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Identification and quantification of phosphate turnover indicators after long-term compost application – long-term and single season effects

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Abstract

Background and aims Soil organic phosphorus (P_{org}) is of interest for plant nutrition because it can comprise between 20 and 80% of total soil phosphate (P). This study aims to examine the effect of compost application on soil phosphatases and microbial biomass, which influence the P turnover and, furthermore, to examine the speciation of P_{org}.

Methods Soil from a long-term field experiment (since 1997) which compares compost application with inorganic fertilization was analyzed for calcium-acetate-lactate extractable P (CAL-P), Olsen-P, acid ($Acid-P_{ase}$) and alkaline ($Alk-P_{ase}$) phosphatase activity and microbial biomass P. P_{org} speciation was additionally analyzed with liquid-state ^{31}P nuclear magnetic resonance spectroscopy (^{31}P-NMR).

Results We found a significant increasing long-term effect of high compost application (equivalent to

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400 kg ha^{-1} N (400)) on Acid-P$_{ase}$ (45%) and Alk-P$_{ase}$ (58%). After compost application, Acid-P$_{ase}$ increased by 41% in treatment 400 (3 days after compost application (DAA)). The ^{31}P-NMR analysis showed a significant increase of inorganic orthophosphate (55%) after high compost application. Furthermore, the total phosphomonoester region was significantly decreased in the treatment 400 (8%).

Conclusions   We demonstrated that long-term compost application increases phosphatase activity which plays a key role in the mineralization of soil P$_{org}$. In particular, the decrease of the concentration of P$_{org}$ species in the phosphomonoester region in the treatment 400 with high compost application highlights that an increased turnover affects this soil P pool and may provide P to plants. This knowledge provides a better understanding of how the P cycle responds to long-term compost fertilization.

Keywords ^{31}P-NMR · Compost · Soil organic P speciation · Long-term field experiment · Microbial biomass P · Phosphatase activity

Abbreviations

P$_{org}$	Soil organic phosphate
P	Phosphate
CAL-P	Calcium-acetate-lactate extractable P
Olsen-P	Olsen extractable P
^{31}P-NMR	^{31}P nuclear magnetic resonance spectroscopy
Acid-P$_{ase}$	Acid phosphatase activity
Alk-P$_{ase}$	Alkaline phosphatase activity
Orth-P	Orthophosphate detected by ^{31}P-NMR
Mic-P	Microbial biomass P
IP$_6$	*myo*-Inositol-1,2,3,4,5,6-hexakisphosphate of phytate
UBS	Unresolved phosphomonoesters represented by an underlying broad signal
100	100 kg Compost-N ha^{-1} a^{-1}
400	400 kg Compost-N ha^{-1} a^{-1}
DAA	Days after application
SDF	Spectral deconvolution fitting

Introduction

The phosphate (P) concentration in the soil solution is generally low due to its high sorption affinity and, therefore, P fertilization with mainly water soluble inorganic P fertilizers is mandatory for plant production (Shen et al. 2011). However, P is also a limited nonrenewable resource (van Vuuren et al. 2010) which increases the need to find alternative P fertilizers such as recycled organic waste as compost. Composts can be an important P fertilizer because they contain a high proportion of potentially plant available P (Frossard et al. 2002; Sharpley and Moyer 2000).

Long-term field experiments are very useful to determine the effect of slow release fertilizers, such as compost, on various soil characteristics like microbial biomass and activity, e.g. phosphatase activity. It has been shown that long-term compost application may increase the amount and alter the composition of soil microorganisms in soil (Liu et al. 2022b). Soil microorganisms play an important role in the soil P cycle by decomposing added organic material and retaining P in the form of microbial biomass P (Mic-P) (Richardson and Simpson 2011). Soil microorganisms and plants can mineralize organic matter by releasing enzymes, for example, phosphatases. Plants, bacteria and fungi can synthesize and secrete acid phosphatase in order to hydrolyze organic soil P (P$_{org}$) species in soil (Ciereszko et al. 2011; He et al. 2022; Quiquampoix and Mousain 2005). However, alkaline phosphatase can only be secreted by soil microorganisms, but not by plants (Kruse et al. 2015; Nannipieri et al. 2010). Furthermore, a spatial separation between acid and alkaline phosphatase activity can be seen in the rhizosphere (Spohn and Kuzyakov 2013).

Acid and alkaline phosphatases catalyze the hydrolysis of monoester bonds of P$_{org}$ with a subsequent release of inorganic P to the soil solution which then can be taken up by plants, soil microorganisms or be adsorbed to soil particles (Blake et al. 2005). Thus, phosphatases are very important enzymes in the soil P cycle (Bünemann 2015). Furthermore, it was shown that soils with a high soil organic matter content exhibit an increased enzyme activity such as acidic and alkaline phosphatase (Lalande et al. 1998; Christopoulou et al. 2021).

Soil P$_{org}$ is of interest for plant nutrition because it can comprise between 20 and 80% of total soil P (Dalai 1977). Liquid-state ^{31}P nuclear magnetic resonance spectroscopy (^{31}P-NMR) is an important technique for soil P$_{org}$ characterization (Cade-Menun 2017) which was used for the first time on soils by Newman and Tate (1980) and since then has

increased the knowledge about the constitution of soil P_{org}. Furthermore, the related extraction and analysis techniques have been improved over the years and, therefore, a more precise characterization of soil P_{org} became possible (McLaren et al. 2020).

Liquid-state ^{31}P-NMR studies showed that the constitution of P_{org} varies worldwide and is usually dominated by phosphomonoesters (Stutter et al. 2012). One prominent P_{org} form in the phosphomonoester region of a ^{31}P-NMR spectrum is *myo*-inositol-hexakisphosphate (IP_6), also known as phytate (Turner et al. 2002) which is a storage form of P in seeds and other plant organs (Raboy 2003). IP_6 is deprotonated between pH 5 and 12 (Barrientos and Murthy 1996) and has several ionic charges, therefore, IP_6 can form complexes with Ca and can be adsorbed to iron/aluminum hydroxides or to specific clay minerals (Turner et al. 2002; Celi and Barberis 2007). IP_6 is adsorbed by their phosphate groups which, for example, reacts the same way with iron oxides, as free phosphate does (Celi and Barberis 2007). Because of the strong adsorption and low release, IP_6 is protected from mineralization and accumulates in soils (Celi et al. 2003). However, also lower order inositol phosphates can be found in the phosphomonoester region of the ^{31}P-NMR spectrum of soils (Reusser et al. 2020b). Furthermore, the phosphomonoester region appears with an underlying broad signal (UBS) in ^{31}P-NMR spectra which is caused by overlapping phosphomonoester species of different molecular weights and of unresolved chemical structure (McLaren et al. 2022; Reusser et al. 2022). These phosphomonoesters of unresolved chemical structure can comprise on average 50% of total P_{org} in soil (McLaren et al. 2020). Thus, quantification is difficult due to overlapping signals of P_{org} species in the phosphomonoester region and, furthermore, this can lead to overestimations of certain P_{org} species. This problem can be reduced by using a spectral deconvolution fitting procedure that includes the UBS (Reusser et al. 2020a).

P_{org} in soil can reach a high concentration and, thus, contribute to plant nutrition, although, it is often not taken into account when making fertilizer recommendations using conventional soil testing methods (e.g. CAL, Olsen) (Steffens et al. 2010). Additionally, if the adsorptions sites are blocked in the soil by P_{org}, the quantity of inorganic P in the soil solution may also increase.

The ^{31}P-NMR analysis has been widely used in agriculture to analyze P species in cropping systems (Cade-Menun 2017). It was shown, for example, that long-term organic fertilization application did not change the P_{org} species composition in soil, but led to an increasing effect on inorganic orthophosphate (Ortho-P) (Ahlgren et al. 2013; Annaheim et al. 2015; Glæsner et al. 2019; Koch et al. 2018; Requejo and Eichler-Löbermann 2014). However, in those studies, soil samples were taken only once in the season and not at planned intervals which could mean that a visible effect in the ^{31}P-NMR spectra directly after application of organic fertilizers was overlooked. Taking one sample, may not give the same results as taking many samples at regular intervals since increased enzyme activity and microbial biomass may decrease the visible effect through mineralization over time.

In the previous studies (e.g. Glæsner et al. (2019) and Koch et al. (2018)) the turnover of compost P in the soil after application was investigated at the process level taking only one sample, however, our approach is to take several samples at planned intervals within a season from seeding to harvest. Additionally, we will determine the effects of enzyme activity and microbial biomass. It was hypothesized that (1) long-term compost application increases P_{ase} activity, Mic-P and changes the composition of the P_{org} species in soil and (2), furthermore, increases the pool of CAL-P and Olsen-P which characterizes plant available P. Additionally, we hypothesized (3) that, immediately following a compost application, the concentration of P_{org} species increases in the beginning and later decreases again, simultaneously, with an increasing P_{ase} activity due to increased mineralization. As a result (4) the phosphomonoesters including the underlying broad signal are not affected by compost application in the long-term.

Material and methods

Study site and soil collection

The compost long-term experiment is located at the experimental station "Heidfeldhof ", belonging to the University of Hohenheim (map coordinates: 48° 42′ 56.8" N, 9° 11′ 36.7" E) and was established in the year 1997. The soil is a loamy soil (Luvisol) originating from alluvial sediments and also known

as Filder loam (Table 1). The randomized complete block design has eight treatments with four replications, respectively. It has a 3-year crop rotation with maize (*Zea mays* L.), winter wheat (*Triticum aestivum* L.) and spring barley (*Hordeum vulgare* L.). Municipal household compost has been applied and incorporated. A mature compost was used with a slightly alkaline pH value (Table 2). Before application, the nitrogen (N) concentration of the actual compost was determined. An annual amount of compost was applied corresponding to 100 kg (100) and 400 kg (400) Compost-N ha^{-1} a^{-1} in compost treated plots. In 2021, 5 t compost ha^{-1} were applied in treatment 100, while 20 t compost ha^{-1} were applied in treatment 400. In the positive control, the three crops have been fertilized with calcium ammonium nitrate (CAN, 17% N) only. In the investigated year 2021, 140 kg N ha^{-1} were applied to maize as CAN. A control treatment remained unfertilized since the establishment of the experiment. Compost and CAN were applied by hand and incorporated with a rotary harrow including the unfertilized control. Then maize was sown in all plots (Cultivar: Ronaldinio, KWS Saat, Einbeck, Germany).

The soil was sampled from the above mentioned four treatments (Control, 100, 400 and CAN) between May and September 2021. Fifteen soil samples (0–10 cm, diameter of the core: 1.5 cm) were taken in each plot per sampling date, then bulked and thoroughly mixed. On each sampling date, the same rows were sampled and the same number of samples were taken in each row. The location of the samples in each row were chosen randomly. Hence, 16 mixed samples (4 treatments × 4 repetitions) were taken on nine sampling dates: 1 day before compost application, 1 day

after compost application (DAA), 3 DAA, 7 DAA, 14 DAA, 28 DAA, 56 DAA, 84 DAA, and 140 DAA. The second sample (1 DAA) was taken after sowing, and the last sample (140 DAA) was taken after harvest. The fresh soil samples of each sampling day were stored in a refrigerator (5 °C) until measurement

Table 2 Chemical properties of the applied compost. The P concentration in the compost extract was determined in CAL, Olsen and NaOH+EDTA extracts. Total P was determined in the aqua regia solution. The determination method is labelled with a small letter

Compost properties	Median
pH$_{CaCL2}$	7.6
C[a] (%)	28
P$_{CAL}$[b] (mg kg^{-1})	937.6
P$_{Olsen}$[c] (mg kg^{-1})	368
P$_{Total}$[b] (mg kg^{-1})	3444.8
Fe$_{NaOH}$[b] (mg kg^{-1})	1822.9
Al$_{NaOH}$[b] (mg kg^{-1})	810.1
Mn$_{NaOH}$[b] (mg kg^{-1})	914.8
Orthophosphate[d] (mg kg^{-1})	2945.5
Total phosphomonoester region[d] (mg kg^{-1})	60.2
IP$_6$[d] (mg kg^{-1})	11.7
β-glycerophosphate[d] (mg kg^{-1})	1.1
Phospholipid-P[d] (mg kg^{-1})	3.0
DNA-P[d] (mg kg^{-1})	4.8
Pyrophosphate[d] (mg kg^{-1})	3.0

[a]Total carbon (C) content was determined by dry combustion (DIN EN 15936:2012–11)

[b]Determination by ICP-OES

[c]Colorimetric determination according to Murphy and Riley (1962)

[d]Determined by ^{31}P-NMR in NaOH-EDTA extracts (Ratio 1:40)

Table 1 Soil physical and chemical properties of the different treatments

	pH$_{CaCl2}$ Median	C[a]	Fe$_{NaOH}$[b]	Al$_{NaOH}$[b]	Mn$_{NaOH}$[b]	Ca$_{NaOH}$[b]	Sand	Silt	Clay
		%	mg kg^{-1}				%		
Control	6.7	1.0±0.02	59.4±39.6	449.5±111.8	5.0±0.7	3021±189	2	64	33
100	6.7	1.4±0.1	138.7±45.0	517.3±37.1	5.5±0.5	3703±278	2	64	33
400	6.9	2.2±0.2	181.7±100.2	412.8±101.3	6.8±0.9	5023±334	2	64	33
CAN	6.5	1.2±0.01	77.1±48.0	459.7±77.6	6.2±0.9	3279±223	2	64	33

[a]Soil total carbon (C) content was determined by dry combustion (DIN EN 15936:2012–11)

[b]Determination by ICP-OES in NaOH+EDTA extracts

[c]Soil texture was determined according to DIN ISO 11277:2002–08 and Köhn (1928)

of phosphatase activity and microbial biomass. The remaining soil was then air dried and sieved (2 mm) for further analysis.

General soil analyses

Calcium-acetate-lactate extractable P (CAL-P) was extracted according to Schüller ([1969](#)) and Olsen-P was extracted according to Olsen et al. ([1954](#)). CAL-P was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, 5110 ICP-OES, Agilent Technologies, Santa Clara, USA) and Olsen-P colorimetrically according to Murphy and Riley ([1962](#)). Total soil P was determined by ICP-OES after microwave pressure digestion with the aqua regia solution (32% hydrochloric acid, 65% nitric acid, 3:2) (VDLUFA [2011](#)). Before the digestion the soil was finely ground.

The pH value was determined in a suspension of the soils with 0.01 M $CaCl_2$ solution (soil to solution ratio: 1:2.5 w/w) (VDLUFA [2016](#)). The total carbon (C) content was determined by dry combustion (DIN EN 15936:2012–11).

Acid and alkaline phosphatase activity

Acid (Acid-P_{ase}) and alkaline phosphatase (Alk-P_{ase}) activity were measured according to Tabatabai and Bremner ([1969](#)) and with a modification in accordance with Rubio et al. ([1990](#)), respectively. Briefly described, 2 g fresh soil were mixed with 2 ml 0.115 M p-Nitrophenylphosphate (pNPP, No. 224–246-5, Carl Roth, Karlsruhe, Germany) and 8 ml modified universal buffer with a pH of 5.5 (Acid-P_{ase}) or 8.5 (Alk-P_{ase}) were added. Soil samples were incubated for one hour at 20 °C in a water bath and afterwards the reaction was stopped with 0.5 M $CaCl_2$. Samples were filtered (MN 619, Macherey–Nagel, Düren, Germany) and 1.20 ml filtrate was mixed with 0.40 ml 0.5 M NaOH and 13.40 ml deionized H_2O. Samples were centrifuged for 10 min at 2500 g and photometrically measured at 400 nm (Spectrophotometer U-2900, Hitachi, Tokyo, Japan). An internal standard was used to detect measurement errors.

Microbial biomass P

Microbial biomass P (Mic-P) was estimated according to Brookes et al. ([1982](#)). The soil samples were

sieved (5 mm) and roots were removed. However, we did not apply other methods, such as described in Mueller et al. ([1992](#)), to remove fine roots. In brief, 10 g fresh soil were fumigated for 24 h with chloroform and then fumigated and unfumigated samples were treated with 0.5 M $NaHCO_3$ (pH 8.5) solution and shaken for 30 min (150 min^{-1}) in a climate-controlled room at 25 °C on an orbital shaker. Then samples were filtered (MN 619, Macherey–Nagel, Düren, Germany) and the phosphate concentration was measured colorimetrically (Spectrophotometer U-2900, Hitachi, Tokyo, Japan) according to Murphy and Riley ([1962](#)). An internal standard was used to detect measurement errors. The P recovery was tested by the addition of a spike of inorganic P equivalent to 25 µg P g^{-1}.

Liquid-state ^{31}P nuclear magnetic resonance (^{31}P-NMR) spectroscopy

Extraction for ^{31}P-NMR was done according to Cade-Menun and Preston ([1996](#)) and with a soil to solution ratio of 1:4 according to McLaren et al. ([2015](#)). Briefly, 8 g of air dried and sieved (2 mm) soil was extracted with 32 ml 0.25 M NaOH + 0.05 M Na_2EDTA (NaOH-EDTA) (ratio 1:4). The compost was extracted with a ratio of 1:40 because a ratio of 1:4 caused line broadening. Then the suspension was shaken for 16 h (160 min^{-1}) in a tempered room at 21 °C on an orbital shaker, centrifuged at 3714 g for 30 min and filtrated (Filter paper: Blue ribbon, 589/3, Schleicher & Schuell, Germany). A 20 ml aliquot was frozen in liquid nitrogen and freeze-dried. Lyophilization yielded 0.55–0.69 g freeze dried material. In the remaining supernatants of the NaOH-EDTA extracts, molybdate reactive P (MRP) was measured with the molybdenum blue method according to Murphy and Riley ([1962](#)) and total P, Al, Fe, Mg and Mn was measured by ICP-OES. The difference between MRP and total P is determined as molybdate unreactive P (MURP).

For ^{31}P-NMR, the treatments control and 400 and sampling dates 1-day prior application, 1 DAA, 28 DAA and 140 DAA) were selected. In total, 16 soil samples and one compost sample were analyzed in a time span of three weeks. Every day, 80 mg of the freeze-dried sample were re-dissolved in 400 µl D_2O (Sigma-Aldrich: 450,510). Then 200 µl of the stock solution was added which contained 140 µl

D_2O, 50 µl 32.2 mM methylenediphosphonic acid (MDP, Sigma-Aldrich: M9508) and 10 µl of 14.2 M NaOD (Sigma-Aldrich: 372,072) for each sample. After mixing the sample with the stock-solution, the solution was vortexed and subsequently centrifuged for 30 min at 10,000 g and analyzed on the same day. In order to reduced weighing errors, a stock solution was prepared that was added to the newly weighed freeze dried soil extract every day.

The compost sample was treated with Na_2S (Sigma-Aldrich: S407410) in order to reduce the amount of paramagnetic ions according to Vincent et al. (2013). Briefly, 120 mg of lyophilized material were re-dissolved in 600 µL of a 38 mM Na_2S solution in D_2O. The solution was left for precipitation for 15 h, vortexed and then centrifuged for 30 min at 10,000 g. An aliquot of 400 µl was mixed with 200 µl of the stock solution and analyzed on the same day.

^{31}P-NMR measurements were recorded on a Bruker 600 MHz spectrometer (Avance III HD, Bruker Corporation, Billerica, MA, USA), equipped with a 5 mm Prodigy BBO cryoprobe, at a ^{31}P frequency of 243 MHz at the Core Facility Hohenheim. The ^{31}P experiments were recorded with 2 k to 4 k scans, depending on the recycle delays and the signal-to-noise ratio. The total measurement time did not exceed 16 h in order to limit degradation. Recycle delays varied from 13 to 16 s for compost treated soils of the treatment 400 and from 18 to 24 s for the control soil samples, being at least 5 times the T1 relaxation time of orthophosphate (as the slowest relaxing compound), which was acquired for each sample individually by inversion-recovery experiments. Spectra were phased and the baseline was corrected automatically with manual adjustments, if needed. Acquisition, processing and determination of non-overlapped integrals were performed using the Bruker TopSpin 3.6.1. software (Bruker Corporation, Billerica, MA, USA). Orthophosphate and peaks in the phosphomonoester region were quantified with a spectral deconvolution fitting (SDF) procedure in MATLAB® R2021b (The Math-Works, Inc., Natick, MA, USA) that fits a Lorentzian/Gaussian line shape to the orthophosphate peak and peaks in the phosphomonoester region. The MATLAB® script is based on the matNMR toolbox (Version 3.9.144, Jacco van Beek) and the peakfit82 function (Version 8.3, ©Thomas C. O'Haver, 2015). Furthermore, it included the UBS as described in Reusser et al. (2020a).

All peaks of P species determined by ^{31}P-NMR were identified by previous spiking experiments. We used phytate (Sigma-Aldrich: P8810), β-glycerophosphate (Sigma-Aldrich: G5422), phosphatidylcholin (Sigma-Aldrich: P3556), DNA (Sigma-Aldrich: D1626) and pyrophosphate (Sigma-Aldrich: P8135).

Data analyses

The statistical analysis was done in SAS 9.4 (SAS Institute, Cary, NC, USA) and in RStudio using the R environment (RStudio Team 2016; R Core Team 2020). The soil sampling dates and the different treatments were compared using a linear mixed model for repeated measures. The model can be described as follows:

$$y_{ijk} = \mu + \alpha_i + \beta_j + \gamma_k + (\alpha\beta)_{ij} + (\beta\gamma)_{ik} + e_{ijk}$$

where y_{ijk} is the measurement of treatment i in block y at date j, μ is the intercept, α_i is the fixed effect of the i-th treatment (Control, 100, 400 and CAN), β_j is the fixed effect of the j-th sampling date, γ_k is the block effect of the k-th block, $(\alpha\beta)_{ij}$ is the fixed interaction effect between the i-th treatment and the j-th sampling date, $(\beta\gamma)_{jk}$ is the fixed interaction effect between the j-sampling date and the k-th block and e represents the error of y_{ijk}. A first order autoregressive variance–covariance structure with date-specific variance was assumed. The residuals of the model were checked for normality and homoscedasticity (despite the heterogeneity already accounted for) via residual plots. Tukey's honest significance test was used to compare means at $\alpha = 0.05$ and letters were used to display the results of the comparison (Piepho 2004, 2012). All graphics were created using the R package *ggplot2* (Wickham 2016).

Results

Soil properties

An overview of the soil chemical and physical characteristics is shown in Table 1. The long-term compost application in the treatment 400 increased the pH value from slightly acidic (pH 6.7) to neutral (pH 6.9). There was no difference in soil pH between the

control and the treatment 100. The lowest pH value of about 6.5 was found in the CAN treatment.

The treatment 400 had a significantly higher total soil C content before compost application (1.9% total C) compared to the other treatments (Control (1.0% total C), 100 (1.3% total C) and CAN (1.2% total C)) and after compost application, the total C content increased significantly from 1.9% until 2.4% 14 DAA (supplementary material, Fig. S1). The compost application in the year 2021 did not show a significant increase of the total soil C content in treatment 100.

One day before compost application, CAL-P (160.8 mg kg^{-1}) was higher in the treatment 400 compared to all other treatments (Control (77.5 mg kg^{-1}), 100 (111.4 mg kg^{-1}) and CAN (76.4 mg kg^{-1})) (Fig. 1). The treatment 100 was found to have higher CAL-P compared to the control and was significantly higher for some sampling days (1 DAA, 14 DAA, 28 DAA, 56 DAA and 84 DAA). Except for the first sampling date, the CAL-P for the CAN treatment was significantly lower than that of the treatment 100. However, the CAL-P of the CAN treatment was not different from that of the control.

In the treatment 400, CAL-P increased significantly on date 3 DAA (186.0 mg kg^{-1}) compared to one day before compost application.

Long-term compost application since 1997 increased soil Olsen-P significantly in the treatment 400 (67.0 mg kg^{-1}) sampled a day before the recent compost application as compared to the control (39.0 mg kg^{-1}) and CAN (39.9 mg kg^{-1}) treatments (Fig. 2). The Olsen-P concentration was higher in sampling dates after compost application in the treatment 400 compared to nearly all other treatments except for one day before compost application and 140 DAA. Generally, compost application in treatment 100 showed a non-significant increase in soil Olsen-P levels compared to the control.

A significant increasing effect after compost application on soil Olsen-P (3 DAA: 83.7 mg kg^{-1}) was found in the treatment 400.
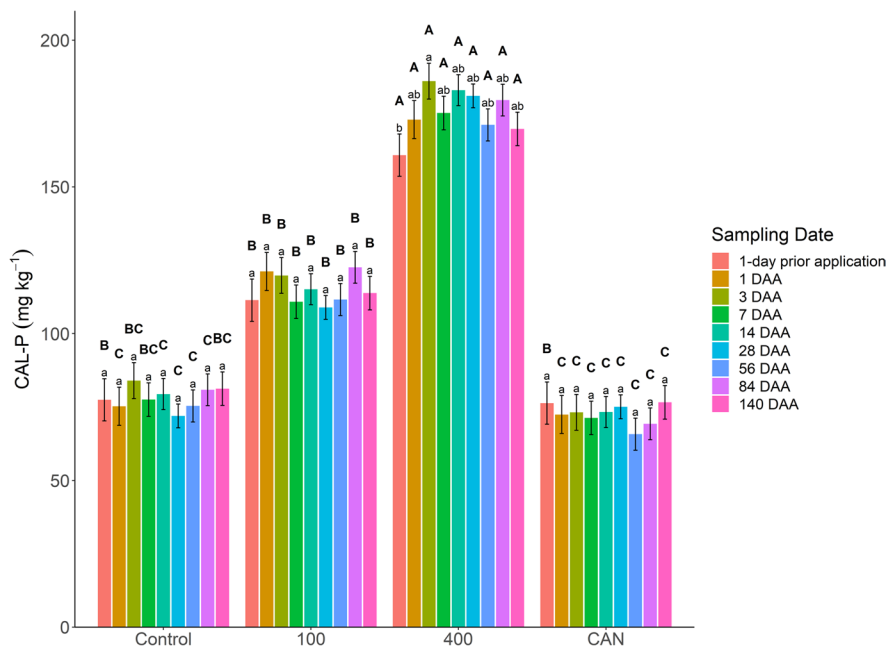

Fig. 1 Soil CAL-P. Soil samples were taken from the treatments: control, compost application rates equally to 100 kg N ha^{-1} a^{-1} (100) and 400 kg N ha^{-1} a^{-1} (400), and mineral calcium ammonium nitrate fertilization 140 kg N ha^{-1} a^{-1} (CAN), before compost application (1-day prior application) and up to 140 days after compost applica-tion (140 DAA). Small letters compare sampling dates within a specific treatment and capital letters compare treatments for each sampling date. Bars with the same letter are not signifi-cantly different according to a linear mixed model for repeated measures ($p < 0.05$). The error bars represent the standard error
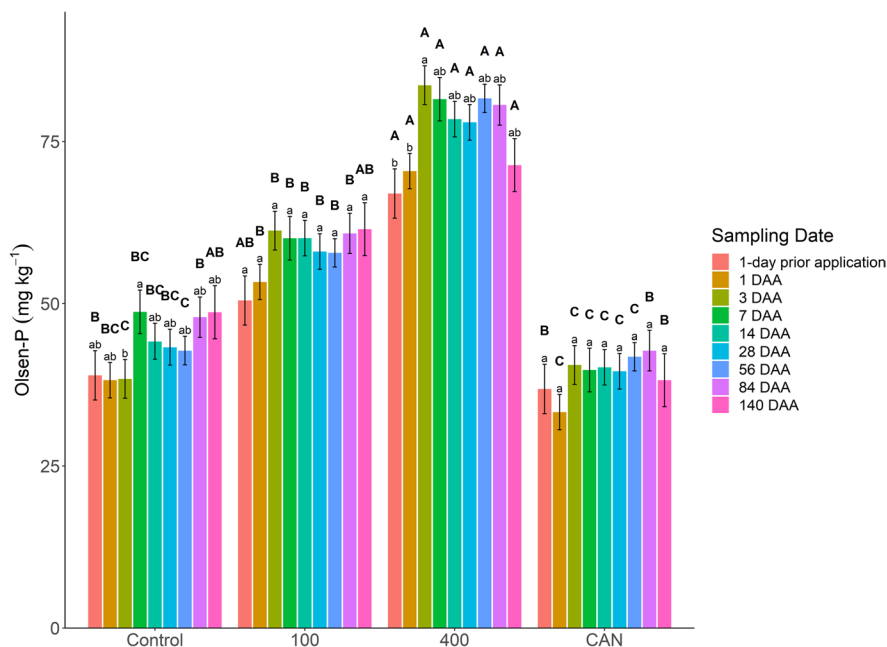
Fig. 2 Soil Olsen-P. Soil samples were taken from the treatments: control, compost application rates equally to 100 kg N ha^{-1} a^{-1} (100) and 400 kg N ha^{-1} a^{-1} (400), and mineral calcium ammonium nitrate fertilization 140 kg N ha^{-1} a^{-1} (CAN), before compost application (1-day prior application) and up to 140 days after compost applica-tion (140 DAA). Small letters compare sampling dates within a specific treatment and capital letters compare treatments for each sampling date. Bars with the same letter are not signifi-cantly different according to a linear mixed model for repeated measures ($p < 0.05$). The error bars represent the standard error

Soil phosphatase activity

At sampling date one day before compost applica-tion, treatment 400 (138.7 µg p-NP g^{-1} DM h^{-1}) showed a significantly higher soil acid phosphatase activity (Acid-P$_{ase}$) compared to the control (95.4 µg p-NP g^{-1} DM h^{-1}) (Fig. 3). Starting with sampling date 3 DAA (195.9 µg p-NP g^{-1} DM h^{-1}), Acid-P$_{ase}$ activity increased in the treatment 400 compared to all other treatments until 56 DAA (285.4 µg p-NP g^{-1} DM h^{-1}). The Acid-P$_{ase}$ activity was not significantly different between the treatment 100 and the control except for sampling dates 56 DAA and 140 DAA. There were no significant differences on most sam-pling dates between 100 and CAN.

All treatments showed a gradual increase in Acid-P$_{ase}$ activity with a peak between 56 DAA (100: 209.8 µg p-NP g^{-1} DM h^{-1}; 400: 285.4 µg p-NP g^{-1} DM h^{-1}; CAN: 184.7 µg p-NP g^{-1} DM h^{-1}) and 84 DAA (Control: 186.5 µg p-NP g^{-1} DM h^{-1}). At 140 DAA Acid-P$_{ase}$ activity dropped significantly in all treatments to the level before application.

The Acid-P$_{ase}$ activity was correlated to soil total C with a Spearman's rank correlation coefficient (R_s): $R_s = 0.44$ ($p = 0.008$) (Fig. S2a).

In the treatment 400 (122.6 µg p-NP g^{-1} DM h^{-1}), soil alkaline phosphatase activity (Alk-P$_{ase}$) was sig-nificantly increased compared to the control (77.5 µg p-NP g^{-1} DM h^{-1}), 100 (93.1 µg p-NP g^{-1} DM h^{-1}) and CAN (77.7 µg p-NP g^{-1} DM h^{-1}) one day before compost application (Fig. 4). Furthermore, Alk-P$_{ase}$ activity was the highest in the treatment 400 and was different for each sampling date compared to the other treatments. A comparison of sampling dates between control, 100 and CAN showed a similar Alk-P$_{ase}$ activity and in most cases no significant differences.

In the treatment 400, compost application increased Alk-P$_{ase}$ activity with an increase up to 7 DAA (247.7 µg p-NP g^{-1} DM h^{-1}) and then Alk-P$_{ase}$ activity decreased to the same level as before application. The same pattern can be seen in the treat-ments control, 100 and CAN. After harvest, Alk-P$_{ase}$ activity decreased close to the initial value in all treat-ments (Fig. 4).
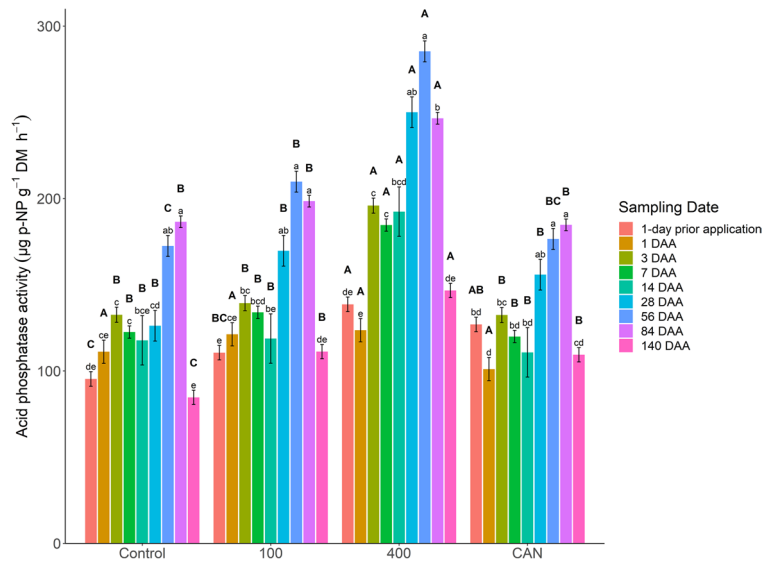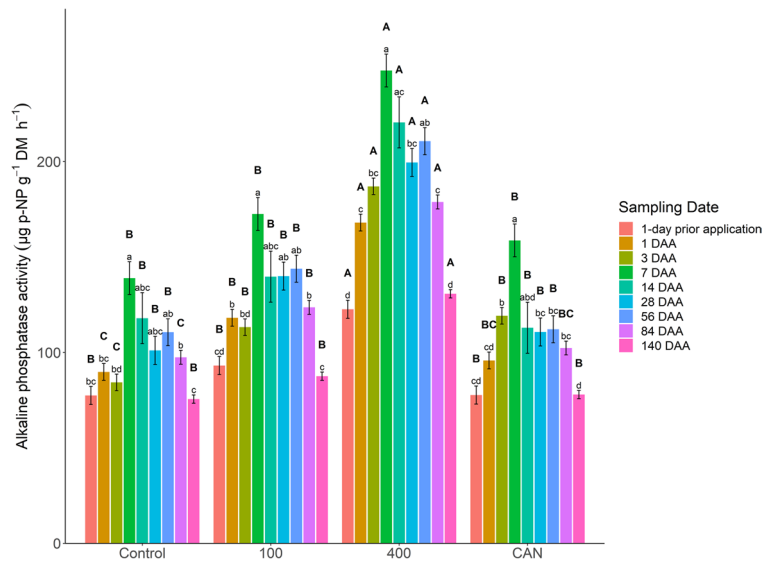
Fig. 3 Soil acid phosphatase activity. Soil samples were taken from the treatments: control, compost application rates equally to 100 kg N ha^{-1} a^{-1} (100) and 400 kg N ha^{-1} a^{-1} (400), and mineral calcium ammonium nitrate fertilization 140 kg N ha^{-1} a^{-1} (CAN), before compost application (1-day prior application) and up to 140 days after compost applica- tion (140 DAA). Small letters compare sampling dates within a specific treatment and capital letters compare treatments for each sampling date. Bars with the same letter are not signifi- cantly different according to a linear mixed model for repeated measures ($p < 0.05$). The error bars represent the standard error

Fig. 4 Soil alkaline phosphatase activity. Soil samples were taken from the treatments: control, compost application rates equally to 100 kg N ha^{-1} a^{-1} (100) and 400 kg N ha^{-1} a^{-1} (400), and mineral calcium ammonium nitrate fertilization 140 kg N ha^{-1} a^{-1} (CAN), before compost application (1-day prior application) and up to 140 days after compost applica- tion (140 DAA). Small letters compare sampling dates within a specific treatment and capital letters compare treatments for each sampling date. Bars with the same letter are not signifi- cantly different according to a linear mixed model for repeated measures ($p < 0.05$). The error bars represent the standard error

Alk-P_{ase} and soil total C showed a strong correlation ($R_s = 0.70$; $p < 0.001$) (Fig. S2b).

Microbial biomass P

Generally, the variability of microbial biomass P (Mic-P) was high in the different treatments as compared to the variability in P_{ase} activity, which is indicated by higher standard errors (Fig. 5). The treatment 400 showed the highest Mic-P on sampling date 14 DAA (75 mg kg^{-1}) compared to all other treatments.

^{31}P-NMR analysis

In the remaining supernatants of the NaOH-EDTA extracts, molybdate reactive P concentration (MRP) showed a significant increase in treatments 400 (515 mg kg^{-1}) compared to the control (330 mg kg^{-1}) (Table 3). However, the mean concentration of molybdate unreactive P (MURP) was higher in the control (75.1 mg kg^{-1}) compared to the treatment 400 (69.6 mg kg^{-1}) (Table 3).

All results of the ^{31}P-NMR analysis are shown in Table 3 and in Fig. S3 to Fig. S6 and Fig. S8. The total P concentration determined by ^{31}P-NMR in NaOH-EDTA extracts was the highest in the treatment 400 (582.1 mg kg^{-1}) compared to the control (414.5 mg kg^{-1}). Specifically, total P was 40% higher in the treatment 400 compared to the control (Table 3).

Inorganic orthophosphate (Ortho-P) had the highest concentration compared to all other P species (401.3 mg kg^{-1}) (Table 3) and also proportionally the highest share of total P (79.9%) (Table S2). Long-term compost application led to a strong increase in total mean Ortho-P in the treatment 400 of about 55%. However, the Ortho-P concentration in the control without compost application also increased at sampling date 1 DAA. In summary, the total mean of the treatment 400 (487.8 mg kg^{-1}) was significantly higher compared to the control (314.7 mg kg^{-1}) (Table 3).

The average of the total phosphomonoester region in the ^{31}P-NMR spectrum (5.30 ppm-2.80 ppm) across the treatments control and 400 was the largest of all P_{org} fractions in this study with a total average
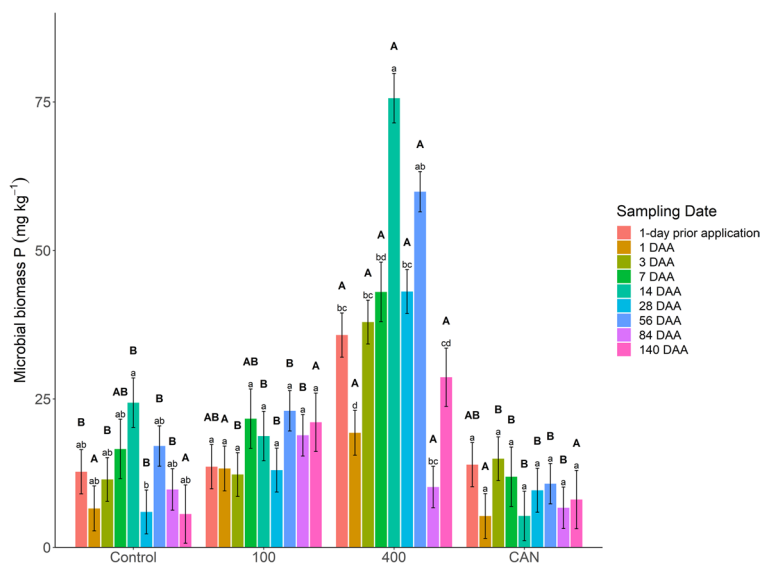

Fig. 5 Soil microbial biomass P. Soil samples were taken from the treatments: control, compost application rates equally to 100 kg N ha^{-1} a^{-1} (100) and 400 kg N ha^{-1} a^{-1} (400), and mineral calcium ammonium nitrate fertilization 140 kg N ha^{-1} a^{-1} (CAN), before compost application (1-day prior application) and up to 140 days after compost applica-

tion (140 DAA). Small letters compare sampling dates within a specific treatment and capital letters compare treatments for each sampling date. Bars with the same letter are not significantly different according to a linear mixed model for repeated measures ($p < 0.05$). The error bars represent the standard error

Table 3 Soil P pools determined by colorimetry and liquid state ^{31}P-NMR analysis of NaOH-EDTA soil extracts. The concentration of total P represents the sum of orthophosphate, the total phosphomonoester region (including e.g. inositol hexakisphosphate (IP6)), phospholipid-P, DNA-P and pyrophosphate-P detected by ^{31}P-NMR in the NaOH-EDTA extract. The underlying broad signal (UBS) represents Porg species which are in the area under the UBS. The p-values refer to the comparison of the means between the treatments control and 400 using a linear model described in the material and methods section. The raw data (n = 2) of the Porg species that was used for calculating the mean can be seen in Table S1

Treatment	Sampling date	MRP	MURP	^{31}P-NMR analysis						Diesters		
				Monoesters								
				Total P (^{31}P-NMR)	Orthophosphate	Total phosphomonoester region	UBS	IP$_6$	β-glycerophosphate	Phospholipid-P	DNA-P	Pyrophosphate-P
		mg kg^{-1}										
Control	1-day prior application	341.0	52.1	375.5	288.8	80.6	73.1	1.9	1.2	2.0	2.7	1.6
	1 DAA	335.0	81.0	471.6	358.2	103.2	93.7	1.6	1.1	3.9	3.7	2.5
	28 DAA	327.0	81.0	426.0	322.3	94.4	79.7	1.7	0.8	3.7	3.4	2.2
	140 DAA	317.0	86.3	384.9	289.7	87.4	74.0	2.0	1.0	3.1	2.9	2.0
400	1-day prior application	507.0	46.3	536.8	445.4	82.2	57.9	2.4	1.4	3.4	3.9	1.9
	1 DAA	519.0	69.3	592.1	502.3	80.3	51.0	1.8	1.7	3.6	3.9	2.0
	28 DAA	518.0	93.1	615.8	516.4	88.4	55.6	1.8	1.4	4.3	4.5	2.3
	140 DAA	516.0	69.1	583.6	487.3	86.8	55.1	2.1	1.3	3.8	3.9	1.9
	Mean control	330.0	75.1	414.5	314.7	91.4	80.1	2.1	1.0	3.2	3.1	2.1
	Mean 400	515.0	69.5	582.1	487.8	84.4	54.9	2.0	1.4	3.8	4.1	2.0
P value		0.006		0.003	0.003	0.008	0.01	0.28	0.02	0.02	0.02	0.68

[a] determined by colorimetry according to Murphy and Riley (1962)

[b] MURP = P determined by ICP-OES—MRP

of 87.9 mg kg^{-1} across all sampling dates, comprising 18.3% of the total P. Furthermore, total phosphomonoester concentration in the control (91.4 mg kg^{-1}) was significantly higher than in the treatment 400 (84.4 mg kg^{-1}). The underlying broad signal (UBS) is a subset of the total phosphomonoester region (described in chapter Spectral Deconvolution Fitting). The P$_{org}$ species which are represented by the area under the UBS also showed a higher concentration in the control (80.1 mg kg^{-1}) compared to the treatment 400 (54.9 mg kg^{-1}) (Table 3; Fig. S8). IP$_6$ did not show a significant difference between the total mean of the control (2.1 mg kg^{-1}) and the treatment 400 (2.0 mg kg^{-1}). β-glycerophosphate is also a part of the orthophosphate phosphomonoester region and the total β-glycerophosphate concentration in the treatment 400 (1.4 mg kg^{-1}) was significantly higher than in the control (1.0 mg kg^{-1}) (Table 3).

The phosphodiesters, phospholipid-P and DNA-P each represent 0.7% of mean total P (Table S2). The phospholipid-P concentration in the treatment 400 (3.8 mg kg^{-1}) was significantly higher than in the control (3.2 mg kg^{-1}). DNA-P also significantly increased in the treatment 400 (4.1 mg kg^{-1}) compared to the control (3.1 mg kg^{-1}) (Table 3). The pyrophosphates did not show a significant difference between the control (2.1 mg kg^{-1}) and the treatment 400 (2.0 mg kg^{-1}).

Discussion

General soil characteristics

The long-term compost application slightly increased soil pH value in the treatment 400, a result which was also found by Diacono and Montemurro (2010). Furthermore, municipal household composts contain high concentrations of calcium (Ca) (Jodar et al. 2017; Montejo et al. 2015), which caused an increase in the Ca concentration in the treatment 400 as compared to the control.

The long-term compost application significantly increased total C in the treatments 100 and 400 compared to the control (Fig. S1) which is due to the increase in soil organic matter. Particularly in sandy soils, high contents of soil organic matter show improving effects on soils, for example concerning water retention and nutrient storage (Lal 2009). Many

factors (e.g. climate conditions, soil microorganisms) affect the long-term soil organic matter accumulation in soils (Wiesmeier et al. 2019). A seasonal total C variation after compost application can only be seen in the treatment 400 with a high compost application. The increase in total C is likely due to the high C input by compost and the decrease after sampling date 14 DAA may be due to the increased activity of enzymes in the soil (Shao et al. 2015).

CAL-P and Olsen-P were significantly increased by long-term compost application in treatment 400 and also showed a short-term compost effect after application (Figs. 1 and 2). This is due to highly plant available P fractions in compost (Frossard et al. 2002), which can accumulate at high compost application rates (Müller and Zhang 2019). Furthermore, high fertilization rates over a long period can cause soil P saturation and decrease the sorption capacity of soils. As a result, soil test P increases and so does the risk of P loss by run off and even by leaching (Hooda et al. 2001). Additionally, P$_{org}$ can also block adsorption sites and cause an increase of P in the soil solution (Hawkins et al. 2022). However, the long-term compost application also increased the soil iron (Fe) and aluminium (Al) concentrations. Depending on the pH value, Fe oxides, Al oxides and CaCO$_3$ are responsible for P fixation in the soil (Penn and Camberato 2019).

Effect of long-term compost application on soil phosphatase activity and Mic-P

The phosphatase activity depends on water and can decrease during drought (Margalef et al. 2017). However, in the year of sampling, it rained frequently and drought was not an issue (Fig. S9). Phosphatases can be bound to soil humic substances and clay minerals, and persist in the soil over time (Olander and Vitousek 2000). This, together with the increased Mic-P biomass, may explain the long-term effect which can be seen in Acid-P$_{ase}$ activity and Alk-P$_{ase}$ activity in the treatment 400 compared to the control (Figs. 3 and 4). This long-term effect is significant, however, it is not as pronounced as for CAL-P or Olsen-P. In the control treatment, an increase in Acid-P$_{ase}$ and Alk-P$_{ase}$ activity can also be seen without compost application in the beginning. This may be explained by soil tillage because all treatments were

cultivated. Soil tillage may have increased the activity of Acid-P_{ase} and Alk-P_{ase} (Deng and Tabatabai 1997).

The Acid-P_{ase} activity showed an increase after compost application in the treatment 400 (Fig. 3). The increase up to 14 DAA might be due to soil microorganisms which release phosphatases such as Acid-P_{ase} since at the beginning, no plants were growing on the field and yet Acid-P_{ase} had increased. In the treatment 100, an increase of Acid-P_{ase} can also be seen (Fig. 3). However, this increase is similar to the control without compost application. The strong increase of Acid-P_{ase} starting 28 DAA in all treatments is very likely due to the beginning of maize growth, with a corresponding exudation of Acid-P_{ase} by the roots. Maize plants are well known for their ability to exude Acid-P_{ase} (He et al. 2022). The results indicate that maize plants may still release Acid-P_{ase} even when CAL-P or Olsen-P are not low.

The Alk-P_{ase} activity increased after compost application, peaking on 7 DAA, before the plants emerged (Fig. 4). This is in contrast to Acid-P_{ase} activity since Alk-P_{ase} is only synthesized by soil microorganisms and not by plants (Kruse et al. 2015; Nannipieri et al. 2010). Alk-P_{ase} and soil total C content showed a strong correlation ($R_S = 0.70$) which indicates a beneficial effect of total C on soil microorganisms (Fig. S2). The large increase 7 DAA was preceded by high precipitation, which may have increased Alk-P_{ase} in combination with freshly applied compost. A similar amount of precipitation before the sampling 84 DAA did not show an increasing effect. However, in general, precipitation can have a positive effect on Alk-P_{ase} (Zhou et al. 2013). Compost application can have an increasing effect on P_{ase} activity and Mic-P, but, the type of compost might also play a role (Lalande et al. 1998).

In this study, Mic-P was particularly pronounced in the treatment 400. Nevertheless, the Mic-P pool was very dynamic in all treatments and those fluctuations can be due to soil temperature and soil moisture (Richardson and Simpson 2011). The variability in Mic-P in our study may also be an artefact as chloroform sensitive fine roots in the soil samples may bias the Mic-P estimation (Martin and Correll 1989; Mueller et al. 1992). Our soil samples were sieved, but no additional technique was applied to remove fine roots before fumigation.

The long-term compost application showed an increasing effect on total C, CAL-P, Olsen-P, P_{ase}

activity and on Mic-P. These increasing effects demonstrate that long-term compost application influences P cycling processes which regulate the P flow in soils. Now that we have discussed the P_{ase} activity and the microbial biomass, we will now turn our attention to how compost application and the increased P_{ase} activity affects P_{org} speciation.

Effect of long- and short-term compost application on soil P_{org} species determined by ^{31}P-NMR

The inorganic orthophosphate (Ortho-P) concentration in NaOH-EDTA extracts detected by ^{31}P-NMR was the largest P fraction in all treatments and increased significantly due to the long-term compost application (Table 3). This is likely the result of a high inorganic P fraction in the composts (Frossard et al. 2002) that accumulated in soil after application over the years.

Phosphomonoesters were the largest P_{org} fraction in this study (Table S2), which is in accordance with other ^{31}P-NMR studies on soil extracts (Xu and Arai 2022). Despite the presence of phosphomonoesters in the compost, the concentration of the phosphomonoesters did not increase in the treatment 400. Furthermore, the mean phosphomonoester concentration was significantly higher in the control than in the treatment 400 (Table 3), which may be explained by a significant higher P_{ase} activity in the treatment 400 (Figs. 3 and 4). Further enzymes may also be increased due to compost application which we did not determine in this study, for example, phytase (Liu et al. 2022a). Due to the increased enzyme activity in treatment 400, mineralization of P_{org} species (e.g. phosphomonoester) may have been increased, which at the same time raised the Ortho-P fraction (Table 3). Furthermore, the addition of organic matter may also have a solubilizing effect on P_{org} species such as competing for sorption sites or influencing the soil surface charge which increases the P concentration in the soil solution (Guppy et al. 2005). In this study, these effects of organic matter may, therefore, be increased by high compost application. This is also suggested by the decreased mean MURP concentration in the treatment 400 compared to the control (Table 3). The phosphomonoester region consists of a variety of different monoesters such as inositol phosphates or β-glycerophosphate which were found in this study. IP_6 is the most prominent inositol phosphate,

however, it is also possible to determine other IP_6 stereoisomers and lower-order inositol phosphates with the ^{31}P-NMR if a prior hypobromite oxidation is done (Reusser et al. 2020b; Turner et al. 2012). In this study, compost application did not show a significant effect on the IP_6 concentration (Table 3) despite the presence of IP_6 in the applied compost (Table 2).

β-glycerophosphate showed an increase after compost application in treatment 400 compared to the control. Doolette et al. (2009) showed that β-glycerophosphate is predominantly a degradation product of phospholipids and not a part of the soil P_{org}. Previously, we showed that Mic-P was increased in treatment 400 which may explain the significant increase of β-glycerophosphate in the treatment 400 compared to the control due to phospholipids of soil microorganisms. This is also highlighted by the fact that the concentration of β-glycerophosphate was higher in treatment 400 than in compost.

Phosphodiesters represent a big proportion of P_{org} input from plants and soil microorganisms (Turner et al. 2003). There are differences in susceptibility to degradation between phosphodiesters species, for example, RNA degrades faster compared to DNA, and therefore, RNA-P cannot be detected in a ^{31}P-NMR spectrum (Turner et al. 2003). DNA-P significantly increased in the treatment 400 compared to the control (Table 3). The applied compost contained DNA-P and may provided DNA-P to the treatment 400. Furthermore, the increased phosphatase activity in the treatment 400 with high compost application suggests that the accumulated DNA-P may also be based on soil microorganisms. However, the origin of DNA-P from plants cannot be fully ruled out (Büne-mann et al. 2008b; Makarov et al. 2005).

Pyrophosphates may be related to soil microorganisms and especially to fungi (Bünemann et al. 2008a). In this study, the mean pyrophosphate concentration of all sampling dates did not show a significant difference between the treatments control and 400 (Table 3). Even though the applied compost contained a higher concentration of pyrophosphate than in treatment 400.

The high microbial biomass P and phosphatase activity and, furthermore, the significantly increased DNA-P and β-glycerophosphate concentrations in the treatment 400 support the presumption that soil microbial activity was the reason for a lower total phosphomonoester concentration in the treatment.

As previously reported by Reusser et al. (2020a), the inclusion of the underlying broad signal (UBS) in the spectral deconvolution fitting (SDF) procedure in our study also substantially reduced the root mean square fitting error and increased the accuracy (R^2) of the model (Table S4). The area under the UBS contains several phosphomonoester species with different molecular weights which overlap and form the UBS (McLaren et al. 2022; Reusser et al. 2022). It was assumed that these compounds are relatively stable to enzymatic hydrolysis and remain unchanged with addition of organic fertilizers (Annaheim et al. 2015; Jarosch et al. 2015). However, the significant lower concentration of the phosphomonoesters which are represented by the area under the UBS in the treatment 400 compared to the control could indicate a degradation of these P_{org} compounds due to compost addition. Hence, this P_{org} pool could function as a P source for soil microorganisms, plants and, therefore, play a role in the soil P cycle.

The decrease of phosphomonoesters, due in part to the enzyme activity in the treatment 400 and the resulting increase of CAL-P and Olsen-P, shows that P_{org} has a potential role in providing P for plants. Nevertheless, most conventional chemical extraction methods, such as CAL or Olsen, which are used for fertilizer recommendations, do not factor in P_{org} in their recommendations (Sulieman and Mühling 2021).

Compost application

This study showed that the high compost application in treatment 400 had the strongest effects, for example, on the phosphatase activity. However, it is important to note that this treatment cannot be directly compared to practical agriculture in many countries due to legally restricted input of N, which is limited in Germany for compost to a maximum of 510 kg N ha^{-1} over a period of three years based on a mean annual input of 170 kg N ha^{-1} per year (BMELV 2017). This treatment was designed to demonstrate effects of compost application on soil and plant growth in a time lapse with a focus on N. This treatment is to be seen as a time lapse in order to recognize long-term positive and negative effects as early as possible. This does also include other nutrients than N and P as reported here including micronutrients and heavy metals (Najar et al. 2016; Reimer et al. 2023).

Conclusion

This study showed that long-term compost application significantly increased the soil P_{ase} activity compared to the control and this also affected the P_{org} speciation. These results indicate that P_{org} speciation is linked to phosphatase activity. The compost application did not have a uniform effect on P species in the soil. In particular, long-term compost application has an increasing effect on soil P_{org} species which can be related to soil microbial activity such as β-glycerophosphate and DNA-P determined by ^{31}P-NMR. This suggests that those P_{org} species did not accumulate in soil, but rather originate from soil microbial organisms that increased in soil of the treatment 400 by long-term compost application. Simultaneously, there was a significant decrease in the P_{org} concentration in the total phosphomonoester region of the treatment 400 compared to the control, which may indicate that compost application increases phosphatases and other enzymes, which mineralize recalcitrant P_{org} species in the phosphomonoester region and especially in the region under the UBS. Those mineralized P_{org} species may provide a considerable share of P to the maize crops. A short-term compost effect on P_{org} species could not be shown. Compost application increased CAL-P and Olsen-P, which indicates that compost provides a high concentration of P which has a high potential plant availability.

The effect of other organic fertilizers on UBS needs to be further evaluated and the importance of P_{org} species in the UBS in relation to plant nutrition needs to be investigated.

Declarations

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