Sylvia Kratz[1], Elke Bloem[1], János Papendorf[2], Judith Schick[1], Ewald Schnug[1], Peter Harborth[2]

Agronomic efficiency and heavy metal contamination of phosphorus (P) recycling products from old sewage sludge ash landfills

Agronomische Effizienz und Schwermetallkontamination von Phosphor (P)-Recyclingprodukten aus mehrjährig deponierten Klärschlammaschen

Abstract

A modified Neubauer pot trial with rye was carried out to investigate the agronomic efficiency of different fertilizer products based on a sewage sludge monoincineration ash (SSA) which had been stored below ground for about ten years. Test products included the stored raw ash from chemically precipitated sewage sludge (SSA 1), an acid leaching treatment without (SSA 2) and with subsequent Ca-P precipitation (SSA 3), and a product subjected to an ion exchange process after acid leaching (SSA 4). For comparison, a thermo-chemically treated ash (SSA-TC) representing the currently available technology was also included. A commercial water soluble P fertilizer (SSP) was used as a reference. NAC-solubility of SSA 2−4 was increased by the acid leaching procedure up to a level around 87−92% of total P, compared to 36.5% in the raw ash (SSA 1) and 63% in SSA-TC. SSA 4 was the only test product with high water solubility (77% of total P). Relative agronomic efficiency related to dry matter yield (RAE-DMY) did not show large variation between products, ranging from 84% (SSA 1) to up to 91% (SSA 2) in comparison to the control (SSP) at the optimum P level (20 mg). A larger variation was displayed when relative agronomic efficiency regarding P uptake (RAE-PU) was calculated. At P level 20, RAE-PU ranged between 53.5% for SSA 1 up to 99% for SSA 4. Thus, the water soluble product clearly distinguished itself from the non-water soluble variants. However, at the highest P level (40 mg), there was a significant decrease in both DMY and PU for SSA 4, which could be explained by Na toxicity related to the high Na content of the product originating from the treatment procedure.

The acid leaching treatment successfully reduced heavy metal contents (As, Cd, Cr, Cu, Ni, Pb, Tl, Zn) of the raw ash, so that the limit values of the German Fertilizer Ordinance were safely met. U concentration was already low (2.9 mg/kg DM) in the raw material. However, even the Ca-precipitation (SSA 3) was not able to reduce the initially high Fe and Al concentrations to a sufficiently low level to prevent the (re-)formation of insoluble Fe/Al-phosphates during the experiment. While the exchange of the cations Al and Fe by Na (SSA 4) was able to enhance the plant availability and uptake of P, it induced other difficulties related to the increase in Na content.

It was concluded that, to make the ash-based recycling fertilizers more attractive, further research is needed to find a procedure which will make the ash-P plant available and at the same time result in a product which is low in growth-reducing contaminants such as sodium or heavy metals.

Key words: Sewage sludge ash, P recycling fertilizer, P solubility, heavy metals

Institute

Julius Kühn Institut (JKI) – Federal Research Institute for Cultivated Plants, Institute for Crop and Soil Science, Braunschweig, Germany[1]
TU Braunschweig, Leichtweiß Institute for Hydraulic Engineering and Water Resources, Braunschweig, Germany[2]

Correspondence

Dr. Sylvia Kratz, Dr. Elke Bloem, Julius Kühn-Institut (JKI), Federal Research Institute for Cultivated Plants, Institute for Crop and Soil Science, Bundesallee 50, 38116 Braunschweig, Germany, E-Mail: sylvia.kratz@julius-kuehn.de, elke.bloem@julius-kuehn.de

Zusammenfassung

In einem modifizierten Neubauer-Gefäßversuch mit Roggen wurde die agronomische Effizienz von Recyclingprodukten untersucht, die aus einer für ca. 10 Jahre deponierten Klärschlammasche aus Monoverbrennung hergestellt wurden. Folgende Produkte wurden getestet: die deponierte Klärschlamm-Rohasche aus chemischer Fällung (SSA 1), ein Säureauszug ohne (SSA 2) und mit anschließender Ca-P-Fällung (SSA 3), und ein Produkt, welches nach dem Säureaufschluss einer Kationenaustauschprozedur unterworfen wurde (SSA 4). Zum Vergleich wurde eine thermochemisch behandelte Klärschlammasche (SSA-TC) mit untersucht, die den gegenwärtigen Stand der Technik repräsentiert. Als Referenz wurde ein kommerzieller wasserlöslicher P-Mineraldünger (Superphosphat, SSP) eingesetzt. Die NAC-Löslichkeit von SSA 2−4 wurde durch den Säureaufschluss auf ein Niveau von 87−92% des Gesamt-P angehoben, im Vergleich zu 36,5% in der Rohasche (SSA 1) und 63% in SSA-TC. SSA 4 war das einzige Testprodukt mit einer hohen Wasserlöslichkeit (77% des Gesamt-P). Die auf den Trockenmasseertrag bezogene relative agronomische Effizienz (RAE-DMY) zeigte keine großen Unterschiede zwischen den Varianten, bei der optimalen P-Stufe (20 mg) variierte sie zwischen 84% des DMY-SSP für die Rohasche SSA 1 und 91% für SSA 2. Die Kalkulation der RAE bezogen auf die P-Aufnahme (RAE-PU) zeigte eine deutlichere Variation: Bei der P-Stufe 20 rangierte die RAE-PU zwischen 53,5% für SSA 1 und 99% für SSA 4. Somit unterschied sich SSA 4, das einzige wasserlösliche Testprodukt, deutlich von den nicht wasserlöslichen Varianten. Allerdings verzeichnete SSA 4 in der höchsten P-Stufe (40 mg) einen deutlichen Einbruch sowohl beim DMY als auch bei der P-Aufnahme. Dies war eine Folge von Na-Toxizität, die durch die behandlungsbedingt stark erhöhte Na-Konzentration dieses Testproduktes verursacht wurde.

Mit der Säurebehandlung konnten die Schwermetallgehalte (As, Cd, Cr, Cu, Ni, Pb, Tl, Zn) der Rohasche signifikant reduziert werden, so dass die Grenzwerte der deutschen Düngemittelverordnung sicher eingehalten wurden. Die Urankonzentration war bereits im Ausgangsmaterial gering (2,9 mg/kg DM). Allerdings war auch die Ca-P-Fällung (SSA 3) nicht in der Lage, die hohen Fe- und Al-Konzentrationen des Ausgangsmaterials hinreichend zu reduzieren, um die (Re-)Formierung von unlöslichen Fe/Al-Phosphaten während des Experiments zu verhindern. Während durch einen Austausch der Kationen Al und Fe gegen Na (SSA 4) die Pflanzenverfügbarkeit und -aufnahme von P erhöht wurden, verursachte diese Behandlung andere, mit den ebenfalls erhöhten Na-Gehalten verbundene Schwierigkeiten.

Das Experiment führte zu der Schlussfolgerung, dass weitere Versuchsansätze erforderlich sind, um P in einer Form aus der Klärschlammasche zu gewinnen, welche zugleich pflanzenverfügbar ist und möglichst geringe wachstumsreduzierende Kontaminanten wie Natrium oder Schwermetalle enthält, damit aschebasierte Recyclingdünger in Zukunft attraktiver werden.

1 Introduction

About 3.4 Mio t (DM) of sewage sludge (SS) are produced in Germany per year (sum of public and private waste water treatment), equal to around 200,000 t/a P_2O_5. The share of SS in the total supply of phosphorus (P) to German agriculture has been dropping considerably over the past decade, down to below 37% of the total amount of SS produced per year in 2013/2014 (Statistisches Bundesamt, 2016).

Germany aims at completely banning the use of untreated SS in agriculture, while only allowing fertilization with SS-based recycling products such as struvite or treated sewage sludge ash (SSA), given their P is plant available and the product meets the legal limit values for organic and inorganic contaminants. The new German Waste Sewage Sludge Ordinance (Abfallklärschlammverordnung, AbfKlärV), which has become effective on Oct 3, 2017, clearly favours P recovery and reuse of P recovered from SS or SSA over the direct use of SS in agriculture. While small waste water treatment plants (< 50.000 population equivalents) will still be allowed in the future to directly apply their SS on agricultural lands, larger waste water treatment plants will be required to recover at least 50% of the P in their sludge, or 80% in the SSA after a transition period of 12 (15) years, depending on their size.

The storage of sewage sludge incineration ash in long-term deposits is permitted provided that: (1) mixing with other wastes, substances and materials and a surface discharge of sewage sludge incineration ash are excluded and (2) it is ensured that a subsequent recovery of phosphate from the landfill remains possible.

Practical experience with such long-term storage of monoincineration SSA is, however, not yet available in Germany. Therefore, comparative investigations have been undertaken over the last 4 years by the State Ministry for Climate Protection, Environment, Agriculture, Nature and Consumer Protection of North Rhine Westphalia with the aim of examining the P recovery from different types of landfills after several years of deposition.

A significant limitation of SSA in terms of its suitability as P fertilizer is its low plant availability. During the incineration process, phosphorus present in the sludge is mainly turned into scarcely soluble Ca-phosphates such as hydroxyapatite or whitlockite (Peplinski et al., 2009; Nanzer et al., 2014a). In addition, like all non-volatile mineral elements in the sludge, heavy metals are concentrated during incineration due to the loss of organic substance. Since 01.01.2015, the heavy metal limit values of the German Fertilizer Ordinance (Düngemittelverordnung, DüMV) are also valid for fertilizers based on SS. According to a survey by Krüger and Adam (2014), about two thirds of the monoincineration ashes currently produced from SS in Germany exceed at least one of these limit val-

SYLVIA KRATZ et al., Agronomic efficiency and heavy metal contamination of phosphorus (P) recycling products ...

Originalarbeit

375

ues and can therefore not be used as fertilizers without further treatment.

Several technologies have been developed to treat SSA in order to turn them into suitable P fertilizers with a high P plant availability and a low level of heavy metal contamination – however, most of them are still under development or only implemented in the form of pilot plants. Therefore, a large amount of monoincinerated sewage sludges will have to be stored for an unknown period of time before they can be treated as required at a large scale. It remains to be seen how this long-term storage affects the properties of the ashes and their suitability as raw material for the production of recycling fertilizers.

HEUSSNER et al. (2016) found that a sequential acid leaching/precipitation strategy was very effective in separating large amounts of heavy metals from SSA, so that the recovered fertilizer completely fulfilled the requirements of the DüMV. However, this strategy was not successful in reducing the high Al/Fe contents typical for sewage sludges and their ashes which underwent chemical P-precipitation. Additional attempts were made to evaluate the effectiveness of these newly obtained recycled fertilizers from deposits.

This paper reports results of a pot trial carried out to investigate the agronomic efficiency of different fertilizer products based on a SSA which had been stored below ground for about ten years in comparison to a treated ash product from fresh SS, which represents the currently available technology.

2 Material and Methods

2.1 Experimental design

Plant availability of P fertilizers is commonly assessed by chemical extraction methods, applying extractants which are supposed to mirror the nutrient solubility in the soil, such as neutral ammonium citrate (NAC). However, chemical extractions only reflect a momentary state, while they are not able to describe the complex solution processes taking place at the soil/fertilizer/plant interface. Therefore, vegetation trials are still the most reliable – but at the same time the most time consuming and costly – method to assess the plant availability of fertilizers. A modified Neubauer pot trial (Fig. 1) was carried out to investigate the agronomic efficiency of different recycling products. In this kind of trial, the plant roots are used as „reactant" to estimate the amount of „root soluble" and thus plant available nutrients in the fertilizer products. To achieve this, a large number of plants (100 rye seeds) are grown in a low amount of (fertilized) substrate (450 g sand) for a relatively short period of time (originally 14–18 days). The plants will use up all soluble nutrients during the experiment (NEUBAUER and SCHNEIDER, 1923; NEUBAUER, 1931) if moisture levels and temperatures are adequate. In the modified form, this experiment is continued after the first harvest until visible symptoms of nutrient deficiency, accompanied by retarded growth, are observed, in order to make sure that it is indeed an

„exhaustion trial", and a second and third harvest are carried out (KRATZ et al., 2010). At the final cut, in addition to above ground biomass (shoots), roots are also harvested and prepared for analysis. The NEUBAUER design was chosen in order to avoid the drawbacks associated with soil-based pot trials, in particular the multiple nutrient content of real soils, which does not allow for nutrient exhaustion within a reasonable amount of time.

Test products included a monoincineration ash produced from chemically precipitated sewage sludge and stored as landfill for about 10 years, subjected to various recycling steps in order to strip it of heavy metals and make its P content plant available (SSA 1–4; **SSA 1**: raw monoincineration sewage sludge ash from the storage site „Raffelberg" (North Rhine-Westphalia, Germany); **SSA 2**: SSA1 recycled by stepwise dissolution in 20% H_2SO_4, and subsequent precipitation of P from the filtrate by addition of KOH (pH 3) and filtration, removal of heavy metals based on the different solubility of P and heavy metals at different pH; **SSA 3**: SSA 1, subjected to the same dissolution process as SSA 2, but precipitation of P as Ca-phosphate to further reduce Al and Fe contents; **SSA 4**: SSA 2 dissolved in acid again, then treated with sodium based ion exchange resins to remove Al, Fe and Ca and thus improve P solubility). For comparison, a thermo- chemically treated sewage sludge ash produced from recently incinerated sludge (**SSA-TC**, a monoincinerated SSA, subjected to a thermo-chemical treatment in a rotary kiln at a temperature of 1000°C and with the addition of Na_2SO_4 to form plant available Ca-Na-phosphates and remove heavy metals) was investigated, representing the fertilizer efficiency of treated ash at the current stage of technical development. A water soluble commercial fertilizer (single super phosphate, SSP) was used as control. A zero control variant without any P addition was also included. P contents and P solubility of the fertilizers used in the experiment are described in Table 1.

Fig. 1.   Modified Neubauer trial with summer rye at day 8 after sowing.

Table 1. P contents and solubility of test products in water and neutral ammonium citrate (NAC$_{eu}$)

Test products		Total P$_2$O$_5$ (%)*	P-water (% of total P)	P-NACeu (% of total P)
Sewage sludge ash raw	SSA 1	8.2	0.06	36.5
SSA recycled	SSA 2	32.6	1.90	86.9
SSA Ca-treated	SSA 3	10.4	0.07	91.8
SSA with ion exchange	SSA 4	6.6	76.90	88.2
SSA thermo-chemically treated	SSA-TC	17.0	0.47	62.7
Single Superphosphate	SSP	21.5	93.30	83.3

* determined by aqua regia digestion

The experiment was set up with three different P levels, which should represent a deficient, an optimum and a luxury supply with P (10, 20 and 40 mg P per pot), based on previous results on P uptake (KRATZ et al., 2010) and an assumed maximum fertilizer use efficiency of 20%. P additions were calculated based on total P contents of the fertilizers after extraction with aqua regia (Table 1). Due to the small amounts of fertilizer to be applied to the limited substrate volume, the test products had to be applied in fine-ground form in order to allow their homogenous distribution in the substrate. All other essential macro- and micro-nutrients except P (i.e. N, K, Ca, Mg, S, Fe, Mn, Zn, Cu, B, Mo) were supplied equally to all pots in liquid form as lab grade chemicals and at optimum rates to make sure no other nutrient deficiency would influence the experiment (fertilization details see Table 2).

450 g of fertilized substrate were filled into transparent polystyrol vessels (diameter 12 cm, height 6 cm) and seeded with 100 dressed summer rye seeds of the variety „Arantes" (1000 grain weight: 41.2 g, germinability: 93%). P-free quartz sand [grading: „fine" sand: 0.1–0.4 mm, coarse sand 0.7–1.2 mm] was used as substrate. Quartz sand was filled into the vessels in three layers: The bottom layer consisted of 50 g coarse and 100 g fine sand, which was mixed with the ground test fertilizers. This layer was also sprinkled with the supplemental fertilizer solutions. On top of this, a layer of 150 g fine sand was placed. Rye seeds were evenly spread on top of the second layer and covered with a third layer of 150 g fine sand. 4 replicates were prepared for each variant.

All pots were brought to approximately 65% of field capacity with de-ionized water. During the trial, water was supplied individually according to pot weight.

The first harvest of above ground biomass took place 16 days after sowing (BBCH 12/13). A second cut was carried out 30 days after sowing (BBCH 11/12), and the third and final cut, including a separate harvest of roots, 51 days after sowing (BBCH 13/14). BBCH-growth stages were defined according to STAUSS et al. (1994). At each harvest, the fresh weight yield was recorded.

2.2 Analytical procedures

For the determination of plant P contents, the plant material was dried in a ventilated oven at 60°C until constancy of weight. The dry weight was recorded for the determination of the dry matter yield. Then the material was fine-ground to a particle size of < 60 μm in a Retsch RS 1 vibrating disc mill with zirconium oxide grinding equipment. 0.5 g plant material was digested with 4 ml HNO$_3$ + 1 ml H$_2$O$_2$ in a microwave (CEM/Mars) at 600 Watt for 27 minutes, raising the temperature up to 200°C. After cooling down, the digest was filled up to 50 ml with

Table 2. Fertilization with other nutrients except P (supplied in liquid form at the start of the experiment, some N was resupplied after the first two cuts)

Nutrient	Supplied as	Total amount (pure nutrient) supplied per pot
N	NH$_4$NO$_3$, KNO$_3$ and Ca(NO$_3$)$_2$	50 mg at the start, 10 mg after 1st and 5 mg after 2nd cut
K	KNO$_3$	60 mg
Ca	Ca(NO$_3$)$_2$	20 mg
Mg, S	MgSO$_4$	4 mg each
Micronutrients	Fe-EDTA solution with MnCl$_2$, ZnCl$_2$, CuCl$_2$, (NH$_4$)$_6$Mo$_7$O$_{24}$, and H$_3$BO$_4$	0.1 mg Fe, 0.05 mg Mn, 0.04 mg Zn, 0.01 mg Cu, 0.0008 mg Mo, and 0.01 mg B

de-ionized water. P concentration was determined by ICP-OES (Thermo icap 6300). A sample of seeds from the same lot as those used in the trial was dried at 40°C, fine-ground and digested in the same way as the plant material to evaluate how much P was added to the pots via the seeds.

For the determination of P contents and solubilities in fertilizers, standard procedures were applied: The original fertilizers were conditioned at 40°C and fine-ground to a particle size of < 60 µm in a Retsch RS 1 vibrating disc mill with zirconium oxide grinding equipment. Total P: Aqua regia (P-AR) digest according to DIN EN 13346/2001–04. Soluble P: Extraction with neutral ammonium citrate (P-NAC) according to EU-method 3.1.4 (EC Regulation 2003/2003), extraction with water (P-water) according to VDLUFA II 4.1.7 (2007). P determination was done colorimetrically (Molybdenum-Blue) according to MURPHY and RILEY (1962) with $(NH_4)_6Mo_7O_{24} \times 4H_2O$, using a spectral photometer (Specord 50, Analytik Jena).

Heavy metal contents of the fertilizers were determined in the aqua regia digests by ICP-OES (Thermo icap 6300) and SF-ICP-MS (Thermo Element XR).

Plant available P contents in the substrate after the experiment were determined by P-CAL (calcium acetate lactate) extraction according to SCHUELLER (1969), which is the standard method for the determination of plant available P in soils in Germany (VDLUFA I A 6.2.1.1, 1991). P determination was conducted colorimetrically (see above).

2.3 Calculations and statistical evaluation

P uptake (PU) was calculated as the product of dry matter yield (DMY) per pot and P concentration in biomass (shoots and roots). The figures show both cumulative dry matter yield and cumulative P uptake as the sum of the three cuts and the roots.

P efficiency was calculated as P uptake in % of P supplied with fertilization, also accounting for the amount of P supplied to the pot with plant seeds:

$$P\ efficiency\ (\%) = \frac{P\ uptake\ per\ pot \times 100}{(amount\ of\ P\ in\ 100\ rye\ seeds + P\ supplied\ with\ fertilizer)}$$

Relative agronomic efficiency (RAE) was calculated for each variant regarding both DMY and PU. Single superphosphate (SSP) was used as a reference. The calculations were performed as follows:

$$RAE\text{-}DMY\ (\%) = \frac{Dry\ matter\ yield\ (variant\ x) \times 100}{Dry\ matter\ yield\ (SSP)}$$

$$RAE\text{-}PU\ (\%) = \frac{P\ uptake\ (variant\ x) \times 100}{P\ uptake\ (SSP)}$$

Differences between variants were statistically tested by one-way ANOVA with a Tukey post-hoc test at a level of significance of $p < 0.05$, using the SPSS 17.0 software package (SPSS Inc., USA).

3 Results and Discussion

3.1 Agronomic efficiency

Only small, in most cases non significant differences between the test fertilizers were observed in DMY (Fig. 2). While the SSP control yielded a significantly higher biomass than the zero P control at all three P levels, the test fertilizers ranged somewhere in between these two. At P level 10, DMY of all test products was significantly higher than the zero P control, however, at P levels 20 and 40, no significant differences were found between SSA 1–3, SSA-TC and the zero P variant. This indicates to a negative effect of these fertilizers when used in higher concentrations, which was most likely due to the input of adverse elements contained in these materials, which increased with increasing P addition (see chapter 3.4). SSA 2 and SSA 3 produced yields which were comparable to the untreated SSA 1 fertilizer at the different P levels (Fig. 2). This was not true, however, for SSA 4, the only water-soluble product, which had been subjected to an ion exchange procedure. SSA 4 produced an even slightly higher DMY than SSP at P level 10, while its DMY dropped down below that of the zero P control at P level 40.

The small variation in DMY of the different tested fertilizers is also reflected by the RAE-DMY which did not show large variation between products in most cases, ranging from 84% for the raw SSA 1 up to 91% for SSA 2 at the optimum P level (20 mg) (Table 3). The highest RAE-DMY was achieved at the lowest P level in most cases, indicating that a fertilizer level of 10 mg/pot was already high enough to cover the P demand of the crops under the conditions of the current experiment.

3.2 P uptake efficiency

A clear differentiation between variants could be shown in P uptake (Fig. 3). All test products had a significantly higher P uptake than the zero control, while the raw ash SSA 1 achieved a significantly lower P uptake than its treated variants. P uptake in the SSA-TC variant was comparable to that in SSA 2 and SSA 3, depending on which P level is looked at. The best performance was again displayed by SSA 4 which achieved a P uptake in the same order of magnitude as the SSP control at P levels 10 and 20. However, at P level 40, P uptake of the SSA 4 variant dropped down considerably as mentioned before.

Accordingly, P efficiency of the test fertilizers was best for SSA 4, which achieved a similar efficiency as the SSP control at P levels 10 and 20 (Fig. 4).

It is important to mention that the „Neubauer trial" is a closed system where negative compounds affect plant growth directly without the buffering capacity of a soil. Fertilizer products cannot really interact with the substrate as this is pure sand. Therefore reactions can take place which would not occur under field conditions. This is especially true for element imbalances which can directly affect plant growth. This way the drastic decrease in plant growth observed for SSA 4 at P level 40 can be explained by Na toxicity affecting the plants. SSA 4 had been treated with NaOH after ion exchange, leading to
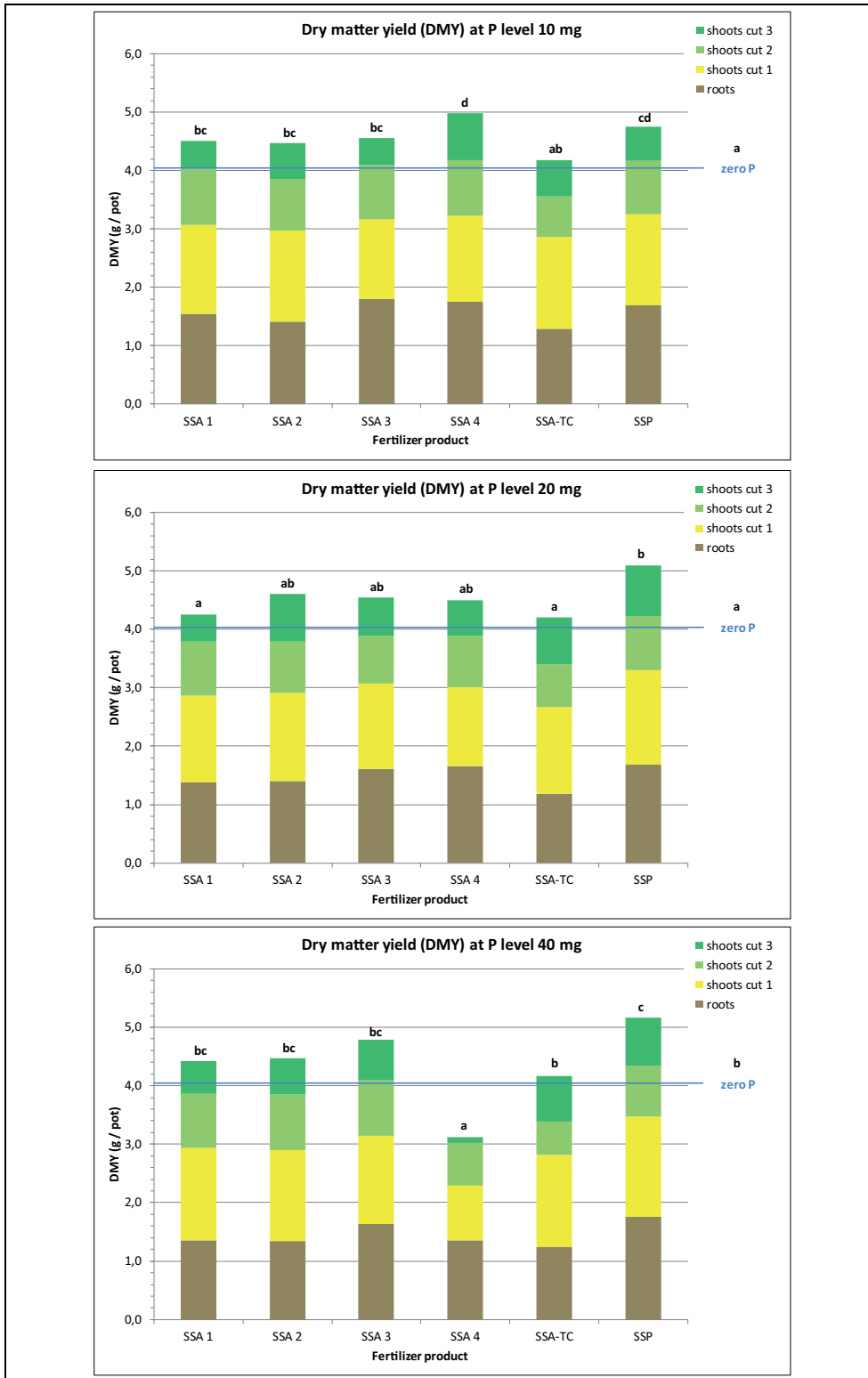
Fig. 2. Cumulative dry matter yield (DMY) of rye for the different tested products. Different letters indicate significant differences between variants at a level of p < 0.05, tested by oneway ANOVA with Tukey post-hoc test.

Na toxicity in the small pots at a high fertilization rate. As shown in Table 7, Na-concentrations of SSA 4 exceeded those of the other products by one order of magnitude, or even two orders of magnitude when looking at the P-related concentrations. While the thermo-chemically treated SSA-TC also contained high amounts of Na, this product also had a much higher P concentration than SSA 4, resulting in a total Na load per pot which was about seven times lower than that supplied with SSA 4. Thus, the SSA-TC variant neither suffered from visible toxicity symptoms, nor from such drastic decreases in DMY as observed for SSA 4.

Table 3. Relative agronomic efficiency (RAE) regarding dry matter yield (DMY) and P uptake (PU), respectively, with single superphosphate (SSP) as reference

	P level (mg/pot)	RAE-DMY (%)			RAE-PU (%)		
		10	20	40	10	20	40
Zero P		83.5	78.5	76.9	59.4	45.6	33.3
Sewage sludge ash raw	SSA 1	94.7	84.1	85.8	69.3	53.5	42.3
SSA recycled	SSA 2	94.1	91.0	86.6	78.1	68.5	56.2
SSA Ca-treated	SSA 3	95.9	90.0	92.2	75.3	61.0	49.2
SSA with ion exchange	SSA 4	104.8	88.9	60.9	104.6	99.2	61.0
SSA thermo-chemically treated	SSA-TC	88.0	84.9	80.7	79.4	71.4	58.0
Single Superphosphate	SSP	100.0	100.0	100.0	100.0	100.0	100.0

In comparison to RAE-DMY, a larger variation was displayed when relative agronomic efficiency regarding P uptake was calculated (Table 3). At the supposed optimum P level (20 mg), RAE-PU ranged between 53.5% for raw SSA (SSA 1) up to 99% for SSA 4. At the lowest P level (10 mg), which seemed to be already high enough to cover the crop demand for P in the current trial, SSA 4 (treated with ion exchange resin) even reached RAE-PU of 105%, strengthening the assumption that P levels may have been calculated too high, in other words, 20 mg P may have been above optimum in this experiment. Thus, regarding P uptake, SSA 4, which was the only product with not only a high NAC-solubility, but also a high solubility in water (see Table 1), clearly distinguished itself from the non-water-soluble products.

3.4 Contamination with heavy metals and other critical elements

Heavy metal concentrations in the treated ashes (SSA 2–4 and SSA-TC) did not exceed the limit values of the German Fertilizer ordinance (Table 4). However, the raw ash SSA 1 would not qualify as a fertilizer, as its concentrations of Cd, Ni and Pb were way above these limit values. Obviously, the treatments were successful in reducing the concentrations of As, Cd, Cr, Ni, Pb and Tl in almost all cases (except As and Tl in SSA 2). It should be noted that the commercial SSP which was used as a reference fertilizer exceeded the limit value for Cd. The current draft for the revision of the European Fertilizer Regulation proposes a stepwise reduction of the Cd limit from 60–40–20 mg Cd/kg P_2O_5, within 12 years after the regulation will become effective (EC, 2016). If the treated ashes shall be marketed as European fertilizers, the limit of 20 mg would also exclude SSA 3 in its current formulation.

However, as shown in Table 1, P concentrations in SSA 3 and SSA 4 were also considerably lower than in the raw ash and in SSA 2. Therefore, in order to evaluate the contamination of these materials as P fertilizers, their heavy metal concentrations were also calculated in relation to their P contents (Table 5). As the calculations show, all three treatments (SSA 2–4) resulted in a considerable reduction of P-related heavy metal concentrations. Heavy metal concentrations in the thermo-chemically treated SSA-TC were more or less in the same order of magnitude as in the other treated ashes, however, their Ni and Pb concentrations were somewhat higher. Whether this is a result of the different raw ashes used or of a more successful treatment in SSA 2–4 cannot be decided as the raw material from SSA-TC was not available.

The treatments of SSA 1 also reduced the concentrations of Cu and Zn (Table 6). Cu and Zn are no longer regulated in the German Fertilizer Ordinance, because it was decided to focus more on their quality as essential micronutrients than as potential contaminants. However, in larger quantities, they can also become toxic to living organisms. Therefore it is still relevant to look at the effects of various treatments on Cu and Zn concentrations in recycling fertilizers.

Uranium is not yet regulated in the German Fertilizer Ordinance as potential contaminant, however, there has been a lot of discussion about it recently, since it often occurs in rather high concentrations in phosphate rock based P fertilizers (Kʀᴀᴛᴢ et al., 2016), and as a heavy metal might have toxic effects on living organisms in the long run. The treatments did not reduce the U concentrations in the products. However, all sewage sludge ash based products displayed considerably lower U concentrations than the commercial SSP (differing by at least one order of magnitude, see Table 6). This should be kept in mind when discussing additional advantages of using recycling fertilizers instead of phosphate rock based products.

An important goal of the Ca treatment (SSA 3) was to further reduce the high concentrations of Al and Fe in the raw ash resulting from chemical P-precipitation with Fe- and Al-salts in the original sewage sludge. However, as the data in Table 7 shows, this attempt was not fully successful. While SSA 3 showed lower Al/Fe concentrations in relation to its dry matter, the Al concentration related
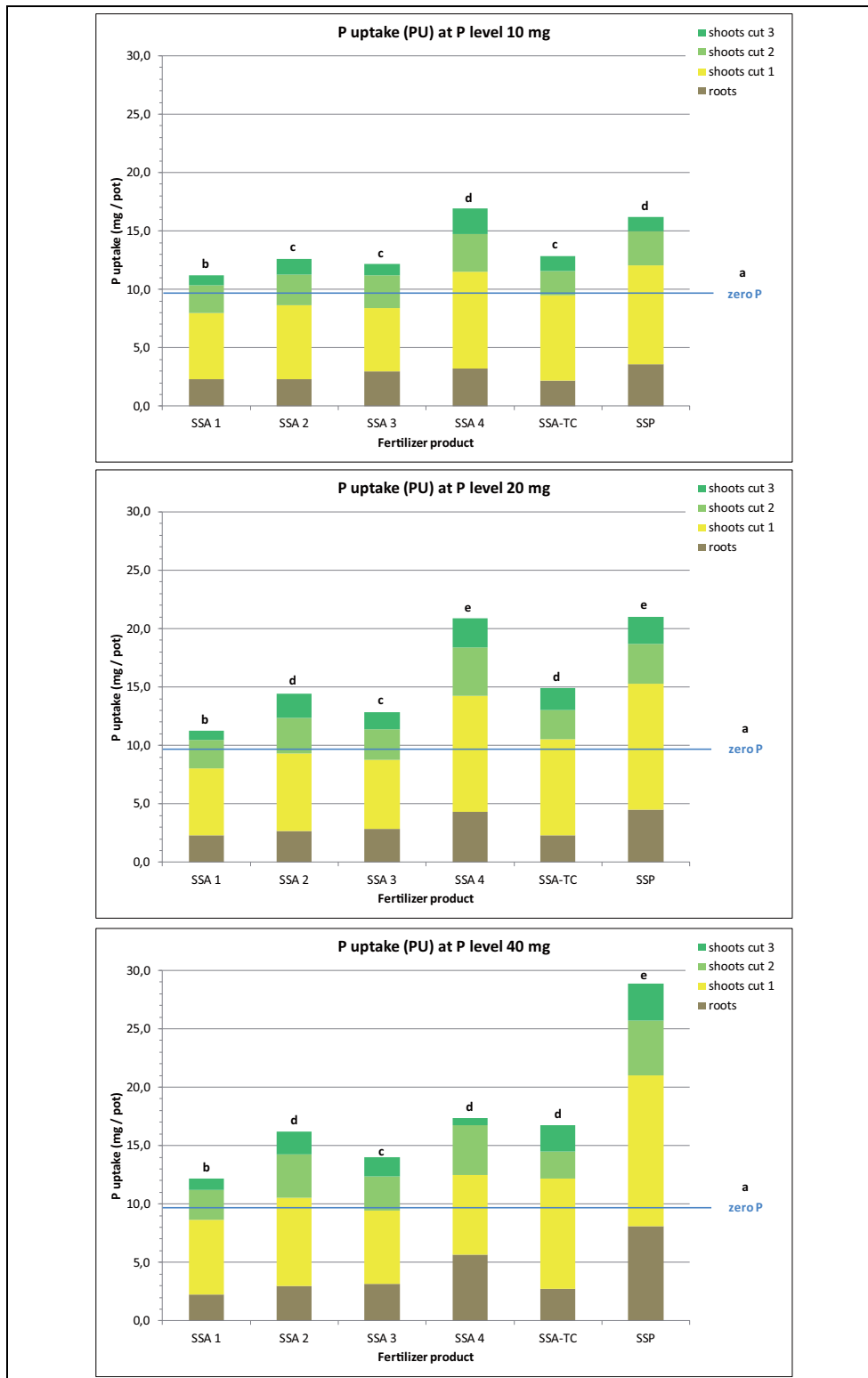
Fig. 3. Cumulative P uptake by rye for the different tested products. Different letters indicate significant differences between variants at a level of p < 0.05, tested by oneway ANOVA with Tukey post-hoc test.

to P contents was almost the same for both SSA 2 and SSA 3, and the amount of Fe (per kg P_2O_5) was only reduced by approximately one third in SSA 3. Obviously, the decrease in concentrations related to dry matter was mainly an effect of dilution of the material caused by the Ca-treatment, which reduced absolute P concentration together with the concentrations of Al and Fe.

3.5 Validity of different extraction procedures
The differentiation in P uptake/P efficiency is only partly mirrored by the different P solubilities in water and neutral ammonium citrate (NAC) (see Table 1). Clearly, the only water soluble variant, SSA 4 (about 77% of P-total are water soluble), performs best. Neither SSA-TC, nor SSA 1, 2 or 3 are water soluble, but they all show some
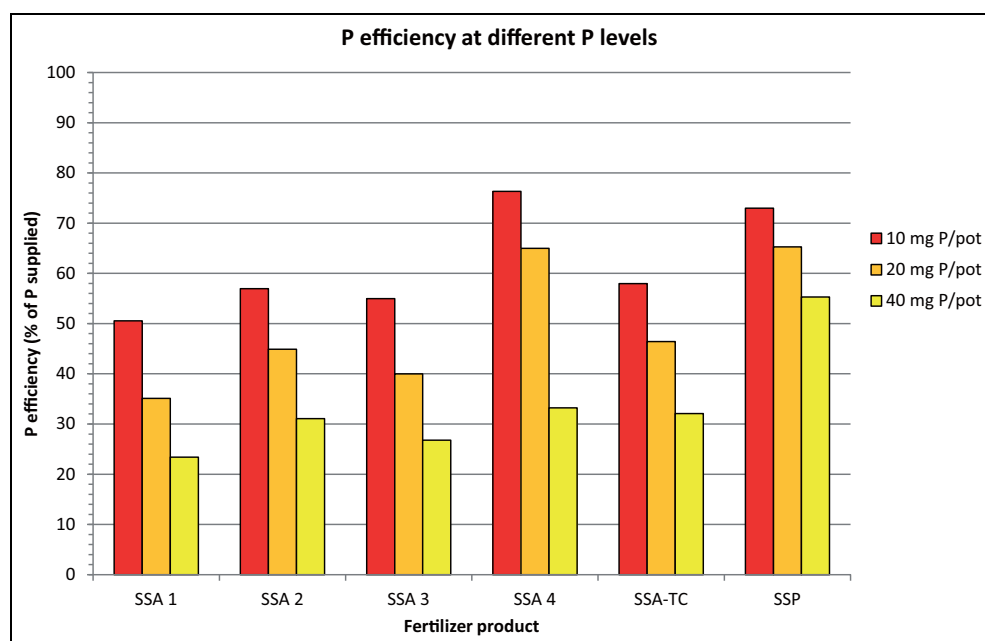
Fig. 4. P efficiency (% of P supplied with fertilizer and seeds) of the tested products at different P-levels

Table 4. Heavy metal concentrations in the tested products in comparison to the limit values of the German Fertilizer Ordinance (Düngemittelverordnung, DüMV)

Fertilizer/product		Concentration (mg/kg DM)						
		As	Cd	mg Cd/kg P_2O_5	Cr	Ni	Pb	Tl
Sewage sludge ash raw	SSA 1	12.2	15.2	186	*1032*	*621*	*418*	0.68
SSA recycled	SSA 2	23.2	4.1	12.7	273	30.7	31.9	0.83
SSA Ca-treated	SSA 3	8.3	2.9	27.6	95.7	18.9	5.6	0.22
SSA with ion exchange	SSA 4	6.0	0.41	6.3	29.6	3.5	1.3	0.11
SSA thermo-chemically treated	SSA-TC	7.1	1.0	6.1	81.8	48.7	39.6	0.24
Single Superphosphate	SSP	5.0	18.4	*85.5*	78.4	42.1	2.3	0.46
Limit values of DüMV		**40**	**	**50**	**(300)***	**80**	**150**	**1**

concentrations exceeding the limits are printed in fat italics
* labeling value (limit value exists only for Cr VI), ** limit value for Cd in P fertilizers is related to their P content

Table 5. Heavy metal contents in the tested products in relation to their P content (mg/kg P_2O_5)

Fertilizer/product		Concentration (mg/kg P_2O_5)					
		As	Cd	Cr	Ni	Pb	Tl
Sewage sludge ash raw	SSA 1	149	186	12582	7574	5099	8.3
SSA recycled	SSA 2	71.0	12.7	838	94.0	97.9	2.5
SSA Ca-treated	SSA 3	80.2	27.6	920	182	54.3	2.1
SSA with ion exchange	SSA 4	90.5	6.3	449	52.3	19.0	1.6
SSA thermo-chemically treated	SSA-TC	41.6	6.1	481	287	233	1.4
Single Superphosphate	SSP	23.3	85.5	365	196	10.6	2.2

Table 6. Concentrations of other potentially critical elements (Cu, Zn, and U) in the tested products (in relation to dry matter and P content, respectively)

Fertilizer/product		Concentration in mg/kg DM			Concentration in mg/kg P₂O₅		
		Cu	Zn	U	Cu	Zn	U
Sewage sludge ash raw	SSA 1	1566	5416	2.9	19093	66048	35.3
SSA recycled	SSA 2	278	377	13.1	852	1157	40.3
SSA Ca-treated	SSA 3	201.0	277	5.5	1933	2664	52.9
SSA with ion exchange	SSA 4	25.1	36.0	2.5	381	546	37.4
SSA thermo-chemically treated	SSA-TC	530	1669	5.8	3118	9818	34.1
Single Superphosphate	SSP	18.1	310	109	84.3	1443	508

Table 7. Concentrations of Ca, Al, Fe and Na in the tested products (in relation to dry matter and P content, respectively)

Fertilizer/product		Concentration in g/kg DM				Concentration in g/kg P₂O₅			
		Ca	Al	Fe	Na	Ca	Al	Fe	Na
Sewage sludge ash raw	SSA 1	74.7	58.2	69.5	2.3	828	710	847	27.6
SSA recycled	SSA 2	3.1	104	40.3	20.7	9.5	320	123	63.5
SSA Ca-treated	SSA 3	277	33.1	9.3	28.2	2626	318	89.0	271
SSA with ion exchange	SSA 4	0.37	3.8	2.5	282	5.1	57.9	37.5	4267
SSA thermo-chemically treated	SSA-TC	92.3	49.7	54.2	102	556	293	319	601
Single Superphosphate	SSP	239	1.2	0.76	3.3	1139	5.7	3.5	15.4

solubility in NAC. The untreated raw ash SSA 1 has by far the lowest NAC-solubility of all variants (about 37% of P-total), which also results in the lowest P uptake. However, SSA-TC with an NAC-solubility of around 63% of P-total shows a P uptake in the same order of magnitude as SSA 2 and SSA 3, although the latter two have significantly higher NAC-solubilities (87 and 92% of P-total, respectively). A possible reason for the high solubility of SSA 2 in NAC, which is not mirrored by a higher P uptake of this variant, is the fact that in this material, P is probably bound to Fe and/or Al in the form of Fe/Al-phosphates, which are soluble in NAC but not available to plants. It has been reported in the literature that NAC extraction will overestimate the plant availability of a P fertilizer if P in this fertilizer mainly occurs in the form of Fe/Al-phosphates (MULLINS et al., 1990). In contrast to this, SSA 3 is the result of a Ca-precipitation process, which most likely converted the Fe-/ Al-phosphates to Ca-phosphates. While these Ca-phosphates may have a higher plant availability, SSA 3 still did not show a higher P efficiency than SSA 2, which was, as discussed above (chapter 3.2), probably related to its high Na content.

The limited ability of standard extraction procedures for P fertilizers to estimate the P plant availability of recycling fertilizers has been noted recently by other researchers (e.g. DUBOC et al., 2017; STECKENMESSER et al., 2017).

They suggest re-assessing the current standards and turning to alternative methods which better mirror the processes taking place at the plant-soil-fertilizer interface, particularly sink-based methods such as Fe-oxide strips, Fe-oxide resin bags or the DGT (diffusive gradient in thin films) method.

Fig. 5 shows the amounts of plant available P (P-CAL) left in the substrate after the end of the experiment, indicating to the amount of available P which could not be used by the plants. At the 10 mg P level, the amount of P which was extracted by CAL was in the same order of magnitude as in the zero P control in case of SSP and SSA-TC, indicating to a more or less complete consumption of available P by the plants at this fertilizer level. Even without P fertilization, plants were not able to use up the complete amount of P supplied by the seeds (on average, P uptake of the zero P variant was 9.8 mg P, while on average 12.2 mg P per pot were added with seeds) during the course of the experiment, causing some P-CAL (0.24 mg/pot) left in the substrate in the zero P control (Figures 5 and 6). An obvious explanation for this is the fact that seed germination capacity was also not 100%, but only 93% (determined by a pre-test). The incomplete utilization of seed P is in line with NANZER et al. (2014b) who report that utilization of seed P depends on P fertilization rate and plant P uptake, with plants un-
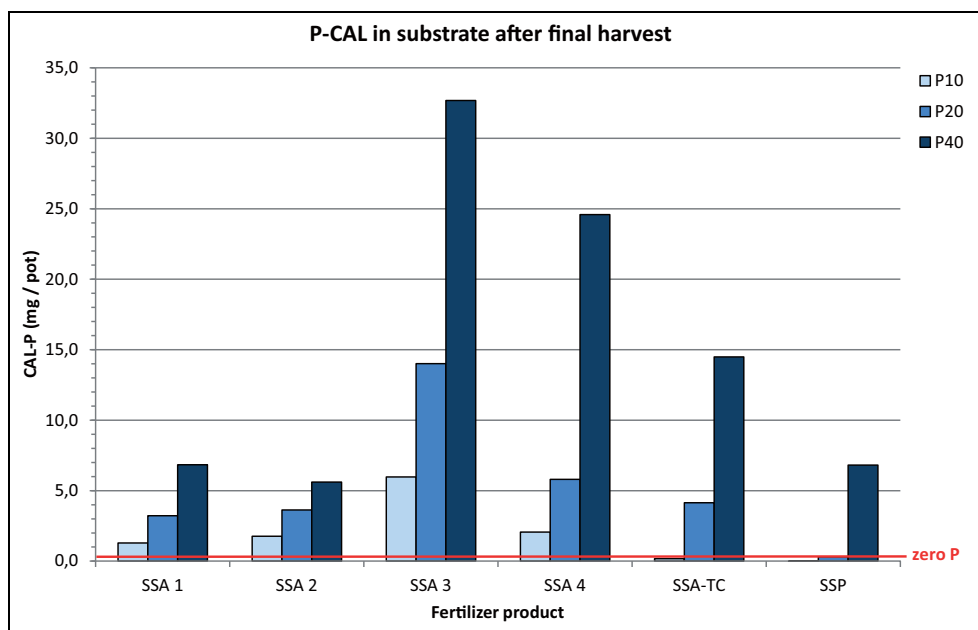
Fig. 5. Plant available P contents (P-CAL) left over by the tested products in the substrate after the final harvest.

der non-limited P supply growing more vigorously and thus being able to utilize all available P sources (including seed P) better than under limited P conditions.

The different variants varied considerably with regard to the amounts of P-CAL left over. The most efficient use of P was observed for the SSP control, which had no P-CAL left at the end of the experiment at P levels 10 and 20. When 40 mg P were supplied, however, about 18% of it could not be used up by the plants during the experiment, indicating to an over-supply with P. For the variants fertilized with SSA 1, SSA 2, SSA 4 and SSA-TC, the amount of P-CAL left in the substrate after the experiment was also low at a P level of 10 mg/pot. At the higher P levels (20 and 40), increasing amounts of P-CAL were left in the substrate. While SSA 1 and SSA 2 both show „left-over" P-CAL in the same order of magnitude as SSP, SSA 3, SSA 4 and (to a lower extent) SSA-TC, display much higher P-CAL contents after the experiment. This is particularly true for the highest P level (40 mg). Apparently, less than 50% of the P supplied with the fertilizer was used up in the SSA 4 variant at that level, and even less than 20% in the SSA 3 variant. The high P-CAL values are in line with the high plant-availability of SSA 3 and SSA 4 indicated by their high solubility in NAC (Table 1). The NAC-solubility of SSA-TC was clearly lower, which explains the lower amount of „left-over" P-CAL in the latter case. Obviously, however, not all of the P added in plant available form could be utilized by the plants and was thus left over at the end of the experiment. This is illustrated more clearly when looking at a simplified balance for the system, comparing the input of total and potentially available P with the sum of P used by plants (P uptake) plus P left in the substrate (P-CAL), termed here as „transferred P" (Fig. 6). Theoretically, the amount of available P added to the system should be found as P taken up by the plants or left over in the substrate in plant avail-

able form, i.e. both columns should have more or less the same height. If this is not the case, it can be assumed that the unaccounted-for rest was immobilized in the substrate in some form (and should be found as insoluble soil P, not analyzed in this study). In the case of SSA 3 and 4, indeed both columns are more or less the same heights at all fertilizer levels. In contrast to this, in the SSA 2 variant, the plants clearly did not use up the complete amount of P offered in „available form", which can be seen by the difference in height between the two columns. This strengthens once more the assumption that a large portion of the P extracted by NAC was not plant available due to its chemical form.

While the SSA 4 variant showed a clear decrease in DMY as a result of Na toxicity at the higher P levels (see above), no such effects in DMY were observed for SSA 3. However, as shown in Table 7, SSA 3 (like SSA-TC) had considerably higher Na concentrations (and, in consequence, was associated with a much higher Na load) than the commercial SSP. This was also reflected in elevated Na concentrations in the plant material of all three variants (data not shown here). It is assumed that this increase in Na uptake by the plants also had an important impact on the uptake of other nutrients, such as P, as the Neubauer trial is a closed system with nearly no buffering capacity due to the sandy substrate.

In contrast to SSA 3 and SSA 4, the untreated raw ash (SSA 1) only displayed a NAC solubility of 36.5%. Accordingly, less usable P was available to the system, which was, however, used up by the plants to a higher degree than in the case of the treated ashes. The low amount and share of P-CAL left over after the experiment is in line with this. It can be assumed that higher shares of non plant available P forms are still left in the substrate. SSA 2 also displayed only a low share of soluble P left over in the substrate (= P-CAL), despite of the fact that the fertilizer
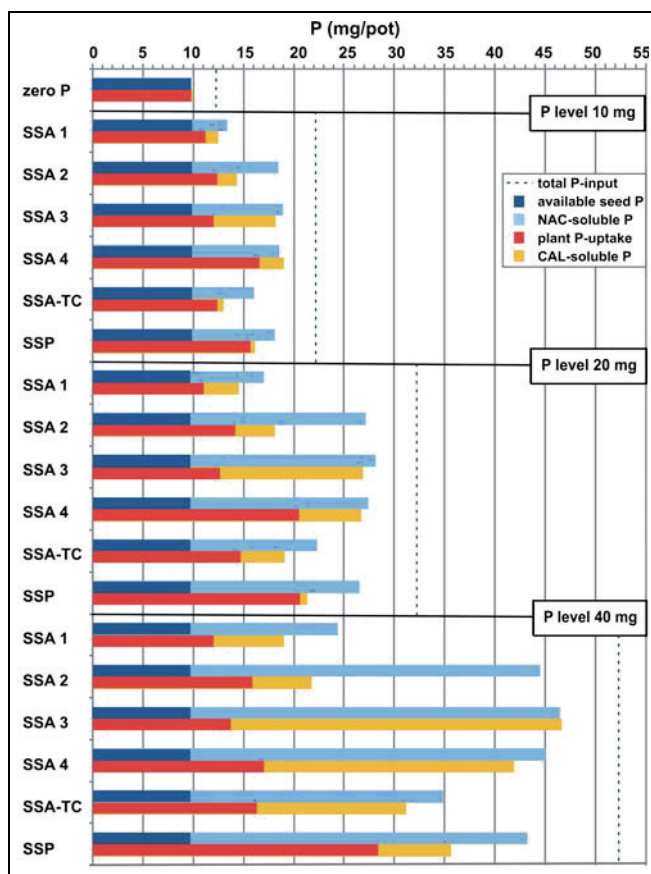
384

Fig. 6. Comparison of *total (= seed plus fertilizer) P input* (dotted green line), the *share of available P* (= available seed P, reflected by P-uptake of the zero P variant, plus NAC-soluble fertilizer P; shown in blue bars) and „*transferred P*" (= P uptake by plants plus soluble P (P-CAL) left over in the substrate after the end of the experiment; shown in red/orange bars) for the different fertilizer variants.

available mineral P fertilizers and to reduce heavy metal concentrations below the limit values of the DüMV.

However, results of the reported trial show that there are still some difficulties to overcome in order to produce viable P fertilizers: The acid leaching procedure alone was not able to reduce the high Al/Fe contents of the products, which caused the preferential formation of non-bioavailable Al-/Fe-phosphates. P uptake achieved by the resulting products remained significantly below that of the commercial mineral P fertilizer used as control.

While an exchange of the cations Al and Fe against Na was able to enhance the plant availability of P, resulting in a P uptake in the same order of magnitude as a commercial P fertilizer, it induced other difficulties related to the resulting increase in Na content, which proved harmful to the plants at the higher fertilization levels. As discussed above, the severe effects observed in the Neubauer experiment were most likely related to the experimental design, using a small volume of a non-buffering sand substrate with a large number of plants, Such a closed, non-buffered system is of course very sensitive to nutrient imbalances, which would probably not occur under field conditions, where plants are growing in a large volume of soil with better buffering capacity. However, these observations highlight the fact that for recycling products – as of course for any other fertilizers as well – it is important to adjust application rates to the actual crop demand and to prevent over-supply in order to minimize the risk of other components to cause imbalances when added to the system at higher concentrations.

It can be concluded that, to make the ash-based recycling fertilizers more attractive, further research is needed to find (or optimize) a procedure which will make the ash-P more plant available and at the same time result in a product which is low in or almost free from growth-reducing contaminants such as sodium or heavy metals, and to deliver a stable plant available P fertilizer product.

Another important question raised by this experiment is the suitability of standard extraction procedures for P recycling fertilizers to estimate their P plant availability. Future research should focus on additional options to describe P solubility of fertilizers more accurately, particularly P sink methods such as Fe-oxide resin bags or DGT.

Finally, the data also revealed that even the untreated ash contains a certain amount of plant available P, which implies that specific measures are necessary when long-term storage of mono-incinerated ash is planned to prevent unwanted P losses to adjacent soils, the groundwater and surface water bodies such as lakes or rivers.

showed a high solubility in NAC (86.9%). Furthermore, at the higher P levels (20 and 40 mg), a considerable share of the input of available P remains unaccounted for in the „transferred P" (Fig. 6). This suggests a low stability of the P forms added by SSA 2, which seem to have re-precipitated as unavailable P minerals again when used as fertilizer.

4 Conclusion

By incinerating sewage sludge and using the resulting monoincineration ash for fertilizer production, up to 90% of the P inflow into the waste water treatment plant can be recovered and utilized (Kʀüɢᴇʀ et al., 2016). Sewage sludge ash-based recycling fertilizers show a good potential to contribute to a sustainable supply of P to agriculture.

The present investigations with sewage sludge ash that had been deposited for several years confirm this finding. The employed acid leaching procedure with subsequent stepwise raising of the solution pH was able to concentrate the phosphates up to the range of commercially

References

DIN EN 13346:2001-4: Characterization of sludges – Determination of trace elements and phosphorus – Aqua regia extraction methods.

Dᴜʙᴏᴄ, O., J. Sᴀɴᴛɴᴇʀ, Fᴀʀᴅ A. Gᴏʟᴇꜱᴛᴀɴɪ, F. Zᴇʜᴇᴛɴᴇʀ, J. Tᴀᴄᴄᴏɴɪ, W.W. Wᴇɴᴢᴇʟ, 2017: Predicting phosphorus availability from chemically diverse conventional and recycling fertilizers. Science of the Total Environment 599/600, 1160-1170.

Originalarbeit

EC Regulation No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilisers (OJ L 304, 21.11.2003, pp. 1-194).

EC, 2016: Commission Staff Working Document Impact Assessment Accompanying the document Proposal for a Regulation of the European Parliament and of the Council laying down rules on the making available on the market of CE marked fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009. http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:52016SC0064.

Hᴇᴜssɴᴇʀ, C., K. Fʀɪᴄᴋᴇ, P. Hᴀʀʙᴏʀᴛʜ, J. Rᴇɪɴʜᴀʀᴅᴛ, F. Kɴᴀᴘᴘᴇ, T. Sᴘᴇɴɢʟᴇʀ, A. Bʀᴇɪᴛᴇɴsᴛᴇɪɴ, K. Kɪᴇᴋʜäғᴇʀ, S. Kʀᴀᴛᴢ, E. Bʟᴏᴇᴍ, 2017: Phosphatrückgewinnung aus Deponien und Altablagerungen – Endbericht. MKLNUV Düsseldorf, 2017 [Online] https://www.umwelt.nrw.de/fileadmin/redaktion/PDFs/umwelt/phosphatrueckgewinnung_aus_deponien.pdf.

Kʀᴀᴛᴢ, S, S. Hᴀɴᴇᴋʟᴀᴜs, E. Sᴄʜɴᴜɢ, 2010: Chemical solubility and agricultural performance of P-containing recycling fertilizers. Landbauforschung vTI Agriculture and Forestry Research 60, 227-240.

Kʀᴀᴛᴢ, S., J. Sᴄʜɪᴄᴋ, E. Sᴄʜɴᴜɢ, 2016: Trace elements in rock phosphates and P containing mineral and organo-mineral fertilizers sold in Germany. Science of the Total Environment – Special Issue. Vol 542 Part B, pp. 1013-1019. Available online under: http://dx.doi.org/10.1016/j.scitotenv.2015.08.046.

Kʀüɢᴇʀ, O., C. Aᴅᴀᴍ, 2014: Monitoring von Klärschlammmonoverbrennungsaschen hinsichtlich ihrer Zusammensetzung zur Ermittlung ihrer Rohstoffrückgewinnungspotentiale und zur Erstellung von Referenzmaterial für die Überwachungsanalytik. UBA-Texte 49/2014.

Kʀüɢᴇʀ, O., K.P. Fᴀᴛᴛᴀʜ, C. Aᴅᴀᴍ, 2016: Phosphorus recovery from wastewater – necessity and possibilities. Desalination and Water Treatment 57, 15619-15627.

Mᴜʟʟɪɴs, G.L., F.J. Sɪᴋᴏʀᴀ, J.M. Bᴀʀᴛᴏs, H.H. Bʀʏᴀɴᴛ, 1990: Plant availability of phosphorus in the water-insoluble fraction of commercial triple superphosphate fertilizers. Soil Science Society of America Journal 54, 1469-1472.

Mᴜʀᴘʜʏ, J., J.P. Rɪʟᴇʏ, 1962: A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27, 31-36.

Nᴀɴᴢᴇʀ, S., A. Oʙᴇʀsᴏɴ, T. Hᴜᴛʜᴡᴇʟᴋᴇʀ, U. Eɢɢᴇɴʙᴇʀɢᴇʀ, E. Fʀᴏssᴀʀᴅ, 2014a: The molecular environment of phosphorus in sewage sludge ash: implications for bioavailability. Journal of Environmental Quality 43 (3), 1050-1060.

Nᴀɴᴢᴇʀ, S., A. Oʙᴇʀsᴏɴ, L. Bᴇʀɢᴇʀ, E. Bᴇʀsᴇᴛ, L. Hᴇʀᴍᴀɴɴ, E. Fʀᴏssᴀʀᴅ, 2014b: The plant availability of phosphorus from thermo-chemically treated sewage sludge ashes as studied by 33P labeling techniques. Plant and Soil 377, 439-456.

Nᴇᴜʙᴀᴜᴇʀ, H., 1931: Die Keimpflanzenmethode nach Neubauer und Schneider. In: Hᴏɴᴄᴀᴍᴘ, F. (Hrsg.): Düngemittel und Düngung. Handbuch der Pflanzenernährung und Düngerlehre, Band 2. Berlin, Springer Verlag, pp. 882-902.

Nᴇᴜʙᴀᴜᴇʀ, H., W. Sᴄʜɴᴇɪᴅᴇʀ, 1923: Die Nährstoffaufnahme der Keimpflanzen und ihre Anwendung auf die Bestimmung des Nährstoffgehalts der Böden. Zeitschrift für Pflanzenernährung und Düngung. A. Wissenschaftlicher Teil. Vol. 2, 329-362.

Pᴇᴘʟɪɴsᴋɪ, B., C. Aᴅᴀᴍ, M. Mɪᴄʜᴀᴇʟɪs, G. Kʟᴇʏ, F. Eᴍᴍᴇʀʟɪɴɢ, F.G. Sɪᴍᴏɴ, 2009: Reaction sequences in the thermo-chemical treatment of sewage sludge ashes revealed by X-ray powder diffraction – a contribution to the European project SUSAN. Zeitschrift für Kristallographie, Suppl. 30, 459-464.

Sᴄʜüʟʟᴇʀ, H., 1969: Die CAL-Methode. eine neue Methode zur Bestimmung des pflanzenverfügbaren Phosphats im Boden. Zeitschrift für Pflanzenernährung und Bodenkunde 123, 48-63.

Sᴛᴀᴛɪsᴛɪsᴄʜᴇs Bᴜɴᴅᴇsᴀᴍᴛ, 2016: Umwelt: Abwasserbehandlung – Klärschlamm. Ergebnisbericht 2013/2014. https://www.destatis.de/DE/Publikationen/Thematisch/UmweltstatistischeErhebungen/Wasserwirtschaft/Klaerschlamm.html.

Sᴛᴀᴜss, R., H. Bʟᴇɪʜᴏʟᴅᴇʀ, H. ᴠᴀɴ ᴅᴇɴ Bᴏᴍᴍ, L. Bᴜʜʀ, H. Hᴀᴄᴋ, M. Hᴇss, R. Kʟᴏsᴇ, U. Mᴇɪᴇʀ, E. Wᴇʙᴇʀ, 1994: Einheitliche Codierung der phänologischen Entwicklungsstadien mono- und dikotyler Pflanzen. Erweiterte BBCH-Skala. Basel.

Sᴛᴇᴄᴋᴇɴᴍᴇssᴇʀ, D., C. Vᴏɢᴇʟ, C. Aᴅᴀᴍ, D. Sᴛᴇғғᴇɴs, 2017: Effect of various types of thermochemical processing of sewage sludges on phosphorus speciation, solubility, and fertilization performance. Wast Management 62, 194-203.

VDLUFA (Hrsg.), 1991: VDLUFA-Methodenbuch Band I: Die Untersuchung von Böden. Darmstadt, VDLUFA-Verlag.

VDLUFA (Hrsg.), 2007: VDLUFA-Methodenbuch Band II.1: Die Untersuchung von Düngemitteln. Darmstadt, VDLUFA-Verlag.

385