



## Considering inorganic P binding in bio-based products improves prediction of their P fertiliser value



Eva Brod<sup>a,\*</sup>, Anne Falk Øgaard<sup>a</sup>, Dorette Sophie Müller-Stöver<sup>b</sup>, Gitte Holton Rubæk<sup>c</sup>

<sup>a</sup> Bioresources and Recycling Technologies, Division of Environment and Natural Resources, Norwegian Institute of Bioeconomy Research, Postbox 115, NO-1431 Ås, Norway

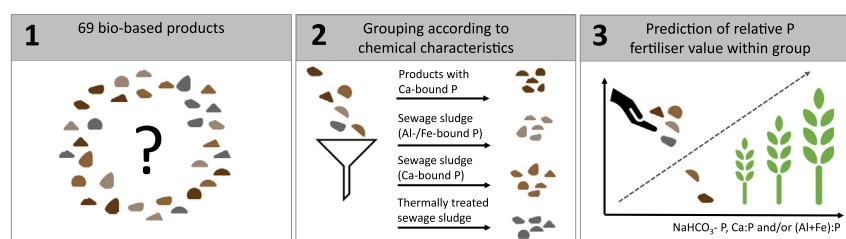
<sup>b</sup> Department of Plant and Environmental Sciences, Faculty of Science, University of Copenhagen, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark

<sup>c</sup> Department of Agroecology, Aarhus University, Blichers Allé 20, DK-8830 Tjele, Denmark

### HIGHLIGHTS

- Unknown P fertiliser value of bio-based products limits recycling in practice.
- Prediction models based on 10 studies with 69 fertiliser products were developed.
- NaHCO<sub>3</sub>-soluble P, Ca:P and/or (Al + Fe):P in the products were tested as predictors.
- Grouping based on expected inorganic P bindings allowed prediction up to R<sup>2</sup> = 79%.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

Editor: Charlotte Poschenrieder

#### Keywords:

Phosphorus recycling  
Solubility  
Relative agronomic efficiency  
Chemical extraction  
Plant availability  
Waste resources

### ABSTRACT

Prediction of the relative phosphorus (P) fertiliser value of bio-based fertiliser products is agronomically important, but previous attempts to develop prediction models have often failed due to the high chemical complexity of bio-based fertilisers and the limited number of products included in analyses. In this study, regression models for prediction were developed using independently produced data from 10 different studies on crop growth responses to P applied with bio-based fertiliser products, resulting in a dataset with 69 products. The 69 fertiliser products were organised into four sub-groups, based on the inorganic P compounds most likely to be present in each product. Within each product group, multiple regression was conducted using mineral fertiliser equivalents (MFE) as response variable and three potential explanatory variables derived from chemical analysis, all reflecting inorganic P binding in the fertiliser products: i) NaHCO<sub>3</sub>-soluble P, ii) molar ratio of calcium (Ca):P and iii) molar ratio of aluminium + iron (Al + Fe):P. The best regression model fit was achieved for sewage sludges with Al-/Fe-bound P ( $n = 20$ ;  $R^2 = 79.2\%$ ), followed by sewage sludges with Ca-bound P ( $n = 11$ ;  $R^2 = 71.1\%$ ); fertiliser products with Ca-bound P ( $n = 29$ ;  $R^2 = 58.2\%$ ); and thermally treated sewage sludge products ( $n = 9$ ;  $R^2 = 44.9\%$ ). Even though external factors influencing P fertiliser values (e.g. fertiliser shape, application form, soil characteristics) differed between the underlying studies and were not considered, the suggested prediction models provide potential for more efficient P recycling in practice.

### 1. Introduction

Despite rock phosphate being a limited resource, bio-based fertiliser products still seldom replace mineral phosphorus (P) fertiliser in practical agriculture. The unknown and variable P fertiliser value of bio-based

products is one of the main bottlenecks for efficient P recycling. In order to promote increased use of recycled nutrients, in 2019 the European Union (EU) issued a new regulation on the use of fertiliser products with specific focus on recycling fertilisers (EU, 2019/1009). To enable estimation of the P fertiliser value of mineral and organo-mineral fertilisers, the new EU (2019/1009) regulation requires extractable P (i.e. water-soluble P and P soluble in neutral ammonium citrate) and total P content to be declared on product labelling. For organic fertiliser products, however, equivalent estimates of P solubility are not required (EU, 2019/1009), owing to

\* Corresponding author.

E-mail addresses: [eva.brod@nibio.no](mailto:eva.brod@nibio.no) (E. Brod), [anne.falk.ogaard@nibio.no](mailto:anne.falk.ogaard@nibio.no) (A.F. Øgaard), [dsst@plen.ku.dk](mailto:dsst@plen.ku.dk) (D.S. Müller-Stöver), [gitte.rubaek@agro.au.dk](mailto:gitte.rubaek@agro.au.dk) (G.H. Rubæk).

lack of knowledge about reliable prediction of the P fertiliser value of alternative products. For example, Kratz et al. (2019) showed that standard chemical extraction methods only have limited predictive value when applied to fertiliser products from recycled materials.

In bio-based fertiliser products, P is usually present as a mixture of various P compounds of differing chemical structure and solubility, resulting in variable P fertiliser values (Kratz et al., 2019). Despite the organic origin of bio-based fertiliser products, P is mainly present as inorganic compounds (Kratz et al., 2016; Brod and Øgaard, 2021), and therefore, P release is determined by the chemical solubility of these inorganic P compounds, rather than by biological decomposition of organic compounds. The P in bio-based fertiliser products is often present as calcium (Ca) phosphates of differing solubility, depending on the Ca:P ratio and degree of crystallisation (Kratz et al., 2019). The solubility of various Ca-phosphates is also pH-dependent, with the P fertiliser value of bio-based products, where P is mainly bound to Ca, increasing with decreasing soil pH (Lindsay, 1979). The P present in bio-based fertiliser products may also be found in iron (Fe) and/or aluminium (Al) compounds or adsorbed to Fe-/Al- (hydr)oxides, especially if Fe-/Al- salts are used for precipitation of P during wastewater treatment (Øgaard and Brod, 2016). The solubility of P bound to Fe and/or Al in fertiliser products increases with increasing soil pH and decreases with increasing (Al + Fe):P ratio (Lindsay, 1979; Øgaard and Brod, 2016).

Farmers are generally only willing to apply bio-based fertiliser products if such products have known P fertiliser values compared to those of mineral fertiliser and if reliable fertilisation plans, in line with crop demands, can be established (Case et al., 2017). Therefore, to achieve efficient P recycling in agriculture, simple and cheap methods for estimating the P fertiliser value of bio-based products must be identified. Growth experiments are the most reliable method for determining the fertiliser value of new fertiliser products, but are time-consuming and costly. Alternatively, extraction of fertilised soil following incubation, using either standard soil P tests or DGT (diffusive gradient in thin film) tests, has been identified as a good approach for establishing the P fertiliser value of bio-based products (e.g. Christel et al., 2014; Christiansen et al., 2020; Duboc et al., 2017; Vogel et al., 2017). However, this approach is also time-consuming and the characteristics of the soil used for the incubation can affect the results. An increasingly popular approach for predicting the P fertiliser value of new fertiliser products is to apply standard soil or fertiliser extraction methods directly to the products and compare the P solubility values against performance in growth experiments (Kratz et al., 2019). The aim is thereby not to extract the absolute amount of available P in the fertiliser product, but rather to extract a P fraction that reflects P release in soils, which is related to P plant uptake.

Previous studies have reached different and partly contradictory conclusions on the most suitable extraction method for predicting the P fertiliser value of bio-based products. For example, Christiansen et al. (2020) compared nine different P extraction methods and concluded that P solubility in an alkaline solution of 0.5 M NaHCO<sub>3</sub> (pH 8.5) was most suitable for predicting the P fertiliser values of the products that included: sewage sludges where P was precipitated with Fe- or Al- salts, compost based on source-separated household/garden/park waste, meat-bone meal, wood ash, biochar based on straw and sewage sludge, and industrial sludge. In a very recent study by Duboc et al. (2022), shoot P content in rye (*Secale cereale* L.) was found to be well correlated with NaHCO<sub>3</sub>-soluble P following application of 42 fertiliser products to a soil with pH (0.01 M CaCl<sub>2</sub>) 7.4. However, no significant correlation with NaHCO<sub>3</sub>-soluble P in the fertiliser products was detected after application to a soil with pH (0.01 M CaCl<sub>2</sub>) 5.5 (Duboc et al., 2022). In the acidic soil, extraction of P with H<sub>2</sub>O combined with adsorption to ferrylhydrate (iron bag method) resulted in the best prediction of P fertiliser values (Duboc et al., 2022). In contrast, a study by Delin (2016) on 14 products, including sewage sludges, manure, straw ash, bone meal, meat meal and digestate based on plant material or slaughterhouse waste, found that the P fertiliser value was better correlated with P extracted with an acid solution of ammonium lactate and acetic acid (pH 3.75) than with H<sub>2</sub>O-soluble P. However, when sewage sludge products

were excluded from that analysis, the best correlation with P fertiliser value was achieved for P extracted in neutral ammonium citrate (Delin, 2016).

The contradictory results obtained to date may be partly explained by many previous studies including large arrays of products with chemically diverse characteristics. Following an extensive literature review, Kratz et al. (2019) concluded that studies including only one specific product type achieved much closer relationships between P extraction and P fertiliser value. A more successful approach for prediction of P fertiliser values might therefore be to group fertiliser products with similar chemical characteristics and to include information on these chemical P characteristics in regression models. To our knowledge, this approach has not been tested to date. Thus this study is the first to combine independently produced data from different studies in development of regression models for predicting the P fertiliser value of bio-based fertiliser products. Specific objectives of the study were to:

- 1) Test the robustness of models using P extraction with 0.5 M NaHCO<sub>3</sub> for prediction of the P fertiliser value of bio-based fertiliser products, by including a wide array of products tested across various experiments.
- 2) Optimise models for prediction of P fertiliser values by grouping fertiliser products according to their origin and chemical characteristics.
- 3) Optimise models for prediction of P fertiliser values by using the molar ratio of Ca:P and (Al + Fe):P in the fertiliser products as potential explanatory variables.
- 4) Present general recommendations on how to predict the P fertiliser value of new fertiliser products compared to mineral fertiliser, information which can be used for the development of fertilisation plans.

## 2. Material and methods

### 2.1. Fertiliser products

Data were taken from 10 independent studies examining crop growth response to P applied with a total of 69 bio-based fertiliser products (Alvarenga et al., 2017; Brod and Øgaard, 2021; Brod et al., 2015b; Christiansen et al., 2020; Lemming et al., 2017a,b; Müller-Stöver et al., 2021; Øgaard, 2017; Øgaard and Brod, 2016). A complete list of the 69 fertiliser products and a description of origin and processing can be found in Table S1 in Supplementary material (SM). The fertiliser products comprised:

- Municipal sewage treated biologically or with Al-, Fe- and/or Ca- salts to remove P before anaerobic digestion, liming, oxidisation, drying, incineration, gasification, pyrolysis, thermochemical treatment and/or acidification ( $n = 41$ ).
- Animal manure originating from cattle, pigs, chicken, horses or salmon, untreated or treated by mechanical separation with or without previous anaerobic digestion, drying and/or pyrolysis ( $n = 18$ ).
- Source-separated household waste and other food waste treated by anaerobic digestion or composting with or without co-substrate ( $n = 4$ ).
- Ash after incineration of timber wood unsuitable for industrial use and/or cereal residues ( $n = 3$ ).
- Meat-bone meal ( $n = 2$ ).
- Other P-rich industrial sludge ( $n = 1$ ).

### 2.2. Preparation and chemical analysis of fertiliser products

An overview of the methods used for chemical characterisation of the 69 fertiliser products, as described in the 10 original studies, is provided in Table S2 in SM. The fertiliser products were dried at 40, 55 or 105 °C, depending on the actual study, and sieved or milled prior to further analysis. To determine total P concentrations, the fertiliser products were digested in various strong acids considered suitable for extracting near-total P amounts in the respective materials, using an ultraclave or microwave (i.e. 7 M HNO<sub>3</sub>, incineration before digestion in H<sub>2</sub>SO<sub>4</sub>, aqua regia or a combination

of HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and HF). Phosphorus in the digested samples was measured spectrophotometrically by the molybdenum blue method according to Murphy and Riley (1962) or by ICP-OES/ICP-MS. Where applicable, total Ca, Al and Fe concentrations were also analysed by ICP-OES/ICP-MS. Total P content and, where available, molar Ca:P and (Al + Fe):P ratio in the fertiliser products are shown in Table S3 in SM.

The solubility in 0.5 M NaHCO<sub>3</sub> of P in the fertiliser products was determined in a solution:sample ratio of 200:1 except in the study by Øgaard and Brod (2016), where the solution:sample ratio was 180:1. Phosphorus extraction with 0.5 M NaHCO<sub>3</sub> was originally developed to estimate plant-available P in soils with a solution:soil sample ratio of 20:1 (Olsen et al., 1954). The solution:sample ratio has since extended to account for the higher P content in fertiliser products compared with soil. Three studies included adjustment of pH in the extraction solution to 8.5 (Brod and Øgaard, 2021; Christiansen et al., 2020; Øgaard and Brod, 2016), as intended by the original method. In most studies the extraction time was 0.5 h, but in two studies the sum of the first two steps in the modified sequential fractionation according to Hedley et al. (1982) was used. Hence P was extracted in H<sub>2</sub>O for 1 h before extraction in 0.5 NaHCO<sub>3</sub> for 16 h in those two studies (Alvarenga et al., 2017; Brod et al., 2015b). Phosphorus concentration in the extracts was analysed spectrophotometrically or by ICP-OES/ICP-MS. For 15 fertiliser products, analysis of NaHCO<sub>3</sub>-soluble P as described above was conducted specifically for the present study. The solubility of P in NaHCO<sub>3</sub>, expressed as ratio of total P in the fertiliser products, is presented in Table S3 (SM).

### 2.3. Pot experiments: mineral fertiliser equivalents

The P fertiliser values of the 69 bio-based fertiliser products relative to mineral fertiliser (as mineral fertiliser equivalents, MFE) was studied in 10 different pot experiments, the set-up of which is described in Table 1. In some pot experiments, MFE of each fertiliser product was tested on two or more soil types, resulting in a total of 94 MFE observations for the 69 fertiliser products. To ensure that only P would be limiting for plant growth, in all pot experiments all other nutrients were applied in solution in amounts regarded as sufficient. Mineral P control treatments were applied as Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> or KH<sub>2</sub>PO<sub>4</sub>. There were three or four replicates per treatment in all pot experiments. Phosphorus uptake was computed by multiplying dry matter (DM) production in aboveground biomass by plant tissue P concentration. Mineral fertiliser equivalents were calculated based

on aboveground P uptake in all pot experiments, but obtained in two different ways. In four studies (b, c, i and j in Table 1), MFE was calculated based on the P response curve as:

$$\text{MFE} = 100 \times \frac{X_1}{\text{P applied}} \quad (1)$$

where:

$$X_1 = \frac{(Y_1 - b)}{a}$$

and *P applied* is amount of P applied with the bio-based fertiliser product; *Y<sub>1</sub>* is P uptake in aboveground biomass as an effect of the bio-based fertiliser product; *X<sub>1</sub>* is amount of mineral P fertiliser resulting in equally high P uptake in biomass as application of the bio-based fertiliser product; and *a* and *b* are slope and intercept, respectively, obtained from linear regression with *Y* = P uptake after mineral P fertiliser application and *X* = increasing application rate of mineral P fertiliser.

In the six remaining studies (a, d, e, f, g and h in Table 1), MFE was calculated directly compared with the P use efficiency of mineral P fertiliser as:

$$\text{MFE} = \frac{\text{PUE}}{\text{PUE (Mineral P fertiliser)}} \quad (2)$$

where:

$$\text{PUE} = \frac{\text{P uptake (P+)} - \text{P uptake (NoP)}}{\text{P applied}} \times 100$$

and *P uptake (P+)* is P uptake in aboveground biomass of plants that received mineral or bio-based P fertiliser product; *P uptake (NoP)* is P uptake in aboveground biomass of plants that received no P fertiliser; and *P applied* is amount of P applied with mineral or bio-based fertiliser product.

The effect of the fertiliser products on soil pH was determined after harvest, in suspension with H<sub>2</sub>O or 0.01 M CaCl<sub>2</sub> solution. Soil pH and MFE for each fertiliser product are presented in Table S3.

**Table 1**

Description of the 10 pot experiments included in model development. P-AL = Phosphorus extracted with 0.1 M ammonium lactate and 0.4 M acetic acid adjusted to pH 3.75 (Egnér et al., 1960); Olsen-P = P extraction with 0.5 NaHCO<sub>3</sub> (Olsen et al., 1954); WEP = water-extractable P.

No.	Reference	Pro-ducts n	Soil	Initial soil pH	Initial soil P level			Pot size L	P rate mg P kg <sup>-1</sup> soil	Crop	Mineral control treatments mg P kg <sup>-1</sup> soil	Type of mineral N fertiliser
					P-AL mg kg <sup>-1</sup>	Olsen-mg P kg <sup>-1</sup>	WEP mg kg <sup>-1</sup>					
a	Alvarenga et al. (2017)	10	Sand/peat mixture	6.5	11	–	–	3	25	Barley	0, 12.5, 25	Ca(NO <sub>3</sub> ) <sub>2</sub>
b	Brod et al. (2015b)	9	Sand/peat mixture	5.5 6.9	11–12	45–48	–	5	12	Ryegrass (1st cut)	0, 6, 12, 18	Ca(NO <sub>3</sub> ) <sub>2</sub>
c	Brod and Øgaard (2021)	14	Sand/peat mixture	6	30	–	0.5	3	15	Barley	0, 7, 5, 15	Ca(NO <sub>3</sub> ) <sub>2</sub>
d	Christiansen et al. (2020)	7	Loamy sand Sandy loam Sand	5.2 5.3 5.2	– – –	12 15 31	2.9 5.0 2.5	3	64	Barley	0, 64	NH <sub>4</sub> NO <sub>3</sub>
e	Lemming et al. (2017a)	3	Sandy loam/quartz; Sand mixture	6.7	–	–	–	1	50	Barley	0, 25, 75, 120	NH <sub>4</sub> NO <sub>3</sub>
f	Lemming et al. (2017b)	2	Sandy loam/quartz	6.7	–	< 20	–	2	80	Barley	0, 80	NH <sub>4</sub> NO <sub>3</sub>
g	Müller-Stöver et al. (2021)	7	Sandy loam/quartz	5.0	–	–	0.7	2.5	80	Spring wheat	0, 50, 80	NH <sub>4</sub> NO <sub>3</sub>
h	Müller-Stöver et al. (unpublished)	3	Sandy loam/quartz Sandy loam	6.5 8.3	– –	– –	1.9 –	2.5	80	Winter wheat	0, 40, 80	NH <sub>4</sub> NO <sub>3</sub>
i	Øgaard and Brod (2016)	11	Sand/peat mixture	7	30	–	0.5	5	37.5	Ryegrass (1st cut)	0, 12.5, 25, 37.5	Ca(NO <sub>3</sub> ) <sub>2</sub>
j	Øgaard (2017)	3	Sand/peat mixture	5.9	–	–	–	4	21	Ryegrass (1st cut)	0, 10.5, 21	NH <sub>4</sub> NO <sub>3</sub>

## 2.4. Data analysis

The 69 bio-based fertiliser products were organised into four groups based on the inorganic P compounds most likely to be present in each product according to the literature (for sources, see Table 2). Within each product group, multiple regression was conducted with MFE as response variable and with three potential explanatory variables: i)  $\text{NaHCO}_3$ -soluble P; ii) molar Ca:P ratio; and iii) molar (Al + Fe):P ratio (Table S3). For each product group, the respective multiple regression model was simplified by excluding those explanatory variables that contributed little to explaining MFE ( $p$ -value > 0.1), until the model was as simple as possible while keeping the coefficient of determination ( $R^2$ ) and adjusted  $R^2$  ( $R^2_{\text{adj}}$ , considering the number of independent variables in the regression model) sufficiently high. Predicted vs. actual plots were also checked for satisfactory accuracy. In situations with curvilinear relationships between variables, explanatory variables were transformed to their reciprocal to achieve better model fit. Residual plots were checked for deviations from the assumptions of normal distribution and equal variance. If the fitted model was strongly determined by single observations, those were excluded from calculation of the regression model and are referred to as outliers. Results are expressed as mean  $\pm$  standard deviation.

## 3. Results and discussion

The suggested grouping of fertiliser products based on inorganic P compounds most likely to be present and the regression model with the best fit for each product group are presented in Table 2.

### 3.1. Fertiliser products with Ca-bound P

The largest group ( $n = 29$ ) comprised fertiliser products where P is usually mainly present as Ca-bound P. This group included animal manure products, source-separated household waste and other food waste products (i.e. digestate, compost), meat-bone meal, ash based on wood/cereal residues and limed industrial chemical sludge (Table S1). According to the literature, in these products most inorganic P occurs in the form of Ca-phosphates of varying solubility, struvite and other magnesium phosphates (Frossard et al., 2002; Toor et al., 2005; Brod et al., 2015a; Bruun et al., 2017).

Total P content in fertiliser products with Ca-bound P was  $26.0 \pm 17.2$  g P  $\text{kg}^{-1}$  DM on average, with the highest P content ( $65.9$  g P  $\text{kg}^{-1}$ ) in

biochar based on swine manure (Brod and Øgaard, 2021) and the lowest ( $6.3$  g P  $\text{kg}^{-1}$ ) in dairy manure (Brod et al., 2015b). The MFE of fertiliser products with Ca-bound P was  $54.7 \pm 26.2\%$  on average, with the highest MFE (127%) being reported for dairy manure (Brod et al., 2015b) and the lowest (11%) for meat-bone meal (Brod et al., 2015b). In the study by Brod et al. (2015a), the P in dairy manure was mainly present as readily soluble inorganic compounds, whereas the P in meat-bone meal was suggested to be mainly present as crystalline and stable Ca-phosphates, such as hydroxyapatite and chlor-fluorapatite, based on XRD and  $^{31}\text{P}$  MAS-NMR analysis.

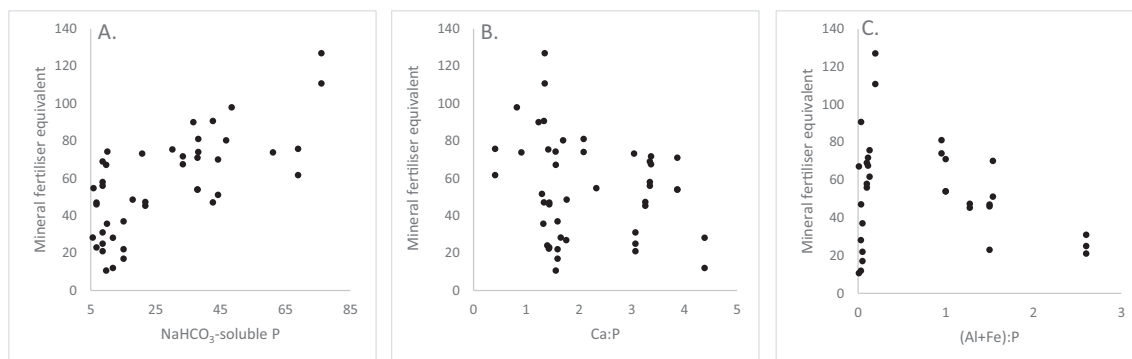
Of the three explanatory variables tested in the present study, the ratio of  $\text{NaHCO}_3$ -soluble P (% of total P) in the bio-based fertiliser products contributed most to explaining their MFE ( $p < 0.001$ ). The higher the ratio of  $\text{NaHCO}_3$ -soluble P in a fertiliser product with Ca-bound P, the higher its MFE (Fig. 1A). One of the principles of P extraction with  $0.5$  M  $\text{NaHCO}_3$  is to estimate the amount of readily soluble Ca-bound P by precipitating  $\text{Ca}^{2+}$  with  $\text{CO}_3^{2-}$  as  $\text{CaCO}_3$  and hence solubilising readily soluble Ca-bound P as orthophosphate in the extraction solution (Kuo, 1994). The pH of the extraction solution (around 8.5) ensures that stable Ca-phosphates remain undissolved (Lindsay, 1979). The molar ratio of Ca:P made the next largest contribution to explaining the MFE of the fertiliser products with Ca-bound P ( $p = 0.09$ ). The higher the Ca:P ratio in the fertiliser product, the lower its MFE, an effect attributable to the low solubility of Ca-phosphates with high Ca:P ratio, e.g. apatite (Ca:P = 1.67) compared with dicalcium phosphate (Ca:P = 1) (Lindsay, 1979). However, the Ca in bio-based fertiliser products can also occur in compounds with elements other than P. In the wood ash product studied by Brod et al. (2015a), the high Ca:P ratio was most likely explained by the presence of  $\text{CaCO}_3$  and  $\text{Ca(OH)}_2$  (Brod et al., unpublished results), as also indicated by its high pH (pH 13). This product was therefore excluded from the prediction model as an outlier. The reciprocal of the Ca:P ratio resulted in a better model fit than the untransformed variable.

In fertiliser products based on animal manure, food waste or other plant-based material, the molar ratio of (Al + Fe):P is commonly low (Table S3). However, as indicated in Fig. 1C, a molar ratio of (Al + Fe):P > 1 can still negatively affect the MFE of fertiliser products where P is mainly present as Ca-bound P. Our dataset comprised in total only six products with (Al + Fe):P > 1 (Table S3), and therefore the explanatory variable was not included in the final prediction model. For further optimisation of the model, we suggest dividing fertiliser products with mainly Ca-bound P

**Table 2**

Grouping of fertiliser products based on inorganic phosphorus (P) compounds most likely to be present according to the literature, and prediction models with the best fit for each product group.

Product group	Fertiliser products	Main P species	Literature suggesting presence of main P species	Prediction model derived in this study
Ca-bound P ( $n = 29$ )	<ul style="list-style-type: none"> <li>- Animal manure</li> <li>- Source-separated household waste and other food waste (i.e. digestate, compost)</li> <li>- Meat-bone meal</li> <li>- Ash based on wood/cereal residues etc.</li> <li>- Industrial sludge post-treated with lime</li> </ul>	<ul style="list-style-type: none"> <li>- Various apatites</li> <li>- Octo-calcium phosphates</li> <li>- Di-/tri-calcium phosphates</li> <li>- Weakly crystalline Ca- and Mg-phosphates</li> <li>- Struvite</li> </ul>	Frossard et al. (2002); Toor et al. (2005); Brod et al. (2015a); Bruun et al. (2017)	<ul style="list-style-type: none"> <li>- MFE = <math>35.4 + 1.1 * \text{NaHCO}_3\text{-soluble P} - 12.0 * 1 / (\text{Ca:P})</math>;</li> <li>- <math>R^2 = 58.2\%</math>, <math>R^2_{\text{adj}} = 56.3\%</math></li> <li>- <math>\text{NaHCO}_3\text{-soluble P}</math>: <math>p &lt; 0.001</math></li> <li>- <math>1/(\text{Ca:P})</math>: <math>p = 0.09</math></li> </ul>
Sewage sludge with Al-/Fe-bound P ( $n = 20$ )	- Sewage sludge where P is chemically precipitated with Al-/Fe-salts	<ul style="list-style-type: none"> <li>- Al-/Fe-bound P</li> <li>- P adsorbed to (amorphous) Al-/Fe-(hydr) oxides</li> </ul>	Frossard et al. (1997); Huang and Shenker (2004); Øgaard and Brod (2016)	<ul style="list-style-type: none"> <li>- MFE = <math>-10.7 + 76.0 * 1 / [(\text{Al} + \text{Fe}):\text{P}]</math>;</li> <li>- <math>R^2 = 79.2\%</math>, <math>R^2_{\text{adj}} = 78.2\%</math></li> <li>- <math>1 / [(\text{Al} + \text{Fe}):\text{P}]</math>: <math>p &lt; 0.001</math></li> </ul>
Sewage sludge with Ca-bound P ( $n = 11$ )	<ul style="list-style-type: none"> <li>- Sewage sludge precipitated with Al-/Fe-salts and thereafter treated with reactive lime</li> <li>- Sewage sludge where P is chemically precipitated with lime</li> <li>- Sewage sludge and other sludge</li> </ul>	<ul style="list-style-type: none"> <li>- Non-crystalline Ca-bound P</li> <li>- Al-/Fe-bound P</li> </ul>	Huang and Shenker (2004); Shober et al. (2006); Alvarenga et al. (2017)	<ul style="list-style-type: none"> <li>- MFE = <math>-20.7 + 1.1 * \text{NaHCO}_3\text{-soluble P} + 2.3 * \text{Ca:P}</math>;</li> <li>- <math>R^2 = 71.1\%</math>, <math>R^2_{\text{adj}} = 56.7\%</math></li> <li>- <math>\text{NaHCO}_3\text{-soluble P}</math>: <math>p = 0.10</math></li> <li>- Ca:P: <math>p = 0.10</math></li> </ul>
Thermally treated sewage sludge ( $n = 9$ )	<ul style="list-style-type: none"> <li>- Sewage sludge ash</li> <li>- Biochar based on sewage sludge</li> </ul>	<ul style="list-style-type: none"> <li>- Crystalline Ca-phosphates</li> <li>- Crystalline Fe-/Al-phosphates</li> </ul>	Nanzer et al. (2014); Müller-Stöver et al. (2021)	<ul style="list-style-type: none"> <li>- MFE = <math>4.1 + 51.2 * \text{NaHCO}_3\text{-soluble P}</math>;</li> <li>- <math>R^2 = 44.9\%</math>, <math>R^2_{\text{adj}} = 38.0\%</math></li> <li>- <math>\text{NaHCO}_3\text{-soluble P}</math>: <math>p = 0.03</math></li> </ul>



**Fig. 1.** Relationship between mineral fertiliser equivalents (MFE, %) of bio-based fertiliser products with Ca-bound P (48 observations) and: A) 0.5  $\text{NaHCO}_3$ -soluble P (% of total P, 48 observations), B) Ca:P ratio in the fertiliser product (48 observations, of which two outliers with Ca:P = 13 not included in the diagram) and C) (Al + Fe):P in the fertiliser product (33 observations).

into two sub-groups, with (Al + Fe):P > 1 and (Al + Fe):P < 1, and creating two separate prediction models.

### 3.2. Sewage sludge products

#### 3.2.1. Sewage sludge with Al-/Fe-bound P

The second largest group ( $n = 20$ ) comprised sewage sludge products in which P was chemically precipitated with Al-/Fe-salts. According to the literature, in Al-/Fe-precipitated sewage sludge P is mainly present as Al-/Fe-bound P or is adsorbed to (amorphous) Al-/Fe-(hydr)oxides (Frossard et al., 1997; Huang and Shenker, 2004; Øgaard and Brod, 2016). However, liming or thermal post-treatment of Al-/Fe-precipitated sewage sludge has been shown to alter P binding forms and P solubility in soil (Shober et al., 2006; Alvarenga et al., 2017). Therefore limed sludge products and thermally treated sewage sludge products were considered as separate groups in this study (Table 1).

Total P content in sewage sludge with Al-/Fe-bound P was  $27.1 \pm 8.5$  g  $\text{P kg}^{-1}$  DM on average. The MFE was  $22.7 \pm 24.4\%$  on average and, according to a  $t$ -test, was significantly lower ( $p < 0.001$ ) for sewage sludge products with Al-/Fe-bound P than for fertiliser products with Ca-bound P.

Of the three explanatory variables considered in the present study, molar (Al + Fe):P ratio in fertiliser products with Al-/Fe-bound P contributed most to explaining MFE ( $p < 0.001$ ). As can be seen from Fig. 2C, the MFE of fertiliser products with Al-/Fe-bound P clearly decreased for products with (Al + Fe):P > 3. Because of the non-linear nature of the decrease, transformation of (Al + Fe):P to its reciprocal resulted in a much better fit of the multiple regression model than the untransformed explanatory variable.

The fraction of  $\text{NaHCO}_3$ -soluble P in fertiliser products with Al-/Fe-bound P products showed a weak relationship ( $p = 0.7$ ) with MFE

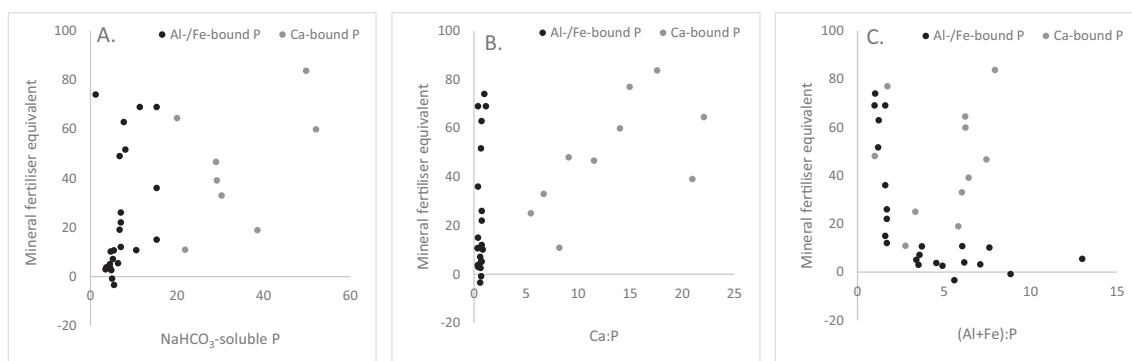
(Fig. 2A). At  $p$ -value > 0.2,  $\text{NaHCO}_3$ -soluble P was not included in the final version of the prediction model for bio-based fertiliser products with Al-/Fe-bound P. Extraction with 0.5 M  $\text{NaHCO}_3$  gives an estimate of the solubility of Al-/Fe-bound P following two main principles (Kuo, 1994): First,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  precipitate as oxides with  $\text{OH}^-$ , resulting in release of phosphate from easily soluble Al-/Fe-bound P to the extraction solution. Second, an increase in negative surface charge results in desorption of sorbed P. Non-labile Al-/Fe-bound P, which is held more strongly to Fe and Al components, is not extracted with 0.5 M  $\text{NaHCO}_3$  (Hedley et al., 1982).

In sewage sludge products where P is chemically precipitated with Al-/Fe-salts, Ca-bound P plays a minor role. Therefore the explanatory variable Ca:P ratio was not included in the final multiple regression model with the best fit (Fig. 2B).

#### 3.2.2. Sewage sludge with Ca-bound P

During post-treatment of Al-/Fe-precipitated sewage sludge with lime, P bound to Al and/or Fe is released as pH increases, and non-crystalline CaP binding forms instead. Alvarenga et al. (2017) used chemical fractionation to demonstrate the shift from Al-/Fe-bound P to Ca-bound P achieved by liming of Al-/Fe-precipitated sewage sludge. In sewage sludge where P is precipitated with Ca-salts, CaP binding dominates (Huang and Shenker, 2004; Shober et al., 2006).

Our dataset included 11 sewage sludge products with mainly Ca-bound P. Total P content in sewage sludge with Ca-bound P (mean  $8.9 \pm 3.3$  g  $\text{P kg}^{-1}$  DM) was significantly lower ( $t$ -test,  $p < 0.001$ ) than in sewage sludge with Al-/Fe-bound P (mean  $27.1 \pm 8.5$  g  $\text{P kg}^{-1}$  DM). This difference can be explained by dilution following lime addition. The MFE of sewage sludge with Ca-bound P was  $46.0 \pm 22.5\%$  on average, which was significantly higher ( $t$ -test,  $p < 0.01$ ) than for sewage sludge products with Al-/Fe-bound P ( $22.7 \pm 24.4\%$ ). The positive effect on MFE resulting from the



**Fig. 2.** Relationship between mineral fertiliser equivalents (MFE, %) of sewage sludge products with Al-/Fe-bound P (25 observations) or Ca-bound P (11 observations) and: A)  $\text{NaHCO}_3$ -soluble P (% of total P; 33 observations), B) Ca:P in the fertiliser products (33 observations, of which one outlier not included in the diagram) and C) (Al + Fe):P in the fertiliser product (34 observations).

shift from Al-/Fe-bound P to more soluble Ca-bound in limed sewage sludge products can be seen in Fig. 2C: Limed sewage sludge products were characterised by relatively high MFE values, despite  $(Al + Fe):P > 3$  for most products. The fraction of  $NaHCO_3$ -soluble P was also significantly higher ( $t$ -test,  $p < 0.001$ ) for sewage sludge with Ca-bound P than for sewage sludge with Al-/Fe-bound P (Fig. 2A).

The MFE of sewage sludge with Ca-bound P was best explained by including  $NaHCO_3$ -soluble P ( $p = 0.1$ ) and the molar ratio of Ca:P ( $p = 0.1$ ) in the prediction model (Table 2). However, the latter only contributed to explaining MFE of sewage sludge with Ca-bound P when a limed sewage sludge product denoted NRA (Øgaard and Brod, 2016) was excluded from the multiple regression model. The MFE of NRA sewage sludge was much lower than expected from its Ca:P ratio, probably because it was still unstable after liming, as indicated by its high pH ( $>11$ ). The explanatory variable  $(Al + Fe):P$  ratio did not contribute to explaining the MFE of sewage sludge with a high proportion of Ca-bound P (Fig. 2C).

### 3.3. Thermally treated sewage sludge products

The smallest group in our dataset comprised thermally treated sewage sludge products ( $n = 9$ ), in the form of sewage sludge ash or biochar based on sewage sludge. In thermally treated sewage sludge products, both Al-/Fe- and Ca-associated P species have been identified (Table 2). There are indications that thermal treatment causes a shift towards more Ca-associated P (Müller-Stöver et al., 2021). Formation of crystalline P-phases as an effect of thermal treatment has also been reported (Nanzer et al., 2014).

The total P content in thermally treated sewage sludge products was  $86.3 \pm 19.7$  g P  $kg^{-1}$  DM on average. The MFE was  $33.4 \pm 20.7\%$  on average, ranging from 6.0% for thermochemically treated sewage sludge ash (TrAsh; Lemming et al., 2017b) to 68% for oxidised biochar based on sewage sludge (PYR-OX; Müller-Stöver et al., 2021).

The  $NaHCO_3$ -soluble P in thermally treated sewage sludge products was the only explanatory variable included here, which contributed to explaining the MFE ( $p = 0.03$ ). The fraction of  $NaHCO_3$ -soluble P was very low on average ( $0.57 \pm 0.27\%$  of total P), despite relatively high MFE compared with untreated sewage sludge (Fig. 3A). However, the latter value might have been biased by including many materials from an experiment by Müller-Stöver et al. (2021), using acidic soil and finely ground fertiliser products, which resulted in overall high MFE values of the thermally treated products.

It is likely that the molar ratio of Ca:P and/or  $(Al + Fe):P$  can also partly explain the MFE of thermally treated sewage sludge products. However, in our dataset there was too little variation within these two explanatory variables for them to be included in our proposed prediction model with the best fit (Fig. 3B, C). This could change with inclusion of more products and observations for further improvement of the prediction models suggested in Table 2.

### 3.4. Implications for practical use: Shortcomings and applicability

The regression models presented in Table 2 give an indication of the MFE of bio-based fertiliser products with unknown fertiliser effect, and can thus be used in devising fertilisation plans for practical agriculture. However, the predictions are still lacking accuracy, with the difference between measured and predicted MFE (Table S3) exceeding  $\pm 20\%$  for:

- 13 of 48 values for products with Ca-bound P
- 3 of 23 values for sewage sludge products with Al-/Fe-bound P
- 2 of 8 values for sewage sludge products with Ca-bound P
- 1 of 10 values for thermally treated sewage sludge products.

Fig. S1 displays a comparison between measured and predicted MFE for each product group.

It can be argued that the main shortcoming of the prediction models suggested in Table 2 is that MFE values are predicted independently of external factors, which might affect their P fertiliser value. External factors of importance include fertiliser shape (e.g. powder or pellets; Müller-Stöver et al., 2021), fertiliser application method (e.g. surface application, incorporation or placing; Pedersen et al., 2020) and the soil type to which the fertiliser products are applied (e.g. Lemming et al., 2020).

Our dataset provided indications that soil pH in particular should be considered as additional explanatory variable in future work to optimise the regression models presented in Table 2. For example, the predicted MFE of meat-bone meal (Brod et al., 2015b) was 29% below the measured value when applied to soil substrate with pH ( $H_2O$ ) 5.5, while it was 28% above the measured value when applied to limed soil substrate with pH ( $H_2O$ ) 6.9. The large differences between measured and predicted MFE values depending on soil substrate can be explained by the P in meat-bone meal mainly being present as crystalline and stable Ca-phosphates, the solubility of which is highly dependent on soil pH (Lindsay, 1979). Accordingly, Delin (2016) identified a significant negative relationship between soil pH and P uptake in ryegrass after fertilisation with 14 P-rich residues. Even though Duboc et al. (2022) anticipated good prediction of the P fertiliser value of 42 fertiliser products based on their fraction of  $NaHCO_3$ -soluble P, a strong correlation ( $R^2 = 0.74$ ) was only achieved on a carbonate-rich alkaline soil with pH (0.01 M  $CaCl_2$ ) 7.4. Since farmers usually test their soils on a regular basis, including soil pH as an explanatory variable would not result in decreased applicability of the prediction models proposed in the present study.

Our dataset did not allow us to include soil pH as an explanatory variable, even though soil pH was measured in almost all of the 10 studies on which our analysis was based (Table S3). This was because only a few of the studies tested the P fertiliser value of a particular fertiliser product on different soils with a wide range of soil pH values. Further, soil pH measurements were not standardised across the different studies (measurement in  $H_2O$  or 0.01 M  $CaCl_2$  solution).

Increased accuracy of the proposed prediction models might also be achieved by extending the dataset to include other fertiliser products and by

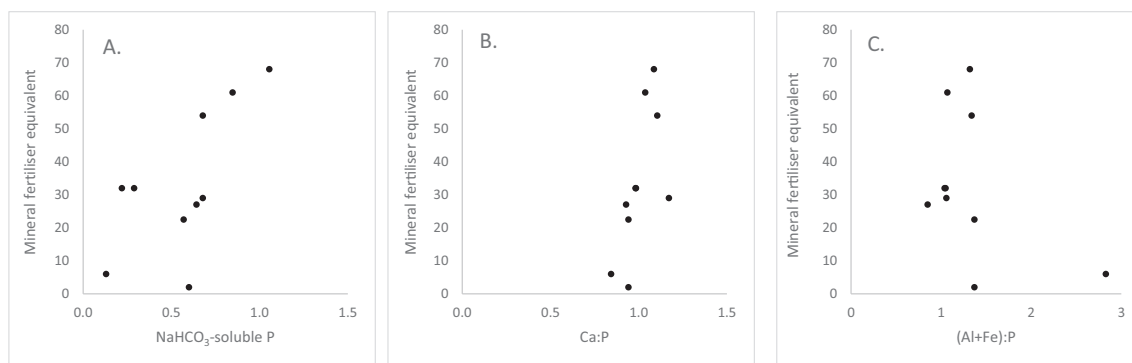


Fig. 3. Relationship between mineral fertiliser equivalents (MFE, %) of thermally treated sewage sludge products (10 observations) and: A)  $NaHCO_3$ -soluble P (% of total P, 10 observations), B) Ca:P in the fertiliser product (10 observations) and C)  $(Al + Fe):P$  in the fertiliser product (10 observations).

including the molar ratio of Ca:P and/or (Al + Fe):P in the models for fertiliser products with Ca-bound P and thermally treated sewage sludge products.

#### 4. Conclusions

Accurate prediction of the P fertiliser value of bio-based fertiliser products is essential for their wider use in practical agriculture. Based on combined results on 69 bio-based fertiliser products from 10 independently conducted studies, we developed regression models for predicting the relative P fertiliser value of four sub-groups of bio-based fertiliser products, distinguished by their chemical characteristics: 1) Fertiliser products with Ca-bound P; 2) sewage sludge with Al-/Fe-bound P; 3) sewage sludge with Ca-bound P; and 4) thermally treated sewage sludge products. To extend the applicability of the proposed prediction models, we suggest that bio-based fertiliser products be labelled with information on: i) total P concentration, ii) ratio of NaHCO<sub>3</sub>-soluble P; iii) molar ratio of Ca:P; and iv) molar ratio of (Al + Fe):P. For further optimisation of the regression models, we suggest considering external factors influencing P fertiliser values (e.g. fertiliser shape, application form, soil characteristics), particularly soil pH.

#### CRedit authorship contribution statement

**Eva Brod:** Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization, Funding acquisition. **Anne Falk Øgaard:** Conceptualization, Methodology, Investigation, Writing – original draft, Project administration. **Dorette Sophie Müller-Stöver:** Investigation, Resources, Writing – review & editing. **Gitte Holton Rubæk:** Conceptualization, Methodology, Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This work was supported by several research projects, two of which were funded by The Research Council of Norway: Kretslop SIS (Sustainable recycling of organic waste resources in the future bioeconomy, grant no. 194051) and Mind-P (Nutrients in a circular bioeconomy: barriers and opportunities for mineral phosphorus independence in Norway, grant no. 268338). The Danish research projects funding the study were supported by the Ministry of Environment and Food of Denmark (Green Development and Demonstration Programme, grant no. 340009-13-0600), the Danish Energy Agency via the EUDP programme (grant no. 64011-0337) and the Market Development Fund and DANVA through a public tender for pre-commercial procurement. We sincerely thank Torfinn Torp for advice on statistical treatment of the data.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.155590>.

#### References

Alvarenga, E., Øgaard, A.F., Vråle, L., 2017. Effect of anaerobic digestion and liming on plant availability of phosphorus in iron- and aluminium-precipitated sewage sludge from primary wastewater treatment plants. *Water Sci. Technol.* 75 (7–8), 1743–1752.

Brod, E., Øgaard, A.F., 2021. Closing global P cycles: the effect of dewatered fish sludge and manure solids as P fertiliser. *Waste Manag.* 135, 190–198.

Brod, E., Øgaard, A.F., Hansen, E., Wragg, D., Haraldsen, T.K., Krogstad, T., 2015a. Waste products as alternative phosphorus fertilisers part I: inorganic P species affect fertilisation effects depending on soil pH. *Nutr. Cycl. Agroecosyst.* 103, 167–185.

Brod, E., Øgaard, A.F., Haraldsen, T.K., Krogstad, T., 2015b. Waste products as alternative phosphorus fertilisers part II: predicting P fertilisation effects by chemical extraction. *Nutr. Cycl. Agroecosyst.* 103, 187–199.

Bruun, S., Harmer, S.L., Bekiaris, G., Christel, W., Zuin, L., Hu, Y., Jensen, L.S., Lombi, E., 2017. The effect of different pyrolysis temperatures on the speciation and availability in soil of P in biochar produced from the solid fraction of manure. *Chemosphere* 169, 377–386.

Case, S.D.C., Oelofse, M., Hou, Y., Oenema, O., Jensen, L.S., 2017. Farmer perceptions and use of organic waste products as fertilisers – a survey study of potential benefits and barriers. *Agric. Syst.* 151, 84–95.

Christel, W., Bruun, S., Magid, J., Jensen, L.S., 2014. Phosphorus availability from the solid fraction of pig slurry is altered by composting or thermal treatment. *Bioresour. Technol.* 169, 543–551.

Christiansen, N.H., Sørensen, P., Labouriau, R., Christensen, B.T., Rubæk, G.H., 2020. Characterizing phosphorus availability in waste products by chemical extractions and plant uptake. *J. Plant Nutr. Soil Sci.* 183, 416–428.

Delin, 2016. Fertilizer value of phosphorus in different residues. *Soil Use and Management* 32 (1), 17–26.

Duboc, O., Santner, J., Golestani Fard, A., Tacconi, J., Zehetner, F., Wenzel, W.W., 2017. Predicting phosphorus availability from chemically diverse conventional and recycling fertilizers. *Sci. Total Environ.* 599–600, 1160–1170.

Duboc, O., Hernandez-Mora, A., Wenzel, W.W., Santner, J., 2022. Improving the prediction of fertilizer phosphorus availability to plants with simple, but non-standardized extraction techniques. *Sci. Total Environ.* 806, 150486.

Egnér, H., Riehm, H., Domingo, W.R., 1960. Untersuchungen über die chemische bodenanalyse als grundlage für die beurteilung des Nährstoffzustandes der Böden. II. Chemische extraktionsmethoden zur phosphor- und kaliumbestimmung. *Kungl. Lantbrukshögskolans Ann.* [Ann. R. Agric. Coll. Sweden] 26, 199–215.

EU, 2019/1009. Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003. <http://data.europa.eu/eli/reg/2019/1009/oj>.

Frossard, E., Bauer, J.P., Lothe, F., 1997. Evidence of vivianite in FeSO<sub>4</sub>-flocculated sludges. *Water Res.* 31, 2449–2454.

Frossard, E., Skrabal, P., Sinaj, S., Bangerter, F., Traore, O., 2002. Forms and exchangeability of inorganic phosphate in composted solid organic waste. *Nutr. Cycl. Agroecosyst.* 62, 103–113.

Hedley, M.J., Stewart, J.W.B., Chauhan, B.S., 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* 46, 970–976.

Huang, X.L., Shenker, M., 2004. Water-soluble and solid-state speciation in stabilized sewage sludge. *J. Environ. Qual.* 33, 1895–1903.

Kratz, S., Schick, J., Øgaard, A.F., 2016. P solubility of inorganic and organic P sources. In: Schnug, E., de Kok, L. (Eds.), *Phosphorus: 100% Zero, Protecting Water Bodies From Negative Impacts of Agriculture: Higher P Utilisation for Reduced P Loads*. Springer, Berlin, pp. 127–154.

Kratz, S., Vogel, C., Adam, C., 2019. Agronomic performance of P recycling fertilizers and methods to predict it: a review. *Nutr. Cycl. Agroecosyst.* 115, 1–39.

Kuo, S., 1994. Phosphorus. In: Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E. (Eds.), *Methods of Soil Analysis Part 3, Chemical Methods*. American Society of Agronomy, Inc, Madison, pp. 869–919.

Lemming, C., Scheutz, C., Bruun, S., Jensen, L.S., Magid, J., 2017a. Effects of thermal drying on phosphorus availability from iron-precipitated sewage sludge. *J. Plant Nutr. Soil Sci.* 180, 720–728.

Lemming, C., Bruun, S., Jensen, L.S., Magid, J., 2017b. Plant availability of phosphorus from dewatered sewage sludge, untreated incineration ashes, and other products recovered from a wastewater treatment system. *J. Plant Nutr. Soil Sci.* 180, 779–787.

Lemming, C., Simmelsgaard Nielsen, M.T., Jensen, L.S., Scheutz, C., Magid, J., 2020. Phosphorus availability of sewage sludges and ashes in soils of contrasting pH. *J. Plant Nutr. Soil Sci.* 183 (6), 682–694.

Lindsay, W.L., 1979. *Chemical equilibria in soils*. Wiley, New York.

Müller-Stöver, D., Thompson, R., Lu, C., Thomsen, T.P., Glæsner, N., Bruun, S., 2021. Increasing plant phosphorus availability in thermally treated sewage sludge by post-process oxidation and particle size management. *Waste Manag.* 120, 716–724.

Murphy, J., Riley, J.P., 1962. A single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27, 31–36.

Nanzer, S., Oberson, A., Huthwelker, T., Eggenberger, U., Frossard, E., 2014. The molecular environment of phosphorus in sewage sludge ash: implications for bioavailability. *J. Environ. Qual.* 43 (3), 1050–1060.

Øgaard, A.F., 2017. Tilgjengelig fosfor i kalkfelt avløpslam. NIBIO report 3 (116), 27 (in Norwegian).

Øgaard, A.F., Brod, E., 2016. Efficient phosphorus cycling in food production: predicting the phosphorus fertilization effect of sludge from chemical wastewater treatment. *J. Agric. Food Chem.* 64 (24), 4821–4829.

Olsen, S.R., Cole, C.V., Watanabe, F.S., Dean, L.A., 1954. Estimation of Available Phosphorus in Soils by Extraction With Sodium Bicarbonate. US Gov Print Office, Washington, pp. 1–19.

Pedersen, I.F., Rubæk, G.H., Nyord, T., Sørensen, P., 2020. Row-injected cattle slurry can replace mineral P starter fertiliser and reduce P surpluses without compromising final yields of silage maize. *Eur. J. Agron.* 116, 126057.

Shober, A.L., Hesterberg, D.L., Sims, J.T., Gardner, S., 2006. Characterization of phosphorus species in biosolids and manures using XANES spectroscopy. *J. Environ. Qual.* 35, 1983–1993.

Toor, G.S., Peak, J.D., Sims, J.T., 2005. Phosphorus speciation in broiler litter and Turkey manure produced from modified diets. *J. Environ. Qual.* 34 (2), 687–697.

Vogel, C., Sekine, R., Steckenmesser, D., Lombi, E., Steffens, D., Adam, C., 2017. Phosphorus availability of sewage sludge-based fertilizers determined by the diffusive gradients in thin films (DGT) technique. *J. Plant Nutr. Soil Sci.* 180 (5), 594–601.