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Article

The Effects of Dissolved Organic Matter Derived from Agricultural Waste Materials on Phosphorus Sorption in Sandy Soils

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Abstract: The effect of organic matter (OM) on soil P-sorption is controversial and needs to be more investigated. The dissolved organic matter (DOM) may be regarded as an influential component on P sorption in natural soils. However, despite the great need for renewable sources of available P and OM in agricultural soils, little is known about interaction between P and DOM in natural soil systems. To uncover if and how soil saturation with DOM derived from different types of abundant agricultural wastes (cattle manure, horse manure, biogas digestate, compost) affects the phosphate sorption, we examined P sorption process in control and DOM-saturated sandy soils. The results indicated that organic matter introduced with agricultural wastes did not always reduce P sorption, but certainly had an effect on impairing P fixation and thus may result in potentially greater P mobility in the soil, including P availability. Up to now, we cannot recommend any of the tested organic amendments to directly overcome the P fixation in arable soils.

Keywords: agriculture waste organic materials; dissolved organic matter; phosphorus sorption; sorption isotherms

1. Introduction

Research on different types of natural and exogenous organic matter, their fractions and effects on phosphorus (P) retention in soil has become a consistent element within issues of global concern [1–9]. Progressive degradation of arable soils – i.a. drought, contamination, soil organic matter losses or the scarcity of plant nutrients (in particular P) – stimulated searching ways to utilize infertile and even degraded soils extremely important. Sustainable use of soil resources has become nowadays an important global problem in response to the increased demand for food production.

Phosphate rock is included in the Critical Raw Materials List by the European Commission in 2014, therefore, reducing the use of mineral fertilizers and making greater use of renewable sources of macronutrients and organic matter is an emerging direction for agriculture [10,11]. Natural organic waste materials applications on agricultural lands seem to be a potentially valuable solution in this matter [10,12–15]. Crop residues, animal manures, composts and other organic materials are frequently used to improve soil quality, enhance organic matter levels, and increasing the bioavailability of soil P may be a favourable outcome of their use in agricultural ecosystems, although the impacts of these types of exogenic organic matter still need extensive studies [16,17].

Behaviour of P in soils remains problematic from both agronomic and environmental perspectives. On the one hand, ensuring the sufficient availability of P – of this essential and limiting plant macronutrient element – poses particular problems regarding the very low efficiency of P mineral fertilization, rising up only 10–20% [18]. Frequent replenishment of bioavailable P forms is necessary but – on the other hand – at the same time rises negative environmental impacts. This leads to a continuous accumulation of strongly bound P accompanying fertilization and the risk of its release from soil into waterways once a certain safe value of soil P saturation is exceeded and the concentration of mobile P forms increases significantly [12,19,20]. This critical value, known in the

literature as a *change point* or *threshold point*, is documented in many studies [21–24]. The P sorption plays a key role in governing the P behaviour in soil environment, including its mobility. This process occurs mainly on mineral surfaces of soil colloidal particles having active sorption sites for P. A particularly important role in this process is attributed to metal oxides and hydroxides commonly found in soils (especially Fe and Al, which activity is high particularly under acidic conditions). At soil pH above 7, Ca ions play an important role in P retention [11,25]. As well as clay minerals (e.g. kaolinite, montmorillonite, illite) – components of the soil sorption complex – participate in P sorption in soils; this occurs mainly at their edges via ligand exchange with surface OH groups.

Organic matter (OM) – due to its complex and still not well understood physical and chemical properties, chemical structure, and mainly due to numerous functional groups with different activity – takes a special place in building up soil sorption properties and also has a significant influence on phosphate sorption in soil. The great diversity in origin, types, forms as well as fractions of organic matter make it very difficult to obtain unambiguous results. Organic matter may affect P sorption in soils as a consequence of various interactions with soil components [26–30], which also have an impact on the stabilisation of OM in soils [31,32] – a process of great importance especially in relation to the progressive loss of organic matter in terrestrial ecosystems. The OM may interact with mineral surfaces by various mechanisms, i.e. ligand exchange, polyvalent cation bridges, and weak interactions, such as hydrophobic interactions including van der Waals forces and H-bonding. Anion exchange between simple coordinated OH groups of the OM is one important mechanism for the formation of strong organo-mineral associations, e.g. Fe-O-C bonds [31]. Ligand exchange between reactive inorganic hydroxyls (OH groups of Fe-, Al-, Mn-hydroxides and edge sites of phyllosilicates) and organic carboxyl and phenolic OH groups is restricted to acid soils rich in minerals with protonated hydroxyl. OM forms strongly complexes with Al and Fe oxides via ligand exchange particularly in acidic soils [31,33]. Organic anions are normally repelled from negatively charged surfaces, but binding occurs when polyvalent cations (such as Ca^{2+} and Mn^{2+} in neutral and alkaline soils and Fe^{3+} and Al^{3+} in acidic soils) are present at the exchange complex and then act as a bridge between two negatively charged sites.

It is generally thought that OM affects the P (ad)sorption in soils by competing for the same sorption sites [19,29]. OM thus blocks P sorption sites resulting in weaker P binding to soil particles. Therefore, an increase in the concentration of available P forms in the soil solution along with increasing OM content has been observed [4,24,29–32]. Consequently, this may be beneficial for agricultural needs but also in certain conditions can contribute to the P leaching from the soil and promote the deterioration of surrounding water bodies by eutrophication.

There is a wealth of evidence for P sorption inhibition by competitive effects and chelation interactions of low-molecular weight organic acids (LMWOAs) that are common in soils [16,27,34–40]. LMWOAs, mainly derived from decomposition of OM and secretion of plant roots and microbes, and they include oxalic acid, citric acid, tartaric acid, malic acid, succinic acid, salicylic acid, p-hydroxybenzoic acid and maleic acid, among others [27]. All of those LMWOAs molecules are components of dissolved organic matter (DOM) – the water-soluble fraction of organic matter – which can be considered as the most active part of OM. This active part of OM contains components that are readily released into the soil solution, for example during rainfalls [26]. Dissolved organic matter is a complexed mixture of organic compounds: humic and fulvic acids, amines, polysaccharides and numerous other C compounds [19]. The ability of DOM to compete with P is mainly determined by the stability of LMWOA [29], and the quality and quantity of DOM is probably the main factor defining the influence of OM on the course of P sorption in soil [41].

The most popular studies using model organic compounds have led to the suggestion that also natural DOM could affect P availability in soils through the competition between DOM and P for mineral adsorption sites. However, some studies found little or no evidence to support an effect of DOM on P sorption and the amount of phytoavailable P under realistic soil conditions [29,38]. Ohno and Crannell [42] have shown that animal manure-derived DOM was less capable of forming complexes with Al and Fe oxides and compete with P for adsorption sites in comparison to those from green manure. They found that green manure-derived DOM inhibited P sorption as a function

of DOC concentration, whereas animal manure-derived DOM enhanced P sorption or had no significant effect [42]. The ability of green manure-derived DOM to inhibit P sorption to a greater extent was attributed to the lower molecular weight of these compounds in comparison to animal manure-derived DOM. Other researchers also have shown that the extent of inhibition is closely related to the chemical structure of both the DOM and the sorbing surface [43]. There is also indication that the formation of DOM-metal complexes can reduce the number of available sorption sites and alter surface charge chemistry (i.e., increase negative surface charge), enhancing dissolution reactions [29]. In contrast, mineral-sorbed or particulate organic matter can also increase P sorption by increasing the number of sorbed cations available to form cation bridges with P [29]. Furthermore, the results with DOM isolated from crop residues, animal manures, and compost showed that the DOM initially leached or dissolved from these amendments was not likely to outcompete orthophosphate for mineral sorption sites [16]. Due to the P bonding to FeOOH through a strong, inner-sphere mechanism, and DOM associating through weaker outer-sphere electrostatic interactions or multiple hydrogen bonds, P outcompetes DOM for adsorption sites at mineral surfaces [16]. Chase et al. presented also the results supporting their earlier studies showing that only aromatic molecules >600 Da can compete with orthophosphate for mineral adsorption sites. Other findings [44] showed that organic compounds with two or more functional groups are more capable of exerting a greater variety of interactions in soils than organic compounds carrying only one functional group.

Hence, the role of organic matter in P sorption is still inconclusive and unclear. Some results show no apparent effect of OM on P, but some also indicate an increase in P sorption under the influence of OM in soil [19,29,36,41,45–48]. These contradicting results could have various reasons. For instance, they could be related to the magnitude of the P adsorption capacity of soil, which depends also on the type of organic matter, soil genesis, or could be an average effect obtained in such complex system as soil. On the one hand, complex structure of OM containing variety of functional groups gives many possible sorption sites for P, on the other hand, can as well block P sorption sites and compete with this component for the same sorption capabilities.

The discrepancies on the effect of OM on P sorption in the literature and the scarcity of studies on the effect of DOM derived from various agricultural waste materials on P sorption in natural soils [29,38,49], as well as the need for renewable sources of available phosphorus and organic matter in agricultural soils call for researching interaction between P and DOM in natural soil systems.

In this paper we present the results of a study on the effect of natural DOM on phosphorus sorption in sandy soil with high content of Al and Fe, varying in properties and land use (agricultural and forest soil; diverse soil material – A horizon (arable); B horizon). The objective was to uncover if and how soil saturation with DOM derived from different types of abundant agricultural wastes (cattle manure, horse manure, biogas digestate, compost) affect the phosphate sorption. We assumed that DOM introduced into soils will interact with mineral surfaces of soil particles, mainly with active sites of Fe and Al oxides, thus blocking the potential P sorption sites and lowering the soil's capacity for P sorption. We also assumed that the different chemical composition of DOM would have a distinctive effect on P sorption due to the type of interactions between OM, Fe/Al oxides and P. The overall aim of the research was to develop a practical approach to overcome the strong P-fixing in certain Northeastern European soils.

2. Materials and Methods

2.1. Materials

2.1.1. Soil material

This research was conducted on light textured soil materials characterized by different basic properties and diverse land uses. Soil 1 (S1) – classified as Brunic Arenosols according to FAO-World Reference Base [50] – located in central Poland (Spała Forest District), occurring in the fresh coniferous forest habitat (with *Pinus sylvestris* and *Picea abies*, with *Quercus petraea* in the

undergrowth). Soil samples were taken from the *sideric* horizon (Bvs). This material showed also the features of *spodic* horizon. S1 is a sand-textured material characterised by pedogenic accumulation of immobile humic complexes with sesquioxides (R_2O_3) and the presence of rusty coatings at mineral grains composed of Fe and Al (not associated with humus), which were formed by silicate weathering and low humic acid synthesis. The features related to the illuvial accumulation of Fe and Al sesquioxides as a result of the podzolic process in the soil horizon are also visible in S1. Soils 2 and 3 (S2; S3) – classified as Eutric Arenosols [50] – arable loamy sand textured soils located in north-eastern part of Germany (S2– Prohn; S3 – Poppendorf). Under natural conditions these soils have been Podzols, but the original litter layer and leached A-horizons have been incorporated into the tilled A-horizon. Beginning in the early 1990ies, deeper ploughing with stronger machinery incorporated the previous oxide-rich spodic horizon material into the surface Ap horizon, causing the problem of phosphate-fixation. This Ap-material has been sampled.

2.1.2. Experimental organic materials and soil incubation

The different types of organic matter derived from agricultural waste materials – compost (CPT), biogas digestate (BD), cattle manure (CM) and horse manure (HM) – have been acquired locally and introduced into the soil in the form of dissolved and colloidal organic matter (abbreviated as DOM). The DOM was extracted using cold tap water at a ratio of 1 : 5 (w : v) of waste to water. After 24h incubation the suspensions achieved passed through a 1-mm-sieve and were filtered through Macherey-Nagel, MN 616 G-filters. We have thus obtained an organic matter fraction from the waste materials, which can be assumed to be naturally the most active in soil, as it has the ability to be rapidly released into solution under natural conditions, such as during rainfall. Next, the air-dry soil samples were placed in beakers and slowly filled up with that dissolved organic matter until the saturation levels of soils were achieved. We have schematically presented the soil filling up procedure with DOM derived from organic waste in **Figure 1**.

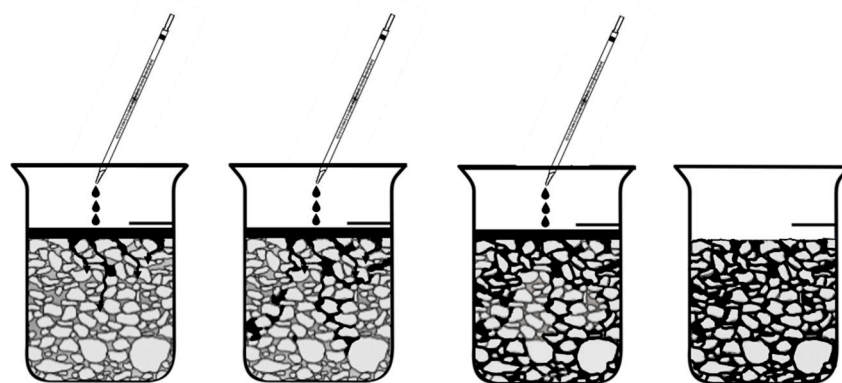


Figure 1. The course of saturation of the soils with waste organic materials.

Our intention was to fill the spaces between the soil particles with DOM to allow the introduced organic matter to occupy the active sorption sites at the soil particles, mainly derived from iron and aluminium oxides and hydroxides (**Figure 2**). Our aim was to block potential sorption sites for P by the introduced organic matter (DOM), which competes with P for the same sorption sites [29]. Thus, we hoped to lower the P sorption capacity of soil and at the same time to increase P availability to plants.

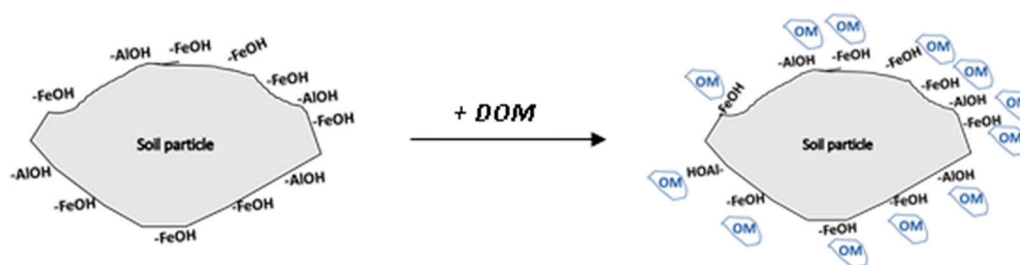


Figure 2. Expected effect of soil mineral particles saturated with dissolved organic matter.

After saturation, the samples were incubated at 70°C and then the soil saturation procedure was repeated several times in the same way. The final amount of DOM added into each soil is shown in Table 1. These soil samples saturated with DOM derived from 4 types of agricultural waste materials were used in P sorption studies in comparison to unamended soils, which were the reference (control) materials.

Table 1. The quantities of DOM additives introduced into the soils (in ml kg⁻¹ of soil) – the experiment variants.

| Soil sample / DOM type | no DOM (control) | DOM-CPT* (ml kg ⁻¹) | DOM-BD (ml kg ⁻¹) | DOM-CM (ml kg ⁻¹) | DOM-HM (ml kg ⁻¹) |
|---------------------------|---------------------|------------------------------------|----------------------------------|----------------------------------|----------------------------------|
| S1 | 0 | 300 | 300 | 300 | 300 |
| S2 | 0 | 520 | 560 | 480 | 520 |
| S3 | 0 | 400 | 480 | 480 | 480 |

*Abbreviations: DOM – dissolved organic matter; CPT – compost, BD – biogas digestate, CM – cattle manure, HM – horse manure.

2.2. Analytical methods

2.2.1. Basic soil chemical characteristic

The following basic properties were determined in soils under study (in fraction < 2 mm): soil texture (data not presented) by hydrometric method [51]; total organic carbon content (C) using a CS-MAT 5500 analyser (Ströhlein GmbH & Co., Kaarst, Germany, currently Bruker AXS Inc., Madison, WI, USA); total nitrogen (N) by the Kjeldahl method using a Buchi Labortechnik GmbH N analyser; pH was determined potentiometrically in 1 m KCl solution at 1:2.5 soil:solution ratio. The total content of Al, Fe and P extracted after digestion in aqua regia (3:1 ratio of concentrated HNO₃ and HCl acids) with microwave-assisted digestion were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin-Elmer Optima 8300 DV, Waltham, MA, USA). The amounts of non-crystalline and poorly crystalline oxides of Al (Al_{ox}), Fe (Fe_{ox}) and P (P_{ox}) were extracted with the solution of oxalic acid and ammonium oxalate at pH 3.0 [52] and measured with the ICP-AES analyser. Then the P sorption capacity (PSC) and degree of P saturation (DPS) of soil were calculated according to the following equations [53–55]:

$$\text{PSC} = 0.5 ([\text{Fe}_{\text{ox}}] + [\text{Al}_{\text{ox}}]) \quad (1)$$

$$\text{DPS} = ([\text{P}_{\text{ox}}] / \text{PSC}) 100 [\%] \quad (2)$$

where PSC and P_{ox}, Al_{ox} and Fe_{ox} are expressed in mmol kg⁻¹.

2.2.2. P-sorption isotherms

Phosphorus sorption process was carried out in soils not saturated (S1, S2, S3) and saturated with DOM derived from waste organic materials: compost (S1-CPT, S2-CPT, S3-CPT), biogas digestate (S1-BD, S2-BD, S3-BD), cattle manure (S1-CM, S2-CM, S3-CM, S3-CM), horse manure (S1-

HM, S2-HM, S3-HM). For this purpose, sorption isotherm was constructed based on 10 doses of phosphorus: 0.0–0.5–1.0–1.5–2.0–3.5–5.0–10–15–20 mg

P · dm⁻³ in the form of KH₂PO₄ with 0.01 mol·dm⁻³ CaCl₂ as a background solution. All the P doses were introduced into 1 g of soil in volume of 25 ml, in 3 repetitions. The samples were equilibrated for 24h on end-over-end shaker, then centrifuged for 15 min at 4500g and filtered. Phosphorus in the supernatants was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin-Elmer Optima 8300 DV, Waltham, MA, USA).

2.2.3. Statistical analyses

The amount of P (ad)sorbed (Q) was calculated from the difference between the amount of P added into the sample (P dose) and the amount of P in the supernatant of equilibrated solution according to Eq. 3, where: Q is the amount of P sorbed (mg kg⁻¹), C_P – the initial concentration of P in solution; P added (mg · dm⁻³), C_{eq} – the concentration of P after 24h-equilibration (mg · dm⁻³).

$$Q = C_P - C_{eq} \quad (3)$$

The Freundlich (4) and Langmuir (5) isotherm equations were applied to describe P adsorption to the soils:

$$Q = K_f C_{eq}^{nf} \quad (4)$$

$$C_{eq} / Q = C_{eq} / Q_{max} + 1 / K_L Q_m \quad (5)$$

where: Q is the amount of P adsorbed to soil at equilibrium concentration (mg kg⁻¹), K_f is the Freundlich unit capacity, C_{eq} is the P concentration in the equilibrated solution (mg dm⁻³), nf is the Freundlich exponent describing the nonlinearity of the adsorption, Q_m is the maximum adsorbed P concentration (mg kg⁻¹), K_L is a constant related to the binding strength of P at the adsorption sites (dm³ mg⁻¹).

The maximum adsorption buffering capacity (MBC, dm³ kg⁻¹) was calculated on the basis of:

$$MBC = K_L \cdot Q_m \quad (6)$$

Phosphorus adsorption isotherm indices (K_L , K_f , nf) and maximum adsorbed P concentration (Q_m) were calculated using the linearized form of the isotherm. The results obtained were fitted to the isotherm models. The standard error (SE), sum SE, variance were calculated to determine R-squared values to evaluate the fit of the results to the sorption models. Adsorption isotherm data were fitted by non-linear Solver function [56] and also the normal linearization method. Fitted parameters by both methods were compared based on goodness of fit measures and the best-fit parameters are finally presented here. It is noteworthy to mention that solver results were found to be more appropriate compared to the linearization technique.

The results obtained were statistically verified using Statistica 13 software [57]. The normal distribution of data was verified using the Kolomogorov-Smirnov test and the Chi-square test. A majority of results did not indicate the nature of the normal distribution. Therefore, non-parametric tests were used for further tests of the data. The differences between groups in the experimental variants were tested using the ANOVA Kruskal-Wallis test. Correlation analysis between data was performed using the Spearman's correlation coefficient. The analysis of principal components (PCA) was conducted and the relationships between the selected parameters were expressed as a correlation coefficient at a statistically significant level of $p < 0.05$.

3. Results and Discussion

3.1. Soils chemical characteristics

3.1.1. Initial properties and P status

The soils S1–S3 differ in their chemical properties. Among the main factors contributing to the different characteristics of these soils are the type of bedrock and land use. Soil S1 (B horizon) is characterized by acidic reaction, typical for the conditions found in coniferous habitats, conducive to the podzolization process. This is a poor soil formed from sand as a bedrock, that is why is characterized by low C content, wide C:N ratio, narrow C:P and N:P ratios. Arable soils (S2 and S3) taken from the surface layer (Ap) have markedly different properties as evidenced by higher pH, C, N and P values and narrower C:N ratio, wider C:P and N:P ratios, most likely originating from arable use, liming and fertilization. Also, these soils have higher total Al and Fe contents (**Table 2**). The Alox and Feox contents of the soils are shown in **Table 3**, and the PSC was estimated from it, which is between 43 mmol kg⁻¹ in S1 and 55 mmol kg⁻¹ in S2. These values are narrow in a relatively low range as compared to data from Northwestern Germany [58]. When the phosphorus bound to Feox and Alox (Pox) is taken into account, the degree of phosphorus saturation (DPS) can be estimated (**Table 3**). The DPS is frequently used as an indicator of threshold for environmental safety, which, if exceeded, can mean a significant increase in the concentration of soluble forms of P in the soil and increased environmental risk associated with P mobility. It has been assessed that this threshold usually occurs at a value of about 25% DPS in sandy soils [21–24]. In S1, the poor forest soil, the DPS is low (18%), while in arable soils (S2, S3) it reaches higher values of 37–40%, which means that the "change point" [22,25,34,59] might have been already exceeded.

Table 2. pH and basic chemical properties of unamended soils (initial properties – S1, S2, S3) and amended with different types of DOM derived from: compost (S1-CPT, S2-CPT, S3-CPT), biogas digestate (S1-BD, S2-BD, S3-BD), cattle manure (S1-CM, S2-CM, S3-CM), horse manure (S1-HM, S2-HM, S3-HM).

| Sample | pH | pH | C | N | P | Al | Fe | C:N | C:P | N:P |
|--------|-------------------|------------------|------|------|------|------|------|------|------|-----|
| | CaCl ₂ | H ₂ O | in % | | | | | | | |
| | | | | | | | | | | |
| S1 | 4.65 | 4.81 | 0.36 | 0.03 | 0.02 | 0.37 | 0.26 | 13.9 | 15.3 | 1.3 |
| S1-CPT | 4.84 | 5.21 | 0.39 | 0.02 | 0.02 | 0.33 | 0.24 | 19.5 | 17.3 | 0.9 |
| S1-BD | 5.84 | 6.28 | 0.49 | 0.05 | 0.03 | 0.35 | 0.25 | 10.0 | 18.6 | 1.9 |
| S1-CM | 5.78 | 6.17 | 0.59 | 0.03 | 0.02 | 0.40 | 0.28 | 17.5 | 23.8 | 1.2 |
| S1-HM | 5.66 | 6.11 | 0.46 | 0.03 | 0.04 | 0.40 | 0.27 | 18.0 | 11.1 | 0.7 |
| S2 | 5.65 | 6.03 | 1.29 | 0.12 | 0.05 | 0.58 | 0.60 | 10.6 | 25.4 | 2.4 |
| S2-CPT | 5.85 | 6.32 | 1.32 | 0.11 | 0.05 | 0.48 | 0.53 | 11.7 | 27.5 | 2.3 |
| S2-BD | 6.10 | 6.55 | 1.40 | 0.14 | 0.05 | 0.48 | 0.55 | 10.3 | 27.4 | 2.7 |
| S2-CM | 6.41 | 6.79 | 1.59 | 0.14 | 0.05 | 0.51 | 0.56 | 11.4 | 30.7 | 2.7 |
| S2-HM | 6.25 | 6.76 | 2.23 | 0.17 | 0.07 | 0.45 | 0.47 | 12.8 | 33.4 | 2.6 |
| S3 | 6.20 | 6.61 | 1.07 | 0.11 | 0.05 | 0.48 | 0.54 | 9.7 | 21.4 | 2.2 |
| S3-CPT | 6.28 | 6.66 | 1.14 | 0.11 | 0.05 | 0.47 | 0.50 | 10.4 | 23.5 | 2.4 |
| S3-BD | 6.38 | 6.72 | 1.21 | 0.12 | 0.05 | 0.45 | 0.50 | 10.1 | 25.4 | 2.5 |
| S3-CM | 6.49 | 6.83 | 1.25 | 0.11 | 0.05 | 0.54 | 0.53 | 11.0 | 26.1 | 2.3 |
| S3-HM | 6.40 | 6.80 | 1.70 | 0.15 | 0.07 | 0.51 | 0.51 | 11.4 | 25.4 | 2.2 |

Table 3. Content of acid ammonium-oxalate extractable Fe, Al, P; Phosphorus Sorption Capacity (PSC) and Degree of Phosphorus Saturation (DPS).

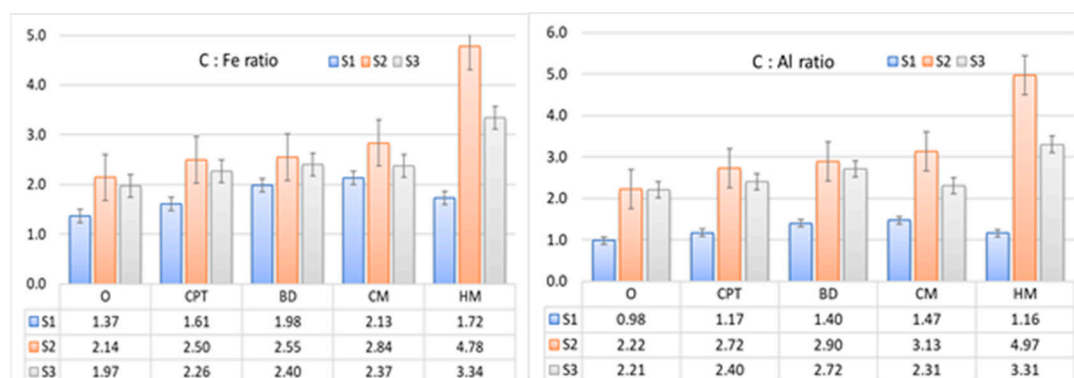
| Soils | Fe _{ox} | | Al _{ox} | | P _{ox} | | PSC | DPS |
|-------|---------------------|-----------------------|---------------------|-----------------------|---------------------|-----------------------|-----------------------|-------------|
| | mg kg ⁻¹ | mmol kg ⁻¹ | mg kg ⁻¹ | mmol kg ⁻¹ | mg kg ⁻¹ | mmol kg ⁻¹ | mmol kg ⁻¹ | % |
| S1 | 1054.7 | 18.9 | 1301.9 | 48.3 | 191.5 | 6.2 | 43.0 | 18.5 |
| S2 | 2029.7 | 36.3 | 1021.9 | 37.9 | 464.5 | 15.0 | 55.3 | 40.5 |
| S3 | 1747.2 | 31.3 | 804.4 | 29.8 | 352.0 | 11.4 | 46.2 | 37.2 |

3.1.2. DOM impact on soil chemical properties

The saturation of soils with different types of DOM caused increased pH values and C contents in all cases (**Table 2**). The highest pH values were observed in S3 and the lowest in S1. DOM derived from compost (DOM-CPT) had the weakest effect on pH increase in all soils. The introduction of DOM-CM (cattle manure) caused the highest pH changes in the cultivated soils (S2 and S3), while DOM-BD (biogas digestate) in soil S1. The DOM saturation increased the C contents. The greatest differences were obtained after DOM-CM introduction in S1 (S1-CM) and after DOM-HM addition in S2 and S3 (S2-HM, S3-HM).

The saturation with DOM had a diverse effect on the total content of basic nutrient elements (**Table 2**). The P content increased significantly only after the addition of DOM-HM. The effect of the other types of DOM on P content either did not cause significant changes or caused a slight decrease in its content, which was observed under the effect of DOM-CPT in all soils. Similarly, slight changes were observed in the Al and Fe contents after DOM saturation. Only in soils S1 and S3 the Al content increased after the addition of DOM-CM and DOM-HM, in other cases the values were rather lower compared to the control soil. In the case of Fe, a slight increase was observed in soil S1 under the influence of DOM-CM and DOM-HM, while in the other cases the content of this component decreased.

The relations between C and some components in the tested samples are worth to mention (**Table 2, Figure 3**). In general, it can be said that the value of C:P ratio increases (**Table 2**) in the studied soils after the DOM saturation according to the following order: O < CPT < BD < CM < HM. An exception is the effect produced after the treatment with DOM-HM to S1 (S1-HM), in which the C:P value is much lower than in O (S1); also in soil S3 the mentioned tendency is less pronounced. The C:Fe and C:Al ratios follow a similar pattern to the C:P relationship, as they increase in all soils according to the order presented above. However, exceptions are observed for DOM-HM in S1 – where C:Fe and C:Al were lower than for DOM-CM. For the C:Al ratio in S3 some divergences are also seen. All values of C:P, C:Fe, C:Al ratios remained in similar relationships in the tested soils and followed the series: S1 < S3 < S2.

**Figure 3.** Effect of DOM on the ratios of C:Fe and C:Al (explanations: O - control soils without DOM; CPT – DOM derived from compost, BD – DOM derived from biogas digestate, CM – DOM derived from cattle manure, HM – DOM derived from horse manure).

3.2. Process of P sorption

3.2.1. P sorption in unsaturated soils (S1, S2, S3)

The results obtained for P sorption in S1-S3 – soils with different P sorption properties – are the reference for the soils saturated with DOM. The early stage of sorption (at the low P doses) in S1 (B horizon) indicates a very high affinity for P, which weakens considerably with the sorption of further P doses (**Figure 4**). The slope of the sorption isotherm decreases then meaningfully and reaches the highest P adsorption value (Q) of approximately 0.2 mg P g⁻¹ soil. The P sorption in arable soils (S2 and S3) at the early stages of isotherms is comparable for these both soils. The much lower slope of the curve – in comparison to S1 – after the sorption of the initial P doses indicates substantially smaller

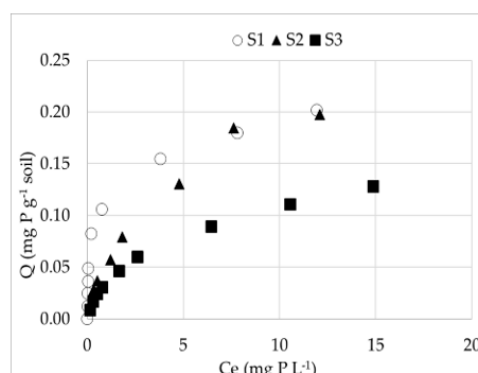


Figure 4. Phosphorus sorption in soils under study (S1, S2, S3). *Explanation: Q – the amount of P adsorbed to soil at equilibrium concentration; Ce – the P concentration in the equilibrated solution.

affinity for P, which is associated with the higher DPS value in both soils (**Table 3**), typical for arable – often overfertilized – soils [58]. The higher doses of P flatten isotherms in both soils and are sorbed better by S2 than S3, which is in agreement with the magnitude of the P sorption capacity in these soils (**Table 3**). The sorption capacity of S2 can be compared to S1 – it reaches also Q value of 0.2 mg P g⁻¹ of soil, while Q is lower in S3 and achieves 0.13 mg P g⁻¹. These results confirm a strong relation with the type of land use of these soils, which seems to be the main factor determining the course of P sorption here. Arable soils (S2 and S3), regularly fertilized with P, have a much higher DPS value, so their affinity for P is much weaker, in contrast to forest soil (S1) with a much lower DPS value (**Table 3**).

The P-sorption isotherms obtained in the studied soils are typical examples of so-called "L" isotherms, in which the concentration ratio of the compound remaining in solution and adsorbed on the solid decreases with increasing concentration of the solute, providing a convex curve [60,61]. The P adsorption by soil is regarded as being a multi-stage kinetic process involving an initial fast adsorption stage (chemical) and then a slower adsorption stage (physico-chemical, physical), and possibly further stages [26,62]. At relatively low P concentrations, the adsorption process is completed rapidly and ion exchange and ligand exchange are probably the dominant mechanisms contributing to the high adsorption rate [26,63]. This quick, chemical phase of adsorption process slows down promptly at high concentrations of added P because available adsorption sites quickly become saturated and P becomes physico-chemically and physically adsorbed from the liquid to the soil at a slower rate, and this process at this point represents the slow adsorption phase [26,62,63]. Then the "L" curve can reach a strict asymptotic plateau when the solid has a limited sorption capacity or the curve does not reach any plateau, when the solid does not show clearly a limited sorption capacity [60]. This is often observed in the case of sorption processes in natural soils, which are polydisperse and highly heterogeneous, and that is why sometimes it may be even difficult to clearly classify the isotherm subtype "L".

3.2.2. DOM effect on P sorption in soils

The saturation of soil samples (S1, S2, S3) with DOM derived from waste organic materials (CPT, BD, CM, HM) resulted in different effects on P sorption (**Figure 5**).

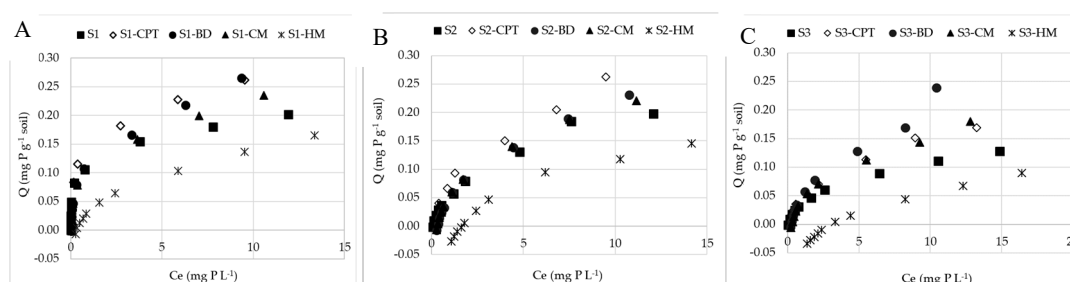


Figure 5. Phosphorus sorption after DOM saturation of soils S1* (A), S2 (B) and S3 (C). *Symbols: S1, S2, S3 – control soils; DOM types: CPT – compost, BD – biogas digestate, CM – cattle manure, HM – horse manure; Symbols for soil 1: S1-CPT – soil 1 with compost DOM addition; S1-CM – soil 1 with cattle manure DOM addition; S1-HM – soil 1 with horse manure DOM addition; S1-BD – soil 1 with biogas digestate DOM. The same pattern was used for other soils); Q – the amount of P adsorbed to soil at equilibrium concentration; Ce – the P concentration in the equilibrated solution.

An increase of P adsorption (Q) at higher P doses was observed as DOM effect in all combinations except for soils saturated with DOM-HM. The highest Q reached about 0.25 mg P g⁻¹ and occurred as a result of DOM-CPT and/or DOM-BD saturation. The enhanced P sorption was also observed as an effect of the DOM-CM treatment in all studied soils. In S2, the DOM-BD and DOM-CM saturations slightly increased the sorption at the highest P dose, but the P sorption process occurred in a very similar way to the control soil in these both cases (S2). Comparable P sorption isotherms were also observed after saturation with DOM-CPT and DOM-CM in the S3 (Q was higher of about 0.05 mg P g⁻¹ than in S3). The soils saturated with DOM-HM behaved undoubtedly differently. In each soil we observed P desorption at the initial stages of sorption (low P doses) and the significant weakening of P sorption (**Figure 5**). A smaller angle of the inclination towards the OX axis indicated a much lower affinity for P in the DOM-HM soil samples than in the control soils, and the decrease of Q was also observed (Q was lower of about 0.05 mg P g⁻¹ than in control soils), unlike others DOM treatments: CPT, BD, CM.

The initial stage of the sorption is determined mainly by conditions related to the properties of reactants important in chemical sorption, i.e. the number of sorption sites on mineral surfaces (including the bonds related to Al and Fe oxides, clay minerals and other soil colloids), PSC or pH. So it can explain the differences in the soils affinity for P as indicated by the slope at the beginning of the sorption curves (**Figures 4 and 5**). The affinity for P weakens in the order: S1 > S2 > S3 and is similar for all cases even after saturation with DOM materials, excluding DOM-HM, which significantly diminished the affinity for P in every soil. At a later stage, when the sorption mechanism goes beyond chemical binding, the type of adsorbent becomes important – so we clearly can observe the differences specific to the type of DOM introduced. The different behaviour of DOM-HM at an earlier stage may be linked to the introduction of increased P amount with this DOM type, which could change the equilibrium of the reaction and lead to previously sorbed P becoming desorbed.

3.3. The P adsorption indices

The P adsorption isotherms were quantitatively described by the two most popular models – Langmuir and Freundlich equations. Results for soils before and after treatments were fitted to these adsorption equations. The values of R-squared were calculated as a quality check (**Table 4**). The Freundlich and Langmuir equations are characterised by the very high values of R² in the soils under study. The weakest R² values were obtained after applications of DOM-HM in S3 (S3-HM).

Table 4. The P isotherm parameters.

| Soil sample / amendment | Freundlich isotherm | | | | | Langmuir isotherm | | | | | MBC mg g ⁻¹ |
|----------------------------|---------------------|----------------|--------------|---------------|----------------|-------------------|----------------|--------------|---------------|----------------|---------------------------|
| | K _f | n _f | sum SE | Variance | R ² | K _L | Q _m | sum SE | variance | R ² | |
| S1 (CONTROL) | 0.1 | 0.27 | 0.001 | 0.0053 | 0.99 | 3.68 | 0.18 | 0.003 | 0.0053 | 0.95 | 0.662 |
| S1-CPT | 0.12 | 0.34 | 0.003 | 0.0089 | 0.97 | 2.78 | 0.24 | 0.003 | 0.0089 | 0.97 | 0.667 |
| S1-BD | 0.1 | 0.43 | 0.002 | 0.0085 | 0.98 | 1.05 | 0.26 | 0.003 | 0.0085 | 0.96 | 0.273 |
| S1-CM | 0.09 | 0.40 | 0.002 | 0.0069 | 0.97 | 1.25 | 0.23 | 0.002 | 0.0069 | 0.97 | 0.288 |
| S1-HM | 0.03 | 0.67 | 0.001 | 0.0035 | 0.98 | 0.12 | 0.26 | 0 | 0.0035 | 0.99 | 0.031 |
| S2 (CONTROL) | 0.05 | 0.56 | 0.001 | 0.0053 | 0.98 | 0.23 | 0.27 | 0 | 0.0053 | 0.99 | 0.062 |
| S2-CPT | 0.06 | 0.63 | 0.001 | 0.0083 | 0.98 | 0.22 | 0.37 | 0.002 | 0.0082 | 0.98 | 0.081 |
| S2-BD | 0.05 | 0.70 | 0.002 | 0.0068 | 0.98 | 0.13 | 0.39 | 0.001 | 0.0068 | 0.99 | 0.051 |
| S2-CM | 0.05 | 0.66 | 0.002 | 0.0064 | 0.97 | 0.16 | 0.34 | 0.001 | 0.0064 | 0.99 | 0.054 |
| S2-HM | 0.008 | 1.12 | 0.005 | 0.004 | 0.88 | 0.01 | 1.34 | 0.005 | 0.004 | 0.87 | 0.012 |
| S3 (CONTROL) | 0.03 | 0.49 | 0 | 0.002 | 0.99 | 0.27 | 0.15 | 0 | 0.002 | 0.99 | 0.041 |
| S3-CPT | 0.04 | 0.55 | 0.001 | 0.0037 | 0.98 | 0.24 | 0.22 | 0 | 0.0037 | 0.99 | 0.053 |
| S3-BD | 0.04 | 0.73 | 0.001 | 0.0064 | 0.98 | 0.09 | 0.45 | 0.002 | 0.0064 | 0.97 | 0.041 |
| S3-CM | 0.04 | 0.64 | 0.001 | 0.004 | 0.98 | 0.15 | 0.26 | 0.001 | 0.004 | 0.98 | 0.039 |
| S3-HM | 0.002 | 1.51 | 0.004 | 0.003 | 0.85 | 0.07 | 0.2 | 0.009 | 0.003 | 0.67 | 0.010 |

3.3.1. Freundlich equation parameters

The capacity factor (K_f). The K_f value, which indicates the number of sorption sites [64], ranges in control soils from 0.03 (S3) to 0.1 (S1). The almost ten times higher value of K_f in S1 than in arable soils reflects a significantly higher P binding capacity of this soil, as we observed on the P sorption curves for the control soils (**Figure 4**). The S1 neither has more Al and Fe nor more Alox, Feox and PSC than the other two soils but its DPS is less than half of soils S2 and S3 (**Tables 2 and 3**), indicating that K_f is determined by available sorption sites in soil, which had been confirmed in the literature [65].

The saturation with DOM revealed divers effects on the K_f parameter (**Figure 6a**). In each soil, a significant increase (by 20-35%) of the K_f parameter was observed after DOM-CPT addition, while a substantial reduction of K_f values (up to 90%) was caused by DOM-HM addition in all soils compared to the control soils. The saturation with DOM-CM and DOM-BD increased the K_f value only in S3 (of about 30%) which indicates the importance of soil properties influencing the value of K_f. No other effects on K_f were observed except for a decrease of about 10% in S1 after DOM-CM saturation (**Figure 6a**). The K_f parameter shows significant negative correlations with the contents of C, N and with pH (**Table 5**). This confirms the important role of organic matter content and pH in building the P sorption capacity in soils and its binding strength and had been observed by other researchers [40,64–66]. This may explain such strong decrease of K_f value after DOM-HM application and the increase of this value in all soils as an effect of the saturation with DOM-CPT. In addition to the basic soil properties, also the total P content has a very strong effect on the course of P sorption which is related to the number of available sorption sites for P in a given soil, as reflected in the DPS values. This was supported by statistically significant negative correlation coefficients between P content and the K_f parameter (**Table 5**), which may contribute to the explanation of the behavior of soils after the saturation with DOM-HM, which resulted in the largest P contents (**Table 2**). The missing significance of correlations of sorption isotherm variable with total contents of Al and Fe are plausible, because the total contents include atoms in the crystals that are not involved in any interaction with phosphate, e.g. internal parts of mineral particles.

Table 5. Correlation coefficients between the sorption isotherm parameters and soil properties. Marked (*) and bold correlation coefficients are significant with $p < 0.05$ ($N=15$).

| Variable | C | N | pH H ₂ O | pH CaCl ₂ | Al | Fe | P | C:Al | C:Fe | Al:P | Fe:P | C:P | N:P |
|----------|--------|-------|------------------------|-------------------------|-------|-------|--------|--------|--------|--------|--------|--------|--------|
| K_f | -0.53* | - | -0.66* | -0.60* | -0.46 | -0.33 | -0.66* | -0.52* | -0.50 | 0.82* | 0.43 | -0.28 | -0.30 |
| n_f | 0.78* | 0.80* | 0.69* | 0.64* | 0.46 | 0.41 | 0.78* | 0.78* | 0.81* | -0.91* | -0.59* | 0.61* | 0.58* |
| K_L | -0.74* | - | -0.67* | -0.61* | -0.43 | -0.36 | -0.73* | -0.73* | -0.76* | 0.90* | 0.60* | -0.58* | -0.53* |
| Q_m | 0.54* | 0.50 | 0.23 | 0.22 | 0.14 | 0.28 | 0.38 | 0.53* | 0.59* | -0.44 | -0.32 | 0.71* | 0.62* |
| MBC | -0.57* | - | -0.71* | -0.65* | -0.45 | -0.31 | -0.67* | -0.55* | -0.56* | 0.86* | 0.54* | -0.34 | -0.35 |
| | | 0.63* | | | | | | | | | | | |

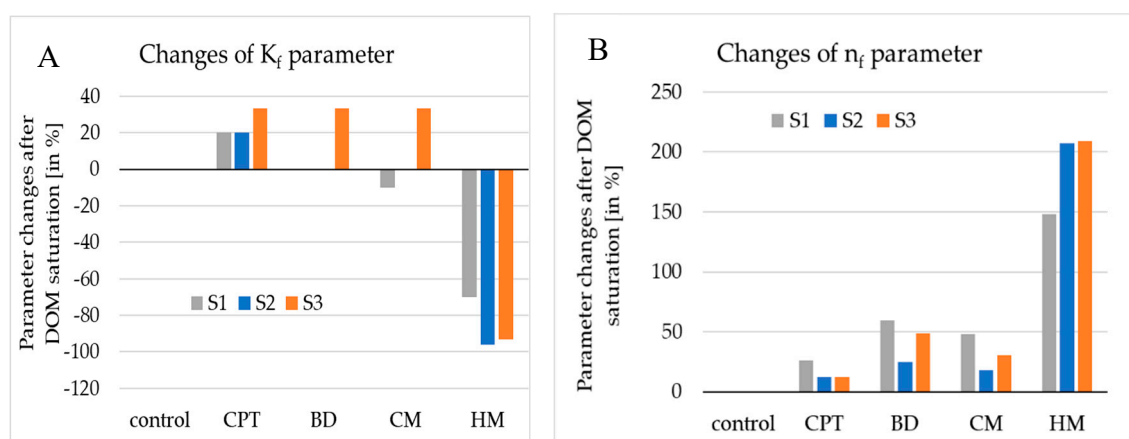


Figure 6. Changes of Freundlich isotherm parameters in S1, S2, S3 soils after DOM application. Changes (expressed in %) for the values of each parameter were related to the values of the control samples, which are displayed here as level 0.

The linearity parameter (n_f). The value of n_f exponent is a measure of the linearity of the function, but sometimes is also considered as an indicator of sorption sites energy heterogeneity [67,68]. In control soils, the n_f value is lower than unity, in range of 0.27 to 0.56 (Table 4). The values obtained are in line with the results of other authors [69]. After the saturation with each type of DOM the exponent n_f was significantly increased, which indicates a substantial increase in the heterogeneity of the energy of P sorbing sites in soils. The effects on n_f value follow the order: HM >> BD > CM > CPT. The highest increase of n_f value after the DOM-HM saturation (Figure 6b), if indicating heterogeneity of P binding sites, eventually points to additional processes such as surface complexation and precipitation [70] that occurred preferably in the DOM-HM samples.

The n_f exponent is positively correlated with C, N, P and pH (Table 5). This implies that saturation with DOM and increase in C content (including elements related to the presence of organic matter: N and P content) and the pH conditions have a dominant effect on increasing the heterogeneity of binding energy in the soils. This may be related to the quantity, but also to the quality of the organic matter introduced into the soil, since it is the structure of the organic molecules that will determine the characteristics of the functional groups active in P sorption. This may also be attempted to explain the major changes in n_f values observed under the influence of DOM-HM, with which, in addition to a significant increase in C content, we also observe the introduction of a large amount of phosphate ions. All these components (DOM, P, Al and Fe), important for P binding in

soils, could probably have interacted with each other in different ways depending on the pH and other reaction conditions such as the contribution of these components. These issues are unfortunately beyond the scope of our study and require further analysis with emphasis on the qualitative characterisation of the organic matter introduced.

3.3.2. Langmuir equation parameters

The maximum adsorption capacity for P (Q_m). The Q_m reflects the number of P adsorption sites per unit weight of soil and is therefore commonly used to estimate P adsorption capacity of soils [26,47,71]. The value of Q_m ranged from 0.15 mg P g⁻¹ (S3) to 0.27 mg P g⁻¹ (S2) in control soils. This value is comparable for S1 and S3 and lower than Q_m in S2. After the saturation with DOM the Q_m value increased in all cases (**Figure 7a**). All types of DOM amendments (CPT, BD, CM, HM) had a comparable effect on Q_m in S1 giving about 30-40% higher values than in control soil (**Figure 7a**). The DOM materials gave a similar effects in S2, excluding the DOM-HM amendment, which greatly increased the calculated Q_m value (by as much as 400% compared to the control sample). This indicates that DOM-HM initiates binding processes that are different from the other soils. A stronger impact on Q_m parameter was observed after the saturation with DOM-BD, DOM-CM and DOM-CPT in S3. The magnitude of this effect followed the order: BD > CM > CPT. In contrast, the DOM-HM impact was negligible compared to control soil (S3).

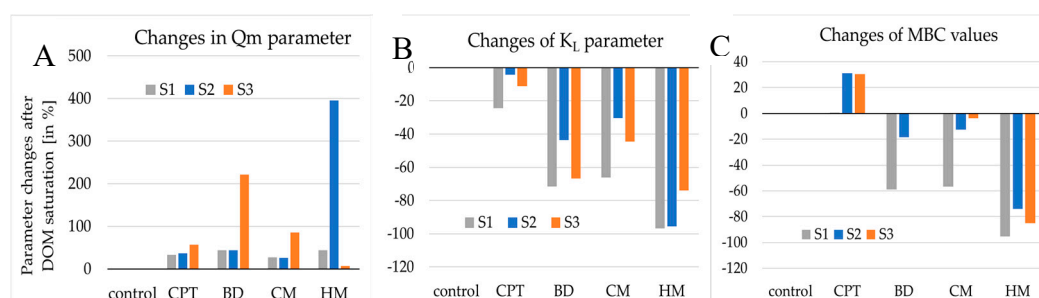


Figure 7. Changes of Langmuir isotherm parameters: (a) Q_m , (b) K_d and (c) MBC in S1, S2, S3 soils after DOM application. Changes (expressed in %) of each parameter values were related to the values of the control samples, which are displayed here as level 0.

Such a comparable effect of the applied DOM types in S1 and S2 suggests that the origin of DOM is unlikely to have a significant effect on the value of the Q_m parameter. Also, the different properties of S1 and S2 did not affect the significant differences in Q_m between the tested variants of the experiment. The increase of Q_m values (**Table 4**) is attributed to an increase of organic matter (OM) content (**Table 2**), which is confirmed by a statistically significant ($p < 0.05$) correlation coefficient ($r = 0.54$) between Q_m and total organic C content (**Table 5**) and remains in line with the results of others [26,47,71,72]. It is likely that DOM has occupied sorption sites potentially available for P – mainly connections to Al and Fe, but providing some new sorption sites for P on its own organic particles, hence the increase in Q_m was observed. There are also results indicating that OM does not have a direct effect on Q_m and the influence of other soil properties is also important [71]. The relationship between Q_m and OM was also shown to be dependent on soil pH [26] after Zhao et al. [73], who found that at pH > 6.0 increasing the OM content increased the amount of P adsorbed by soils but decreased the amount of P adsorbed by soils at pH < 6.0. In our study we observed this relation as an increase in Q_m value with an increase of C content at pH > 6.

Numerous studies have reported the effect of soil organic matter on inhibiting P adsorption in soil by blocking adsorption sites on metal oxides, such as Al and Fe oxides, or by forming metal-SOM-P complexes with flexible structures [26,27,29,36,39,68]. Nevertheless, our results conducted on different types of DOM do not confirm this based on the Q_m value analysis. The Q_m value higher than in control soils indicates that new sorption sites for P are likely to be generated after soil saturation with DOM. This is clearly demonstrated in S2 after DOM-HM saturation, where significantly higher number of sorption sites can be related to the higher amount of introduced DOM and the higher

content of Al and Fe (especially amorphous Al and Fe – Al_{ox}, Fe_{ox}; **Table 2, Table 3**). Possibly, in this case, the sorption sites for P were not blocked, but a different sorption mechanism/s prevailed. It is not known clearly what the role of the high concentration of P introduced together with DOM-HM might have been. Possibly in the presence of high concentration of P, the behaviour of organic molecules was different than in other cases. Competition and mutual blocking of these components may have occurred. Although it is also possible that the DOM saturation may have caused in this case that, on the one hand, DOM interacted with the surface functional groups of Al and Fe, but, on the other hand, generated additional sorption sites for P associated with the organic molecules' sorption active functional groups. It is possible that the high P concentration may also have favoured the formation of monodentate, rather than bidentate, bonds with P on active surfaces, which tended to bind P more weakly in the soil, thereby increasing the P pool that can more readily pass into solution. The probability of multilayer P sorption, formation of monodentate bonds on sorptive surfaces or increased P leaching under high P loading conditions has been repeatedly observed in the literature [74–77]. In the presence of much P bi- or more-layer bonding and co-precipitation may occur as well. Another possibility is that DOM-HM could support the disintegration of Al-/Fe-oxide microaggregates making more sorption sites available. All these mechanisms [70] may have resulted in such a large increase in the maximum P sorption capacity (Q_m) calculated from our results and correlations ($Q_m : C$) we obtained (**Table 5**). The question remains in this area as to the effect of high P concentration in the presence of DOM on the activity of the introduced organic matter, and what is the organic matter activity in blocking/enhancing P sorption depending on its qualitative nature [28,78].

The P bonding energy constant (K_L). The K_L parameter reflects the P bonding energy and is one of the most important indicators describing the soil affinity for P. A higher K_L value indicates stronger P sorption, and spontaneous sorption may occur more readily as the P supply becomes less intense [62]. The K_L parameter values calculated for control measurements can be ordered in the following way: $S2 < S3 \ll S1$. The comparable K_L values lower than 0.3 were calculated for arable soils (S2, S3), while the forest soil had the K_L value at least ten times higher (**Table 4**). These differences reflect various soil properties, first of all the mineralogy that governs P-binding sites and the land use/management history, e.g. the former P fertilization at the arable soils S2 and S3. This view is supported the apparent much higher DPS values in arable soils compared to forest soil S1.

The K_L parameter decreased considerably as a general effect of the saturation with DOM materials (**Figure 7b**). This indicates that the introduced organic materials weakened P binding energy in all 3 soils. The new sorption sites likely generated under the DOM influence are energetically weaker in holding P than the Al and Fe bonds [31,70], thus the marked reduction in the K_L parameter, which was greatest in S1 compared to other soils. A comparable effect of soil organic matter on K_L values was observed by Yang et al. [26] in studies on phaeozem soils that received addition of humic substances. The largest negative effect on K_L was observed after the saturation with DOM-HM, followed by DOM-BD, DOM-CM, and the weakest effect was observed after the introduction of DOM-CPT (**Figure 7b**). The strongest impact of DOM-HM is probably related to the large amount of P incorporated into the soil (**Table 2**), so P fixation is much weaker in such material and probably forming single bonds with P that are definitely more easily desorbable from soil.

The Maximum Buffering Capacity (MBC). The MBC is an joined parameter that combines the effects of Q_m and K_L values [26,62]. The higher MBC means that more P can be sorbed by soil. We observed an increase of MBC value (**Figure 7c**) solely as an influence of DOM-CPT in S2 and S3 (S1-CPT had no effect). The other DOM types predominantly caused a decrease in MBC value (**Figure 7c**), which was the strongest after DOM-HM saturation in all soils. No influence was observed in S3-BD and S3-CM.

The different response to the DOM-CPT introduction may be related to the specific nature of the raw organic waste composted and, above all, to the transformation of OM during the mineralisation and humification processes [79,80]. This probably allowed the production of a material that more strongly retains P in the soil, e.g. DOM with a more aromatic character than the others, because aromatic moieties exert the largest binding energies for phosphate among various organic

functionalities [70]. Although the effect of CPT on Q_m is similar for other types of DOM (**Figure 7a**), it stands out as having the weakest effect on the reduction of the K_L parameter (**Figure 7b**) compared to other DOM materials, thus the effect on MBC finally is positive or not present after the introduction of DOM-CPT. However, confirmation of this is possible in further studies of the nature and composition of CPT organic matter.

3.4. Relationships affecting P sorption in DOM-treated soils

The PCA displays the relationship between analysed data, soil samples saturated and unsaturated with DOM materials and estimates which parameters or parameter combinations best characterize the variability between data (**Figure 8**). Each axis, in a two-dimensional representation, explains a certain percentage of the total variability that exists between samples. Principal components 1 (PC1) and 2 (PC2) explained together 82.01% (68.74 + 13.27) of the total variability among the selected properties of DOM-amended soils and control soils and gives the two-dimensional representation of the components to describe the sample characteristics. The total content of P, C, N, pH, C:P, C:Al and Al:P ratios, and the values of K_t , K_L , MBC are the main contributors in PC1, while the Fe:P ratio seems to be the main contributor in PC2. The parameters with vectors situated closer to each other indicate parameters that may have a high positive correlation. These include: the sorption parameters K_L , K_t , MBC and Al:P ratio. In contrast, they are negatively correlated with some basic soil properties, such as pH, C, N, P and the C:P, C:Al, C:Fe ratios. These results are confirmed by statistically significant, strong coefficients correlations (**Table 5**). The vectors that form an angle close to 90°, such as Fe:P and sorption parameters (K_L , K_t , MBC) may not present significant correlation. We observed statistically significant correlation coefficients for Fe:P ratio with n_f exponent, K_L and MBC (**Table 5**).

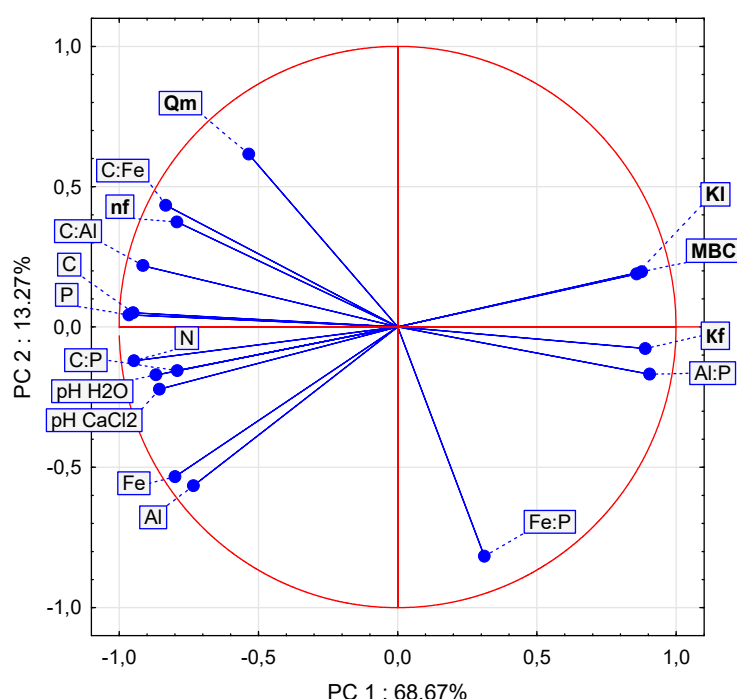


Figure 8. Projection of variables onto the factor plane (1x2).

The position of the soil samples displayed in **Figure 9** reveals that all variants S2 and S3 (arable soil) are located in two quadrants of the graph, indicating the similar character of these samples. They are comparable in their basic chemical properties, and strongly differ from soil S1. Soil S1 and its DOM-treated variants, having different characteristics, are situated in the same area in which the Al:P, K_L , K_t and MBC parameters appear. These parameters probably are most significantly determined the dissimilarity of soil S1 compared to S2 and S3. This is undoubtedly related to the

different land use as forest of soil S1, but also to the different genetic material of collected soil. Within these two separated groups of soils a certain type of differentiation due to the type of DOM applied is also interesting: the DOM-HM group stands out the most clearly in the top of the chart, followed by the DOM-BD group. The subsequent variants already show a much weaker specificity, but DOM-CPT are usually slightly higher than DOM-CM and the control samples, which (apart from S1) appear in the lowest position in **Figure 9**.

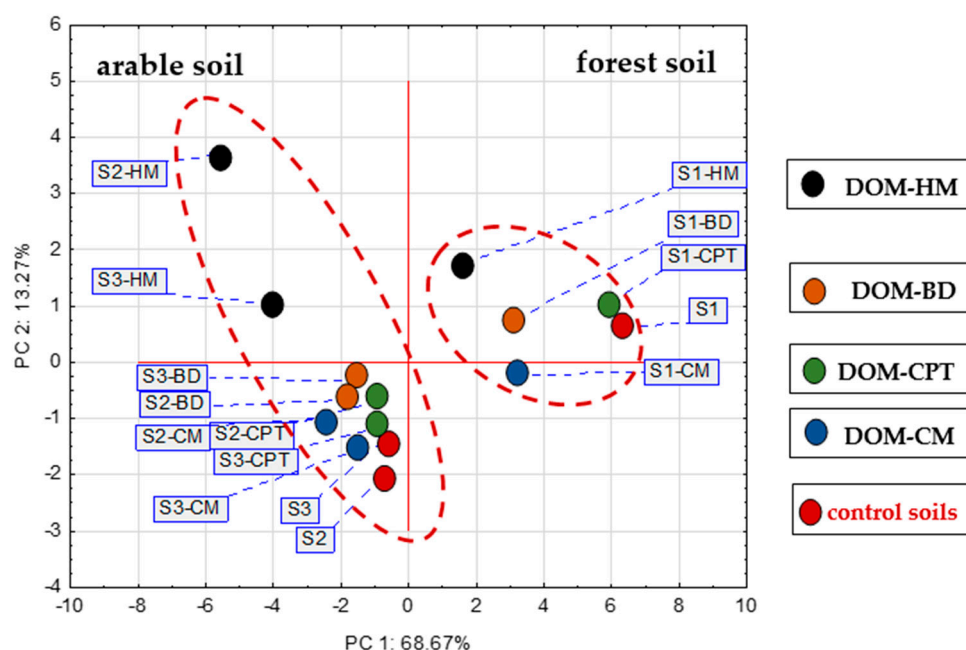


Figure 9. Projection of cases onto the factor plane (1x2).

The PCA and strong significant correlation coefficients obtained between total organic C content and all sorption parameters confirm important role of soil organic matter in P sorption process in soils. It is worth noting that Q_m parameter, that was the weakest correlated sorption parameter, also showed a significant positive relations with C content and C-related ratios. The proportion of Al and Fe content to total organic carbon (C:Al, C:Fe) and total phosphorus content (Al:P, Fe:P) are of great importance in relation to P sorption in studied soils, as evidenced by high correlation coefficients revealed between these indices and the isotherm parameters (**Table 5**). This approves our hypothesis that an increasing amount of organic matter in the form of added DOM interacts with active sorption sites on Al and Fe (hydr)oxides blocking them and in this manner affects P sorption in the soil. The strong positive correlations between n_f (and negative for K_f , K_L and MBC) with the C:Al and C:Fe (and C:P) ratios, together with the significant negative correlations between n_f (and positive for K_f , K_L , MBC) with the Al:P and Fe:P ratios provide evidence for this thesis. This indicates the importance of the increasing proportion of total C content in relation to Al and Fe (as well as to P) and, in parallel, the decreasing relation of the Al and Fe content to the total P content in the P sorption process.

4. Conclusions

Our study indicates that dissolved organic matter (DOM) introduced with agricultural wastes did not always reduce phosphorus sorption, but certainly had an effect on impairing P fixation and thus may result in potentially greater P mobility in the soil, including P availability.

Our hypothesis, that P sorption sites, derived in sandy soils mainly from Fe and Al oxides, would be blocked by introduced organic matter in form of DOM was only partially confirmed. On the one hand, DOM derived from compost (DOM-CPT), biogas digestate (DOM-BD) and cattle manure (DOM-CM) increased the P adsorption (Q) in the Ap horizons of arable soils and in the B horizon of forest soil (**Figure 5**). On the other hand, DOM from horse manure (DOM-HM) caused a

significant decrease of P sorption in all soils under study (**Figure 5**). However, the highest content of total P in soils after DOM-HM saturation, in contrast to the other DOM types, indicates that the P added with DOM-HM probably is the main reason causing the inhibition of further P sorption in these three soils.

As an effect of the saturation with DOM, we observed a substantial increase in the heterogeneity of the energy of P sorbing sites (n_f) and a weakening of the P bonding energy (K_L), while at the same time an increase in the sorption capacity (Q_m). The DOM (excluding the impact of DOM-CPT) affected the Maximum Buffering Capacity (MBC) in the studied soils and decreased the potential soil activity in P retention (**Table 4, Figure 7c**).

Up to now, we cannot recommend any of the tested organic amendments to directly overcome the P fixation in arable soils. The effect of DOM saturation that we observed is an averaged result of the activity of functional groups of DOM, and the predominant nature of these groups will determine the soil P binding capacity and its mechanism. For this reason, qualitative studies of different types of DOM and its ability to compete with P for the same sorption sites are an important direction for further research on the application of organic wastes in terms of sustainable management of P availability in soil.

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