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Simulation of soil phosphorus dynamics and crop yield for organic and mineral fertilization treatments at two long-term field sites

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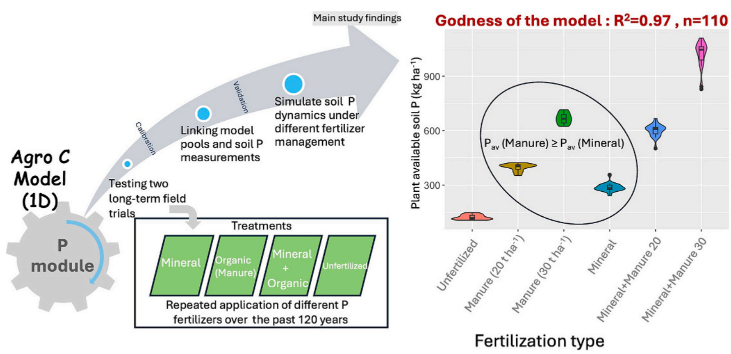
HIGHLIGHTS

- Model calibration linked simulated P pools with P_{CAL} and P_{DGT}-measured fractions.
- Validation showed AgroC's accurate simulation of soil P dynamics and crop yields.
- Combined manure and mineral fertilizers enhanced soil P availability and crop yield.
- Long-term manure use matched mineral fertilizers in maintaining soil P levels.
- MIX treatments showed the highest yield and positive soil P balance over time.

GRAPHICAL ABSTRACT



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ABSTRACT

The efficacy of phosphorus (P) based fertilizers is frequently compromised by soil dynamics that render much of the applied P unavailable for crops. This study aimed to: (i) validate a new P model's prediction of plant-available P; (ii) analyze the effects of organic versus mineral fertilization on P availability and crop yield; and (iii) examine temporal changes in P pools under various fertilization regimes. Data were collected from two long-term field trials, Dikopshof and Bad Lauchstädt, in Germany, using organic (FYM), mineral (MIN), a combination of organic and mineral (MIX) fertilizers, and unfertilized treatments. The AgroC model, incorporating a new P module, accurately predicted P dynamics in cropped plots. At both sites, MIX presented the highest yield, P removal, total P and available soil P. After 120 years of repeated P fertilization, simulations at Dikopshof revealed a positive P balance in MIN (11.1 % with observed 13 %) and in MIX (15 % with observed 15 %), but negative in FYM (−4.9 % with observed −5 %). However, at Bad Lauchstädt, the P balance was negative in all treatments except in MIN (+1.04 %), indicating P depletion. Among crops, cereals showed the most variated yields, with P-use efficiency ranging from 50 % to 99 %, while sugar beet presented the highest P-use efficiency (up to 122 %). The lowest P application rates exhibited, FYM treatment, the highest P-use efficiency for all crops. Model pools were successfully linked to field-measured soil P fractions using CAL and DGT methods, providing initial predictions of various soil P fractions across different fertilization strategies.

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1. Introduction

Phosphorus (P)-based fertilizers have been critical for modern agriculture, yet much applied P becomes unavailable to plants due to soil processes like adsorption and precipitation (Eriksson et al., 2016; Mohammed et al., 2017; Niu et al., 2013; Richardson et al., 2009). This contributes to widespread P deficiency, impacting over 40 % of global arable land (Tilman et al., 2002; Vance, 2001). Accurate quantification of plant-available P and crop uptake is essential to optimize fertilizer use, balancing resource conservation with crop yields (Magid et al., 2006; Seidel et al., 2021; Smith and Schindler, 2009; Yan et al., 2020). Monitoring soil P dynamics in cropped soils is crucial for understanding long-term fertilizer effects on P availability (Otabbong et al., 1997; Zhao et al., 2010). Techniques like the Calcium Acetate Lactate (CAL) method (Schüller, 1969) and Diffusive Gradients in Thin Films Technology (DGT) (Mason et al., 2010; Six et al., 2012) assess plant-available P but can be time-consuming, highlighting the need for faster, reliable methods.

Modeling is a powerful tool for understanding the dynamics and fate of P in the soil-plant system. Models allow to distinguish P fluxes that would have been impossible to measure at the field scale (Das et al., 2019; Jones et al., 1984a; Jones et al., 1984b; Mollier et al., 2008). However, one of the major drawbacks limiting model use as a reliable management tool is their purely conceptual definition. The model pools are usually defined by a turnover or exchange rate lacking a direct link to measurable P fractions. Although efforts have been made to bridge the gap between model pools and measurable P fractions, this challenge basically remains largely unsolved. By linking model simulations with measured P fractions (using PCAL and DGT methods), the study provides a unique and novel approach to accurately predict plant-available P, offering insights into P fluxes that are challenging to measure directly at the field scale.

Our study evaluated the performance of various fertilizer management practices in enhancing soil organic P and P availability for crops. We simulated P dynamics following regular fertilizer applications using a new P module integrated into the AgroC soil-crop-atmosphere model. Data from two long-term field trials, which included different crops, mineral fertilizers, and organic manure treatments, were used to assess the model's effectiveness in describing observed P dynamics under field conditions. The model enabled us to distinguish P fluxes that could not be measured directly at the field scale. We hypothesized that long-term application of different fertilization strategies (organic, mineral, and combined) would alter plant-available P pools and consequently affect crop yields due to their varying biochemical compositions and mineralization potentials. The aim of this study was to test this hypothesis by integrating computational modeling with field observations. Towards this end, the objectives of this work were: (i) to assess how well the new P module simulates crop yield; (ii) to analyze the effects of organic versus mineral fertilization on P availability and crop yield across the long-term experimental sites; (iii) to validate the AgroC model's predictions of plant-available P against actual measurements from these long-term fertilization trials; and (iv) to examine the temporal changes in P pools and their influence on crop performance under various fertilization regimes.

2. Materials and methods

2.1. Field studies

For this study, two long-term fertilizer experimental sites in Germany were considered. The first long-term trial is located at the Dikopshof farm (50° 48′ 21″N, 6° 59′ 9″E) “LTFE Dikopshof” situated south of Cologne, Germany, on the intermediate terraces of the River Rhine. The second site is Static Fertilization Experiment Bad Lauchstädt (51° 23′ 35″N, 11° 52′ 45″E) located at the experimental field station of the Helmholtz-Centre for Environmental Research in Bad Lauchstädt, Sachsen-Anhalt, central Germany. Due to the absence of true replicates at the plot level, where only a single measurement was taken within each plot, the measurements from the same plots across the strips of the target site were averaged.

2.1.1. LTFE Dikopshof (Dikopshof)

Established in 1904, the Dikopshof climate is Atlantic with mean annual temperature of 10.1 °C and a mean annual rainfall of 630 mm (1906–2014). The soil is a silt loam Luvisol and contains on average 24 % clay, 63 % silt, and 13 % sand in the plough layer (Seidel et al., 2021). A five-crop rotation during the monitoring period included sugar beet (*Beta vulgaris*), winter wheat (*Triticum aestivum*), winter rye (*Secale cereale*), the fodder legume ‘persian clover’ (*Trifolium resupinatum*), and potato (*Solanum tuberosum*). Crop residues were removed except for roots and senesced potato leaves. However, it was acknowledged that a small portion, approximately 10 % of the residues, would inevitably remain due to the practical limitations of achieving complete removal.

The plot size is 18.5 × 15 m with a core plot of 10 × 9 m, in this study, four different treatments have been evaluated (farmyard manure amendment, FYM (official treatment ID: +m); full mineral NPKCa fertilization, MIN (official treatment ID: NPKCa); full mineral NPKCa fertilization plus FYM, MIX (official treatment ID: NPKCa+m) and a control treatment without fertilization CTR (official treatment ID: unfertilized). The FYM was applied on the plots cultivated with sugar beet, potato, and winter rye plots at an annual average rate of 20 Mg FM ha^{-1} (FM is Fresh Matter) after the preceding crop was harvested. Table 1 summarizes the application levels for both manure and mineral fertilizers, along with their respective chemical compositions. Details on the long-term experiment are given in Seidel et al. (2021).

2.1.2. Static fertilization experiment Bad Lauchstädt (BL)

Established in 1902, it is managed now by the UFZ Centre for Environmental Research Leipzig-Halle, central Germany. Average annual temperature is 10.1 °C and the average annual rainfall is 489 mm (1996–2018). The soil is a silt loam Haplic Chernozem and contains on average 25 % clay, 66 % silt, and 6 % sand in the plough layer (Altermann et al., 2005; Siebers et al., 2023). The four-crop rotation during 1902–2014 was sugar beet (*Beta vulgaris*), spring barley (*Hordeum vulgare*), potato (*Solanum tuberosum*), and winter wheat (*Triticum aestivum*), from 2015 the root crops were replaced by maize. Over the monitoring period, some crop varieties changed and simultaneously, the use of pesticides was intensified in recent decades. Additionally, crop residues were systematically removed, only the root system remained in the soil. Analogous to the LTFE Dikopshof, around 10 % of the residues were assumed to unavoidably remain on the field due to practical limitations.

The experimental field covers an area of 4 ha and is divided into 8 strips of 200 × 25.5–28.5 m called “Schlaghälfte”(SH). Six treatments, varying in amendment type and application level, have been evaluated (farmyard manure amendment at 20 Mg FM ha $^{-1}$ rate, FYM_20 (official treatment ID: 12); farmyard manure amendment at 30 Mg FM ha^{-1} rate, FYM_30 (official treatment ID: 6); full mineral NPKCa fertilization, MIN (official treatment ID: 13); full mineral NPKCa fertilization combined with FYM of 20 Mg FM ha^{-1}, MIX_20 (official treatment ID: 7); full mineral NPKCa fertilization combined with FYM of 30 Mg FM ha^{-1}, MIX_30 (official treatment ID: 1); and control without amendment (CTR, official treatment ID: 18). FYM was only applied on plots cultivated with sugar beet or potato. Table 1 details the application levels and chemical compositions of both manure and mineral fertilizers. Details on the long-term experiment are given in Merbacha and Körschens (2002).

2.2. Field data collection and measurements

The study period for Dikopshof spans from 1953 to 2018, whereas for BL it was 1996 to 2018, limited by data availability. Tables SI-1 and SI-2 in Supplementary Information (SI) summarize the crop, soil, and climate data used in this study (Ahrends et al., 2020; Medinski et al., 2018; Merbach and Schulz, 2013; Seidel et al., 2021; Siebers et al., 2023).

The crop yield and biomass data were obtained as follows: at the BL site, the mean annual yield for each treatment was calculated by averaging the four replicate plots within each treatment. At Dikopshof, the mean annual crop yield and biomass were calculated from measurements taken across five strips.

The available soil P was determined by different methods, calcium acetate lactate (P_{CAL}), double-lactate (P_{DL}) and diffusive gradients in thin films (P_{DGT}). The CAL extraction method was employed for measuring plant available P in soils (P_{CAL}) in Dikopshof and P_{DL} and P_{DGT} were employed in BL. P_{CAL} was driven from P_{DL} data using the equation (van Laak et al., 2018):

$$P_{CAL} = 8 + 0.61.P_{DL} \tag{1}$$

Where P_{CAL} is P fraction measured by calcium acetate lactate method in mg kg^{-1}, and P_{DL} is P fraction measured by double-lactate method in mg kg^{-1}.

Data in BL was collected on a yearly basis over a 19-year period from 1996 to 2015, while the Dikopshof field was sampled irregularly 5 times between 1972 and 2015. To measure P_{CAL} as described by Schüller (1969), the soil samples were shaken with a buffered extraction solution containing calcium lactate, calcium acetate, and acetic acid (pH 3.7–4.1), then filtered over a paper filter. Extracts were reacted with molybdenum blue solution and ascorbic acid, then measured photometrically.

Following the recommendation of Siebers et al. (2021), available soil P for plant uptake was assessed using the DGT approach. The DGT sampler consists of a hydrogel layer containing an ion resin that is covered by a diffusion layer and protected by a membrane. The DGT device was deployed to the soil brought to 100 % water holding capacity for 24 h at 21 °C. After deployment, the DGT units were dismantled and the ferrihydrite gel eluted in 1 mL of 1 M HCl solution for at least 24 h. The P DGT concentrations were calculated according to standard DGT formulae described by Zhang et al. (1998).

2.3. Modeling approach

2.3.1. Modeling of the carbon, nitrogen and phosphorus cycle

The one dimensional mechanistic crop model AgroC includes four modules i) the coupled SOILCO$_2$/RothC model (Herbst et al., 2008) for simulating hourly or daily soil water fluxes using the Richards equation, heat fluxes using the convection-diffusion equation, the solute transport applying the convection-dispersion equation, and C turnover in the soil-profile with the C turnover model RothC (Coleman and Jenkinson, 1996), ii) the SUCROS model for crop growth and root system development (Spitters et al., 1989), iii) a module that combines elements of RothC and SWATNIT models (Vereecken et al., 1991) to simulate nitrogen (N) transformation in the soil and iv) another module for P transformation in soil. Detailed concepts and equations of P module are available in the Supporting Information (SI), only a brief description of the module is given here. The P module accounts for the major processes that determine sources, transformations, and sinks of P in agricultural soils (Fig. 1). All these processes are assumed to follow first order kinetics. The P module differentiates organic and inorganic P forms in soil, which was not the case in P models, inorganic P is divided into three pools: labile, active, and stable. The liquid-phase labile pool is available for plant uptake. Inorganic P fertilizer is assumed to be in a soluble form and contributes to the labile pool. The labile pool is in equilibrium with the active pool and rapid exchange may occur. The active pools are assumed to be equilibrium with the stable pool and the exchange between those two pools is expected to be slower.

Organic P transformations follow the same pool concept as organic N, based on the RothC model for organic C turnover, except for the microbial biomass pool, which is replaced by a microbial C/P ratio. Soil organic matter is divided into three pools: decomposable plant material (DPM), resistant plant material (RPM), and humified organic matter (HUM). Organic P is partitioned between these three pools. The internal cycling of C in the three organic pools has a P demand regulated by a fixed C/P ratio (ro_P) of the soil biomass. This C/P ratio controls the release/immobilization of soil mineral P from the three organic pools.

Organic P fertilizer is assumed to enter the DPM and RPM pools, except for a small fraction (set to 20 %) that is assumed to be in a soluble form and directly feeds the labile mineral P pool. Plant residues from above and belowground are estimated based on crop type and are assumed to split at harvest into DPM and RPM. Both DPM and RPM decompose to HUM, contributing to the increase in P in the humus pool. The decrease of soil organic P in the three pools due to mineralization contributes to the increase in labile P pool.

The P uptake is modeled using a similar approach to the N uptake model suggested by Huwe and van der Ploeg (1991), with two key differences: (i) the P content of the plant is not organ-specific but constant for the entire crop, and (ii) the convective uptake of P by plant is limited to a minor component compared to the diffusive uptake. Both leaching and plant uptake are added as sink terms to the convection-dispersion equation that simulates liquid-phase P transport in soil profile.

Table 1
Amounts and chemical compositions of manure and mineral fertilizers applied on soil.

	LTFE Dikopshof			Static Fertilization Experiment Bad Lauchstädt				
Amendment	MIN	FYM	MIX	MIN	FYM_20	FYM_30	MIX_20	MIX_30
Organic manure								
Mg FM ha^{-1}	–	20	20	–	20–22	30	20–22	30
C/N	–	10	10	–	10	10	10	10
C/P	–	100	100	–	100	100	100	100
C [kg C ha^{-1}][b]	–	1.8	1.8	–	1.8–2.0	2.7	1.8–2.0	2.7
Mineral fertilizer								
P [kg P ha][c]	31	–	31	60	–	–	28	12
K [kg K ha]	116	–	116	230	–	–	110	50
N [kg N ha^{-1}][a]								
Potato	50	–	50	140	–	–	120	120
Winter wheat	60	–	60	100	–	–	80	80
Winter rye	40	–	40		–	–		
Spring Barley				80	–	–	60	60
Sugar beet	80	–	80	170	–	–	150	150

[a] The N application rate varied based on the crop being cultivated.
[b] Calculations rely on two assumptions: first that dry matter constitutes 25 % of the fresh manure applied, and second that the carbon content of the dry matter is 36 % (Herbst et al., 2018).
[c] Triple superphosphate constitutes 45 % of the P mineral fertilizer applied on soil.

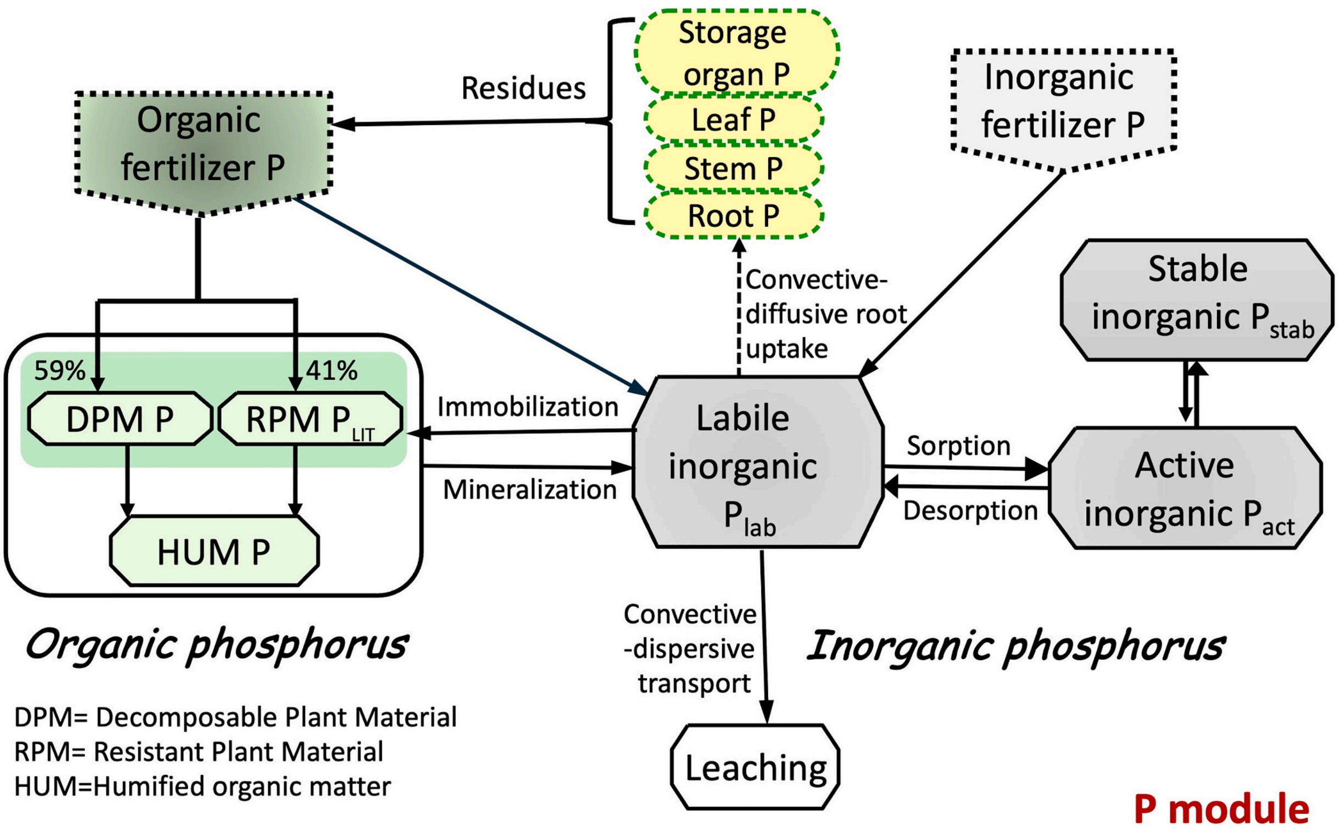

Fig. 1. Structure of the P module.

2.3.2. Model set-up

2.3.2.1. Initial conditions. The soil organic C, and P pools were initialized using the pedotransfer function (PTF) of Weihermüller et al. (2013). This PTF requires only two inputs: total organic C (TOC) and clay content. The initial organic N and P pools were estimated in dependence of the C pools based on a C/N ratio of 10 and a C/P ratio of 100. After setting the initial pools, the model was additionally run for a warm-up period of 800 years to ensure equilibrium.

2.3.2.2. Water flow parameters. We employed the Van Genuchten (1980) model to characterize both the soil water retention and unsaturated hydraulic conductivity. We estimated the required hydraulic parameters using the pedotransfer function developed by Vereecken et al. (1991). For the Dikopshof long-term experiment, measured water content data was available, which allowed to estimate the hydraulic parameters through inverse modeling using the Simplex algorithm proposed by Nelder and Mead (1965).

2.3.2.3. P module calibration. For each site, the treatment with the highest P input from the combination of mineral and manure fertilizers was used for model calibration at BL (1996–2014) and Dikopshof (1953–1992). these parameter sets were validated by comparing the model performance against observation data of the yield, biomass, soil P and crop removal form Dikopshof and for BL. The model predictions were validated over the study period through periodic soil sampling of the ploughed layer (0-30 cm) after crop harvesting. Soil samples were taken both in plots that received fertilizer and unfertilized plots.

The maximum photosynthesis rate A_{max}, which is the potential CO_2 assimilation rate of a unit leaf area at light saturation in kg CO_2 ha^{-1} h^{-1}, along with the crop N and P demand parameters, were manually adjusted to better align the simulated outcomes for P removal (as described below in the next section) with the observed harvested biomass and yield. A single value for the crop N demand parameter was applied across all treatments. The values for P demand and A_{max} parameters were adjusted for each crop variety individually. This was done to account for differences in either biomass production or P removal measurements between the various crop varieties, as some varieties changed during the study period.

To achieve a good fit between observed and simulated values for total soil P and soil P fractions (P_{CAL}, P_{DGT}), the Simplex algorithm was used to adjust two P sorption parameters: the non-sorption coefficient PSP [−] defined as the fraction of P that remains in the labile pool and the stable to active pool size ratio.

2.3.2.4. P removal calculation. The P removal by crop (kg P ha^{-1}) represents the net P uptake by crops after accounting for P recycled back into the soil via crop residue incorporation. In other words, P removal equals the total P in crops minus the P returned to the soil from decomposing crop residues left behind. The organ-specific fraction of biomass that remains on the field is a crop-specific model parameter. For instance, winter wheat, winter rye, and barley produce residues that account for 25 % of the stem biomass and 100 % of the root biomass. The calculated P removal by the model was compared to observed data. The measured P content in the harvested straw was multiplied by the measured straw biomass. Similarly, the P content in the harvested grain was multiplied by the crop yield. The total observed P removal was determined by adding the results of these two calculations.

2.3.3. Linking of measured P fractions to model pools

2.3.3.1. Plant-available P_{av}. Since P_{CAL} is considered a reliable predictor of plant available P in German soils (Gocke et al., 2021), the measured P_{CAL} values in this study were assumed to be equivalent to the plant available fraction in the soil. In terms of model P pools this corresponds to:

$$P_{av} = P_{CAL} = P_{lab} + P_{act} + \alpha.P_{stab} \quad (2)$$

Where: P_{av} is the plant-available P pool and P_{lab}, P_{act}, P_{stab} are respectively labile, active, and stable P model pools, and P_{CAL} is the P fraction measured by the CAL extraction method. The correction factor α adjusts for the overestimation of plant-available P by the P_{CAL} method, accounting for the fact that not all stable P in soil is accessible to plants under natural conditions.

2.3.3.2. Plant uptake P_{up}. Degryse et al. (2009) found that DGT is a good predictor of the P plant uptake when the uptake is diffusion rate limited. To account for the ability of DGT to mimic plant root uptake of available soil P, in this study the DGT-measured *P* values were directly related to the P uptake by plants and assigned to the corresponding model P pools using the following equation suggested by Herbst et al. (submitted):

$$P_{up} = P_{DGT} = P_{lab} + P_{act}.\frac{PSP}{1 - PSP}.t_{P_{DGT}}.r_{rev} \quad (3)$$

Where P_{up} is the plant P uptake, *PSP* [−] is the non-sorption coefficient defined as the fraction of P that remines in the labile pool, $t_{P_{DGT}}$ is the diffusion period of the DGT method (=1 day), r_{rev} is the desorption rate modifier (r_{rev}=0.1 d^{-1}) and P_{DGT} is the P fractions measured by the DGT approach. In Eq. (2), the right-hand side has two elements. The first element is the model estimate of the P mass in the liquid phase, and the second element represents the portion of the active mineral P pool that potentially desorbed over the course of the P_{DGT} experiment.

2.3.4. Statistical analyses and modeling performance

Statistical analyses were performed using R Studio and Python (3.8.16). The Shapiro–Wilk test and Bartlett's test were applied to the observed data to evaluate normality and homogeneity, respectively. Tukey Kramer HSD test was performed to test if crop yields differed significantly among treatments. Graphical comparisons and the following statistical criteria: root mean square error RMSE, the coefficient of model efficiency EF proposed by Nash and Sutcliffe (1970), and the coefficient of determination R^2 were used to quantify the performance of the model against observations.

3. Results and discussion

3.1. P dynamics in soils: measurements and modeling

3.1.1. Total soil P

The total soil P content measured in the topsoil layer (0–30 cm depth) during 2016 for Dikopshof and 2015 for BL was compared against the corresponding simulated values from the model. For both sites, except for the CTR treatments, the simulated total P fell within the observed error range for the measurements (Fig. 2), indicating better model efficiency in the amended soils than in CTR treatments where the P content was underestimated. In measured, the total P increased in the following order between 1953 and 2018 for Dikopshof: CTR < FYM = Min < MIX, while in simulated it followed CTR < FYM < Min < MIX. The same order was also found for BL in observed total P: CTR < FYM_30 = MIN < MIX_30. Nevertheless, the simulated total P in FYM treatment with a higher dose of manure addition (30 t ha^{-1}) was greater slightly than MIN: CTR < MIN < FYM_30 < MIX_30.

3.1.2. Total P removal from soil

At Dikopshof, the model accurately simulated the increase in total P removal after crop harvest from 454 to 1324 kg P ha^{-1} between 1953 and 2018, following the order: CTR < MIN < FYM < MIX. Field observations supported this pattern, with observed total P removal ranging from 432 to 1340 kg P ha^{-1}, aligning with the model's sequence (Table 2). The model's performance for total P removal was acceptable (Table 3), with RMSE values ranging between 4.2 and 6.6 kg P ha^{-1}. The MIX treatment exhibited the highest simulated total P removal over the experimental period, attributed to the high available soil P (Fig. 4a) due to the cumulative input of 1612 kg P ha^{-1} from mineral P fertilizer and 702 kg P ha^{-1} from organic amendment over 65 years (Table 2).

At BL, the simulated total P removal between 1996 and 2018 increased from 296 to 611 kg P ha^{-1} with the following order: CTR < FYM_20 < FYM_30 < MIN < MIX_20 < MIX_30 (Table 2, Fig. SI 3c). From the field observations, the values of total P removal ranged from of 206 to 645 kg P ha^{-1} increasing in the same order as the simulation results, except for the MIX_20 and MIX_30 treatments, which showed almost the same value (a difference of about 1 kg P ha^{-1}) (Table 2). The RMSE values varied between 4.3 and 6.2 kg P ha^{-1} falling within the same error range as the Dikopshof (Table 4). As for Dikopshof, the mixed treatment Mix_30 exhibited the highest total P removal over the experimental period. This is a consequence of the highest available soil P (Fig. 3 and Fig. 4b) and occurred despite that Mix_30 did not receive the highest P inputs. The total amount of mineral and organic P applied to soil increased in the following order CTR < FYM_20 < FYM_30 < MIX_30 < MIX_20 < MIN. The finding of higher total P removal in MIX_30 could be attributed to the organic portion of P in manure. This organic form is not immediately available to crops and may remain in the soil for a long period. It is slowly mineralized to plant-available inorganic forms and thus increase overall P availability (Johnston and Steen, 2002). Mineral fertilizers, on the other hand, are immediately

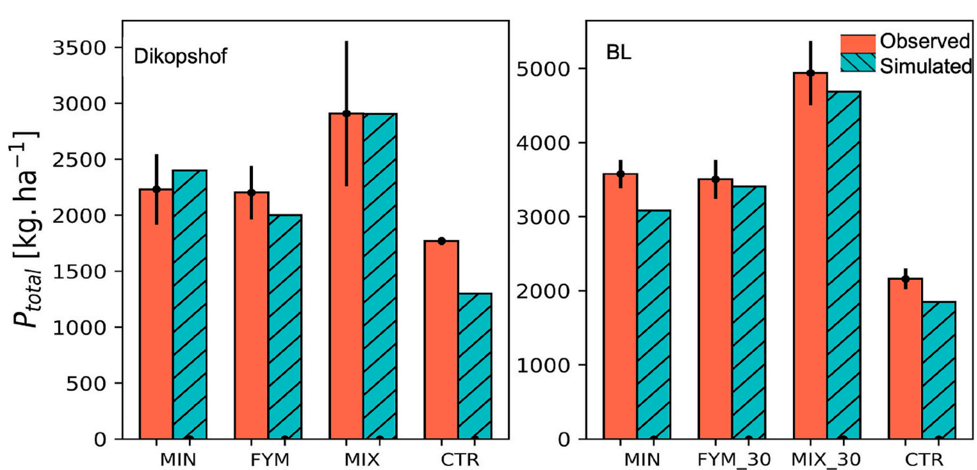

Fig. 2. Comparison between simulated (in hatched bars) and observed (in plain bars) P_{total} concentrations (in kg P ha^{-1}) for different treatments at the two study sites: (a) Dikopshof site and (b) Bad Lauchstädt site.

Table 2
Comparison between simulated and observed P balance, P loss and P gain at Dikopshof and Bad Lauchstädt sites over the studied period.

	Dikopshof (1953–2018)				BL site (1996–2018)					
	MIN	FYM	MIX	CTR	MIN	FYM_20	FYM_30	MIX_20	MIX_30	CTR
Initial total P	4623	5331	6426	3655	6359	7890	7065	8113	8916	4656.4
Inputs of P by mineral and organic amendments [in kg P ha^{-1}]										
Mineral	1612	–	1612	–	660	–	–	308	132	–
Organic	–	702	702	–	–	200	300	200	300	–
Outputs of P (observed) [in kg P ha^{-1}]										
Removal P	1000	990	1340	432	570	419	501	645	644	206
Leached P	n.m[¥]	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m
Outputs of P (simulated) [in kg P ha^{-1}]										
Removal P	1100	968	1324	454	573	407	491	607	611	296
Leached P	2	1.6	1.7	2	0.38	0.46	0.43	0.38	0.38	0.57
Phosphorus balance (∑inputs- ∑outputs) [in kg P ha^{-1}]										
Simulated	510	−268	988	−456	87	−207	−191	−99	−179	−297
Observed	610	−290	972	−434	90	−219	−201	−137	−212	−207
Phosphorus gain (+) or Phosphorus loss (−) [in %]										
Simulated	11.1	−4.9	15	−12	1.4	−2.6	−2.7	−1.2	−2.0	−6.4
Observed	13	−5	15	−11	1.4	−2.8	−2.8	−1.7	−2.4	−4.5

¥: n.m: no measurement.

Table 3
Statistical indices for the yield, biomass, and plant P removal for Dikopshof site, RMSE = root mean square error, EF = model efficiency.

Treatment	RMSE	EF	R^2
Crop Yield [Mg ha^{-1}] [–] [–]			
Mineral (MIN)	1.18	0.84	0.86
Manure (FYM)	1.63	0.81	0.83
Mineral plus Manure (MIX)	1.65	0.80	0.84
Control (CTR)	1.17	0.69	0.80
Crop Biomass [Mg ha^{-1}] [–] [–]			
Mineral (MIN)	2.28	0.62	0.80
Manure (FYM)	2.40	0.78	0.80
Mineral plus Manure (MIX)	3.58	0.63	0.85
Control (CTR)	1.83	0.58	0.74
Removal P [kg P ha^{-1}] [–] [–]			
Mineral (MIN)	4.2	0.72	0.73
Manure (FYM)	5.2	0.55	0.6
Mineral plus Manure (MIX)	6.6	0.56	0.67
Control (CTR)	4.2	0.27	0.37

Table 4
Statistical indices for the yield, biomass, and plant P removal Bad Lauchstädt site, RMSE = root mean square error, EF = model efficiency.

Treatment	RMSE	EF	R^2
Crop Yield [Mg ha^{-1}] [–] [–]			
Mineral (MIN)	1.20	0.88	0.88
Manure with a rate of 20 Mg FM .ha^{-1} (FYM_20)	2.20	0.62	0.73
Manure with a rate of 30 Mg FM .ha^{-1} (FYM_30)	1.80	0.70	0.85
Mineral plus Manure, manure applied at 20 Mg FM .ha^{-1} (MIX_20)	1.30	0.73	0.91
Mineral plus Manure, manure applied at 30 Mg FM .ha^{-1} (MIX_30)	1.40	0.70	0.85
Control (CTR)	1.20	0.41	0.74
Crop Biomass [Mg ha^{-1}] [–] [–]			
Mineral (MIN)	2.30	0.77	0.88
Manure with a rate of 20 Mg FM ha^{-1} (FYM_20)	3.01	0.46	0.74
Manure with a rate of 30 Mg FM ha^{-1} (FYM_30)	3.01	0.45	0.80
Mineral plus Manure, manure applied at 20 Mg FM ha^{-1} (MIX_20)	2.20	0.73	0.88
Manure plus Manure, manure applied at 30 Mg FM ha^{-1} (MIX_30)	2.20	0.68	0.90
Control (CTR)	1.80	0.53	0.75
Crop Removal P [kg P ha^{-1}] [–] [–]			
Mineral (MIN)	4.4	0.52	0.75
Manure with a rate of 20 Mg FM ha^{-1} (FYM_20)	5.8	0.27	0.28
Manure with a rate of 30 Mg FM ha^{-1} (FYM_30)	5.6	0.5	0.5
Mineral plus Manure, manure applied at 20 Mg FM ha^{-1} (MIX_20)	4.4	0.56	0.79
Manure plus Manure, manure applied at 30 Mg FM ha^{-1} (MIX_30)	4.3	0.57	0.74
Control (CTR)	6.2		0.51

available in the soil and are either taken up by plants or subject to sorption in the soil.

3.1.3. P balance

The P balance accounting for P inputs from organic and mineral amendments and P outputs, including removal and leaching, as obtained by the model for the various treatments (Table 2). P losses by leaching over the studied periods were evaluated at depths of 1.6 m and 1.2 m at Dikopshof and BL, respectively. The P loss (−)/gain (+) was calculated as the difference in the P mass in the soil at the end of the simulation to the initial total P content (Table 2).

At BL site, all treatments except MIN showed negative P balances, indicating that more P is being removed from the soil than supplied, leading to depletion of soil P stocks. These findings are in accordance with the results reported by Medinski et al. (2018). Simulations revealed P losses ranging from −1.2 % to −6.4 % between 1996 and 2018, with the order of loss being: MIX_20 < MIX_30 < FYM_20FYM_30 < CTR. The highest P loss of the CTR treatment was expected, as no amendments were applied. Conversely, the MIN treatment showed a 1.4 % increase in P stock. At Dikopshof, P balances from 1953 to 2018 were negative for FYM (−4.9 %) and CTR (−12 %) treatments, but positive for MIX (+15 %) and MIN (+11 %) treatments. Similar to BL, soil P depletion occurred in the FYM treatment, while P stocks increased in the MIN and MIX treatments. These differences can partially be attributed to the varying

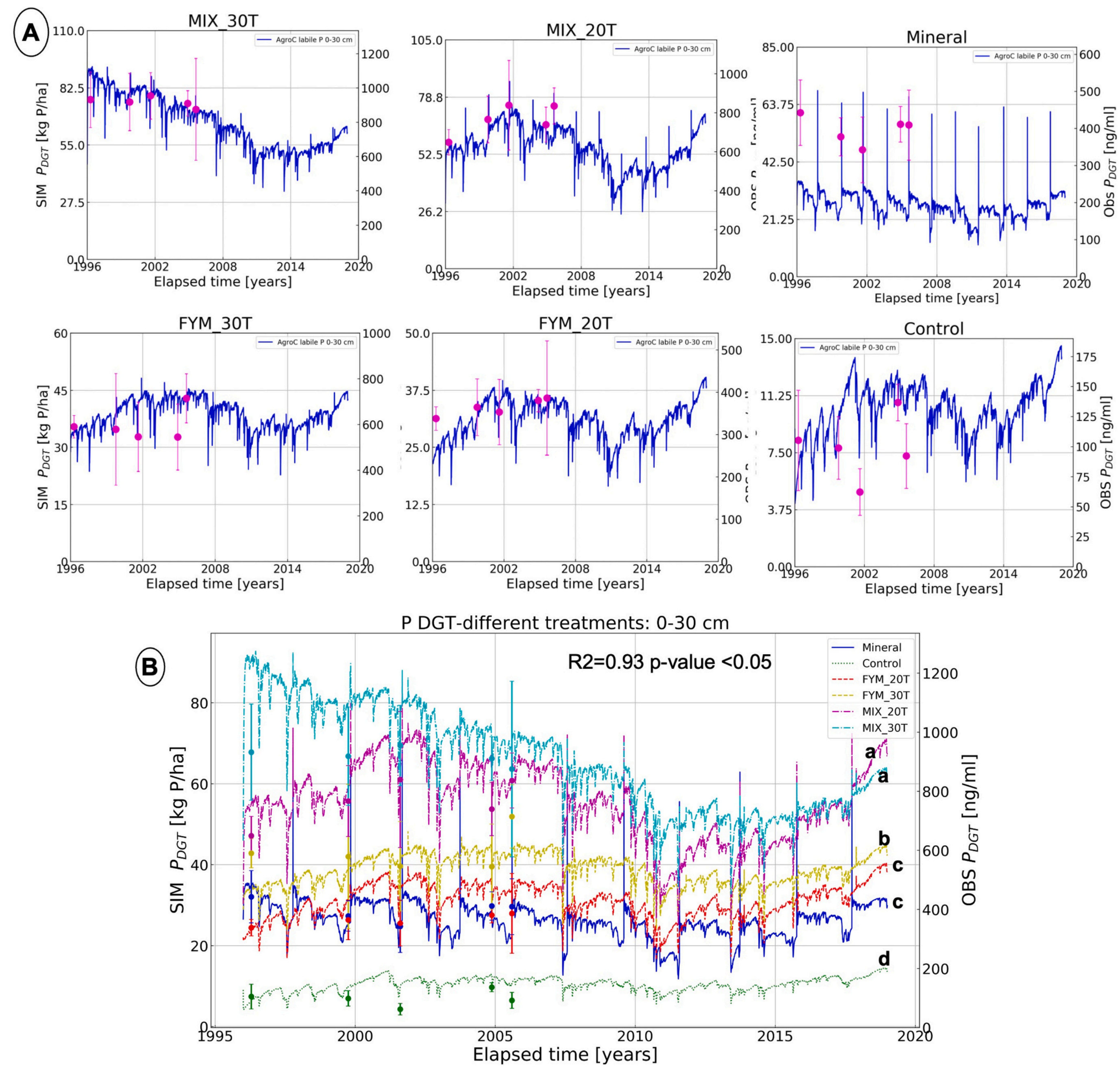

Fig. 3. Comparison between fitted P_{DGT} concentrations (in kg ha^{-1}, shown by lines) and observed values (in ng mL^{-1}, drawn by markers) (in kg P ha^{-1}) across treatments at the Bad Lauchstädt site: (A) represents treatments individually, (B) represents multiples comparison. Lowercase letters (a, b, c, d) represent the Tukey's HSD test results.

amounts of P inputs applied to each treatment (Table 2).

3.2. Plant-available P

By linking measured P fractions to model pools, we were able to simulate the available soil P, as measured by P_{DGT} and P_{CAL}. Thereby, the Tukey's HSD test was conducted separately for both P_{DGT} and P_{CAL} measurements at each site to assess significant differences between treatments (Fig. 3 and Fig. 4, Table SI 3 and Table SI 4). The results showed that P_{CAL} measurements were significantly different across all treatments at both sites. For P_{DGT} measurements at the BL site, significant differences were observed between treatments, except for MIX_20 and MIX_30, which showed no significant difference. Available soil P in FYM treatment was found comparable to MIN treatment.

3.2.1. Soil P_{DGT}

The soil P_{DGT} in the topsoil layer (0–30 cm) at the BL site was related to the model pools according to Eq. (3) (Fig. 3). Data for the Dikopshof site were not available. The temporal trend of the measured P_{DGT} concentrations followed the order: CTR < MIN ≤ FYM_20 < FYM_30 < MIX_20 ≤ MIX_30. Available P to plant uptake in FYM_30 presented higher than MIN, same results was found by Omara et al. (2017) who found after repeated application of beef manure, the P level was far beyond winter wheat requirements in a long-term site in Oklahoma. The fitted values calculated by Eq. (3) across different treatments are in good agreement with the measured P_{DGT} values as confirmed with high R^2 of 0.93 (p-value <0.01) across all treatments and follow the same trend as measured (CTR < MIN ≤ FYM_20 < FYM_30 < MIX_20 ≤ MIX_30). The simulated average P_{DGT} concentration trends from 1996 to 2019 in kg P

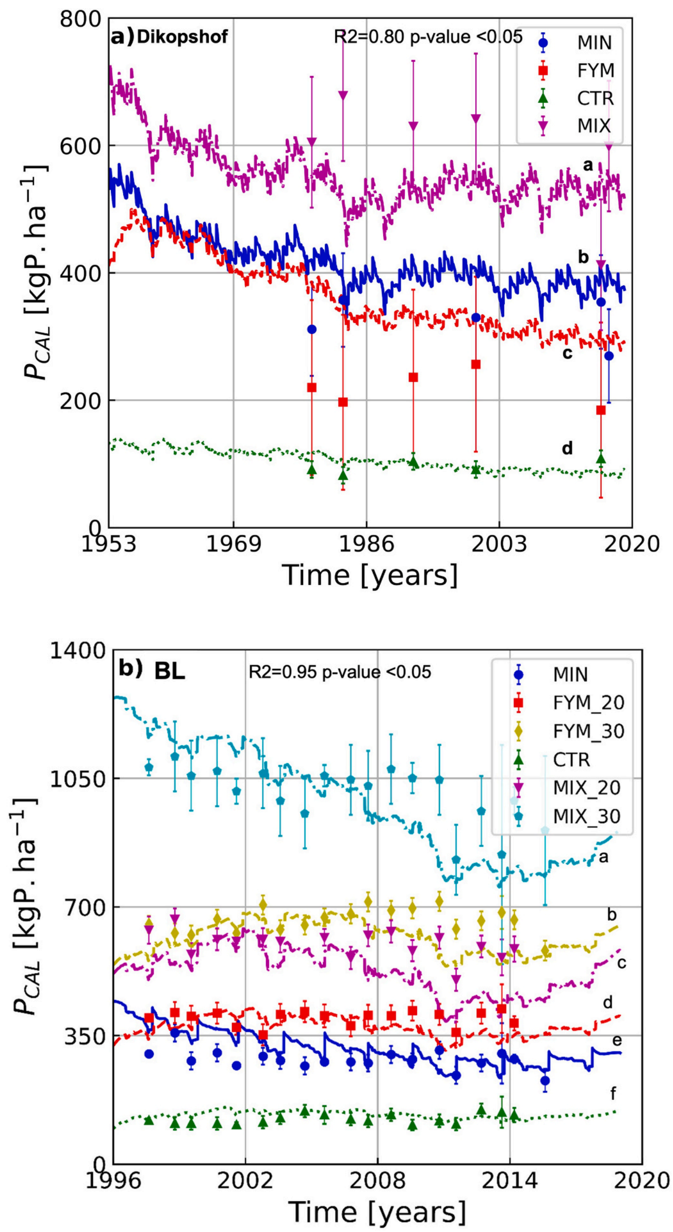

Fig. 4. a, b: Comparison between simulated and observed P_{CAL} concentrations (in kg P ha^{-1}) for different treatments at the two study sites: (a) Dikopshof and (b) Bad Lauchstädt. Lowercase letters (a, b, c, d, e, f) represent the Tukey's HSD test results.

ha^{-1} were 65.9 ± 12.6 for the MIX_30 treatment, 55.4 ± 9.4 for MIX_20, 38.6 ± 3.9 for FYM_30, 31.0 ± 4.2 for FYM_20, 26.4 ± 4.3 for MIN and 10.4 ± 1.7 for CTR, known that the unit of P-DGT of measured data is ng ml^{-1} and of simulated data is kg P ha^{-1}. A graphical comparison showed that the model trends for the MIN and FYM_20 treatments as well as for MIX_30 and MIX_20 treatments appeared to be close to each other. The simulated trend for the CTR, exhibited the lowest amount of P_{DGT}, whereas the combined treatment showed the highest. These simulated P_{DGT} results, despite using different units, show consistency with the pattern seen in the P_{DGT} measurements (Fig. 3), indicating that the model prediction and plant-available P as measured by DGT fractions agree under various fertilization conditions.

3.2.2. Soil P_{CAL}

The P_{CAL} content in the first soil layer (0–30 cm) at both sites of the study was related to the model pools according to Eq. (2). Initially, the parameter α in this equation was set to 0.003 using data from the combined treatment (MIX_30). Following this adjustment, the calibrated equation was validated against data from the other treatments (Fig. 4). The P_{CAL} value measured at the Dikopshof site increased in the following order: CTR < FYM < MIN < MIX, while they increased in the following order for BL: CTR < MIN < FYM_20 < MIX_20 < FYM_30 < MIX_30 (Fig. 4). Predicted values indicated the same orders and generally fell within the observed error for the measurements, as confirmed by relatively high values of R^2 being 0.80 and 0.95 (P-value <0.05) for all treatments for Dikopshof and BL, respectively (Fig. 4). The simulated average P_{CAL} concentration trends from 1995 to 2019 at the Dikopshof site were: 555.4 ± 48.2 for the MIX treatment, 365.0 ± 60.3 for FYM, 418.0 ± 44.9 for MIN and 52.6 ± 10.9 kg P ha^{-1} for CTR. Meanwhile, at the BL site, the simulated average P_{CAL} concentration trends from 1996 to 2019 were 980.4 ± 152.6 for the MIX_30 treatment, 525.2 ± 60.5 for MIX_20, 614.5 ± 41.8 for FYM_30, 373.8 ± 25.4 for FYM_20, 317.6 ± 46.9 for MIN and 133.9 ± 10.1 kg P ha^{-1} for CTR.

At both sites, the repeated addition of farmyard manure in amended treatments was found to provide P to plants at levels equal to or even higher than those achieved with mineral fertilizers. These findings suggest that the application of different soil amendments may significantly influence P availability in soils, and the modeling approach by AgroC might be used to provide a preliminary dynamic prediction on plant-available P contents in a field.

3.3. Crop response

3.3.1. Crop yield and biomass simulations

Our initial simulation, employing a uniform set of crop parameters across treatments at each site, yielded reasonably accurate predictions for crop yield and biomass in most cases (Table 3 and Table 4). Nevertheless, the long-term exposure to nutrient stress tends to reduce crop growth rate via reduced radiation interception and radiation use efficiency (Fischer, 1993; Garcia et al., 1988; Green, 1989; Green, 1987; Hay, 1999; Van Keulen and Seligman, 1987; Green, 1989; Hay, 1999), with potato being the most sensitive crop. Thus, we refined the value of the maximum photosynthetic rate (A_{max}) for potato for only the CTR treatment (see Figs. SI 1 and SI 2). Consequently, at the Dikopshof, we set the A_{max} value for potato to 9 kg CO_2 ha^{-1} h^{-1} across all treatments, except for the CTR treatment, which had an A_{max} of 4.5 kg CO_2 ha^{-1} h^{-1}. Similarly, at the BL site, an A_{max} of 20 kg CO_2 ha^{-1} h^{-1} was applied to all treatments, except for the CTR treatment, with an A_{max} value of 9 kg CO_2 ha^{-1} h^{-1}.

Hence, the model demonstrates sufficient accuracy in predicting crop yield and biomass for most amended treatments for both sites (Figs. 5 and 6). Overall, the model's predictive power is robust, with coefficients of determination (R^2) ranging from 0.73 to 0.91 for yield predictions and 0.74 to 0.90 for biomass predictions for both sites (Tables 3 and 4).

At Dikopshof, the model showed varying levels of accuracy across different treatments (Table 3). The MIX treatment showed the highest discrepancy between simulated and observed biomass, with a root mean square error (RMSE) of 3.58 Mg ha^{-1}. In contrast, the control treatment, which received no fertilizer inputs, displayed the lowest errors, with an RMSE of 1.83 Mg ha^{-1}. The small error in the control treatment can simply be attributed to the lower values of yield and biomass production. At the BL site, the mineral treatment had the highest model efficiency for yield (0.88) and biomass (0.77) (Table 4). The control treatment showed slight overestimation, with the lowest RMSE of 1.2 Mg ha^{-1}.

3.3.2. The fertilization levels impact on crop yield

The crop yields obtained from the different treatments at Dikopshof are below the potential ones mainly due to inadequate fertilizer application (Seidel et al., 2021). However, the observed yields across different treatments indicated that crops exhibit varying degrees of sensitivity to fertilizer inputs, as detailed in Table SI 3 using Tukey's HSD

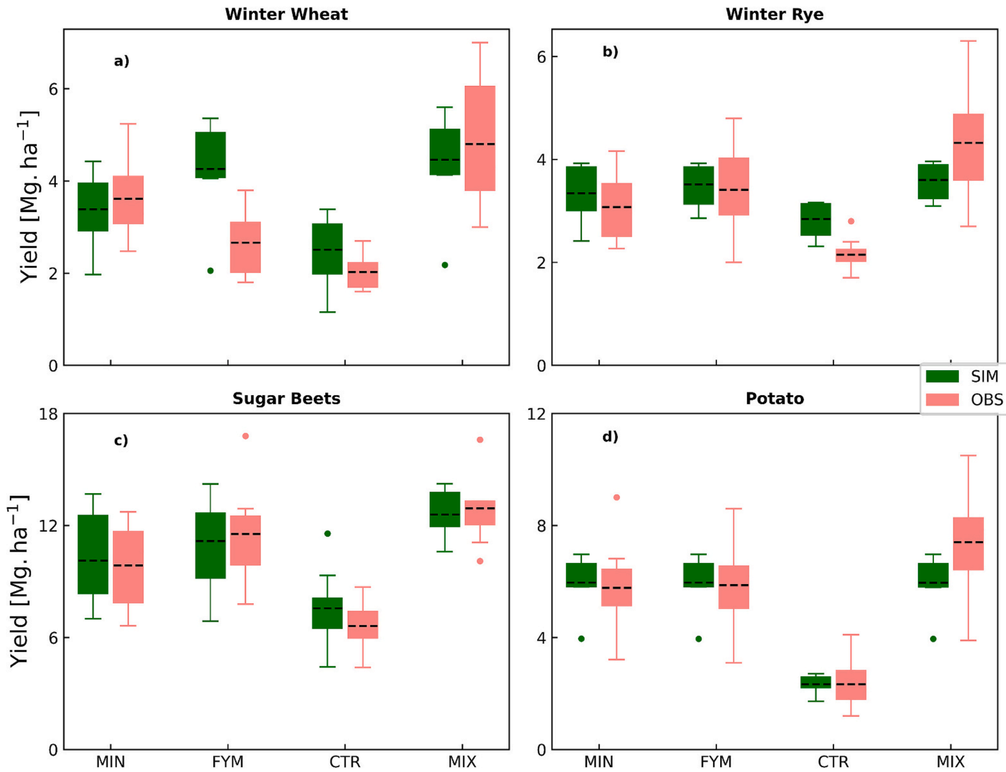

Fig. 5. Comparison of observed (purple) and predicted (green) crop yields for (a) winter wheat, (b) winter rye, (c) sugar beets, (d) potato under different treatments at the Dikopshof site. Circles represent the outliers, and the dashed black lines indicate the averages.

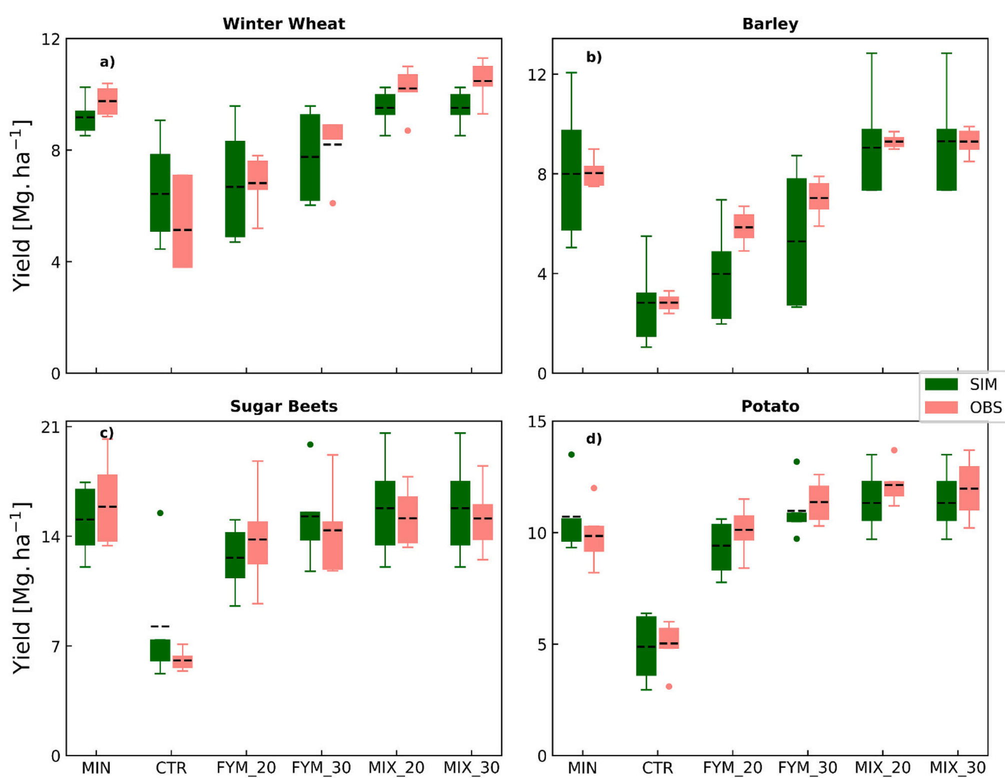

Fig. 6. Comparison of observed (purple) and predicted (green) crop yields for (a) winter wheat, (b) barley, (c) sugar beets, (d) potato under different treatments at the Bad Lauchstädt site. Cercles represent the outliers, and the dashed black lines indicate the averages.

test results. Winter wheat showed the highest sensitivity to fertilizer levels, with clear yield variations among the treatments (Fig. 5). Over a 40-year period (1953–1992), the measured average yields of winter wheat in t. ha^{-1} were 4.71 ± 1.5 for the MIX treatment, 2.6 ± 0.9 for FYM, 3.6 ± 0.7 for MIN, and 2.02 ± 0.6 for CTR. The FYM treatment likely experienced P and N stresses that limited winter wheat production, as it did not receive supplemental inorganic fertilizer.

Interestingly, clover as a legume did not exhibit significant yield differences across fertilized treatments, regardless of the application level. This suggest that yield response of clover was less sensitive to varying fertilizer inputs compared to other crops. This is probably also a consequence of the simulated N fixation of 125±40 kg N ha^{-1}. year on average as a legume species. The yield of potato and sugar beet was highest under the MIX treatment and lowest under the CTR treatment. However, there was no significant difference in yield between the MIN and FYM treatments, suggesting that these crops require only low levels of phosphorus fertilization. Overall, the yield of different crops highlighted a varying sensitivities to P fertilizer inputs, with winter wheat being the most responsive and clover being the least responsive among the crops studied.

Similar trends were observed at BL, where yield variations reflected the impact of different fertilization levels (Merbach and Schulz, 2013). However, when comparing the MIX_30 and MIX_20 treatments specifically, no statistically significant yield differences were observed across all crop types (Fig. 6). This lack of significant variation was confirmed through Tukey's Honest Significant Difference (HSD) test, with detailed results presented in Table SI 3 of the supplementary information. Potato and sugar beet behaved similarly to the potato and sugar beet at the Dikopshof in four treatments (MIX_30, MIX_20, FYM_30, FYM_20), confirming the same finding. Observed Barley yield was very similar across all treatments except the control, which presents the lowest yield. Winter wheat showed the highest sensitivity to the fertilizer level. Treatments that received mineral fertilizers presented the highest measured yield of winter wheat and no significant difference was observed between them (MIX_20, MIX_30 and MIN treatments). These findings are consistent with the studies of Holík et al. (2018) and Medinski et al. (2018), which found that mineral fertilizer treatments led to higher winter wheat yields compared to treatments using only organic manure.

3.3.3. P removal variations across different crops

The model effectively simulated P removal at the BL site, with EF values over 0.5 for most treatments, except FYM_20 (Table 4). At Dikopshof, results were accurate for all treatments except CTR treatment that had EF values below 0.5, likely due to variability in crop uptake and soil conditions. These findings are consistent with challenges in modeling P dynamics under varying conditions (Qin et al., 2018). At Dikopshof, the presence of clover further affected accuracy due to unknown cutting dates.

The effect of different crops on P removal was evaluated by analyzing P removal data across various treatments using Tukey's HSD test. The findings are detailed in Tables SI 3 and SI 4. The results indicate that P removal for each crop studied at both sites was significantly different in the CTR plot compared to the amended treatments, while P removal in the amended treatments was generally similar. For winter rye, potato, and clover at the Dikopshof, as well as potato and barley at the BL site, there were no significant difference in P removal among the MIX, MIN, and FYM treatments. However, for winter wheat, significant differences were observed between amended treatments at both sites, with FYM deviating significantly from MIX but being similar to MIN. Notably, when a higher amount of farmyard manure (30 Mg FM ha^{-1}) was applied in the FYM_30 treatment, the P removal for winter wheat increased, aligning more closely with the levels observed for the MIN treatment. A similar trend was observed for sugar beet. These findings highlight the complexity of P dynamics in agricultural systems and suggest that management practices, such as the application rate of farmyard manure, are crucial for optimizing P use efficiency, particularly for winter wheat.

3.3.4. P-use efficiencies

To assess how efficiently crops utilized fertilizers, P-use efficiency ratios were calculated (Table 5). This metric is the ratio of P removed by the crop to the amount of P fertilizer applied. Higher ratios indicate more efficient use of the applied fertilizer. Among the treatments studied, the treatment with the lowest P application levels exhibited the highest P-use efficiency. Specifically, the FYM treatment at Dikopshof, and the FYM_20 and FYM_30 treatments at BL, showed superior P efficiency. However, this high efficiency led to a decreasing P balance over the study period, indicating a non-sustainable practice with respect to soil P.

Sugar beet exhibited the highest P-use efficiency among all crops at both sites (Table 5). In the FYM treatments, the P-use efficiency exceeded 100 %, indicating that more P was removed by sugar beet than supplied through fertilizer. This can be attributed to the P acquisition strategies of sugar beet roots, which are adapted to acquire P from the soil (Medinski et al., 2018). During the early stages of root development, sugar beet requires a substantial amount of P from the soil for the production and transport of sugars and proteins (Sinclair and Vadez, 2002). Consequently, an adequate supply of P early in the season is crucial for achieving high sugar beet yields. In contrast, potato exhibited the lowest P use efficiency at both sites. This may be due to the shallow root system and low total root length of potatoes, which comprise approximately one fourth of the root density of wheat (Hopkins et al., 2014; Mikkelsen, 2015). Consequently, potatoes may have limited access to soil P reserves, leading to lower P utilization efficiency.

Winter wheat used around 75–99 % of provided P in BL in all treatments except MIN, but the cereal crops at Dikopshof in all treatment and in MIN treatment at BL only utilized around 50 % of the provided P in the soil (Table 5). This indicates that the P fertilizer might be applied in excess in was not fully utilized by the crops. This finding agrees with Seidel et al. (2021) that showed cereal's yield loss due to P omission was only 7–8 %. This resulted in sorption and accumulation of P in the soil, as evidenced by the P gain in the soil by 11 % in MIN treatment and 15 % in MIX treatment at Dikopshof site (Table 2). However, the higher removal of P by sugar beet is compensated by the P fertilizer not taken up by other crops grown in the crop rotation system, leading to the P balances presented in Table 2. In contrast, at BL site, cereal crops exhibited a P-use efficiency near to 100 % in FYM_20 and between 50

Table 5
P-use efficiency ratios of different crops at Dikopshof and Bad Lauchstädt sites, determined as P removal to the amount of P applied with fertilizers ratio.

Treatment	P-use efficiency ratio [−]				
	Winter wheat	Winter rye	Potato	Sugar beet	Clover
Dikopshof site (1953–2018)					
Mineral (MIN)	0.40	0.50	0.34	0.53	0.87
Manure (FYM)	0.42	0.65	0.44	0.86	0.95
Mineral plus Manure (MIX)	0.55	0.34	0.27	0.52	0.66
Bad Lauchstädt site (1996–2018)					
Mineral (MIN)	0.5	–	0.25	0.58	–
Manure with a rate of 20 Mg FM ha^{-1} (FYM_20)	0.99	–	0.84	1.22	–
Manure with a rate of 30 Mg FM ha^{-1} (FYM_30)	0.77	–	0.58	1.03	–
Mineral plus Manure, manure at 20 Mg FM ha^{-1} (MIX_20)	0.74	–	0.37	0.76	–
Mineral plus Manure, manure at 30 Mg FM ha^{-1} (MIX_30)	0.8	–	0.49	0.82	–

and 80 % in other treatments. The results presented in Table 2 agree with Medinski et al. (2018). They report similarly small losses or gains for comparable fertilizer treatments. In this study soil P was lost at −1.7 % and −2.4 % for MIX_20 and MIX_30 and slight soil P gain by 1.4 % in MIN treatment was observed. Generally, manure use, whether applied independently (FYM) or combined with mineral fertilizers (MIX), showed similar effectiveness to mineral fertilizer alone for a range of crops and treatments when applied at the same P levels. This points to manure as a viable alternative to mineral P fertilizer. Further, it potentially enables a reduction in fertilization costs compared to costly mineral fertilizers without significantly increasing risks such as nutrient leaching (Lu et al., 2021; Sun et al., 2022).

4. Conclusion

This study underscores the importance of combining long-term field data with detailed analyses to better understand soil phosphorus dynamics and optimize fertilization strategies. The use of the new P module within the AgroC framework provides an effective means for assessing plant-available P under different fertilization regimes. This enables evaluation of crop responses and establishes a strong link between theoretical understanding and practical field observations. The results suggest that using both organic and mineral fertilizers can sustain or even improve soil P levels and crop production, offering a viable alternative to relying solely on mineral fertilizers. This is especially valuable for regions facing challenges with P depletion and declining soil fertility.

Additionally, this work highlights the value of assessing long-term changes in P availability, offering insights that are not always apparent through field measurements alone. As agricultural systems adapt to pressures from climate change and the need for more sustainable practices, the findings from this study can help improve the management of fertilizer use, balancing productivity with environmental considerations. Future research should aim to fine-tune the application of these approaches across various soil types and climatic conditions, ensuring broader applicability.

CRediT authorship contribution statement

Gihan Mohammed: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Formal analysis, Data curation, Conceptualization. **Nina Siebers:** Writing – review & editing, Writing – original draft, Validation, Project administration, Investigation, Formal analysis, Conceptualization. **Ines Merbach:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis. **Sabine J. Seidel:** Writing – review & editing, Validation, Investigation, Formal analysis. **Michael Herbst:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Gihan mohammed reports financial support was provided by Forschungszentrum Jülich Institute of Bio- and Geosciences Agrosphere 3. Gihan Mohammed reports a relationship with Forschungszentrum Jülich Institute of Bio- and Geosciences Agrosphere 3 that includes: employment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177517.

Data availability

The data that has been used is confidential.

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