Effect of anaerobic digestion and liming on plant availability of phosphorus in iron- and aluminium-precipitated sewage sludge from primary wastewater treatment plants

Emilio Alvarenga, Anne Falk Øgaard and Lasse Vråle

ABSTRACT

More efficient plant utilisation of the phosphorus (P) in sewage sludge is required because rock phosphate is a limited resource. To meet environmental legislation thresholds for P removal from wastewater (WW), primary treatment with iron (Fe) or aluminium (Al) coagulants is effective. There is also a growing trend for WW treatment plants (WWTPs) to be coupled to a biogas process, in order to co-generate energy. The sludge produced, when stabilised, is used as a soil amendment in many countries. This study examined the effects of anaerobic digestion (AD), with or without liming as a post-treatment, on P release from Fe- and Al-precipitated sludges originating from primary WWTPs. Plant uptake of P from Fe- and Al-precipitated sludge after lime treatment but without AD was also compared. Chemical characterisation with sequential extraction of P and a greenhouse experiment with barley (Hordeum vulgare) were performed to assess the treatment effects on plant-available P. Liming increased the P-labile fraction in all cases. Plant P uptake increased from 18.5 mg pot$^{-1}$ to 53 mg P pot$^{-1}$ with liming of Fe-precipitated sludge and to 35 mg P pot$^{-1}$ with liming of the digestate, while it increased from 18.7 mg pot$^{-1}$ to 39 and 29 mg P pot$^{-1}$ for the Al-precipitated substrate and digestate, respectively. Thus, liming of untreated Fe-precipitated sludge and its digestate resulted in higher P uptake than liming its Al-precipitated counterparts. AD had a negative impact on P mobility for both sludges.

Key words | anaerobic digestion, lime treatment, phosphorus recycling, sludge stabilisation

INTRODUCTION

The continuous growth in the world’s population is a major concern for future food production and supply (Cordell & Neset 2014). Finite natural resources that are not renewable, such as phosphorus (P), play an important role in the food chain. Phosphorus is essential for the metabolism and functioning of plants and animals, and hence there is a strong dependence on P in the agriculture sector in order to maintain or increase crop yield levels. However, agricultural practices have led to a surplus of highly soluble P from mineral fertilisers in soils that is further transported to water bodies (Huang & Shenker 2004) and then irreversibly lost to the sea, affecting the P cycle globally (Rittmann et al. 2011; März et al. 2014).

The fast rate of depletion of P mineral resources, which are located in only a few countries, is leading to concerns about the impact of potential future scarcity of the resource on global markets and food costs, so the focus is now turning to more effective use of P (Rittmann et al. 2011). This change in focus is increasingly reorienting agricultural practices towards recycling P safely, together with other macronutrients such as nitrogen, by managing organic residues such as manure and dewatered sewage sludge. Ott & Rechberger (2012) show how critical P has become as a resource, with e.g. only 1.2 kg P year$^{-1}$ per capita reaching the consumer from the 4.7 kg P year$^{-1}$ per capita imported to Europe. Management of this resource is of great relevance for the future food supply, and therefore recovering and recycling P would contribute to closing the P balance regionally in Europe and worldwide, reducing the dependence on P mineral reserves (Schoumans et al. 2015).

doi: 10.2166/wst.2017.056
The collection and use of P-rich wastes is a suitable alternative for recycling P through the agriculture sector. A large amount of P is collected in sewage sludge, since on average 98% of P in the human diet is discharged to the sewage system as urine and faeces (Smil 2000). In a European context, sewage sludge is widely reused for agricultural purposes. For example, in Norway 60% of sewage sludge is used in agriculture (Hamilton et al. 2015). However, a precondition for efficient replacement of mineral P fertiliser with P-rich wastes is high plant availability of the P in the wastes. Different types of wastes have specific fertilisation effects associated with their chemical properties (Boen & Haraldsen 2013; Brod et al. 2015). In particular, sewage sludge produced by chemical precipitation of P in sewage with aluminium (Al-) and/or iron (Fe-) salts often results in sludge with a low P fertilisation effect, and therefore most of the P it contains is stored in the soil when applied (Frossard et al. 1996; Maguire et al. 2001; O’Connor et al. 2004; Krogstad et al. 2005; Plaza et al. 2007). The expansion of the biogas industry has broadened the options for effective management of the P resource in biodegradable waste and sewage sludge, providing the possibility to produce methane as an energy carrier and digestate for nutrient recycling. The biogas process also stabilises the sewage sludge (odour reduction and hygienisation) and reduces its volume. The processing of sludge can be continued after anaerobic digestion (AD) by post-treatment of the AD residue (ADR) with slaked lime (Ca(OH)2) to further stabilise the substrate and facilitate further dewatering. Quicklime (CaO) can also be used, with the aim of hygienisation in addition to stabilisation.

Sludge stabilisation treatments may influence the plant availability of P in Fe- and/or Al-precipitated sludge. Therefore, exploring the effects of these post-treatments on plant availability of P is of great interest. Aerobic digestion studies have shown conclusively that the plant availability of P is considerably influenced by the metabolic processes that solubilise P (Wild et al. 1997; Bachmann et al. 2014; Christel et al. 2014; Hupfauf et al. 2015). For example, Bachmann et al. (2014) demonstrated that the performance of soil microorganisms in remobilising P is influenced when ADR is used for maize production. However, those studies did not consider the effects of Fe- and Al-precipitation of the sewage sludge. Studies on the behaviour of soluble P in anaerobically digested Fe- and Al-precipitated sewage sludge are limited (Kahliluoto et al. 2015). The reduction of Fe³⁺ during AD could release adsorbed phosphates. However, simultaneous P re-precipitation (with Fe²⁺) could decrease the solubility of the nutrient in the digestate through formation of secondary minerals (e.g. as vivianite with Fe²⁺), as shown by Cheng et al. (2015). Similarly, Kahliluoto et al. (2015) found that AD of Fe-precipitated sludge reduced the plant availability of P. However, there is a knowledge gap concerning the role of such reduction processes in AD for Al-bound P. Any re-precipitation and/or adsorption of P during or after AD could proceed differently for Fe- and Al-precipitated sludge. For example, Fe-precipitation is frequently well described by Langmuir isotherms, whereas Al-precipitation follows Freundlich adsorption pathways (Bratby 2006). For that reason, post-treatments such as liming could be expected to release the P from Fe- and Al-precipitated sludge, whether anaerobically digested or not, in different ways.

Liming of sewage sludge is commonly used in the Norwegian wastewater (WW) industry as a treatment for stabilisation or sanitisation of the sludge. Liming the sludge also gives a porous structure, improving the separation between liquid and solid in further processing of the digestate (Deneux-Mustin et al. 2001). Such treatment can increase P plant uptake, as indicated in studies by Illmer & Schinner (1995) and Illmer et al. (1995), Krogstad et al. (2005) and Øgaard & Brod (2016). However, knowledge about the effect on plant availability of P in liming of Fe- and Al-precipitated sludge is lacking. Moreover, the effect of combined AD and Fe/Al-precipitation of sludge, with liming as a post-treatment step before dewatering, is unknown.

The aim of this study was thus to compare the effects of AD and liming, both separately and in combination, on P plant availability in Fe- and Al-precipitated sludge. The stabilisation treatments carried out were thermophilic AD in a semi-pilot scale digester and liming with two products (CaO and Ca(OH)2). The different sludges were characterised by sequential extraction of P and, in addition, the plant availability of P was evaluated in a greenhouse experiment with barley (Hordeum vulgare L.) as a crop.

MATERIALS AND METHODS

Sludges

The substrates, which are referred to hereafter as untreated (UT) Fe- or Al-precipitated sludges, were sampled on March 2014 at two WW treatment plants (WWTPs): FREVAR KF (FRE) and Ullensaker Gardermoen (ULL). The streams considered were sewage sludge chemically precipitated with iron chloride (FeCl₃) at FRE and sewage adsorption.
sludge chemically precipitated with aluminium sulphate (Al₂(SO₄)₃) at ULL. Both streams were thickened in the WWTPs to increase their dry matter (DM) content prior to sampling. Both streams were sampled at the inlet of the thermophilic biogas process (60°C for FRE and 55°C for ULL) coupled to the WWTP. The samples were stored at 4°C until analysis of their physicochemical parameters. The UT sludges were analysed using standard methods for analysis of water and WW, as shown in Table 1 (APHA 2012). An overview of the subsequent post-treatments is shown in Figure 1.

### Anaerobic digestion treatment

Two 25-L continuous stirring tank reactor (CSTR) systems were used for AD of each sludge (Fe- or Al-precipitated). The inoculum used in the reactors was collected along with the samples from the FRE and ULL WWTPs and stored at 37°C for 2 days before being added to the CSTR reactors.

The start-up procedure for the AD process was as described by Estevetz et al. (2014). In the start-up phase, 9 L of each inoculum was added and diluted with water to 15 L (nominal working volume) and stirred at 20 rpm. Only one hydraulic retention time (HRT) was considered for AD treatment of the UT sludges. A HRT of 22 days was considered for the Fe-precipitated sludge and 15 days for the Al-precipitated one. The operating temperature for the whole AD treatment was 60°C for FRE and 55°C for ULL (the same temperature as used at the respective WWTPs). Gas chromatography was used to monitor the composition of the biogas. Some physicochemical parameters of the ADRs are presented in Table 2.

### Liming treatment

Liming of the UT sludges and ADRs was performed according to the schedule in Figure 1. Solid Ca(OH)₂ was added to a final concentration of 26% (0.35 g Ca(OH)₂/g TS) in the UT sludge/ADR and solid CaO was added to a final concentration of 27% (0.39 g CaO/g TS) only in the UT sludge. Both lime types were of industrial reagent quality and were provided by the company Miljøkalk AS, Norway.

The lime was dispersed at 100 rpm for 10 min in 800 mL of sludge/ADR by means of a Jar-test device manufactured by Phipps & Bird™. The limed products were then decanted and dried at 105°C to constant weight.

### Pot experiment

A total of 10 different sludges were obtained from the treatments described above. The relative plant availability of P in the sludges compared with that in mineral P fertiliser (MinP)

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**Table 1 | Physicochemical parameters of the primary untreated (UT) sludges at the FRE and ULL WWTPs**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FRE</th>
<th>ULL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dry solids (TS, %)</td>
<td>9.5 ± 0.06</td>
<td>5.9 ± 0.04</td>
</tr>
<tr>
<td>Volatile solids (VS, % of TS)</td>
<td>71 ± 0.65</td>
<td>72 ± 0.45</td>
</tr>
<tr>
<td>pH (25°C)</td>
<td>6.2 ± 0.2</td>
<td>5.9 ± 0.2</td>
</tr>
<tr>
<td>Conductivity (mS cm⁻¹)</td>
<td>9.64 ± 0.02</td>
<td>4.53 ± 0.02</td>
</tr>
<tr>
<td>Fe</td>
<td>115 ± 0.1</td>
<td>7.5 ± 0.1</td>
</tr>
<tr>
<td>Al</td>
<td>11 ± 0.1</td>
<td>60 ± 0.1</td>
</tr>
<tr>
<td>Ca</td>
<td>9.6 ± 0.08</td>
<td>5.9 ± 0.2</td>
</tr>
<tr>
<td>K</td>
<td>5.5 ± 0.1</td>
<td>3.5 ± 0.1</td>
</tr>
<tr>
<td>Na</td>
<td>3.8 ± 0.03</td>
<td>0.91 ± 0.01</td>
</tr>
<tr>
<td>Mg</td>
<td>1.9 ± 0.1</td>
<td>2 ± 0.1</td>
</tr>
<tr>
<td>P_total</td>
<td>8.8 ± 0.1</td>
<td>12 ± 0.1</td>
</tr>
<tr>
<td>P_org</td>
<td>0.6 ± 0.14</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>N</td>
<td>14 ± 0.1</td>
<td>24 ± 0.1</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05 ± 0.002</td>
<td>0.022 ± 0.001</td>
</tr>
<tr>
<td>Cu</td>
<td>0.074 ± 0.0008</td>
<td>0.076 ± 0.0008</td>
</tr>
<tr>
<td>Mn</td>
<td>0.079 ± 0.0007</td>
<td>0.15 ± 0.0002</td>
</tr>
<tr>
<td>Ni</td>
<td>0.014 ± 0.002</td>
<td>0.013 ± 0.001</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0004 ± 6e-5</td>
<td>0.0005 ± 6e-5</td>
</tr>
<tr>
<td>Pb</td>
<td>0.013 ± 0.001</td>
<td>0.035 ± 0.0002</td>
</tr>
<tr>
<td>Zn</td>
<td>0.25 ± 0.01</td>
<td>0.24 ± 0.01</td>
</tr>
</tbody>
</table>

*Organic P.

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**Figure 1 | Sequence of treatments of the untreated metal-precipitated sludges. UT = untreated; AD = anaerobic digestion; SL = slaked lime; QL = quicklime.**
The sand and peat mixture was mixed homogeneously with the sludges, except for a top layer of approximately 2.5 cm without sludge to avoid negative effects of the sludge on germination. Holes (1 cm depth) were made in the soil and 18 seeds of barley were sown. The number of plants was adjusted to 15 after germination.

Deionised water was applied three times a week to about 60% of water-holding capacity. Light was provided by 400 W fluorescent lamps (model Osram Powerstar HQI-BT®). The photosynthetic flux in the room was 200 μmol m⁻² s⁻¹ at plant height, with a 16 h/8 h light/dark cycle. Heating was provided if the temperature dropped below 18 °C during the light period and 15 °C during darkness. The average air temperature oscillated between 14.5 and 22 °C, with an average temperature during the whole experiment of 18 °C. The plants were harvested approximately 7 weeks after sowing, when they were at start of heading. The plants were cut roughly 2.5 cm above the soil surface, stored in a paper bag per pot and dried at 60 °C to constant weight.

### Analytical methods

#### Biogas treatment control

Biogas production was controlled by continuously measuring biogas composition, pH, ammonium (NH₄⁺) concentration, alkalinity (total inorganic carbon (TAC) as mg L⁻¹ CaCO₃) and volatile organic acids (FOS) as mg L⁻¹ of acetic acid in the ADR. The TAC and FOS values were determined by means of a "TitroLine® 6000" basic titration unit with a magnetic stirrer TM 235 produced by SI Analytics GmbH. The titration was controlled by a pH combination electrode A 7780 1M-DIN-ID. The pH of the ADR was measured with a Thermo Orion pH meter model Dual Star. The TS and VS concentrations were determined by a gravimetric method at 105 °C and 550 °C, respectively, at constant weight. The NH₄⁺ concentration was determined by the ion selective electrode method using a Thermo Scientific Orion electrode model 9512HPBNWP connected to a Thermo Orion Dual Star device.

The four CSTRs (FRE-1, FRE-2, ULL-1 and ULL-2) were connected to a gas chromatograph (GC) model 8610C in order to continuously monitor the biogas composition (concentrations of methane (CH₄) and carbon dioxide (CO₂)) from the start-up phase until the end of the HRT period for each reactor. The GC was equipped with a thermal conductivity detector and a 2 m Haysep-D column. Chromatography, data acquisition and integration were performed using the PeakSimple 3.88 software for Windows.

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Table 2 | Physicochemical parameters of the AD residues (ADR, from two reactors) of sewage sludge from the FRE and ULL WWTPs after one HRT

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FRE-1</th>
<th>FRE-2</th>
<th>ULL-1</th>
<th>ULL-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dry solids (TS, %)</td>
<td>4.48 ± 0.06</td>
<td>4.54 ± 0.05</td>
<td>3.00 ± 0.04</td>
<td>2.90 ± 0.06</td>
</tr>
<tr>
<td>pH (25 °C)</td>
<td>8.01 ± 0.2</td>
<td>7.93 ± 0.1</td>
<td>7.97 ± 0.2</td>
<td>7.89 ± 0.2</td>
</tr>
<tr>
<td>P_initial (g kg⁻¹ TS)</td>
<td>15.2 ± 0.05</td>
<td>n.d.</td>
<td>21.8 ± 0.88</td>
<td>n.d.</td>
</tr>
<tr>
<td>P_initial (g kg⁻¹ TS)</td>
<td>2.1 ± 0.2</td>
<td>n.d.</td>
<td>3.4 ± 0.6</td>
<td>n.d.</td>
</tr>
<tr>
<td>N-NH₄⁺ (mg L⁻¹)</td>
<td>2,210 ± 0.2 n.d.</td>
<td>2,335 ± 0.1 n.d.</td>
<td>2,545 ± 0.05 n.d.</td>
<td>2,455 ± 0.04 n.d.</td>
</tr>
</tbody>
</table>

n.d., not determined.

was studied in a pot experiment with barley (Hordeum vulgare L. cv. Heder) as the reference crop.

This pot experiment was conducted using 3-L pots filled with 3.65 kg DM of a 'soil' consisting of a limed mixture of nutrient-deficient sand and 4 weight-% sphagnum peat. The soil had a very low content of plant-available P, 11 mg P kg⁻¹ measured by the ammonium lactate-extractable P method (PAL, (Egnér et al. 1960)) and consisted of 1% clay, 2% silt and 97% sand. Sludge dose was calculated based on total P (P_initial) content and amounted to 90 mg P pot⁻¹, equivalent to 60 kg P ha⁻¹ (assuming 20 cm topsoil depth). The P fertilisation effect of the sludges was compared with that of a top layer of approximately 2.5 cm without sludge to avoid negative effects of the sludge on germination. Holes (1 cm depth) were made in the soil and 18 seeds of barley were sown. The number of plants was adjusted to 15 after germination.

Deionised water was applied three times a week to about 60% of water-holding capacity. Light was provided by 400 W fluorescent lamps (model Osram Powerstar HQI-BT®). The photosynthetic flux in the room was 200 μmol m⁻² s⁻¹ at plant height, with a 16 h/8 h light/dark cycle. Heating was provided if the temperature dropped below 18 °C during the light period and 15 °C during darkness. The average air temperature oscillated between 14.5 and 22 °C, with an average temperature during the whole experiment of 18 °C. The plants were harvested approximately 7 weeks after sowing, when they were at start of heading. The plants were cut roughly 2.5 cm above the soil surface, stored in a paper bag per pot and dried at 60 °C to constant weight.

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The injector, detector and column were operated at 41, 153 and 81 °C, respectively. Helium was used as a carrier gas, at 20 mL min⁻¹. A standard gas mixture (CH₄/CO₂) at 65/35% was used for calibration of the GC.

**Sludge analyses**

All the substrates obtained from the processes illustrated in Figure 1 were sequentially extracted using a modified Hedley fractionation of P for manure and compost (Hedley et al. 1982; Sharpley & Moyer 2000). The fractionation scheme consisted of five fractions obtained by extraction of 1 g of dried substrate with 200 mL of deionised water for 1 h, followed by 200 mL of 0.5 M NaHCO₃ (P-labile), 0.1 M NaOH (P-Al/Fe) and 1 M HCl (stable Ca-P), each for 16 h. Residual P was determined following digestion with ultrapure and concentrated HNO₃ and HCl in a high performance microwave reactor (HPMR) (model IV, MLS GmbH) for 4 h at 260 °C and 50 bar. All the extracts except residual P were filtered through 0.45 μm membranes and the ortho-P in the filtrate was analysed by colorimetry using the molybdenum blue method in a Stasar II Giford Instrument® spectrophotometer at 882 nm (Murphy & Riley 1962). The P_total concentration in the filtered extracts and in the residues of the fractionation was analysed using an inductively coupled plasma (ICP) optical emission spectrometer (OES) (Perkin-Elmer model 5300 DV). The Fe, Al, Ca and Mg concentrations in the filtrates and residues were determined by ICP-OES.

The P_total, Fe, Al, Ca, K, Na and Mg and heavy metals Cr, Cu, Mn, Ni, Cd, Pb and Zn concentrations in all the dry sludges were determined by microwave digestion and ICP-OES as described in the previous paragraph for the residues of the fractionation. Organic P (P-org) was estimated by solubilising the inorganic P with 12 N H₂SO₄ in a water bath at 70 °C for 10 min and subtracting the value from P_total (Møberg & Petersen 1982).

**Plant and soil analyses**

The dried plants from each pot were milled (Laboratory Mill 3100, Perten Instruments, mesh size 0.5 mm) and digested with ultrapure and concentrated HNO₃ at 260 °C and 50 bar in the HPMR. The P_total and heavy metal concentrations (Cr, Cu, Mn, Ni, Cd, Pb and Zn) were analysed by ICP mass spectrometry model Agilent Tech. 8800 Triple Squad. In addition, total N was determined by means of infrared spectroscopy in a LECO TruSpec® CHN device in the milled samples. After completion of the pot experiment, soil samples were analysed for pH (ISO 2015) and P-AL (Egnér et al. 1960). Uptake of P (mg pot⁻¹) in aboveground biomass was computed by multiplying P concentration by aboveground DM yield.

**Statistical methods**

In the AD treatment, two replicates per UT sludge were used in the reactors. Three replicates were used for the fertiliser, plant and soil analyses, with the inclusion of the standard deviation for quality assurance of the data. Analysis of variance was performed to study the effect of the sludges on plant P uptake. To perform multiple comparisons, the Tukey’s honest significant difference multiple comparison test was used (α = 0.05).

**RESULTS AND DISCUSSION**

**Anaerobic digestion treatment**

From the control parameters (pH, FOS, TAC, etc.), it was possible to ensure that the biogas process was running effectively throughout the start-up phase and the HRT (Figure 2(a) and 2(b)). The HRT started on 13 April 2014 for FRE-1, FRE-2 and ULL-1. The case of ULL-2 was slightly different due to low pH values and high FOS/TAC ratio (Figure 3). A very high content of FOS and production of volatile fatty acids in the ADR decreased the pH to 6.5, and thus the biogas process was inhibited (Yuan & Zhu 2016). The start-up process stabilised after 16 April and the first feeding of the HRT was made on 24 April. The process was considered under control for pH values in the ADR of between 7.5 and 8 (25 °C) and a FOS/TAC ratio below 2 (Drosg 2013).

The normalised biogas CH₄ concentration (% by weight) was determined daily as an additional control of the HRT for all reactors (Figure 4(a) and 4(b)). The lower CH₄ concentration for ULL compared with FRE is most likely attributable to the degradation of organic compounds in a biological treatment step in ULL prior to the chemical precipitation, whereas FRE has no such biological step. ULL therefore had a lower VS content than FRE.

**Anaerobic digestion and lime treatment effect on plant-available P**

The effect of AD and liming on plant availability of P was studied with two approaches. The first involved chemical characterisation of the different sludges (UT and treated)
Figure 2 | Measured pH and FOS/TAC ratio of the anaerobic digestion residue (ADR) for the biogas reactors (a) FRE-1 and (b) FRE-2 during the start-up and HRT periods.

Figure 3 | Measured pH and FOS/TAC ratio of the anaerobic digestion residue (ADR) for the biogas reactors (a) ULL-1 and (b) ULL-2 during the start-up and HRT periods.

Figure 4 | Daily normalised CH₄ concentration (% by weight) in the biogas from reactors (a) FRE-1 and ULL-1 and (b) FRE-2 and ULL-2. The HRT was 22 days for FRE-1 and FRE-2 and 15 days for ULL-1 and ULL-2.
with a modified scheme for sequential P extraction, while the second involved a growth experiment with barley.

**Sequential P extraction**

By the sequential extraction of P, the distribution of P in pools of different solubility could be studied.

As can be seen from Figure 5(a) and 5(b), there was a very low H₂O-P (loosely bound P) concentration in all UT and treated sludges. Both the UT sludges and the non-limed AD sludges also contained a considerable low P-labile fraction (NaHCO₃-P). The effect of AD treatment was not significant for this P fraction. Moreover, the P-Fe/Al (NaOH-P) fraction was the highest for both of these substrates.

The liming treatment (both slaked lime and quicklime) had a positive effect in increasing the P-labile fraction significantly. However, this positive impact on plant availability of P was significantly higher for slaked lime than for quicklime. This difference was more pronounced for the FRE sludges than the ULL sludges, with slaked lime increasing the P-labile fraction in FRE sludges by more than twice as much as quicklime.

**Growth experiment**

Phosphorus uptake at the two pH levels tested in the control treatments was similar, and therefore only the results for the lowest pH level (pH 6.5) are shown. The P uptake by barley in all treatments is shown in Figure 6(a) and 6(b).

A poor effect on P uptake was achieved from AD without liming. Plant uptake of P in that treatment was not significantly different from that in the UT sludge and the control (receiving 0 kg P ha⁻¹). The P plant uptake results confirmed the findings from the P-fractionation analysis that the liming treatments gave the highest availability of P (see Figure 6). Moreover, the NaHCO₃-P fractionation gave similar results, with a close correlation with plant P.
uptake for both FRE and ULL UT and treated sludges (Figure 7(a) and 7(b)).

The highest P plant uptake occurred with slaked lime treatment of the UT sludges, and these values were significantly higher than those obtained by slaked lime treatment of AD sludges (Figure 6). There is thus a negative effect of AD on comparing with the slaked lime treatment of UT (UT + SL). Moreover, plant P uptake was significantly higher (1.2-fold) for slaked lime treatment of UT than for quicklime treatment of the UT substrates from both FRE and ULL. The P fractionation of the fertilisers showed a similar trend for ULL (with 1.08-fold higher P uptake for SL liming), as seen from Figure 7.

RAE, or the relative P fertilisation effect compared with MinP, was markedly low for the AD treatment, only 0.7% for FRE and 4.3% for ULL (Table 3). Therefore, AD had scarcely any P fertiliser effect. In contrast, liming increased the RAE values substantially. The highest RAE (81.3%) was obtained by Fe-precipitation and liming (UT + SL).

### Effects of liming of Fe- and Al-precipitated sludge on plant-available P

Liming of sludge led to increased concentrations of P-labile and Ca-P and a reduced concentration of P-Fe/Al, as shown by the sequential P fractionation. This improved the plant availability of P and plant P uptake compared with unlimed sludges, where the majority of the P was bound to Fe or Al. This can be explained by the increased pH value in limed sludge being reflected in the fertilised soil (Table 4). As a result, Fe/Al-(hydr)oxides were less positively charged and the solubility of P-Fe/Al increased with increasing pH (Lindsay 1979). Simultaneously, the Ca-concentration was raised by liming, resulting in a shift of Fe-/Al-bound P to Ca-bound P in the sludges. This Ca-bound P was most likely a non-crystalline type of Ca-phosphate in the sludges (Øgaard & Brod 2016). However, Al-hydrolysis products have previously been reported to desorb P at a lower rate than Fe-hydrolysis products, as the pH increases following liming (Haynes 1982; Singh et al. 2005; Achat et al. 2016).

For soils, Achat et al. (2016) have found that the concentration of phosphate ions in the soil solution had a stronger negative correlation with Al than with Fe extracted with ammonium oxalate (correlation coefficient = −0.42 and −0.17, respectively; p < 0.05). In similar findings by Singh et al. (2005), the corresponding correlation coefficients were −0.68 (p < 0.05) and −0.49 (non-significant) for Al and Fe, respectively. Thus, from a chemical extraction point of view, the P binding is most likely stronger for Al- than for Fe-oxides. This is explained by lower solubility of Al-phosphate than Fe-phosphate, and thus stronger and

### Table 3 | RAE of P fertilisation for the primary precipitated untreated sludges from the FRE and ULL WWTPs and their treatments

<table>
<thead>
<tr>
<th>Treatment</th>
<th>FRE (%)</th>
<th>ULL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UT</td>
<td>7.7</td>
<td>8.2</td>
</tr>
<tr>
<td>UT + SL</td>
<td>81.3</td>
<td>51.3</td>
</tr>
<tr>
<td>UT + QL</td>
<td>62</td>
<td>36.6</td>
</tr>
<tr>
<td>AD</td>
<td>0.7</td>
<td>4.3</td>
</tr>
<tr>
<td>AD + SL</td>
<td>44.2</td>
<td>30.6</td>
</tr>
</tbody>
</table>

UT, untreated; AD, anaerobic digestion; SL, slaked lime (Ca(OH)2); QL, quicklime (CaO).

![Figure 7](https://iwaponline.com/wst/article-pdf/75/7/1743/454078/wst075071743.pdf)
AD in combination with liming had a negative effect on P availability. Liming with slaked lime was more effective than liming with quicklime. Liming with both slaked lime and quicklime increased P availability from the solid fraction of pig slurry as compared to untreated sludge. This suggests that a combined treatment scheme comprising Fe-precipitation of sludge, AD and liming is the optimal approach for maximising energy and P recycling.

Table 4 | Soil pH value after seven weeks of the pot experiment

<table>
<thead>
<tr>
<th>Fertiliser</th>
<th>Soil pH at the end of the pot experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRE</td>
<td>6.1 ± 0.06</td>
</tr>
<tr>
<td>UT</td>
<td>6.1 ± 0.06</td>
</tr>
<tr>
<td>UT + SL</td>
<td>8.2 ± 0.05</td>
</tr>
<tr>
<td>UT + QL</td>
<td>8.3 ± 0.06</td>
</tr>
<tr>
<td>AD</td>
<td>5.8 ± 0.04</td>
</tr>
<tr>
<td>AD + SL</td>
<td>7.3 ± 0.03</td>
</tr>
<tr>
<td>ULL</td>
<td>6.1 ± 0.05</td>
</tr>
<tr>
<td>UT + SL</td>
<td>7.6 ± 0.06</td>
</tr>
<tr>
<td>UT + QL</td>
<td>8.4 ± 0.03</td>
</tr>
<tr>
<td>AD</td>
<td>5.8 ± 0.04</td>
</tr>
<tr>
<td>AD + SL</td>
<td>7.1 ± 0.03</td>
</tr>
</tbody>
</table>

UT, untreated; AD, anaerobic digestion; SL – slaked lime (Ca(OH)$_2$); QL – quicklime (CaO).

Treatment scheme suggestions for sludge

AD is a treatment needed in order to recycle energy and nutrients contained in the sewage sludge at WWTPs. AD can mineralise organic P, but if the concentration of Fe$^{3+}$ or Al$^{3+}$ is high in the inlet stream of the biogas plant, P released by mineralisation will be adsorbed to Fe/Al. Further post-AD treatment, such as liming, is required for Fe-/Al-precipitated sludge in order to significantly improve P recycling. In the present study, liming increased plant availability of P to a greater extent for Fe-precipitated sludge than for Al-precipitated sludge. This suggests that a combined treatment scheme comprising Fe-precipitation of sludge, AD and liming is the optimal approach for maximising energy and P recycling.

CONCLUSIONS

- Liming with both slaked lime and quicklime increased P uptake in barley, particularly for Fe-precipitated sludge.
- Liming with slaked lime was more effective than liming with quicklime in increasing plant P uptake, for both Fe- and Al-precipitated sludges.
- AD in combination with liming had a negative effect on plant availability of P for both Fe- and Al-precipitated sludges, whereas AD without a liming post-treatment had no significant effect on P availability.

ACKNOWLEDGEMENTS

This work was part of the research project ‘Biosolids in Food Production – Phosphorus Recycling and Food Safety’, which was funded by the Research Council of Norway (Grant No. 207811) and industry partners.

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First received 12 August 2016; accepted in revised form 16 January 2017. Available online 27 January 2017