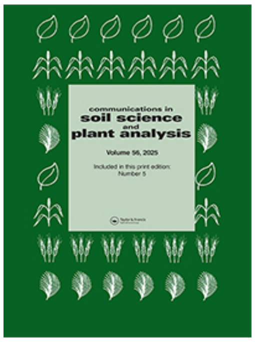

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Phosphorus Fractionation of Dairy Processing Waste Recycled Fertilizers Reveals Inadequacy of the Standards, Measurement and Testing (SMT) Protocol

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ABSTRACT

The Standards, Measurements and Testing (SMT) protocol is widely used to fractionate phosphorus (P); however, it lacks the focus on defining the solubility of P-fractions, which is usually performed independently. In this paper, the addition of a separate pre-wash step with H_2O as a first step prior to the SMT protocol was tested to account for the solubility of P. Results were compared to a control unmodified SMT experiment. The differences in P-fractions were analyzed to determine the origin of the readily available P (soluble P). Six different dairy processing waste treatment products were investigated in the form of sludge, hydrochar, and ash. Water-soluble P (WSP) was correlated with weakly bound calcium (Ca), aluminum (Al) and iron (Fe). However, the SMT protocol failed to correctly identify the different pools of P as unexpected correlations were found between P and Ca, Al and Fe. Moreover, large concentrations of organic P were present in ashes (>10 mg P g^{-1}). The organic P fraction included substantial amounts of Fe that correlated highly with P ($R^2 = 0.84$). No association between WSP and any of the pools of P defined by SMT was detected, with the exception of total P and inorganic P. The paper concludes that SMT erroneously classifies P into different discrete fractions across various recycled P-products with fertilizer potential. A critical reevaluation of the SMT protocol is recommended, by abandoning the categorization of P into discrete pools and switching to solvent-based categories referring to the chemicals used in each extraction.

Highlights

- SMT fractionation protocol was modified to assess water soluble phosphorus
- The modified SMT protocol was performed on 6 different P-recycled products (fertilizers)
- SMT protocol fails to identify correctly different fractions of phosphorus
- A critical reevaluation of SMT protocol is recommended

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Introduction

The recovery of phosphorus (P) from industrial waste streams has been gaining increasing attention for environmental and agronomic reasons. On one side, offloading phosphorus into marine and terrestrial ecosystems imposes severe environmental concerns over potential eutrophication and water poisoning in the absence of proper management (Liu et al. 2019). On the other side, an increasing scarcity of phosphate rocks threatens agricultural production for lack of access to P, labeled consequently as critical raw material by the European Union (EU) (Bertrand et al. 2016). The significant concentration of P in industrial waste streams presents a potential secondary source for P and an opportunity to address the environmental losses of P. Studies have shown that recovering phosphorus from sewage sludge can provide 12–15% of the total P demand (Cordell, Drangert, and White 2009). Recovering P aims to provide this fertilizer-essential nutrient either directly through novel fertilizers or indirectly as additives used to enrich fertilizers. Recently, several techniques have been developed to recover P from different sources, including raw and processed industrial waste streams (Delgado Sancho et al. 2019; Hu et al. 2021; Jupp et al. 2021). One relevant source of P for recycled P-products is dairy processing waste (DPW), which consists of intermediate streams and additives used during the production and treatment of dairy products (Kolev Slavov 2017). DPW usually contains P concentrations of up to 5% dry weight and are beneficial in terms of their relatively low concentrations of contaminants (Hu et al. 2021).

Transitioning toward the use of recycled P products derived from DPW as fertilizers, however, raises an array of challenges. Recycled P-products are more diverse and chemically complex than those derived from phosphate-rock (Delgado Sancho et al. 2019; Liu et al. 2019). P in recycled fertilizers is generally classified into different inorganic P-molecules (such as calcium (Ca), aluminum (Al) or iron (Fe) phosphates) or organic P forms (Ghanim, Kwapinski, and Leahy 2018). However, P-fractions present in soil and other solid samples can be heterogeneous in terms of solubility and chemical properties. For instance, the solubility of P from hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is lower than that of P from triple super phosphate ($Ca(H_2PO_4)_2 \bullet H_2O$, TSP), even though both are considered Ca-P molecules (Xiong et al. 2018; Zwetsloot, Lehmann, and Solomon 2015). The solubility of strengite ($FePO_4 \bullet 2\,h_2O$) is lower than vivianite ($Fe_3(PO_4)_2 \bullet 8\,h_2O$) (Lundager Madsen and Bruun Hansen 2014), and the solubility of aluminum phosphate ($AlPO_4$) is lower than aluminum hydroxide phosphate ($AlHO_5P^{-4}$) (Berthon and Daydé 2013). The P-compounds mentioned above were proven to be present in DPW streams and their products (McIntosh et al. 2022; Oliveira et al. 2016; Sibrell, Penn, and Hedin 2015). It has also been demonstrated that organic P forms such as phospholipids are easily decomposable (Veum, Lorenz, and Kremer 2019) in contrast to other organic molecules like phytate (Liu et al. 2022). These contrasts have strong implications regarding the variability of P solubility in species having similar elemental composition, which raises the question regarding the correlation between identifying elemental composition and defining solubility of P in recycled P as fertilizers since crops can only benefit from the more soluble forms of P. Previous literature revealed that products derived from dairy sludge possess significant agronomic performance, particularly in terms of recycled P (Shi et al. 2022). Therefore, it is necessary to develop an accurate method for assessing the different fractions of P present in dairy-based P-recycled products while accounting for the solubility of the fractions.

It is also relevant to identify the forms of P present in the novel recycled P fertilizers from a legislative perspective. The European Fertilizer Regulation 1069/2019 stipulates in Article 2 that producers of recycled fertilizers must report amounts of water-soluble P (Delgado Sancho et al. 2019). Part II of Annex III in the same regulation declares that it is essential to report the quantity of water-soluble P in products qualifying as organo-mineral fertilizers (European Commission 2019). It is likely that future regulations will also cover the chemical fractions of P as their fertilizer equivalent values are possibly different from each other (Khomenko et al. 2023; Shi et al. 2022).

The most common ways to characterize the different pools of P involve sequential fractionations or extractions with different acids or bases that extract operationally defined pools of P. Different fractionation techniques have been reported in literature including the techniques of Jackson & Chang (1957), Hedley's, Stewart, and Chauhan (1982) or Tiessen & Moir (2008)

(Condron and Newman 2011). The majority of these sequential fractionation schemes include early steps in which the P-fractions with higher solubility, commonly associated with plant uptake, are first quantified. For instance, Jackson & Chang's used ammonium chloride (NH_4Cl) and the Hedley's and Tiessen & Moir's made use of resin strips and sodium bicarbonate ($NaHCO_3$) in P-quantification (Condron and Newman 2011).

For the characterization of P in wastes and sediments, a universal, non-sequential method was proposed by the European Commission under the framework "Standards, Measurements, and Testing" (Ruban et al. 1999). This procedure is also known as the SMT protocol and is based on the Williams P fractionation for soils and sediments (Williams, Mayer, and Nriagu 1980). According to Clarivate Web of Science (2024), both protocols, Ruban et al. (1999) and Williams, Mayer, and Nriagu (1980), have received 270 and 139 citations respectively. The SMT protocol has been widely used in the characterization of P forms in waste materials (Nilsson et al. 2022; Tiwari et al. 2024; Xu et al. 2015). The SMT protocol has several advantages, including its simplicity and universal application. Since it is not a sequential fractionation, its application is easier than other techniques such as Hedley's P fractionation (Hedley, Stewart, and Chauhan 1982), which involves many steps with a higher probability of introducing errors (Cao et al. 2022). SMT divides P into 5 operationally defined pools; total P (TP), organic P (OP), inorganic P (IP), apatite P (AP) and non-apatite inorganic P (NAIP). However, one of the drawbacks of the SMT protocol is the lack of identification of the most soluble P-forms, which is the major pool of interest for the production of bio-based fertilizers (García-Albacete, Martín, and Cartagena 2012). Some authors suggested that the most available forms of P are the NAIP and OP, since they are easily mobilizable and weakly bound to sample matrices (Cristina et al. 2022; García-Albacete, Martín, and Cartagena 2012; Ghanim, Kwapinski, and Leahy 2018). Other studies suggested that AP has a higher bioavailability for plants compared to the less available NAIP (Li et al. 2015; Takahashi et al. 2001).

In this study, a modified SMT protocol to assess the water-soluble P (WSP) of each fraction identified by the protocol was executed for different DPW products with fertilizer potential. Furthermore, the paper aimed to assess the contribution of different P pools to the newly added WSP pool by quantifying the different SMT P pools before and after water extraction. The main hypothesis was that, by comparing the results of the washed samples with those of unwashed samples, it would be possible to trace the origin of WSP in P-fractions in DPW.

Materials and methods

Modified SMT protocol

A modified version of the SMT protocol was conducted in which water-soluble P (WSP) was first extracted on a separate batch of samples after an extraction with water for 16 h (washed) and, in parallel, this process was compared to a standard fractionation following the SMT protocol (control) (Figure 1) (Pardo, López-Sánchez, and Rauret 2003; Wang et al. 2020). The experiment was set up as a completely randomized design with three replicates.

Products analysed

Six different recycled P products with fertilizer potential were characterized (Supplementary material, Table S1). The set of materials includes two sludges (SL) from dairy processing waste and the subsequent products derived from them: hydrochar (HC) and ash (AS). SL1 originated from a dairy factory in Denmark and SL2 originated from a dairy plant in Ireland. Both SL1 and SL2 received chemical treatments with Fe to precipitate P. AS1 and AS2 were produced after combustion of SL1 and SL2, respectively, at 250°C for 2 h followed by 3 h at 550°C, following the ASTM D2584 ISO 3451 procedure (Nurul and Mariatti 2013). HC1 was produced by adjusting the dry matter (DM) content of SL1 to 15%, adjusting the pH to 5 and

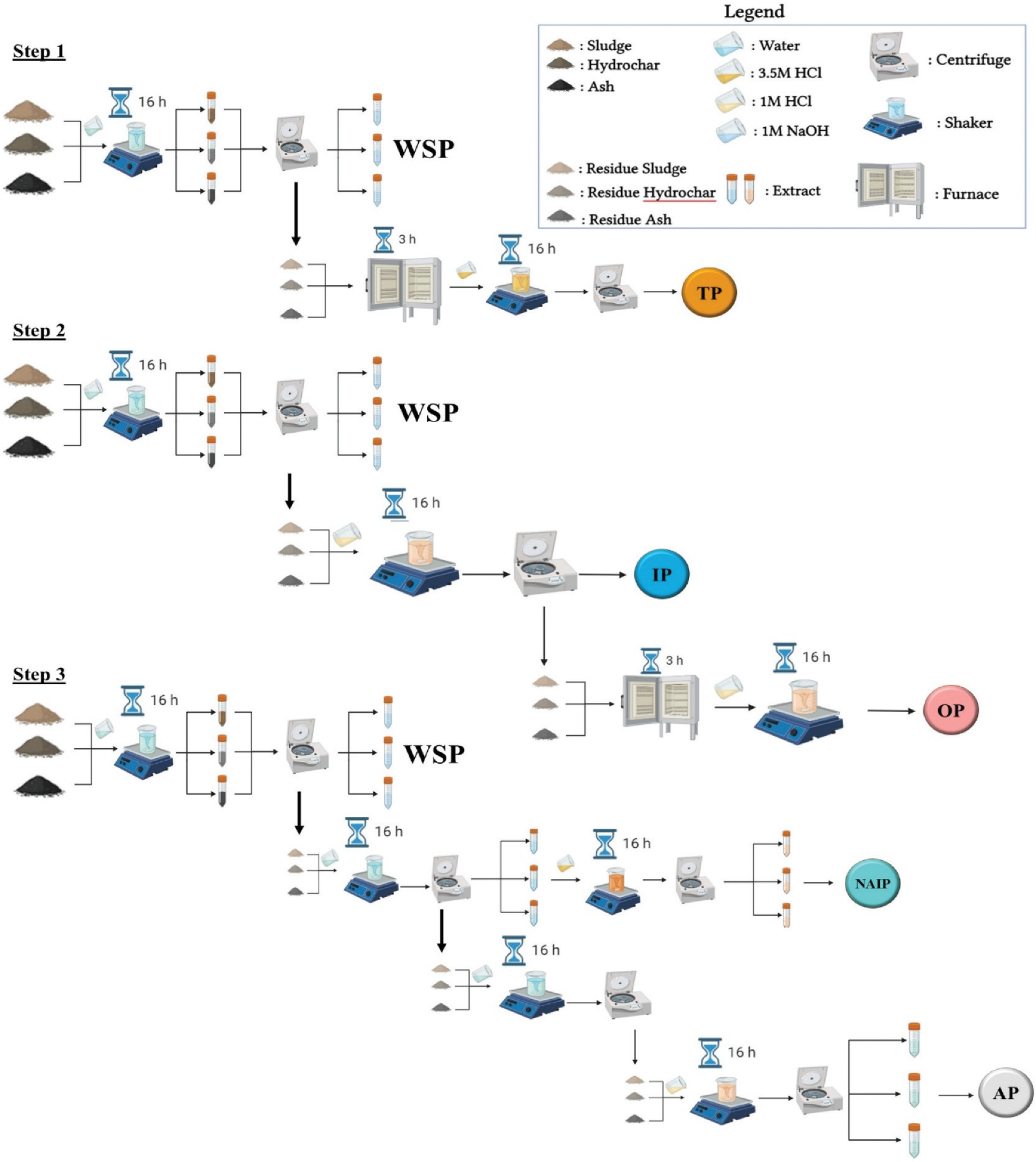

Figure 1. Flowchart of the modified fractionation protocol. The three steps of the SMT protocol (steps 1, 2 and 3) refer to the procedures followed to detect each of total P (TP), organic & inorganic P (OP & IP), and apatite and non-apatite P (AP & NAIP). Each of the three steps is conducted with (modified SMT protocol) and without (original SMT protocol) an initial step to determine water soluble P (outcome of first centrifuge step) by shaking samples with H_2O for 16 h, referred to as the washing treatment. The share of SMT in each of the original SMT P pools can thus be determined by comparison of the P content in each fraction with and without washing. Each extraction (each step with and without washing) was conducted on separate samples for 6 different recycled P fertilizers (supplementary material, table S1) in triplicates.

carbonizing at 225°C for 1 h. Adjusting the DM content and pH was performed simultaneously through the addition of specific volume of 3.5 M HCl. Meanwhile, HC2 was produced from SL2 by preserving the DM content at 19%, the pH to 8.3 and carbonization temperature was adjusted to 180°C for a residence time of 2 h. The differences between the produced ashes and hydrochars were intended to expand the study pool upon which the modified SMT protocol is assessed.

SMT measurements

The SMT protocol has been described extensively in several research papers previously, and what follows is a thorough description of the modified SMT protocol adopted from the standard procedure explained previously (García-Albacete, Martín, and Cartagena 2012). For each fertilizer, 3 samples were tested for each fraction: total P (TP), inorganic P (IP), organic P (OP), non-apatite inorganic P (NAIP), and apatite P (AP) for washed and unwashed versions of the SMT protocol. For WSP, 9 samples were analyzed for each fertilizer. In total, 108 samples were measured in this experiment. All solid samples were dried at 105°C for 24 h before the start of the experiment.

For the determination of water-soluble phosphorus (WSP), 0.2 g of sample was placed into shaking tubes with 20 mL of demineralized H_2O. After 16 h of shaking in an orbital shaker, samples were centrifuged for 5 min at 4190 ×g. The duration of shaking was fixed to 16 h of extraction time to ensure consistency with the rest of extractions in the unmodified SMT protocol. The supernatant was collected for analysis, and the residue was used to continue with the measurements of the SMT protocol. For the samples which followed the standard SMT protocol, this first wash with H_2O was not performed.

To determine total P (TP), the samples were placed in porcelain crucibles and calcined at 450°C in a muffle oven for 3 h. Afterwards, the residue from the sample was placed into shaking tubes with 20 mL of 3.5 M HCl. After 16 h of shaking at room temperature in an orbital shaker, the samples were centrifugated at 4190 ×g for 5 minutes. The extract was collected for TP measurement.

For determination of inorganic (IP) and organic P (OP) the samples were shaken with 20 mL of 1 M HCl for 16 h and then centrifugated at 4190 ×g for 5 minutes. The supernatant was collected separately to assess the IP fraction. To quantify OP, the residue from the 1 M HCl extraction was initially calcined at 450°C and then extracted with 20 mL of 1 M HCl for 16 h. After centrifugation, the extract was separated from the residue for follow-up measurements.

Finally, for the measurement of non-apatite inorganic P (NAIP) and apatite P (AP), samples were first shaken for 16 h with 20 mL of 1 M NaOH. After centrifugation, 10 mL of extract was collected and 4 mL of 3.5 M HCl was added to each sample. The acidified supernatant was incubated at room temperature for 16 h for NAIP measurement. To obtain the AP fraction, the residue from the 1 M NaOH extraction was collected and underwent shaking with 20 mL of 1 M HCl. After centrifugation, the supernatant was collected for AP determination.

P, Ca, Fe and Al were determined through ICP-OES by following the standard procedure reported in literature (Krachler et al. 2012) in all collected extracts. The outcome of the measurement was divided into 6 categories: WSP extract, TP extract, IP extract, OP extract, NAIP extract, and AP extract.

Statistical analysis

The effect of the washing treatment and product type was assessed by a two-factor analysis of variance (ANOVA). Model residuals were inspected for normality, homogeneity and heteroscedasticity assumptions. Correlations were performed to show which cation or anion dominated the P binding forms (P-Ca, P-Fe or P-Al) in each extract. When ANOVAs indicated significant effects ($p < .05$), differences between products were tested using Tukey's HSD test. Moreover, the relationships between the chemical composition and the wash treatment were explored by conducting a principal component analysis (PCA) for each of the three steps of the SMT protocol separately.

All statistical analyses and figures were made using the software RStudio v1.4.1717 (R Core Team 2022). The following packages were used: ggplot2 (Wickham 2016), psych (Revelle 2024), emmeans (Lenth 2024), multcompView (Graves, Piepho, and Dorai-Raj 2024), ggpubr (Kassambara 2023), factoextra (Kassambara and Mundt 2020), grid (R Core Team 2022) and PerformanceAnalytics (Peterson and Carl 2020).

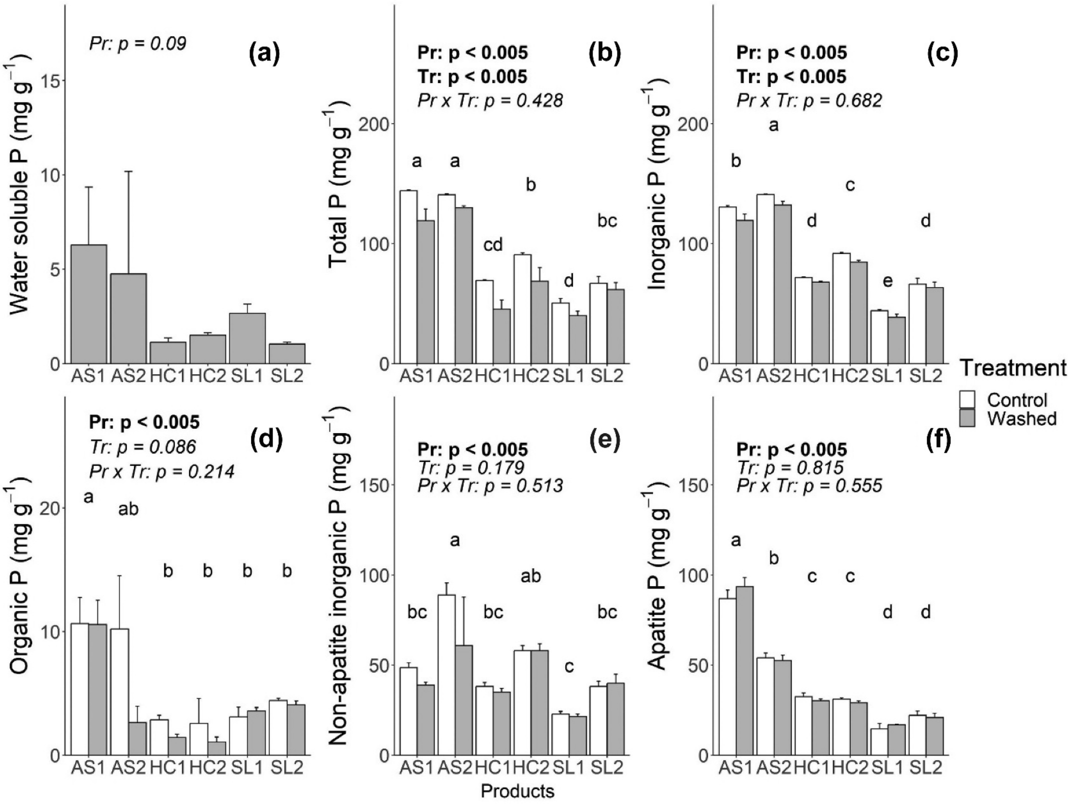

Figure 2. P content of the different SMT P fractions with (washed, grey bars) and without (control, white bars) the additional water washing step. Values are expressed in mg P by g of dry weight. Error bars represent the standard error of the mean (*n* = 9 for panel a and *n* = 3 for panels B to F). Pr = product, tr = washing treatment. Letters show statistical differences between products. Bars indicate standard error, *n* = 3. Bold characters are used to highlight significant effects.

Original dataset is available at ZENODO online repository (Velasco-Sánchez et al. 2023).

Results

Differences between products and washing treatment

The different products analyzed did not show statistical differences in water soluble P (WSP) ($p = .09$) (Figure 2, panel A). Ashes showed higher values of WSP (5.3 ± 1.8 mg P g^{-1} for AS1 and 4.7 ± 3.1 WSP for AS2) compared to hydrochars and sludges, but their high variation led to no statistical differences. AS1 and AS2 showed the highest TP, IP and OP values (Figure 2, panels B, C, and D). NAIP was highest in AS2, and AP was highest in AS1 (Figure 2, panels E and F). SL2 and HC2 showed higher amounts of TP, IP and NAIP than their SL1 and HC1 counterparts. No differences were found in OP between sludges and hydrochars. Hydrochars showed a higher amount of AP than sludges. The recovery of P in the unwashed samples was complete for IP + OP and NAIP + AP for the ashes and hydrochar (Supplementary material, Table S2). The fractional recovery of P–defined as the amount of initial P-fraction retained in the DPW products–for the sludges was below 90% for the NAIP + AP fractions (Supplementary material, Table S2).

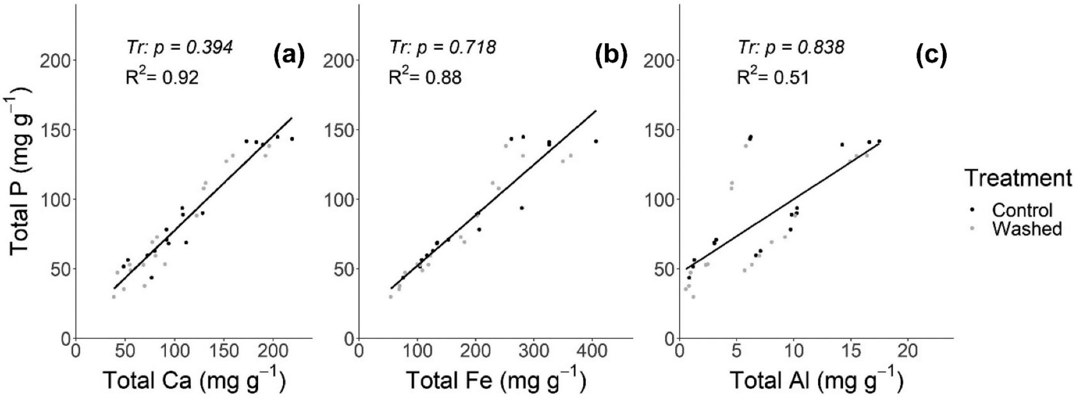

Figure 3. Correlations between total P and total Ca (A), Fe (B) and Al (C). Solid lines indicate significant correlations, $p < .05$. Tr = treatment effect. Values are expressed in mg P by g of dry weight. Solid black color stands for unmodified SMT protocol and grey symbols represent the modified one.

A significant effect of the washing treatment occurred only in the TP and IP fractions, showing a reduction in extracted P in the washed samples (Figure 2, panels B and C). For the remaining pools of P (OP, NAIP and AP) no statistically significant effect was observed after washing with water ($p > .05$).

Water soluble Ca was highest in AS1, AS2 and HC2 with 23.4 ± 4.3, 14.4 ± 14.2 and 8.2 ± 0.3 mg Ca g,$^{-1}$ respectively. No differences in water soluble Fe occurred among the products with an average extracted of 3.2 ± 2.3 mg Fe g^{-1}. With respect to water soluble Al, no differences across products occurred. Negligible amounts of water-soluble Al were detected in any of the products with the exception of AS1 in which a small amount was detected, 0.25 ± 0.17 mg Al g^{-1}.

Correlations of P with Ca, Al and Fe

TP showed a significant correlation with total Ca and Fe and to a lower extent Al, showing adjusted R^2's of 0.92, 0.88 and 0.51, respectively (Figure 3). Fe was predominant in the TP extract, with values ranging roughly from 50 to 450 mg Fe g^{-1}. Ca was the second most abundant element with values in the range between 50 and 250 mg Ca g^{-1} in the TP extract. The value of Al ranged roughly between 0 and 20 mg Al g^{-1}.

WSP was found to be positively correlated ($p < .05$) with water soluble Ca and Fe and to a lower extent Al (Figure 4). Ca was the most soluble element with values recovered in the

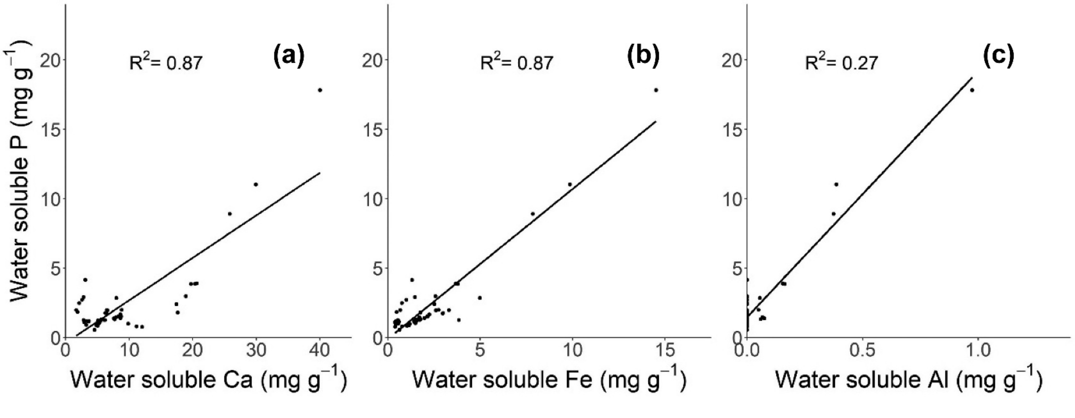

Figure 4. Correlations between water soluble P and water-soluble Ca (A), Fe (B) and Al (C). Solid lines indicate significant correlations, $p < .05$. Values are expressed in mg P by g of dry weight.

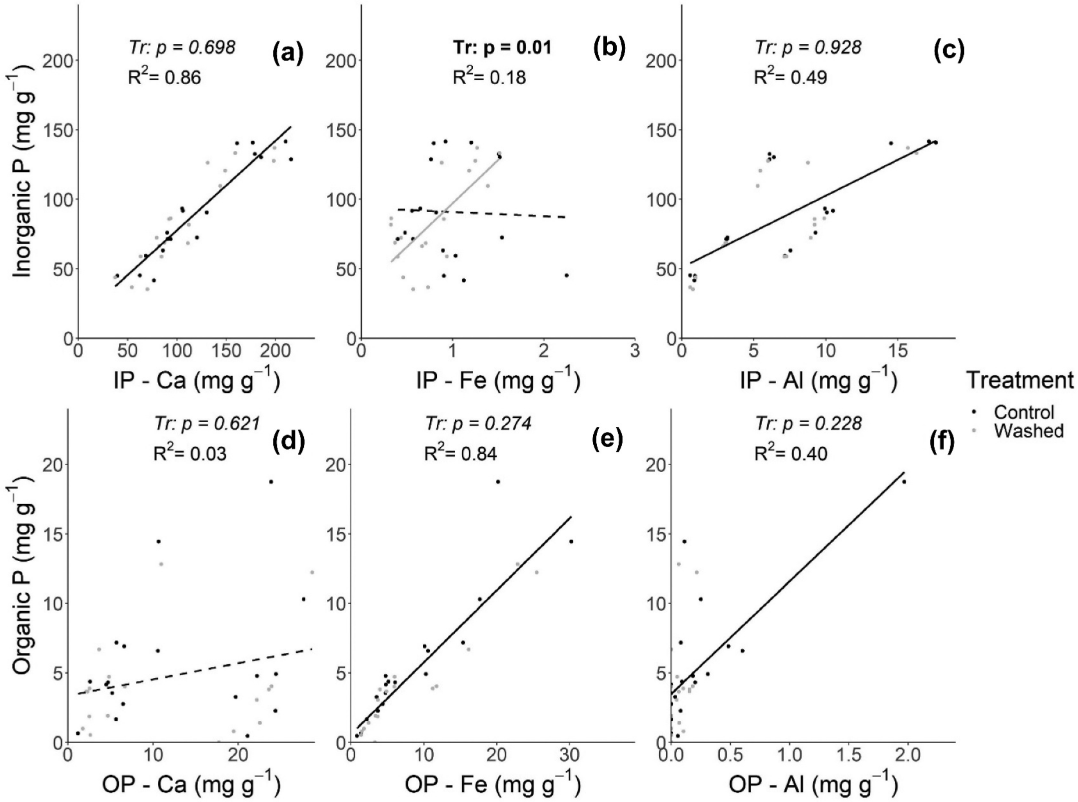

Figure 5. Correlations between P and Ca, Fe and Al for in the inorganic P (IP) and organic P (OP) extracts. Values on the x axis show the concentration of Ca, Fe and Al in the IP (upper row) and OP (lower row) extracts. Solid lines indicate significant correlations, $p < .05$. Dashed lines indicate non-significant correlations. Tr = treatment effect. Values are expressed in mg P by g of dry weight. Solid black-color represents the unmodified SMT protocol and grey the modified one.

water extract ranging roughly from 0 to 50 mg Ca g^{-1}. Fe in the water extract ranged approximately from 0 to 15 mg Fe g^{-1}, yet most of the samples had values of water-soluble Fe below 5 mg Fe g^{-1}. Al was poorly soluble in water as the highest value found was less than 1 mg Al g^{-1}.

IP was strongly correlated with Ca in the IP extract (Inorganic Ca); to a lesser extent with inorganic Al; and only marginally with Fe (Figure 5). Very slight amounts of Fe were extracted in the IP extract (<3 mg Fe g^{-1}). The values of Al and Ca extracted in the IP extract were in the same range as those from the TP extract (Figure 3). For the correlations with OP, both Fe and Al in the organic P extract correlated significantly with OP. The adjusted R^2's were 0.84 and 0.4 respectively. No significant correlation between OP and Ca in the OP extract was observed. Large amounts of Ca and Fe were found in the OP extract, roughly ranging from 0 to 30 mg g^{-1}.

NAIP was only correlated with Al in the NAIP extract, $R^2 = 0.93$ (Figure 6, panel C). The NAIP extract contained relatively large amounts of Al, being in the same range as total Al. The correlation between AP and Ca in the AP fraction was significant and showed a high adjusted R^2. Al in the AP extract was also positively correlated with AP. Fe in the AP extract was not correlated with AP.

The results of the principal component analysis (PCA) showed great overlap between the wash and control treatments. This indicated non-significant differences in chemical composition between the washed samples and control ones. This was found for the three steps of the SMT protocol (Figure 1). The results of the PCA can be found in the supplementary material (Supplementary material, Figure S1).

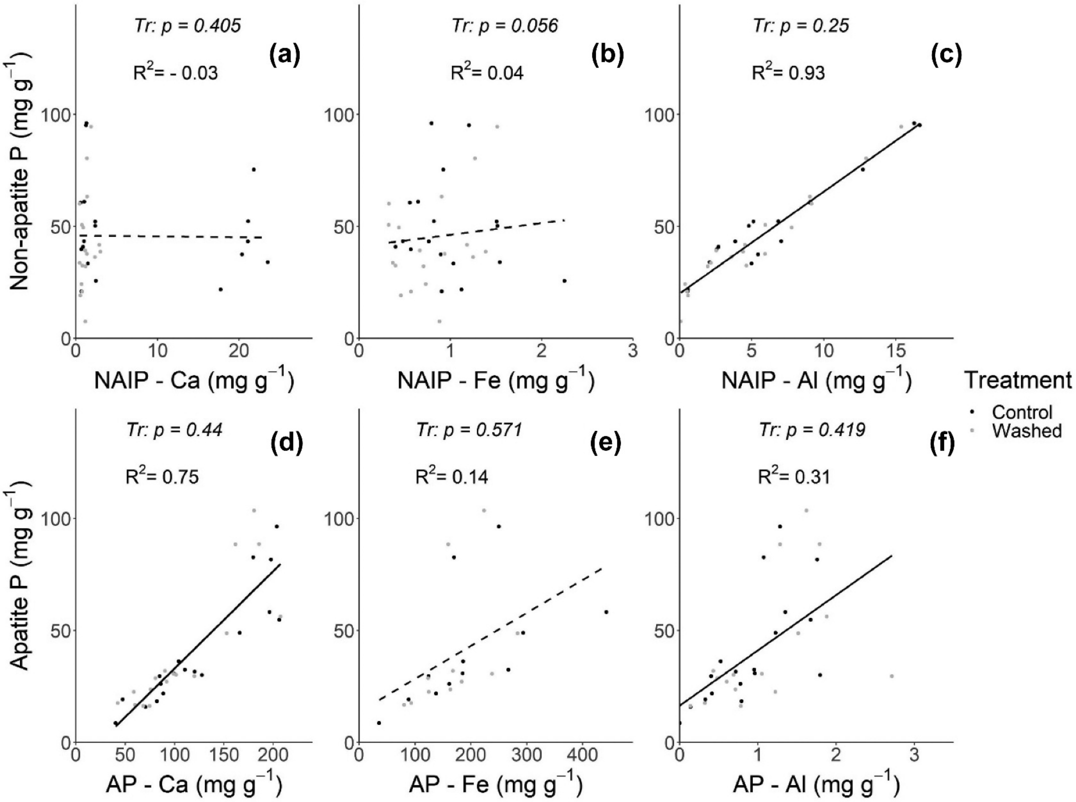

Figure 6. Correlations between P and Ca, Fe and Al for each fraction in the non-apatite (NAIP) and apatite (AP) extracts. Values on the x axis show the concentration of Ca, Fe and Al in the NAIP (upper row) and AP (lower row) extracts. Solid lines indicate significant correlations, $p < .05$. Dashed lines indicate non-significant correlations. Tr = treatment effect. Values are expressed in mg P by g of dry weight. Solid black-color represents the unmodified SMT protocol and grey the modified protocol.

Discussion

Water soluble P

The aim of the paper was to modify the SMT protocol by adding a step in which WSP is assessed and to investigate which forms of P contributed most to the WSP pool. The observed levels of WSP were similar across all the products studied (Figure 2, panel A). Ashes showed higher levels of WSP compared to the other products, but due to their increased variation no statistical differences were found. Neither the ashing nor the hydrothermal carbonization reduced the levels of readily soluble P compared to the sludge. This contrasts with earlier findings of lower solubility from ash and hydrochar compared to their raw original material (Delgado Sancho et al. 2019; Khomenko et al. 2023; Lemming et al. 2020).

To assess which forms of P contributed more to the WSP pool, it was suggested that washing samples with water as a first step would result in the removal of all the WSP forms and, therefore, a reduction of P across the different pools (as compared to the traditional protocol) would be observed. This would reveal the pools of P that contributed most to WSP and their correlation with water-soluble Ca, Fe and Al (Figure 4). In particular, WSP correlated strongly with Ca and Fe and poorly with Al, as very low amounts of Al were found. This would suggest that WSP comes from loosely bound forms of Ca and Fe. This is not uncommon, as Fe-P and Ca-P are among the more common forms of P across recycled fertilizers (Delgado Sancho et al. 2019). However, an exclusive reduction of P in the TP and

IP pools was observed after the washing step (Figure 2, panels B and C). No reduction was observed for the OP, NAIP or AP fractions, and in some cases even more P was extracted after the wash (Figure 2, panels D to F and Supplementary material, Table S2). This is surprising as AP and NAIP can be comprised of a wide range of soluble P-Ca and P-Fe molecules (Hertzberger, Cusick, and Margenot 2020; Wu et al. 2019; Zwetsloot, Lehmann, and Solomon 2015). The lack of reduction in the OP, NAIP and AP fraction is suggested to be linked to the inadequacy of the SMT protocol to allocate P into different pools of P.

SMT protocol inadequacy and labelling misconceptions

The SMT protocol led to mismatches between observations and the purported meaning of the SMT fractions. For example, almost no Fe was extracted in the IP pool (Figure 5, panel B) despite Fe-P being an important constituent of ashes, hydrochars and dairy processing sludge (Belibagli et al. 2022; Hu et al. 2021; Yu et al. 2022), but large amounts of Fe were found in the OP extract that correlated strongly with the P contained in this fraction (Figure 5, panel E). In the NAIP extract, very small amounts of Fe were detected, even though Fe is more abundant than Al in the samples studied (Figures 3, panels B and C, and Figure 6, panel B). In contrast, large amounts of Fe were detected in the AP extract (Figure 6, panel E). Significant amounts of OP were extracted from ashes (Figure 2, panel D), which was unexpected as ashes contain little to no organic molecules after pyrolysis at 550°C (Vassilev, Baxter, and Vassileva 2013).

These inconsistencies can be attributed to erroneous assumptions adopted by the SMT protocol and its interpretation. First, the protocol assumes that no organic P is extracted after 16 h of extraction in 1 M HCl (Figure 1). This is highly unlikely as 1 M HCl is strong enough to dissolve large amounts of carbon (Silveira et al. 2008; Worsfold et al. 2008), which could result in the solubilization of significant amounts of OP. The most readily soluble forms of OP may therefore have been ascribed as IP. Similarly, after calcination and extraction with HCl, SMT assumes that only OP is extracted. The results of this paper demonstrated the inaccuracy of this assumption as significant amounts of Ca and Fe were measured in this extract, which could be associated with Ca-P and Fe-P that were not dissolved in the previous step (Figure 5). The strong correlation between OP and Fe in the OP fraction could also imply that non soluble Fe-P salts were being extracted (Figure 5, panel E).

The assumption of the SMT protocol is that NaOH selectively extracts P from cations such as Fe and Al. However, it is not clear that most insoluble forms of NAIP are extracted with 1 M NaOH and, more importantly, there is no reason that prevents the solvent from extracting P from soluble organic or from Ca-P forms (Sano et al. 2012). If not all the Fe-P and Al-P forms were extracted by NaOH, they could potentially be extracted later by the 1 M HCl extraction as shown by the large amounts of Fe found in this extract (Figure 6, panel E). Other authors have already demonstrated that acids such as HCl or HNO_3 can successfully extract significant amounts of Fe-P (Elomaa et al. 2019; Sano et al. 2012).

Ultimately, one of the main reasons for the confusion caused by the SMT fractionation is the compartmentalization of P into different pools and not into groups related to the chemicals used. For example, the SMT scheme refers to 1 M HCl extractable P as IP or the 1 M NaOH extractable as NAIP (Figure 1) (García-Albacete, Martín, and Cartagena 2012; Pardo, López-Sánchez, and Rauret 2003; Wang et al. 2020). As reflected by the results of this study, such correlation between the nomenclature and the actual nature of the extracted fractions can be inaccurate, as it is unlikely for the extraction to solely account for the corresponding P-fractions specified in the protocol. Using an operationally defined nomenclature in which the extractant is linked to the pool of P could be more accurate for assessing the extracted fractions (Gu and Margenot 2021). This is already the case in other fractionation schemes, such as Hedley's, Stewart, and Chauhan (1982) in which P is allocated into resin-P, NaOH-P, 1 M HCl-P etc (Hedley, Stewart, and Chauhan 1982). or in the earlier versions of the SMT protocol (Ruban et al. 1999).

P fractionation schemes limitations

The erroneous attribution of groups of P to various extracts or fractions has also been shown in other fractionation schemes in soils and sediments (Barrow et al. 2021; Gu et al. 2020). In a noteworthy paper, Barrow et al. (2021), analyzed hydroxyapatite, Al oxide and goethite using the Chang and Jackson (1957) and Zhang and Kovar (2009) fractionation procedures (Chang and Jackson 1957; Zhang and Kovar 2009). Large amounts of Ca-P were detected in both goethite and Al oxides regardless of the scheme followed. Similarly, Fe-P was found in Al oxides and Al-P was found in hydroxyapatite and goethite. The false detection of OP in ashes revealed in the present study (Figure 2, panel D) is also in line with the results of Barrow et al. (2021).

The main hypothesis of this study was that washing samples with water would remove all WSP from the samples causing a reduction in the measured pools of P. The lack of responses for AP, NAIP or OP found in this study could also be associated with the misconceptions of the precipitate-particulate theory (Barrow et al. 2021). In this sense, P would be present in the materials as a continuum and not as a set of discrete fractions (Barrow 2021). Barrow et al. (2021) and Barrow (2021) extensively describe the impossibility of allocating P into different discrete groups using P fractionations schemes, suggesting that P is controlled by adsorption-diffusion and not by a precipitation-particulate phenomenon (Barrow 1999, 2021; Barrow et al. 2021). The washing step could have then caused P to be re-distributed across the reactive surfaces in the materials, thus reducing the ability to conveniently trace back soluble P across the discrete fractions. The lack of differences between the modified and unmodified SMT samples in most fractions supports this suggestion.

Conclusion

This paper demonstrated that the conventional SMT fractionation method is inconsistent in describing the different pools of P in recycled fertilizers. The results of the study suggest: (i) that the assumptions of the selective extractions of P in the SMT protocol are erroneous; (ii) that allocating P into discrete pools might be nonrealistic; and (iii) that naming P extracts as representing functional, discrete pools is potentially inaccurate and could be misleading.

The necessity to achieve environmentally viable P-recycled fertilizers demands a higher degree of precision and standardization in identifying P-groups. Therefore, it is recommended to adjust the nomenclature of the SMT protocol and to develop new methods that can characterize agronomically relevant pools of P in line with the EU fertilizer regulation. Adjusting the extraction time, temperature and extractants used to mimic plant absorption would be essential for the correct assessment of the fertilizer value of recycled P products with fertilizer potential.

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