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Fractionation and distribution of phosphorus in acid soils: Review

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Abstract

Phosphorus (P) availability is commonly assumed to limit productivity in many tropical soils, yet there is relatively little information on the phosphorus chemical forms, distribution, and transformations that P acid soil. The best way to obtain of separate fractions of phosphorus in soil using series of solvents of different strength is sequential analysis. The method used was Chang and Jackson sequential analysis. Formation of the forms of soil phosphorus and their binding largely depends on soil pH. In neutral and alkali soils the main phosphate compounds are calcium phosphates, and their solubility depends mainly on the ratio Ca/PO₄. In such soils, the activity of Ca ions increased resulting in reduced solubility of phosphate while in neutral and acidic soil the adsorption and desorption of phosphate mainly occurs at Al and Fe oxide surfaces.

Keywords: Chemical forms, phosphorus, sequential

Introduction

Phosphorus (P) is one of the essential nutrients for plant growth, and is of particular interest in highly weathered tropical and sub-tropical soils (Brady and Weil, 2002) ^[18]. Phosphorus (P) is a limiting nutrient for terrestrial biological productivity. Next to N, P has more widespread influence on both natural and agricultural environments than any other essential elements (Brady and Weil 2002) ^[18]. Several authors reported that P supply and cycling rate act as fundamental control on nitrogen fixation, carbon and sulfur dynamics, and P availability limits overall productivity in many natural ecosystems (Pieri, 1992) ^[36].

The forms, contents, distributions, transformations, and availability of P in soils vary among soil types and may depend on one or combinations of soil properties. The soil properties that influence soil P pools are discussed by (Borggaard *et al.* 1990) ^[17]. Strong correlation between these soil properties and various P pools were reported. These soil properties include soil pH (Brady and Weil, 2002) ^[18], clay content and nature of clay minerals (Pandey *et al.*, 2000) ^[35], soil organic matter (Summer, 1997) ^[45], soil CEC. Amorphous and crystalline Al and Fe oxides in acidic soils and calcareous compounds in basic soil have close relationships with P pools (Borggaard *et al.*, 1990) ^[17]. Strong correlation between these soil properties and various P pools does not show direct influence of the properties on the P pools. Correlation analysis may inadequately describe relationships because correlation does not insure that direct-cause-effect relationship exists (Wright, 1921) ^[49]. Direct-cause-effect relationship also cannot be done by straight regression, either simple or multiple, because soil properties are commonly intercorrelated. To predict direct cause-and-effect relationships between soil properties and soil P pools path analysis model is important statistical tool which is also adopted by most agricultural and other biological scientists.

Sequential analyses

The ways phosphates bound to soil particle are the parts of a puzzle whose solution can give many answers concerning their availability to plants and the possible leaching down the soil profile. The best way to obtain the answers is isolation of separate fractions of phosphorus in soil using series of solvents of different strength, i.e. sequential analysis.

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Chang and Jackson sequential analysis

Most operationally defined schemes available address inorganic forms of phosphate. The main inorganic forms of P are the fraction adsorbed by exchange sites and referred to as loosely bound, labile or exchangeable P, the fraction associated with Al, Fe and Mn oxyhydroxides, and the fraction in Ca-bound compounds generally referred to as apatite P or Ca-bound (Ruban *et al.* 1999b) ^[38].

Fraction of soil P extracted by 1M solution of ammonium-chloride (water-soluble P)

This fraction of phosphorus is closely linked with the dynamics of P bounding in soil. Such bounding of phosphorous ions can be characterized as an initial reaction. And it represents a non-specific adsorption and ligand exchange on mineral edges or by amorphous oxides and carbonates. This fraction is bound to Mn isolated in step 2 from Table 1 (Mn II) ($r=0.994$, **), which indicated its sorption on hydrated oxides of manganese. Due to specific further bounding of phosphorus, this fraction is very low in quantity (less than 1 % of the total mineral phosphorus) in acidic soils such as Stagnosol. Passage of this form of phosphorus into bounded-to-aluminum phosphorus is a process characteristic for acidic soils. The reverse process is also possible (correlation coefficients 0.974 and 0.780 for 0-30 and 30-60 cm, respectively). A very strong correlation between water-soluble P and available P (0.945 and 0.715 for 0-30 and 30-60 cm, respectively) proved that this form of phosphorus was available for plants.

Fraction of soil P extracted by 0.5M NH₄F solution (Al bound P)

Such an isolated fraction of phosphorus is a characteristic for monodent and bident bounds (Tisdale *et al.*, 1993) ^[40]. Consequently, these compounds are very labile and are described as pseudo sorption (Van der Zee *et al.*, 1988). In acid mineral soils, such as Podzols, P is mostly retained by Al and Fe oxides by the ligand exchange mechanism where the OH- or H₂O groups of sesquioxides surfaces were displaced by dihydrogenphosphate anions (Simard *et al.*, 1995) ^[42]. In certain soils, this bound is not strictly confined to Al but can bound bind to Si, as well (Manojlovic, *et al.* 2007) ^[30]. However, in the studied Stagnosol, the strong correlation of Al-P with Al extracted in the step 2 (Al II) could be attributed to carbonates and aluminosilicates ($r=0.998$ **)

Fraction of soil P extracted by M NaOH solution (Fe bound P)

Fraction of soil P isolated by such a strong reagent may have a high content in soil and mainly is greater than that bound to Al (Manojlovic *et al.*, 2007) ^[30], ranging between few hundred mg per kilogram. From the chemistry viewpoint, such bounded P is characteristic for the slow-flowing processes involving formation of covalent Fe-P or Al-P bonds on Fe and Al oxide surfaces (Willett *et al.*, 1988) which can be an additional source of available P (Beck & Sanchez, 1994) ^[10]. However, the strength of this bound is quite high. Therefore, its availability is limited. That determines the absence of correlation between the mentioned fraction and the available P. However, in the

layers of soils such as Stagnosol, due to constant wetting and alteration of oxidative – reductive conditions, the content of this form of P can be as low as less than 1 mg per kilogram due to passage into other forms (reducible and occluded). Its movement along the soil depth is also limited as indicated by the absence of correlation between the values at different depths. Sequential analysis didn't show marked correlation with the fraction of Fe, but the correlation with DTPA-extractable Fe was recorded (0.665*).

Fraction of soil P extracted by M Na dithionite, Na citrate solution (Reducible P)

In contrary to the previous types of bounding of P in soil, this fraction is characterized by the bounds within the particle. Such bounding results in the process of occlusion where the phosphate is adsorbed to the surface of Al hydroxide and is bound by poorly crystalline Fe oxides from that occluded in the crystalline Fe oxides (Delgado & Scalenghe, 2008) ^[22]. In this structure, the phosphate binds the Al- with Fe³⁺ hydroxide so the surface of Al phosphate particle is enveloped by a Fe³⁺ hydroxide skin. Such adsorbed phosphates are only indirectly available to plants. Thus, in the conditions determined by reduction processes the reduction of iron Fe²⁺ and the breakage of the earlier formed bounds take place, which makes this form of P available for plants. Although this fraction is small compared to other fractions of P in soils, under the oxidized conditions Fe-P represents the dominant fraction (Manojlovic *et al.*, 2007) ^[30]. But under the conditions of soil undergoing alterations of wet and dry regimes with high content of available Fe (Cakmak, D. *et al.*, 2010) ^[13] the reducible-P can be of significant concentration up to 30% from the total mineral P. The high correlation found between the reducible and Al bound P ($r=0.97$ **) indicates the indirect availability of this form of P under the alteration reduced conditions in Stagnosol.

Fraction of soil P extracted by M NaOH solution (Occluded P)

Chang & Jackson (1957) ^[21] noticed that during the sequential extraction some soils, rich in Fe oxides, contain significant amounts of Fe-phosphate occluded within the oxide, which cannot be extracted by sodium dithionite and sodium citrate. This occluded phosphate can be extracted by repeated alkali solution. The P tied in this manner might be increased in quantity by constant addition of mineral phosphate fertilizer where its total content ranges between few milligrams to tens of milligram per kg soil; i.e. in small amounts from 1% to about 10% from the total mineral P (Manojlovic *et al.*, 2007, Mustapha *et al.*, 2007) ^[30]. Under the alteration of reduced and oxidized conditions that predominate in Stagnosol, this form is chemically tied to the reducible form of P, especially, in the upper soil layer ($r=0.890$ **). Also, within such soil particle, Al-phosphate can be present, which can be available under certain conditions within Fe-oxide (Fig.4). Its migration along the soil depth is limited and is of very low mechanic intensity. Absence of correlation with DTPA extractable Fe indicates the un-availability of Fe in such compounds.

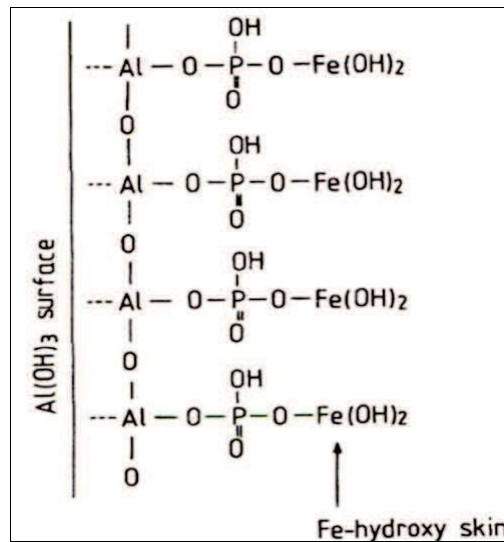


Fig 1: Fe-hydroxy skin covering the phosphate adsorbed to Al oxide/hydroxide (Mengel & Kirkby, 2001)

Fraction of soil P extracted by M H2SO4 solution (Ca bound P)

In neutral to calcareous soil the concentration of phosphate in soil solution is governed mainly by the formation and dissolution of calcium phosphates. This in turn depends on soil pH and Ca²⁺ concentration in soil solution. The lower are Ca/P ratios in the Ca phosphates -the higher is their solubility in water. However, in acidic soils in spite of significant amount of this fraction (up to 40% from total mineral forms) the Ca-P was widely dispersed in soil minerals and it was weakly changeable. This is supported by the absence of significant correlation between exchangeable

Ca and Ca- bound P. Therefore, in such soils fertilization does not result in significant changes in the content of Ca-bound P (Hartikainen, 1989) [23]. However, relative increase of this fraction is possible in the subsurface soil layer due to leaching and accumulation of Ca ions, under acidic conditions, in deeper layers where it is transformed into non-labile phosphate fractions. This process of phosphate ageing is especially rapid in acid soils with a high adsorption capacity. The start of this process can also be detected by the negative significant correlation between water-soluble P and DTPA extractable Ca (-0.590*)

Table 3: Phases of soil phosphorus and the reagents used for their sequential extraction

Procedure	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6
Manojlovic (2007) [30] modified from Chang & Jackson (1957) [21] BCR (Ruban <i>et al.</i> , 2001) [38]	1M NH4Cl	0.5 M	0.1 M NaOH	0.3 M Na dithionite, Na	0.1 M NaOH	0.25 M H2SO4
	Water soluble P	NH4F Al bound P	Fe bound P	citrate	Occluded P	Ca bound
				Reducible P		P
	1M NaOH	3.5 M HCl	1M NaOH	1M HCl + calcination	3.5 M HCl + calcination	
	NaOH - P	HCl - P	Inorganic P	Organic P	Conc HCl - P	

Fraction of soil P extracted by 1M NaOH (Al-Fe-Mn bound P)

This fraction of phosphorus bound to oxides and hydroxides of aluminum, iron and manganese, so called oxide-hydroxide fractions was extracted in step 1 (Tab. 3). The associations of P and Fe are often found in sediments, where phosphorus is tied to complex compounds of iron through changes of ligands (Stumm & Morgan, 1981). In soils such as Stagnosol, this fraction of phosphorus is correlated with Ca from the second phase (Ca II, Table 1) (r=0.951, **) that indicates binding of phosphorus with carbonate fraction. Such bounds are quite labile, what is supported by a strong correlation between Al-Fe-Mn bound P with available P with corresponding coefficients 0.782 and 0.813 (for 0-30 and 30- 60 cm, respectively). The correlation coefficients between HCl -P and available P were 0.939 and 0.902 (for 0-30 and 30-60 cm, respectively). The good correlation of the Al-FeMn fraction with Al-P fraction from Chang and

Jackson method (r=0.775, **) explains the leaching of Al-Fe-Mn bound P fractions from the surface to the subsurface soil layer (r=.901, **) (Fig. 5).

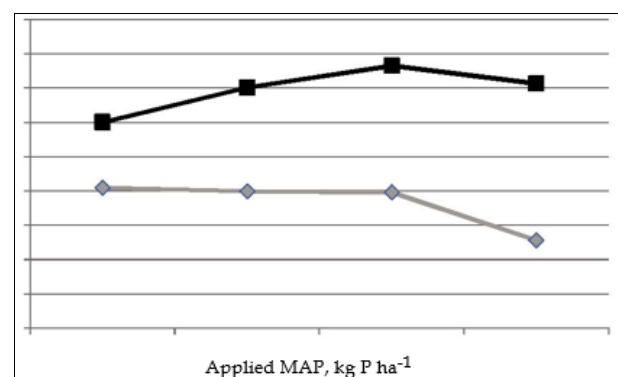


Fig 2: Ratio of NaOH bound P (BCR) to Al bound P (Chang & Jackson) in the 0-30 cm and 30-60 cm soil intervals

Fraction of soil P extracted by 3.5 M HCl (Ca bound P)

This fraction generally represents the phosphorus in apatite (Williams *et al.*, 1976; William *et al.*, 1980)^[48] and phosphorus bound to Ca (Golterman, 1996, 1982) and was extracted in step 2 (Tab. 3). The adsorption of phosphorus in calcium carbonate is one of the mechanisms of formation of calcium phosphate in sediments. However, apart from the

Fe bound phosphorus, formation of CaPO₄ is possible by sedimentation. The behavior and distribution of this fraction is similar to the fraction described above (HCL-P/CaII, $r=0.965, **$). Its distribution along the soil profile is also analogous to the above described fraction of phosphorus (Fig. 3).

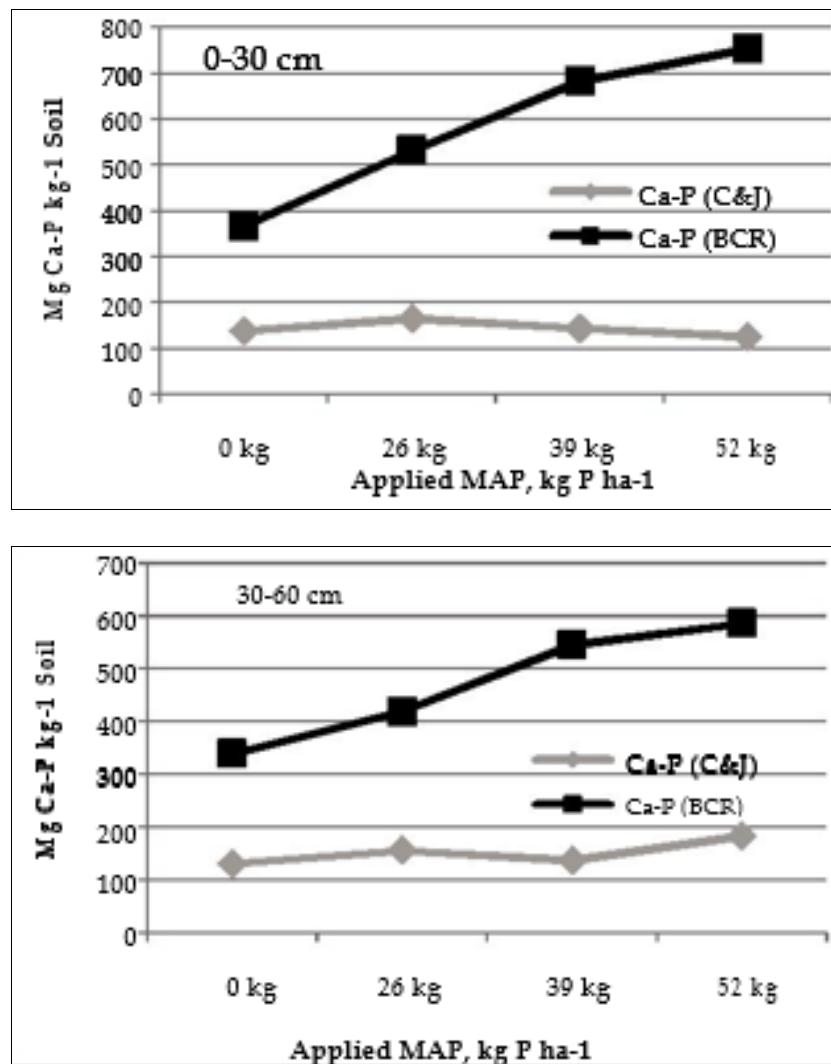


Fig 3: Distribution of Ca bound P in the two applied methods: Chang & Jackson and BCR in the two soil intervals upon 40-years application of phosphate fertilizer

Fraction of soil P extracted by 1M NaOH (Inorganic P; IP):

This fraction is supposed to consist of the later two fractions (Al-Fe-Mn bound P and Ca-P) however, due to the different extracting reagent used for their separation, we have isolated this fraction by extraction in step 3 (Tab. 3). The fraction of inorganic phosphorus in our study was highly correlated with Ca II (Tab. 1), what is the consequence of the decrease of bioavailable phosphorus in the soil. Good correlation of IP with Ca and Al extracted in step 3 of the sequential analysis (Tab. 1) highlights the roles of Ca and Al in the fixation of phosphorus in soil. The decrease of the bioavailability of this fraction is supported by a moderately good positive correlation with the occluded phosphorus ($r=0.619 *$).

Soil physical characteristics

Long-term application of phosphate, besides the direct influence on the content and forms of P in soil, also

influences the other soil properties. It can affect the structure of clay minerals where fractions of P can replace Al ions from the tetrahedral structure thus destructing the structure and pulverizing clay minerals (Rajan, 1975)^[37]. Long-term fertilization with MAP distinguished that phenomenon since the changes in soil texture were due to the amount of added P, i.e. in the experiment a significant increase of clay fraction was detected correspondingly to the rates of fertilizer, which is the result of fragmentation of clay particles.

Soil chemical characteristics

Acidity (pH)

Mineral fertilizers can change the soil pH depending on the dominance of alkali or acidic components. Because in MAP the acidic components predominates, since in soil the process of nitrification leads to formation of nitrate ions, the long-term fertilization unavoidably results in acidification

(Magdof *et al.*, 1997) [29]. Since the amounts of nitrogen components in the applied fertilizer were small and due to the negligible effect of phosphoric components, the decrease in soil pH after 40-years of application of MAP was slight but significant ($p < 0.05$ (Tab. 4). It should be mentioned that the other phosphoric fertilizers without nitrogen components did not have a negative impact on soil pH even after long application.

Available phosphorus (Al-method)

Available phosphorus is a fraction of P that is considered available for plants. Chemical extraction is based on solvents, which more or less imitate adsorptive power of plant root. Phosphorus in the first four fractions obtained by the Chang & Jackson method by definition is more or less available to plants but this fact was not confirmed in the 40-year field experiment of application of MAP on Stagnosol. Absence of correlation between the available P and Fe-P is

probably due to the low amount of Feposphate found in this experiment ($< 1 \text{ mg kg}^{-1}$). Based on the results of coefficient of correlation, the direct correlation between the available forms of P is recorded for water soluble P and the P bound to Al at both depths (for 0-30 cm is 945** and 987** respectively; for 30-60 cm 715** 888** respectively). On the other hand, reducible phosphate is indirectly correlated with the available P via water-soluble and Al bound P. The bounds of occluded P in the first depth with water-soluble ($r = .585^*$) and in the second depth with water-soluble and Al-P indicates on its possible availability under the extreme conditions of wetting and drying, characteristic for Stagnosol. Except the Ca-bound phosphorus, all the fractions of soil P showed increasing trends accordingly to the applied phosphate fertilizers where the Al-bound phosphorus showed the clearest increasing tendency (Fig. 4).

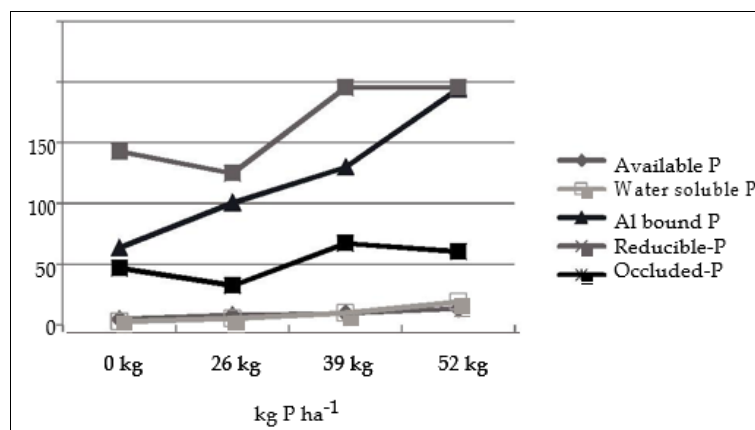


Fig 4: Concentrations soil P extracted by different methods upon 40-years application of phosphate fertilizer

Mobile Al: One of the indirect consequences of phosphate fertilization that acidifies the soil is the increase in the amount of mobile Al. Soil acidity is caused by the formation of H⁺ ions in the soil solution, which is neutralized by Al and Fe oxy/hydroxy complexes (Schwertmann *et al.*, 1987) [41] where the end product of neutralization are species of Al cations such as Al³⁺, Al (OH)²⁺, Al (OH)²⁺. Connection of these two processes is confirmed by a high correlation between soluble Al and decreases in soil pH ($r = .897^{**}$). It is known that the solubility of Al progressively increases below 5.5 soil pH (H₂O) (Mrvic *et al.*, 2007) [34]. In our experiments, in the 26 kgPha-1, treatment in the subface soil the amount of mobile Al is doubled versus to control (Tab. 4).

Exchangeable cations and CEC: A recent research showed that the decrease of exchangeable Ca and Mg with P fertilization is caused by their replacement with H⁺ ions and leaching to layers down the soil profile (Belay *et al.*, 2002) [11], immobilization by phosphates, and by their assimilation by plants. However, destruction of clay minerals as affected by phosphorus and increase in CEC reduces the leaching. In soils with pH above 5.0, increases in acidity results in destruction of minerals, i.e. exchangeable Ca²⁺ and in lesser degree Mg²⁺, might be derived from structure of soil primary minerals thus increasing the Ca availability in soil solution (McLaughlin & Wimmer, 1999) [32]. This process of releasing Ca and Mg is much weaker than that of Al because the release of cations is proportional to charge,

which results in higher amounts of cationic species in the soil solution. Under 40-years of phosphate application, the amount of exchangeable Ca is increased (Tab. 4), although the increase was not regular but significant in the surface soil due to the mentioned reverse processes.

Microelements

The content of microelements in the soils depends on their amounts in the soil-forming rocks and on the soil-forming processes. The role of microelements in the physiological and the biochemical processes is immeasurably great. Soil is a source of microelements for plants, animals and humans. Deficiency or excess amount of microelements in fodders and food products lead to the disturbance of exchange of substances and the appearance of diseases in plants, animals and people. Basic for the vital activity of the plants and other living organisms are manganese, copper, boron, zinc, molybdenum, nickel, cobalt, fluorine, vanadium, iodine. One of the anthropogenic sources of microelements in soil is agriculture, including the application of phosphate fertilizers.

Iron solubility

Is controlled both by pH and redox potential. Iron becomes more soluble at lower pH values and under reduction condition. Iron solubility is largely controlled by the solubility of the hydrous Fe³⁺ oxides. At higher pH levels the activity of Fe³⁺ in solution decreased for 1000 time for each pH unit rise (Lindsay, 1974). When soil is

waterlogged, the reduction of Fe^{3+} into Fe^{2+} increases the solubility of Fe. On the other hand, application of phosphate and its immobilization by formation of compounds with Fe, results in decrease in the amount of DTPA-extractable Fe, what is supported by the absence of correlation between mobile Fe with reducible and occluded P. Application of phosphate during 40- years determined the antagonistic processes fully took place, i.e. a small increase in DTPA extractable Fe in the treatments where the processes of acidification are active was detected ($p < 0.05$) (Tab. 7).

Zinc solubility is decreased with increasing of soil pH (Cakmak, I. *et al.*, 1996) [14] where phosphates can immobilize Zn as zinc phosphate $\text{Zn}_3(\text{PO}_4)_3 \cdot 4\text{H}_2\text{O}$, although this theory is not fully proved (Jurinak & Inouye 1962) [26]. However, application of MAP has shown opposite results for the second depth (30-60 cm) (Tab. 6, 7). Consequently, in the subsurface soil the content of the total Zn increases ($p < 0.05$) versus control. This in turn probably resulted in leaching of Zn due to acidification of the surface soil. On the other hand, the decrease of the amount of DTPA-extractable Zn is evident ($p < 0.05$) what can explain the prevalence of the processes of immobilization of Zn by phosphorus.

Copper similarly to Zn responded to the changes in soil pH. However, its solubility is quite lowered due to very strong bounds of Cu with soil organic matter (Mc Bride 1989). Reduced conditions in Stagnosol ties Cu with iron forming cuprous ferrite, possibly controlling Cu solubility, which depends on the solubility of Fe (Shuman, 1985) [43], which was reflected in significant correlation between soluble Fe and Cu. The amount of fluorine in phosphate fertilizers depends on geographic origin of the raw material and the degree of its treatment. In fertilizers such as MAP this amount is not negligible (Tab 5). There was no significant increase in the amount of total F (Tab. 6, 7); the values were near or within the world's average (Helmke, 2000) [24]. Solubility of fluoride ions is controlled by the soil pH and the amount of soil Ca and P (Hurd-Karrer 1950) [25]. But it should be noted that P affects the availability of F only in case of very high amounts of P in soil. Therefore, in our experiments a statistically significant increase of soluble F was detected in the both soil depths in accordance with the rates of the applied fertilizer, which presumably were induced by the decrease of soil pH ($r = -0.92$ $p < 0.01$) (Loganathan *et al.*, 2006) [28]. The significant increase of the amount of soluble F in the subsurface soil might be due to its leaching from the upper soil layer.

Conclusion

Formation of the forms of soil phosphorus and their binding largely depends on soil pH. In neutral and alkali soils the main phosphate compounds are calcium phosphates, and their solubility depends mainly on the ratio Ca/PO_4 . In such soils, the activity of Ca ions increased resulting in reduced solubility of phosphate while in neutral and acidic soil the adsorption and desorption of phosphate mainly occurs at Al and Fe oxide surfaces. The bounds Al-O-P forms much more labile forms than formations with double bounds of P. Al bound P is the most labile form that supplies the plants with P-nutrient, and is the most responsible form for the movement of P along the soil profile and replenishment of other soil P-fractions. Both sequential analyses used for P fractionation proved that Al bound P fraction is closely related to the mobile Al of soil solution. Application of

mineral phosphates results in the increase of Al bound P fraction thus increasing the amount of plant-available phosphorus in soil. In acidic soils, the application of MAP doesn't results in considerable changes in the amount of Ca-bound P and of organic P in soil. Also, the 40-year application of MAP destroys the structure of the clay minerals what in its turn increases the soil CEC. The long-term application of MAP didn't result in the accumulation of potentially toxic elements in their considerable concentrations, i.e. their concentrations were negligible in Stagnosol. An important outcome is that soil P can exist in a series of "pools", which can be defined in terms of the extractability of P in different reagents. Also, the P in these pools can be related to the availability of P to plants, recognizing that there is a continuum of both extractability and availability. The most important concept is the reversible transfer of P among the most of soil phosphorus pools, what opens a possibility of the effective use of the applied phosphorus. These complex transformations of soil phosphorus grant wide opportunities for further researches.

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