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The Influence of Municipal Solid Waste Compost on the Tranformations of Phosphorus Forms in Soil

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Abstract: Searching for a renewable phosphorus (P) source for agricultural soils has become a challenge of particular importance on a global scale. Depletion of the world's phosphate resources as well as the risk of environmental problems caused by excessive P mobility have placed this topic among the most important environmental issues. The aim of this study was to analyse the transformation of phosphorus forms in municipal solid waste compost (MSWC) at different maturity stages, to assess the effects of their application on soil phosphorus status and to evaluate the suitability of MSWC for agricultural soils as a potential phosphorus source. The application of MSWC to the soil had a positive effect on the content of available P. The content of potentially mobile P forms increased significantly in the soil, primarily after the introduction of immature MSWC and confirmed by the significant correlations with the applied P indicators. However, the results indicate that the MSWC does not pose a serious environmental risk and could become a potential source of P in the soil, although the material used for this purpose should be mature. This study also indicated that the assessment of using compost as a P source should not be based on P total content alone, but should include the content of different P forms and specific P-related indicators, to reflect both the P availability and the potential environmental risks.

Keywords: environmental P indicators; P availability; P behaviour in soil; P mobility; organic waste utilisation; renewable P source

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1. Introduction

Considering the limited worldwide range of phosphorus (P) reserves [1–4], which as phosphorites were included in the Critical Raw Materials List by the European Commission in 2014 [1,2], the problem of finding new P sources for agricultural soils has become a challenge for modern generations. Hence, reducing the use of mineral fertilisers and making greater utilisation of renewable P sources has become an emerging direction for agriculture.

Phosphorus is an essential macronutrient in plant nutrition, and therefore, is an important issue for agriculture. The low efficiency of P fertilisation, i.e., not higher than 15–30%, which results from strong P sorption in soils, is the main reason for the deficiency of available P forms in soil. Therefore, continuous P fertilisation is necessary to meet the requirements of crops. This, in turn, contributes to the accumulation of P in arable horizons of cultivated soils in forms that are strongly fixed and not available to plants. At subsequent P doses, when a certain level of P is exceeded, over-fertilisation can occur, which refers to the level at which the sorption sites for P are no longer available (P saturation is reached). Then, P is poorly held in the soil and the risk of mobilisation and leaching of excess P into the environment rises significantly, causing undesirable effects of eutrophication in aquatic ecosystems. These aspects must be taken into account when P fertilisers are introduced into soil.

One of the possible and reasonable solutions is to look for naturally available resources in the environment that can be reused. In particular, this is currently recommended, in light of another alarming problem, i.e., ever-increasing global consumption. Therefore, one of the goals of waste management is to utilize instead of landfilling. The application of natural organic waste materials to agricultural soils appears to be a valuable solution as a potential P source, mainly due to a sufficiently high abundance of phosphorus in the waste materials. The application of compost, formed by processing waste biomass including municipal waste, in agricultural practice is one of the particularly promising and profitable directions [5–13]. A particular strength of organic waste applications is that they have been shown to increase the bioavailable P content in soils [1,14–20]. The fundamental issue, from an agronomic point of view, is the soil available P dynamics, which depend on many factors, most often related to the effect of pH, clay content, and the elemental composition of Al, Fe, or Ca in soil solution. The role of organic matter is also important with respect to P availability, however, we often encounter ambiguous and even contradictory findings in the literature regarding its effect on P sorption, and therefore also on P (bio)availability [3,21–24]. Several studies have shown that organic matter introduced with organic amendments reduced P fixation and enhanced P uptake in soils [21]. It is also worth noting that inorganic P bound in the soil as part of organic matter—which makes up a significant proportion of soil P—is less stable than P minerals in the soil, and therefore can shift more quickly to a pool of available P [25]. Therefore, organic waste materials introduced into the soil can be a potential substitute for limited non-renewable phosphorus resources; however, the type and formation conditions may contribute to different phosphorus contents and P form proportions in organic amendments, as well as their effectiveness as a source of P in the soil. Environmental considerations should also be kept in mind when using different qualities and quantities of organic waste.

The mineralization and transformation of organic matter in the composting of organic waste, including municipal solid waste, provides a stable product that has high fertilising potential, which can improve the chemical and physical properties of cultivated soils and, consequently, can have a positive impact on soil quality [7,26–30]. During the composting process, which involves the transformation of organic matter, there are also significant transformations in the P content and proportions between different P forms, which can have a significant impact on the suitability of such material as a source of P in soil. Detailed studies on phosphorus transformations in composts and treated soils are still scarce [8,19,31–33]. Further research in this area is of great importance in relation to the amounts and relative distribution of P forms and P availability, as well as the environmental risk of possible P leaching from compost [3,32,34,35].

Therefore, the purpose of this study was to analyse the transformation of phosphorus forms in municipal solid waste compost (MSWC) at different maturity stages, in order to assess the effects of MSWC application on soil phosphorus status, including environmental risks of P mobilisation, and to evaluate the suitability of MSWC as a potential phosphorus source for agricultural soils.

2. Materials and Methods

2.1. Composting Material and Pot Experiment

Municipal solid waste compost (MSWC) at different maturity stages, obtained from the Katowice agglomeration in Poland (50.293238, 19.069045), and soil material used in the pot experiment were studied to identify the effect of the MSWC on the soil properties.

The raw material from the composting plant, working according to the hybrid bioreactor DANO/open pile semi-dynamic technology [36], was composted for 279 days. As described earlier by Jamroz et al. [2], the main technological device in a DANO system is the biostabiliser, which consists of two basic elements that determine the course of composting: a closed fermentation chamber, in which optimal conditions prevail for an intensive course of technological processes, and a slow-speed drum crusher, in which waste dispersion occurs through abrasion and tearing. The raw material was obtained after 36 h of waste dispersion into the biostabiliser. Further composting took place outdoors in piles of size: 4 m long, 2 m wide, and 1.5 m high. The composted material was mixed every 10–15 days, the moisture was maintained at 50% w/w, and the temperature was measured daily [2]. Samples were taken from about 20 places in the pile, after 36 days (after the thermophilic phase, CPT-1), 95 days (after biodegradation phase, CPT-3), and 159 and 279 days (during the stabilisation, CPT-6 and CPT-9) of composting time, then mixed, and the final weight of a sample was 2.5–3 kg of fresh material. Then, the samples were dried at room temperature, ground, and sieved (1 mm). The total organic carbon (TOC) was analysed with a CS-mat 5500 instrument (Strohlein GmbH & Co., Kaarst, Germany, currently Bruker AXS Inc., Madison, WI, USA); the total nitrogen (TN) was determined following the Kjeldahl method using a Buchi Labortechnik GmbH N analyser; pH was determined potentiometrically; ash content (Ash) was determined after burning in a furnace at 550 °C; and the contents of amorphous Fe and Al (Fe_{ox} and Al_{ox}) were extracted in oxalic-oxalate solution, pH 3.0, according to the Tamm method [37,38]. All results obtained are presented on a dry matter weight basis.

The pot experiment was conducted according to the scheme shown in Table 1. The MSWC at various maturity stages (1, 3, and 9 months from the beginning of composting (CPT-1, CPT-3, CPT-9)) was introduced into the loamy soil (LS) in two doses: 100 and 400 t ha^{-1}. The aim of the pot experiment was to test the possibility of using composts produced from municipal solid waste as components of horticultural substrates. Since commercial peat-based potting substrates contain a significant amount of organic matter, the amount of MSWC applied in the pot experiment was adequately adjusted to provide conditions similar to potting substrates in terms of organic matter content; hence, the lower dose of MSWC was 100 t ha^{-1}. The use of a higher dose (400 t ha^{-1}) of compost was intended to determine the risk of using doses of composts produced from municipal solid waste, especially immature composts, that were too high for plants. The soil used in the pot experiment was taken from a 0–30 cm depth of Phaeozem [39] and was characterized by 57% sand, 16% silt, and 27% clay content, pH (KCl) of 6.7, as well as a TOC of 12 g kg^{-1}. These data have already been discussed in an earlier paper [40].

Table 1. Scheme of the pot experiment using compost at different maturity stages.

Dose of Compost (t ha^{-1})	Compost (CPT) Maturity in Months:		
	1 (MSWC-1)	3 (MSWC-3)	9 (MSWC-9)
0	LS	LS	LS
100	LS + 100 CPT	LS + 100 CPT	LS + 100 CPT
400	LS + 400 CPT	LS + 400 CPT	LS + 400 CPT

Symbols: MSWC—municipal solid waste compost; LS—loamy soil.

2.2. Phosphorus Extraction Procedures

The following phosphorus forms were determined in the research material: the total content of P after digestion in concentrated $HClO_4$ [41,42] in the aluminium block at a temperature of 130 °C (P_t); the content of organic P (P_{org}), calculated from the differences between the P content measured in 0.5 M H_2SO_4 extracts of the samples burned in a furnace at 550 °C for 2 h (P_t) and samples not subjected to burning (P_{min}) [43]; the P oxalic-oxalate extractable (P_{ox}), according to Tamm method, using a mixture of 0.175 M $(NH_4)_2C_2O_4{\cdot}H_2O$ and 0.1 M $H_2C_2O_4{\cdot}H_2O$ (pH 3.0) at a ratio of 1:50 (m/v), then shaken for 4 h in darkness, and centrifuged [37,38]; the available P (P_{M3}), with the Mehlich III method [44] after a 5 min reaction time with a solution of 0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.13 M HNO_3 + 0.001 M EDTA used at a 1:10 ratio (m/v); the water-extractable P (P_w) form, extracted in ultrapure water at a ratio of 1:15 (m/v), then shaken for 1 h, and centrifuged, the solutions after filtration were acidified to pH 2 with HCl to prevent precipitation of phosphate compounds [45]; the soluble P (P_{CaCl2}), extracted in 0.01 mol·dm^{-3} $CaCl_2$ at a ratio of 1:10 (m/v) after 2 h of shaking, at a temperature of 20 °C [46]. Solutions were centrifuged, filtered, and then acidified. Concentrations of P were measured following the ICP-EAS method. All measurements were done in 3 replicates.

2.3. Indicators Related to the P Forms

The solubility index (I) of the most mobile forms, represented as the percentage of water-extractable (P_w) or easily soluble (P_{CaCl2}) P forms in relation to the total P content (P_t), was calculated according to the following equations:

$$I_w = (P_w/P_t) \times 100\ [\%],$$

$$I_{CaCl2} = (P_{CaCl2}/P_t) \times 100\ [\%].$$

The phosphorus activation coefficient (PAC) represents the degree of difficulty with which transformations between total P and available P occurs. The PAC is an important indicator of soil fertility and the transformation of P fractions; its higher values indicate higher P bioavailability to promote plant growth [47]. The PAC was calculated as the available P (P_{M3}) to total P (P_t) ratio [48]:

$$PAC = P_{M3}/P_t \times 100\ [\%].$$

The P sorption capacity (PSC) and degree of P saturation (DPS) were calculated on the basis of the contents of Al_{ox}, Fe_{ox}, and P_{ox}, expressed in mmol kg^{-1}, according to the following equations [49–52]:

$$PSC = 0.5\ ([Fe_{ox}] + [Al_{ox}])\ [mmol\ kg^{-1}],$$

$$DPS = ([P_{ox}]/PSC) \times 100\ [\%].$$

The phosphorus saturation ratio (PSR) allows a threshold value to be established that corresponds approximately to a set critical solution P concentration and is applicable to a wide variety of soils [53]. Despite methodology differences in obtaining a threshold PSR value, most soils tend to have a PSR value in the 0.1–0.15 range [54]. The PSR is equivalent to DPS, but without a corrective constant ($\alpha = 0.5$) associated with the DPS definition [55], and was calculated in accordance to Nair [54]:

$$PSR = [P_{ox}]/([Fe_{ox}] + [Al_{ox}]).$$

The soil phosphorus storage capacity (SPSC) was calculated according to [56,57]:

$$SPSC = (\text{threshold PSR} - \text{soil PSR}) \times (\text{sum of extractable Al and Fe}),$$

where the value of 0.15 was used as the best approximation of threshold PSR value [56] corresponding to the critical P solution concentration of 0.10 mg dm^{-3} P, as proposed by Breeuwsma and Silva [55,56].

2.4. Statistics

The pot experiment was performed in 3 replicates. Averaged samples of MSWC (20 places) and soil from the variants of the pot experiments were taken from all replicates, from which determinations were made in 2 repetitions, and each measurement was repeated 3 times.

A statistical analysis was conducted using the Statistica 13 software [58]. The data were subject to analysis of variance (ANOVA) to determine significant differences among the groups of MSWC maturity, as well as between treatments of the pot experiment, the different levels of MSWC doses and the different stages of MSWC maturity. Significance of effects using mean values for properties were statistically compared among the compost maturity stages and between the pot experiment variants by the Tukey HSD post hoc test, at a confidence level of $p < 0.05$. The Kolmogorov–Smirnov test ($p < 0.05$) was applied to check the normality of data distribution. Significant parameter correlations were determined using the Pearson correlation coefficient (r).

3. Results and Discussion

3.1. Basic Compost Properties

The basic properties of the compost under study (Table 2) have been presented in detail by [6]. According to the progress of the composting process, the content of organic matter decreases, resulting in a gradual decrease in the content of total organic carbon (TOC) from 17.7% to 14.4%, accompanied by an increase in ash content and changes in the content of TN from 11.5 to 13.0 g kg^{-1}. The progress of mineralization and humification processes is illustrated by the values of the C/N ratio, which narrows during composting, starting from a value of 15.4 (CPT-1) and ending at a value of 11.2 (CPT-9). The alkaline reaction of the tested compost gradually increases, taking on pH values in the range of 7.5–8.1. The water-extractable and total contents of heavy metal in MSWC were also determined [6]. Decreasing concentrations of water-extractable forms of heavy metals were found associated with the maturity stages of the composts (results not shown). There was no evidence of environmental risks associated with the heavy metal content in the compost [6]. These results have been confirmed by previous studies on the influence of heavy metal concentrations in MSWC on the chemical composition of soils and cultivated plants [59]. The proportion of amorphous Fe and Al oxides (Fe_{ox} and Al_{ox}) increases with the maturation of the compost, with Fe being dominant. The significant changes observed in the content of these components in the early stage of composting are probably due to the intense organic matter mineralization at this stage of the process. In the later stages of the process during the stabilisation of the compost, the changes in their content also stabilise. These components are important in creating sorption sites for phosphorus in soils, but also in composts [3,60,61]. Therefore, P sorption capacity (PSC) and degree of P saturation (DPS) are estimated based on their content in soils [62,63]. These indicators can probably also be applied to solid organic waste (including composts) and provide a useful tool for estimating the proportion of potentially available sorption sites for phosphorus and the rate of their occupancy, as we discuss below.

Table 2. Basic properties of MSWC at different maturity stages: composting times of 1 month (CPT-1); 3 months (CPT-3); 6 months (CPT-6); 9 months (CPT-9). Data modified on the basis of [6].

Compost Maturity Stage.	TOC [1] g kg^{-1}	TN g kg^{-1}	C/N	pH	Ash g kg^{-1}	Fe_{ox} g kg^{-1}	Al_{ox} g kg^{-1}
CPT-1	177.3	11.5	15.4	7.5	572.5	5.4	3.5
CPT-3	158.3	12.5	12.7	7.8	603.2	8.8	5.5
CPT-6	146.7	13.0	11.3	7.7	613.1	8.9	5.4
CPT-9	144.3	12.9	11.2	8.1	637.2	7.1	5.5

[1] TOC—total organic carbon; TN—total nitrogen; C/N—the TOC: TN ratio; Fe_{ox}, Al_{ox}—amorphous forms of Fe and Al.

3.2. Dynamics of P Forms in Compost at Different Maturity Stages

The contents of P forms in the compost are presented in Table 3, while their percentages of P_t are shown in the Figure 1.

P total (P_t). The total P content (P_t-$HClO_4$) in the compost ranges between 2.5 and 3.3 g kg^{-1} (after wet digestion with concentrated $HClO_4$). The lowest content is reached in the initial stage of composting (CPT-1) and, in the later stages, it increases. These changes are related to weight loss due to decomposition of composted waste. Comparable P_t values were obtained after extraction in a solution of weakly dilute sulfuric acid in compost ash samples (P_t-H_2SO_4). The differences between the results of both these extractions are within 5–10% (Figure 1). In most cases, the P_t-H_2SO_4 values are lower; in CPT-9, the value was slightly higher than the P_t-$HClO_4$ value. These data are comparable with data reported in the literature [3,42]. Other authors have found that dry combustion followed by P extraction in 0.5 M H_2SO_4 slightly underestimated P_t, which was attributed to incomplete oxidation of organic matter, volatilization of P, and formation of insoluble P crystals during dry combustion at 550 °C [64,65].

Table 3. Phosphorus forms in compost at different maturity stages (composting times of 1 month (CPT-1); 3 months (CPT-3); 6 months (CPT-6); 9 months (CPT-9)).

Compost Maturity Stage	**P_t ($HClO_4$)**	**P_t (H_2SO_4)**	**P_{min}**	**P_{ox}**	**P_{org}**	**P_{M3}**	**P_{CaCl2}**	**P_w**
	mg kg^{-1}							
CPT-1	2571.2	2355.1	1909.4	1107.0	445.7	156.3	31.6	50.9
CPT-3	3328.2	3158.6	2888.4	2180.8	270.2	163.4	12.1	24.0
CPT-6	3340.1	3492.3	3272.4	2118.4	219.9	185.1	8.9	24.6
CPT-9	2928.4	3276.7	3071.6	1949.8	205.0	185.3	14.6	25.6

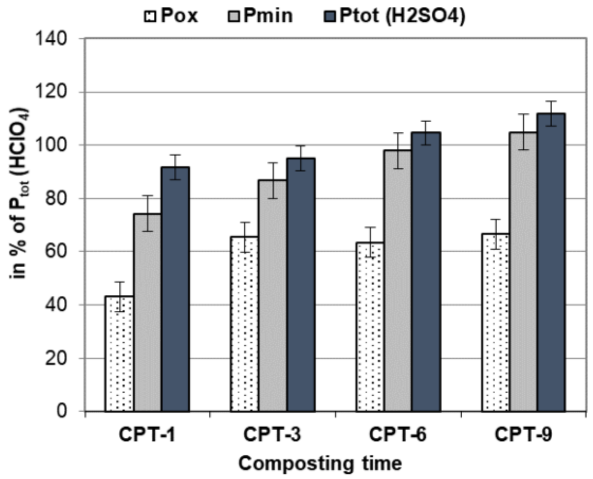

Figure 1. Relation of P_t, P_{min}, and P_{ox} content (in % of P_t-$HClO_4$) during the composting process (CPT-1, CPT-3, CPT-6, and CPT-9 composting months). The bars indicate the standard error.

Inorganic P (P_{min}). The P_{min}, defined as P extractable in 0.5 M H_2SO_4, prevailed as a P fraction in compost with the content between 74 and even 105% of P_t ($HClO_4$). The value higher than 100% results from the P_{min} calculations based on the results of extraction in H_2SO_4, which, in this sample, showed higher values than in $HClO_4$ (Figure 1). Comparable results of inorganic P (P_{min} extracted with 0.5 M H_2SO_4) have been obtained in other studies [3] for different types of compost (69–89%).

Oxalate P (P_{ox}). The P_{ox}, extracted with acid ammonium-oxalate, showed essentially lower contents in compost compared to P_{min}. In an earlier study [43], it was shown that the the fraction of inorganic P (P_{min}) consisted of acid-extracted Ca-P and a portion of secondary inorganic phosphorus (unoccluded P), which probably caused the difference between these two values. The lowest values of P_{ox} were obtained in immature compost (CPT-1), and then increased in later stages of organic matter conversion, ranging from 1 to 2.1 g kg^{-1}, which reflected 43–67% of P_t (Table 3 and Figure 1). Our results for P_{ox} were slightly lower compared to data presented by [3], who reported P_{ox} content as high as 55–74% of P_t in different types of compost.

Organic P (P_{org}). The content of P_{org} coincides with the processes that organic matter undergoes during composting. Just a small portion of P_t is present in organic form in compost, which is in agreement with other authors [3,32,66]. The P_{org} content reaches 17% of P_t in the initial stages of the composting process (CPT-1, P_{org} = 446 mg kg^{-1}) and gradually decreases in the later stages to about 7–8% of P_t (Figure 2). Due to the mineralization of organic residues as a result of the activity of microorganisms, organic P, which is a component of organic structures, is released and transformed into mineral forms. In later stages of organic matter transformations, P_{org} can also be a component of newly formed connections with organic molecules of high resistance to decomposition, which are organic structures that can undergo continuous remodelling. As a result of these transformations, the relations between P_{min} and P_{org} go through a fundamental altering during composting (P_{min}/P_{org} ratio), where the domination of the inorganic forms (P_{min}) significantly increases from 4:1 (CPT-1) to 15:1 (CPT-6, CPT-9). The P inorganic forms expressed as P_{ox} content keep the same tendency and represent about nine times higher concentrations than P_{org} in the later composting stages (Figure 2).

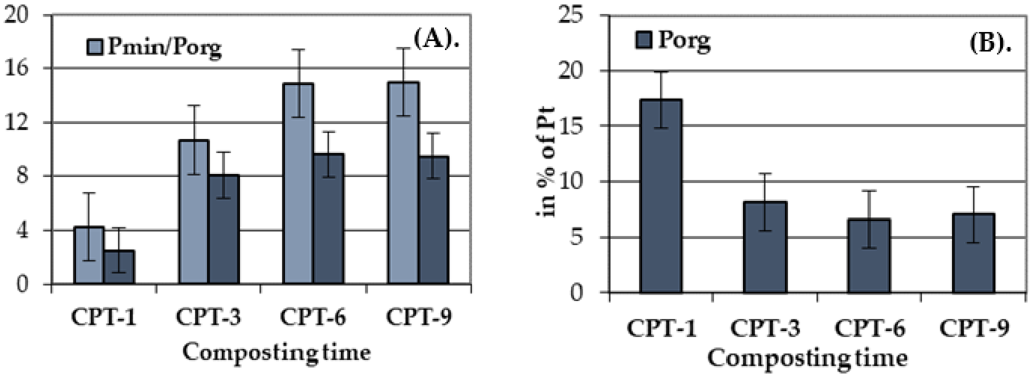

Figure 2. The organic P transformations in MSWC: (**A**) The mineral P to organic P ratios (P_{min}/P_{org} and P_{ox}/P_{org}); (**B**) P_{org} content as a % of P_t (the bars indicate the standard error).

Indicators of P status in MSWC. The content of Pox is considered as the amount of P bound mostly by non-crystalline Al and Fe oxides (Alox, Feox), which are one of the major inorganic P sorbing elements in soils. The sorption capacity of compost related to P also largely depends on the activity and the amount of Al/Fe oxides and hydroxides. Therefore, their contents are commonly used to estimate the DPS in soil, mainly to determine the risk of P leaching into the environment. Here, we now try to use the DPS as a useful tool in estimating the stock of potentially available P in composts (MSWC), a value which, when introduced into soils, can potentially increase the P available to plants and, in extreme cases, pose a risk of P mobilisation into the environment. The DPS value in the studied MSWC is 31.5% in the initial stage of composting and reaches 38–38.7% in its subsequent phases (Table 4). These medium-high DPS values mean that MSWCs have potential as a P fertiliser for crops. The composts contain higher inorganic P reserves after passing the thermophilic phase, i.e. after the stage of intensive mineralisation of organic matter. At this stage of composting, the processes of tranformation of Porg into inorganic P forms are already slowing down, also the amount of Al and Fe stabilises, hence the DPS values are higher. The PSR values confirm these results. The SPSC calculations show negative values in MSWC (Table 4), which in the case of soils could indicate that the safe concentration of P in solution is exceeded and that there may be an increased release of mobile P forms into the environment, but in the case of composts, we can only conclude that the amount of P contained in MSWC may increase the pool of available P after the application to the soil.

Table 4. Phosphorus indicators in compost of different maturity stages (composting times: 1 month (CPT-1); 3 months (CPT-3); 6 months (CPT-6); 9 months (CPT-9)).

Compost Maturity Stage	PSC * (mmol kg^{-1})	DPS (%)	PSR	SPSC (mmol kg^{-1})	PAC (%)	I_{CaCl2} (%)	I_w (%)
CPT-1	113.6	31.5	0.16	−1.66	6.08	1.23	1.98
CPT-3	181.8	38.7	0.19	−15.89	4.91	0.36	0.72
CPT-6	180.4	37.9	0.19	−14.29	5.54	0.27	0.74
CPT-9	165.7	38.0	0.19	−13.24	6.33	0.50	0.87

* PSC—phosphorus sorption capacity; DPS—degree of phosphorus saturation; PSR—phosphorus saturation ratio; SPSC—soil phosphorus storage capacity; PAC—phosphorus activation coefficient; I_{CaCl2}—solubility index related to P_{CaCl2}; I_w—solubility index related to P_w.

Available P (P_{M3}). The content of bioavailable P (P_{M3}) increased during the composting time (Table 3). The lowest values (156 mg kg^{-1}) at the beginning of composting (CPT-1) stabilise after 6 months, reaching a value of 185 mg P kg^{-1} (CPT-6 and CPT-9). The PAC value accounts for from 4.9 to 6.3% of the compost (Table 4 and Figure 3) and gradually increases as composting progresses, indicating a transformation of P towards enhancement of P activation. It is important to note the lower proportion of P_t in the first stages of composting.

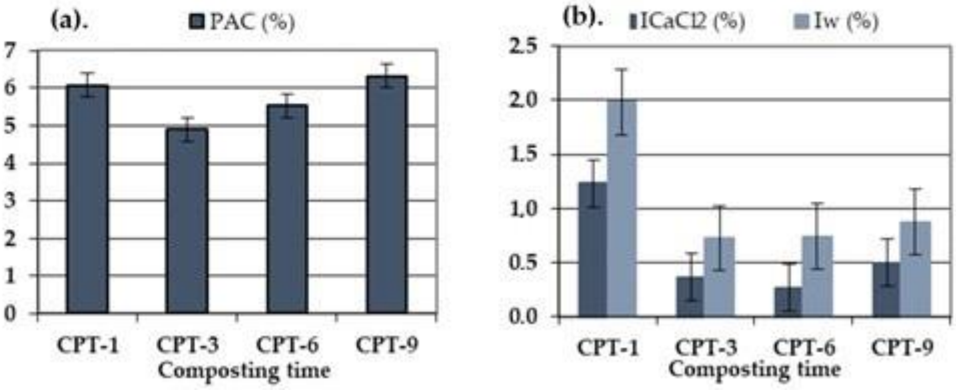

Figure 3. Phosphorus activation coefficient (PAC) (**a**) and solubility indices (I_{CaCl2} and I_w) (**b**)in MSWC (the bars indicate the standard error).

Water-soluble (P_w) and easily soluble (P_{Cacl2}) forms of P, and solubility indices (I). These two forms of P are highly soluble and extractable in water-based solutions and are used as an indicator of the potential for P loss in surface runoff [67,68] These forms of P are both typically found in low concentrations in the range of 0.8–8 mg P kg^{-1} [69]. P_w is very easily leached into the environment, for example, during rainfall, and their presence in increased concentrations may indicate a risk of leaching from the surface, but also deep into the soil profile [70,71]. However, the extraction solution of 0.01 M $CaCl_2$ moves the P_{CaCl2} form into solution under chemically similar conditions to those in the soil solution. The similar ionic strength allows the release of mobile P, which is weakly bound to soil particles. Thus, the high content of P_{CaCl2} also indicates a significant environmental hazard. We observed a relatively high content of I_w (CPT-1) reaching the level of 2% (Table 4 and Figure 3) in the initial stage of composting (Figure 3b), which corresponded to 51 mg kg^{-1} P_w (Table 3). In the later stages of composting, the P_w content stabilised at a much lower level of about 25 mg kg^{-1}, which corresponded to 0.7–0.9% of I_w (CPT-3, CPT-6, and CPT-9). The content of readily soluble P (P_{CaCl2}) was similarly shaped; the highest value was observed in CPT-1 (I_{CaCl2} = 1.2%) and corresponded to over 30 mg P kg^{-1} (Table 3). After 3 months, the content of P_{CaCl2} stabilised at a comparable level and decreased to a value of about 10 mg kg^{-1} at CPT-3, CPT-6, and CPT-9, taking the lowest value (I_{CaCl2} = 0.25%) in the sixth month of composting. A slightly higher I_{CaCl2} (0.5%) was observed after 9 months (Figure 3) of composting (CPT-9). The lower values of P_{CaCl2}, compared to those measured in distilled water (P_w), are typical due to differences in the ionic strength effects of the extraction solutions [53,72–74].

The relatively high contents of mobile P forms (P_{M3}, P_{CaCl2}, and P_w) are closely related to the transformation and contents of the mineral and organic P forms, which are closely dependent on the course and conditions of the composting process, as has been confirmed by studies by other authors [6,29]. The largest transformations in organic matter occur in the initial phase of composting, mainly during the 20-40 days of composting [28]. The first stage of the composting process is dominated by the processes of hydrolysis and oxidation of organic matter, followed by the decomposition of rapidly biodegradable organic substances, such as carbohydrates or proteins and their components, with a gradual increase in temperature. These components, with hydrophilic character, are mainly composed of polysaccharides, proteins, peptides, and amino acids [6,29], which promote the release of phosphate residues along with other products formed at this stage (NH_3, CO_2, and H_2O). These are related to the higher proportion of low-molecular-weight organic acids and to the largest content of easily degradable OM components, such as aliphatic chains, polysaccharides and alcohols, which are chemically or biologically oxidised in immature compost. The composting process transforms the heterogeneous raw OM into a compositionally homogeneous product at the end of the process, so the mature compost contains more aromatic structures with greater stability. Therefore, the above changes in MSWC may be the reason for significantly increased amounts of soluble forms of P (P_w and P_{CaCl2}) just in CPT-1 compared to subsequent MSWC maturity stages. The significant increase in these forms of P released from the OM may indicate a lack of sorption sites for P in CPT-1. This may be explained by the high content of low molecular weight organic acids, which qualitatively and quantitatively abundant functional groups may interact with Fe/Al oxides and hydroxides, blocking access of P to their sorption sites and limiting its binding to Fe and Al. The higher concentrations of these mobile forms of P in the early stages of composting can therefore be explained by a mechanism of competition for sorption sites between P and OM in MSWC, as already documented in numerous papers, e.g. Guppy et al. [23]. The rate of mineralization of organic phosphorus is generally well correlated with the rate of nitrogen mineralization and the release of CO_2. In addition, the values of C, N, P mineralization tend to be proportional to the content of these elements in MSWC. This is also confirmed by our results (Figure 4), which we illustrate using the quantitative C/N, C/P and N/P ratios that reflect the transformations accompanying the decomposition and conversion of organic matter during the composting process. All values of these ratios between macronutrients decrease gradually with the progress of composting time. A decrease in TOC and an increase in the proportion of Ac in the compost (Table 2 and Figure 4a) significantly affect the decrease in C/N and C/P ratios (Figure 4b,c), which are also accompanied by simultaneous mineralization and release of N and P from organic structures. The N/P ratio is more stable, decreasing gradually to values below 4, indicating more dynamic N transformation than P conversion (Figure 4d).

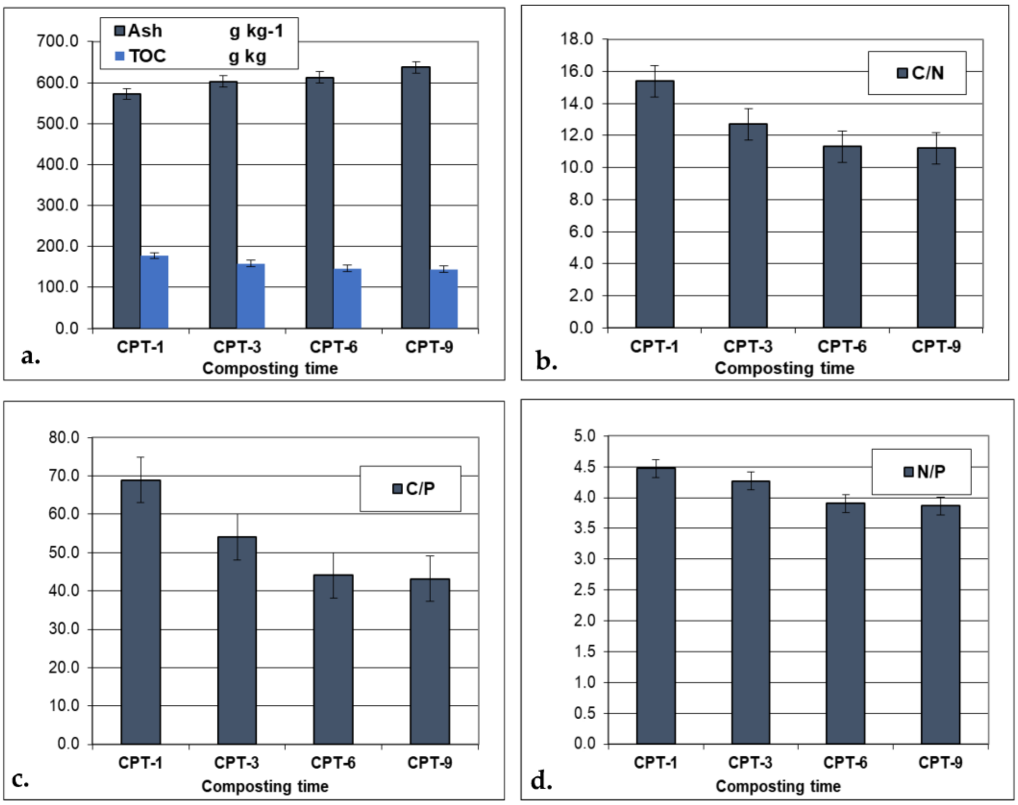

Figure 4. (**a**) Ash content (Ash) and TOC ratio; (**b**) C/N ratio; (**c**) C/P ratio; (**d**) N/P ratio, in the subsequent maturity stages of the MSWC (the bars indicate the standard error).

3.3. Dynamics of P Forms in Compost-Amended Soil

Enrichment of agricultural soils with organic waste materials continues to gain supporters and, providing that the necessary legal guidelines are followed, organic waste materials are considered to be a valuable source of macronutrients, including P. Unfortunately, there are still many aspects in this area that require further studies. These include the transformation and stability of P, which has often been analysed only in terms of its total content. The potential of compost application is very high, but may present some environmental limitations. The lower and higher doses of composts at different maturity levels applied in our study are meant to indicate both potentially undesirable and positive effects of introducing such materials into soils. The results of the pot experiment are displayed in Table 5 and in Figure 5a–f.

Table 5. The P indicators and the content of P_{ox} and P_{org} forms in compost-amended soil, expressed in % of P_t.

Soil Sample	I_w			I_{CaCl2}			PAC			P_{ox}			P_{org}		
	(in % of P_t)														
	CPT-1	**CPT-3**	**CPT-9**	**CPT-1**	**CPT-3**	**CPT-9**	**CPT-1**	**CPT-3**	**CPT-9**	**CPT-1**	**CPT-3**	**CPT-9**	**CPT-1**	**CPT-3**	**CPT-9**
LS	4.8	4.3	4.7	2.1	2.0	1.8	37.6	28.7	29.9	53.1	51.8	56.0	46.4	58.8	62.9
LS + CPT (100 t/ha)	4.9	3.9	4.7	2.3	1.8	2.0	38.7	37.5	42.7	51.1	55.0	58.5	34.9	47.2	44.7
LS + CPT (400 t/ha)	3.6	2.8	2.7	1.7	1.2	1.1	35.2	40.8	32.9	49.1	53.1	49.0	44.5	33.3	30.9

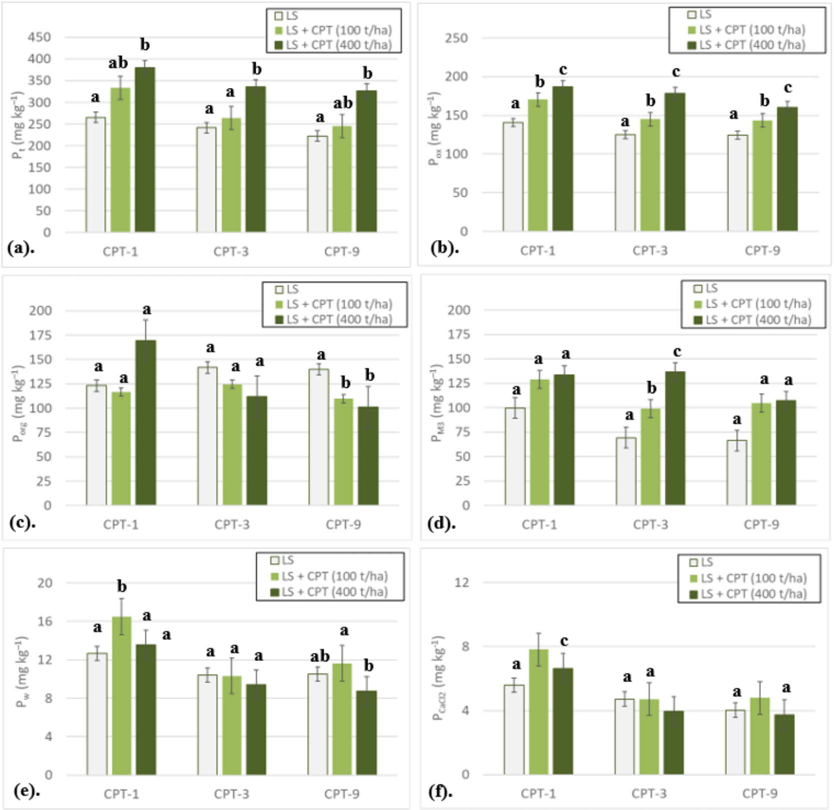

Figure 5. The effect of different compost doses and maturity on the content of P forms in the soil investigated: (**a**) P_t content; (**b**) P_{ox} content; (**c**) P_{org} content; (**d**) P_{M3} content; (**e**) P_w content; (**f**) P_{CaCl2} content. Explanation: LS—loamy soil; CPT—compost; CPT-1, CPT-3, CPT-9—compost maturity stages at 1, 3, and 9,months; LS + CPT (100 t/ha) and LS + CPT (400 t/ha)—compost-amended soil with 100 t/ha and 400 t/ha doses of compost. P forms: P_t—total content of P; P_{ox}—oxalic solution extractable P; P_{org}—organic forms of P; P_{M3}—available P; P_w—water soluble P; P_{CaCl2}—easily soluble P. Letters a, b, and c indicate significance of differences by RIR Tukey test at $p < 0.05$ (values marked with the same letter are not statistically significantly different). The bars indicate the standard error.

P total (P_t). The P_t content in the studied soil increased significantly after the application of compost only under the influence of the higher dose of compost in CPT-1, CPT-3, and CPT-9. The introduction of the lower dose (100 t ha^{-1}) did not cause statistically significant changes in P_t content (Figure 5a).

Organic P (P_{org}). The content of P_{org} increased only after the introduction of the higher dose of CPT-1 compost, but this was not a statistically significant result (Figure 5c). There were also no significant differences in P_{org} observed for the variants with CPT-3. However, the introduction of mature compost (CPT-9) resulted in a significant reduction in the content of organic P forms after the application of both the lower and the higher doses. The significant decomposition and remodelling of organic matter and the accompanying mineralization of P_{org} during composting at the mature stage only produced the effect seen in the cultivated soil. The content of P_{org} accounted for between 31 and 47% of P_t in the soil after the application of compost and, typically, these values were higher after the introduction of the lower dose.

Oxalate P (P_{ox}). The content of mineral forms of phosphorus, expressed as P_{ox}, was observed in the range of 49–58.5% of P_t in soil amended with compost, and increased significantly after compost application in all variants. The effect of the amount of compost applied was significant, and higher P_{ox} values were always observed after the introduction of the higher dose (Figure 5b).

Available P (P_{M3}). The content of bioavailable P also increased in all samples compared to the control soil (LS). Changes in the content of P_{M3} were paralleled by trends of P_{ox} content. However, only the effects after the introduction of CPT-3 were statistically significant, where both the lower and the higher doses induced higher P_{M3} content. This was reflected in the PAC value in the soil after the introduction of compost, which was within the range of 33–43%, and this was higher compared to LS. This effect is highly desirable and beneficial for the quality of cultivated soils (Figure 5d).

Water soluble P (P_w). A significant increase in P_w content was observed in the soil after application of the lower dose of CPT-1 compost. The higher dose did not cause significant differences. The amendment with CPT-3 and CPT-9 compost did not cause significant changes in P_w content in relation to LS (Figure 5e). The I_w index was within the range of 2.7–4.9% in the soils after compost introduction (Table 5). The above observations show that the large amounts of water-extractable forms of P released from the compost, especially at the initial stage of composting (CPT-1), pose less risk of leaching after introduction into the soil; however, caution should still be exercised during the application of immature composts, such as CPT-1.

Easily soluble P (P_{CaCl2}). The easily leachable phosphorus (P_{CaCl2}) increased markedly when immature compost (CPT-1) was added to the soil, with both the lower and higher doses causing statistically significant increases in P_{CaCl2} content (Figure 5f). However, the effect of the higher dose of compost was weaker. A significant increase in P_{CaCl2} content was also caused by the addition of CPT-9 compost, but the effect was evident only when the lower dose was introduced. After the application of mature compost, the effect of the increase in P_{CaCl2} content was definitely weakened, similar to that observed for P_w. The content of mobile forms of phosphorus in compost-fertilised soil showed similar trends. Higher concentrations were always observed for P_w compared to those for P_{CaCl2}, in the results for CPT-1, CPT-3, CPT-6, and CPT-9 composts. In compost-fertilised soils, the I_{CaCl2} content was in the range of 1.0–2.3%, indicating a level more than twice as low as that obtained for I_w. This relation ($I_w > I_{CaCl2}$) was expected, as has been evidenced by numerous reports from previous studies [53,72–74]. Higher P concentrations in deionised or distilled water extracts are associated with lower ionic strengths and the effect of different soil solution compositions on P solubility [75,76]. The easier transition of P into the water phase (P_w) relative to the weak salt solution phase (P_{CaCl2}) may represent a potential environmental problem. In particular, this may be a concern when organic matter is being extensively mineralised, for example, during composting, and when composts are used in agricultural areas where the availability of P to plants is essential, but an excess of its soluble form may pose a risk to surrounding watercourses [77,78].

Indicators of soil P status. An important issue associated with this topic is the effects of compost application on soil status in relation to P, which is assessed on the basis of P sorption capacity (PSC) and the degree of P saturation (DPS), according to which the environmental risks associated with the release of P are commonly estimated [79,80]. We also used other indicators (Table 7) that are considered to be useful for assessing environmental risks associated with problematic phosphorus management [54,56,57], which were the soil P storage capacity (SPSC) and P saturation ratio (PSR), previously mentioned in the Section 2. The estimations of these properties were based on the content of oxalate-extractable active forms of Al and Fe expressed in mmol kg^{-1} (Table 6) and P_{ox} associated with them (Figure 5b). Increases in the Al_{ox} and Fe_{ox} contents were observed in compost-amended soil, which was simultaneously reflected in the improvement of PSC in the soil (Table 7), allowing more P to be retained. The best effects were observed after the introduction of the higher dose of mature compost. The degree of phosphorus saturation (DPS) in MSWC-treated soils ranged between 28.2 and 38.3% (Table 7), which indicated higher values compared to the control soil (LS). At the same time, it was observed that the environmental threshold point (25%) of DPS was exceeded after the introduction of MSWC, mainly immature compost (CPT-1). A value of up to 25% of the DPS is a safe level of P saturation, described in the literature as a 'threshold point', 'environmental threshold' or 'point of change', exceeding which may be associated with the potential for increased release of P to the environment (water) from the soil [53,81–83]. Our study showed that this threshold was exceeded as a result of the addition of MSWC, but it should be noted that a threshold value of 25% was originally proposed for Dutch acidic and sandy soils, and for the whole soil profile up to 90 cm. This means that the values we obtained for the Ap level in MSWC amended-textured soils do not pose a serious environmental risk due to the higher mobility of P. In our soils, the increase in DPS only applies to the 0–30 cm level, while deeper in the soil profile the DPS values would probably be lower and unchanged by the addition of MSWC, although our pot experiment does not allow us to confirm this assumption. The issue of safe DPS levels, however, still requires more thorough research with regard to the application of composts to cultivated soils. The PSR values in the studied soils (Table 7) also indicate exceeding or approaching the environmentally safe PSR threshold [54]. The PSR shows the highest values after the application of immature compost (CPT-1). Composting time resulted in decreasing PSR values. The effect of compost on the PSR of the soil is apparent, its application rate resulted in an increase in PSR versus the control soil (SL). The SPSC is an indicator that shows the ability to retain P in the soil. When it takes on negative values, it indicates a very poor ability to maintain P in the soil, thus, showing that the ”change point” has been exceeded and the P concentration in solution has increased. In this case, when immature compost is applied, it takes on negative values. As the compost matures, the SPSC achieves higher values (positive), although negative values are still observed in soils fertilised with a higher dose of MSWC. The reflection of the values of these indices in the concentration of readily soluble forms of P has been repeatedly cited in the literature, and was also confirmed by our results, which we present using the PSR (DPS shows a twin relationship), SPSC, and PSC as examples (Figures 6 and 7).

Table 6. The content of oxalate-extractable Fe_{ox} and Al_{ox} in the studied soils.

Soil Sample	Fe_{ox} (g kg^{-1})			Al_{ox} (g kg^{-1})		
	CPT-1	CPT-3	CPT-9	CPT-1	CPT-3	CPT-9
LS	0.97	0.97	0.92	0.31	0.29	0.32
LS + CPT (100 t/ha)	0.93	1.08	0.97	0.33	0.34	0.31
LS + CPT (400 t/ha)	1.05	1.13	1.11	0.39	0.40	0.45

Table 7. Indicators of P status in the studied soils: Phosphorus sorption capacity (PSC), degree of P saturation (DPS), soil P storage capacity (SPSC), and P saturation ratio (PSR).

Soil Sample	PSC (mmol kg^{-1})			DPS (%)			PSR			SPSC (mmol kg^{-1})		
	CPT-1	CPT-3	CPT-9	CPT-1	CPT-3	CPT-9	CPT-1	CPT-3	CPT-9	CPT-1	CPT-3	CPT-9
LS	14.43	14.06	14.22	31.51	28.70	28.28	0.16	0.14	0.14	−0.22	0.18	0.25
LS + CPT (100 t/ha)	14.38	15.89	14.44	38.29	29.46	32.09	0.19	0.15	0.16	−1.19	0.09	0.33
LS + CPT (400 t/ha)	16.51	17.57	18.32	36.48	32.74	28.20	0.18	0.16	0.14	−1.07	−0.48	−0.30

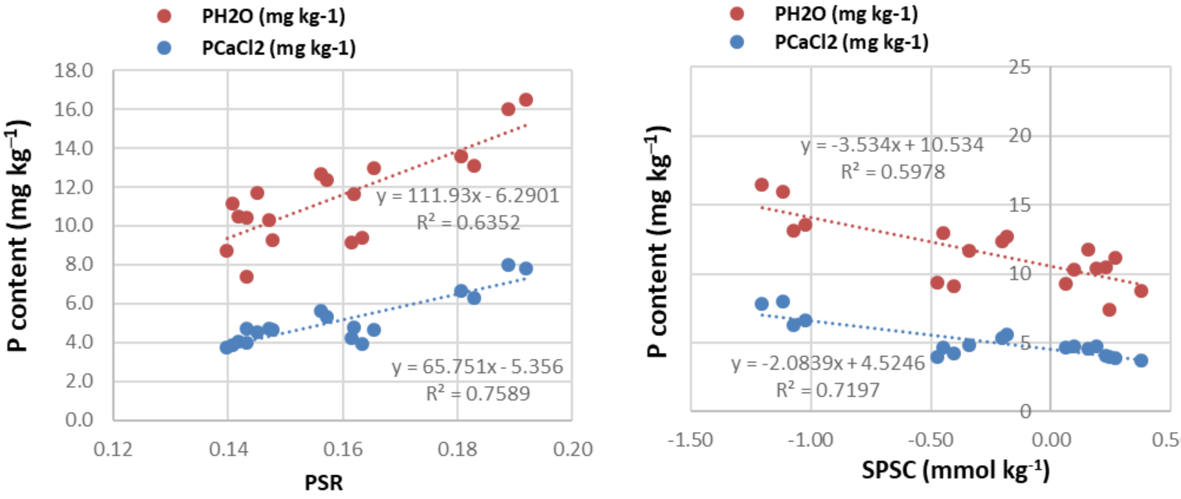

Figure 6. The relationship between the PSR and SPSC and the content of mobile P in P_{CaCl2} and P_w forms.

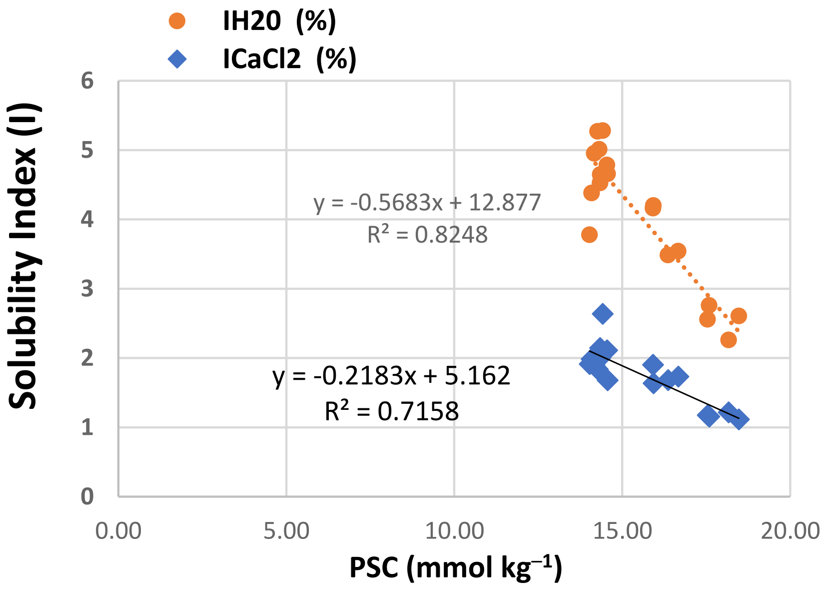

Figure 7. The relationship between the PSC and solubility indices (I_{CaCl2} and I_w).

In Table 8, the results of the correlations obtained between the values of the calculated P indicators and the forms of phosphorus are presented. The results confirm the trends and transformations of P forms observed as a result of using lower and higer doses of compost at different maturity stages. Based on these results, we can, once again, confirm the usefulness of these indicators for estimating the P status in soils and environmental risks associated with the P mobility (P_{CaCl2} and P_w) and, based on the PAC values, we can confirm the bioavailability of P in the conditions of the experiment.

Table 8. Correlation coefficients between P indicators and P forms in studied soils ($N = 18$, $p < 0.05$, significant coefficients marked with *).

Variable	PSC	DPS (%)	PSR	SPSC	PAC (%)	I_{H2O} (%)	I_{Ca} (%)
P_w (mg kg^{-1})	−0.51 *	0.80 *	0.80 *	−0.77 *	0.03	0.62 *	0.72 *
P_{CaCl2} (mg kg^{-1})	−0.32	0.87 *	0.87 *	−0.85 *	−0.23	0.35	0.67 *
P_{M3} (mg kg^{-1})	0.07	0.36	0.36	−0.35	0.63 *	0.03	−0.04
P_{org} (mg kg^{-1})	−0.20	0.18	0.18	−0.22	−0.37	0.06	0.08
P_{min} (mg kg^{-1})	0.44	0.78 *	0.78 *	−0.79 *	−0.41	−0.35	−0.02
P_{ox} (mg kg^{-1})	0.63 *	0.71 *	0.71 *	−0.73 *	−0.46	−0.55 *	−0.32
Pt_{HClO4} (mg kg^{-1})	0.66 *	0.63 *	0.63 *	−0.64 *	−0.64 *	−0.65 *	−0.41
Pt_{H2SO4} (mg kg^{-1})	0.31	0.79 *	0.79 *	−0.82 *	−0.54 *	−0.29	0.02

4. Conclusions

Our findings showed that the dynamics of P forms which occur, along with the progress of composting time are closely related to the transformations that organic matter undergo in the process. Thus, with the advancement of the composting stages, an increase in mineral P forms was observed, as well as a significant reduction in the content of P_{org}, resulting from intensive mineralization and remodelling of organic matter. The highest contents of mobile P forms, which were observed in immature compost (CPT-1), were also associated with this. In later composting stages, the content of P mobile forms was already much lower. The availability of phosphorus was higher in mature MSWC. The application of MSWC to the soil had a positive effect on the content of available P. The content of potentially mobile forms of P also increased significantly in the soil, primarily after the introduction of immature compost and confirmed by the significant correlations with the applied P indicators. However, the results indicate that the MSWC we studied does not pose a serious environmental risk due to excessive P mobility and could become a potential source of P in the soil, contributing thus to a reduction of the need for mineral P fertilisers. An indisputable benefit of using MSWC (and other organic amendments) as a renewable source of P in agriculture is the supporting role of organic matter in reducing the P sorption in the soil, which we observed in as an increase in the available and soluble forms of phosphorus in the soil. Therefore, it is important to monitor the use of composts on soils with a very high available P content (and high DPS), as this may result in undesirable over-activation of P into the environment, especially for the case of immature composts. In conclusion, the use of MSWC in agricultural soils is possible and potentially profitable, although the material used for this purpose should be mature. The evaluation of compost suitability as a P fertiliser or amendment should not be performed only on the basis of the total content of P, but needs to be developed showing the dynamics of different P forms that reflect the level of P availability, but also indicate potential environmental threats, such as the high value of DPS and the content of easily leached P forms.

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