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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- The P-submodel of DayCent has been calibrated and tested using four long-term experiments in Europe.
- The model captures the main P fluxes over time under a wide variety of management in European conditions.
- The P_{Total} of five different soils was reproduced well by the model.
- The model is a promising tool for assessing policy, practical applications, and management and climate scenarios.



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ABSTRACT

CONTEXT: Phosphorus (P) is a non-renewable geological macronutrient that plays an essential role in food security. The excessive use of P as a fertilizer and its subsequent diffuse loss leads to the deterioration of water quality, eutrophication, and loss of biodiversity. Ecosystem process-based models are a powerful tool to depict the P cycle, investigate the effects of management practices and climate change, and ultimately assess policy interventions that affect biogeochemical cycles. Of the limited number of P models in agricultural production systems, none have been tested in temperate conditions for periods of decades using long-term field experiments. *OBJECTIVE:* The objective of this study is to evaluate the ability of the detailed P submodel from DayCent to: simulate the magnitude and temporal dynamics of P outputs; assess changes in P soil pools from European agricultural long-term experiments; and interpret the main causal factors inducing the differences between the observed vs. the simulated pools and fluxes.

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METHODS: We used data from four long-term experiments to calibrate and test the P submodel of DayCent. The experiments involve five different soils, mineral and organic fertilizer treatments, management intensity levels, various crop rotations, crop residue management, and irrigation.

RESULTS AND CONCLUSIONS: The DayCent model captured the gross P budget (input minus output) in the four long-term experiments, and it performed well in simulating their soil total P (P_{Total}) over time. The model application simulated the soil available P ($P_{Available}$) in the same range as the measured data, but the temporal dynamic did not always match the observed trends. P modelling is subject to a wide range of uncertainties with respect to both input data (particularly the unknown initial distribution of the different pool sizes of P and the uncertainty of the measurements) and the representation of processes influencing the P cycle that are not yet accounted for in the model. Despite these uncertainties and calls for further model assessment and developments, the results show that DayCent was capable of satisfactorily predicting the main P fluxes over time under a wide variety of management practices and European site conditions.

SIGNIFICANCE: The model may be used to assess different scenarios with a changing climate, a change in management or land-use, and to analyse potential feedback between the terrestrial and the climate system. This makes this model a promising tool for assessing policy and practical interventions.

1. Introduction

Phosphorus (P) is an essential macronutrient that plants take up in substantial amounts (Cordell et al., 2009). Its supply from fertilizers plays an important role in food security, especially given the growing world population (UN, 2019). Fertilization of P predominantly uses non-renewable geological P deposits or organic sources such as manure (Einarsson et al., 2020). However, mined rock phosphate is becoming increasingly limited due to finite rock phosphate supplies, an increasing P demand, potential geopolitical issues, and technical, economic, and quality constraints such as heavy metal contamination and price fluctuations (Köhn et al., 2018, Ulrich et al., 2014, Penuelas, 2020, Mogollón et al., 2018).

In soil, P is present in different forms with varying availability to plants (Hedley et al., 1982; Yang and Post, 2011). The plant available P contents are assessed by various methods worldwide, with the Olsen method being widely used in Europe and correlating relatively highly to plant P uptake (Steinfurth et al., 2021; Zehetner et al., 2018). While reaching plant available P concentrations for optimal crop production through fertilization, it is important to stay below the soil P saturation level to minimize losses to the environment (Bai et al., 2013). Excessive use of P as a fertilizer and the subsequent diffuse losses to freshwaters and oceans leads to the deterioration of the water quality, eutrophication, and loss of biodiversity (Ceulemans et al., 2014; Cordell et al., 2009). In the European Union (EU), more than half of the surface waters are not in a good ecological or chemical status, with nutrients being one of the major causes of degradation (EEA, 2018). The current P flow from arable land to fresh- and ocean water is considered to be beyond the safe operating space for sustainable human development (Carpenter and Bennett, 2011; Steffen et al., 2015) and a threat to the Sustainable Development Goals (SDGs) 6 (clean water and sanitation) and 14 (life below water) (Langhans et al., 2021).

To address these environmental challenges, policy tools such as the Farm to Fork Strategy of the European Commission aim to reduce the nutrient losses by at least 50% while ensuring no deterioration of soil fertility and the reduction of fertilizer use by at least 20% by 2030 (European Commission, 2020). Ecosystem process-based models are a powerful tool for depicting the nutrient cycle (which includes uptake from the soil, assimilation, and remobilization in plants) and investigating the effects of management practices and changing climate on the biogeochemical fluxes. Therefore, they can be of assistance in developing or assessing environmental policy to decrease P losses and increase the P use efficiency.

To test these models, it is essential to use measured field observations, especially from long-term experiments with detailed information about the local weather, soil properties, land management, and crop yield, ideally with a high frequency of data collection. Long-term experiments hold key information about the trends and dynamics which is necessary to evaluate the tendency of the agroecosystem to accumulate or lose nutrients as well as to identify the change of the different soil nutrient soil pools (Körschens, 2006; Sandén et al., 2018). Long-term experiments also provide more stabilized conditions as the management is often maintained for a prolonged time (Ilari et al., 2019).

Compared to the large number of models developed to simulate the carbon (C) and nitrogen (N) cycles, there is a limited number of models that simulate P dynamics in agricultural production systems (Das et al., 2019; Sattari, 2014). Models that incorporate P are generally biogeochemical models with a P submodel (Das et al., 2019) that simulate inorganic and organic soil P dynamics in interaction with the N and C cycles. Various agricultural oriented models have been developed and described in literature with varying complexity and included processes according to their purpose and the level of information required (Das et al., 2019; Lewis and Mcgechan, 2002; Sattari, 2014). Some studies have enabled the P submodels to assess the P use efficiency of a specific crop in P-limited conditions from mostly highly weathered soils (e.g., DSSAT (Amin et al., 2018; Dzotsi et al., 2010); APSIM Ahmed et al., 2018). In another study, four field-scale P dynamic model concepts (ANIMO, GLEAMS, DAYCENT, and MACRO) were compared to each other, and their constituent processes were analysed with particular reference to the equations used (Lewis and Mcgechan, 2002). The authors concluded that the models partially represent the processes, and a new hybrid version of the four models would bring the best results.

The APSIM model has been assessed in a tropical/subtropical case study (i.e., Vertisols in Australia) to simulate soil P dynamics and crop responses in two long-term P studies (Raymond et al., 2021). APSIM was able to predict crop yields within an acceptable modelling performance but showed an inconsistent linear correlation between the modelled plant available P pools and the measured labile-P. The model APSIM has also been tested by comparing the P concentration in plant export and a final measure of soil labile P taken at the end of the modelling process (e. g., Ahmed et al., 2018). Ideally, more robust calibration can be done comparing simulated changes in soil P concentrations over time against measured soil concentrations (Das et al., 2019). The EPIC model has been tested on soils from the Swiss Soil Monitoring Network, but the calibration of the model was only partially successful, with statistical evaluation criteria giving contradictory results and poor predictions for the validation subset (Della Peruta et al., 2014). The grid-based version of the EPIC model (PEPIC) has been applied to estimate global P losses from maize, rice, and wheat, for a time period of 4 years (Liu et al., 2018). None of the described models have been tested in temperate conditions for longer periods using long-term field experiments as quality control. This lack of validated process-based P model hinders the prediction of P pools and flows, as well as the knowledge of the interactions of the P cycle with other biogeochemical elements in the agricultural system.

The DayCent model is a process-based terrestrial ecosystem model that has a detailed representation of the soil biogeochemistry, including water, nutrient cycle, crop yields, and agricultural management such as crop rotation, irrigation, tillage, and fertilizer application (Grosso et al., 2002; Parton et al., 1998, 2020; Parton et al., 1988). It simultaneously simulates the daily dynamics of organic C, N, sulfur (S), and P. DayCent has been developed and parameterized to simulate a wide range of crops (Sansoulet et al., 2014). It has been successfully applied in long-term experiments on simulating soil C (with the monthly CENTURY version) and the N cycling (Lugato et al., 2007; Dal Ferro et al., 2016). It also includes a detailed P submodel that was set up in 1988 but has only been used to compare model concepts (Lewis and Mcgechan, 2002), assess agro-environmental measures for organic P leaching for the Veneto region (Dal Ferro et al., 2017). It has not yet been tested to simulate the P cycle components in measured long-term field experiments.

The objectives of this study are to: (i) evaluate the ability of the detailed P submodel from DayCent to simulate the magnitude and temporal dynamics of P outputs; (ii) assess the changes in P soil pools from European agricultural long-term experiments and; (iii) interpret the main causal factors inducing the differences between the observed vs. simulated pools and fluxes. For this purpose, data from four long-term experiments established in the 60's and 70's in Italy and Switzerland are used to calibrate and test the P submodel of DayCent. The experiments involve five different soil types, different mineral and organic fertilizer treatments, management intensity levels, various crop rotations, crop residue management, and irrigation.

2. Materials and methods

2.1. Experimental design of long-term trials

Our dataset for the model calibration and testing consisted of four long-term trials at two field locations in Italy and Switzerland (SI 1.1) with different soil types, various fertilization intensities, different types of fertilizers, crop rotations, as well as cover crop and crop residue management with or without irrigation (Fig. 1). The crop rotation experiment (CR) conducted three crop rotations (mono, two-years, and four-years) in high- and low-input cropping systems, factorially combined. In addition, there is a high-input maize monoculture experiment (MMo), which includes various fertilization intensities and different types of fertilizers. In the same experimental farm, the soil and fertilization experiment (SF) included three different soil types reconstructed in lysimeters with contrasting textures and organic carbon contents with organic, mineral, and mixed fertilization. While not being an open field experiment, this long-term trial provides valuable information due to the contrasting soil types and the detailed soil P measurements. Lastly, a long-term field trial in north-western Switzerland (DOK) included four farming systems in plot experiments, two conventional and two organic farming systems. All data sets used for the simulation and their main physical and chemical characteristics are listed in Table 1, while a comprehensive description of the inputs and crop rotations follows in the subsections and the Supporting Information (SI 1.2). Collectively, the dataset consisted of 88 treatments running between 12 and 37 years. The managements used in the trials represent a broad range of typical land management in the respective regions. The treatments of the different trials range from no fertilization to full mineral or full organic fertilization. The five different soils provided a high variability in soil mineralogy and chemistry with a big range in soil texture (Fig. S2, SI 1.1) and pH (4.9-8.1).

2.1.1. Crop rotation experiment (CR)

The long-term field experiment CR trial is located at the experimental farm of the University of Padova (Veneto Region, NE Italy $45^{\circ}21'$ N; $11^{\circ}58'$ E; 6 m a.s.l.) with a sub-humid local climate. The annual rainfall is approx. 850 mm, with the highest rainfall in a median year in June (100 mm) and October (90 mm) and the lowest in winter (50–60 mm). Temperatures are lowest in January (average: 1.5 °C) and highest in July (average: 27.2 °C). The site has a shallow water table ranging, on average, from about 0.5–1.5 m in late winter-early spring to 1–2 m in summer. Each crop rotation is replicated three times and arranged in a split-plot design, with the different crops of the crop rotation growing in parallel in the respective years. At the beginning of the trial, the total P content (P_{Total}) in the top layer was 0.7 g kg⁻¹, with 47.2 mg kg⁻¹ available P measured as P-Olsen. P_{Total} was determined by ignition and HCl extraction.

The experimental layout is a 7.8 m \times 6 m split-plot with three replicates. The treatments considered in this study were a factorial combination of three crop rotations (1-, 2-, and 4-year), three mineral fertilization rates (control (O), single rate (M), double rate (MM)), and two management intensification levels (high input and low input) (SI 1.2). The variables that determine the management intensity have been switched every 12 years to investigate emerging agronomic problems



Fig. 1. Overview of the long-term experiment dataset and included input parameters used as a basis to calibrate and validate the P submodel of the process-based biogeochemical model DayCent.

Table 1

Data sets used and main physical and chemical characteristics of the topsoil layer at the beginning of the trials. The CR and the MMO trials are conducted in the same soil type and characteristics.

Trials	Crop rotation experiment (CR) & high-input maize monoculture (MMo)	Soil and fertilization experiment (SF clay)	Soil and fertilization experiment (SF sandy)	Soil and fertilization experiment (SF peat)	Bio-Dynamic, bio-Organic, and "Konventionell" (DOK)
Site locations Soil type (WRB)	Padova, Italy Fluvi-Calcaric	Padova, Italy Reconstructed Stagnosol	Padova, Italy Reconstructed Arenosol	Padova, Italy Reconstructed Histosol	Therwil, Switzerland Haplic Luvisol
Considered timeframes	1964–2001 (in 3 cycles)	1964–2001	1964–2001	1964–2001	1978–2019
Sand (g kg ⁻¹)	470	250	934	380	119 ^d
Silt (g kg $^{-1}$)	380	230	60	136	707^{d}
Clay (g kg $^{-1}$)	150	520	6	484	154 ^d
BD g cm ⁻³	1.26	1.10	1.44	0.95	1.32 ^d
pH (H ₂ O)	7.8	7.9	8.1	4.9	6.3 ^d
Organic carbon (%)	1.2	1.45	0.17	10.5	1.67 ^d
Total N (g kg $^{-1}$)	0.99	1.5	0.15	6.7	1.48 ^d
Total P (g kg $^{-1}$)	0.7	2.8	0.5	1.1	0.7^{d}
Available P (mg kg ⁻¹)	47.2 ^a	161 ^a	26 ^a	100 ^a	2.596 ^{b, d}
Type of fertilizer	mineral, FYM ^c , slurry	mineral, FYM	mineral, FYM	mineral, FYM	mineral, FYM, slurry, slightly aerobically rotted FYM, composted FYM
Treatments included	54 & 8	6	6	6	8
Reference	(Giardini, 2004; Lugato et al., 2007; Morari et al., 2006)	(Giardini, 2004; Lugato et al., 2007; Pizzeghello et al., 2011)			(Mäder et al., 2002; Mayer et al., 2015)

^a Measured with the Olsen method.

^b Measured using CO₂ saturated water.

^c FYM = farmyard manure.

^d Soil sample was taken in rotation unit c.

without changing the crop rotations (see SI 1.2). The trial started in 1962, yet we report the results from 1964 onwards as the parameters initialized the first 2 years.

The cropping systems received three mineral fertilization rates (O, M, MM) and, in some phases, additional organic fertilization: (O - control) no fertilization; (M) 70, 31, and 75 kg ha⁻¹ year⁻¹ of N, P, and K, respectively; (MM) 140, 61, and 149 kg ha⁻¹ year⁻¹ of N, P, and K, respectively. Average rates of 20 t ha⁻¹ year⁻¹ FYM (20% d.m., 0.5% N, 0.1% P, 0.6% K) and 40 t ha⁻¹ year⁻¹ of liquid manure (10% d.m., 0.4% N, 0.1% P, 0.3% K) were applied prior to ploughing in certain phases of the trial (SI 1.2). All the rotations receiving FYM had crop residues removed with the logic that they would be used for the livestock bedding. In the second cycle, the low input treatments without manure application received an extra application of mineral fertilization of 100, 22, and 117 kg ha⁻¹ year⁻¹ of N, P, and K, respectively, as well as crop residue incorporation into the soil to match the NPK supply with the corresponding intense treatment. Whenever present in the M and MM treatments, the cover crops also received 70 and 140 kg ha⁻¹ year⁻¹ of N, respectively. No mineral N was applied to soybean and alfalfa.

The 1- year rotation was a continuous maize succession. The 2-year rotation was maize–wheat. The 4-year rotation was sugarbeet–maize–wheat–maize. The maize following sugarbeet in the crop rotation was substituted for soybean (*Glycine* max L.) in the period 1989–2001. Soil tillage was a medium-depth autumn ploughing followed by the normal operations of seedbed preparation at different times according to crop. These involved the use of vigorous rotary hoeing.

2.1.2. Maize monoculture experiment (MMo)

The maize monoculture trial has been conducted on the same soil type as the CR trial. The experimental treatments were a combination of three replicates of four treatments with two management intensification levels (high input and low input). A total of 24 plots were cultivated. The four treatments contrasted different types of fertilization with only mineral – (M2), only organic – (L2), mixed mineral/organic fertilization

(LM), and no fertilization (O). When present, the nutrient input was the same for all treatments: 300, 66, and 348 kg ha⁻¹ year⁻¹ of N, P, and K, respectively. The main crop maize included intra-annual succession maize – forage crop for the first cycle for both intensity levels (1962–1975) and in the second cycle (1977–1988) only for the low-intensity plots. The main intensification variable was residue incorporation as well as the input of liquid manure instead of FYM in the last third cycle (1989–2001) for the intensive treatments.

2.1.3. Soil and fertilization experiment (SF)

The SF trial was also conducted at the experimental farm of the University of Padova. This trial was carried out in 4 m² lysimeter plots with concrete walls to 80 cm depth and an open bottom. The treatments were a factorial combination of three types of soil (clay, sandy and peaty) with six mineral, organic or mixed fertilization methods, organized in two randomized blocks, totalling 36 cultivated plots. The soils were excavated in the 1960's from the south-western plain (clay), the central coastal area (sandy), and the southern plain (peat) of the Veneto region (Italy) and reconstructed in lysimeters. The clay soil had a montmorillonitic clay content higher than 50% (Table 1) with the highest initial soil total P and available P (Polsen) contents (2.8 g kg⁻¹and 161 mg kg⁻¹, respectively). The sandy soil has a sand content of higher than 93%, with a low initial total P and available P content (0.5 g kg^{-1} and 26 mg kg^{-1} , respectively). The peat soil was characterized as a minerothrophic peat with a low pH of 4.9 and an initial total P and available P content of 1.1 g kg⁻¹ and 100 mg kg⁻¹, respectively (Morari et al., 2006). The three soils of this trial have been assessed also for other P pools and P extractions (Pizzeghello et al., 2011, 2014, 2016). P_{Total} was determined by ignition and HCl extraction, and organic P (Porg) as the difference between an ignited and an untreated sample (Pizzeghello et al., 2014). The concentration at which the clay soil is saturated with P (measured in Olsen) could be determined as 54 mg kg⁻¹ (Pizzeghello et al., 2016). The fertilization treatments included mineral (m2), organic (12), or mixed fertilization (lm), as well as reduced mineral (m1), reduced organic (l1), and no fertilization (O). The nutrient inputs were:

(O - control), no fertilization; (lm) 20 t (fresh weight) ha^{-1} year⁻¹ FYM + 100, 22, and 116 kg ha^{-1} year⁻¹ of N, P, and K, respectively; (l2) 40 t (fresh weight) ha^{-1} year⁻¹ FYM; (m2) 200, 44, and 232 kg ha^{-1} year⁻¹ of N, P, and K; (l1) half of l2; (m1) half of m2, respectively. The FYM, generally applied between October and November, had the same composition as in the CR trial. The trial started in 1964 and is still running today.

The crops grown in this trial were a 2-year maize (*Zea mays* L.)– wheat (*Triticum aestivum* L.) rotation until 1984, an open rotation with various horticultural crops from 1985 to 1992, followed by a 3-year rotation of tomato (*Lycopersicon esculentum* Mill.)–sugarbeet (*Beta vulgaris* L.)–maize from 1993 onwards. The wheat received only one-half the fertilizer or manure rate applied to maize. In all treatments, the crop residues were removed. In the fall, manual minimum tillage of the surface soil (ca. 0–20 cm layer) was carried out.

2.1.4. DOK trial

The DOK trial experimental site is located in Therwil (Basel Country Region, Switzerland 47°30'N, 7°33'E; 309 m a.s.l.) with a temperate climate and a small inclination of 5%. The mean annual temperature is 10.5 °C and rainfall is 842 mm. The trial was originally initiated to compare different organic and conventional farming systems at standard and reduced fertilization levels. The experiment is arranged in a split-split-plot design with four replicates as well as three replicates of each crop rotation arranged in a shifted design with differing crops growing in parallel in the respective years, resulting in 96 plots in total. At the beginning of the trial, the total P content in the topsoil (0-30 cm) was 0.76 g kg⁻¹, with 2.596 mg kg⁻¹ available P measured in CO₂-saturated water (Flisch et al., 2017). P_{Total} , P_{Org} and inorganic P contents were determined with the ignition method of Saunders and Williams (1955).

All treatments of the DOK trial have the same crop rotation and similar soil tillage. Their differences arise in the plant protection management and fertilization quality and quantity associated with the four farming systems: bio-dynamic (D1, D2), bio-organic (O1, O2), mixedconventional (K1,K2), mineral-conventional (M), and the unfertilized control (N). The bio-dynamic, bio-organic, and mixed-conventional systems are separated into half (e.g., D1) and full (e.g., D2) fertilization levels. Full fertilization (level 2) corresponds to a nutrient amount of 1.4 livestock units (LU), whereas the first two crop rotation periods were fertilized with 1.2 LU. At half fertilization (level 1) 50% fertilizers of the full fertilization were applied. One livestock unit equals 105 kg N, 15 kg P, and 149 kg K (SR 814.201 GSchV). Since the organic rate varied, we implemented average organic P inputs per treatment for each crop rotation period (every 7 years). The fertilization treatments included: (D) aerobically composted FYM and slurry amended biodynamic preparations $(1.2/1.4 \text{ LU ha}^{-1} \text{ year}^{-1})$; (O) slightly aerobically rotted FYM and slurry $(1.2/1.4 \text{ LU ha}^{-1} \text{ year}^{-1})$; (K) anaerobically rotted FYM and slurry (1.2/1.4 LU ha⁻¹ year⁻¹) plus mineral fertilizers up to the recommended level of the plant-specific Swiss standard recommendation; (M) exclusively mineral fertilizers since 1985; 1978-1984 non-fertilized; (N) non-fertilized since 1978. Average P fertilization was 0 for the control (N); $35 \text{ kg P ha}^{-1} \text{ year}^{-1}$ (M); between 20 and 37 kg P ha $^{-1}$ year $^{-1}$ for the full (D2, O2 & K2), and between 10 and 19 kg P ha⁻¹ year⁻¹ in the reduced fertilized treatments (D1, O1, K1). The average N and K fertilization rate can be seen in (Oehl et al., 2002).

The crops grown in the DOK trial were a 7-year rotation, including potatoes, green manure, winter wheat, fodder intercrop, white cabbage, winter barley, beetroot, and grass-clover. Eventually, from the 4th crop rotation, soybean, and silo maize were integrated into this rotation.

2.2. Model

2.2.1. P submodel description

The present study used the version DD13centEVI of DayCent with enabled C, N, and P submodels. An overview of the P cycle is given in SI

1.3. The P submodel comprises organic (Porg) and five mineral P pools: Plabile, Psorbed, Pstrongly sorbed, Pparent, and Poccluded (Parton et al., 2020). Plabile, equivalent to resin P (PResin), represents the plant available P in soil solution that rapidly equilibrates with the P_{sorbed} fraction. The size of the Plabile pool controls plant uptake, immobilization, and leaching of P. The equilibrium relationship between Plabile and Psorbed is defined by two parameters, sorption maximum (SORPMX), which indicates the maximum amount of P which can be sorbed, and the sorption affinity (PSLSRB), which controls the slope of the sorption curve. In turn, P_{sorbed} is in dynamic equilibrium with a more strongly sorbed P pool (Pstrongly sorbed) which may translocate P to an occluded pool (Poccluded). Phosphorus can enter the P cycle by weathering of parent material (P_{parent}), typically apatite, or by mineral or organic fertilization events. Porg is divided into several pools which follow the decomposition of the soil organic matter pools (structural, metabolic, slow and passive) characterized by different CP ratios. Phosphorus losses from the system occur due to crop removal, leaching of Plabile and Porg, soil erosion, grazing, and biomass burning. Phosphorus can be added as inorganic P fertilizer or organic matter additions such as manure or compost with varying decomposition rates.

The model was evaluated by assessing its ability to simulate the magnitude and temporal dynamics of P changes in agricultural soils, P export through crop harvest and residue removal, and the overall P budgets. Additionally, the resulting dynamics are compared to literature values. The gross P budget was calculated as:

$$Gross P budget = P_{Mineral Fertilizer} + P_{Manure} + P_{Chemical Weathering} - P_{Grain Harvest}$$
(1)
-P_Residue Removal

Processes that have a marginal contribution in the experimental fields compared to those included in Eq. (1), such as P input through seeds, and atmospheric deposition, were not included in the P budget of the long-term trials. Erosion was not included as the experimental fields are in a flat position or soil was confined in lysimeters, thus the P removal through soil erosion is likely far below the estimated average of 1 kg ha⁻¹ year⁻¹ in Europe (Alewell et al., 2020; Panagos et al., 2022a). Atmospheric deposition of P is approximately 0.3 kg P ha⁻¹ year⁻¹ (Tipping et al., 2014) which is negligible compared to the other P inputs in the long-term trials. Leaching was also not included in the budget as no data was available from the long-term experiments to test the model. Also reported losses of <0.01 to 3.2 kg P ha⁻¹ year⁻¹ (average values of 0.3 kg P ha⁻¹ year⁻¹) (Leinweber et al., 1999) from a study involving 20 differently managed lysimeters are, again, low compared to the terms included in Eq. (1). Nevertheless, it was checked, if the model simulates negligible organic or inorganic P losses as leachates. Lastly, the P input coming from the "horn manure" preparations in the biodynamic plots of the DOK trial was also excluded, as the amount of P is negligible.

2.2.2. Model parameterization

Site-specific input data included climate, soil texture, bulk density, pH, soil depth, soil organic C, mineral and organic N, and mineral and organic P contents as determined at the beginning of the trial. As the CR and the SF trials have been successfully simulated with both Century (the monthly version of DayCent) and DayCent for the C and N cycles (Lugato et al., 2007; Dal Ferro et al., 2016), certain initial site-specific input data came from previous initialization/calibration. Calculated soil parameters such as field capacity, wilting point, and saturated hydraulic conductivity were either measured or calculated with pedotransfer functions (PTF) depending on the experiments (Saxton et al., 1986). Management information was adapted according to the longterm trials, such as dates of planting, harvesting, irrigation, ploughing, and fertilization. The meteorological data inputs (maximum and minimum monthly air temperature and monthly cumulated precipitation) came from meteorological stations located close to the two experimental sites in Padova and Therwil.

The strategy for model parameterization and calibration of the P

submodel included these sequential steps: i) the initialization of soil P pools with data at the beginning of the experiment or first data available; ii) the calibration of the crop uptake, soil P pool exchange parameters and adjustment of initial P pool sizes, if necessary. Since the three of them interact in regulating P supply and demand, they were calibrated iteratively by trial and error, with the objective of minimizing the root mean square of observed and simulated average P export and budget. Thus, the soil P pools of the topsoil (30 cm) were manually initialized according to the measured values of P_{Total}, P_{Available}, and, if present, P_{org} using the data at the beginning of the experiments. Besides $\ensuremath{P_{Total}}$ and P_{Available}, the sizes of other P pools were observed only qualitatively since the long-term experiments data did not include a complete fractionation of P in soil as in the P submodel (which is based on Hedley et al., 1982). The relative pool size distribution of the unknown mineral pools was estimated by subtracting the measured PAvailable and Porg from the P_{Total} pool and distributing the rest over the pools P_{Occluded}, P_{Strongly} sorbed, and PParent based on literature partitioning of similar soils (Yang and Post, 2011). The parameters determining the flows between the mineral P pools P_{Occluded}, P_{Strongly sorbed}, P_{Sorbed}, and P_{Parent} resulted in very small flows and were left unchanged from the model default values except for the flow from the strongly sorbed to the P_{Sorbed} and P_{Available} pool. This flow was enabled by adding low site-specific values (Table S4, SI), as the default was equal to 0, to allow exchange with the P_{sorbed} pool.

As there was a lot of variability in some PAvailable measurements and the initial values were not always known, the initial pools were based on the first data available and adjusted as explained before. Unfortunately, the available P in the trials and the model referred to different extraction methods, while all reflecting a soluble P form that is accessible for plants: resin extractable P (DayCent model), the Olsen method (the CR, the SF, and the MMo trials), and the PCO₂ method (DOK trial). This is a recurring issue in working with P data. Because a change of the standard method would decrease the comparability of data, the use of conversion equations has been established to allow the combination or comparison of data derived by different methods (Steinfurth et al., 2021). However, conversion equations are strictly empirical, highly dependent on the soils used to establish the equation, and should therefore only be conducted if necessary. As none of the measured data was assessed with the same method as the DayCent outputs refer to (i.e., resin extractable P), it is unavoidable that conversion equations are used in this case. The H₂O-CO2 method used in Switzerland (Dirks and Scheffer, 1930; CO2-saturated water, soil to solution ratio 1:2.5, extraction time 60 min) has a coefficient of 16 to calculate Polsen (Eq. (2)) (Neyroud and Lischer, 2003 according to Steinfurth et al., 2021). For the conversion of P_{Resin} to Polsen, a correlation formula derived from 30 alkaline soils was used (Nesse et al., 1988) (Eq. (3)). Therefore, from here on, the plant available P (P_{Available}), including the modelled P_{labile}, is given as the measured or modelled values transformed to the Olsen method.

$$P_{\text{Olsen}} = P_{\text{CO2}}^{*} 16 \tag{2}$$

$$P_{Olsen} = P_{Resin}^* \ 0.62 - 1.98 \tag{3}$$

Secondly, the equilibrium between P_{labile} and P_{sorbed} had to be defined (Fig. S4, SI 1.3). The SORPMX was based on the change point, which is the $P_{Available}$ threshold, after which P loss via runoff and leaching increases dramatically. The soil-specific change point was used when available (SF clay). Otherwise, the values were based on reported change points between 20 and 112 mg kg⁻¹ (McDowell, 2001; Nair et al., 2004; Bai et al., 2013; Xue et al., 2014). PSLSRB was adjusted with the objective of matching the P gross budget and, secondly, to minimize the difference between modelled and measured $P_{Available}$ in the time series.

Whenever P_{org} was measured (SF soils, DOK soil), the CP ratios of the soil organic matter pools were adapted from the default values so that their sums matched the measured P_{org} staying within the suggested ranges by the model (SI 1.1.3). When measured data were not present, as

for the CR and MMo trials, the organic P pool was initialized by central values suggested by the model for relatively unweathered soils. These values coincided with values from literature (Kirkby et al., 2011; Tipping et al., 2016; Zechmeister-Boltenstern et al., 2015).

In DayCent, all organic P pools and thus also the daily P uptake are a function of plant biomass and CP ratios. Crop production is controlled by moisture, temperature, solar radiation, and nutrient supplies (the most limiting nutrient constrains production). For the crop parametrization, the parameters included in (Lugato et al., 2007), such as maximum potential growth rate (PRDX), the harvest index (HIMAX), and CN ratios, were kept unchanged. Depending on the nutrient demand and supply, the CP ratios are allowed to range within set minimum and maximum values, which may constrain the production in case of nutrient limitations (SI Fig. S5). The maximum and minimum CP ratios (PRAMX, PRAMN) were therefore calibrated for each crop species, using all treatments from all trials to represent the trends in the P uptake by the various crops over the 40-year experimental period. The aim was to have crop CP ratios that are not location specific but crop type specific. The control treatments allowed to define the maximum CP ratios at deficient nutrient availability. One new crop was created to represent horticultural crops, such as white cabbage. In the model, P uptake was insensitive to a parameter that controls the fraction of the labile P available to plants (FAVAIL(2)). Therefore, the calibrated CP ratios compensate for this insensitivity, as well as other possible missing P uptake processes (e.g., microbial solubilization, root exudation, root phenotypes, mycorrhizal association). Thus, the CP ratios may deviate from literature CP ratios in plant tissues, although those data are quite rare and variable. This study did not enable the sulfur submodel, and other nutrients such as potassium or micronutrients are not considered in DayCent.

3. Results and discussion

3.1. Soil surface P budget

The average annual P inputs from mineral and organic sources for the various treatment combinations of all trials ranged from 0 to 11.35 g m^{-2} (equivalent to 0–113.5 kg ha⁻¹). This range is within those of the different phosphorus legislation and guidelines in Europe (1.7–12.5 g m^{-2} year⁻¹, Amery and Schoumans, 2014), and reflect thus representative P inputs. The observed and simulated P input, P export, and the resulting P budget for the 1-year low-intensity CR trial is shown as example (Fig. 2). In the depicted CR trial, the P input (Fig. 2a) came both from mineral and FYM fertilization, with the inputs changing over time. Other treatments simulated in this study are presented in the supplementary section (SI 1.4).

The model represented the average P export in all treatments well, except for some underestimated treatments of the high input CR trial (Fig. 3a). The measured P export ranged from 1.18 to 13.67 g m⁻² (mean of 3.4), and the modelled P export from 0.31 to 11.0 g m⁻² (mean of 2.7). Both measured and modelled P exports are in line with P removed by crop harvesting and residues found in a recent regional study (1.7–2.2 g m⁻² for the Veneto Region, Panagos et al., 2022b), indicating the representativeness of the data used in this study. The modelled P export, which considered biomass removal, including crop harvest, crop residues, and intercropping, showed the same magnitude and temporal dynamics as the measured data (e.g., Fig. 2b).

When comparing the three fertilization rates of the low input CR trial (Fig. 2a), it becomes visible that a higher modelled fertilization lead to a higher modelled P export (Fig. 2b). For the CR trial, and all trials in general, the model performed worse in simulating observed P export in the control treatments that received little to no fertilization. The reasons can be that the model still did not reflect the CP ratios at low $P_{Available}$ conditions or crop specific mechanisms to increase P availability (e.g., microbial solubilization, root exudation, root phenotypes, mycorrhizal association (Alori et al., 2017; Niu et al., 2013; Wang and Lambers,



Fig. 2. Simulated vs. observed P input, P export and P budget of the three fertilization rates in the 1-year low input crop rotation; (•) measured; (—) modelled using DayCent. The unit [g m⁻²] equals [kg ha⁻¹]/10.



Fig. 3. a) Average P export estimated from the measured data compared to the P export predicted by DayCent for the CR (both intensities), the MMo, the SF and the DOK trials; b) Average P budget estimated from the measured data compared to the P budget predicted by DayCent for the CR (both intensities and all cycles separated), the MMo, the SF and the DOK trials. The lines indicate the 1:1 line ± 1 g/m2.

2020)). The abrupt changes in P export in 1975 and 1988 stemmed from a change in management (e.g., lower fertilization, changed crop rotation) or a change in crop variety (e.g., with higher yields). The other trials show similar behaviour as the CR trial (SI 1.4). For instance, the modelled average crop export (2.87 g m⁻²) from the DOK trial was slightly lower than the measurements suggest (2.92 g m⁻²) due to the lower modelled export for the low fertilized treatment.

There was a strong linear relationship (r^2 value = 0.95) between observed versus simulated P budgets for all the trials considered in this study (Fig. 3b). The modelled P budget (shown as one example in Fig. 2c) also closely followed the amount and temporal dynamics of the measured data. The range of the measured balance was from -4.2 to 8.6 g m⁻², which was a little wider than the modelled range of -3.34 to 7.9 g m⁻², confirming the model capacity for simulating both P surplus and deficit conditions. In general, in the high input treatments the model overestimated the P budget, and in the little to not fertilized treatments it underestimated the budget slightly.

The type of fertilizer did not seem to affect the ability of the model to accurately simulate the P budget, as shown in the treatments of the SF, MMo (SI 1.4) and DOK trials that included organic or mineral fertilization. Nevertheless, in the SF trials, the organically fertilized treatments had slightly higher modelled P budgets than the mineral fertilized treatments, due to a lower P export. In literature, there is no consensus yet, on whether and under which conditions organic fertilizers increase or decrease P sorption and thus affect P uptake (Pizzeghello et al., 2016); but often they are associated with increased P solubility and P uptake,

which seems conflicting to the P export behaviour of the model.

The majority of the long-term experiments included in this study leaned toward high intense farming with high export and input. Piccoli et al. (2021) have already described the nutrient balance predictions based on the CR and MMo trials as more optimistic than those based on real fields since the crops are generally over-fertilized. This might have helped the model performance as the P submodel of DayCent has been described as limited applicable for soils in which P is the major limiting nutrient (Gijsman et al., 1996). However, none of the treatments are solely P limited since the nutrients were generally added together, potentially masking the model's response when looking at P effect alone.

3.2. P dynamics in agricultural soils

The observed and modelled P_{Total} were in the same magnitude of values (Fig. 4a). Being mass balance consistent, P_{Total} reacted to the P budget so that a positive and negative P budget increased and decreased modelled P_{Total} values, correspondingly. This mass balance consistency was not always recorded in the measured P_{Total}. When looking at all trials conducted on the native soil of Padova (CR, MMo), it stands out that the P_{Total} increased disproportionately between the two measurement years compared to the amount of P added through fertilization (e. g., Fig. 5). For instance, the measured P_{Total} of the unfertilized control treatment increased equal to the highly fertilized MM treatment. This indicates a high uncertainty of the sampling and/or the analysis possibly coming from different laboratories, operators, and samplers. Thus, the differences between the individual modelled and measured P_{Total} values of the CR and the MMo trials may not indicate poor model performance, especially in the MMo trial where only one P_{Total} measurement exists that might be unfoundedly high. The P_{Total} measurements of the SF trial (Fig. 6) followed their respective P budgets more, although, for some treatments, there were small P_{Total} increases in the 1980's despite negative P budgets (SI 1.4). The P_{Total} measurements of the DOK trial were consistent with their P budgets, with a general decrease in P_{Total} in the negative P budget plots, except for the mineral-conventional (M) treatment.

The average $P_{Available}$ stocks measured in the soils of all treatments were within the range of 0–30 g m⁻². The model generally overestimated the $P_{Available}$ for all trials except the SF. As the P budget is well reflected in the model, this overestimation was mainly an issue of soil P dynamics. The reasons for such an increase in modelled $P_{Available}$ can include setting the soil's sorption capacities too low, mechanisms are still missing in the P submodel such as re-sorption, or the conversion equations from the available P methods do not capture the true P_{Available} pool. In the CR, MMo, and the initial phase of the DOK trial, the modelled P_{Available} accumulated over time, driven by a positive budget. This was the result of a lower sorption affinity setup, which resulted in a closer relation between change in P budget and P available (Fig. 7). The modelled soils seem to have reached the saturation point, and the crop uptake is at its maximum uptake capacity so that P added through fertilizers accumulates as P_{Available}. On the other hand, the soils of the CR and SF trials showed a high sorption affinity. Their measured PAvailable was quickly sorbed when provided by fertilization but also exchanged back from the sorbed pool when depleted by crop uptake. That made those soils more invariant to the P budget (Fig. 7), particularly in the CR and MMo soils rich in carbonates. The model parameterization of the SORPMX parameter, which defines the maximum P sorption potential, was set within levels suggested by literature and slightly calibrated together with PSLSRB (SI Fig. S4). Indeed, when sorption affinity was increased, the crop uptake diminished significantly, as shown by the sensitivity analysis (Fig. S6 SI). This may indicate, as discussed, that plants in field conditions are capable of P uptake at low P availability, likely by some mechanisms not incorporated in the model. It is also important to note that measured and modelled PAvailable refer to different methods of P extraction, which increases uncertainty in defining the extent of plant availability, despite the use of conversion equations. In essence, due to this trade-off in fitting PAvailable and P uptake, the priority was given to reproducing the gross P budget instead of perfectly matching the P fraction in soils, still subject to large uncertainty. As leaching and erosion of P would happen in smaller amounts compared to the P_{Available} increase, it is not likely that these are the missing processes. When running the model at different soil pH values (4.8, 6, 7.8), a very low reactivity of the P_{Available} to the soil pH was found.

In the CR trial, the modelled accumulation of $P_{Available}$ markedly increased with fertilization (Fig. 5). In the soil of the DOK trial, the modelled $P_{Available}$ also increase stronger than the measured up to a certain threshold (data not shown). After this threshold, the modelled $P_{Available}$ followed the measured data at an increased level, with the mineral-conventional treatment diverging the most from the measured (SI 1.4.2). One reason for the modelled initial increase of $P_{Available}$ can be that the model pools were not yet in equilibrium. Instead, the modelled $P_{Available}$ in the SF trial followed the measured values, remaining in the



Fig. 4. a) Average P_{Total} estimated from the measured data compared to P_{Total} predicted by DayCent; b) Average $P_{Available}$ estimated from the measured data compared to $P_{Available}$ predicted by DayCent. Measured and modelled values are transformed to the Olsen method via conversion equations; c) Average P_{Total} compared to $P_{Available}$ estimated from the measured data (red) compared to predicted by DayCent (blue) for all trials (treatments are represented by the same symbol as in the graphs a & b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Simulated and observed soil total (black) and available P (orange) in the 0–30 cm topsoil of the three fertilization rates 1-year low input crop rotation of the CR trial; (—) modelled; (•) measured.



Fig. 6. Simulated and observed soil total P (black), and available P (orange) for in the 0–30 cm of topsoil of three fertilization rates of the SF trial of the clay, sandy and peat soils; (–) modelled; (•) measured; O = control; L2 = organic fertilizer; M2 = mineral fertilization.



Fig. 7. Annual rate of the available P change in relation to the P budget in measured and simulated data for (a) the CR in the period 1974–2000 (LI = low input; HI = High input), and (b) the SF in the period 1982–2001, (min = mineral; mix = mixed; org = organic fertilization). * relations are statistically significant at p < 0.05.

range of the measurements, notably quite wide (Fig. 6). This might be due to the lower retrogradation of $P_{Available}$ in those soils and more information from previous studies (Pizzeghello et al., 2016) to set the SORPMX parameter at least for the SF clay trial.

The deviation of the modelled vs. measured $P_{Available}$ behaviour was also evident from the relationship between P_{Total} and $P_{Available}$ (Fig. 4c). A flat relation generally indicates conditions far from the saturation of the soil with P available forms, as depicted by the measured data. The model set up toward a lower sorption affinity resulted in a condition closer to a $P_{Available}$ saturation. In all soils of this study, both the measured and the modelled $P_{Available}$ initially account for 0.4–11% of P_{Total} . This corresponds well with literature values, where $P_{Available}$ typically accounts for 1–10% of the P_{Total} (Le Noë et al., 2020; Ringeval et al., 2017). In the course of the trials, the measured percentages of $P_{Available}$ from P_{Total} increased for all soils except the soils of the SF clay and SF peat trials, where $P_{Available}$ decreased with respect to the year and fertilization rates, likely affected by the discussed measurement uncertainty.

Fig. 7 also indicated a difference in $P_{Available}$ depending on the type of fertilizer. In the CR trial (Fig. 7a), the measured high input treatments (dotted line) that received more organic fertilizer had a higher intercept and lower slope than the low input treatments, suggesting a better availability of P with the use of organic fertilizers. Also in the SF trial (Fig. 7b), the organically fertilized treatments seem to have higher measured $P_{Available}$ at the same P budget. This is in accordance with literature that suggests that organic fertilization influences the P chemistry in soil and promotes the solubilization of P (Wandruszka and Ray., 2006). This higher availability due to the type of fertilizer cannot be observed in the modelled data, likely due to the pathway of P transformation implemented. In the P submodel, the P added as organic fertilizer has first to become available for crop uptake by mineralization of organic carbon pools, whereas mineral P addition is directly added to the mineral P pool.

A recent study developed and calibrated a model of inorganic P dynamics using the observations from 147 soils worldwide (Wang et al., 2022), that can be the basis for inorganic P dynamics for global land models. They have found that the bioavailability of soil P depends not only on the desorption rates of labile and sorbed pool, inorganic

phosphorus fractions, the slope of P sorbed against solution P concentration, but also on the ability of biological uptake to deplete solution P concentration. Additionally, the modelled parameters found by Wang et al. from 147 soils worldwide vary by several orders of magnitude, which shows the need of more experimental data to tune the soil P dynamic in DayCent.

The remaining mineral soil pools $P_{strongly sorbed}$, P_{parent} , and $P_{occluded}$ can only be assessed qualitatively, as there are no measurements in the long-term trials. All soil P pools reacted slowly over the timeframe of the trials. P_{parent} and $P_{occluded}$ slowly lost P to the more labile pool, as in agreement with literature in the timeframe of the simulation. The $P_{strongly \ sorbed}$ pool lost or gained P to/from the more labile pool, depending on the equilibrium with $P_{Available}$. The P submodel was also checked for P losses through mineral or organic leaching. Leaching of organic P, related to the decomposition of the active soil organic carbon pool and its CP ratio, was a constant flux in minimal amounts. Leaching of mineral P, however, was not recorded. Even though the leaching rates are low, a functioning leaching would be beneficial for large-scale and scenario modelling, thus more model development is needed.

3.3. Yield

The comparison of observed vs. modelled yield is important for modelling P export, as it is directly dependent on the yield via the CP ratios. Yield was modelled as the annual sum of the economic yield of C in grain, tubers and forage biomass. The crops included in this study were maize, forage maize, winter wheat, sugarbeet, soybean, tomato, potatoes, fodder intercrop, white cabbage, winter barley, grass-clover, and white cabbage. The model did predict the observed harvest quite accurately ($r^2 = 0.76$) for the trials CR, MMo and SF and in response to the different treatments (Fig. 8). The measured yields in the clay and peat soils of the SF trial, were higher than those modelled likely due to a more efficient management compared to open field conditions for which the model is calibrated. The ranges of the crop yields of the different trials can be seen in the SI 1.4.1.



Fig. 8. Measured vs. modelled average biomass removed by crop harvest for all trials except the DOK trial with stdev bars in grey.

4. Conclusion and future model developments

The DayCent model captures the P budget (input minus output) in six long-term experiments with high accuracy, especially for the medium high fertilized treatments. $\ensuremath{P_{\text{Total}}}\xspace$ reacted to the P budget as the model is mass balance consistent, so a surplus in the P budget increased P_{Total} (and vice versa). The model application was able to reproduce measured PAvailable values in the same range but sometimes with contrasting temporal dynamics. P modelling is subject to a wide range of uncertainties with respect to both input data (particularly the unknown initial distribution of the different P pool sizes and the uncertainty of the measurements) and the representation of processes influencing the P cycle that are not yet accounted for in the model. The reason for the $P_{Available}$ not being easily reproducible might be because (1) information of the initial P pool sizes was not fully known, (2) the model was not fully reflecting all P uptake processes, (3) immobilization might have been too low in certain conditions (eg., calcareous soils). To decrease the uncertainty, more research on the individual P pools will help to improve the available P dynamic in the soils. Data with a complete fractionation of P (Hedley et al., 1982) in soils with diverse mineralogy and chemistry would be needed, especially from several samplings in time from long-term experiment sites. Also, the C-N-P relationship with its specific mechanisms and interactions is still poorly understood. A deeper understanding would help to reflect the C, N, and P cycles in the model better. In order to use the model on a global scale, it should also be tested on more crops and other world regions with more weathered and P limited soils.

Supplementary to more detailed P pool measurements, model development might be needed to improve the simulated P transformation in soil. Mechanisms that could improve the model are the movement of P sorbed to particles through micro- and macropores of the soil (Simard et al., 2000), different root strategies of plants that can exude organic acids to increase the P availability (Hocking, 2001), and pH dependant sorption (Barrow, 2017). An important mechanism to be tested further is the P dynamic of organic fertilizers. We have seen that the availability of P from organic fertilizers is reduced compared to mineral fertilizers in Daycent, which is not in accordance with the measured values (Morari et al., 2008).

Additionally, some model parameters affecting the P cycle did not perform as intended, such as "favail", the fraction of labile (non-sorbed) P in the surface layer available to plants, and fleach(4), the leached fraction of $P_{Available}$. Favail did not seem sensitive to any changes. As the CP ratio of the crops could bypass it, it did not affect the model performance. Additionally, it should be investigated why mineral P leaching does not react to changes in the leaching parameter, even though the leaching rates of mineral P would be low. Further investigations and adjustments to the model would help gain a deeper understanding of the processes taking place and increase its applicability.

Despite these uncertainties and calls for further model assessment and developments, there was an urgent need for a process-based biogeochemical model that includes not just N and C cycles but also P. As this was the first attempt to assess a process-based model on longterm experiments in European conditions, the results are encouraging. The work sheds light on the complex processes involved in the P cycle and the interpretation of long-term P dynamics better disentangled by comparing model projection and measured data. Past simulation results, focussing on C and N, have shown that the DayCent model was able to reproduce the major effects of climate, soil, and management on crop production (Lugato et al., 2017; Necpalova et al., 2017; Quemada et al., 2020; Stehfest et al., 2007). Thus, the model may be used to assess different scenarios with a changing climate, a change in management or land-use, and to analyse potential feedbacks between the terrestrial and the climate system. This makes this model a promising tool for assessing policy and practical applications that advocate for a change in nutrient inputs and agricultural management. Finally, this work may trigger a stronger engagement of the modelling and experimentalist community to address pressing environmental challenges, such as the efficiency of using a non-renewable resource like phosphorous.

Additional information

Correspondence and requests for materials should be addressed to A. M. The model input files will be made available upon request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The model input files will be made available upon request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.agsy.2022.103595.

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