



Earthworms affect reactive surface area and thereby phosphate solubility in iron-(hydr)oxide dominated soils

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ABSTRACT

Sustainability of agricultural systems is at stake, as phosphorus (P) is a non-renewable resource while its global reserves are limited. Stimulating earthworm activity can be a technology to increase the level of readily plant-available phosphate (PO₄). However, conclusive evidence on the mechanisms underlying an earthworm-enhanced PO₄ solubility is yet missing. This study aimed to reveal possibly overlooked pathways by which earthworms affect PO₄ solubility, and quantify the relative importance of all contributing mechanisms. Therefore, we set up a greenhouse pot experiment in which we investigated the large increase in water-extractable PO₄ in casts of three earthworm species (*Lumbricus rubellus*, *Aporrectodea caliginosa*, *Lumbricus terrestris*) in soils with either predominantly Fe- or Al-(hydr)oxides. Oxalate-extractable PO₄ was increased in earthworm casts compared to bulk soil which can be attributed to the mineralisation of natural organic matter (NOM). Surface complexation modelling was used to elucidate the mechanisms that control earthworm-enhanced PO₄ solubility. The results of our modelling showed that the increase in pH in earthworm casts relative to bulk soil affects PO₄ solubility only to a minor extent. Besides NOM mineralisation, two major mechanisms contributing to earthworm-enhanced PO₄ solubility are (i) a decrease in the reactive surface area (RSA) of the metal-(hydr)oxide fraction; and (ii) a decrease in the competition between NOM and PO₄ for binding sites of the metal-(hydr)oxides. As the newly discovered decrease of the RSA was only found for Fe-(hydr)oxide-dominated soils, earthworms have the largest potential to enhance PO₄ solubility in those soils.

1. Introduction

Phosphorus (P) is an important element in the environment. It is often the limiting factor for plant growth (Hinsinger, 2001), and therefore P fertilisers are widely used in agriculture. However, phosphate rock, the prime source of mineral P fertiliser, is non-renewable, and its long-term availability is increasingly at stake (Cordell et al., 2009; Sharpley et al., 2018). Furthermore, the distribution of phosphate rock reserves is limited mostly to a few countries, which might lead to geopolitical tensions in the future (Cordell and White, 2015; United States Geological Survey, 2021). On the other hand, P fertilisation

beyond plant needs imposes large risks to the environment (Carpenter et al., 1998; Shepherd et al., 2016). To decrease the use of P fertilisers, many ways of improving the utilisation of soil P are currently explored (Rowe et al., 2016; Stutter et al., 2012). One of these techniques considers the effect of stimulating earthworm activity, which can temporally and locally increase the level of readily plant-available phosphate (PO₄) in soil (Le Bayon and Milleret, 2009), and thereby improve the P uptake of grass and enhance its biomass production (Mackay et al., 1982; Ros et al., 2017; Vos et al., 2014). While this may increase the sustainability of agricultural systems by decreasing the use of P fertilisers, earthworm-enhanced solubility of PO₄ may negatively affect

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agricultural sustainability as well, as it can be responsible for increased P losses by particulate and dissolved P forms in water runoff (Le Bayon et al., 2002; Sharpley and Syers, 1976).

The effect of earthworms on the solubility of soil P is large. In earthworm casts, the readily-available PO₄ concentration can be several hundred times higher than in the surrounding bulk soil (Van Groenigen et al., 2019). The extent to which PO₄ solubility is enhanced varies strongly among earthworm species but is not distinctly related to their ecological classification (Vos et al., 2019). Various mechanisms for the increase of soil P by earthworms have been proposed as discussed in detail in previous studies (Le Bayon and Milleret, 2009; Ros et al., 2017; Vos et al., 2019; Vos et al., 2014). Summarised, the proposed mechanisms are: (a) desorption of PO₄ from mineral surfaces due to an increase of pH in earthworm casts; (b) release of PO₄ due to competitive binding of natural organic matter (NOM) from the earthworm gut to reactive sites of metal-(hydr)oxides; (c) release of additional PO₄ due to stimulated mineralisation of NOM through enhanced microbial activity in the earthworm gut; and (d) selective feeding by earthworms on soil particles with a higher P content. However, there is little conclusive evidence yet on the relative importance of each of these pathways.

To understand and quantify the solubility of PO₄ as a function of soil properties, surface complexation modelling (SCM) can be used. Following this approach, Ros et al. (2017) proposed increased NOM binding to Fe- and Al-(hydr)oxide particles as a major mechanism explaining the increase in water-extractable PO₄ in earthworm casts. However, those authors noted that the NOM surface loadings required to explain the observed PO₄ concentrations in casts were very high compared to the typical NOM loading of Dutch agricultural soils (Hiemstra et al., 2010b; Hiemstra et al., 2013). Another reason to question these results is the use of goethite as a proxy for the natural metal-(hydr)oxide fraction in the model approach, while ferrihydrite (Fh) particles may be responsible for most of the reactivity towards PO₄ (Mendez et al., 2020; Mendez et al., 2022).

Furthermore, due to the lack of precise chemical characterisation of casts, additional pathways of earthworm-enhanced PO₄ solubility may have been overlooked to date. Such an unconsidered pathway could be a change in the reactive surface area (RSA) of soil metal-(hydr)oxide particles during passage through the earthworm gut, as a decrease of the RSA results in less binding capacity for PO₄ at the metal-(hydr)oxide

surface and a subsequent release of PO₄. Such a change in the RSA can be assessed with the probe-ion method (Hiemstra et al., 2010a; Koopmans et al., 2020), and could be caused by the chemical conditions inside the earthworm gut as a consequence of intense microbial processes. In the earthworm gut, NOM is rapidly decomposed resulting in the production of soluble organic molecules as a by-product of mineralisation (Kalbitz et al., 2000), as well as in the consumption of oxygen and other electron acceptors. These microbially-induced processes stimulate anoxic conditions (Drake and Horn, 2007), which may affect the RSA of the metal-(hydr)oxide fraction, particularly if this fraction is dominated by redox-sensitive Fe (Zhou et al., 2019).

The aim of the present study was firstly to reveal if a change in the RSA of metal-(hydr)oxides could be an overlooked pathway by which earthworms affect PO₄ solubility, and secondly, to quantify the relative importance of all contributing mechanisms that have been mentioned above. We used four soils with contrasting contents of Fe- and Al-(hydr)oxides and for the bulk soils and casts the RSA was derived with the probe-ion method. The Fe-(hydr)oxide speciation was determined both structurally and chemically. For all soils, various types of earthworm species and earthworm-free controls with and without mineral P fertilisation were tested to induce variation in the intensity of NOM decomposition and soil chemical properties. This allowed us to unravel and quantify the various processes contributing to earthworm-enhanced PO₄ solubilisation in soils.

2. Materials and methods

2.1. Greenhouse experiment

A greenhouse pot experiment was used to generate earthworm casts and bulk soil samples. The experiment was set up as a full factorial randomized block design with soil type (four soils) and earthworm species (five treatments) as independent factors. Each treatment was replicated four times. To elucidate the role of the type of metal-(hydr)oxides, the selected soils consisted of two soils where Fe-(hydr)oxides are more abundant than Al-(hydr)oxides, and two soils with predominantly Al-(hydr)oxides. These soils were topsoils (0–25 cm) from the Netherlands with different physico-chemical properties (Table 1; analytical procedures are described in appendix A.1). The earthworm

Table 1
Physico-chemical characteristics of the four soils used in this study.

	S1	S2	S3	S4
Coordinates [lat, long]	52°31'32.8"N 5°32'22.5"E	52°12'57.8"N 6°13'26.4"E	51°59'32.7"N 5°34'58.4"E	51°59'28.5"N 5°35'04.4"E
Land use	Intensively managed crops	Extensively managed pasture	Extensively managed pasture	Intensively managed pasture
Sand [%]	32.0	67.3	89.0	88.9
Silt [%]	33.0	14.5	6.1	4.2
Clay [%]	20.3	13.1	1.6	2.2
CaCO ₃ [%]	7.4	–	–	–
NOM [g kg ⁻¹]	46	47	41	40
pH-CaCl ₂ [-]	7.5	4.9	6.0	5.8
P-AL [mmol kg ⁻¹]	4.7	0.1	3.4	8.4
PO ₄ -ox [mmol kg ⁻¹]	11.1	3.1	4.9	13.0
P _{ox} [mmol kg ⁻¹]	11.9	5.7	8.8	18.7
Fe _{ox} [mmol kg ⁻¹] ^a	68.1 (82 %)	125.8 (87 %)	11.3 (16 %)	12.5 (18 %)
Al _{ox} [mmol kg ⁻¹] ^a	15.3 (18 %)	18.6 (13 %)	60.6 (84 %)	58.7 (82 %)
α [mol/mol] ^b	0.14	0.04	0.12	0.26
Fe-DCB [mmol kg ⁻¹]	140.6	797.3	13.3	15.6
Fe _{ox} /Fe-DCB [%] ^c	48	16	85	80
Non-crystalline Fe-(hydr)oxides [%] ^d	100	16	82	75
Crystalline Fe-(hydr)oxides [%] ^d	0	84	18	25

^a The percentage between parentheses gives the relative amount of Fe and Al present in the oxalate pool, showing that this pool is dominated by Fe-(hydr)oxides in soils S1 and S2, and by Al-(hydr)oxides in soils S3 and S4.

^b The P loading of reactive metal-(hydr)oxides was calculated as $\alpha = P_{ox}/(Fe_{ox} + Al_{ox})$ with all oxalate-extractable elements in mol kg⁻¹.

^c This molar ratio represents the fraction of non-crystalline Fe-(hydr)oxides according to chemical extractions.

^d Calculated by scaling the Fe of the non-crystalline (Fh) and crystalline (goethite, lepidocrocite, and hematite) Fe-(hydr)oxides on the total pool of Fe-(hydr)oxides derived by XAS.

treatments included *Lumbricus rubellus* Hoffmeister, 1843 (Lr; feeds on surface litter), *Aporrectodea caliginosa* (Savigny, 1826) (Ac; feeds on roots, soil, and soil-associated NOM), *Lumbricus terrestris* Linnaeus, 1758 (Lt; ingests some soil, but mainly feeds on surface litter) (Bouché, 1977; Drake and Horn, 2007), a control without earthworms (PO), and a control without earthworms but with additional mineral P fertilisation (P+; 100 kg P ha⁻¹ = 1.4 mmol kg⁻¹ soil). All pots (diameter: 20 cm; height: 23 cm) were filled with 7 kg of soil and sown with perennial ryegrass (*Lolium perenne*). After a pre-growing period of 35 days, the earthworms were added after which the experiment lasted for 33 days. During the experiment, soil moisture was kept gravimetrically at 60 % of the water holding capacity of each soil by adding water through a watering tube placed in the centre of each pot. Further experimental details are described in appendix A.2.

2.2. Chemical analyses

Earthworm casts and bulk soil of the two control treatments without earthworms (PO and P+) were collected as described in appendix A.3. The moisture content of both matrices was determined by drying subsamples at 40 °C for 24 h. The dried material was extracted with 0.2 M acid ammonium oxalate to determine the amounts of total P, PO₄ (P_{ox}, PO₄-ox), and non-crystalline Fe- and Al-(hydr)oxides (Fe_{ox}, Al_{ox}) (Schwertmann, 1964). Concentrations of P, Fe, and Al were measured with inductively coupled plasma-atomic emission spectroscopy (ICP-AES). A subsample of the filtrate was diluted ten times with 0.01 M HCl to eliminate the interference of oxalate during PO₄ measurement (Hass et al., 2011) by segmented flow analysis (SFA) using the molybdenum blue method (Murphy and Riley, 1962). As the amount of cast was insufficient, the total (non-crystalline and crystalline) amount of Fe-(hydr)oxides was solely determined for the PO bulk soils using a dithionite-citrate-bicarbonate extraction (DCB) (Holmgren, 1967; Mehra and Jackson, 1960). Structural characterisation of Fe in the PO bulk soils and some cast samples was obtained by Fe K-edge X-ray absorption spectroscopy (XAS) (using reference spectra for Fh, goethite, lepidocrocite, hematite, and Fe in clay minerals; appendix C).

A modified P-Olsen method (Olsen et al., 1954) was used in the probe-ion approach (Hiemstra et al., 2010a; Koopmans et al., 2020) to calculate the RSA of casts and bulk soils in combination with SCM. For the extraction of 0.2 g dried material with 0.5 M NaHCO₃ (pH = 8.5) at a solution-to-solid ratio (SSR) of 50 L kg⁻¹, 0.2 g washed powdered activated carbon was added in excess to facilitate NOM removal. Suspensions were shaken for 257 h (~10 days) at 20 strokes minute⁻¹ in an end-over-end shaker at 20 °C. After centrifuging for 10 min at 3000 rotations minute⁻¹, the suspensions were filtered over a 0.45 µm-filter, acidified with 0.3 M HCl to pH = 2.0, and put in an ultrasonic bath to remove the released CO₂. Subsequently, PO₄ was measured by SFA.

Since soil drying and rewetting increases P and dissolved organic carbon (DOC) release in water and weak salt extracts (Koopmans et al., 2006; Koopmans and Groenenberg, 2011), moist material was used for the extraction of casts and bulk soils with water as a proxy for the soil solution. Water extracts were prepared by adding ultra-pure water to moist material at a SSR of 10 L kg⁻¹ after correcting for the initial moisture content. The suspensions were shaken horizontally for 24 h with 75 strokes minute⁻¹ at 20 °C, centrifuged for 10 min at 3750 rotations minute⁻¹, and the supernatants were filtered through a 0.45 µm-filter. The pH and electrical conductivity (EC) of the filtrates were measured, after which EC was converted to ionic strength (*I*) (Griffin and Jurinak, 1973). Aliquots of the filtrate were taken to measure (i) PO₄, NH₄, NO₃, total dissolved N (TDN), total dissolved C (TDC), and dissolved inorganic C (DIC) by SFA; (ii) total dissolved P (TDP) with inductively coupled plasma-mass spectrometry; (iii) Ca, Mg, Na, K, and S by ICP-AES. Dissolved organic N (DON) was calculated from the difference between TDN and mineral N forms (NH₄ and NO₃), DOC from the difference between TDC and DIC, and dissolved organic P (DOP) from the difference between TDP and PO₄.

2.3. Surface complexation modelling

2.3.1. Reactive surface area

To describe the adsorption of cations and anions on metal-(hydr)oxide surfaces, we used SCM based on a combination of the charge distribution model (Hiemstra and Van Riemsdijk, 1996) and the multi-site ion complexation model (Hiemstra et al., 1996) (together further referred to as CD model). The probe-ion method (Hiemstra et al., 2010a; Koopmans et al., 2020) was used to calculate the RSA (m² kg⁻¹ cast or soil) of casts and bulk soils, by interpreting the measured equilibrium PO₄ concentration in the NaHCO₃ extracts in the absence of NOM with the CD model. During equilibration in NaHCO₃, the total amount of reversible adsorbed PO₄ (R_{ev} in mol kg⁻¹) will be distributed over the solid and solution phase:

$$R_{ev} = RSA \times \Gamma + SSR \times C. \quad (1)$$

where R_{ev} is represented by PO₄-ox, Γ (mol m⁻²) the PO₄ loading of the reference oxide, SSR the solution-to-solid ratio employed during NaHCO₃ extraction (50 L kg⁻¹), and C the measured equilibrium PO₄ concentration in the NaHCO₃ extracts (M). The probe-ion method results in a RSA representing all soil surfaces that contribute to PO₄ binding. While those surfaces can consist of both metal-(hydr)oxides and oxidic clay minerals (Gérard, 2016; Mendez et al., 2020), only metal-(hydr)oxides were included in our SCM as clay minerals did not significantly contribute to the RSA of a wide range of Dutch topsoils (Mendez et al., 2020). The reference oxide for each matrix was either goethite (as proxy for crystalline Fe-(hydr)oxides) and/or Fh (as proxy for non-crystalline Fe-(hydr)oxides), as for both oxides a consistent set of CD model parameters is available (appendix B) (Hiemstra et al., 2010a; Hiemstra and Zhao, 2016; Mendez and Hiemstra, 2019; Mendez et al., 2020). The choice for the reference oxide for each soil was based on the solid Fe speciation given by XAS analyses (appendix C).

Subsequently, the RSA resulting from Eq. 1 can be scaled on the pool of metal-(hydr)oxides into the specific surface area (SSA in m² g⁻¹) and the corresponding mean spherical oxide particle size (*d* in nm). This calculation, which requires particle size-dependent values of the molar mass and mass density of the Fe- and Al-(hydr)oxides, was based on the set of equations and parameter values given by Hiemstra (2018) and Mendez et al. (2020) (appendix D).

2.3.2. Natural organic matter loading

As NOM can compete with PO₄ for reactive surface sites, the NOM loading of metal-(hydr)oxides may affect the PO₄ concentration in solution (Hiemstra et al., 2010b). Therefore, this NOM loading was calculated for casts and bulk soils based on the obtained RSA (section 2.3.1), PO₄-ox, and the conditions in the water extracts.

Firstly, the free ion concentrations of NH₄, NO₃, Na, K, Ca, Mg, and (H)CO₃ were calculated from their measured concentrations in the water extracts, pH, and *I* using ECOSAT which includes the NICA-Donnan model. Ion complexation with inorganic ligands and dissolved organic matter (DOM) was included in our model calculations and competition between protons and cations for binding to DOM was considered (Hiemstra et al., 2013; Weng et al., 2012). For the modelling, half of the DOM concentration was interpreted as generic fulvic acid (FA) (Ros et al., 2010) and the DOM concentrations were calculated from the measured DOC concentrations assuming a C content of 50 %. Generic NICA-Donnan model parameters were used for proton and cation binding to FA (Milne et al., 2001; Milne et al., 2003).

Secondly, the RSA and the reference oxides used for its calculation, in combination with the calculated free ion concentrations and the pH and *I* of the water extracts, as well as the measured PO₄-ox of the casts and bulk soil samples were used as input for the CD model to derive the NOM loading of each sample. In our model approach, three Fe-NOM surface species were defined (Hiemstra et al., 2013) (appendix B). The NOM loading (µmol m⁻²); the total of all three included Fe-NOM surface

species) was derived as a fitting parameter while the PO_4 concentration was fixed at the measured value using ECOSAT in combination with the program FIT (version 2.581) (Kinniburgh and Tang, 2004).

Statistical analyses were performed in R, version 4.0.2, and are described in appendix E.

3. Results and discussion

3.1. Soil properties and earthworm survival

The NOM content was 40–47 g kg^{-1} for all four soils, but the soils varied largely in their pH (4.9–7.5) and $\text{PO}_4\text{-ox}$ content (3.1–13.0 mmol kg^{-1} ; Table 1). The latter was 54–93 % of P_{ox} , which is comparable to other Dutch topsoils (Mendez et al., 2020), and showed that the risk of eutrophication can be overestimated when P_{ox} instead of $\text{PO}_4\text{-ox}$ is used for the calculation of the degree of P saturation of soils (Koopmans et al., 2004; Van der Zee and Van Riemsdijk, 1988). In soils S1 and S2, the metal-(hydr)oxide fraction consisted predominantly of Fe-(hydr)oxides, whereas this fraction was Al-(hydr)oxide-dominated in soils S3 and S4 (Table 1). The latter two soils had been part of a long-term (>30 years) P fertilisation trial on grassland and differed in the amount of P fertiliser they had received, resulting in differences in their P-status.

Earthworm survival during the greenhouse experiment was on average 77 % but varied between earthworm species (Ac showed a survival of 63 % while this was 87 % and 83 % for Lr and Lt). Since Ac produced smaller amounts of cast than the other species, all four replicates had to be pooled to obtain sufficient material for chemical analysis, but even then not all analyses could be performed.

3.2. Controlling mechanisms of earthworm-enhanced PO_4 solubility

3.2.1. Mineralisation and pH

For earthworm casts, PO_4 concentrations in the different soil extracts (oxalate, NaHCO_3 , water) were elevated relative to the P0 bulk soil (Fig. 1 and Table F.2). This could (partly) be caused by selective feeding of the earthworms, as NOM particles enriched with small embedded oxide particles will have a relatively larger P content than the average NOM particle (Ros et al., 2017; Vos et al., 2019). Furthermore, additional PO_4 entering the system through NOM mineralisation by earthworms could result in the observed increased amount of $\text{PO}_4\text{-ox}$ in casts. Enhanced mineralisation by earthworms is indicated by the elevated water-extractable DOC concentrations of the casts (Table F.1). This agrees with literature (Bolan and Baskaran, 1996; Ros et al., 2017; Van Groenigen et al., 2019; Vos et al., 2019) and can be caused by the excretion of DOC-rich substances by the earthworms (e.g. mucus) (Lopez-Hernandez et al., 1993) or stimulated mineralisation inside the earthworm gut (Brown et al., 2000; Satchell and Martin, 1984; Wolters, 2000), resulting in the production of soluble organic molecules as a by-product of mineralisation (Kalbitz et al., 2000). Enhanced mineralisation is evidenced by the increased DON, S, and DOP concentrations in the water extracts of the casts (Table F.1). The increase of these NOM constituents shows a good correlation with the increase of DOC (appendix G). Additionally, there is a general increase in cation and anion concentrations and I of the water extracts of the casts (Table F.1), which is likely related to enhanced mineralisation inside the earthworm gut. Concentrations of elements that are not directly released by NOM mineralisation can still be increased, as mineralisation can lead to elevated NH_4 concentrations (Decaëns et al., 1999), which can subsequently be exchanged for other cations like Na or K at the soil cation exchange complex (Ros et al., 2017).

Focusing on the differences in the casts of the various earthworm species, the concentrations of DOC and the other mentioned components of the water extracts are generally higher for Lr than Lt. For Ac, our dataset is incomplete, but based on the DOC concentrations observed for this species in previous studies (Vos et al., 2019; Vos et al., 2014), the expected contribution of Ac to mineralisation is lower than for Lt. The

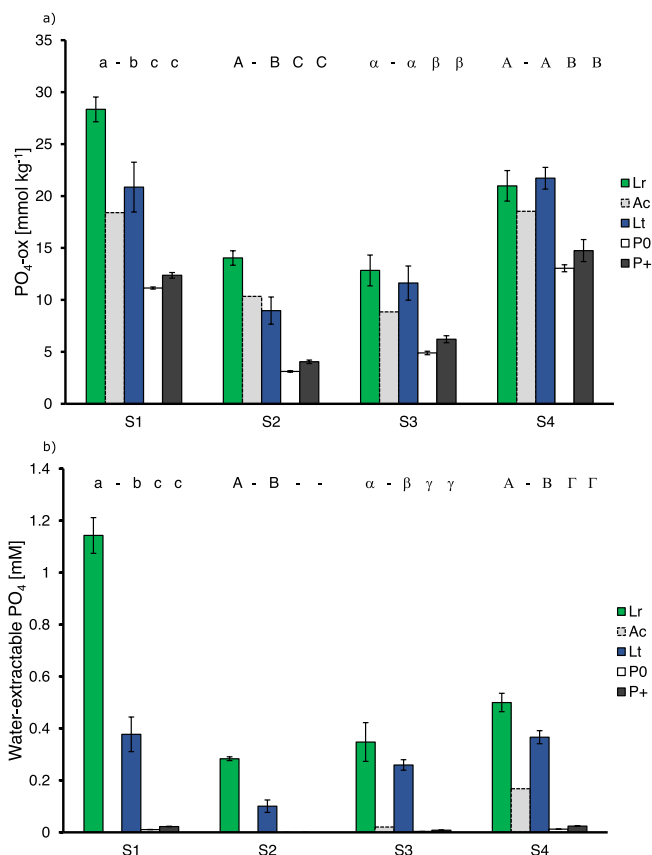


Fig. 1. Oxalate-extractable PO_4 (a; $\text{PO}_4\text{-ox}$) and water-extractable PO_4 (b) of the four soils and earthworm casts. The water-extractable PO_4 concentrations of soil S2 (P0 and P+) were below the detection limit of the SFA. Due to limited cast production by Ac, water-extractable PO_4 could not be determined for soils S1 and S2, and only without replicates for soils S3 and S4. Hence, Ac was excluded from statistical analysis and, when available, its value is presented with a dotted bar. Error bars denote standard deviations. The significance of differences was determined for each soil separately.

suggested order of intensity of mineralisation is, therefore, $\text{Lr} > \text{Lt} > \text{Ac}$. This agrees with measurements on N mineralisation in the casts of these species (Postma-Blaauw et al., 2006), and matches the expected mineralisation potential based on the NOM quality in the food these earthworms ingest (section 2.1).

The production of CO_2 by mineralisation inside the earthworm gut results in the enhancement of $p\text{CO}_2$, and the associated release of protons. However, often these protons are buffered by the production of alkalinity (HCO_3^-) during NOM mineralisation (Ros et al., 2017). This production of alkalinity can be the reason for the observed pH increase in earthworm casts for three of our soils (S2, S3, S4; Table F.1), although other causes, like the earthworms' calciferous glands (Briones et al., 2008) and the presence of anoxic conditions in the earthworm gut leading to proton consumption (Kögel-Knabner et al., 2010; Pan et al., 2014), are also possible. This pH increase in casts is widely recognised in literature (Basker et al., 1994; Jiménez et al., 2003; Kuczak et al., 2006; Sharpley and Syers, 1976; Van Groenigen et al., 2019; Vos et al., 2019) and may result in larger PO_4 desorption from mineral surfaces. However, in soil S1, we observed a decrease in the pH of casts. For this calcareous soil with a high pH an additional mechanism for the consumption of the produced alkalinity is present, as HCO_3^- release may lead to precipitation of Ca and neutralisation of the produced alkalinity according to $\text{HCO}_3^- + \text{Ca} \leftrightarrow \text{CaCO}_3(\text{s}) + \text{H}^+$. Because of the pH decrease in soil S1, the final pH in the casts from all soils was rather similar ($\text{pH} \approx 7.5$). Hence, earthworms seem to create a more or less constant pH in their casts, regardless of the pH of the surrounding bulk soil.

3.2.2. Reactive surface area

The increase of $\text{PO}_4\text{-ox}$ because of the additional PO_4 added by mineralisation will affect the water-soluble PO_4 concentration, but a quantitative interpretation requires modelling for which the RSAs of casts and bulk soils are pivotal. The reference oxides required to determine the RSAs were given by XAS, which showed that the solid Fe speciation of the casts was identical to that of the corresponding bulk soils. The Fe-(hydr)oxides of soil S1 consisted solely of Fh, while in the other soils, also crystalline Fe-(hydr)oxides (i.e. goethite, lepidocrocite, and hematite) were present (Table C.1). For all soils but soil S1, the fraction of non-crystalline Fe-(hydr)oxides according to XAS was in close agreement with the amount found by chemical extraction using oxalate and DCB (Table 1). For soil S1, however, the ratio $\text{Fe}_{\text{ox}}/\text{Fe-DCB}$ is much lower than seen by XAS. This may be due to the limited sensitivity of XAS for identifying different types of Fe-(hydr)oxides in samples in which most Fe is associated with clays, as is the case for soil S1 (only 22 % of total Fe is present in the form of (hydr)oxides; Table C.1). Another explanation might be the incomplete dissolution of non-crystalline Fe-(hydr)oxides after the two-hour oxalate extraction of soil S1 (Schwertmann et al., 1982). In our SCM, the relative occurrence of non-crystalline and crystalline Fe-(hydr)oxides measured with XAS will be used and brought to the absolute scale using the total amount of Fe-(hydr)oxides measured with DCB. Since for extraction with DCB no sufficient cast material was available, the total amount of Fe-(hydr)oxides in the casts was taken to be the same as in the corresponding bulk soils. The minor differences (2 ± 5 %) between Fe_{ox} of the casts and corresponding P0 soils support this assumption (Table F.2).

In soils S3 and S4, the Fe-(hydr)oxides are predominantly non-crystalline, while the total metal-(hydr)oxide fraction consists largely of non-crystalline Al-(hydr)oxides (Table 1). Therefore, the small fraction of crystalline Fe-(hydr)oxides compared to the total pool of metal-(hydr)oxides was ignored in our further calculations. Presently, no specific proxy with a consistent set of parameters for the CD model is available for natural Al-(hydr)oxides, but according to recent work with Al-(hydr)oxide-dominated weathered tropical soils, Fh was an adequate proxy in the CD modelling (Mendez et al., 2022). Therefore, Fh was chosen as reference oxide for soils S3 and S4. Fh was used as well for soil S1, but for soil S2 a mixture of goethite and Fh was used in the ratio measured by XAS (84 % and 16 % respectively; Table 1).

The RSA of our soils can be assessed with the PO_4 probe-ion method (Hiemstra et al., 2010a; Koopmans et al., 2020) using either Fh or a mixture of Fh and goethite as a proxy. For soils S1, S3, and S4, the procedure is relatively straightforward as only one proxy (i.e. Fh) is used in the interpretation of the data from the NaHCO_3 extracts, as described by Eq. 1 (section 2.3.1). Subsequently, these RSAs can be scaled on the pool of metal-(hydr)oxides into the SSA to derive the corresponding mean spherical size of the oxide particles according to the set of equations provided in section D.1. This scaling requires the amount of non-crystalline oxides in each sample: $\text{Fe-DCB} \times \text{non-crystalline fraction XAS}$ (Fe-(hydr)oxides) and Al_{ox} (Al-(hydr)oxides) (Table 1).

For soil S2, the calculation of the RSA differs from the approach followed for soils S1, S3, and S4 because of the large contribution of crystalline Fe-(hydr)oxides to the total pool of metal-(hydr)oxides. The calculations were only possible if the SSA of one of the reference oxides was fixed at a chosen value (section D.2). Therefore, the SSA of the crystalline Fe-(hydr)oxide fraction (SSA_{crys}) was set to $\text{SSA}_{\text{crys}} = 40 \text{ m}^2 \text{ g}^{-1}$, which falls within the range of values reported for synthetic goethite samples ($\approx 20\text{--}110 \text{ m}^2 \text{ g}^{-1}$) (Hiemstra et al., 1989) and which results in realistic SSA values for the non-crystalline fraction ($\text{SSA}_{\text{ncrys}}$) that are consistent and comparable with the results for the other Fe-(hydr)oxide-dominated soil S1 (appendix H). Although uncertain, the precise value of our estimate of SSA_{crys} did not influence our main conclusions. Further scaling of the RSA of soil S2 on the pool of metal-(hydr)oxides into the total SSA of non-crystalline and crystalline metal-(hydr)oxides and the corresponding mean spherical oxide particle size, requires the amounts of non-crystalline and crystalline Fe-(hydr)oxides. Consistently

with the approach followed for non-crystalline Fe-(hydr)oxides, the amount of crystalline Fe-(hydr)oxides was estimated by $\text{Fe-DCB} \times \text{crystalline fraction XAS}$.

The effect of short-term P fertilisation on the RSA and particle size follows from comparing the P0 and P+ treatments of each soil in Fig. 2. This shows that the addition of P in our relatively short pot experiment did not lead to significant differences. The effect of long-term P fertilisation on the RSA and particle size can be assessed from a comparison of soils S3 and S4. These soils were taken from a long-term P fertilisation trial and have similar soil properties, but soil S4 received P fertiliser for >30 years, whereas soil S3 did not. This long-term P fertilisation has led to a suppression of particle growth in soil S4, therefore yielding a much larger RSA and smaller particle size for the different matrices, which agrees with previous observations (Borch et al., 2007; Makris et al., 2005; Schwertmann, 1991). In the Fe-(hydr)oxide-dominated soils S1 and S2, the RSA of the casts was lower than for the corresponding bulk soils, while the particle size of the casts was larger. We explain this based on the prevailing redox conditions of chemical reduction in the earthworm gut which are due to the intense process of mineralisation (Drake and Horn, 2007; Zhou et al., 2019), consuming oxygen and other electron acceptors. Such anoxic conditions can lead to the formation of small amounts of Fe^{2+} and Fe reduction has been shown to occur in the earthworm gut (Zhou et al., 2019). Subsequently, this Fe^{2+} can act as a catalyst for the aging process of Fe-(hydr)oxides as is observed in synthetic systems (Hansel et al., 2005; Jones et al., 2017; Pedersen et al., 2005), although this process can be inhibited by PO_4 associated with the

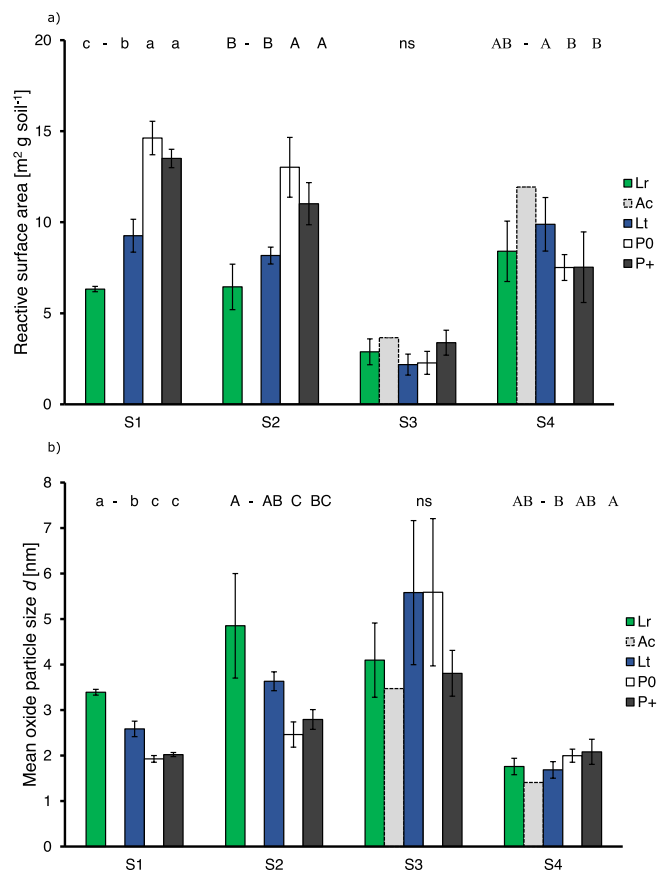


Fig. 2. Reactive surface area (a; RSA) and mean oxide particle size (b; d) of the four soils and earthworm casts. Due to limited cast production by Ac, the RSA and d could not be determined for soils S1 and S2, and only without replicates for soils S3 and S4. Hence, Ac was excluded from statistical analysis and, when available, its value is presented with a dotted bar. Error bars denote standard deviations. The significance of differences was determined for each soil separately.

Fe-(hydr)oxides (Kraal et al., 2022; Kraal et al., 2020). This Fe²⁺-catalysed aging process results in larger Fe-(hydr)oxide particles and thereby decreases the RSA of the casts. In contrast to Fe, Al is not redox-sensitive and Al-(hydr)oxides will therefore not be affected. Indeed, the RSA and particle size of the casts and bulk soils for the Al-(hydr)oxide-dominated soils either showed no significant differences (soil S3) or only relatively small and opposite differences to those in the Fe-(hydr)oxide-dominated soils between Lt and P+ (soil S4; Fig. 2). However, as Fh was used as a proxy for soils S3 and S4, while the metal-(hydr)oxide fraction of these soils was dominated by Al-(hydr)oxides, the specific differences for soil S4 should be considered with care as they can be the result of less accurate model parameters.

The decrease of the RSA in the casts from Fe-(hydr)oxide-dominated soils will lead to a higher PO₄ solubility in the water extracts as less RSA is available for PO₄ adsorption. Hence, a decrease of the RSA in combination with an increase in PO₄-ox due to additional PO₄ input by enhanced mineralisation both contribute to the strong increase in PO₄ solubility for soils S1 and S2. For the Al-(hydr)oxide-dominated soils S3 and S4, earthworm-enhanced PO₄ solubility is likely primarily due to enhanced mineralisation, as the RSA of casts did not decrease compared to bulk soils.

When the increase in particle size of the metal-(hydr)oxides is related to a low redox potential in the earthworm gut, differences in particle size between earthworm species may be expected as their intensity of mineralisation may differ. More intense mineralisation by Lr than by Lt (section 3.2.1) could result in more growth of Fe-(hydr)oxide particles, leading to a lower RSA and larger particle size for Lr than for Lt. This was indeed found in soils S1 and S2, although the difference was not significant for soil S2. For the Al-(hydr)oxide-dominated soils, no significant differences in RSA and particle size were observed between earthworm species.

3.2.3. Natural organic matter loading

Another proposed mechanism to explain the increase in the water-solubility of PO₄ in earthworm casts is a change in competitive adsorption between NOM and PO₄ (Le Bayon and Milleret, 2009; Lopez-Hernandez et al., 1993; Ros et al., 2017). This contribution has been evaluated here with the CD model, by deriving the NOM loading (i.e. the total of the adsorbed Fe-NOM surface species in $\mu\text{mol m}^{-2}$) of the metal-(hydr)oxide surfaces. Using solely PO₄-ox (as R_{ev}) and RSA as model input, measured PO₄ concentrations are often underpredicted by the model, which can be attributed to the absence of competitive binding between PO₄ and NOM in the model approach (Hiemstra et al., 2010b). This was the case for soils S1 and S2, and including NOM competition would increase the predicted PO₄ concentration. The data for PO₄-ox and RSA can be unified with the PO₄ concentration measured in the water extracts by fitting the required NOM loading.

The results are depicted in Fig. 3, which shows an inverse relationship between the fitted NOM loading and adsorbed PO₄. The bulk soils have a high NOM loading and a low PO₄ loading, but in the earthworm gut, PO₄ is released, which increases the PO₄ loading. In the Fe-(hydr)oxide-dominated soils S1 and S2, this PO₄ release is caused by mineralisation and a decrease of the RSA, and it varies per earthworm species matching the hypothesis of more intense mineralisation by Lr than Lt as Lr has a higher PO₄ loading than Lt. The consequence of the increased PO₄ loading is a decrease in the NOM loading and a decrease in the competitive effect of NOM adsorption on the PO₄ solubility of casts compared to the bulk soil. This finding is different from the suggestion made by Ros et al. (2017) who proposed an increase in the NOM loading of the metal-(hydr)oxides in casts. These authors did not measure the RSA of both bulk soil and casts and assumed there were no differences in the SSA of metal-(hydr)oxides between both matrices (Ros et al., 2017), which can explain this discrepancy. The NOM loadings required to explain the measured PO₄ concentrations in water extracts from casts in Ros et al. (2017) were very high (>2 $\mu\text{mol m}^{-2}$), considering that the NOM loading of Dutch agricultural soils is typically $1.6 \pm 0.3 \mu\text{mol m}^{-2}$

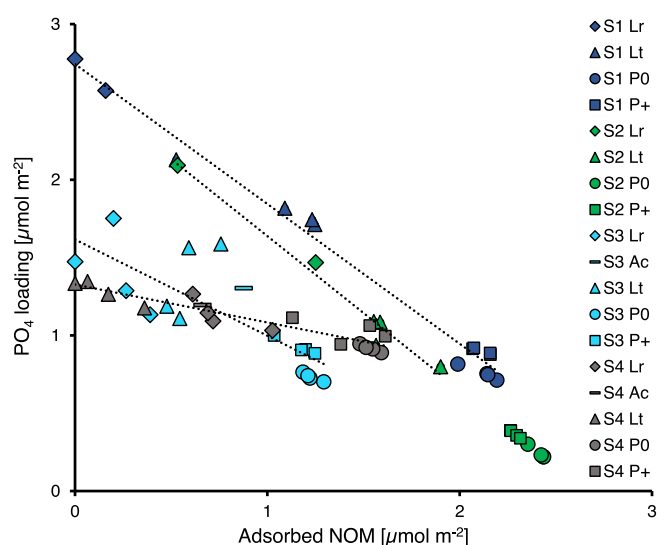


Fig. 3. Relationship between the NOM and PO₄ loading of metal-(hydr)oxides for the four soils and earthworm casts. For the bulk soil samples (P0 and P+) of soil S2, no NOM loading could be modelled as the water-soluble PO₄ concentration was below the detection limit of the SFA. The NOM loading of these samples has been calculated from the regression line between the NOM and PO₄ loading of the casts from this soil but should be interpreted with care as it is based on extrapolation. Colours refer to soils and symbols to treatments. Dotted lines are regression lines for each soil. The calculations for the Al-(hydr)oxide-dominated soils S3 and S4 were done using adapted values for the RSA (see text).

(Hiemstra et al., 2013). In our study, a more realistic NOM loading of $1.1 \pm 0.6 \mu\text{mol m}^{-2}$ for the casts of the Fe-(hydr)oxide-dominated soils was obtained.

For the Al-(hydr)oxide-dominated soils S3 and S4, we followed a different approach to fit the NOM loading, as for some cast samples the predicted PO₄ concentration in the absence of NOM competition in the CD modelling was already higher than the measured PO₄ concentration in the water extracts. This was likely due to the combination of a low to very low NOM loading of casts and, in part, an underestimation of the RSA by the probe-ion method. We did additional measurements to improve our RSA estimates, but those did not yield satisfying results (appendix I). In our alternative approach, we therefore increased the RSA in the CD modelling for one sample of soil S3 for which water-extractable PO₄ was most overpredicted until the fitted NOM loading became zero. Subsequently, this RSA was applied to all other samples of soil S3 as no differences in the RSA were observed between treatments (section 3.2.2). Fixing the RSA allowed us to fit the NOM loading of the other samples of soil S3. The same approach was followed for soil S4. Similar to the Fe-(hydr)oxide-dominated soils, the NOM loading of the Al-(hydr)oxide-dominated soils was lower for the casts than for the corresponding bulk soils (Fig. 3). This strengthens the validity of our conclusions on the importance of the release of PO₄ from mineralisation and the decrease in the RSA of the Fe-(hydr)oxide-dominated soils being the major mechanisms for enhancing PO₄ solubility in the cast, while the competitive effect of NOM adsorption on the PO₄ concentration in the water extracts decreases in casts compared to the bulk soil.

3.3. Scenario analysis

The contribution of the different controlling mechanisms of earthworm-enhanced PO₄ solubility in earthworm casts is illustrated in Fig. 4. Overall, the strong increase of pH in soils S2, S3, and S4 (a; Table F.1) has relatively little effect on the increase in PO₄ solubility. A major contribution is made by PO₄ addition to the system through stimulated mineralisation inside the earthworm gut, leading to an

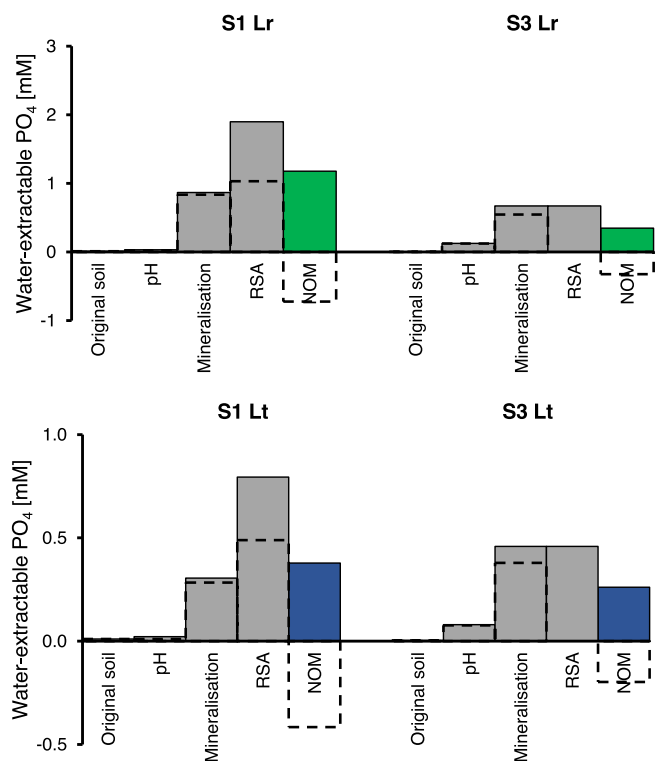


Fig. 4. Additive effects of the controlling mechanisms of earthworm-enhanced PO₄ solubility on water-extractable PO₄ for soils (columns: soil S1 (left) as representative of a Fe-(hydr)oxide-dominated soil and soil S3 (right) as representative of an Al-(hydr)oxide-dominated soil) and earthworm species (rows: the two species for which sufficient cast material was collected for replicates of the corresponding measurements, Lr and Lt). The controlling mechanisms indicated on the x-axis are: change in pH (pH), increased NOM mineralisation releasing additional PO₄ (Mineralisation), a decrease in RSA increasing water-soluble PO₄ as there is less surface area available for PO₄ adsorption (RSA), and a decrease in competition for adsorption sites between PO₄ and NOM (NOM) as the NOM loading becomes lower in earthworm casts. Starting point for each figure is the condition of the controlling mechanisms of earthworm-enhanced PO₄ solubility in the P0 soil (original soil). Subsequently, the CD model was used to predict the PO₄ concentration in the water extracts by changing consecutively the pH, PO₄-ox, and the RSA to the values measured in earthworm casts. Lastly, the fitted NOM content was included. This approach is shown by the different bars in each figure, in which every sequential grey scaled bar represents the additive effect of a controlling mechanism and the coloured bars match with the observed PO₄ concentration for the specific treatment (Fig. 1b). Dotted bars indicate the separate effect of a controlling mechanism, which is calculated as the additive effect of each successively mentioned mechanism minus the additive effect of the previously mentioned mechanism(s). Because of the possible effects of the interplay of the controlling mechanisms, the calculation of the separate effects might yield different values of the dotted bars.

increase of PO₄-ox (b; Fig. 1a). Both mechanisms were already acknowledged in the literature (Le Bayon and Milleret, 2009; Ros et al., 2017; Vos et al., 2019; Vos et al., 2014). A new finding in our work is the decrease in the RSA of casts (c). We observed this only for the Fe-(hydr)oxide-dominated soils, whereas this process is absent or minor in the Al-(hydr)oxide-dominated soils (Fig. 2a). Another new conclusion is related to the role of competitive binding between NOM and PO₄, as, in contrast to a previous suggestion (Ros et al., 2017), we observed a lower NOM loading in earthworm casts than in the bulk soil (d; Fig. 3). This decrease in interfacial NOM is a feedback process resulting from the increase in PO₄ loading induced by processes (a)–(c). Consequently, the competitive effect of NOM adsorption exerted on PO₄ solubility decreases in casts compared to their corresponding bulk soils.

All these controlling mechanisms of earthworm-enhanced PO₄

solubility are directly or indirectly related to the capacity of an earthworm to mineralise the organic material it ingests, which therefore governs the ability of the various earthworm species to enhance PO₄ solubility in soils. Although the magnitude of earthworm-enhanced PO₄ solubility, therefore, differs per earthworm species, the same controlling mechanisms are relevant for each soil.

The identification and understanding of the various mechanisms involved in earthworm-enhanced PO₄ solubility in our study show how nature can teach us how to decrease P fertiliser inputs while still increasing the level of readily plant-available soil P to support optimal plant growth. As the decrease of the RSA was only present in soils where the metal-(hydr)oxide fraction was dominated by Fe-(hydr)oxides, earthworms have the largest potential to enhance PO₄ solubility in those soils. This makes that especially Fe-(hydr)oxide-dominated soils are promising to study the effect of earthworms on enhancing PO₄ solubility further, by investigating more earthworm species and species interactions. However, since the redox sensitivity of Fe-(hydr)oxide-dominated soils contributed to increased PO₄ solubility, this can potentially be relevant for other oxyanions with a high affinity for binding to soil metal-(hydr)oxides like arsenate (As(V)) (Stachowicz et al., 2008). In As(V)-contaminated soils, a decrease of the RSA caused by earthworms might lead to increased levels of soluble As(V), translating into higher toxicity. Such side-effects of earthworm-enhanced PO₄ solubility should be taken into account when considering the use of earthworms to make the P nutrition of our agricultural systems more sustainable.

4. Conclusions

This research showed that earthworms can enhance the solubility of PO₄ in their casts via: (a) a relatively small effect of the increase of pH in casts; (b) a major contribution of PO₄ addition through stimulated mineralisation inside the earthworm gut; (c) a potentially major effect of a decrease in the RSA of casts by particle growth which is catalysed by the formation of Fe²⁺ during the reducing conditions caused by mineralisation; and (d) a decrease in the competition between NOM and PO₄ for binding sites on metal-(hydr)oxides in casts compared to the bulk soil. All these controlling mechanisms of earthworm-enhanced PO₄ solubility are directly or indirectly related to the capacity of an earthworm to mineralise the organic material it ingests, which therefore governs the ability of the various earthworm species to enhance PO₄ solubility in soils. The reduction of the RSA was only observed for Fe-(hydr)oxide-dominated soils, whereas it was absent or minor in Al-(hydr)oxide-dominated soils. Although the effect of earthworm-enhanced PO₄ solubility is finite as it can only increase the solubility of P already present in the soil, this study demonstrated that soil mineralogy influences earthworm-enhanced PO₄ solubility and suggests that earthworms have the largest potential to enhance PO₄ solubility in Fe-(hydr)oxide-dominated soils.

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

Data will be made available on 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.geoderma.2022.116212>.

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