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Phosphorus: Chemism and Interactions

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1. Introduction

Phosphorus (P) is a limiting nutrient for terrestrial biological productivity. The availability of "new" P in ecosystems is restricted by the rate of release of this element during soil weathering. Soil P exists in inorganic and organic forms. Inorganic P forms are associated with amorphous and crystalline sesquioxides, and calcareous compounds. Organic P forms include the relatively labile phospholipids and fulvic acids and the more resistant humic acids. The intergrades and dynamic transformations between the forms occur continuously to maintain the equilibrium conditions (Hedley et al., 1982). Its low concentration and solubility (< 0.01 mg P kg^{-1}) in soils, however, make it a critical nutrient limiting plant growth.

In natural soil ecosystems the main source of inorganic phosphorus is rocks where the primary minerals are of the greatest importance, where in turn calcium phosphates are the most important (e.g. apatite) (Fig.1). In weathered soils, leaching of Ca ion results in formation of Al-phosphate (e.g. berilinite) and Fe-phosphate (e.g. stregnite); the complete list were given by Lindsay, (1979) and Lindsay, et al., (1989). By the definition, these minerals are characterized with three-dimensional atomic structure. As far as phosphorus concentration in the soils is concerned, it can be very low from 50 mg kg^{-1} and high up to 3500 mg kg^{-1} (Foth & Ellis, 1997; Frossard et al., 1995). Application of phosphorus from mineral phosphate results mainly in formation of amorphous compounds with soluble Al, Ca and Fe where the phosphorus is adsorbed on the surfaces of clay minerals, Fe and Al oxyhydroxides or carbonates and physically occluded by secondary minerals.

In natural ecosystems, P availability is controlled by sorption, desorption, and precipitation of P released during weathering and dissolution of rocks and minerals of low solubility (Sharpley, 2000). Due to high fixation and immobilization of phosphorus in the soil, the agriculturists apply high amounts of p-fertilizer, what results in greater input of P into soil that plant uptake. Application of phosphates can maintain or improve crop yields, but it can also cause changes in the chemical and physical properties of the soil, both directly and indirectly (Hera & Mihaila, 1981; Acton & Gregorich, 1995; Aref & Wander, 1998; Belay et al., 2002). The cumulative accumulation of available P in agricultural soils may partially saturate the capacity of a soil for P sorption, with resulting increase of P leaching into the subsoil layers (Ruban, 1999), or may sometimes reach depth more than 90 cm (Chang et al., 1991), suggesting that erosion, rather than leaching, would cause a threat to water bodies (Zhou and Zhu, 2003). Such a process of leaching is especially effective in soils of Stagnosol type with clear E horizon due to their lower adsorption capacity, with relatively shallow

ground waters (Tyler, 2004; Väänänen et al., 2008). Fertilization with mineral P in the inorganic pools explains 96 % of the variation in the level of available phosphorus (Beck & Sanchez, 1994).

Great number of researchers studied many aspects of fate and behavior of applied P. However, the chemical processes and following plant availability of soil P remains a big challenge for scientists since it offer wide spectrum of uncertainties, and contradictions. This Chapter is devoted to explanation of mechanisms and distribution of different forms of phosphorus, its transformation and dynamics in the soil based upon the 40-years of experience in phosphate field application.

2. Materials and methods

2.1 Site description

The investigation was conducted at the Varna experimental station, 44°41'38'' and 19°39'10'' (near Belgrade, Serbia), where a wide range of different fertilization treatments has been undertaken since 1968. The soil type is Stagnosol (WRB, 2006), a loam textured Pseudogley developed on Pliocene loam and clay materials under aquic conditions at 109 m above sea level. Average annual precipitation of the site is 705 mm, and the average temperature is 12°C. The mineralogical composition of the studied soil was as follows: illite (50–70%), vermiculite (10–30%), and other clay minerals (kaolinite, chlorite, feldspar, quartz and amphibolites) (Aleksandrovic et al., 1965). The cultivated crops were winter wheat (*Triticum aestivum* L.) and corn (*Zea maize* L.), with crop residues removed. The soil cultivation was performed by a standard plowing to 25 cm depth.
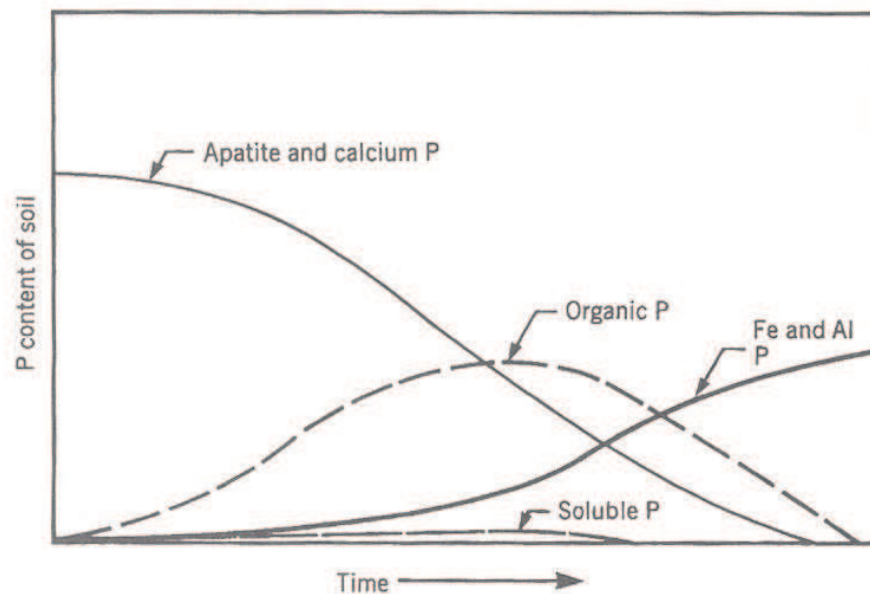

Fig. 1. Relative distribution of the major forms of soil P vs time of the soil development (Foth & Ellis, 1997)

Three rates (26, 39, and 52 kg P ha−1) of monoammonium phosphate (MAP) fertilizer (NH4H2PO4) were applied in combination with a consistent rate of N (urea) (60 kg ha−1) and K (KCl) (50 kg ha−1) for 40 yr of the experiment. The fertilized treatments were

compared to the control, with no fertilizer applied. The experiment was arranged as a randomized block design, with each treatment randomized in three blocks for a total of 12 plots. Each plot was 5 by 11 m. Composite samples of five soil subsamples were taken from each plot in the three field replications from two depths: surface (0–30 cm) and subsurface (30–60 cm) layers in spring 2008.

2.2 Methods

Soil pH was determined with a glass electrode pH meter in a 1:2.5 water solution. Soil total C and N were measured with an elemental CNS analyzer, Vario model EL III (ELEMENTAR Analysasysteme GmbH, Hanau, Germany; Nelson & Sommers, 1996) Available P and K were determined by the Al-method of Egner–Riehm (Enger & Riehm, 1958), where 0.1 M ammonium lactate (pH = 3.7) was used as an extract. After the extraction, P was determined by spectrophotometry after color development with ammonium molybdate and $SnCl_2$ (Enger & Riehm, 1958). Soil Ca and Mg were extracted by ammonium acetate and determined with a SensAA Dual atomic adsorption spectrophotometer (GBC Scientific Equipment Pty Ltd, Victoria, Australia; Wright & Stuczynski, 1996). Determination of CEC was performed by the steam distillation method after the treatment with 1 M ammonium acetate (Sumner & Miller, 1996). Exchangeable Al was determined by the titration method by Sokolov: the extraction with 1 M KCl (1:2.5) followed shaking for 1 h and titration with 0.01 M NaOH (Jakovljević et al., 1985).

Trace elements were determined with an ICAP 6300 ICP optical emission spectrometer (Thermo Electron Corporation, Cambridge, UK), after the soils were digested with concentrated HNO_3 for extraction of hot acid-extractable forms, and by diethylenetriaminepentaacetic acid (DTPA) for extractable elements (Soltanpour et al., 1996). The F content was determined by ion-selective electrode, after the soil had been fused with NaOH for total F and after extraction with water for available F (Frankenberger et al., 1996). Soil granulometric composition was performed using the pipette method (Day, 1965). All chemical analyses were performed in two analytical replications. The Merck standards were used for the determinations on ICP and SensAA Dual. Before the determination of samples, three blank samples were read, which allowed correcting the results. For the verification of the results, a referent soil sample was determined for all the studied elements (NCS ZC 73005 soil, CNAC for Iron and Steel, Beijing).

Statistical analyses were performed with the SPSS version 16 software. The effects of treatments on all the variables were tested by ANOVA. Statistical differences between the treatments were determined using the *t* test (95%) Pearson for Fisher's LSD. The significance of their correlations was analyzed via the Pearson correlation matrix (SPSS, 2007).

3. 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.

3.1 Sequential extraction procedure

One of the most common phase divisions for sequential extraction was used in the experiment:

Exchangeable or *sorptive* (*adsorptive and ion exchange*) *phase*. This phase is used to estimate the maximum quantity of sorbed ions that geological material can release, without visible decomposition of some mineral phases. Neutral solutions of salts (NH_4OAc, $MgCl_2$, $CaCl_2$, $BaCl_2$, KNO_3, etc.) are usually used for this extraction phase. Their concentrations (and ion forces) must be high enough to initiate the most complete ion exchange and desorption from all substrates.

"*Easily reducible*" *phase*. Weak reduction means (for example, hydroxylamine) are used for selective reduction (solvent) of manganese oxyhydrates, but they are also used for the most mobile fraction of amorphous iron oxides. All the present microelements co-precipitated in these oxides to be detected in the solution.

"*Moderate reducible*" *phase*. For the amorphous iron oxides and the more crystalline manganese oxides, some stronger reduction means are used – oxalic acid, sodium dithionite and similar methods.

Organic-sulfide phase. Distinguishing of organic and sulfide metal fractions in a geological material is one of the disadvantages of sequential extraction. This problem is still unresolved. Pure nitric acid or its combinations with other acids is very effective, but it leads to a noticeable decomposition of silicate material. The use of hydrogen peroxide is acceptable at higher temperatures and low pH (about 2).

Residual phase. This is the least interesting phase of the ecochemical aspect as it includes silicate and oxide materials as well as incorporated metal ions, i.e. in natural conditions this fraction cannot be mobilized from geological material. Concentrated mineral acids and their mixtures are usually used for decomposition of this crystal matrix (Petrovic, et al., 2009) (Tab. 1).

Procedure	Step 1†	Step 2	Step 3	Step 4	Step 5
Petrovic et al. (2009)	1 M CH_3COONH_4 Exchangeable	0.1 M $NH_2OH \cdot HCl$ Bound to carbonates and easily reducible	0.2 M $(NH_4)_2C_2O_4$ and 0.2 M $H_2C_2O_4$ Moderately reducible	30 % H_2O_2 + 3.2 M CH_3COONH_4 Organic-sulphide	6M HCl Residual

Table 1. Reagent in the sequential extraction procedure used to study substrates metals (Fe, Al, Mn and Ca) and P

3.2 Chang and Jackson sequential analysis
3.2.1 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. However, due to application of mineral fertilizers and accumulation of phosphorus (Jaakola, et al. 1997) the processes of saturation of free spaces for adsorption of P in the soil (Vu et al, 2010) result in its significant increase, by about 6 times compared to the control plots in the studied experiment. Considering the low movement of phosphate ions along adepth the soil profile, which is

slower than in the processes of bounding them into less soluble forms, such increase of P ions concentration is expressed distinct in the surface soil layer 0-30 cm.

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.

3.2.2 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). Consequently, these compounds are very labile and are described as pseudo sorption (Van der Zee et al., 1987; 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 H_2O groups of sesquioxides surfaces were are displaced by dihydrogenphosphate anions (Simard et al., 1995). In certain soils, this bound is not strictly confined to Al but can bound bind to Si, as well (Manojlovic, et al. 2007). 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 alumosilicates (r=0.998**). Somewhat increased content of this fraction versus to the available phosphorus indicates that not only modettant bounds are involved (Fig. 3).
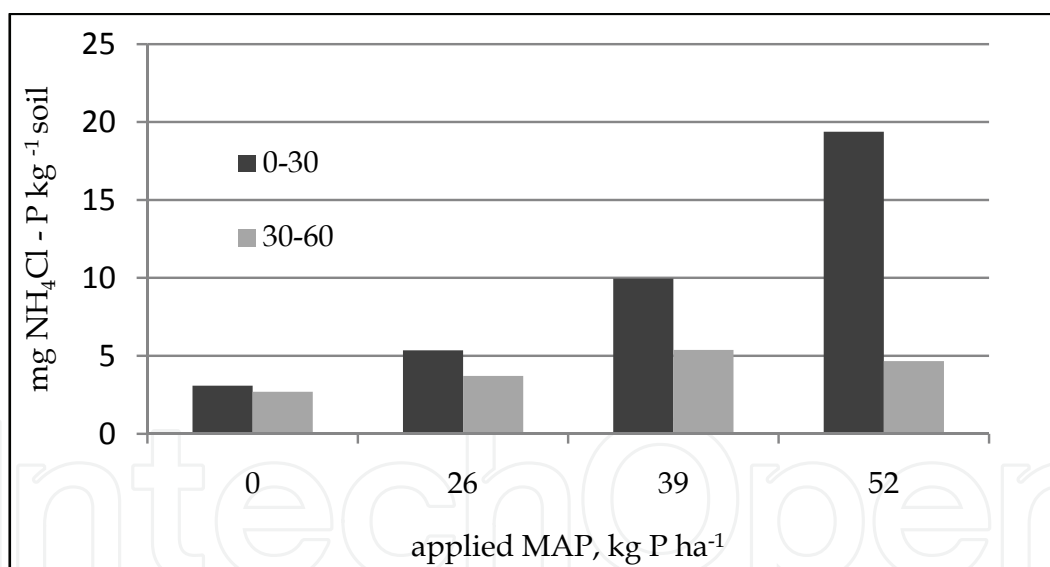

Fig. 2. Content of ammonium-chloride extractable P upon 40-years of phosphate application (water-soluble P)

It is obvious that this fraction of soil phosphorus is the most important for plants since there is a high correlation between the Al bound P and the available forms of phosphorus extracted by the Al-method (r=987**). Also, application of mineral phosphorus influences this fraction of soil P the most with the recorded increase of its content from 16.08% in the control to 34.51% in the treatment with 52 kg P ha⁻¹. This fraction of P is responsible for migration of phosphorus along the soil depth, which is confirmed by a significant correlation between the values at two depths (0.876**), as well as for the replenishment of the pool of other fractions of soil P.
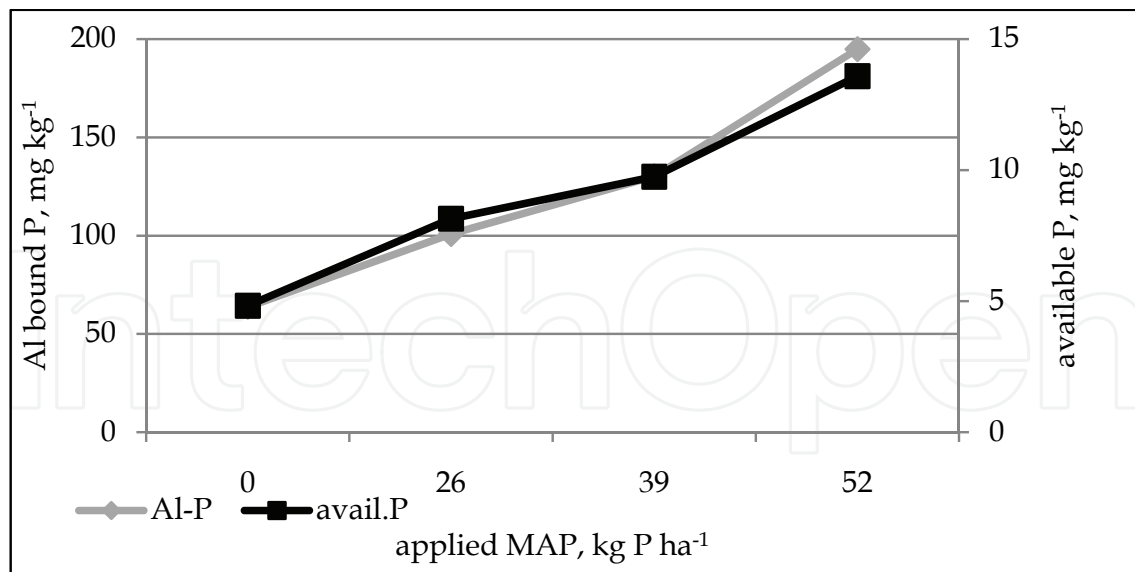
Fig. 3. Content of Al bound P and available P upon 40-years of application different amounts of phosphate fertilizer

3.2.3 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, Mustapha et al., 2007), 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). 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*)

3.2.4 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). In this structure, the phosphate binds the Al- with Fe^{3+}hydroxide so the surface of Al phosphate particle is enveloped by a Fe^{3+}hydroxide skin. Such adsorbed phosphates are only indirectly available to plants. Thus, in the conditions determined by reduction processes the reduction of iron Fe^{2+} 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, Mustapha et al., 2007). But under the conditions of soil

undergoing alterations of wet and dry regimes with high content of available Fe (Cakmak, D. et al., 2010) 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.

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

Chang & Jackson (1957) 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).

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.
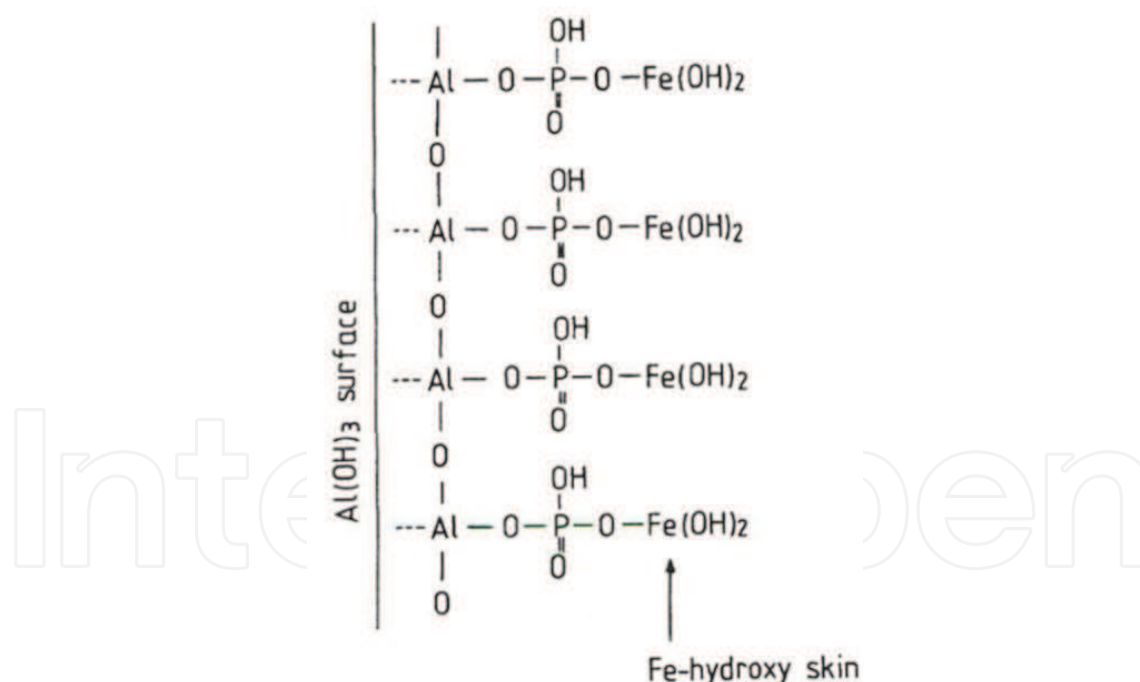

Fig. 4. Fe-hydroxy skin covering the phosphate adsorbed to Al oxide/hydroxide (Mengel & Kirkby, 2001)

3.2.6 Fraction of soil P extracted by M H_2SO_4 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 Ca^{2+} 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). 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*).

4. BCR analysis

BCR method according to SMT standard protocol was applied for determination of P in soil (Ruban et al., 1999). BCR is a non-specific extraction procedure for determination of phosphorus in freshwater sediments, developed in the frame of the European Program, Standards, measurements and Testing (SMT) is used for certification campaign for a reference material. The SMT protocol was extended to soil material because bioavaialable forms of phosphorus are important not only for analysis of sediments but also of soils. The detailed description of the SMT protocol is given at Ruban et al., (2001). The Certified Reference material CRM 684 (River Sediment Extractable Phosphorus, from Po River, Italy) was analyzed to verify the results of analyses.

4.1 BCR procedure

Among numerous extraction schemes used, the procedures widely adopted are those developed by Williams (1976), Hieltjes & Lijklem (1980), Rutenberg (1992) and Galterman (1993). Together with the cited procedures, in the literature can be found other sequential schemes (Delaney, et al., 1997; Kleberg et al., 2000). Due to the large number of the existing procedures for extraction of phosphorus and due to the impossibility of comparison of the results from different source samples obtained via different laboratory procedures, the Program of Standardization of extraction scheme was initiated (Ruban et al, 1999).

To overcome the incompatibility of results a Program of the European Commission (SMT: Standards, Measurements and Testing, earlier BCR) initiated the project for selection of sequential extraction procedures for determination of forms of phosphorus in lake sediments. This project targeted the homogenization of extraction schemes to investigate a selected scheme in inter-laboratory investigations that includes expert European laboratories and to certificate traces in the referent material of the sediment. Four methods (Tab. 2) were chosen for testing. These methods were applied in the inter-laboratory investigations and served as the base for development of homogenized procedure for phosphorus extraction from lake sediments. For the determination of phosphorus, all the laboratories used spectrophotometry (Murphy & Riley, 1962). Along with this method, some laboratories used ion-chromatography such as ICP-AES. However, using the laters proved to be unsuitable, since ICP-AES allows determination of total phosphorus, while the method of ion-chromatography determines only orthophosphate.

Procedure	Advantages	Disadvantages
Williams	Simple and practical	Partial resorption of phosphorus extracted with NaOH onto CaCO3
Hieltjes - Lijklem	Simple and practical	Dissolution of small amounts of Fe-P and Al-P with NH4Cl; hydrolysis of organic phosphor is unavoidable; no responce to bioavailability
Golterman	Extraction of specific compounds; allows extraction of organic P; supports information about bioavailability of fraction	Not practical; NTA i EDTA contaminate the determination of phosphorus; complicated preparation of the solution; in some sediments the extraction must be undertaken more times to obtain valid results
Rutenberg	Possibility of differentiation of different types of apatite; no distribution of phosphorus on the residual particle surfaces during extraction	Very long; extraction with butanol is very difficult

Table 2. Advantages and disadvantages of the methods for sequential extraction of soil P fractions (adapted from Ruban et al., 1999)

Based on the results of inter-laboratory investigations, the modified Williams scheme named SMT (1998) was proposed. The SMT scheme allows definition of the following forms of phosphorus: NaOH-extractable phosphorus (NaOH-P); phosphorus bound to oxides and hydroxides of Fe, Al and Mn; (Fe-Al-Mn-P) HCl-extractable phosphorus (HCl-P); phosphorus bound to Ca (Ca-P); organic phosphorus (Org-P), inorganic phosphorus (IP); concentrated HCl phosphorus, (conc. HCl-P); total phosphorus(TP) (Ruban et al., 1999).

After the compilation of the extraction scheme, certification of extractable phosphorus from the referent material CRM 684, sampled from Po River (Italy) near the Gorina city, was undertaken within the Project (SEPHOS - sequential extraction of phosphorus from fresh water sediment) (Ruban et al., 2001). After acceptance and certification of SMT procedure, valid comparison of worldwide results became possible, what is of great importance for understanding of biogeochemical cycle of phosphorus in actual systems.

In Tab. 3 there are phases of phosphorus and the reagents used for their extraction in both procedures: modified Chang & Jackson and BCR

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

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

4.1.1 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-Fe-Mn 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).
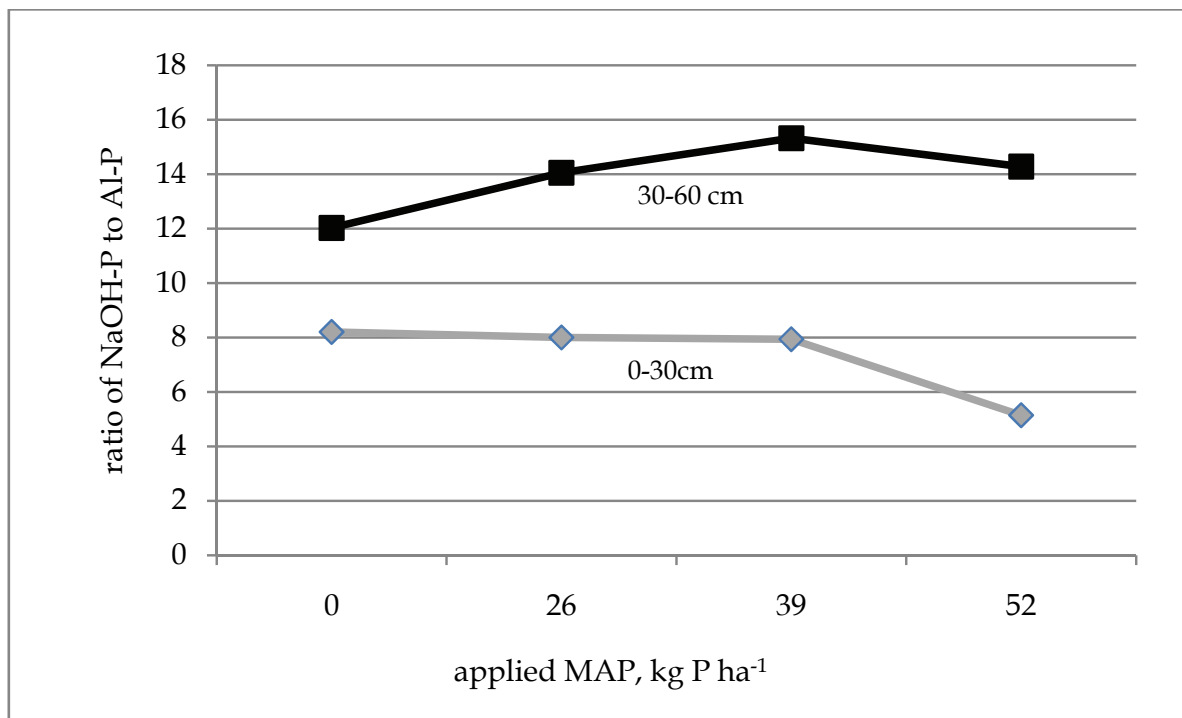

Fig. 5. Ratio of NaOH bound P (BCR) to Al bound P (Chang&Jackson) in the 0-30 cm and 30-60 cm soil intervals

4.1.2 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) 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 $CaPO_4$ is possible by sedimentation. The behavior and distribution of this fraction is similar to the fraction described above (HCL-P/CaII, r=0965,**). Its distribution along the soil profile is also analogous to the above described fraction of phosphorus (Fig. 6).
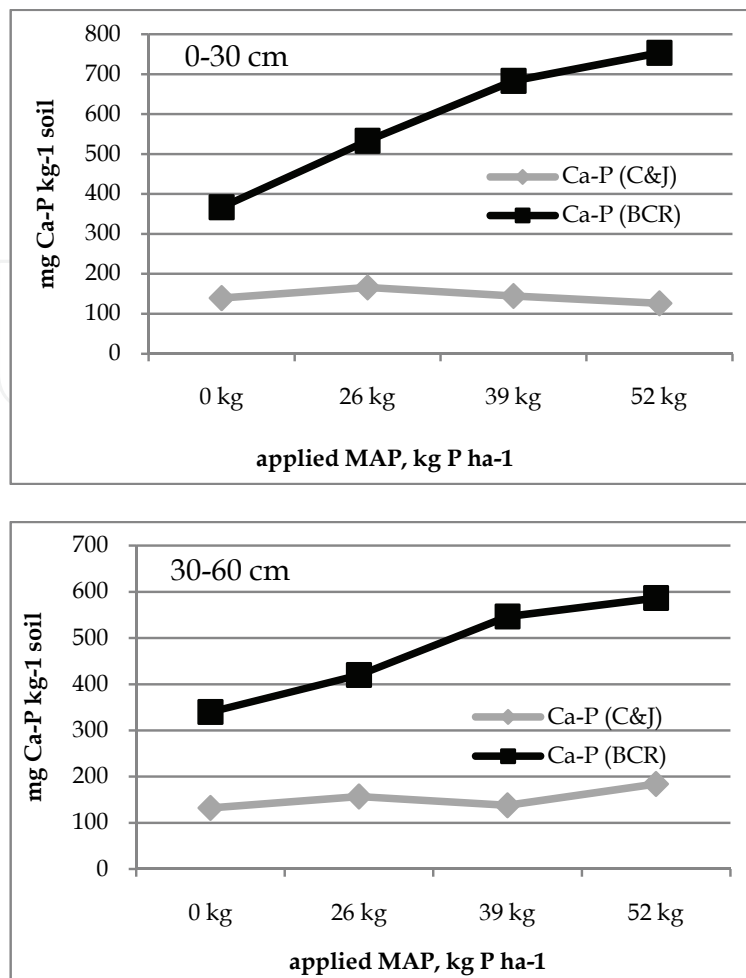
Fig. 6. Distribution of Ca bound P in the two applied methods: Chang&Jackson and BCR in the two soil intervals upon 40-years application of phosphate fertilizer

4.1.3 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=.619 *).

4.1.4 Fraction of soil P extracted by 1M HCl+calcinations (Organic P; Org.P)

This fraction of phosphorus is an exact fraction with not precisely defined constitution that partially consists of phitite (De Groot & Golterman, 1993). The extraction of the organic P fraction was performed in step 4 (Table 3). Most of the organic soil phosphorus is present in the form of the inositol phosphate ester while the proportion of phospholipids and nucleic acids in soils is small due to the fact the two groups of phosphate esters are quickly dephosphorylated by microbial phosphatases (Flaig, 1966).

The moderately good correlation of the organic P with Fe extracted in step 4 (Table 1) indicates the importance of this phase in bonding of organic phosphorus. In contrary to other phosphorus fractions determined by BCR method the organic P fraction didn't show increases after 40-years of application of phosphate fertilizer on Stagnosol.

The absence of changes in the content of organic phosphorus after the 40-years of application of phosphate fertilizer (Fig.7) obviously was due to its low mobility; the microorganisms easier consumed the applied mineral phosphorus from fertilizer, which resulted in negligible changes of organic phosphorus.
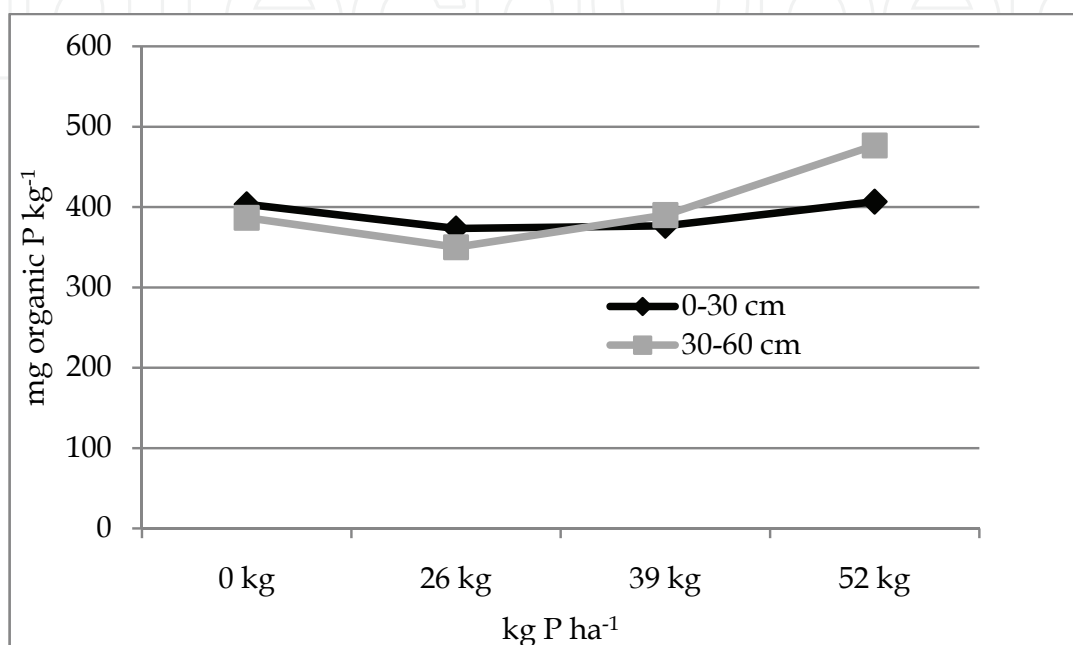

Fig. 7. Response of soil organic phosphorus after 40-years application of phosphate fertilizer

5. Microwave digestion method (Ethos Milestone) using HNO_3, HCl and HF (completely total P; TP)

Long-term application of mineral phosphate fertilizer on Stagnosol not only determined the changes in the content of total P extracted by these extraction solutions: known that more than 90% of phosphorus present in soil as insoluble and fixed. Because in soil the process of bounding of phosphate into unavailable forms takes place constantly, the content of total phosphorus can give information about which amount of added phosphate is tied, i.e. unused. Fertilization increases the amount of total forms of P both on surface and subsurface soil layers. But the ratio of the increase in the content of P between the sum of the entire mineral fraction extracted by Chang&Jackson method and the total P by microwave method is 1:6, which indicates the presence of very clear process of fixation and accumulation of P, i.e. formation of the secondary minerals (Fig. 8).

As mentioned earlier, for such type of soil, often due to mineral fertilization there are no increases in the amount of organic P (Sharpley & Smith 1983, Adeptu & Corey, 1976). The process of immobilization of P in deeper layers is closely linked to the mobility of Al-P, where according to the unpublished data, the correlation with the total P was r=0.721[**]. Therefore, in such soils fertilization by phosphate demands a special caution, i.e. finding the exact ratio between the process of immobilization and the plant demands.
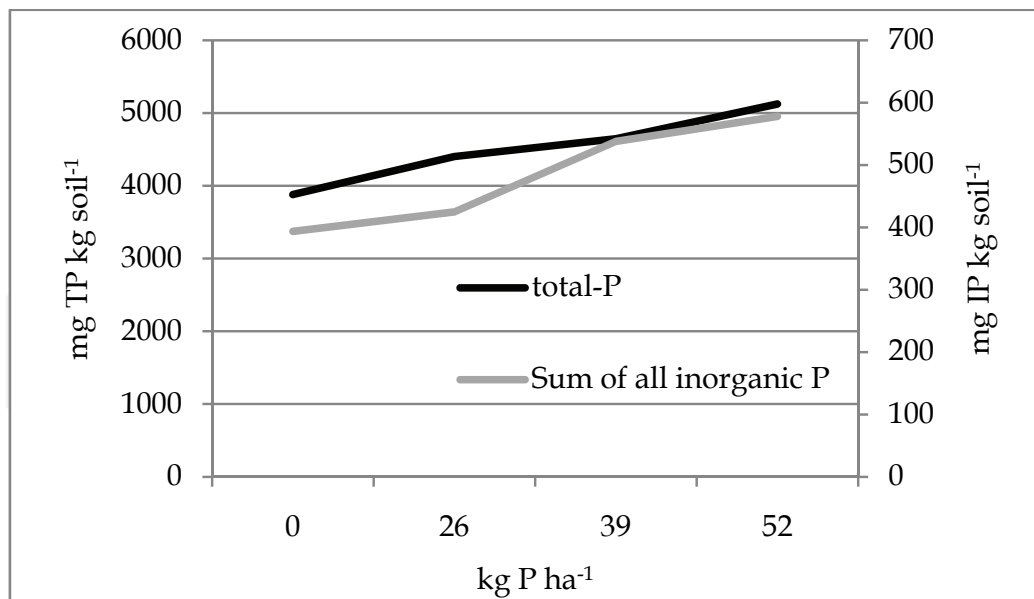
Fig. 8. Changes in the concentrations of total P extracted by microwave digestion and the sum of all inorganic P from Chang&Jackson method upon 40-years application of different rates of MAP

6. Soil agrochemical properties

The change in the basic soil properties and accumulation of micro- and trace elements, some with toxic species, upon the application of phosphate fertilizers are the important factors both for crop yield and for ecological concerns. They can maintain or improve crop yields, but they can also cause changes in the chemical and physical properties of the soil, both directly and indirectly (Hera & Mihaila, 1981; Acton & Gregorich, 1995; Aref & Wander, 1998; Belay et al., 2002). By affecting the basic soil properties (pH, organic C and N, cations, CEC, granulometic composition), phosphate fertilization may influence the solubility of certain elements, such as Al, F, Ca, and Mg (Lindsay, 1979; Kabata-Pendias & Pendias, 2001; Loganathan et al., 2006). On the other hand, mineral phosphate fertilizer could provide an abundance of available phosphorus in soil and increase the efficiency of metal-phosphate mineral formation (Ma et al., 1993; Berti & Cunningham, 1997; Hettiarachhchi et al., 1997; Cooper et al., 1998). Metal-phosphate minerals were shown to control metal solubility in soil suspension when available P was added (Santillian-Medrano & Jurinak, 1975) by inducing the formation of heavy metal phosphate precipitates (Cotter-Howells & Capron, 1996). Additionally, raw materials for P fertilizers contain certain amounts of trace elements and microelements, which may be incorporated into mineral fertilizer (Goodroad & Caldwell, 1979; Adriano, 2001; Kabata-Pendias & Pendias, 2001). The effect of fertilization on soil quality can be best evaluated through the use of long-term experiments (Mitchell et al., 1991; Nel et al., 1996). The general soil-chemical properties are given in Table 4.

Only 15% of the applied phosphorus is consumed by plants quickly after addition (Greenwood, 1981), the rest transforms into insoluble forms and non-labile fractions. Consumption of the applied P by plants becomes more and more difficult each year. However, constant application of fertilizer from year to year can replenish the capacity for the adsorption, and consequently the amount of the available phosphate (Stewart & Sharpley 1987; McCollum, 1991; Maroko, et al., 1999).

As would be expected, the content of P in the soil increased significantly (p < 0,01) depending on the amount of applied phosphate. So, in the treatment with 52 kg/Pha^{-1} an increase by about 3 times was detected in Stagnosol (Figure 9). In the deeper soil layer due to low mobility of phosphates this increase was only by 2 times as compared to the control treatment (Cakmak, D. et al., 2010).

6.1 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). 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 (Fig. 9). In spite the mineral fertilization causes decreases in soil CEC (Belay et al., 2002) especially if the amount of organic matter did not change, in our case due to the increased content of clay the slightly significant increase of CEC in the treatments with 39 and 52 kg P ha^{-1} (p < 0,01) was recorded. The consequence is increases of the value of sum of base in the second depth under the higher rates of fertilizer (p < 0.05).

Treatment	Organic C	Total N	Avail. P†	Exch. Ca^{2+}†	Exch. Mg^{2+}	Mobile. Al	pH	CEC†	Sum of base
g P ha^{-1}	— — % — —			— — — mg 100 g^{-1} — — —				— — cmol kg^{-1} — —	
				0-30 cm					
0	0.99 ± 0.03	0.11 ± 0.001	4.8a‡ ± 0.6	237a ± 9	40.7 ± 4.2	3.7a ± 0.9	4.95a ± 0.0	16.4a ± 0.6	8.67a ± 0.2
26	1.06 ± 0.02	0.12 ± 0.003	8.2b ± 0.4	267b ± 2	43.8 ± 2.3	6.9b ± 1.5	4.80b ± 0.1	18ab ± 0.4	9.07b ± 0.2
39	1.03 ± 0.05	0.12 ± 0.004	9.6.c ± 0.3	251ba ± 7	45.9 ± 1.7	7.1b ± 1.0	4.84b ± 0.0	18.4b ± 0.2	9.34b ± 0.3
52	1.06 ± 0.04	0.12 ± 0.003	13.5d ± 2.8	241ba ± 6	43.8 ± 2.2	7.9c ± 0.9	4.76c ± 0.0	18.8b ± 0.4	8.94b ± 0.3
P	NS§	NS	***	*	NS	*	*	**	*
				30-60 cm					
0	0.81 ± 0.02	0.10 ± 0.000	3.5a ± 0.7	277 ± 3	48.1 ± 0.9	4.07 ± 0.6	5.03 ± 0.0	17.1 ± 0.5	9.87a ± 0.2
26	0.77 ± 0.05	0.09 ± 0.00	5.2b ± 1.6	262 ± 9	49.9 ± 4.4	5.51 ± 1.1	4.95 ± 0.1	16.9 ± 0.6	9.34a ± 0.5
39	0.83 ± 0.09	0.10 ± 0.01	6.1c ± 1.2	264 ± 16	48.2 ± 4.9	4.37 ± 0.1	5.02 ± 0.1	17.5 ± 0.4	10.44b ± 0.4
52	0.74 ± 0.03	0.09 ± 0.00	7.0d ± 1.5	272 ± 10	50.8 ± 1.8	4.68 ± 0.4	5.03 ± 0.0	17.9 ± 0.9	10.7b ± 0.6
P	NS	NS	***	NS	NS	NS	NS	NS	*

* Significant at P < 0.05.
** Significant at P < 0.01.
*** Significant at P < 0.001.
† Avail., available; Exch., exchangeable; CEC, cation exchange capacity.
‡ Within each depth increment, means with the same letter are not significantly different.
§ NS, not significant.

Table 4. Soil chemical characteristics of Stagnosol in 40-years phosphate fertilization experiment
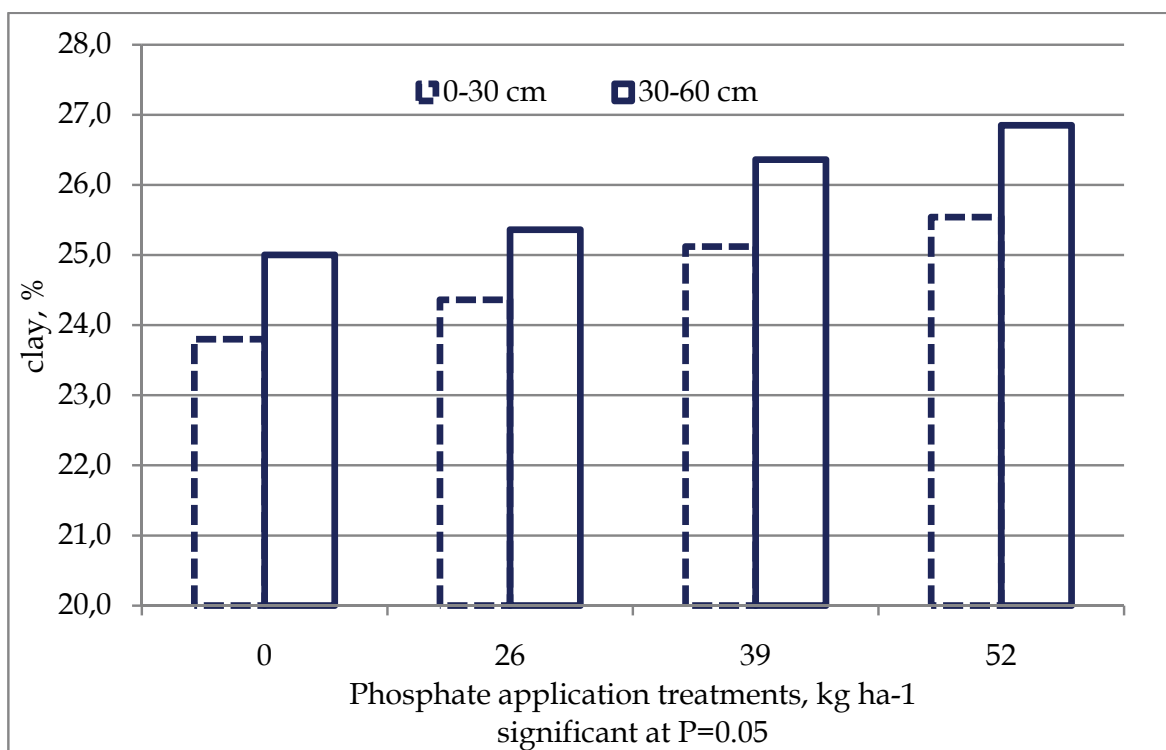
Fig. 9. Amount of clay fraction under long-term application of different rates of phosphate fertilizer in two depths on a Stagnosol soil.

6.2 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; Belay et al., 2002; Saleque et al., 2004). 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 Fe-phosphate found in this experiment (< 1 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. 10).
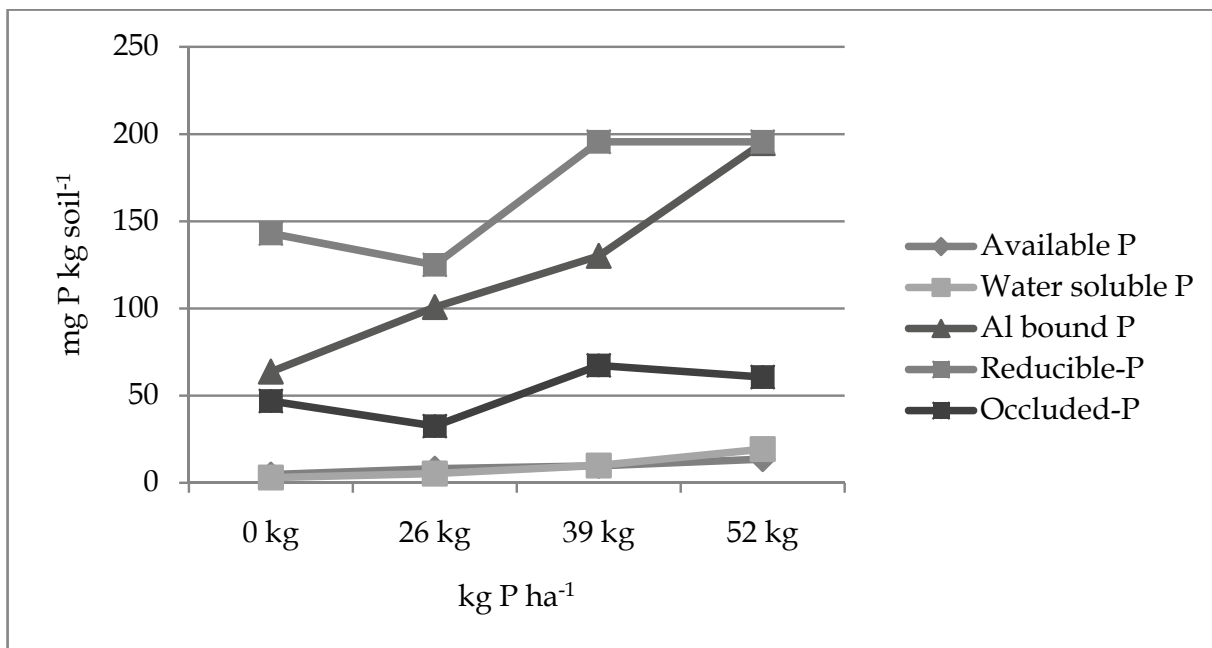

Fig. 10. Concentrations soil P extracted by different methods upon 40-years application of phosphate fertilizer

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) where the end product of neutralization are species of Al cations such as Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$. 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 (H_2O) (Abrahmsen, 1984; McKenzie & Nyborg, 1984; Mrvic et al., 2007). In our experiments, in the 26 kgPha^{-1} treatment in the subrface soil the amount of mobile Al is doubled versus to control (Tab. 4).

Exchangeable cataions 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), 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 Ca^{2+} and in lesser degree Mg^{2+}, might be derived from structure of soil primary minerals thus increasing the Ca availability in soil solution (McLaughlin & Wimmer, 1999). 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.

7. 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 Fe^{3+} oxides. At higher pH levels the activity of Fe^{3+} 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) where phosphates can immobilize Zn as zinc phosphate $Zn_3(PO_4)_3 4H_2O$, although this theory is not fully proved (Jurinak & Inouye 1962). 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 controling Cu solubility, which depends on the solubility of Fe (Shuman, 1985), 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 (Gooroad & Caldwell, 1979). 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; Glandey & Burns, 1985). Solubility of fluoride ions is controlled by the soil pH and the amount of soil Ca and P (Hurd-Karrer 1950). 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 ($r=-0.92$ $p < 0.01$) (Pickering, 1985; Barrow & Ellis, 1986; Loganathan et al., 2006). The significant increase of the amount of soluble F in the subsurface soil might be due to its leaching from the upper soil layer.

7.1 Trace elements

The dominant sources of fertilizer contaminants are the raw materials used to manufacture phosphate fertilizer. The most common contaminant metals and metalloids found in phosphate rock are arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), selenium (Se) and fluoride. Therefore, phosphate fertilizer is considered as one of the most important sources of trace element contamination in agricultural soils. The content of some trace elements used in our 40-year experiment is given in Table 5.

Element	As	Hg	F	Cr	Cu	Zn	Cd	Ni	Pb	Fe
			$-------$ mg kg^{-1} $--------$							
Concentration	4–15	0.003–0.005	19,600–26,700	15–315	10–20	10–38	3–16	4–39	10–20	4000–5000

Table 5. Content of trace elements in the applied monoammonium phosphate

7.2 Lead (Pb)

Amount of Pb in phosphate fertilizers ranges between 7-225 mg kg^{-1} (Kabata-Pendias, 2001). The amount of Pb in the applied phosphate ranged between 10 and 20 mg kg^{-1} (Stevanovic et al., 2009). It is known that lead-containing compounds are weakly soluble (Davies, 1995), but application of phosphates affects their solubility, resulting in their greater immobilization (McGowen et al., 2001; Dermatas et al., 2008).

Hettiarachchi & Pierzynski (1996) had more success with the solubility equilibrium approach. They studied the influence of P additions on Pb solubility in a Pb-contaminated soil. Prior to P additions, the soil was in equilibrium with cerrusite ($PbCO_3$), but after addition of a soluble P the equilibrium was shifted to the Pb controlled by hydroxypryromorphite [$Pb_5(PO_4)_3OH$], a less soluble Pb mineral phase (Sims & Pierzynski, 2005).
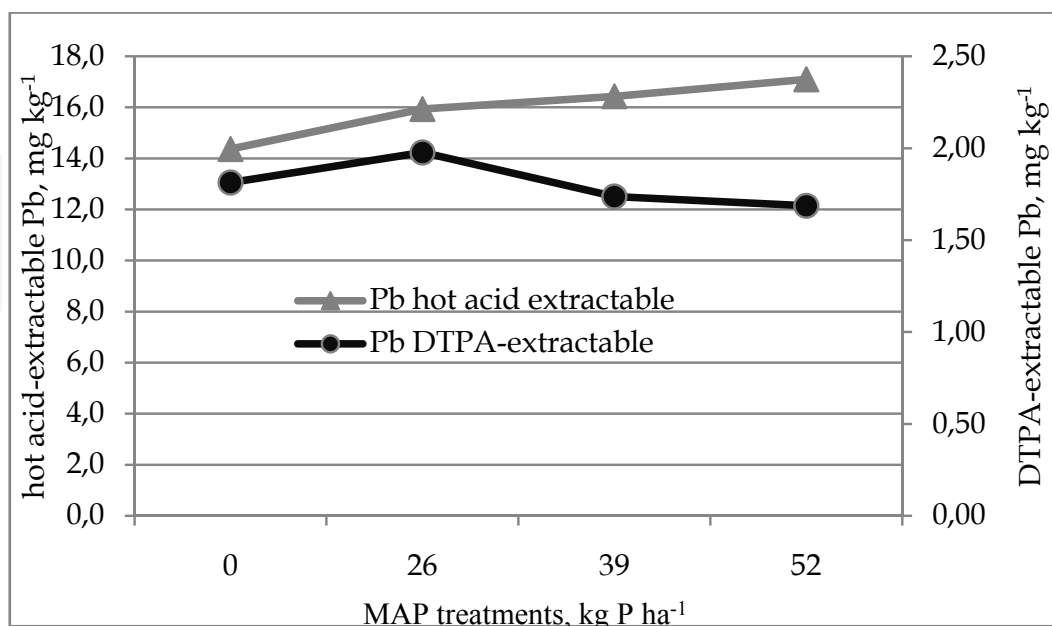

Fig. 11. Distribution of hot acid-extractable and diethylenetriaminepentaacetic acid (DTPA)-extractable Pb under different rates of phosphate fertilization on a Stagnosol soil

In our experiment, the amount of hot acid-extractable Pb in the 0- 30 cm soil interval increased significantly ($p < 0.05$) in accordance with the amount of added P fertilizers (Tab. 6). Significance was observed between the control and all the treatments. The content of hot acid-extractable Pb in the 0-30 cm interval of the control was less than that in the 30-60 cm interval, whereas in the fertilized treatments its content was higher in the upper than in the lower soil depth. Relatively small but significant increase of total P after the 40-years of phosphate application was due to the low content of P in the applied fertilizer, and to the low applied rates of fertilizer. Expectedly, based on the above-mentioned results, in contrast to the hot acid-extractable form, the amount of DTPA-extractable Pb decreased significantly ($p < 0.05$) in the 0-30 cm soil with the increase in fertilization rates (Fig. 11).

7.3 Cadmium (Cd)

Cadmium is in fertilized soils as divalent cation Cd_2^+ and the associated organic and inorganic complexes. As the cation, Cd solubility is highest in acidic soils, in soils with low CEC and soils with high anionic ligands (Hahne & Kroontje, 1973; Garcia-Miragaya & Page, 1976; Garcia-Miragaya & Page, 1978; Chubin & Street, 1981). Cadmium present in granular fertilizers rapidly dissolves and the solid-phase Cd in the fertilizer moves into the soil as free Cd_2^+. In contrast to the other trace metals such as Cu and Zn, organic ligands do not bind strongly free Cd_2^+ ions or the Cd complexes. In inorganic ligands the dominant Cd species present in soil solution tend to be more mobile than other trace metals, including Pb and Cu (Alloway, 1995).

Cadmium is a trace metal that is often bound to P fertilizers, especially to rock phosphates and it proved to be less mobile than the P carrier itself in the soil profile (Mulla et al., 1980; Adriano 2001; Kabata-Pendias & Pendias, 2001). However, the fertilizer we used (MAP) contains low concentrations of Cd (3–16 mg kg^{-1}) (Stevanovic et al., 2009). The low measured concentrations of this element and its solubility resulted in almost the same concentrations of Cd in both soil intervals. The minor changes in Cd observed in our studies were clearly due to the low levels of Cd in the source material (Tab. 6). About 71% of the accumulated Cd resided in the surface soil (0 to 15 cm) compared with only 45% for P (Adriano, 2001).

Treatment					Hot acid-extractable					
	Total F	Cu	Zn	Ni	Pb	Cd	Co	Cr	As	Hg
kg P ha^{-1}	— — — — — — — — — — mg kg^{-1} — — — — — — — — — —									
					0–30 cm					
0	334 ± 16.5†	12.7 ± 0.2	32.0 ± 0.4	26.3 ± 0.5	14.4a† ± 0.7	0.20a ± 0.00	11.5 ± 0.1	18.7a ± 0.6	4.5a ± 0.00	0.049a ± 0.001
26	337 ± 2.6	12.6 ± 0.1	32.3 ± 1.1	27.2 ± 0.3	15.9b ± 0.2	0.20a ± 0.00	12.5 ± 0.7	17.4ab ± 0.5	4.9ab ± 0.17	0.060b ± 0.004
39	339 ± 15.7	13.7 ± 0.8	32.0 ± 0.8	26.8 ± 1.2	16.4b ± 1.0	0.27b ± 0.02	11.3 ± 0.2	16.9ab ± 1.0	5.0b ± 0.20	0.061b ± 0.005
52	358 ± 8.5	12.6 ± 0.3	31.9 ± .03	26.2 ± 0.7	17.1c ± 0.1	0.27b ± 0.02	12.0 ± 0.4	15.9b ± 0.5	4.9a ± 0.13	0.092c ± 0.002
P	NS‡	NS	NS	NS	*	**	NS	*	*	***
					30–60 cm					
0	323a ± 10.1	12.5 ± 0.1	30.9 ± 0.1	27.0 ± 0.5	16.7a ± 0.3	0.20 ± 0.03	12.8 ± 0.8	18.6ab ± 0.8	4.7ab ± 0.2	0.04a ± 0.001
26	331a ± 6.4	13.3 ± 0.2	33.0 ± 0.8	28.0 ± 0.7	14.6b ± 0.6	0.20 ± 0.03	13.1 ± 0.4	19.9a ± 1.1	4.6a ± 0.1	0.06b ± 0.002
39	342a ± 3.1	12.8 ± 0.5	31.1 ± 0.6	27.1 ± 0.6	14.0b ± 0.8	0.20 ± 0.00	12.2 ± 0.8	16.8b ± 0.5	4.5a ± 0.1	0.06b ± 0.003
52	351b ± 11.2	13.3 ± 0.5	31.7 ± 0.1	27.3 ± 0.3	15.0ab ± 0.3	0.27 ± 0.02	12.0 ± 0.4	19.0a ± 0.6	5.0b ± 0.1	0.09c ± 0.002
P	*	NS	*	NS	**	NS	NS	*	*	***

Table 6. Concentrations of hot acid-extractable trace elements in Stagnosol of long-term phosphate fertilization experiment

Treatment	Water-extr. F	DTPA-extractable					
		Cu	Zn	Ni	Pb	Cd	Fe
kg P ha^{-1}		— — — — — — — — — mg kg^{-1} — — — — — — — — —					
				0–30 cm			
0	0.32a† ± 0.01	1.60a ± 0.04	0.77 ± 0.09	1.11 ± 0.08	1.81ab ± 0.09	0.07 ± 0.011	158a ± 3.4
26	0.69b ± 0.22	1.67ab ± 0.04	0.73 ± 0.03	1.31 ± 0.11	1.98b ± 0.04	0.07 ± 0.003	196b ± 8.4
39	0.76b ± 0.12	1.70b ± 0.01	0.74 ± 0.07	1.32 ± 0.12	1.74ab ± 0.08	0.06 ± 0.002	195b ± 9.4
52	0.92c ± 0.09	1.65a ± 0.02	0.88 ± 0.09	1.38 ± 0.07	1.65a ± 0.15	0.07 ± 0.008	194b ± 4.3
P	*	*	NS‡	NS	*	NS	**
				30–60 cm			
0	0.14a ± 0.03	1.57a ± 0.01	0.56 ± 0.02	1.22 ± 0.03	1.57 ± 0.02	0.04 ± 0.008	162 ± 6.2
26	0.31b ± 0.10	1.57a ± 0.02	0.47 ± 0.05	1.24 ± 0.07	1.64 ± 0.01	0.03 ± 0.002	173 ± 9.9
39	0.31b ± 0.05	1.57a ± 0.04	0.47 ± 0.06	1.29 ± 0.04	1.43 ± 0.10	0.04 ± 0.005	167 ± 5.4
52	0.38b ± 0.04	1.49b ± 0.02	0.41 ± 0.02	1.19 ± 0.06	1.45 ± 0.12	0.04 ± 0.004	166 ± 5.8
P	*	*	*	NS	NS	NS	NS

Table 7. Concentrations of water-extractable F and DTPA-extractable trace elements in Stagnosol of long-term phosphate fertilization experiment.

7.4 Arsenic (As)

Application of phosphates can enhance As mobility, phytoavailability, and phytotoxicity in lead arsenate contaminated soils amended with MAP (Peryea, 1991). The degree of arsenic toxicity depends on the phosphate concentration in the nutrient solution in certain soil-plant environments (Hurd-Karrer, 1939). The main predicators of As solubility are soil mineralogy, organic matter, soil pH and As oxidation state. Arsenic may form insoluble compounds with Fe and Al oxides, be absorbed by the organic matter or hydroxyl groups on clay minerals (Mitchell & Barr, 1995). Among various potassium and sodium salts, potassium phosphate was the most effective in extracting arsenic, attaining more than 40% extraction (Alam, et al., 2001). Phosphate could displace adsorbed or fixed As from sorbing complexes and thereby initially increase the amount of soluble As in soils. (Kabata-Pendias, & Pendias, 2001).

Because As is often a contaminant in phosphate fertilizers (Adriano, 2001; Kabata-Pendias & Pendias, 2001) produced from rock phosphates (O'Neill, 1995) we expected a higher concentration of As in the upper soil interval. However, because of their position in the periodic table of elements, where phosphorus, an essential element capable of being absorbed in relatively large amounts, and arsenic, a highly toxic element, chemically much like phosphorus, these elements often behave as antagonists. Anion antagonism between P and As (Parfitt, 1978), and their similar solubility under certain soil pH (Alloway, 1995), resulted in the movement of As down the soil profile (Tab. 6).

7.5 Chromium (Cr)

The content of Cr in phosphate fertilizers ranges between 66-245 mg kg^{-1} (Kabata-Pendias & Pendias, 2001). However, in the fertilizer used in our experiments the content of Cr was wider and ranged from 15-315 mg kg^{-1}. Chromium in soil could be found mainly in two forms: Cr^{3+} and Cr^{6+}. In the majority of soils, the relatively insoluble and less mobile Cr(III) form predominates and it geneally occurs as insoluble hydroxides and oxides (McGrath, 1995). Phosphorus states in soil and soil pH can determine the similarity of adsorption and solubility behavior between Cr^{3+} and Al^{3+}. Although the amount of Cr entering soil via the

use of phosphate fertilizers is uncertain, it is likely to exist as Cr(III). Chromium (Cr III) in soil is not likely to be toxic (McGrath, 1995). Presence of Cr 6^+ in the soil surface horizons is due to its linkage to the oxidizing conditions and redox potentials. Once Cr is oxidized into the hexavalent form in the soil, it becomes more mobile and leachable (Adriano, 2001). Ions of $H_2PO_4^-$ and $HCrO_4^-$ are antagonists what is reflected in the increased mobility and solubility of Cr ion in soil solution. Data in the Table 4 confirms this hypothesis since in the control at both depths the concentration of Cr was nearly equal; however, at the surface depth the concentration of Cr is significantly decreasing correspondingly with the applied rate of phosphate; whilst at the subsurface depth the concentration of Cr significantly increases after the addition of phosphate (Adriano, 2001).

7.6 Nickel, Cobalt, Mercury (Ni , Co, Hg)

The content of Ni and Co did not show any differences in any of the treatments. The concentrations of these trace elements in the studied soil were within the range of average world concentrations. Most commercial fertilizers have Hg content below 50 ng per gram, but considerably higher amounts occur in phosphate fertilizers. Hg may be derived partly from the phosphate rocks and partly from the sulphuric acid used for dissolution of phosphates (Steinnes, 1995). Because of the initially low concentrations of hot-acid extractable Hg in the control treatment, the increased concentrations of Hg detected at both soil depths (Tab. 6) under the fertilized treatments are obviously due to the applied MAP. However, in spite of statistically significant increases in the content of Hg, its absolute amount is small and doesn't pose a risk for the environment even after 40-years application of MAP in Stagnosol.

8. Conclusions

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 does'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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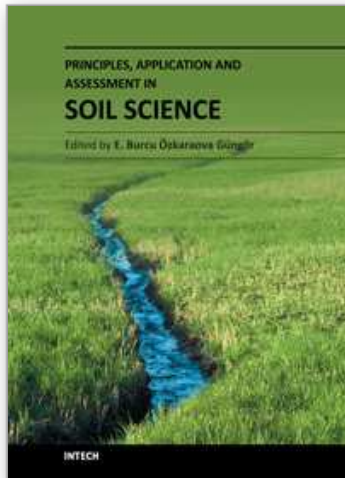
Principles, Application and Assessment in Soil Science

Edited by Dr. Burcu E. Ozkaraova Gungor

Our dependence on soil, and our curiosity about it, is leading to the investigation of changes within soil processes. Furthermore, the diversity and dynamics of soil are enabling new discoveries and insights, which help us to understand the variations in soil processes. Consequently, this permits us to take the necessary measures for soil protection, thus promoting soil health. This book aims to provide an up-to-date account of the current state of knowledge in recent practices and assessments in soil science. Moreover, it presents a comprehensive evaluation of the effect of residue/waste application on soil properties and, further, on the mechanism of plant adaptation and plant growth. Interesting examples of simulation using various models dealing with carbon sequestration, ecosystem respiration, and soil landscape, etc. are demonstrated. The book also includes chapters on the analysis of areal data and geostatistics using different assessment methods. More recent developments in analytical techniques used to obtain answers to the various physical mechanisms, chemical, and biological processes in soil are also present.

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