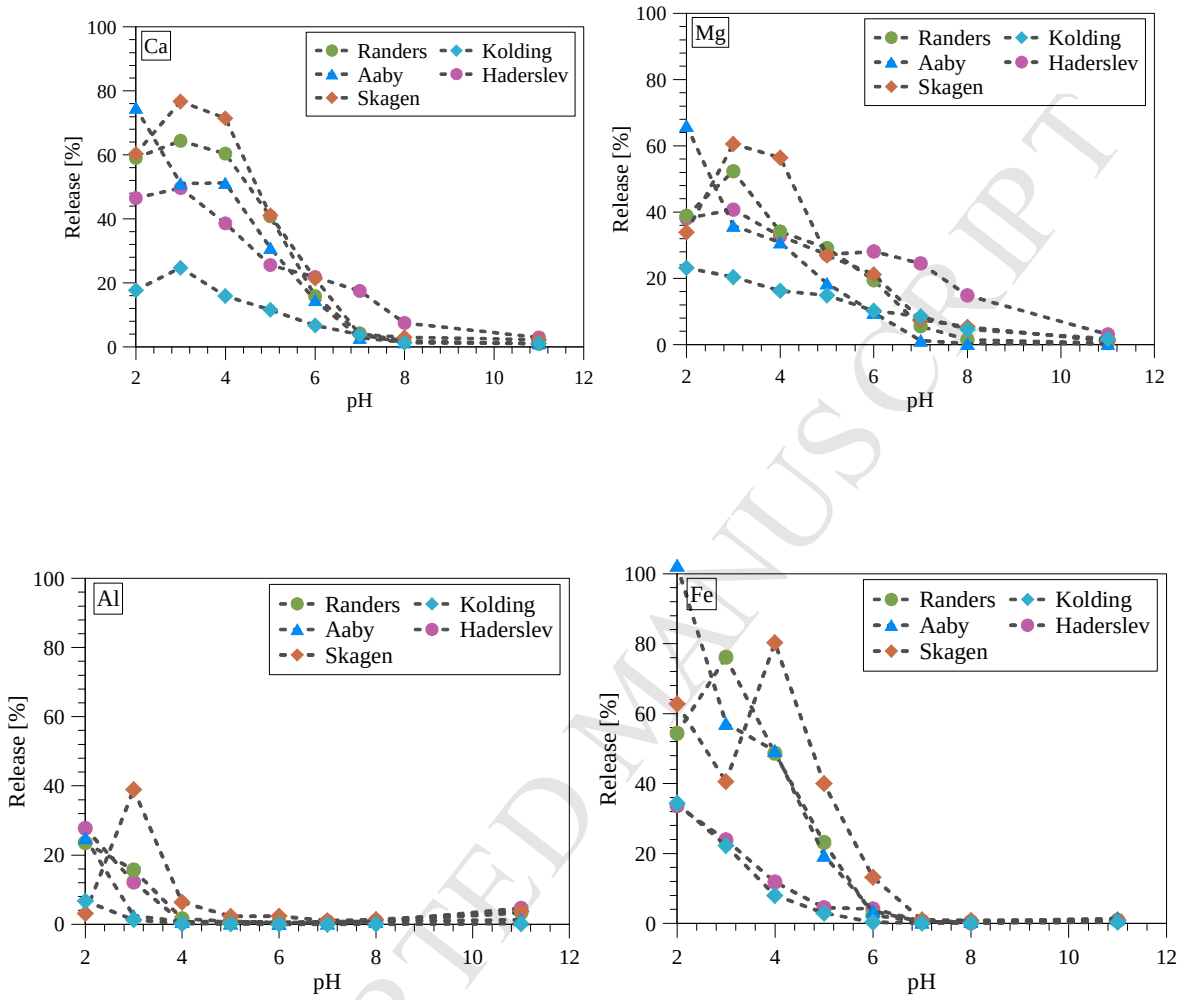
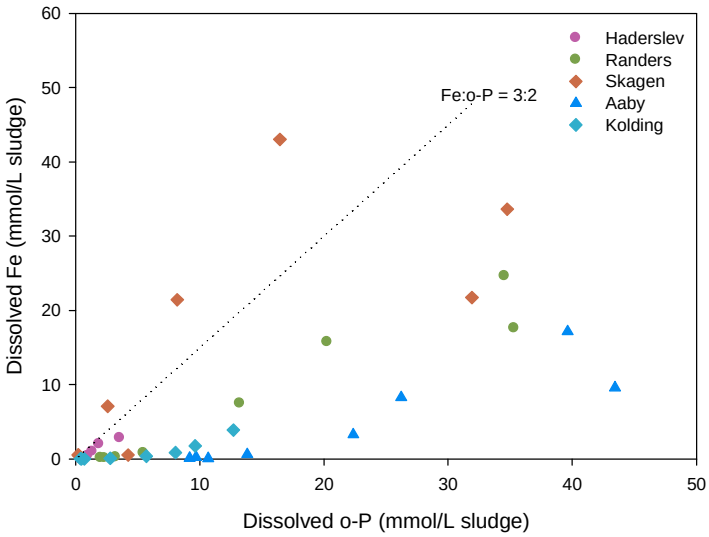


Figure 8: Metal concentration in the liquid phase with respect to the concentration in raw sludge.

In several papers, it is reported that phosphate precipitate as vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$ as the main product after addition of iron coagulant (Frossard et al., 1997; Wilfert et al., 2016) i.e. the stoichiometry for Fe:o-P is equal to 1.5. Looking at data for all plants, except Skagen WWTP, more than 10 – 20 mM phosphorus is released before any iron is dissolved, after which the ratio between Fe and o-P release is close to 1.5 (Figure 9a). Thus, the data indicates that vivianite may be one of the P-minerals dissolved during acidification, but it is not the only mineral. The data support the idea of Levlin and Hultman (Levlin and Hultman, 2007), who

295 report that part of the phosphorus can be dissolved without a high release of iron. Sludge also contains
296 $Ca_5(PO_4)_3OH$ (Yi and Lo, 2003) where the stoichiometry Ca:o-P is equal to 1.67. Plotting the release of Ca
297 as function of o-P indicates that the first mineral released may be calcium phosphate (Figure 9b), since
298 calcium release is higher with respect to iron in the beginning. The molar amount of released o-P is more
299 than 9-10 times higher than the released amount of magnesium and 15 times higher than the released amount
300 of aluminium e.g. only minor amount of phosphate is bound as aluminium or magnesium salts.



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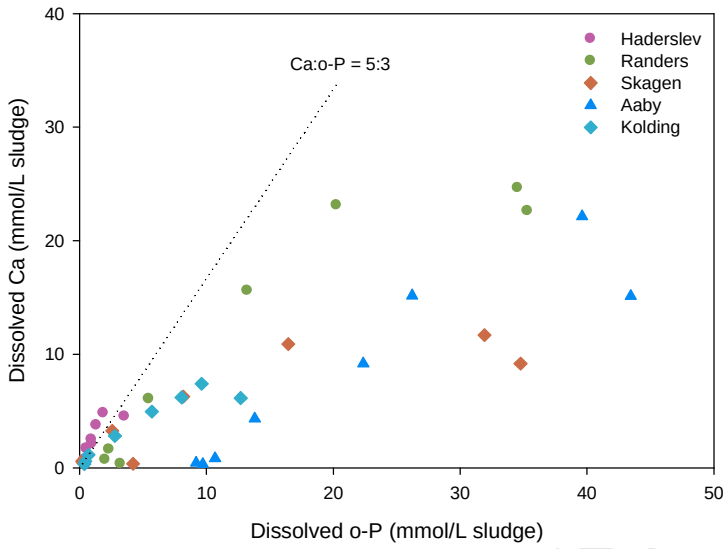
302 (a)



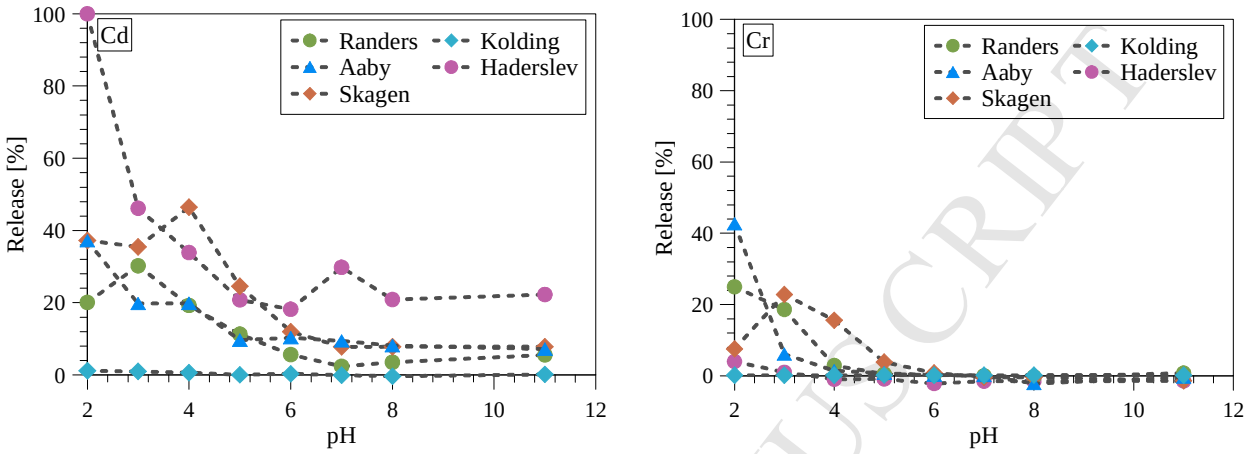
(b)

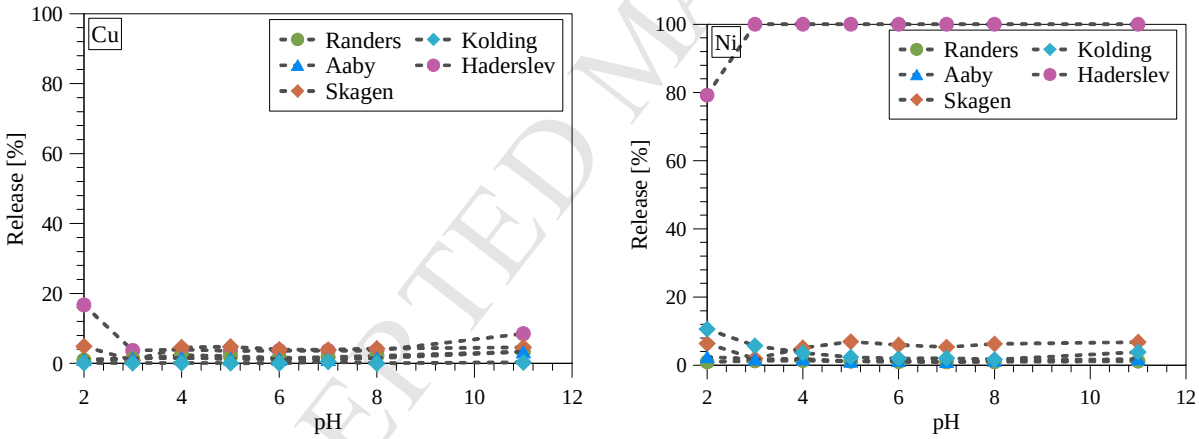
Figure 9: Stoichiometry release for (a) Fe:o-P and (b) Ca:o-P

Release of heavy metals during acidification

Acidification of sludge was previously used as a method to release heavy metals into the liquid phase in order to easily extract them from sludge (Mingot et al., 1995; Naoum et al., 2001; Stylianou et al., 2007). Heavy metals are often found in different fractions in sludge including soluble, exchangeable, adsorbed, bound to organics and sulfides, bound to carbonate and residual components (Tessier et al., 1979; Wang et al., 2005). There are two ways to view the heavy metal release from sludge:It can be considered negative as the released heavy metals can easily be incorporated into the phosphorus fertilizer product, or positively, as it is easier to remove the heavy metals from sludge when the heavy metals are released to the liquid phase. According to Naoum et al. (Naoum et al., 2001), the remaining heavy metals in the sludge after acid treatment are stabilized in the sludge (Naoum et al., 2001). In this study, the release of heavy metals is in general low (<30%) for all the wastewater treatment plants (Figure 10), the exceptions being Zn and Cd which show a higher release at some WWTPs.

The main concern regarding heavy metal dissolution in this study is related to the risk of incorporation into a precipitated fertilizer product. Therefore, some preliminary precipitation experiments have been performed by simply increasing pH as discussed in the following section.





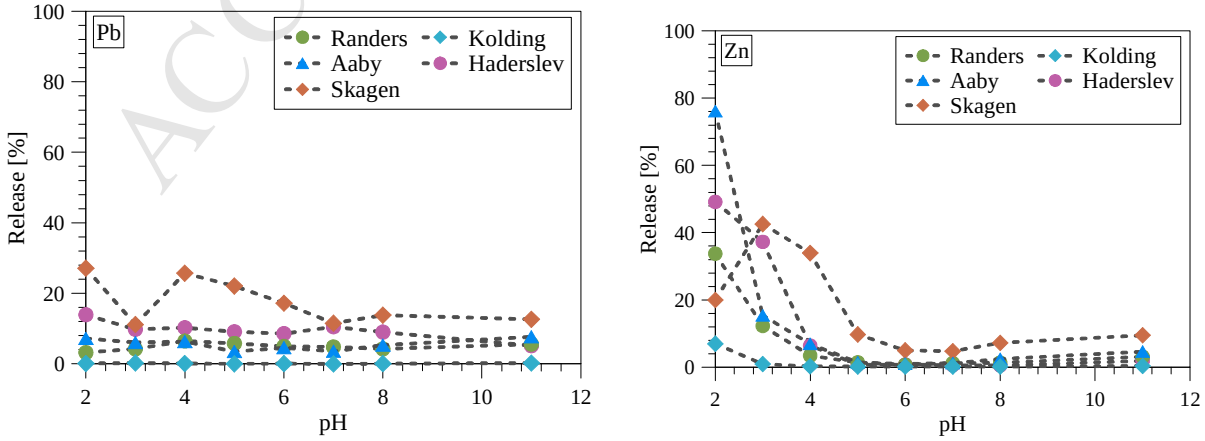


Figure 10: Release of heavy metals into the liquid phase at various pH-values, a) Cd, b) Cr, c) Cu, d) Ni, e) Pb and f) Zn.

Recovery of released phosphorus after acidification

The solid material was removed from acidified samples (pH 2) by centrifugation after which phosphorus was precipitated from the liquid phase by adding NaOH to pH 6, 7, 8 and 9. The phosphorus recovery increases from 53.7% at pH 6 to 80.8% at pH 9 with respect to the o-P concentration at pH 2. Besides phosphorus, the precipitate contains high amounts of calcium and iron. This indicates that phosphorus was mainly precipitated as iron phosphate and calcium phosphate (Figure 11). In the acidified sludge from Kolding WWTP more calcium was precipitated with respect to Randers WWTP. Iron precipitation was decreasing as pH was increased, and the same trend was observed for phosphorus. On the other hand, calcium precipitation increased with pH, which can be due to calcium sulfate precipitation. Calcium carbonate precipitation is unlikely, since CO_2 was removed during acidification. The removal of CO_2 might also ensure, that there are more cations in the solution that precipitate with phosphorus, since the metal-carbonate compounds originally present in the sludge is no longer an issue. Only very low amounts of Zn, Al and Mg were found in the precipitate, and thus the purity was high. The data in Figure 11 shows that precipitation follows the same trend as the dissolution of P, metals (Figure 8) and heavy metals (Figure 10) and is also in accordance with the sludge composition before acidification (Table 3), where for instance Zn has a higher concentration compared to the other heavy metals.

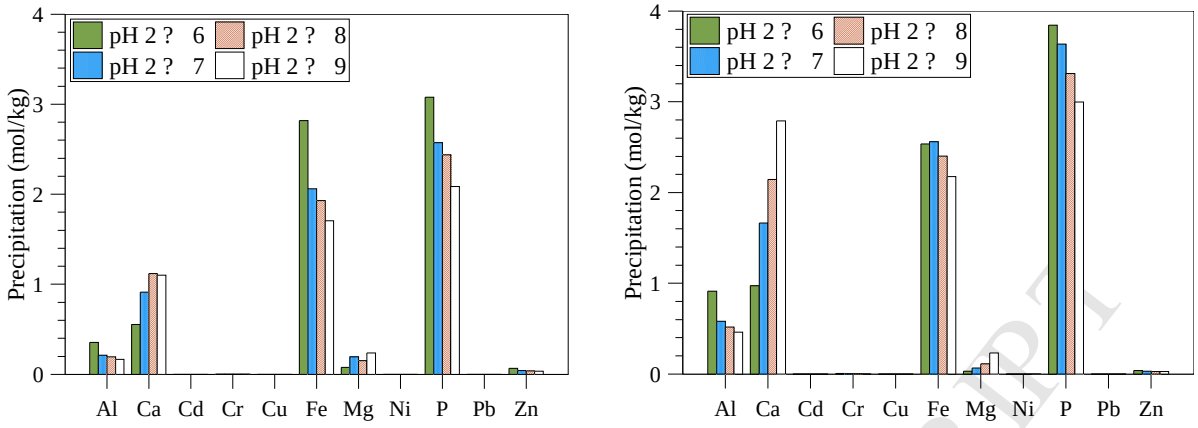


Figure 11: Precipitation at different pH (a) Randers; (b) Kolding.

Economic evaluation of sludge acidification

Acidification of sludge improves phosphorus recovery, in particular from digested sludge. However, today it might not be cost competitive with respect to mining since the use of chemicals are rather high for acidification (0.2-0.44 mole H_2SO_4/kg sludge). Moreover, the subsequent recovery of phosphorus by either precipitation (increasing pH) or other methods also limits the economic feasibility. It is more likely that phosphorus recovery will be politically driven or that phosphorus is in high risk of depletion. In this study, the cost of acidification is around 4€/kg P based on Figure 7 and a price of H_2SO_4 (95%) of 0.13€/kg. Equipment and operational costs have not been taken into account. According to (Egle et al., 2016), recovery from sludge ash is 5-6 €/kg P, recovery from digester supernatant is 6-10 €/kg P and from acidified sludge it is 9-16 €/kg P. However, the ash is used directly and separation of heavy metals is not considered, as in this study. Moreover, recovery from supernatant normally only recovers around 30-50% of the phosphorus (Pinnekamp et al., 2013), thus acidification can be a potential solution for a high phosphorus recovery process.

Conclusion

Digested and non-digested sludge from five wastewater treatment plants were acidified by addition of H_2SO_4 to dissolve phosphorus. For the five tested sludge types, 60-100 mmol o-P was released per added mol H_2SO_4. The highest phosphorus release was observed when pH was lowered to pH 2 (The sludge was exposed to acid for 1h for all the experiments). More acid was required for digested sludge as CO_2 stripping increases the acid consumption. However, more phosphorus can be released from digested sludge (up to 80%) compared to non-digested sludge (25%). Simultaneously release of heavy metals was low and not a major concern. The most critical release of heavy metals were observed for Cd, Zn and Ni after acidification of non-digested sludge. High amounts of iron was released during acidification, which can be a potential problem if iron is unwanted in the phosphate product. Preliminary precipitation experiments by pH increase proved that iron is the main precipitant together with phosphorus.

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- Phosphate precipitates with iron at increased pH.