



Phosphorus in recycling fertilizers - analytical challenges

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ABSTRACT

The importance of secondary raw materials for phosphorus (P) fertilizer production is expected to increase in the future due to resource depletion, supply risks, and heavy metal contamination of fossil phosphate resources. Municipal wastewater is a promising source for P recovery. In Germany for instance, it contains almost 50% of the total amount of P that is currently applied as mineral fertilizer. Several procedures have been developed to recover and re-use P resulting in a growing number of recycling fertilizers that are currently not regulated in terms of fertilizer efficiency. We tested various materials and matrices for their total P content, solubility of P in neutral ammonium citrate (P_{nac}) and water, and performed robustness tests to check if existing analytical methods are suitable for those new materials. Digestion with inverse aqua regia was best suited to determine the total P content. P_{nac} sample preparation and analyses were feasible for all matrices. However, we found significant time and temperature dependencies, especially for materials containing organic matter. Furthermore, several materials didn't reach equilibrium during the extractions. Thus, strict compliance of the test conditions is strongly recommended to achieve comparable results.

1. Introduction

Phosphorus (P) is essential for all animate beings. Amongst others, it is crucial for energy metabolism (ATP-ADP cycle), storage and expression of genetic information (DNA, RNA), and bone structure. In contrast to other raw materials, P cannot be replaced. The recommended daily intake of P is 700 mg for adults (Young et al., 1997). This P is eventually removed from farmlands by crops and has to be replaced to allow for sustainable farming. The demand for P is expected to increase in the future with increasing world population. Even though some of the required P already comes from recycling sources like agricultural fertilizer and fermentation residues, a significant amount of P is applied as mineral fertilizer. Those are produced from phosphate rock that is a fossil and limited resource. In Germany, for instance, 26% of the more than 550,000 t/a P that is used to fertilize farmlands comes from that source (Gethke-Albinus, 2012). The use of phosphate rock for fertilizer production is connected with three major problems: resource depletion, supply risks, and heavy metal contamination. The possible P scarcity is under vigorous discussion for decades (Ulrich and Frossard, 2014). However, numbers suggest that the P resources will not run out in the immediate future, with current estimates of the static range of more than 300 a (USGS, 2016). The supply risks are of greater concern since the production of P rock is concentrated either in countries with a high domestic demand

(USA, China) or in politically unstable regions (Morocco and Western Sahara). Europe, for instance, does not possess significant deposits and completely depends on imports and is thus susceptible to world market price fluctuations and economic and political crises. For this reason, the European Commission put P on its list of critical raw materials in 2014 (EU Commission, 2014). Furthermore, phosphate rock is contaminated with U, Cd, and Th (Al-Shawi and Dahl, 1995; Dissanayake and Chandrajith, 2009; Ulrich et al., 2014; Kratz et al., 2016) that may pose environmental and health hazards. The German Federal Protection Agency estimates that more than 160 t/a U is put to German farmlands by mineral P fertilizer (UBA, 2012). The utilization of alternative P sources is in order to encounter these risks.

Recently, several studies were conducted to determine P mass flows (Li et al., 2015; Kerstens et al., 2016; Wu et al., 2016), identify possible P recovery potentials (Krüger and Adam, 2015; Theobald et al., 2016; van Dijk et al., 2016), and assess P flow management strategies (Metson et al., 2016; Zoboli et al., 2016). Municipal wastewater is a promising source for P recovery since it contains significant amounts of this element (Hukari et al., 2016; Krüger et al., 2016). P can be recovered from various points of wastewater treatment (Montag, 2008), for instance as struvite that can be crystallized from the sludge liquor or precipitated from the sludge (Jaffer et al., 2002; Katakai et al., 2016). Sewage sludge or sewage sludge ashes (Adam et al., 2009; Guedes et al., 2014; Herzel et al., 2016) are also possible sources for P

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recovery or in the case of sludge, directly used as fertilizer. However, the former approach is subject to discussion since sewage sludge contains organic and inorganic contaminants that might pose environmental risks (Marani et al., 2003; Harrison et al., 2006). Biomass ashes (Tan and Lagerkvist, 2011) or municipal solid waste incineration ashes (Kalmykova and Karlfeldt Fedje, 2013) are also discussed as possible P sources.

All these efforts result in a large and growing number of recycling products that are either used as fertilizer directly or utilized for fertilizer production. Even though not many of those procedures, aside from struvite precipitation, are operational on technical scale right now, their usage, amount, and importance is expected to increase in the future. One of the most important points regarding fertilizers is their nutrient content and the respective bioavailability. However, the existing regulations and analytical methods cover conventional fertilizers and do not consider the new emerging recycling products (EC, 2003; Düngemittelverordnung, 2012). Currently, those regulations are being adapted to include also organic fertilizers. Since the existing analytical methods were not developed for fertilizers from secondary raw materials, they have to be tested whether they are suitable to assess the fertilizer efficiency. There are several parameters and methods that can be applied for that purpose. Even though the new regulations are not yet in effect, three parameters are expected to be the most important. Those are the total amount of P that is usually determined after acid digestion (Dancer et al., 1998; Jameson et al., 2016), the solubility in neutral ammonium citrate (P_{nac}) that is considered to indicate the mid- to long-term plant availability of P, and water solubility (P_{ws}) as a measure of immediate availability (Kratz et al., 2010).

We performed robustness tests of 10 materials that are used as secondary P sources or precursor for fertilizer production and a mineral fertilizer as reference. We applied and compared 6 different reagent mixtures for determination of the total P content as well as P_{nac} and P_{ws} extractions. We altered the test conditions of P_{nac} extraction both in terms of temperature and time to see if the method works for the different materials and matrices. Furthermore, we determined the influence of different filtration techniques.

2. Materials and methods

2.1. Sample acquisition

We obtained the samples, which are described in Table 1, courtesy of operators of three different WWTP (sludge 1 and 2, SSA), operators of P recovery facilities (struvite 1 and 2, recycling P 1 and 2), and providers of conventional fertilizer (TSP). We got P rock samples courtesy of Christian Kabbe from the Berlin Centre of Competence for Water.

Table 1
Primary and secondary raw materials for fertilizer production.

Sample	Description
Sludge 1	Dried sewage sludge from a municipal WWTP
Sludge 2	Thickened sewage sludge from a municipal WWTP
Struvite 1	Magnesium ammonium phosphate, crystallized from sludge liquor
Struvite 2	Magnesium ammonium phosphate, precipitated from digested sludge
Recycling P 1	Calcium phosphate, crystallized from sewage
Recycling P 2	P precipitated from dairy wastewater
SSA	Sewage sludge ash from fluidized bed incineration
P rock magmatic	Phosphate rock of magmatic origin
P rock sedimentary	Phosphate rock of sedimentary origin
TSP	Triple super phosphate, mineral fertilizer as reference

Table 2
Digestion and extraction methods.

Digestion	Reagent mixture, (amounts in brackets [mL])	Weighed-in quantity [g]
Per ^a	HNO ₃ (4), HClO ₄ (1.5), HF (0.5); 2nd step: H ₃ BO ₃ (5.0)	0.1
Aqua regia ^a	HNO ₃ (1.2), HCl (3.6), H ₂ O (0.5)	0.5
Inv ^a	HNO ₃ (4), HCl (1), H ₂ O (0.5)	0.3
H ₂ O ₂ /HNO ₃ ^a	H ₂ O ₂ (1), HNO ₃ (5)	0.3
H ₂ O ₂ /HNO ₃ /H ₂ SO ₄ ^a	H ₂ O ₂ (1), HNO ₃ (5), H ₂ SO ₄ (0.5)	0.1
NaOH ^d	2% NaOH _{aq} (10); after digestion: HCl (5)	0.1
P_{nac} ^b	Neutral ammonium citrate solution (100)	1.0
P_{ws} ^c	Double distilled water (50)	1.0

^a Based on DIN ISO 11466.

^b According to DIN EN 15957.

^c According to VDLUFA II.1; 4.1.7.

2.2. Sample preparation

The samples were air-dried, divided representatively by dividing cross and grinded with a tungsten carbide vibratory disc mill down to a grain size < 63 µm. The samples were dissolved by microwave-assisted digestion (according to (DIN ISO 11466, 1997)). Approximately 0.1 g of milled SSA was weighed in on 0.1 mg and mixed with the reagent mixture as stated in Table 2. The solution was filled up with doubly distilled water to 50 mL. All reagents were purchased in analytical grade, all acids from AppliChem GmbH, Darmstadt and LiNO₃ (for the elemental analysis, see below) from Merck KGaA, Darmstadt. P solubility in neutral ammonium citrate (P_{nac} ; (DIN EN 15957, 2011)) and water (P_{ws} ; (VDLUFA, 1995)) were determined according to the respective standards. All experiments were carried out in triplicates. Results were considered to be significant if the differences exceeded the respective standard deviations. We discussed only those significant results.

2.3. Elemental analysis

The P mass fractions in the samples as well as P concentrations in the P_{nac} and P_{ws} extracts were determined by means of ICP-OES (inductively coupled plasma optical emission spectroscopy; 213.618 nm; axial). Solutions from digested solid samples were spiked with 10 g/L LiNO₃ and the respective acids to even out matrix effects and measured undiluted according to the respective standard (DIN EN ISO 11885, 2009) with a Thermo Scientific iCAP 7400. P_{nac} extracts were measured from 100-fold dilution and P_{ws} extracts undiluted. Extracts as well as the respective standards were acidified with 1.5% HNO₃. We took part in a round robin test for P_{nac} and P_{ws} extraction (VDLUFA M2/2015) for quality control. We received two organic NPK fertilizers (compost), which were dried at 105 °C and sieved to 0.5 mm particle size. We analyzed the samples according to the methods and standards mentioned above. The mean values of the round robin test with 11 participants were (values stated in mg/kg): sample 1: P_{nac} 3370 (tolerance 2580–4260; our value 2966); P_{ws} 289 (217–370; our value 305); sample 2: P_{nac} 2655 (2056–3329; our value 2392); P_{ws} 261 (178–359; our value 261). All our results are well within the tolerance range and P_{ws} values are basically on the spot. However, P_{nac} are about 10% lower than the round robin test mean values. Presumably, this is due to the fact that we used pressure membrane filtration instead of the stipulated folded filter (see results and discussion section). We applied this to avoid blocking of the ICP-OES with fine particles. Even though we probably measured P_{nac} a little bit on the low side, we do not expect this to hamper our conclusions, since we discuss relative differences according to the experimental boundary conditions.

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