ORIGINAL ARTICLE

Fate of P from organic and inorganic fertilizers assessed by complementary approaches

Yue Hu · Klaus A. Jarosch · Mareike Kavka · Bettina Eichler-Löbermann

Abstract Long-term field experiments (LTFEs) can provide an extensive overview on the effectiveness of phosphorus (P) management. In order to have a detailed insight into the availability and distribution of the P in soil as affected by organic and inorganic fertilizers (no P, triple-superphosphate (TSP), compost and compost + TSP), soil samples collected at a LTFE established in 1998 in Northern Germany at different sampling dates and soil depths were subjected to P characterization including the double-lactate method (P-dl) as standard soil test, the degree of P sorption (DPS), the sequential P fractionation and isotopic exchange kinetics. While the type of fertilizer had rarely an effect on the soil P pools, higher amounts of P applied resulted in increased values of P-dl, labile P fractions and P that was isotopically exchangeable within 1 min ($p < 0.05$). The DPS values varied from on average 40.2% (no P) to 47.2% (compost + TSP) with small variations during the experimental time. In contrast, significant shifts from less available to readily available P pools were measured between the sampling in autumn 2017 and spring 2019. The differences in the P budgets between the treatments corresponded to the differences of the total P stocks in 0–90 cm, yet with an estimated upward or downward movement of P between the soil depths as consequences of long-term deficit or surplus of fertilizer P. The use of complementary methods in this study contributed to a better understanding of the potential availability of P in soil in a long term perspective.

Introduction

Phosphorus (P) is a critical resource for the bio-economy and for food security in the European Union and at the global level. However, not only the P shortage might be problematic for future (agricultural) production, but also a regional oversupply of P with corresponding ecological consequences, calling for a rapid resolution of this imbalance (Cordell and White 2014; Leinweber et al. 2018; Lun et al. 2018). The

Y. Hu · *Present Address:*
M. Kavka
Satellite Collections North, Genebank Department, Leibniz Institute of Plant Genetics and Crop Plant Research (IPK), Malchow, Poel, Germany

Y. Hu · M. Kavka · B. Eichler-Löbermann (✉)
Agronomy and Crop Science, University of Rostock, Rostock, Germany
e-mail: bettina.eichler@uni-rostock.de

K. A. Jarosch
Agroecology and Environment, Agroscope, Zurich, Switzerland

urgency to solve this P paradox is also highlighted by the fact that the global biogeochemical P flux has been described as one of the "Planetary Boundaries" that has already been exceeded (Steffen et al. 2015). Optimizing the use of different P sources, including P from waste materials, is seen as option to increase the sustainability and efficiency of P management in agronomic systems (Lun et al. 2018; Pavinato et al. 2020).

Organic fertilizers have a large potential as P sources in plant production and the P fertilizer effect of organic amendments can be similar to or even higher than that of highly soluble synthetic fertilizers as shown for instance for digestates (Möller and Müller 2012; Zicker et al. 2020), sewage sludge (Kahiluoto et al. 2015), and compost (Lemming et al. 2019). The type of P source also affects the availability of the surplus P, i.e. the fraction of soil P that is derived from fertilizers but was not taken up by plants (Sattari et al. 2012; Sharpley et al. 2013). Knowledge about the size and accessibility of the soil P pools is needed to enable adequate fertilizer management.

Worldwide, various methods to determine soil test P values as a proxy for plant available P are in use (Jordan-Meille et al. 2012; Nawara et al. 2017; Steinfurth et al. 2022). The chemical extraction of homogenized soil samples is widely used because it is easy to handle. However, the chemical extractants cannot completely reflect the real pool of P that can be taken up by plants. Some of the soil P tests are chemically so strong that they can dissolve P equivalent to hundreds of kg P ha^{-1} while others, such as water or CaCl$_2$ are so mild extractants that they may underestimate the amount of P which could be mobilized and taken up by plants (Jordan-Meille et al. 2012). The double-lactate method (P-dl) is one of the German standard soil P tests. It uses double-lactate in an acid medium and is mainly applied for soils with a pH < 6 (Siebers et al. 2021).

In order to better describe agricultural and environmental P cycles methods other than standard soil P tests are in use (Kruse et al. 2015). Sequential P extraction schemes have been developed to quantify fractions of organic and inorganic soil P in dependence to their chemical extractability. Often-used approaches based on the method developed by Hedley et al. (1982) assume that soil P can be segregated into several defined pools with different solubility and contribution to plant P nutrition (Milić et al. 2019).

This method has also proven useful to evaluate P solubility especially regarding biological processes across a soil weathering gradient (Cross and Schlesinger 1995).

Simultaneously, other approaches have been developed to describe P behavior and availability in soil. The soil P sorption capacity (PSC) was established to determine the potential of a soil to sorb P, based on the amounts of iron and aluminum oxides (Fe-ox and Al-ox). The more P is sorbed on these sorption sites, the higher the degree of P saturation (DPS) and thus potential loss of P from soil (Lookman et al. 1995; Blombäck et al. 2021). Alternatively, soil P exchangeability can be determined by using isotopic tracers. The ^{32}P or ^{33}P isotopic exchange kinetics (IEK) are used to quantify how many inorganic P ions can be exchanged between the soil solution and the soil solid phase and thus can become plant available within a specific time frame (Frossard and Sinaj 1998; Frossard et al. 2011). This dynamic perspective on soil P availability has proven useful to better understand the influence of long-term P fertilization strategies on the availability of soil P and soil P fluxes (Oehl et al. 2002; Borda et al. 2014; van der Bom et al. 2019; Lemming et al. 2019).

Practical P management is mostly guided by analyzing topsoil samples. However, although P contents commonly decrease with increasing depth the subsoil should be considered as relevant P reservoir (Siebers et al. 2021). The vertical P translocation depends on agronomic management and a full understanding of P cycling processes is only possible if deeper soil depths are considered, too (Glæsner et al. 2011; Rubæk et al. 2013; van der Bom et al. 2017).

Long-term field experiments (LTFEs) can provide an extensive overview on the effectiveness of P management strategies (Knapp et al. 2012; Rodríguez et al. 2018). However, it became evident that P budgets are not always linked to results from standard soil P tests in the topsoil and that the fate of applied P may remain partly unclear (Oehl et al. 2002; Jordan-Meille et al. 2012; Nawara et al. 2017; Zicker et al. 2018; Pavinato et al. 2020). Consequently, it was suggested to extend the analytical spectrum in order to improve the assessment of soil P pools as affected by fertilizers. However, due to the large analytical effort studies applying various approaches to describe the P availability and exchangeability in soil often only used single sampling dates or focused on one soil

layer (Requejo and Eichler-Löbermann 2014; van der Bom et al. 2017, 2019; Rodríguez et al. 2018; Koch et al. 2018; Lemming et al. 2019).

The present study focusses on the evaluation of long-term P fertilizer strategies established in a field experiment in 1998 in Northern Germany. Soil P pools were analyzed at different experimental times and in different soil depths, allowing to extend the knowledge gained from previous studies on soil P pools and dynamics between them. Soil samples were taken in three soil depths (0–30, 30–60 and 60–90 cm) after 21 years of continuous management. Furthermore, temporal variations of P pools were monitored by analyses on stored samples. Besides chemical P extractions (P-dl, oxalate soluble P (P-ox) and sequentially extracted P fractions) we determined the isotopic exchangeability of P over time in order to examine the dynamic of soil P availability and variations of soil P pools in dependence of P fertilizer form and amount.

The specific objectives of this study were (I) to determine the availability and distribution of P in the soil profile as affected by P budget and type of fertilizer, (II) to compare the results of P availability by standard soil tests with methods that provide deeper insights into P pools and P dynamics, and (III) to assess the extent to which management-induced differences in P pools and P dynamics vary during the experimental time.

Material and methods

Experimental site and soil sampling

The LTFE was established at the experimental station of the University of Rostock in autumn 1998. The experimental site is located in a maritime-influenced region in northeast Germany (54°3′41.47″ N; 12°5′5.59″ E), about 15 km south of the Baltic Sea shore. The average annual temperature in this region is 8.1 °C and the mean annual precipitation is around 600 mm. The soil texture at this site is loamy sand and the soil is classified as Stagnic Cambisol according to the World Reference Base for Soil Resources (IUSS Working Group WRB 2015).

The field trial was designed as randomized split plots, with organic fertilizer supply as main-plots (408 m^2 each) and inorganic fertilizer supply as

Table 1 Phosphorus (P) input, P offtake and P budget accumulated for 21 years after no P fertilizer application (no P) or with triple-superphosphate (TSP), bio-waste compost (compost) or both (compost + TSP) since 1998. Mean ± standard deviation (n = 4)

Treatment	P input kg ha^{-1}	P offtake	P budget
No P	0.0	454.3 ± 30.1	− 454.3 ± 30.1
TSP	498.8	494.5 ± 17.5	4.3 ± 17.5
Compost	459.9	508.4 ± 6.4	− 48.5 ± 6.4
Compost + TSP	958.7	529.3 ± 18.5	429.4 ± 18.5

sub-plots (120 m^2 each) in four replications as previously described by Zicker et al. (2018) and Eichler-Löbermann et al. (2021). From in total nine fertilizer treatments, four were selected for this study: a treatment without P supply (no P), with triple-superphosphate (TSP), bio-waste compost (compost) and a combination of both fertilizers (compost + TSP). From 1998 to 2013, TSP was applied annually at a rate of 21.8 kg P ha^{-1} yr^{-1} and increased in 2014 to 30 kg P ha^{-1} yr^{-1} to balance the negative P budget. Compost was produced as sanitized compost based on green garden and landscape waste residues and was applied every three years beginning in 1998 at a rate of around 30 t ha^{-1}. Due to varying P concentrations in the compost, the P supply differed on the individual application dates. The total amounts of P applied from 1998 until the sampling in spring 2019 were about 500 kg ha^{-1} in the treatments with TSP and about 460 kg ha^{-1} in the treatments with compost resulting in about 960 kg ha^{-1} in the combined treatment compost + TSP. Concrete P supply and P budgets for each treatment are given in Table 1. Nitrogen fertilization was applied as calcium ammonium nitrate annually according to the crop requirements after determination of mineral nitrogen (Nmin) in 0–30 cm soil depth in autumn resulting in only slight differences in N supply between treatments. Magnesium and potassium were supplied in form of MgSO$_4$ and KCl according to the recommendation of the regional agricultural advisory service.

For this study soil samples were taken in spring 2019 (21 years after the establishment of the experiment) from three soil depths (0–30, 30–60 and 60–90 cm). Furthermore, stored samples from previous sampling dates taken at a depth from 0–30 cm in autumn 1999, 2003, 2008, 2012 and 2017 were

included. Soil samples were taken and mixed from three randomly selected spots in each repetition of every treatment with an auger. Air-dried soil samples were sieved (2 mm) for standard soil P tests, P sorption determination and sequential P fractionation. Samples from 2019 were used additionally to determine isotopic exchange kinetic parameters.

The crops cultivated on the studied plots in the respective sampling years were spring rape in 1999, winter wheat in 2003, maize in 2008, winter rye in 2012, spring barley in 2017, and winter wheat in 2018.The precipitation and temperature in the sampling years are illustrated in Supplementary Figure S1.

P budget, standard soil test and P sorption

The P offtake was determined as the product of the plant P concentration and dry weight of harvested biomass. The plant P concentration was determined after dry ashing and HCl digestion (2 g dry material digested in 20 mL of 25% boiling HCl in a 100 mL volumetric flask) by inductively coupled plasma optical emission spectroscopy (ICP-OES; ICP Serie Optima 8300DV, PerkinElmer, USA). The 21-year-fertilisation and cultivation resulted in a negative P budget in the no P treatment (-454.3 ± 30.1 kg ha^{-1}), nearly balanced in the compost (-48.5 ± 6.4 kg ha^{-1}) and TSP treatment (4.3 ± 17.5 kg ha^{-1}), and positive in the compost+TSP treatment (429.4 ± 18.5 kg ha^{-1}) (Table 1).

Soil pH was measured in 0.01 M CaCl$_2$ at a soil:solution-ratio of 1:2.5 using a pH electrode (pH 1100 L, VWR International, Germany). Soil organic matter (SOM) from sampling year 2019 was determined as the difference of soil weight (air-dried and sieved through 2 mm) between before and after incineration (550 °C in muffle furnace).

The content of P-dl was determined with a modified method after Riehm (1948). Briefly, 12 g air-dried and sieved soil (2 mm) were mixed with 150 mL solution consisting of calcium lactate (0.4 M C$_6$H$_{10}$CaO$_6 \times$5H$_2$O) and hydrochloric acid (0.5 M HCl) at pH 3.6 and shaken overhead for 90 min with 35 rpm. After filtration (cellulose round filter, 3–5 μm), P concentration in the filtrate was determined by ICP-OES.

The P-ox, Fe-ox, and Al-ox in soil were determined using a method modified from Schwertmann (1964) and DIN ISO 19684-6 (1997). Briefly, 1.5 g of 2 mm sieved dry soil was extracted with 30 mL oxalate buffer according to DIN ISO 19684-6 (1997) and shaken for 2 h using an overhead shaker in the dark with 35 rpm. After filtration (cellulose round filter, 3–5 μm), 1 mL filtrate was transferred into a 15 mL centrifuge tube and mixed with 11 mL deionized water for dilution. P-ox, Fe-ox and Al-ox in the diluted solution were determined by ICP-OES. The PSC was calculated by

$$\text{PSC} = 0.5 \times (\text{Al-ox} + \text{Fe-ox}), \tag{1}$$

where 0.5 is a scaling factor and PSC, Al-ox and Fe-ox are expressed in mmol kg^{-1} (Börling et al. 2001; Maguire et al. 2001). The DPS was calculated by

$$\text{DPS} = 100 \times \frac{\text{P-ox}}{\text{PSC}}, \tag{2}$$

where P-ox is expressed in mmol kg^{-1} and DPS is expressed in percentage.

Sequential phosphorus fractionation

A modified sequential fractionation method based on the approaches from Hedley et al. (1982), Tiessen et al. (1984) and Tiessen and Moir (1993) was used to extract different P fractions from the soil (Supplementary Figure S2). For that, 0.5 g dry fine-ground soil was weighed into 50 mL centrifuge tubes with 30 mL deionized water. Samples were shaken overhead at 22 rpm for 18 h with subsequent centrifugation at 3500 rpm for 20 min and decanted. Afterwards, samples were sequentially extracted with 30 mL of 0.5 M NaHCO$_3$, 0.1 M NaOH and 1 M H$_2$SO$_4$. No rinsing of the residual soil was performed between different extraction steps. After filtration (cellulose round filter, 3–5 μm), total P concentration in each extract was determined by using ICP-OES. Concentration of inorganic P (Pi) in the extracts was measured by the molybdenum blue method (Öhlinger 1996) colorimetrically (Specord 50, Analytik Jena, Germany). Concentration of organic P (Po) in the extracts was calculated by subtracting Pi from total P concentration in the extracts. Total P in soil (P-tot) was determined using a method modified from DIN EN 14,436

(2004). In brief, 0.5 g dry fine-ground soil was dissolved with 8 mL of Aqua regia (6 mL 37% HCl plus 2 mL 65% HNO_3) overnight and digested for 20 min at 180 °C in a microwave-digestion system (Mars 6, CEM, Germany), then transferred to a volumetric flask and filled up to 50 mL for the measurement with ICP-OES. Concentration of not extractable P (P-residual) was calculated as the difference between the sum of all P fractions (P-sum) and P-tot in the soil. Total P stocks in each soil depth (0–30, 30–60 and 60–90 cm) were computed from the P-tot content with a soil bulk density of 1.2 g cm^{-3} for 0–30 cm and 1.3 g cm^{-3} for 30–60 and 60–90 cm.

Phosphorus-33 (^{33}P) isotopic exchange kinetics

For the soil sampled in 2019, the amount of isotopically exchangeable P was determined by an IEK experiment for describing the dynamics of Pi ions between the soil solution and the soil solid phase. For that, 10 g of 2 mm sieved and dried soil was gently shaken with 99 mL Millipore water in a 250 mL Nalgene bottle for 16 h on a horizontal shaker. After shaking, the bottle was placed on a magnetic stirrer plate and 1 mL carrier free ^{33}P labeled orthophosphate (0.53 ± 0.08 kBq mL^{-1}, Hartmann Analytic, Germany) was added at time 0. After 1, 4, 10, 30, 60, and 90 min, about 5 mL suspension was sampled with a syringe and immediately passed through a membrane filter (0.2 μm). The radioactivity in the filtrate (r) was determined by liquid scintillation counting (1 mL filtrate + 5 mL Rotiszint eco plus scintillation cocktail) with a Liquid Scintillation Counter (Tri-Carb 4810TR 110 V, PerkinElmer, USA). 100 min after ^{33}P addition, 15 mL suspension was sampled and filtered for determination of orthophosphate concentration (Cp, mg L^{-1}) using the molybdenum blue method (Öhlinger 1996) with a spectrophotometer (Beckman DU-640, GMI, USA).

The measured ratios of remaining radioactivity r at different sampling time points (r(t)) over initially added radioactivity R (r(t)/R) as well as the different sampling times were log10 transformed and correlated with a nonlinear regression function. The intercept of this linear function (parameter m) relates to the rapid reaction of exchangeable Pi and is closely linked to the fraction of radioactivity remaining in the soil solution after 1 min of tracer addition (Oehl et al. 2002). The slope of the linear function (parameter

n) relates to the slow physicochemical reactions and reflects isotopically exchangeable Pi over time (Sen Tran et al. 1988).

The isotopic exchange of ^{33}P ions in solution was described by Fardeau (1993) as follows:

$$r(t)/R = m\left(t + m^{\frac{1}{n}}\right)^{-n} + \frac{r_{\inf}}{R} \tag{3}$$

The ratio $r_{\inf}/R$ describes the maximum possible dilution of the isotope at infinite time as is approximated by the ratio of Pi ions in the soil solution ($10 \times Cp$) over total Pi in the soil. Total Pi in the soil (Pi-tot) was determined as the difference between P-tot from the Aqua regia extraction and total organic P in soil (Po-tot) determined with ignition method by Saunders and Williams (1955).

The amount of exchangeable P (mg kg^{-1}) within a specific time (E(t)) was extrapolated from the IEK experiment for different time intervals using the following formula:

$$E(t) = 10 \times Cp \times R/r(t) \tag{4}$$

In this study, the following time increments were chosen: P exchangeable within 1 min (E1min), P exchangeable within 1 h (E1hour), P exchangeable between 1 h and 3 months (E1hour-3months) and P exchangeable longer than 3 months (E > 3 months). E > 3 months was calculated as the difference between Pi-tot and exchangeable P within 3 months (E3months). E1hour-3months was calculated as difference between E3months and E1hour.

Statistical analyses

All statistical analyses were performed with R version 4.0.4 (R Core Team 2021) in the RStudio development environment (RStudio Team 2020). Data of all treatments within each year were analyzed with two-way ANOVA including the factors treatment and block. Data of all treatments between selected years were analyzed with Repeated Measures ANOVA with treatment and year as fixed effect, and block as random effect. Functions lme and ACF from the car package (Fox and Weisberg 2019), function lsmeans from the lsmeans package (Lenth 2016), and function cld from package multcomp (Hothorn et al. 2008) were used for the Repeated Measures ANOVA. When the effect of the factors was significant ($p < 0.05$),

post-hoc comparisons were carried out by Duncan's new multiple range test ($\alpha = 0.05$) with function duncan.test from the agricolae package (de Mendiburu and Yaseen 2020). Normal distribution of residuals and homogeneity of variance were checked in all statistical models using the function shapiro.test and leven.test from the car package (Fox and Weisberg 2019). If normality assumption were not met, data was transformed through the boxCox function from the car package (Fox and Weisberg 2019). Correlations between selected parameters from standard soil tests, the sequential fractionation and IEK in each soil depth were estimated with Pearson's correlation coefficient and the correlations were displayed with heat maps using the package ggplot2 (Wickham 2016). A principal components analysis (PCA) was performed with package factoextra (Kassambara and Mundt 2020) and FactoMineR (Lê et al. 2008).

Results

Standard soil test P

In 2019, 21 years after the beginning of the experiment, the fertilizer treatments had a clear effect on P-dl contents in the 0–30 cm soil depth, with highest values found for the compost + TSP treatment ($p < 0.05$) (Table 2). The single application of compost or TSP had higher values of P-dl in comparison to the no P treatment ($p < 0.05$).

Treatment differences became already evident after one year (1999) of trial run (Fig. 1). During the experimental time the concentrations of P-dl in the no P treatment reduced from 35.9 mg kg^{-1} in autumn 1999 to 26.0 mg kg^{-1} in autumn 2017, while they remained almost stable in the TSP and compost treatment, though with variations between the sampling dates. In the compost + TSP treatment, no significant increase was measured at all sampling dates in comparison to 1999. Soil samples taken in spring 2019 showed higher values of P-dl in all treatments in comparison to autumn sampling in 2017.

Although the P budgets were similar in the TSP and compost treatments, the soil P-dl contents in 0–30 cm were found to be higher in the compost treatment in autumn 1999, 2008, 2012, and 2017. On average of all sampling dates, the order of the P-dl in 0–30 cm soil depth was determined as follows: compost + TSP (55.4 ± 8.6 mg kg^{-1}) ≥ compost (47.2 ± 5.3 mg kg^{-1}) ≥ TSP (40.8 ± 7.5 mg kg^{-1}) ≥ no P (32.6 ± 6.1 mg kg^{-1}).

The P-dl contents decreased with soil depth ($p < 0.05$) but followed the same pattern between the treatments as in 0–30 cm (Table 2). Differences were found between no P and compost + TSP treatment in

Table 2 Soil organic matter (SOM), pH in $CaCl_2$ (pH ($CaCl_2$)) and double lactate extractable P (P-dl) of the soil samples taken in spring 2019 in three soil depths (0–30, 30–60 and 60–90 cm) after no P fertilizer application (no P) or with triple-superphosphate (TSP), bio-waste compost (compost) or both (compost + TSP) since 1998

Treatment	Depth cm	SOM %	pH ($CaCl_2$)	P-dl mg kg^{-1}
No P	0–30	1.9 ± 0.2Ab	5.6 ± 0.1Bb	32.4 ± 4.2Ac
	30–60	1.5 ± 0.6Aa	5.8 ± 0.1Aa	18.2 ± 4.4Bb
	60–90	1.8 ± 0.4Aa	5.9 ± 0.1Aa	7.2 ± 1.7Cb
TSP	0–30	2.0 ± 0.2ABb	5.6 ± 0.2Bab	42.2 ± 8.9Ab
	30–60	1.7 ± 0.2Ba	5.8 ± 0.0ABa	25.7 ± 10.8Bab
	60–90	2.1 ± 0.1Aa	6.1 ± 0.4Aa	8.9 ± 5.1Cab
Compost	0–30	2.3 ± 0.2Aa	5.8 ± 0.2Bab	46.8 ± 5.5Ab
	30–60	1.8 ± 0.3Ba	5.8 ± 0.0Ba	38.2 ± 14.3Aa
	60–90	1.9 ± 0.3Ba	6.1 ± 0.1Aa	14.9 ± 2.6Ba
Compost + TSP	0–30	2.3 ± 0.2Aa	5.9 ± 0.2Aa	60.5 ± 7.9Aa
	30–60	1.7 ± 0.3Aa	5.8 ± 0.1Aa	39.3 ± 8.3Ba
	60–90	1.9 ± 0.5Aa	6.0 ± 0.1Aa	15.4 ± 6.6Ca

Letters in capital case indicate significant difference between soil depths and letters in lower case indicate significant difference between treatments within same soil depth (Duncan's new multiple range test with $p < 0.05$). Mean ± standard deviation (n = 4)
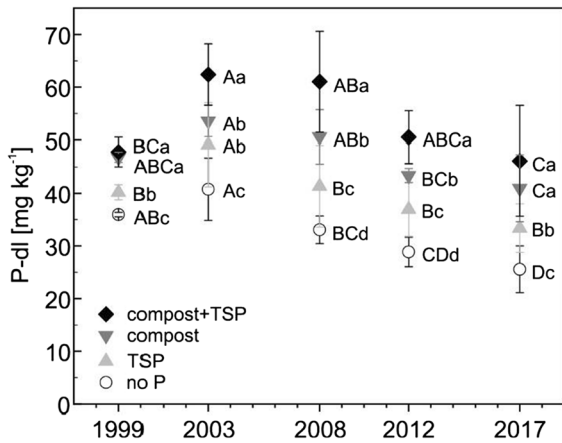
Fig. 1 Double lactate extractable phosphorus (P-dl, mg kg^{-1}) of soil samples taken in autumn of 1999, 2003, 2008, 2012 and 2017 after no P fertilizer application (no P) or with triple-superphosphate (TSP), bio-waste compost (compost) or both (compost + TSP) since 1998. Letters in capital case indicate significant differences between sampling dates within the same treatment and letters in lower case indicate significant differences between treatments within the same sampling date (Duncan's new multiple range test with $p < 0.05$). Mean ± standard deviation (n = 4)

both 30–60 cm and 60–90 cm depth ($p < 0.05$). In tendency, the P-dl values were higher in the compost than in the TSP treatment, yet differences were not significant.

P sorption and degree of P saturation

In 2019, the P-ox contents in 0–30 cm soil depth were found to be higher in the treatments with fertilizer supply than in the no P treatment ($p < 0.05$) (Table 3). The differences between the fertilizer treatments were less pronounced as for P-dl (see Standard soil test P), and in none of the examined soil depths the compost + TSP treatment resulted in significantly higher P-ox values than the TSP or compost treatment. Likewise, the sampling time was less relevant for the P-ox than for the P-dl contents (Fig. 2a). During the experimental time only for the no P treatment clear changes of P-ox contents were measured with a steady reduction from 2003 to 2019. Differently to the P-dl contents, the P-ox contents were not clearly raised at the spring sampling 2019 in comparison to the autumn sampling of the previous years (Table 3 and Fig. 2a).

Table 3 The oxalate-soluble contents of aluminum, iron and phosphorus (Al-ox, Fe-ox and P-ox), P sorption capacity (PSC) and degree of P saturation (DPS) of the soil samples taken in spring 2019 in three soil depths (0–30, 30–60 and 60–90 cm) after no P fertilizer application (no P) or with triple-super-phosphate (TSP), bio-waste compost (compost) or both (compost + TSP) since 1998

Treatment	Depth cm	Al-ox mg kg^{-1}	Fe-ox	P-ox	PSC mmol kg^{-1}	DPS %
No P	0–30	549.4 ± 65.2Ab	1576.8 ± 216.8Aa	264.9 ± 48.1Ab	24.3 ± 3.1Aa	35.1 ± 3.3Ab
	30–60	636.1 ± 47.6Aa	1794.2 ± 253.9Aa	233.0 ± 22.2Aa	27.8 ± 2.5Aa	27.2 ± 3.7Bb
	60–90	511.6 ± 138.5Aa	1585.2 ± 627.1Aa	123.4 ± 30.6Bb	23.7 ± 8.0Aa	17.7 ± 4.0Ca
TSP	0–30	650.5 ± 67.9Aab	1839.1 ± 190.9Aa	363.4 ± 43.1Aa	28.5 ± 2.9Aa	41.1 ± 2.8Aa
	30–60	599.0 ± 75.6ABa	1942.4 ± 178.3Aa	266.4 ± 56.8Ba	28.5 ± 2.2Aa	30.2 ± 6.0Bab
	60–90	524.4 ± 27.7Ba	1857.7 ± 571.1Aa	146.0 ± 24.0Cab	26.3 ± 5.1Aa	18.1 ± 2.4Ca
Compost	0–30	633.9 ± 34.2Aab	1782.8 ± 52.2Aa	358.5 ± 30.1Aa	27.7 ± 1.0Aa	41.7 ± 2.4Aa
	30–60	603.6 ± 69.7Aa	1911.4 ± 279.7Aa	315.3 ± 44.1Ba	28.3 ± 3.8Aa	36.1 ± 2.9Ba
	60–90	539.4 ± 69.3Aa	1732.1 ± 324.2Aa	166.5 ± 18.7Ca	25.5 ± 3.7Aa	21.4 ± 3.6Ca
Compost + TSP	0–30	654.2 ± 32.7Aa	1891.0 ± 91.9Aa	397.2 ± 32.4Aa	29.1 ± 1.3Aa	44.1 ± 2.6Aa
	30–60	603.5 ± 99.8ABa	1928.9 ± 172.3Aa	312.6 ± 55.0Ba	28.5 ± 3.3Aa	35.5 ± 5.1Ba
	60–90	537.1 ± 161.7Aa	1774.9 ± 405.0Aa	162.3 ± 32.4Cab	25.8 ± 6.2Aa	21.3 ± 7.3Ca

Letters in capital case indicate significant difference between soil depths and letters in lower case indicate significant difference between treatments within same soil depth (Duncan's new multiple range test with $p < 0.05$). Mean ± standard deviation (n = 4)

The PSC which was calculated on the basis of Al-ox and Fe-ox did differ neither between the treatments nor between the soil depths (Table 3 and Fig. 2b). Consequently, the DPS followed very much the pattern of P-ox with lower values for the no P than for the treatments with P supply in 0–30 cm as well as 30–60 cm soil depth. In 0–30 cm, the DPS in the fertilizer treatments was above 40% at all sampling dates (Fig. 2c).

Sequentially extracted P fractions and total P

In 2019 the labile soil P fraction (sum of P-H$_2$O and P-NaHCO$_3$) ranged in 0–30 cm from 125 to 163 mg kg^{-1} with higher values found for higher P budgets (Fig. 3 and Supplementary Table S1). Differences between the treatments were mainly caused by varying P-H$_2$O contents, while for P-NaHCO$_3$ relatively small differences were found. Moderately labile P (corresponding to NaOH-extractable P), ranging in 0–30 cm from 224 to 243 mg kg^{-1}, was not influenced by fertilization. Stable P (sum of H$_2$SO$_4$-extractable P and residual P), ranging in 0–30 cm from 155 to 230 mg kg^{-1}, were found to be higher for the compost + TSP treatment than for the no P treatment, while the single application of TSP or compost did not result in raised values in comparison to no P. The P-tot, ranging in 0–30 cm from 504 to 636 mg kg^{-1}, was highest in the compost + TSP treatment followed by the compost treatment ($p < 0.05$) (Supplementary Table S1), while for the TSP and no P treatment no significant differences were found.

Generally, the same patterns between treatments as observed in 0–30 cm soil depth were also observed in deeper soil depths, yet with hardly any significant differences between the treatments at 60–90 cm soil depth (Fig. 3). While the P content in the labile and moderately labile fractions decreased with increasing soil depth, this was not the case for the stable fraction, which comprised considerable proportions of P (> 50% of P-tot) in the depth 60–90 cm. This was caused in particular by the P-residual. In contrast to the P fractions, for P-tot, clear differences between the treatments were measured in 60–90 cm, and the compost + TSP treatment was found to accumulate considerably more P in this depth than in the other treatments (Table 4 and Fig. 3). While in the depth of 0–30 cm, the P-tot content in the compost treatment

Fig. 3 Phosphorus (P) concentrations of labile (sum of P-H$_2$O and P-NaHCO$_3$), moderately labile (P-NaOH), stable (sum of P-H$_2$SO$_4$ and P-residual) and total P fractions (P-tot) of soil samples taken in spring 2019 from three sampling depths (0–30, 30–60 and 60–90 cm) after no P fertilizer application (no P) or with triple-superphosphate (TSP), bi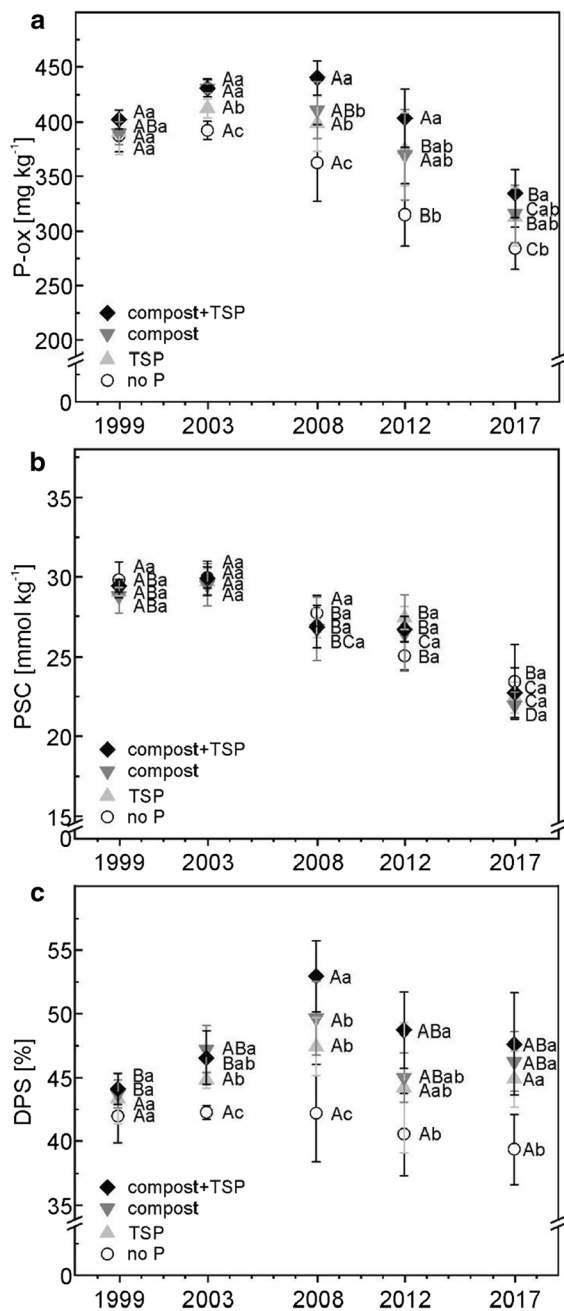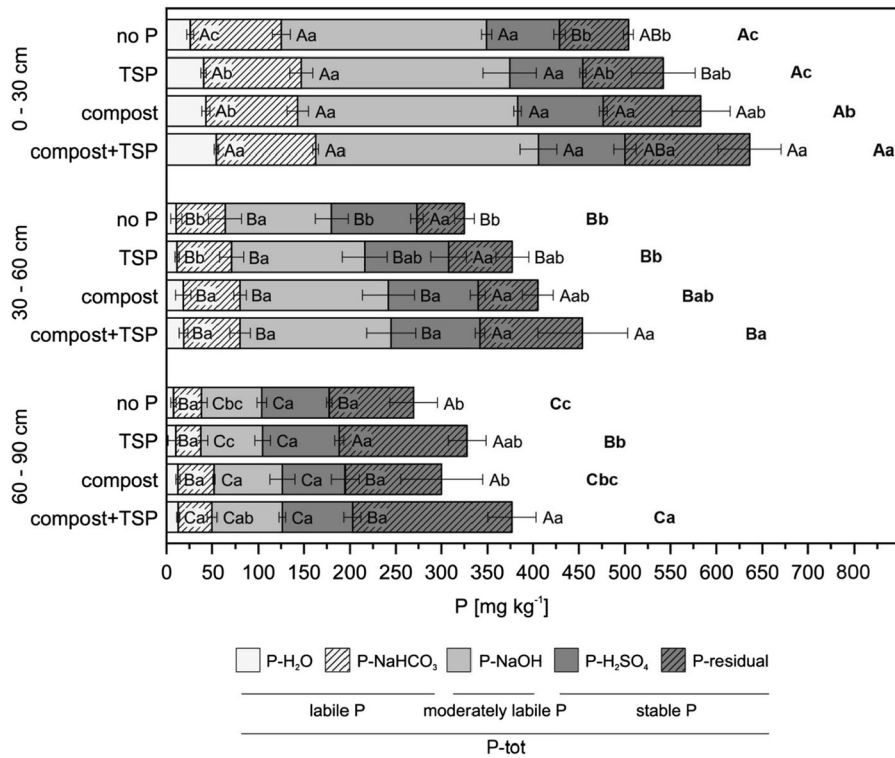o-waste compost (compost) or both (compost + TSP) since 1998. Letters in capital case indicate significant difference between soil depths within same treatment and letters in lower case indicate significant difference between treatments within same soil depth (Duncan's new multiple range test with $p < 0.05$). Bold letters at the rightmost position indicate differences for P-tot. Mean ± standard deviation (n = 4)

Table 4 Total phosphorus stocks (P-tot) of the soil samples taken in three soil depths (0–30, 30–60 and 60–90 cm) and their sum in profile (0–90 cm) in spring 2019 after no P fertilizer application (no P) or with triple-superphosphate (TSP), bio-waste compost (compost) or both (compost + TSP) since 1998

Treatment	0–30 cm kg ha^{-1}	30–60 cm	60–90 cm	0–90 cm
No P	1814 ± 51	1268 ± 93	1052 ± 138	4133 ± 194
TSP	1951 ± 149	1336 ± 222	1279 ± 66	4566 ± 213
Compost	2099 ± 67	1580 ± 187	1170 ± 96	4848 ± 213
Compost + TSP	2290 ± 73	1770 ± 275	1492 ± 104	5682 ± 374

Mean ± standard deviation (n = 4)

was higher than in the TSP treatment, in the depth of 60–90 cm P-tot tended to be lower in the compost treatment.

Inorganic P fractions accounted with about 70–80% for most parts of the P-sum in 0–30 cm and the proportion of Pi even increased in deeper soil depths (Supplementary Table S2). No significant differences between organic and inorganic P fertilizer supply were found within the Po fractions, though the compost treatment tended to have a higher proportion of Po in deeper soil layers than TSP.

Fig. 4 Phosphorus (P) concentrations of labile (sum of P-H$_2$O and P-NaHCO$_3$), moderately labile (P-NaOH), stable (sum of P-H$_2$SO$_4$ and P-residual) and total P fractions (P-tot) of soil samples taken in autumn of 1999, 2003, 2008, 2012 and 2017 after no P fertilizer application (no P) or with triple-superphosphate (TSP), bio-waste compost (compost) or both (compost + TSP) since 1998. Letters in capital case indicate significant difference between sampling dates within same treatment and letters in lower case indicate significant difference between treatments within same sampling date (Duncan's new multiple range test with $p < 0.05$). Bold letters at the topmost position indicate differences for P-tot. Mean ± standard deviation (n = 4)
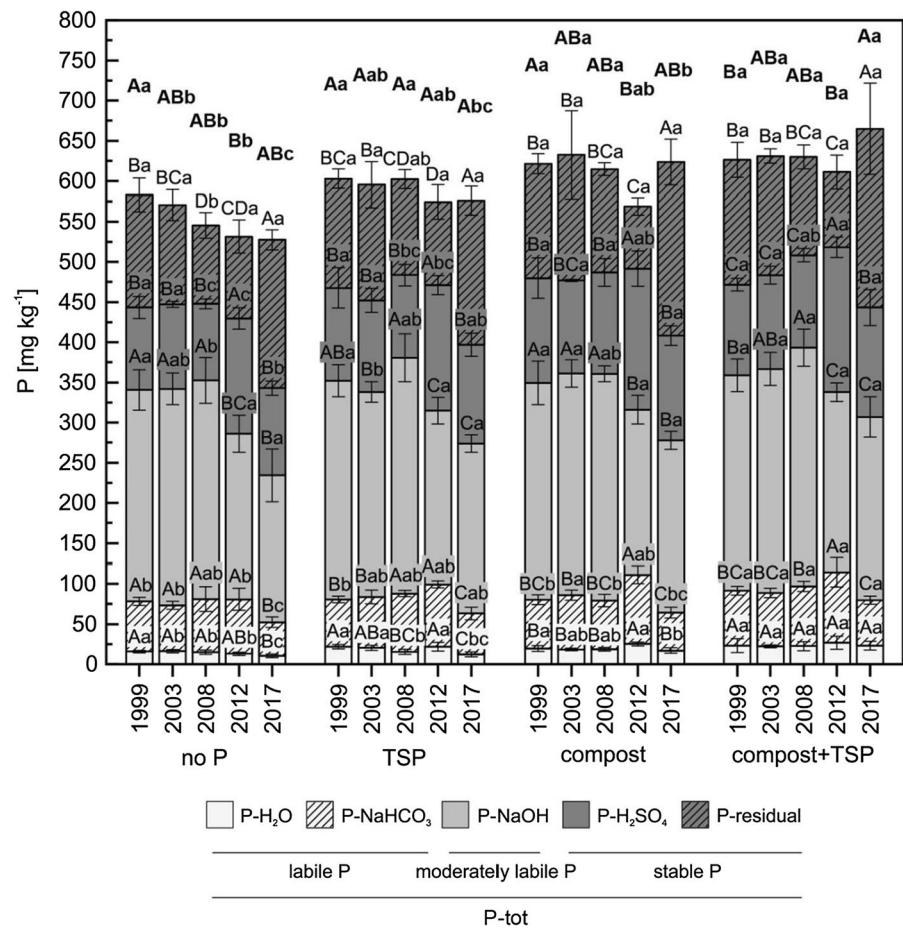
With respect to development over time, the differences of P-H$_2$O in 0–30 cm between the four treatments became considerably greater with time (Fig. 4). In comparison to the no P treatment (defined as 100%), P-H$_2$O in the compost + TSP treatment increased to 145% in 1999, 152% in 2008, 206% in 2012 and 221% in 2017. Increasing differences over time, though not as distinct, were also measured for P-H$_2$SO$_4$, while the differences between the treatments did not increase during the experimental period for P-NaHCO$_3$ and P-NaOH (Fig. 4).

Similar to P-dl, the contents of labile P in 0–30 cm were higher in spring 2019 than in autumn samplings of previous years (Figs. 3, 4). In contrast, P-H$_2$SO$_4$ was found to be lower in 2019 than in the other years. With respect to changes

of P-tot in the 0–30 cm soil depth, the decrease in the no P treatment was more pronounced than the increase in the compost + TSP treatment over the experimental time.

Isotopic P exchange kinetics

The Cp measured by the IEK method in 2019 showed a clear differentiation between treatments with lowest values in the no P, similar values in the TSP and compost and highest values in the compost + TSP treatment (Table 5). Cp in 0–30 cm ranged between 4.7 and 10.8 mg kg^{-1} and decreased about tenfold in 60–90 cm. Pi-tot showed little response to treatment and decreased by about half in 60–90 cm (average 185 mg kg^{-1}) compared to 0–30 cm (average 362 mg kg^{-1}).

Table 5 Indicators of phosphorus (P) availability measured with the isotopic exchange kinetics approach (parameter m and n of the exchange kinetics, orthophosphate concentration (Cp), total inorganic P (Pi-tot), exchangeable P within one minute (E1min), within one hour (E1hour), from one hour to three months (E1hour-3months), within three months (E3months) and not exchangeable within three months (E > 3 months)) of the soil samples taken in 2019 in three soil depths (0–30, 30–60 and 60–90 cm) after no P fertilizer application (no P) or with triple-superphosphate (TSP), bio-waste compost (compost) or both (compost + TSP) since 1998

Treatment	Depth cm	m	n	Cp mg kg^{-1}	Pi-tot
No P	0–30	0.87 ± 0.08Aa	0.25 ± 0.06Ca	4.7 ± 0.3Ac	326.5 ± 79.4Aa
	30–60	0.64 ± 0.09Ba	0.31 ± 0.04Ba	2.0 ± 0.4Bb	216.5 ± 43.4Ba
	60–90	0.26 ± 0.03Ca	0.37 ± 0.03Aab	0.4 ± 0.1Cb	174.2 ± 49.0Ba
TSP	0–30	0.70 ± 0.10ABa	0.33 ± 0.03Ba	6.7 ± 0.9Ab	349.7 ± 34.1Aa
	30–60	0.74 ± 0.17Aa	0.31 ± 0.04Ba	3.2 ± 1.7Bb	223.8 ± 48.3Ba
	60–90	0.38 ± 0.18Ba	0.42 ± 0.04Aa	0.6 ± 0.4Cab	189.1 ± 61.6Ba
Compost	0–30	0.79 ± 0.11Aa	0.25 ± 0.03Ba	6.9 ± 0.2Ab	377.4 ± 69.2Aa
	30–60	0.77 ± 0.08Aa	0.28 ± 0.03Ba	4.1 ± 0.6Bab	252.2 ± 44.2Ba
	60–90	0.43 ± 0.14Ba	0.36 ± 0.02Ab	0.9 ± 0.4Cab	175.6 ± 15.5Ca
Compost + TSP	0–30	0.77 ± 0.14Aa	0.26 ± 0.04Ba	10.8 ± 1.6Aa	395.4 ± 44.3Aa
	30–60	0.86 ± 0.12Aa	0.27 ± 0.03Ba	5.8 ± 1.5Ba	261.0 ± 35.3Ba
	60–90	0.35 ± 0.17Ba	0.35 ± 0.03Ab	1.1 ± 0.9Ca	199.9 ± 48.6Ca

Treatment	Depth cm	E1min mg kg^{-1}	E1hour	E1hour-3months	E > 3months	E3months %
No P	0–30	6.0 ± 0.5Ac	14.8 ± 2.1Ab	69.2 ± 35.2Ab	242.4 ± 84.7Aa	26.4 ± 12.3Bb
	30–60	3.3 ± 0.6Bc	10.3 ± 0.9Bb	64.2 ± 8.4Aa	142.1 ± 46.0Ba	35.4 ± 8.2Aa
	60–90	1.5 ± 0.3Cb	6.7 ± 1.5Cb	66.1 ± 19.4Aa	101.3 ± 31.2Ba	41.9 ± 4.5Aa
TSP	0–30	10.4 ± 2.3Ab	34.4 ± 10.1Aa	162.0 ± 25.5Aa	153.3 ± 59.6Aa	56.8 ± 13.8Aa
	30–60	4.6 ± 1.8Bbc	13.7 ± 4.6Bab	77.3 ± 24.3Ba	132.8 ± 47.0Aa	41.2 ± 11.3Aa
	60–90	1.5 ± 0.6Bb	7.7 ± 1.6Bab	86.7 ± 8.3Ba	94.6 ± 53.8Aa	53.0 ± 12.6Aa
Compost	0–30	9.4 ± 1.0Abc	23.3 ± 2.2Aab	94.8 ± 15.9Aab	259.3 ± 71.5Aa	32.0 ± 7.2Aab
	30–60	5.7 ± 0.9Bab	15.5 ± 2.8Bab	71.8 ± 13.7Aa	164.8 ± 57.6Ba	35.9 ± 10.3Aa
	60–90	2.0 ± 0.3Cab	8.1 ± 1.2Cab	66.7 ± 10.8Aa	100.8 ± 16.4Ba	42.7 ± 6.5Aa
Compost + TSP	0–30	14.9 ± 2.9Aa	38.5 ± 12.3Aa	139.7 ± 56.5Aa	217.2 ± 37.3Aa	44.3 ± 13.1Aab
	30–60	7.3 ± 1.5Ba	18.3 ± 2.9Ba	77.7 ± 17.4Ba	165.0 ± 19.1ABa	36.6 ± 3.9Aa
	60–90	2.8 ± 1.2Ca	10.8 ± 4.0Ba	81.2 ± 24.7Ba	107.9 ± 22.2Ba	45.6 ± 3.4Aa

Letters in capital case indicate significant difference between soil depths and letters in lower case indicate significant difference between treatments within same soil depth (Duncan's new multiple range test with $p < 0.05$). Mean ± standard deviation (n = 4)

Treatments had no significant effect on IEK parameters m and n. Parameter m decreased with increasing soil depth ($p < 0.05$; average 0.78 in 0–30 cm, 0.75 in 30–60 cm and 0.36 in 60–90 cm) while the parameter n increased with increasing soil depth ($p < 0.05$; average 0.27 in 0–30 cm, 0.29 in 30–60 cm and 0.38 in 60–90 cm; Table 5).

The E1min and E1hour both had lowest values in the no P and highest values in the compost + TSP treatment ($p < 0.05$) in all soil depths, whereas no differences were found between the TSP and compost treatment. The E1min and E1hour decreased in all treatments with increasing soil depth. The E1hour-3months values showed significant ($p < 0.05$) differences only in the soil depth of 0–30 cm between treatments TSP (162 mg kg^{-1}) and compost + TSP (140 mg kg^{-1}) on the one hand and treatment no P (69 mg kg^{-1}) on the other hand. E1hour-3months showed similar values through all soil depths for treatments no P and compost, while they reduced with depth for treatments TSP and compost + TSP. The fraction of P that was not
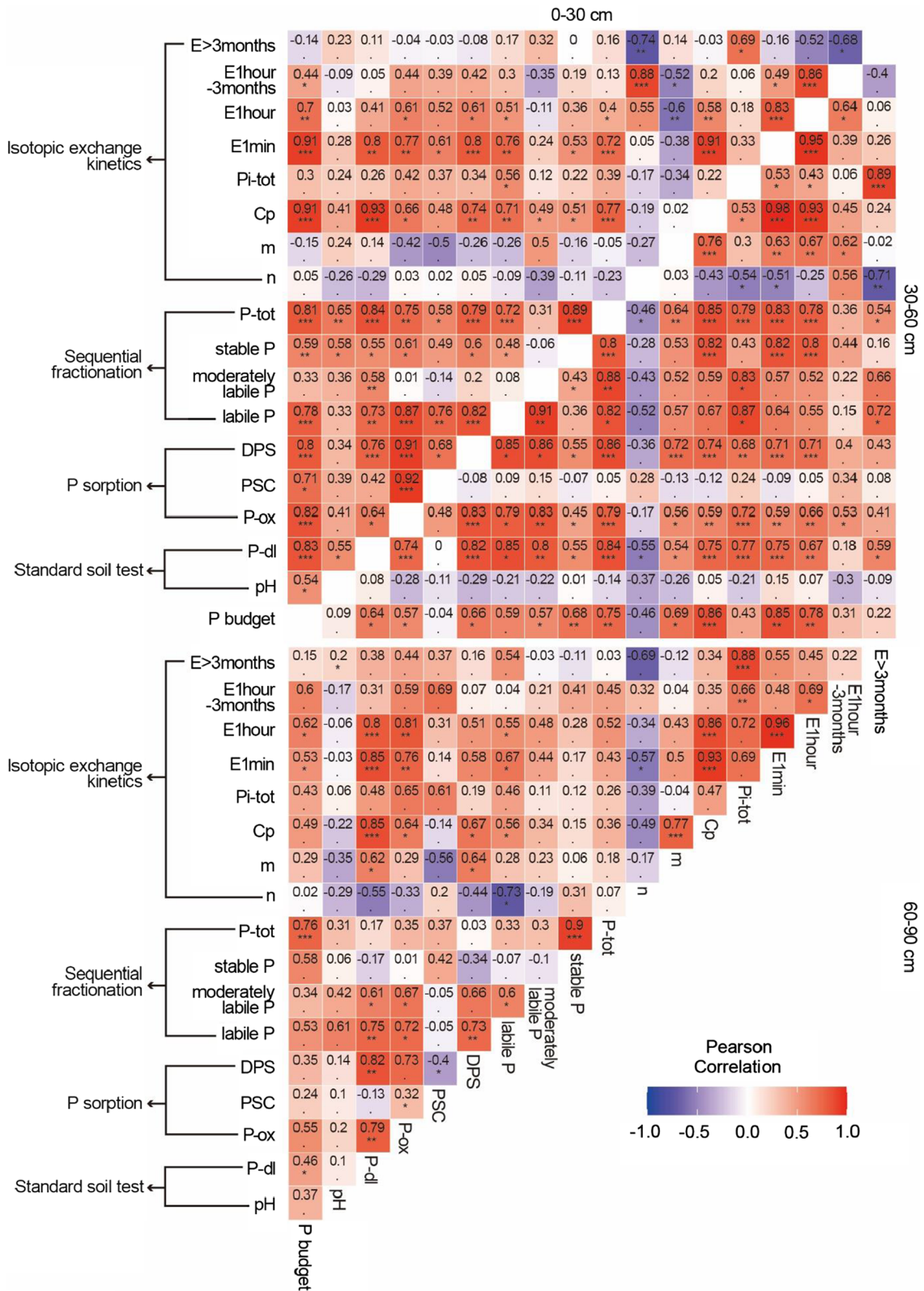
◄ **Fig. 5** Heat map showing Pearson's correlation coefficients among selected parameters of soil samples taken in spring 2019 from three sampling depths (0–30, 30–60 and 60–90 cm) across all treatments. Parameters are grouped in P budget, standard soil test, P sorption, sequential fractionation and isotopic exchange kinetics. ***, **, * and . indicate significances at $p < 0.001$, $p < 0.01$, $p < 0.05$ and $p > 0.05$, respectively

exchangeable within three months (E > 3 months) was not affected by any treatment and decreased with soil depth, though not significantly for TSP. The percentage of P that can be exchanged within a period of three months (E3months) ranged from 26% (no P) to 57% (TSP) in 0–30 cm soil depth but became more similar between treatments in 60–90 cm soil depth (42–53%).

Correlations between soil characteristics and P budgets

The P budget was closely correlated with several soil characteristics in 0–30 cm depth (Fig. 5), particularly P-dl ($r = 0.83$, $p < 0.001$), P-ox ($r = 0.82$, $p < 0.001$), labile P ($r = 0.78$, p < 0.001), P-tot (0.81, $p < 0.001$), Cp ($r = 0.91$, $p < 0.001$) and E1min ($r = 0.91$, $p < 0.001$). Below the 0–30 cm depth, the P budget correlated with soil properties, too, though less closely. The strongest correlation in 60–90 cm were found between P budget and P-tot (0.76, $p < 0.001$).

Between the soil characteristics usually positive correlations were observed, particularly between P-dl, P-ox, Cp, E1min and labile P, as well as between P-tot and stable P. The strength of these correlations usually decreased with increasing soil depth, but for P-dl increasing correlation strengths with P-ox and E1min were found in deeper soil.

Water extractable Pi as determined by IEK (Cp) correlated strongly with water extractable P from the sequential fractionation (Pi-H_2O) over all soil depths (Fig. 6a). However, Cp reached in average only 16% of the concentrations of Pi-H_2O. Total inorganic P (Pi-tot) determined by ignition method for IEKs showed strong positive correlation with the sum of inorganic fractions from sequential fractionation (Pi-sum; Fig. 6b). The sum of H_2O- and NaHCO$_3$-extractable Pi was significantly correlated with isotopically exchangeable inorganic P within one hour (E1hour) ($r = 0.81$, $p < 0.001$; Fig. 6c). The

correlations became weaker with stronger extraction agent and longer exchange time (NaOH-extractable Pi and E1hour-3months: $r = 0.47$, $p < 0.01$; Fig. 6d; H_2SO_4-extractable inorganic P and E > 3 months: $r = 0.31$, $p > 0.05$; Fig. 6e).

PCA

A PCA biplot was created to visualize the similarity between soil samples and the influences of each parameter (Fig. 7). Two principal components (PC1 and PC2) explained most variation (79.1%). P-NaOH and E > 3 months were clustered closely and had higher vector loading to PC1 than other parameters, whereas stable P and P-residual from sequential extraction showed higher vector loading to PC2. The labile P pool, Pi-tot and E1min were closely clustered as well. Soil samples distributed along the PC1 direction with increasing soil depths, e.g. 0–30 < 30–60 < 60–90 cm, whereas along PC2 direction the order changed to 60–90 < 0–30 < 30–60 cm. In most cases, the differentiation between the depths was more pronounced than between the treatments. Within each soil depth, the treatments in PC1 direction followed the order no P > TSP > compost > compost + TSP. In each soil depth of the compost + TSP treatment behaved strongly differently to the other treatments.

Discussion

Long-term fertilizer management affects mainly the topsoil and labile P pools

In order to comprehensively assess the effect of long-term P fertilizer strategies various analytical approaches were used, which were also expected to explain the fate of P in soil in more detail than standard soil tests. The P-dl method was used as standard soil test as suggested for soils with pH values lower than 6 (Buczko et al. 2018).

For P fertilizer recommendation, target P-dl values in the topsoil are used, which are deduced from field experiments that record yield response to increasing P-dl values. According to the soil P classification of the German federal state of Mecklenburg-Western Pomerania (Kape 2019), the P-dl content in the no P, TSP and compost treatments were in 2019 in the
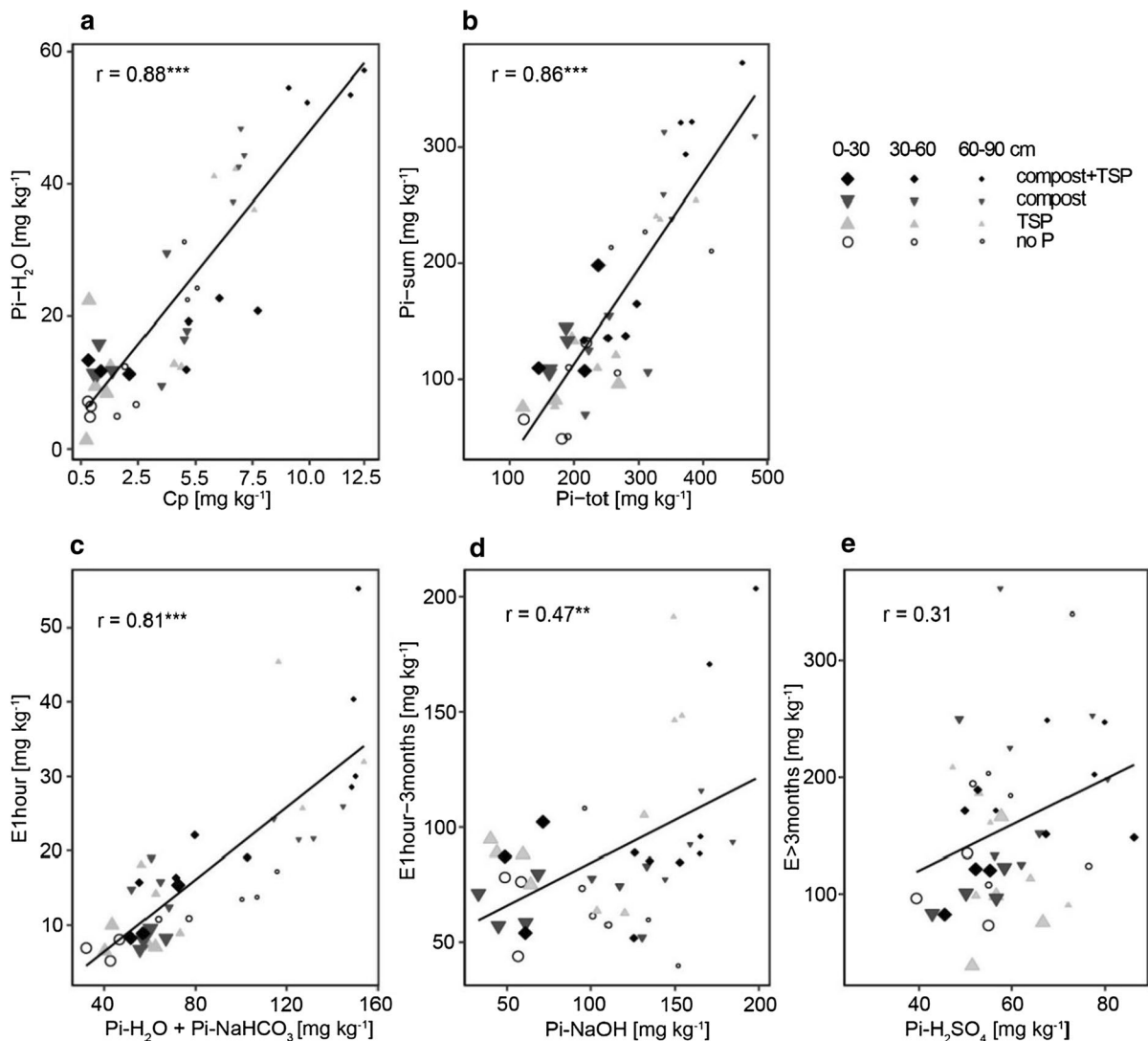
Fig. 6 Correlations between sequentially extracted fractions and isotopically exchangeable inorganic P of soil samples taken in spring 2019 from three sampling depths (0–30, 30–60 and 60–90 cm) after no P fertilizer application (no P) or with triple-superphosphate (TSP), bio-waste compost (compost) or both (compost+TSP) since 1998. H_2O-extractable inorganic P (Pi-H_2O) from sequential fractionation correlated with water extractable Pi (Cp) determined by IEK (**a**), sum of inorganic fractions from sequential fractionation (Pi-sum) correlated with total inorganic P (Pi-tot) determined in IEK (**b**), sum of H_2O- and $NaHCO_3$-extractable inorganic P (Pi-H_2O+Pi-$NaHCO_3$) correlated with P exchangeable in 1 h (E1hour) (**c**), NaOH-extractable inorganic P (Pi-NaOH) correlated with P exchangeable between 1 h and 3 months (**d**), and H_2SO_4-extractable inorganic P (Pi-H_2SO_4) correlated with P only exchangeable over 3 months (E > 3 months) (**e**). Fitted lines were illustrated after linear regression

same target P fertility class B corresponding to 31 to 55 mg kg^{-1} and indicating slightly sub-optimal P contents. Despite the positive P budgets over 21 years the P content in the compost+TSP treatment was still in P fertility class C indicating optimal P contents from 56 to 80 mg kg^{-1}. Fertilization affected P-dl also in

deeper soil depths with elevated values especially for the treatments compost and compost+TSP. However, considering that subsoils are often compacted the availability of this P pool to crops may be limited (Kautz et al. 2013). The P-dl contents in the topsoil were closely correlated with the P budgets ($r = 0.83$,

Fig. 7 Biplots generated from PCA with the percentage of variance explained by the first two components for selected parameters of soil samples taken in spring 2019 from three sampling depths (0–30, 30–60 and 60–90 cm) after no P fertilizer application (no P) or with triple-superphosphate (TSP), bio-waste compost (compost) or both (compost + TSP) since 1998

$p < 0.001$). However, P budgets were mainly determined by differences in P supply, and less by varying P withdrawals with crop harvest. Previous studies on this field experiment have shown that long-term differences in P fertilization affected the plant-available P levels but not necessarily crop yields, and especially the yields of winter cereals and mixed crops were insensitive to P supply (Zicker et al. 2018; Eichler-Löbermann et al. 2021).

At our experimental site the DPS was relatively high, which was mainly linked to the low Al-ox and Fe-ox contents in soil and consequently low PSC values. The PSC values of our soil were with about 25 mmol kg^{-1} in the lower range estimated for various Dutch soils (Koopmans et al. 2006), that formed under similar conditions, and clearly lower than the PSC of many northern European soils (Uusitalo and Tuhkanen 2000; Rubæk et al. 2013; Blombäck et al. 2021) with values between about 50 to 400 mmol kg^{-1}. Previous investigations have shown that DPS values ranging from 25 to 40% have an increased risk of P loss (Breeuwsma et al. 1995;

Siebers et al. 2021). Thus, relevant P losses or translocation into deeper soil depths would have to be expected even for the no P treatment in which the lowest DPS of about 35% was found in 2019. However, because P stocks in the soil profile down to 90 cm soil depth were roughly equivalent to P budgets in the treatments, we can largely rule out shifts to depths greater than 90 cm in our study (see below). When evaluating the results, one must also take into account the oxalate extraction may overestimate the amount of sorbed P because calcium phosphates, which represented the second most important P form in this soil after P associated with Fe- and Al-(hydr) oxides (Koch et al. 2018), can be also dissolved during the oxalate extraction (Blombäck et al. 2021).

The sequential fractionation was used to differentiate between labile, moderately labile and stable P fractions. The labile fraction (P-H$_2$O and P-NaHCO$_3$) in 0–30 cm followed the expectations with higher P contents when the P budgets were higher ($r = 0.78$, $p < 0.001$). The labile fraction was also closely correlated to the P-dl ($r = 0.76$, $p < 0.001$) but was about three times higher than the P-dl, which should be taken into account in terms of practical fertiliser recommendations. The P-NaOH and P-H$_2$SO$_4$ in 0–30 cm was less clearly affected by the budgets and less correlated to other soil characteristics than the labile P. Insensitivity of P-NaOH and P-H$_2$SO$_4$ following moderate rates of P application to agricultural soils was previously reported. These fractions were only affected at very high P additions of 90 kg ha^{-1} yr^{-1} (Negassa and Leinweber 2009) or long-term P budgets of about 1800 kg ha^{-1} (Rodríguez et al. 2018). In our study, the P supply in the compost + TSP treatment (about 40 to 45 kg ha^{-1} yr^{-1}), though evidently above the P demand of crops, was probably not high enough to clearly influence the moderately labile and stable P fractions. The lower sensitivity of P-NaOH and P-H$_2$SO4 to P management could also be explained with a study of Klotzbücher et al. (2019), showing that from the third extraction step onwards, sequential fractionation can fail to assess binding strengths between P forms and minerals.

In the subsoil the effect of P budget was noticeably lower than in the topsoil, and site-specific soil properties would have mainly influenced the P fractions, as also shown for a stagnic Cambisol in a study of Baumann et al. (2020). In this context, weathering from

primary minerals was described as a principal process responsible for P solubility and availability in deeper soil depth in a study of Kautz et al. (2013).

Similar to the approach of Helfenstein et al. (2020) we related distinct P fractions of the sequential fractionation with amounts of P that were isotopically exchangeable within certain time frames. While for the labile P fraction, a strong correlation was found, the correlations became weaker the longer the time period considered and the stronger the extractant used. This suggests that E-values especially for longer time-periods could not be well predicted from sequentially extracted P fractions. In difference to Helfenstein et al. (2020), we correlated only the inorganic P fractions with specific E-values, which we believe is more coherent with the assumption that only the exchange of inorganic P is determined with the IEK experiment. Indeed, if the correlations were calculated with total P instead of inorganic P for each P fraction, the correlations would mostly become even weaker (data not shown). This indicates that for the analysis of P dynamics at specific sites, both the sequential fractionation and the IEK approach may be useful to complement each other, but that one method alone cannot fully replace the other.

When using E1min as indicator for soil P availability, all treatments were well supplied with P in the 0–30 cm soil depth, since only E1min values lower than 5 mg kg^{-1} are considered P limiting for crops (Gallet et al. 2003). For soil depths below 30 cm there was a clear trend of increased E1min and E1hour values with increasing soil P budgets. This trend diminished for E-values larger than 1 h, indicating that only the P fractions with an exchangeability within one hour were reaching deeper soil depths in case of a positive budget. The topsoil of all treatments appeared to exhibit a low soil P sorption, indicated by IEK parameter m values of > 0.7. This is supported by DPS values > 35% in all treatments (see above).

The differences in the P budgets between the treatments increased over the course of the experimental years and were about 900 kg ha^{-1} when comparing the no P with the compost + TSP treatment and about 400 to 450 kg ha^{-1} when comparing the no P with TSP or with compost (Table 1) in 2019. The differences regarding the P stocks in the soil depth of 0–30 cm (no P 1813 kg ha^{-1}, TSP 1951 kg ha^{-1}, compost 2098 kg ha^{-1}, compost + TSP 2290 kg ha^{-1}), represented roughly about 40 to 50% of the theoretical

differences in the P stocks expected on the basis of the P budgets. However, the P stocks in the whole soil depth from 0–90 cm (no P 4133 kg ha^{-1}, TSP 4566 kg ha^{-1}, compost 4848 kg ha^{-1}, compost + TSP 5552 kg ha^{-1}) differed almost equally to the differences in the P budgets. Thus, it can be assumed that no relevant losses occurred neither that P was located into deeper soil depths than 90 cm during the experimental period. The distribution of P stocks in the soil profile was as follows: 43% for the 0–30 cm depth, 31% for the 30–60 cm depth, and 26% for the 60–90 cm depth (average of all treatments). With not even half of the total P stocks in soil occurring in the top 30 cm, deeper soil depth plays an important role as P reservoir. Although the 60–90 cm soil depth may be less relevant for plant nutrition (see above), our results support previous recommendations to focus more on subsoil when describing the fate of surplus P (Rubæk et al. 2013).

Type of fertilizer did not affect P pools

Not only the P budgets, but also the type of fertilizer was expected to affect the soil P pools. Especially for the readily available P in the topsoil we assumed higher contents when water soluble P was applied with TSP than after compost application. However, no differences in the labile P fractions were found between both fertilizer treatments and for P-dl even higher contents could be measured after application of compost compared to TSP. The P supply with TSP and compost was about the same on average over the years, but while TSP was applied every year, compost was applied only every three years, but in three times the amount. However, this cannot be a reason for the increased P-dl contents, since the samples were taken at different periods after the respective compost applications.

Despite the different C input with the fertilizers, the ratio of organic and inorganic P fractions in the 0–30 cm depth was not altered by the type of fertilizer (see Supplementary Table S2) and the total Pi and total Po ratios were about 75 and 25%, in both, the TSP and the compost treatment. The independence of soil P forms from the type of fertilizer can be explained with turnover processes whereby the application of organic compounds usually raises the activity of microbes in the soil and consequently the microbial immobilization of

inorganic P, mineralization of organic P and microbial P synthesis (Bünemann et al. 2008; Richardson and Simpson 2011). Additionally, the inorganic P is converted into organic P by the plant P uptake which supplies the soil with organic P through dead below- and aboveground plant biomass (Bünemann et al. 2008). One has also to consider, that organic fertilizers do not necessarily contain only organically bound P. In the case of mature compost in particular, a large proportion is already mineralized and in the compost applied in this study, the organic P accounted for only 10 to 15% of the total P (Requejo and Eichler-Löbermann 2014). In the subsoil, we found a tendency to higher shares of Po for the compost than for TSP treatment (21% vs. 14%). Relatively high Po contents in subsoils were also reported in a review paper by Kautz et al. (2013) and were explained by the translocation of Po into the subsoil via the root system especially under high supply of organic fertilizers.

Considering the isotopically exchangeable P fractions, the fraction of P that could be recovered as available in less than 3 months was in tendency lower for compost than for TSP, while compost addition favored the increase of P fractions that are slower exchangeable than within 3 months. In a study of Lemming et al. (2019) compost P was also found to be less rapidly exchangeable than other recycling products such as sewage sludge. However, this contradicts somehow the findings of the sequential fractionation and the P-dl method, where P applied with compost was found to be as readily available as P given with TSP (see above). One has to consider that despite the lower E3months values in the compost compared to the TSP treatment, purely arithmetical, the E3months value in the compost treatment in the 0–30 cm depths corresponds to about 340 kg ha^{-1} and is thus considerably higher than the expected annual P withdrawal of the plants. That the compost application did not limit the crop yields on this site was shown before by (Zicker et al. 2018; Eichler-Löbermann et al. 2021).

In comparison to TSP the compost treatment tended to have higher P contents in the depths of 0–30 cm and 30–60 cm, but tended to have lower P contents in the depth 60–90 cm. This agrees with a study of Lemming et al. (2019) where compost, unlike other recycled products, retained in the topsoil. Lower vertical P translocation after application of organic amendments to sandy soils were also found in a study of Debicka et al. (2016) and were explained by the substantial role of organic matter for P binding.

Only slowly increasing differences in the P pools between the treatments

Besides soil samples taken from different depths in spring 2019, stored soil samples from selected previous sampling dates beginning in 1999 were analysed to assess the management-induced differences in P pools and P dynamics with experimental time. Though the P-dl in 0–30 cm correlated with the P budgets (see Correlations between soil characteristics and P budgets) it became clear that differences in P-dl between treatments have not increased as much as one would have expected based on the budgets. Especially in the compost + TSP treatment, the P surplus was not adequately reflected by the P-dl contents and neither by other methods used. The analyses of deeper soil depths showed that surplus P was shifted vertically (see Long-term fertilizer management affects mainly the topsoil and labile P pools). In our experiment on a Stagnic Cambisol, the fate of the surplus P could only be explained when considering the P-tot in a soil depth until 90 cm, while in a study with the same experimental duration of 21 years on a Haplic Luvisol developed on loess the subsoil until 50 cm could almost completely account for P lost from the topsoil (Oehl et al. 2002).

But not only downward movement of P happened in our field experiment, also an upward P movement can be expected, especially in the treatment without P with higher soil P pools than estimated. This upward movement of P can be related to plant uptake that returned P back to the topsoil and is expected to increase as the total and available P in the topsoil decrease (Oehl et al. 2002). Besides the spatial availability, crops can also enhance the chemical availability of P. Crop induced P mobilization is mainly found under P deficiency (Hinsinger 2009; Devau et al. 2011; Hinsinger et al. 2011; von Tucher et al. 2018; Eichler-Löbermann et al. 2021), which may have counteracted the increasing depletion of the available P pools over time in the no P treatment. Although in our experiment no fixed crop rotation was applied, the wide variety of cultivated crops during the

experimental time may have contributed to mobilize P from chemically less available pools.

While the differences in the P pools between the fertilizer treatments did not increase as expected over time, significant differences were already measured after only one year of the experiment in 1999. Immediate changes in readily available P after P application was also found for a large number of short-term experiments. That means that fertilisation measures initially have a clear effect, at least on soils poor in P, but in a longer term the P availability may remain at a relative constant level, without a pronounced dependency on fertilizer supply. This presumption can be strengthened by results from other LTFEs differing in soil types and climatic conditions (Oehl et al. 2002; Rodríguez et al. 2018; von Tucher et al. 2018) and should be considered when deriving fertilizer recommendations from field experiments.

With the exception of the compost + TSP treatment, a decreasing trend from 2008 to 2017 was measured for P-dl, P-ox and the moderately labile P fraction in the 0–30 cm depth. For the no P treatment this decrease can be explained by the P removal with the crop harvest, but this decrease is in contrast to the balanced fertilizer supply in the TSP and compost treatment. Apart from a vertical P translocation, this observation can be explained with a shift from more readily available to less readily available P over time, as the stable P fraction increased in this period. A general decrease in soil test P content was also observed in another German field experiment by von Tucher et al. (2018). The P forms in the soil are also subject to strong seasonal fluctuations. For the spring sampling in 2019, significantly higher readily available P contents (P-dl and labile P fractions) were measured compared to the autumn sampling in 2017, while the P-H_2SO_4 was found to be lower in 2019 than in the other years. That means there was a shift from stable to labile P and the high contents in the labile pool were offset by very low contents in the stable pool. Seasonal changes of the soil P fractions were also analyzed in other field experiments and were mainly related to microbial activity and increasing mineralization of organic P fractions (Fabre et al. 1996; Yang et al. 2015). This can also explain the lower percentage of organic fractions in spring 2019 as compared with the autumn sampling of the previous years (Supplementary Table S2 and S3).

Conclusions

The use of complementary methods for soil P stocks and P dynamics in this study allowed a better understanding of potential P availability and a better explanation of the effects of P fertilisation over time than individual methods could provide. The P budgets closely correlated with readily available and rapid exchangeable pools (P-dl, P-H_2O and E1min) or the P-tot while the moderately labile and stable fractions (P-NaOH and P-H_2SO_4) were less sensitive to P supply. Accumulation or depletion of P in the topsoil can affect the P stocks in deeper soil depths with an estimated upward movement of P in the case of a long-term P deficit and a downward movement in the case of a long-term P surplus. However, despite the high DPS values at our experimental site, no relevant P translocation deeper than 90 cm soil depth was detected. Variations in readily available P pools between spring and autumn sampling need to be considered in practical fertilizer recommendations, and further research should be conducted to better explain the role of biological P mobilization in this regard. Since P supply from compost contributes at least as much as TSP to readily available P pools, the results also suggest that organic waste products can replace chemical fertilizers in a long term perspective.

Declarations

Conflict of interest We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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