Heliyon 10 (2024) e40160

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Challenges in developing reliable phosphorus predictive models: Unpredictable release under soil redox changes

Filippo Saiano, Riccardo Scalenghe [*]

Dipartimento Scienze Agrarie, Alimentari e Forestali, Università degli studi di Palermo, Italy

ARTICLE INFO

Keywords:
Null point
Maximum adsorption capacity
Overfertilized soils

ABSTRACT

Phosphorus (P), crucial for plant nutrition, is unevenly distributed in the Earth's crust, necessitating its supplementation in agriculture through fertilizers. However, excessive use can lead to water pollution. Our research focuses on the P adsorbing complex, investigating P release due to flooding, using 12 well-characterized soils with contrasting properties. Our research measures directly the P-adsorbing complex using adsorption/desorption isotherms. We observed that the P concentration in the solution —sufficient to prevent desorption yet low enough to avoid further sorption by the soil— decreases when the soil undergoes complete reduction (anoxia). When grouped by similarity, calcareous soils exhibit higher maximum P adsorption capacities (X_{max}) under alternating reducing conditions (ARC) compared to continuous reducing conditions (CRC). In slightly acidic soils, CRC leads to a wider spread in X_{max} values than ARC. For acidic, organic matter-rich soils, ARC results in the highest X_{max} values (123 mmol P kg^{-1} soil) compared to CRC, whereas in acidic, light-textured soils, CRC shows significantly higher mean X_{max} values than ARC. Nevertheless, we were unable to develop a predictive model for soil P desorption based on key intrinsic properties and climate. When an environmental or anthropogenic transformation induces anoxia, the P released does not follow a predictable pattern.

1. Introduction

Phosphorus (P) plays a strategic role in supporting plant nutrition, yet it is not uniformly distributed across the Earth's crust; instead, it is found in concentrated deposits. In areas where soils lack P, it's supplemented with fertilizers. However, excessive addition of P to soil can lead to eutrophication when it leaches into surface waters. These interconnected factors underscore the importance of effective management practices, particularly within the agricultural sector. Creating soil distribution maps would greatly aid in decision-making processes, and significant strides have been made in this regard in recent years [1,2]. Progress has been notable, moving from enhanced cartographic resolutions to a focus on assessing various P pools within the soil, rather than just total P, which is less relevant for management purposes. For instance, Ringeval et al. [3,4] modeled the global distribution of soil P with a good (0.5° × 0.5°) spatial resolution although considering topsoils only, 0–30 cm (corresponding to LUCAS sampling guidelines), with no vertical discretization. Furthemore, soil P pools were considered (GPASOIL model) according to Hedley scheme (inorganic P in soil solution, labile inorganic P, moderately labile inorganic P, primary inorganic P, labile organic P, stable organic P, and occluded P. Indeed, van Doorn et al. [5] add precision using high-resolution digital soil mapping: they considered amorphous iron (Fe)- and aluminium (Al)-(hydr)oxides to better interpret the behaviour of soil P. However, the challenge lies in the abrupt changes that P undergoes in soil

---

[*] Corresponding author.
E-mail address: riccardo.scalenghe@unipa.it (R. Scalenghe).

https://doi.org/10.1016/j.heliyon.2024.e40160
Received 4 April 2024; Received in revised form 4 November 2024; Accepted 4 November 2024

behaviour, often in response to minor environmental fluctuations. It is widely acknowledged that even temporary water excess or slight alterations in the soil's redox potential can trigger rapid solubilization of P [6]. This can lead to subsequent reoxidation, resulting in greater P adsorption in some soils and less in others. In natural soils, redox cycles occur regularly under normal conditions. However, in cultivated soils, such cycles can happen frequently throughout the year, particularly due to common agronomic practices like irrigation. Therefore, the fundamental inquiry becomes: is it possible to effectively map P in soil while incorporating a predictive capability that accounts for its potential release in a practical way?

The chemistry of soil P is known to be controlled by various type of reactions, such as adsorption/desorption and precipitation/dissolution [7–9]. These reactions usually concern P in solution, or the Intensity factor. Other reactions, i.e. oxidation/reduction, do not affect P *per se* but have a drastic influence on the soil components, Fe and Mn oxides, that constitute the Quantity factor in adsorption/desorption phenomena. The reduction of Fe and Mn to more soluble forms implies that soils that undergo anoxia become a P source [10]. Two previous works had studied as the solution changes following a continuous submersion period [11] or cycles of oxidation and reduction [12] in twelve agricultural soils very different for their physico-chemical properties. Under alternating redox conditions, P release in solution exhibited a rapid peak followed by a decline. This decrease in concentration is attributed to re-adsorption by undissolved crystalline oxides, the exposure of new sorption sites through the dissolution of Fe coatings, or the formation of iron precipitates under anoxic conditions. It had been reported that, after repeated cycles of oxidation and reduction, soil P has a tendency to transition towards less stable forms, which can be readily released upon subsequent reduction [13,14]. A change in the P adsorption/desorption behaviour of the soils can then be postulated as a consequence of the transformation of the adsorbent matrix.

In this paper, we investigate the transformations of the P-adsorbing complex as a result of anaerobiosis, continuous or intercalated by short periods of oxidation, to quantify this transformation directly. We search for a prevalent pattern capable of elucidating the behaviour and facilitating the prediction of P concentration in soils.

2. Materials and methods

This study examines the main physical and chemical properties of twelve benchmark overfertilized soils from diverse agricultural regions in Germany, Great Britain, Italy, and Spain. Selected for their extreme phosphorus adsorption characteristics, these soils vary in pH, organic matter content, carbonates, iron and aluminum oxides, and phyllosilicate types. The soils were classified as overfertilized based on a criterion where the available phosphorus, determined by regional soil P tests, was at least twice the critical level needed for an average crop. We used very well studied soils [11,12,15–24] ranging taxonomically from Regosols (Entisols),[1] to Vertisols (Vertisols) typically dominating in Mediterranean environments, to Chernozems (Alfisols and Mollisols) of the cooler mid-latitudes, and from xeric to udic in soil moisture regime and frigid to thermic in soil temperature regime. These twelve soils cover a wide range of geo-ecological settings and of total soil P content and the capacity of phosphate sorption (Fig. 1).

Three–gram samples of soil were weighed into 20-mL vials to which 15 mL 0.01 M $CaCl_2$ was added. The vials were sealed in an anaerobic box (298 K) and, at intervals up to two years, a batch of vials was shaken for 20 min and centrifuged. At the end of the experiment, solid phases were freeze-dried and analysed for P (details in Ref. [11]).

In another experiment 3 grams of the same twelve soil and 15 mL of 0.01M $CaCl_2$ were incubated under anoxic conditions (20 days, 298 K) then oxidised (1 day) and dried (1 day). The entire cycle was repeated 11 times (details in Ref. [12]). Gases in the anaerobic box ($pN_2 = 0.88$; $pCO_2 = 0.08$; $pH_2 = 0.04$) were chosen to reflect the components most likely present under anoxic natural conditions.

On the solid phase, P and Fe were extracted with 0.2 M acid ammonium oxalate at pH 3 [27], as adapted by Darke et al. [28], and an estimate of plant available P[2] was determined according to Olsen et al. [29].

Adsorption characteristics were estimated by adding different amounts of KH_2PO_4 (from 0.1 to 50 μg P mL^{-1}) to 0.2 g of soil in 0.01M $CaCl_2$, shaking end-over-end for 24 h and analysing P in solution with the molybdate blue method [30] or the malachite green method [31] depending on the P concentration in solution.

Phosphorus adsorption isotherms were used to characterize each soil's capacity to remove dissolved P from solution; they were prepared by plotting mmol PO_4^{3-}-P adsorbed or precipitated per kg of soil as a function of P remaining in solution after equilibration (24 h) at a constant temperature (298 K) with 0.1, 2, 5 and 10 mmol P L^{-1}. P adsorption properties were described through their Null Point (NP), where adsorption equals desorption, or by the maximum adsorption capacity of the Langmuir equation (X_{max}) for those soils whose NP was impossible to establish. The NP is the solution concentration of P that is just high enough to prevent desorption from the soil and just low enough to prevent further adsorption [8]. This approach necessitates two assumptions: i) the amount of phosphate remains in the adsorbed form decreases with time (t), and ii) the adsorbed phosphate is in equilibrium with the phosphate in solution and that this can be described by a Freundlich equation. If a soil has a significant amount of phosphate, the easiest way to represent this is with the variable q, the native phosphate. Therefore, the total sorbed phosphate is $S + q$, where S is the adsorbed plus penetrated phosphate. So, considering this factor along with the influence of temperature [8], we get this equation:

$$S = kc^{b1}\left(exp\left(-\frac{E}{RT}\right)t\right)^{b2} \qquad \text{(eq. 1)}$$

---

[1] The first name is according to the World Reference Base [25]; the designation according to US Soil Taxonomy [26] is in parenthesis.

[2] In this paper, we use the terms P_o and Fe_o to refer to P and Fe extracted by acid ammonium oxalate at pH 3 and to P_{Ols} to refer to P extracted by $NaHCO_3$ at pH 8.5.

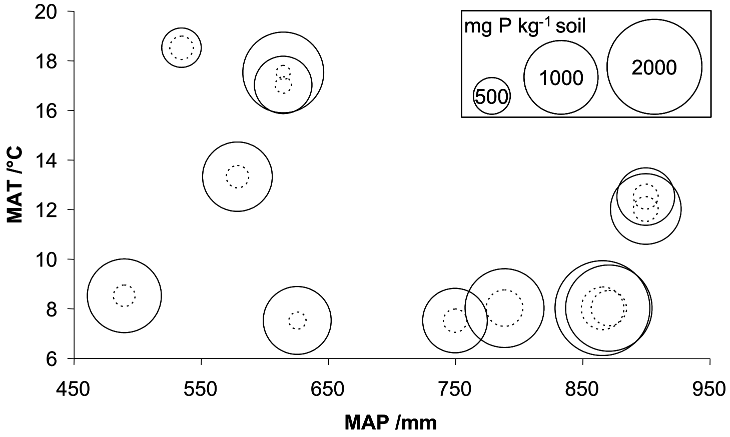

Fig. 1. Distribution of selected soils in a MAP–MAT graph (relationship between mean annual temperature, MAT in Celsius degrees and precipitation, MAP in mm) where lines represent total P and dotted lines Phosphate Adsorption Capacity Index, PACI. PACI [($Fe_o + Al_o$) + (Fe_d–Fe_o)/5] is calculated assuming that the P adsorption capacity per mol of Fe or Al is about one fifth for crystalline Fe oxides (estimated as Fe_d–Fe_o) of that for amorphous oxides (estimated as $Fe_o + Al_o$) [17].

where k is a constant, c is the initial solution concentration, E is an activation energy, T (Kelvin) is the temperature, and R is the gas constant, b_1 and b_2 are coefficients. Equation (1) is expressed with sorption S as the main variable. However, the measurements were taken for the concentration c.

3. Results and discussion

Within a soil, an aqueous phase can be separated from its solid phase by decanting it throughout, blocking certain substances while letting others pass through. A distinctive pattern is observable if groupings of our soils are considered under oxic condition.

The Phosphate Adsorption Capacity Index, PACI,

$$\text{PACI} = (Fe_o + Al_o) + (Fe_d - Fe_o)/5 \qquad \text{(eq. 2)}$$

assumes that the P adsorption capacity per mol of Fe or Al, about one fifth for crystalline Fe oxides of that for amorphous oxides (Fig. 1), is strictly correlated to the maximum quantity of phosphorus that a soil can adsorb, X_m, ($r = 0.96^{**}$) [17] and to the A parameter of the Elovich equation that describes P slow adsorption reactions ($r = 0.73^{*}$) [19]. But, under reducing conditions all these absorption/desorption properties are greatly influenced: the reduction induces a marked increase of the X_m and a dramatic decrease of the value of the null point (Fig. 2). The phosphate concentration in the solution is sufficiently elevated to hinder desorption from our twelve soils, 1.5 mg P L^{-1} solution in average, as a result of the reduction this value drops to 0.1 mg P L^{-1}. The specular X_{max} pattern is on average 0.7 g P kg^{-1} soil under oxic conditions; it increases to a maximum of 1.4 following reduction. However, soils with a high X_{max} might still have low NPs if adsorb P even at low concentrations. Conversely, soils with high NPs might not necessarily have high X_{max} if they have a limited overall capacity to hold P but requires a high initial concentration to begin adsorption.

The soils are grouped into (1) calcareous, C, (E1, E2 and I3), (2) slightly acid, SA, (D1, D2, E3 and I2), (3) acid and rich in organic matter, AOMR, (G3, G6 and G9), and (4) acid and light-textured, ALT, (D3 and I1) (Table S1).

For an equivalent reduction period of 60 days, oxidation pulses enhance the phenomenon by 15 % in the C soils. However, in the AOMR soils, the cycles tend to reduce the maximum adsorption as the decline continues. The alternation of cycles in the short period interferes on the reaction kinetics of adsorption-desorption magnifying the potential release of P. If considered globally, the alternation of cycles of oxidation does not substantially modify the phenomenon over years (Fig. 2).

In the first month, no significant changes are observed; however, the soils, despite their differences, begin to converge over time. Notable variations emerge after 220 days, and both cycles and continuous are found to be equivalent (i.e., interspersing periods of oxygenation with anoxia does not affect the solid phase of the soils. However, other studies on the same soils have shown that the liquid phase is significantly influenced). In the long run, the differences between the soil remain so that the system is rebalanced. We can say that within a temporal horizon of months the characteristics converge, with an annual time horizon the starting characteristics emerge again. On the long run, NP moves away from 1 (indicating the starting conditions, not anoxic) and, specularly, X_{max} increases greatly (Table S2). The figure highlights two distinct phases: a relatively rapid change occurring over weeks and a slower, long-term transformation that spans years.

Managing P availability to plants over short time periods may offer advantages both agronomically and potentially in an environmental context [32]. When exposed to oxic conditions, the P adsorption–desorption curves of these twelve soils indicate that the amount of phosphorus released to a dilute electrolyte tends to be proportional to the P concentration in the soil solution raised to a power that decreases with an increasing solution to soil ratio [24]. Under continuous reducing conditions, the water-extractable P significantly increases, leading to a substantial P solubilization [11,33]. This scenario could be exacerbated during a sequence of

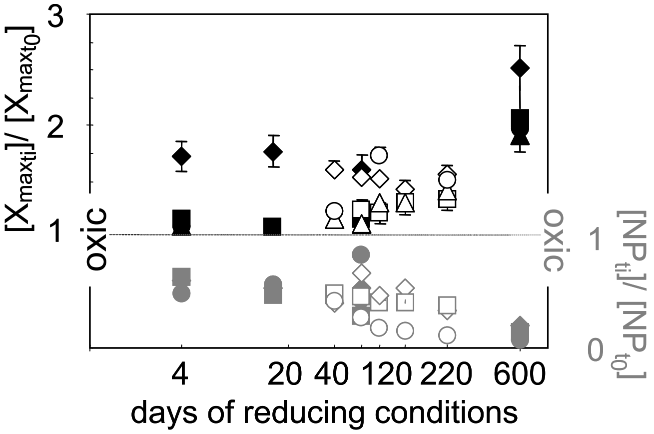

Fig. 2. Changes in maximum adsorption capacity of the Langmuir equation (X_{max}) in black above and below in grey the null points, NP (P solution concentration that is just high enough to prevent desorption from the soil and just low enough to prevent further sorption). From oxic condition represented by the dotted line, their transformations during pulsed reducing conditions (open symbols) and continuous reducing conditions (filled symbols). Results, calculated using equation (1), are expressed as a ratio of the respective initial X_{max} and NP (t_i/t_0 where t_0 and t_i are the concentrations at time '0' and 'i' respectively) and averaged (± standard error of the mean) for the soil groups: (⋄) calcareous (C), (□) slightly acid (SA), (△) acid OM rich (AOMR) soil, (◯) acidic light-textured (ALT) soil are extreme for properties, long-term paddy or very heavily overfertilized. Full data, expressed on an oven-dry basis at 378 K, are in Table S2 (P sorption isotherms, with NP in µmol P L^{-1} solution and X_{max} in mmol P kg^{-1} soil).

pulsed redox conditions, where up to two-thirds of total soil P is susceptible to a change in extractable form. Current findings suggest that changes in the organic and calcium-associated P fractions are particularly evident in such situations [12].

Olsen extractable P, used to represent an extraction method that has been widely adopted for advisory purposes, showed wide changes in concentrations: from 8 to 79 mg P_{Ols} kg^{-1} soil. In general, they followed one of three trends, three calcareous soils (E1, E2 and E3) declined, while two (I3 and D3) remained relatively unaffected (<10 % change from the initial value) and the remaining soils all showed an increase over time (data from Ref. [12]). Organic matter addition appears to hinder the effect of Ca dissolution on P release from soil [14]. The intricate nature of P adsorption-desorption processes in soil is closely linked not only to the characteristics of the soils themselves but also to the dynamic behavior of water within the soil matrix [13,34].

After the 4th cycle, the molybdate reactive phosphorus (MRP) fraction (representing inorganic orthophosphate) experiences a rapid decline, indicating a shift towards less soluble forms of P. This transformation is likely due to the system approaching a biological and chemical equilibrium, similar to what was observed in the continuous reduction experiment [11]. Notably, there is no evident correlation with a standard soil test, such as Olsen, which could be significant. Additionally, the change in MRP concentrations often exceeds that of P_{Ols}, even in the case of calcareous soils. During the cycles in our twelve soils, the Fe–P ratio becomes stoichiometrically de-coupled from the hypothesised *iron redox wheel* [35,36]. Further, the absence of a clear correlation with a standard soil test, specifically Olsen, holds potential significance. This is because the alterations in P adsorption properties differ from those observed in P_{Ols}, indicating a general incapacity of this routine P extraction test to predict short-term physico-chemical changes in P solubility [12]

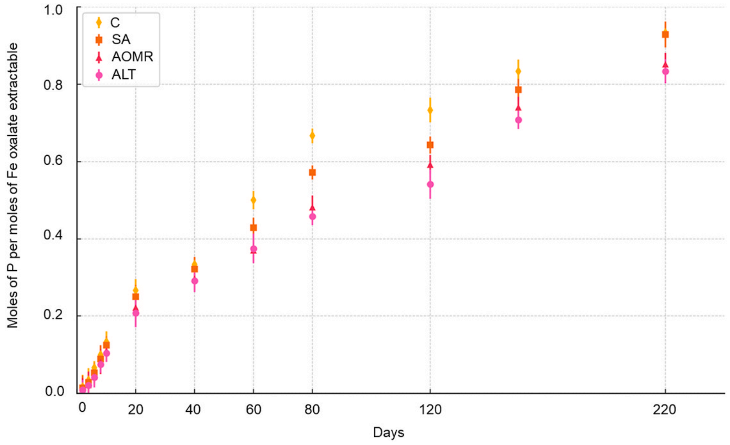

Fig. 3. Moles of P in respect to moles of Fe as extracted by oxalate from soils experiencing both continuous and pulsed reducing conditions over 220 days. Data from Ref. [23].

and medium-term shifts in P adsorption properties.

The mobility and solubility of P decrease due to the formation of insoluble compounds. A fundamental mechanism for immobilization involves the modification of solution pH. Adsorption and precipitation of P by Ca are dominant phosphate removal mechanisms, with the efficiency of the process being linked to the amount of CaO and/or Ca^{2+} released in solution through hydration and dissolution processes [37]. While P concentrations significantly increased in most soils, they remained stable in soils with high clay content. The onset of flooding triggers P release [38] associated with the liberation of Ca, Mg, and Mn, suggesting that P release may be controlled by the dissolution of Mg and Ca phosphates and reductive dissolution of Mn phosphates [14].

Predictions carry a high degree of uncertainty, as evident when compared to published field data. Flooding induces an increase in extractable poorly-crystalline Fe forms (Fe_o) in most soils, although not universally. This may lead to an elevation in allophane concentrations and, consequently, increased adsorption of PO_4^{3-} [20,39,40]. The chemistry of P and Fe is closely intertwined in both soils and sediments [41,42]. In soils, poorly crystalline Fe and P extracted by ammonium oxalate are well-known to be correlated [18,24,43]. This occurs in our untreated twelve soils (r 0.72*), this correlation is lowered cycle by cycle. The moles of P for each mole of Fe initially are very different from soil to soil. The gradual transformation induced by cycles of reduction and oxidation tends to “normalise” the system. After eleven oxidation/reduction cycles, the extraction in ammonium oxalate obtains 1 mol of P every 2 mol of Fe for most soils, as has been verified by measurements (Fig. 3). As the reduction conditions continue, their molar ratio tends to increase. The discrepancy in oxalate-extractable elements under oxic and reducing conditions, following incubation with mixed resins ([23], in their table 3), elucidates the connection between P bound to the resin after 32 days of submersion, represented as a Q factor, and P in solution, as highlighted in our Fig. 2. The gradual increase in amorphic components of the absorbing complex under anoxic conditions triggers the dissolution of oxides and carbonates, subsequently leading to the release of P [23]. However, it seems that the presence of P in solution is not governed by the solid phase [44].

These soils are susceptible to erosion, wherein smaller soil aggregates would be selectively displaced. In such instances, although the overall potential loss of P would be higher compared to the initial whole soil, the finer and more easily transported material might contribute to a reduced solution P concentration compared to coarser-sized fractions. The total P content within specific particle size classes decreases as the dispersive energy required increases [22]. However, if during the erosive processes different aggregate size fractions of these soils were mixed, measured P in water is lower than the predicted P [21]. And, the mixes of the calcareous aggregates (E1, E2, and I3) follows the same pattern as water soluble P in the mixes of non-calcareous aggregates [21], despite differences in the mechanisms of P retention [22].

The determination of soil P is sometimes problematic due to the sensitivity of its measurement, so the possibility of predicting the content in P, occasionally becomes useful for the management of soils for agronomic and environmental purposes. On relatively similar soils (Haplic Luvisols and Gleyic Cambisols [25]) under oxic conditions, Hosseini et al. [45] predicted P content in soils using models: genetic algorithms, partial least squares regression, and artificial neural network. Among the soil properties investigated, they found that soil P was most closely related to organic matter (i.e. all these soils are OM poor soils). Despite the promising results, careful attention must be paid to the predictive inference of phosphorus. It can work, as in this case, when the soils are very similar, as well as environmental conditions. Our results show that if the soil is subjected to temporary anoxia, any prediction is fallacious. To formulate adequately accurate predictive equations, a substantial amount of material should serve as the foundation for their development. Additionally, soils should likely be categorized based on other soil properties that could explain variations in P adsorption capacity [46]. Despite this structural alignment, reduction and the ensuing pH alterations result in elevated concentrations of P in solution during flooding.

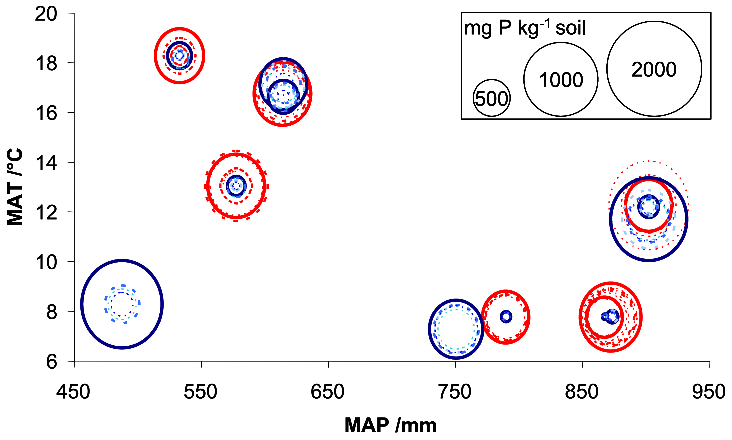

Fig. 4. The twelve soils plotted against salient climatic characteristics, precipitation in abscissa and temperature in ordinate. Colours indicate P desorption (red) or P adsorption (blue). The solid lines indicate C/X after 220 days of reduction alternating with moments of oxidation, the dashed lines the intermediate points (four measuring points in the range 0–220 days, 40, 60, 80 and 120 days). Soil D3 divided by 100.

In the past decade, more frequent extreme weather, including atmospheric rivers and heavy rainfall, has led to prolonged flooding of agricultural soils, potentially increasing MRP concentrations. This rise is due to the solubilization of P, reduction of Fe^{3+} binding to P, and the release of dissolved organic carbon from disrupted soil aggregates [36]. Fig. 4 provides a graphical comparison of two P concentration ratios (C/X at C_i and C_{10}) in untreated soils over 220 days under pulsed reducing conditions, such as flooding and anoxia. The null point (X) represents the P solution concentration where the soil neither adsorbs nor desorbs P, indicating a balance. The graph depicts the impact of these environmental changes on the P concentration ratios, showcasing the dynamic behaviour of P in soils over time and under varying conditions, highlighting how different soils respond to reducing conditions. The distribution of behaviour concerning adsorption properties is uneven when sorted by geo-ecological zones (Fig. 4).

3.1. *Is it possible to evaluate the soil P cycle by considering factors beyond P budgets?*

Muntwyler et al. [47] achieved through unprecedented spatial resolution an estimate on the P budget. Upscaling the calibrated DayCent model (i.e. the daily time-step version of the CENTURY biogeochemical model) [48], they generated higher-resolution maps depicting the average P budgets during a decade by executing the model with a low maximum sorption capacity (0.5-times) and maximal sorption affinity (a), as well as by running the model with a low maximum sorption capacity (1.5-times) and minimal sorption affinity. Muntwyler et al. [47] introduced a robust model framework that effectively: i) identifies surplus or deficit P balances in target areas at high spatial resolution, ii) highlights areas warranting further investigation and where alterations in agricultural practices could enhance achievement of policy objectives related to environmental pollution and resource efficiency for critical raw material P, and iii) evaluates potential reactions of the P cycle to changes in agricultural management in future scenarios. Their conclusion is that future research should explore diverse scenarios, including additional soil conservation measures, conservation agriculture practices (e.g., reduced tillage or grass margins), mulching, recycled P fertilizer utilization, changes in soil organic carbon (SOC), climate variations, and global-scale model scaling.

Modeling P inputs and outputs, they reveal a slightly positive annual P balance in EU and UK agricultural soils, where national averages range from -2.5 to 5.2 kg P ha^{-1} $year^{-1}$, with P surpluses (positive balances) posing an environmental pollution risk. The highest surpluses were modeled in Denmark, Cyprus, Malta, Portugal, Ireland, Spain, North-Western France, Northern Belgium, Central Poland, Northern Ireland, Western England (>2 kg P ha^{-1} $year^{-1}$). Conversely, P deficits were modeled in the Czech Republic, France (excluding the North-West), Finland, Germany, Slovakia, Western Netherlands, South-Western Austria, Northern Italy, and parts of the UK (South-Eastern England, and Scotland) (<-1 kg P ha^{-1} $year^{-1}$). These models take into account the fluxes through the soil but, notably, they are unable, at this spatial resolution, to consider the thermodynamic properties of soils, especially in terms of P desorption/adsorption. The limited scope of the 12 soils only captures a narrow range of situations across four countries. While the level of detail is informative, it emphasizes that attempting to extrapolate predictive characteristics or trends for P dynamics, considering various environmental factors, is challenging. A significant discrepancy is apparent concerning German soils, which, in our analysis, face a high risk of P loss despite being perceived as deficient in other assessments. As soils become more alkaline, saturated with bases and P, and with sorption capacity exceeded, there is an elevated risk of P losses to aquatic ecosystems [49].

Modeling cannot incorporate all analytical details available in a specific study. The comparison reveals substantial interpretative discrepancies, prompting reflection on whether simplifying scenarios to the extent of risking implausibility was a meaningful approach.

Furthermore, soil nutrients in agricultural systems are influenced by a combination of natural factors and field management practices [50]. Among these factors, water and soil movement play a crucial role in shaping, in particular, the P distribution. Runoff transports dissolved P, while bound P can be important to note that total P, although commonly measured, does not effectively predict the availability of P for plants or its potential release into water. The picture is made even more complicated considering that the interaction of climate change, alterations in land use and cover, and different management practices can intensify the dispersion of nutrients, leading to more significant fluctuations in total P loads [51]. The system is even more complicated in coastal areas, when in addition to a change in the redox conditions of the soils there is a combined increase in ionic strength [52]. So, further research is required to evaluate methods for mapping soil legacy P and the risk of MRP release across different scales [53].

4. Conclusion

Our results show that the maximum P adsorption capacity (X_{max}) can double under reducing conditions, shifting from 0.7 g P kg^{-1} under oxic conditions to 1.4 g P kg^{-1}, alongside a mirror decrease in the null point from 1.5 mg P L^{-1} to 0.1 mg P L^{-1}. The convergence of adsorption properties across different soil types after prolonged exposure (e.g., up to 220 days) points to the need of adaptive management strategies tailored to soil group-specific behaviors. In fact, our investigation reveals that the transformations of the P-adsorbing complex under anaerobic conditions, whether continuous or intermittently oxidative, lack a consistent pattern, thus precluding the development of a predictive model for soil P desorption based on intrinsic properties and climate, particularly during events leading to anoxia such as flooding. The concentration of P in the solution needs to be finely balanced – high enough to prevent desorption but low enough to hinder further adsorption by the soil. This delicate equilibrium is disrupted when soils are subjected to flooding, a phenomenon observed across various soil types in the mid to long term. This observation underscores the tendency for adsorption properties to converge, irrespective of soil type or location. Importantly, while flooding may alter certain aspects, the fundamental nature of the soil remains unchanged, and the reactivity of P specific to a particular soil type persists. Consequently, there is no distinct management option for geographically distinct soils saturated with phosphorus. The development of overarching strategies to control P losses on a continental scale must account for the inherent diversity of soils. To address this challenge, regionalization and the implementation of best practices in water management at the catchment level become crucial.

CRediT authorship contribution statement

Filippo Saiano: Writing – review & editing, Validation. **Riccardo Scalenghe:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: The corresponding author is a Section Editor of this journal (Soil Science section). First author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This dedication is extended to Tony Edwards, expressing the heartfelt wish for a swift and complete recovery.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e40160.

References

[1] P. Panagos, J. Köningner, C. Ballabio, L. Liakos, A. Muntwyler, P. Borrelli, E. Lugato, Improving the phosphorus budget of European agricultural soils, Sci. Total Environ. 853 (2021) 158706, https://doi.org/10.1016/j.scitotenv.2020.158706.

[2] T.L. Van Staden, K.J. Van Meter, N.B. Basu, C.T. Parsons, Z. Akbarzadeh, P. Van Cappellen, Agricultural phosphorus surplus trajectories for Ontario, Canada (1961–2016), and erosional export risk, Sci. Total Environ. 818 (2022) 151717, https://doi.org/10.1016/j.scitotenv.2021.151717.

[3] B. Ringeval, et al., Phosphorus in agricultural soils: drivers of its distribution at the global scale, Glob. Change Biol. 23 (2017) 3418–3432, https://doi.org/10.1111/gcb.13618.

[4] B. Ringeval, et al., A global dataset on phosphorus in agricultural soils, Sci. Data 11 (2024) 17, https://doi.org/10.1038/s41597-023-02751-6.

[5] M. van Doorn, et al., High-resolution digital soil mapping of amorphous iron- and aluminium-(hydr)oxides to guide sustainable phosphorus and carbon management, Geoderma 443 (2024) 116838, https://doi.org/10.1016/j.geoderma.2024.116838.

[6] A.N. Sharpley, Soil phosphorus dynamics: agronomic and environmental impacts, Ecol. Eng. 5 (2–3) (1995) 261–279, https://doi.org/10.1016/0925-8574(95)00027-5.

[7] N.J. Barrow, The slow reaction between soil and anions: 1. Effects of time, temperature and water content of a soil on the decrease in effectiveness of phosphate for plant growth, Soil Sci. 118 (1974) 380–386.

[8] R.E. Mendoza, N.J. Barrow, Characterizing the rate of reaction of some Argentinean soils with phosphate, Soil Sci. 143 (1987) 105–112, https://doi.org/10.1097/00010694-198702000-00004.

[9] D. Pizzeghello, A. Berti, S. Nardi, F. Morari, Phosphorus forms and P-sorption properties in three alkaline soils after long-term mineral and manure applications in north-eastern Italy, Agric. Ecosys. Environ. 141 (2011) 58–66, https://doi.org/10.1016/j.agee.2011.02.011.

[10] A.C. Edwards, P.J.A. Withers, Linking phosphorus sources to impacts in different types of water bodies, Soil Use Manag. 23 (Suppl. 1) (2007) 133–143, https://doi.org/10.1111/j.1475-2743.2007.00120.x.

[11] R. Scalenghe, A.C. Edwards, F. Ajmone-Marsan, E. Barberis, The effect of reducing conditions on P solubility for a diverse range of European agricultural soils, Eur. J. Soil Sci. 53 (2002) 439–448, https://doi.org/10.1046/j.1365-2389.2002.00462.x.

[12] R. Scalenghe, A.C. Edwards, E. Barberis, F. Ajmone-Marsan, Are agricultural soils under a continental temperate climate susceptible to episodic reducing conditions and increased leaching of phosphorus? J. Environ. Manag. 97 (2012) 141–147, https://doi.org/10.1016/j.jenvman.2011.11.015.

[13] D. Kumaragamage, D. Flaten, O.O. Akinremi, C. Sawka, D. Ige, F. Zvomuya, Impact of manure phosphorus fractions on phosphorus loss from manured soils after incubation, J. Environ. Qual. 41 (2012) 845–854, https://doi.org/10.2134/jeq2011.0415.

[14] E.A.G.S. Amarawansha, D. Kumaragamage, D. Flaten, F. Zvomuya, M. Tenuta, Phosphorus mobilization from manure-amended and unamended alkaline soils to overlying water during simulated flooding, J. Environ. Qual. 44 (2015) 1252–1262, https://doi.org/10.2134/jeq2014.10.0457.

[15] E. Barberis, F. Ajmone Marsan, R. Scalenghe, A. Lammers, U. Schwertmann, A.C. Edwards, R. Maguire, M.J. Wilson, A. Delgado, J. Torrent, European soils overfertilized with phosphorus: Part 1. Basic properties. Fert, Res. 45 (1996) 199–207, https://doi.org/10.1007/BF00748590.

[16] A. Delgado, J. Torrent, Phosphate-rich soils in the European Union: estimating total available-plant phosphorus, Eur. J. Agron. 6 (1997) 205–214.

[17] A. Delgado, J. Torrent, The release of phosphorus from heavily fertilized soils to dilute electrolytes: effect of soil properties, Agronomie 19 (1999) 395–404.

[18] A. Delgado, J. Torrent, Phosphorus forms and desorption in heavily fertilized calcareous and limed acid soils, Soil Sci. Soc. Am. J. 64 (2000) 2031–2037, https://doi.org/10.2136/sssaj2000.6462031x.

[19] A. Lammers, Phosphatformen und Phosphatfreisetzung in Hochgedüngten Böden Europas, DE, Herbert Utz Verlag, München, 1997, p. 179p.

[20] R.O. Maguire, A.C. Edwards, M.J. Wilson, Influence of cultivation on the distribution of phosphorus in three soils from NE Scotland and their aggregate size fractions, Soil Use Manag. 14 (1998) 147–153, https://doi.org/10.1111/j.1475-2743.1998.tb00633.x.

[21] R.O. Maguire, A.C. Edwards, J.T. Sims, P.J.A. Kleinman, A.N. Sharpley, Effect of mixing soil aggregates on the phosphorus concentration in surface waters, J. Environ. Qual. 31 (2002) 1294–1299, https://doi.org/10.2134/jeq2002.1294.

[22] R. Scalenghe, A.C. Edwards, E. Barberis, Phosphorus loss in overfertilized soils: the selective P partitioning and redistribution between particle size separates, Eur. J. Agron. 27 (2007) 2–80, https://doi.org/10.1016/j.eja.2007.02.002.

[23] R. Scalenghe, A.C. Edwards, E. Barberis, F. Ajmone-Marsan, Release of phosphorus under reducing and simulated open drainage conditions from overfertilised soils, Chemosphere 95 (2014) 289–294, https://doi.org/10.1016/j.chemosphere.2013.09.016.

[24] J. Torrent, A. Delgado, Using phosphorus concentration in the soil solution to predict phosphorus desorption to water, J. Environ. Qual. 30 (2001) 1829–1835, https://doi.org/10.2134/jeq2001.3051829x.

[25] IUSS Working Group WRB, World Reference Base for Soil Resources. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps, fourth ed., International Union of Soil Sciences (IUSS), Vienna, Austria, 2022, p. 234.

[26] Soil Survey Staff, Keys to Soil Taxonomy, twelfth ed., USDA, Natural Resources Conservation Service, U.S. Gov. Print. Office, Washington, DC USA, 2022.
[27] U. Schwertmann, Diefferenzierung der eisenoxide des bodens durch extraction mit ammoniumoxalat-losung, Z. Pflanz. Boden. 105 (1964) 194–202, https://doi.org/10.1002/jpln.3591050303.
[28] A.K. Darke, M.R. Walbridge, B.G. Lockaby, Changes in Al and Fe crystallinity and P adsorption capacity in a floodplain forest soil subjected to artificially manipulated flooding regimes in field mesocosms, Wetl. Ecol. Manag. 4 (1997) 235–244, https://doi.org/10.1007/BF02150537.
[29] S.R. Olsen, C.V. Cole, F.S. Watanabe, L.A. Dean, Estimation of available phosphorus in soils by extraction with sodium bicarbonate, USDA circular 939, US Gov. Print. Office, Washington, DC, USA (1954).
[30] J. Murphy, J.P. Riley, A modified single solution method for determination of phosphate in natural waters, Anal. Chem. Acta 27 (1962) 31–36, https://doi.org/10.1016/S0003-2670(00)88444-5.
[31] E. Barberis, F. Ajmone-Marsan, E. Arduino, Determination of phosphate in solution at different ionic composition using malachite green, Commun. Soil Sci. Plant Anal. 29 (9–10) (1998) 1167–1175, https://doi.org/10.1080/00103629809370017.
[32] OECD, Linkages between agricultural policies and environmental effects. Using the OECD Stylised Agri-Environmental Policy Impact Model, OECD Publishing, London, 2010, p. 176p.
[33] M. Rodgers, M. O'Connor, M.G. Healy, C. O'Driscoll, Z.Z. Asam, M. Nieminen, R. Poole, M. Müller, L. Xiao, Phosphorus release from forest harvesting on an upland blanket peat catchment, For. Ecol. Manag. 260 (2010) 2241–2248, https://doi.org/10.1111/10.1007/s10342-014-0815-5.
[34] J. Ma, Y. Ma, R. Wei, Y. Chen, L. Weng, X. Ouyang, Y. Li, Phosphorus transport in different soil types and the contribution of control factors to phosphorus retardation, Chemosphere 276 (2021) 130012, https://doi.org/10.1016/j.chemosphere.2021.130012.
[35] Y. Li, S. Yu, J. Strong, H. Wang, Are the biogeochemical cycles of carbon, nitrogen, sulfur, and phosphorus driven by the "FeIII/FeII redox wheel" in dynamic redox environments? J. Soils Sediments 12 (2012) 683–693, https://doi.org/10.1007/s11368-012-0507-z.
[36] T. Rupngam, A.J. Messiga, A. Karam, Solubility of soil phosphorus in extended waterlogged conditions: an incubation study, Heliyon 9 (2023) e13502, https://doi.org/10.1016/j.heliyon.2023.e13502.
[37] T.K. Udeigwe, P.N. Eze, J.M. Teboh, M.H. Stietiya, Application, chemistry, and environmental implications of contaminant-immobilization amendments on agricultural soil and water quality, Environ. Int. 37 (2011) 258–267, https://doi.org/10.1016/j.envint.2010.08.008.
[38] V. Weerasinghe, I. Amarakoon, D. Kumaragamage, N.J. Casson, S. Indraratne, D. Goltz, X. Gao, Release of phosphorus and metal(loid)s from manured soils to floodwater during a laboratory simulation of snowmelt flooding, J. Environ. Qual. 53 (2024) 470–481, https://doi.org/10.1002/jeq2.20564.
[39] L. Lilienfein, R.G. Qualls, S.M. Uselman, S.D. Bridgham, Adsorption of dissolved organic and inorganic phosphorus in soils of a weathering chronosequence, Soil Sci. Soc. Am. J. 68 (2004) 620–628, https://doi.org/10.2136/sssaj2004.6200.
[40] M. Velázquez, M.C. Del Campillo, J. Torrent, Temporary flooding increases iron phytoavailability in calcareous Vertisols and Inceptisols, Plant Soil 266 (2005) 195–203, https://doi.org/10.1007/s11104-005-1095-0.
[41] A.K. Darke, M.R. Walbridge, Al and Fe biogeochemistry in a floodplain forest: implications for P retention, Biogeochemistry 51 (2000) 1–32, https://doi.org/10.1023/A:1006302600347.
[42] M. Hosomi, M. Okada, R. Sudo, Release of phosphorus from lake sediments, Environ. Int. 7 (1982) 93–98, https://doi.org/10.1016/0160-4120(82)90078-2.
[43] H. Shahandeh, L. Hossner, F. Turner, A comparison of extraction methods for evaluating Fe and P in flooded rice soils, Plant Soil 165 (1994) 219–225, https://doi.org/10.1007/BF00008065.
[44] V.D. Quang, J.E. Dufey, Effect of temperature and flooding duration on phosphate sorption in an acid sulphate soil from Vietnam, Eur. J. Soil Sci. 46 (1995) 641–647, https://doi.org/10.1111/j.1365-2389.1995.tb01360.x.
[45] M. Hosseini, S.R. Agereh, Y. Khaledian, H.J. Zoghalchali, E.C. Brevik, S.A.R. Movahedi Naeini, Comparison of multiple statistical techniques to predict soil phosphorus, Appl. Soil Ecol. 114 (2017) 123–131, https://doi.org/10.1016/j.apsoil.2017.02.011.
[46] R. Uusitalo, E. Aura, A rainfall simulation study on the relationships between soil test P versus dissolved and potentially bioavailable particulate phosphorus forms in runoff, Agric. Food Sci. 14 (2005) 335–345, https://doi.org/10.2137/145960605775897713.
[47] A. Muntwyler, P. Panagos, S. Pfister, E. Lugato, Assessing the phosphorus cycle in European agricultural soil: looking beyond current national P budgets, Sci. Total Environ. 906 (2024) 167143, https://doi.org/10.1016/j.scitotenv.2023.167143.
[48] W.J. Parton, M.D. Hartman, D.S. Ojima, D.S. Schimel, DAYCENT: its land surface submodel: description and testing, Global Planet. Change 19 (1998) 35–48, https://doi.org/10.1016/S0921-8181(98)00040-X.
[49] G.K.G. Cunha, K.P.V. Cunha, F. Araújo, R. Angelini, Urbanization increases the risk of phosphorus loss in sandy soils of tropical ecosystems, Chemosphere 349 (2024) 140937, https://doi.org/10.1016/j.chemosphere.2023.140937.
[50] K.E. Schilling, P.J. Jacobson, C.F. Wolter, Using riparian zone scaling to optimize buffer placement and effectiveness, Landsc. Ecol. 33 (2018) 141–156, https://doi.org/10.1007/s10980-017-0589-5.
[51] J. Wu, C.-X. Qin, Y. Yue, S.-P. Cheng, H. Zeng, L.-Y. He, Comprehensive effects of climate, land use/cover, and management practices on runoff and nutrient variations in a rapidly urbanizing watershed, Chemosphere 349 (2024) 140934, https://doi.org/10.1016/j.chemosphere.2023.140934.
[52] C. Gu, S. Joshi, M.H.H. Fischel, E.J. Tomaszewski, P. Northrup, D.L. Sparks, Saltwater intrusion increases phosphorus abundance and alters availability in coastal soils with implications for future sea level rise, Sci. Total Environ. 931 (2024) 172624, https://doi.org/10.1016/j.scitotenv.2024.172624.
[53] A.R.H. Wiegman, G.H. Myers, I.C. Augustin, M.L. Kubow, M.J. Fein-Cole, V.L. Perillo, D.S. Ross, R.M. Diehl, K.L. Underwood, W.B. Bowden, E.D. Roy, Potential for soil legacy phosphorus release from restored riparian wetlands within an agricultural landscape, Biogeochemistry 161 (2022) 137–156, https://doi.org/10.1007/s10533-022-00972-2.