The chemical characteristics of soil which determine phosphorus partitioning in highly calcareous soils

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Abstract: Phosphorus fractions from three highly calcareous soils (average, 24.9 ± 4.8 % CO_3^{2-}) from sampling sites with a Mediterranean climate were isolated by sequential extraction. In order to provide a more reliable basis for the definition of the obtained P-fractions, principal component analysis was applied and from the chemical characteristics of the 14 investigated soils, those characteristics which define the content and association features of the P-fractions were assessed. The soils are characterized by a relatively high pH (8.0 – 8.2) and by significantly differing contents of organic mater, acid-soluble Mg and total P. These differences affected the various association features of the P-fraction with the soil constituents. The NH_4F–P fraction (isolated with 0.5 M NH_4F, pH 8.2) is defined by the contents of the main metals of the oxide–hydroxide–clay associations (Al, Fe, Mn) or by the the redox potential (*E*h) of Mn. The accumulation of NaOH–phosphorus (extractable with 0.1M NaOH) depended on the constituents of the oxide–hydroxide–clay association, the humic substances and *E*h-related factors. In those soils in which NaOH–P is defined by the oxide–hydroxide–clay assoiation, the participation of Fe as a bridge-forming metal is proposed. The main part of total P, *i.e.*, $\Delta P = TP - (NH_4F–P + NaOH–P)$ is defined by the status of Mn– and Fe–humic complexes or by the concentration of hydroxyl-ions.

Keywords: NH_4F–extractable P, NaOH–extractable P, phosphorus-associations, principal component analysis.

INTRODUCTION

Several decades ago, the associations of phosphorus-compounds with the constituents of soils and sediments was one of the main interest of agrochemical and ecochemical investigations, as the mobility of phosphorus and its availability to the biota depends on the nature of its associations.[1–6] The partitioning of inorganic

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and organic phosphorus-species between soil constituents is very complex,[2] and depends on many interrelated soil characteristics, such as the concentration of re-active Al-, Fe- and Mn-species, Ca- and Mg-species, pH, Eh and organic lig-ands.[7–11] However, it is possible to differentiate the following principal associa-tions of phosphorus:[12] (*i*) adsorptionally and exchangeably bound P, (*ii*) phospho-rus associated with aluminum (phosphates of Al, and P-species bound to Al-hy-droxides and oxides), (*iii*) phosphorus associated with iron or manganese (phos-phates of Fe and Mn, and P-species bound to Fe- and Mn-hydroxides and oxides), (*iv*) phosphorus occluded by oxides and hydroxides of Al, Fe and Mn, (*v*) phospho-rus associated with calcium (the different sparingly soluble phosphates of Ca as well as P-species bound on the surfaces of Ca-carbonate particles). These P-frac-tions are mainly operationally defined because it is not always possible to make a consistent distinction in a chemical and/or structural sense between these frac-tions.[11,13,14] Two main shortcomings of the current fractionation procedures should be mentioned: (*i*) the difficulty to reliably differentiate between inorganic and organic phosphorus-fractions as a consequence of the hydrolytic action of the majority of extraction agents on organic P-compounds,[1,15] and (*ii*), the lack of se-lectivity in the determination of Al- and Fe-associated phosphorus in certain soils.[11,16,17]

Fundamental investigations of ion associations in soils and sediments empha-size the existence of more complex phosphorus-substrate associations, *i.e.,* struc-tures consisting of two or more of the P-substrates found by sequential fractiona-tions. For example, particle surfaces having hydroxyl groups (oxides, hydroxides, alumosilicates) bind orthophosphate ions *via* a metal ion-bridge, $\equiv$S–O–M–phos-phate.[18,19] Similarly, Boers and DeBles[9] proposed the formation of complex associ-ations consisting of a functionalized organic matter, metal ion-bridge and phosphate. Obviously, in such structures, P is associated simultaneously with several substrates, for example, an oxide- or hydroxide-forming metal (Fe, Al, Mn) or organic matter, and a bridge-forming metal (Fe, Al, Mn, Ca, Mg). One of the determining factors in the formation of such complex associations could be the pH of zero point charge,[20,19] pH_{zpc}, of a potential P-substrate. Consequently, the formation of these associations is favoured by an increase in the pH of the environment.[19]

The aim of this investigation was the assessment of the more mobile fractions of phosphorus in highly calcareous soils because these fractions are related to the available P-fractions.[15,21,22] Due to the high content of carbonates, mainly Ca-car-bonates (CO_3^{2-} ranges from 15.9 to 31.7 %) a preferential association of phospho-rus with calcium could be expected.[23] In addition, as a consequence of the estab-lished relatively high pH (mean value: 8.08 ± 0.05), the majority of potential P-substrates are probably already negatively charged, thus tending to repulse phos-phate ions, but simultaneously highly active in the formation of complex associ-ates *via* metal ion bridges. The relatively high content of acid-soluble aluminium

(average 30.4 ± 6.8 g/kg) indicates a rarely found high content of active Al-species. Moreover, aluminium prevails over acid-soluble iron, the atomic ratio of Al/Fe being 2.9. Therefore, the fractionation procedure according to Chang and Jackson[12] was applied with several modifications, despite the difficulty in the reliable differentiation of Al- and Fe-associated phosphorus.[16,17] In order to avoid possible shortcomings in the assignment of individual P-fractions, firstly, the principal soil characteristics, defining the soils, were assessed by principal component analysis, PCA.[24] Then the scores of these characteristics were computed for each sample and correlated with the individual P-fractions, according to Miura and Badayos,[25] with the aim of determining the soil characteristics which most clearly define the P-fractions, as well as their association features.

EXPERIMENTAL

Sampling site characteristics

The investigated area, Ćemovsko Field, is located about 2 km southeast from the town Podgorica, at an altitude of 10–50 m and has a Mediterranean climate with a mean annual temperature of 15 °C, and growing season rainfall ranging from 38.5 mm (July) to 238.5 mm (November). The sampling sites are 2.5 to 7 km west of the Aluminium factory "KAP", which processes bauxite.

The soil is a rendzina on a fluvioglacial deposit consisting of carbonates (calcite, dolomite).[26] The content of soil skeletal material is on average 75 %, consisting mainly of particles between 0.5 and 2 cm. In the fine soil fraction (< 2 mm), the sand content is 50 to 90 %, silt 8–35 %, and clay ranges between 2 and 15 %.[26] A deep amelioration followed by cultivation (vineyards) of sections of the Ćemovsko Field began successively more than 29 years ago: section Aerodrom in 1976/77, Centar in 1980 and section Šipčanik in 1981.

Sampling and sample preparation

Twenty-six surface samples (0 – 30 cm) were taken in the middle of May, after the plant material from the top soil (1 cm) had been removed. One sample per 55000 m² was taken. Rock particles greater than 1 cm and plant debris were handpicked from the samples (*ca.* 1.5 kg.). The samples were air-dried and then homogenized in a porcelain mortar, to pass through a standard 2 mm sieve. Subsamples of about 400 g were taken and ground in a stainless steel ball-mill (Retsch) to pass trough a standard 0.15 mm sieve.

Analytical methods and data processing

The moisture content was determined by drying at 105 °C until constant mass was achieve.[27]

The carbonate carbon, C_{carb}, was determined by a standard volumetric method.[28]

The total organic carbon, C_{org}, was determined by elemental microanalysis on a Pregl apparatus,[29] after treatment of the dried samples with 6 M HCl in order to eliminate C_{carb}.

The pH-value was determined with a combined glass–calomel-electrode in soil/deionized water suspension, 2.5 (w:v).[30]

The total phosphorus, TP, was determined after the treatment of samples with $HNO_3 + HClO_4$ and subsequently with HCl, according to Hesse.[1] In the resulting solutions, the total P was determined by inductively coupled plasma emission spectroscopy (ICPAES), on a Shimadzu 7500 instrument.

The acid soluble total metals (TMg, TCa, TA1, TMn and TFe) were determined in the same solutions used for TP, by atomic absorption spectrometry (AAS) on a Varian SpectrAA 55 instrument. The detection limits for the AAS method for the metals were as follows: Al – 0.2 mg dm⁻³, Fe – 0.03 mg dm⁻³, Mn – 0.01 mg dm⁻³, Ca – 0.005 mg dm⁻³ and Mg – 0.002 mg dm⁻³.

The sorbed and exchangeable phosphorus,[12,15] P_{exch}, was extracted by shaking 5.000 g of sample with 50 cm^3 0.5 M KCl for 4 h, at room temperature. The determination was performed by ICPAES.

The ammonium fluoride–phosphorus, NH_4F–P, was extracted by shaking for 1 h (at room temperature), 1.000 g of sample with 50.0 cm^3 of 0.5 M solution of NH_4F (the pH of which had been adjusted to 8.2 with ammonia solution).[12] The supernatant was separated by centrifugation and the NH_4F–P in the resulting solution was determined by ICPAES. The solid residue was washed twice with a saturated solution of NaCl.

The sodium hydroxide–phosphorus, NaOH–P, was extracted from the washed residues after the NH_4F–P extraction with 50 cm^3 of 0.1 M NaOH solution for 17 h at room tempeature.[12] During the first and the last two hours, the suspensions were shaken. Separation of the solution and determination of P was performed in the same manner as for the NH_4F–P. However, in order to exclude possible interference from extracted humic substances, the solutions were treated with HNO_3 and $HClO_4$ before P-determination by ICPAES.

The NH_4F–metals and NaOH–metals, co-extracted during the NH_4F- and NaOH- extractions, respectively[12] (Mg, Ca, Al, Mn and Fe), were determined by ICPAES, using a Shimadzu 7500 instrument. The detection limits for the ICPAES method were as follows: for P, Mg and Al – 0.05 mg dm^{-3}, for Fe – 0.03 mg dm^{-3} and for Ca and Mn – 0.01 mg dm^{-3}. For both the ICPAES and the AAS method, the concentrations were calculated from calibration curves obtained with standard solutions. In order to avoid possible matrix-effects during the AAS-measurements, special standard solutions containing similar amounts of macro-cations as the investigated sample solutions, were employed.

Data processing and statistical methods

All the concentrations are expressed the basis of the weight of the sample drying at 105 °C. After rejection of the two samples showing extreme values for particular parameter concentrations an application of the Q-test, the remaining twenty-four samples were processed with the SPSS® 10.0 Program (mean value with standard deviation, principal component analysis with matrix rotation and correlation).

Principal component analysis

Factor analysis with principal component extraction was performed using the program SPSS® 10.0, for Windows.[24] Principal component analysis (PCA) represents an effective statistical tool for analysing data trends and relationships.[24,25] In principle, this is a data reduction technique, whereby the original set of correlated variables is transformed into a new set of mutually non-correlated variables, *i.e.,* the factors, which contain the principal components. The scope of PCA is to group chemical species according to the similarities of their variations and to assign physical and chemical significance to these groups.

RESULTS AND DISCUSSION

A general overview of the characteristics of the soils and the distribution of phosphorus- and related metal-fractions is given in Table I.

TABLE I. Mean values and standard deviations of the determined parameters (concentrations in mmol/kg) for all samples, and for the samples from a particular location (significantly differing mean values with $p < 0.05$ are underlined, and with $p < 0.01$ are marked in bold)

Parameter	All samples (*n* = 24)	Aerodrom (*n* = 8)	Centar (*n* = 8)	Šipčanik (*n* = 8)
pH	8.08 ± 0.05	8.09 ± 0.07	8.06 ± 0.04	8.08 ± 0.05
C_{carb}	4100 ± 800	4400 ± 700	4300 ± 600	3700 ± 1000
C_{org}	2440 ± 450	2710 ± 410	2640 ± 440	2150 ± 370
TP	33.87 ± 7.47	**40.42 ± 6.47**	33.33 ± 3.45	**27.85 ± 6.24**
TMg	926.57 ± 189.50	**1104.64 ± 90.25**	**950.7 ± 134.51**	**725.01 ± 91.97**

TABLE I. Continued

Parameter	All samples (n = 24)	Aerodrom (n = 8)	Centar (n = 8)	Šipčanik (n = 8)
TCa	3806.67 ± 502.82	3950.91 ± 493.71	3964.63 ± 386.06	3504.46 ± 530.35
TA1	1126.7 ± 252.7	1049.0 ± 264.4	1080.0 ± 181.9	1251.1 ± 282.4
TMn	11.44 ± 2.53	10.82 ± 2.46	10.61 ± 1.68	12.89 ± 2.93
TFe	388.09 ± 81.25	368.49 ± 81.49	365.40± 58.01	430.37 ± 92.82
$NH_4F–P$	1.71 ± 0.066	**2.16 ± 0.56**	**1.43 ± 0.33**	1.53 ± 0.81
$NH_4F–Al$	7.47 ± 2.93	**9.32 ± 1.99**	**6.11 ± 2.17**	6.98 ± 3.63
$NH_4F–Mn$	0.03 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.03 ± 0.01
$NH_4F–Fe$	0.27 ± 0.14	0.29 ± 0.12	0.30 ± 0.20	0.23 ± 0.10
NaOH–P	1.47± 0.62	1.44 ± 0.43	1.69 ± 0.86	1.29 ± 0.49
NaOH–Al	93.29 ± 19.25	96.51 ± 18.84	93.41 ± 17.32	89.96 ± 23.20
NaOH–Mn	0.10 ± 0.05	0.09 ± 0.03	0.11 ± 0.07	0.09 ± 0.06
NaOH–Fe	1.34± 0.84	1.14 ± 0.50	1.64 ± 1.00	1.25 ± 0.95

The principal chemical characteristics of the investigated soils are the relatively high pH, the high content of carbonates (C_{carb}) and the rather high atomic ratio od solubilized Al and Fe during oxidative acid digestion (TA1/TFe = 2.9). The content of organic carbon is relatively low, 2440 mmol/kg or 2.9 %, whereas the total phosphorus content, TP, of 33.9 mmol/kg or 0.1 % appears to be satisfactory.

The content of carbonate stoichiometrically exceeds the total content of Ca, TCa and for the location sections Aerodrom, Centar and Šipčanik, the average differences $\Delta C_{carb} = C_{carb} - TCa$ were 452, 332 and 235 mmol/kg, respectively. Despite containing several percent of dolomite, the surplus carbonate in these soils cannot be simply attributed to magnesium because the total content of magnesium TMg, is on average 2.7 times greater than the ΔC_{carb}-values. Therefore, TCa as well as TMg extracted from samples by oxidative acid treatment, besides being of carbonate origin could have an additional source, such as the partial dissolution of some silicates and/or the solubilization of humic-bound Ca and Mg. Magnesium particularly can accumulate in soils as a residue after the degradation of chlorophylic plant material. However, TMg was positively correlated with the actual C_{org} content only for the Centar-soil ($R = 0.645$, $p = 0.042$).

The loosely sorbed and exchangeable P-fraction (P_{exch}) was extracted with 0.5 M KCl, but the concentrations were below the detection limit of ICPAES. This shows either, (*i*) the inorganic as well as the organic sorbed and/or exchangeably-bound P is actually below 0.02 mmol/kg as a result of the ample presence of strong binding substrates, or (*ii*) the obtained result is an artifact, *i.e.,* the temporarily solubilized P_{exch}-fraction in the high-pH suspension reacted subsequently with Ca-ions or with other potential substrates, thus forming insoluble species. The

concentrations of NH_4F–Mg, NH_4F–Ca, NaOH–Mg and NaOH–Ca were also below the respective detection limits.

The differences in the soil composition (Table I) re-enforced the similarities but also the differences existing between particular sections. A decrease of the concentrations of C_{carb}, C_{org}, TMg and TP, from the section Aerodrom to Centar, to Šipčanik can be observed. The existing differences in the soil composition of the particular location sections could have resulted in significantly different chemical characteristics of the soil, thus affecting the formation of specific P-associations. Therefore, it was decided to perform an investigation of the P-distribution for each of these sections separately.

Section Aerodrom

By applying principal component analysis[24] on 14 parameters and after matrix rotation, six factors were extracted with eigenvalues higher than 1, having a total variance of 98.9 % (Table II).

TABLE II. Factor analysis for Aerodrom-soil: eigenvalues, cumulative value, factor composition and communality estimates for 14 soil characteristics (significant factor loadings are shown in bold)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Commun.
Eigenvalue	6.55	2.41	1.46	1.26	1.09	1.08	
Cumulative %	46.8	64.0	74.4	83.4	91.2	98.9	
NaOH–Mn	**0.970**	−0.027	0.021	0.038	0.176	0.142	0.995
TA1	**0.932**	0.149	0.201	0.126	0.167	0.155	0.999
NaOH–Fe	**0.928**	−0.174	−0.082	0.126	0.222	0.156	0.988
TFe	**0.913**	0.216	0.333	−0.082	−0.010	0.054	1.000
TMn	**0.904**	0.292	0.296	−0.035	0.028	0.026	0.993
C_{carb}	**-0.886**	−0.207	−0.344	−0.146	0.065	−0.117	0.986
NaOH–Al	**0.864**	0.033	−0.013	−0.197	0.365	0.006	0.920
TCa	−0.636	−0.562	−0.448	−0.210	−0.100	−0.161	1.000
TMg	−0.023	**−0.991**	−0.074	0.086	−0.065	0.018	0.999
NH_4F–Fe	0.149	**0.873**	0.162	0.373	0.201	0.072	0.996
NH_4F–Al	0.298	0.186	**0.911**	−0.192	−0.083	0.005	0.997
pH	0.010	0.143	−0.163	**0.915**	0.140	0.264	0.973
NH_4F–Mn	0.348	0.256	−0.079	0.186	**0.874**	−0.026	0.992
C_{org}	0.238	0.040	0.027	0.248	-0.022	**0.938**	1.000

Factor 1 consist of three groups of parameters: group I with TA1, TFe and TMn, representing the hydroxide–oxide–clay association of the soil, group II with NaOH–Mn, NaOH–Fe and NaOH–Al, and group III with C_{carb}, which is negatively correlated with the members of groups I and II. The NaOH–metrals, being extracted in high pH suspensions, most probably represent, with the possible partial exception of NaOH–Al, the

humic substance–complexes (HSc) of these metals. Bearing in mind their significant correlations with the total extractable metals (TA1, TFe, TMn), it can be assumed that the NaOH–metals represent native complexation equilibria in these soils. In accordance with this assumption could be the similarity in the ratio of [(NaOH–Fe)/(NaOH–Mn) = 12.4] and the ratio of the conditional stability constants (pH 7.0) of the Fe(III)– and Mn(II)–humic acid complexes,[31] $K_{Fe–Hum}/K_{Mn–Hum} = 10.0$. Finally, group III, the content of carbonatic carbon (C_{carb}), being negatively correlated with groups I and II, represents the main soil constituent, which is complementary to the oxide–hydroxide–clay association, the carbonate group. Considering the above discussion, Factor 1 defines the soil through the status of the oxide–hydroxide–clay association, the carbonates, and the status of humic substances.

Factor 2 consists of TMg (–0.991) and NH_4F–Fe (+0.873). Taking into account the reasonable correlation between TMg and TCa ($R = 0.590$, $p = 0.062$), TMg belongs mainly to the Ca-carbonate-group, which is complementary to the oxide–hydroxide–clay group. The iron dissolved as the NH_4F–Fe fraction at pH 8.2 does not correlate with any other parameters, including TFe. According to Sholkovitz and Copland[32] and Spaks,[33] Fe(III)–humic acid complexes are quite soluble at high pH values and Fe, as well as Al, forms the most stable complexes with humic substances.[33,34] In addition, it can be shown by calculations that at pH 8.2 no detectable Fe(III)- or FeF_4^--ions can exist in solution. It may be assumed then that the NH_4F–Fe can only be in the form of stronger humic substance complexes (HSc), which are extractable or which are formed at pH 8.2. Therefore, Factor 2 is likely to represent the status of the humic substances.

Factor 3 is represented by the amount of aluminium extracted with NH_4F solution at pH 8.2, the NH_4F–Al fraction. Its significant correlations, positively with TFe, and negatively with TCa, indicate the relationship of this Al-fraction with the hydroxide–oxide–clay association. However, its poor correlation with TA1 and the fact that the extraction was performed with NH_4F, indicates that the NH_4F–Al fraction probably represents a mixture of Al-species, *i.e.,* it is at least composed of Al–humic substance complexes and the expected AlF_6^{3-}. Therefore, NH_4F–Al is likely to represent the status of Al established during the extrraction with the NH_4F – reagent, *i.e.,* the operationally established status of Al.

Factor 4 is represented by the pH value of the soil. The lack of correlations with any of the parameters shows that this Factor represents an essential unique soil characteristic, the pH status of the soil.

Factor 5 is represented by NH_4F–Mn (Table II), which does not significantly correlate with any other parameter. Manganese is present in soils in many oxidation states Mn(II)-, Mn(III), Mn(IV)- and mixed-species, including carbonates, oxides, hydroxides, adsorbed and/or precipitated species on calcite, clay minerals, Fe-oxides/hydroxides or organic matter, as well as complexed with organic matter.[35] Under high pH conditions and a low content of organic matter as is the case in the currently investigated soils, a distinct *E*h-dependent shift towards the prevalence of Mn(III, IV)-spe-

cies is observed,[35] and this in turn affects the type of association between Al-, Fe- and Mn-species. Considering that the Mn(III,IV)-species, besides nitrates, represent the most sensitive redox-species of soils,[36] Factor 5 may be considered to represent the Eh-status – or more concretely – the status of Mn in the soils.

Factor 6 consists only of C_{org} (Table II), which does not significantly correlate with any other parameter. This factor expresses the content and the characteristics of the organic matter in the soils and is, therefore, named the organic matter status.

The Factor scores[25] of particular Factor from Table II and the correlations of the phosphorus fractions with these scores are presented in Table III for the Aerodrom-soil.

The content of total phosphorus is inversely proportional to the pH value (Table III; scores of Factor 4). As the $NH_4F–P$ and the $NaOH–P$ fractions did not correlate with the pH-scores, it is obvious that a quantitatively significant fraction within the total phosphorus, defined as ΔP_{AER} (Eq. (1)), was inversely proportional to the pH of the soil.

$$TP_{AER} = TP – (NH_4F–P + NaOH–P) = 40.42 – (2.16 + 1.44) = 36.82 \text{ mmol/kg.} \quad (1)$$

TABLE III. Aerodrom-soil: Factor scores and correlation matrix for TP, $NH_4F–P$, $NaOH–P$ ($n = 8$). Fl: oxide–hydroxide–clay group + carbonate group + humic substance status; F2: humic substance status at pH 8.2; F3: status of Al at pH 8.2; F4: pH of soil; F5: status of Mn; F6: organic matter status. (statistically significant correlation coefficients are shown in bold)

		F1 score	F2 score	F3 score	F4 score	F5 score	F6 score	TP	$NH_4F–P$
TP	R	0.171	–0.092	0.004	**–0.743***	–0.276	–0.415		
	p	0.343	0.414	0.496	**0.017**	0.254	0.153		
$NH_4F–P$	R	0.123	0.321	0.214	0.133	**0.700***	–0.312	0.023	
	p	0.385	0.219	0.306	0.377	**0.027**	0.226	0.478	
$NaOH–P$	R	**0.824****	0.265	0.183	-0.371	0.239	0.108	0.239	0.259
	p	**0.006**	0.263	0.333	0.183	0.284	0.399	0.284	0.268

*, ** Significant at the 0.05 and 0.01 probability levels (1-tailed), respectively

This part amounts 91.1 % of TP, and it was attempted to closer assess its associations by means of correlation analysis with particular substrate-representing parameters. The negative, statistically insignificant correlation of ΔP_{AER} with C_{org} probably excludes organic matter as an important substrate for this main part of the total P. The positive, but insignificant, trends of ΔP_{AER} with TCa and with $\Delta Fe = TFe – (NH_4F–Fe + NaOH–Fe)$ suggest the distribution of ΔP_{AER} between several substrates, but some preference for Ca and for Fe is indicated. As for the inverse proportionality between the TP content (or ΔP_{AER}) and pH, this could be the effect of either: (*i*) the competitive exchange between hydroxyl ions and ions of P-species[19] resulting in a decrease of ΔP_{AER}-retention, and/or (*ii*) a gradual increase of the negative charge on the potential phosphate-binding species with values of

$pH_{zpc} > 8.0$, such as α-Al_2O_3, γ-$AlOOH$, α-Fe_2O_3 and amorphous $FeOOH$, MgO.[20] Thus, with increasing pH, the amount of phosphorus-species directly bound on these substrates decreases.[37] The experimentally documented inverse proportionality between pH and orthophosphate sorption on Fe(III)- or Al-hydroxides by Lijklema[38] is in accordance with both assumptions.

The amount of NH_4F–P is defined by the status of manganese (Table III, scores of Factor 5). This phosphorus fraction should contain only phosphorus bound to Al-species.[12] However, for many soils an unsatisfactory selectivity of the NH_4F-reagent (*i.e.,* a contribution of Fe–phosphorus) was observed.[16,17] The most indicative characteristics related to the NH_4F–P fraction were the following: (*i*) simple correlation analysis indicated no association of NH_4F–P with Al- or Fe-species; (*ii*) considering the great stoichiometrical difference between NH_4F–P and NH_4F–Mn, *i.e.,* 2.16 *vs.* 0.04 mmol/kg, the role of NH_4F–Mn as a bridge-forming metal must be excluded; and (*iii*) NH_4F–P is significantly correlated only with NH_4F–Mn. Taking into account all these, it can be proposed that the NH_4F–P fraction is partitioned between several substrates and this partition feature is probably related to the actual redox equilibrium.

The content of NaOH–P (the Fe-associated P)[12] is defined by the status of the oxide–hydroxide–clay group and the status of the humic substances; (Table III; scores of Factor 1). This finding is in accordance with the investigations of Cassagne *et al.*[39] who proposed NaOH–P to be chemisorbed on Al- and Fe-species or associated with humic substances. A high proportion of humic-asssociated phosphorus in the NaOH–P fraction was also determined by Makarov *et al.*[4] The NaOH–P fraction should strictly consist of P-species associated with Fe-oxide/hydroxides,[12] which are liberated during extraction by exchange with OH^--ions from the NaOH-reagent. However, it is reasonable to assume than any P-substrate association susceptible to such exchange reactions, including also the P-organic compounds or associations, will contribute to the NaOH–P fraction. For example, Taranto *et al.*[40] extracted di-esters of phosphoric acid with $NaHCO_3$ at pH 8.5 (Olsen-P), and mono-esters (Fe-phytates) with NaOH. Vig *et al.*[22] concluded that the NaOH–P in calcareous soil is positively correlated with the Olsen-P. Similarly, Blagojević *et al.*[21] also found a significant correlation of NaOH–P with the plant-available P in a calcareous chernozem.

Section Centar

Applying the same procedure[24] as for section Aerodrom, five Factors, which define the soils, were extracted having a total variance of 98.7 % (Table IV).

TABLE IV. Factor analysis for the Centar-soil: eigenvalues, cumulative value, Factor composition and communality estimates for 14 soil characteristics (significant Factor loadings are shown in bold)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Commun.
Eigenvalue	5.09	3.00	2.45	2.12	1.15	
Cumulative %	36.3	57.8	75.3	90.5	98.7	
TMn	**0.964**	–0.050	–0.078	0.216	–0.073	0.991

TABLE IV. Continued

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Commun.
TA1	**0.964**	0.125	−0.015	0.126	−0.011	0.961
TFe	**0.920**	0.010	−0.067	−0.329	0.195	0.998
C_{carb}	**−0.915**	0.074	0.097	−0.329	0.195	0.998
NH_4F–Al	0.580	0.321	−0.234	0.485	0.490	0.970
C_{org}	−0.125	**0.891**	0.406	−0.304	0.237	0.095
NaOH–Al	0.283	**0.852**	0.304	0.237	0.095	0.964
pH	−0.116	**−0.818**	0.231	−0.22	0.457	0.999
TMg	−0.552	**0.717**	−0.245	0.253	0.201	0.984
NaOH–Mn	−0.093	0.134	**0.985**	−0.039	−0.006	0.998
NaOH–Fe	−0.037	0.073	**0.974**	−0.178	−0.012	0.987
NH_4F–Mn	0.372	0.175	−0.299	**0.857**	0.008	0.993
NH_4F–Fe	0.488	0.345	0.030	**0.797**	−0.037	0.995
TCa	−0.638	0.013	−0.010	−0.022	**0.761**	0.987

Factor 1 is represented by two groups of parameters: (*i*) Mn, TAl, TFe, and (*ii*) C_{carb} (Table IV). The members of the first group represent the oxide–hydroxide–clay association and correlate negatively with C_{carb}, the complementary carbonate group. Factor 1 defines the soil by the status of the oxide–hydroxide–clay and the carbonate groups.

Factor 2 defines the Centar-soil also with four parameters belonging to two inversely proportional groups (Table IV): (*i*) with C_{org}, NaOH–Al and TMg and (*ii*) with the pH value (− 0.818). Taking into account the close relationship between NaOH–Al and C_{org} ($R = 0.839$, $p = 0.005$) as well as the high stability of complexes of Al–humic substance,[33,34] it can be proposed that this aluminium-fraction consist mainly of Al–HSc. However, the formation of this complex as well as of aluminates depends on the status of the Al-species, which in turn depends on pH. Therefore, the NaOH–Al fraction represents the status of Al. A better correlation of TMg with C_{org} ($p = 0.042$) than with C_{carb} ($p = 0.108$) points to a preferential relation of Mg with organic matter rather than with the carbonate group, but demonstrates also the diverse associations of magnesium in the soil compounds. The inverse proportionality between NaOH–Al or C_{org} and pH can be explained as an effect of the increased mobility of the humic part of organic matter or of relevant Al-species (*e.g.* aluminates, Al–HSc) with increasing pH. Considering all these, Factor 2 defines the Centar-soils in terms of organic matter, Al-species, Mg-species and pH.

Factor 3 defines the soils by the NaOH–Mn and NaOH–Fe fractions, *i.e.,* the amount of Mn and Fe which are in solution under the high pH-conditions of NaOH-extraction, a fact which points to their coordinative nature. In addition, their positive trends with C_{org} (for NaOH–Mn: $R = 0.528$, $p = 0.089$; for NaOH–Fe: $R = 0.468$; $p = 0.121$), may indicate a relationship with humic substances. It can be pro-

posed that these two NaOH–metals express the status of Mn– and Fe–humic substance complexes.

Factor 4 is represented by the NH_4F–Mn and NH_4F–Fe fractions (Table IV). On the basis of a detailed analysis of all correlations, it can be proposed that these NH_4F–metals represent the operationally established status of Mn and Fe.

Factor 5 is represented by the total extractable calcium, TCa, which is positively correlated only with C_{carb} and fairly well with TMg. The stoichiometrical relationships between these three parameters were introductorily discussed and considered all these, Factor 5 defines soils by the status of calcium.

TABLE V. Centar-soil: Factor scores and correlation matrix for TP, NH_4F–P, NaOH–P ($n = 8$). F1: oxide–hydroxide–clay group + carbonate status; F2: organic matter status + Al-status + Mg-status + pH-status; F3: Mn– and Fe–humic substance complex status; F4: Mn- and Fe-status at pH 8.2; F5: Status of Ca (statistically significant correlation coefficients are shown in bold)

		F1 score	F2 score	F3 score	F4 score	F5 score	TP	NH_4F–P
TP	R	0.450	0.260	**0.728***	0.006	–0.265		
	p	0.131	0.267	**0.020**	0.494	0.263		
NH_4F–P	R	**0.677***	-0.239	0.516	0.369	0.113	0.588	
	p	**0.032**	0.285	0.095	0.184	0.395	0.062	
NaOH–P	R	0.168	**0.865***	–0.047	0.218	–0.141	0.428	–0.003
	p	0.345	**0.003**	0.456	0.302	0.370	0.145	0.498

*,** Significant at the 0.05 and 0.01 probability levels (1-tailed), respectively

The content of total phosphorous of the Centar-soil is defined by the status of Mn– and Fe–humic substance complexes (Table V; scores of Factor 3), *i.e.,* the concentration of TP is directly proportional to the amount of NaOH–Mn and NaOH–Fe, which express the status of the complexes of these two metal–humic substances. As the two P-factions, NH_4F–P and NaOH–P were not related to the NaOH–metals, it can be concluded that a quantitatively significant P-fraction within the TP is related to the status of Mn– and Fe–humic substance complexes. An attempt to assess closer the associations of this main part of the TP, amounting to 90.6 % (Eq. (2)), gave no unambiguous response, thus pointing to a partitioning of ΔP_{CEN} between several soil constituents. On the basis of simple correlation analysis, the most probable binding sites of ΔP_{CEN} would be on the organic matter and on Fe- and Mn-species.

$$\Delta P_{CEN} = TP – (NH_4F–P + NaOH–P) = 33.33 – (1.43 + 1.69) = 30.21 \text{ mmol/kg.} \quad (2)$$

The amount of NH_4F–P (considered as Al–associated P)[12] is defined by the status of the oxide–hydroxide–clay group (Table V; scores of Factor 1), *i.e.*, the content of this P-fraction is directly proportional to the TA1, TFe and TMn. As a consequence of the high degree of direct proportionality between the constituents

of the oxide–hydroxide–clay group, it was not possible to allocate the proportions of Al-and Fe-species acting as possible substrates.

Finally, the amount of NaOH–P (considered as Fe–associated phosphorus)[12] is defined by the status of the organic matter, of aluminium, magnesium and pH (Table V; scores of Factor 2). As the correlation between NaOH–P and NaOH–Al seems to be an artifact (two distant groups of data points; not shown), the organic matter and/or Mg-species are most probably involved in the pH-dependent accumulation of NaOH–P. However, no clear indications of an association of NaOH–P with Fe-species were found.

Section Šipčanik

The Šipčanik soil was also characterized by 5 Factors with a total variance of 96.9 % (Table VI).

TABLE VI. Factor analysis for the Šipčanik-soil: eignvalues, cumulative value, Factor composition and communality estimates for 14 soil characteristics (significant Factor loadings are shown in bold)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Commun.
Eigenvalue	4.96	3.08	2.56	1.49	1.48	
Cumulative %	35.4	57.4	75.7	86.3	96.9	
NH_4F–Al	**0.921**	0.156	0.219	0.125	–0.192	0.973
TMn	**0.848**	0.334	0.284	0.165	0.234	0.993
TFe	**0.828**	0.369	0.289	0.206	0.196	0.986
TA1	**0.807**	0.292	0.316	0.261	–0.158	0.930
C_{carb}	**–0.748**	–0.331	–0.513	–0.226	–0.071	0.987
NaOH–Al	0.615	0.444	0.494	0.396	–0.069	0.987
NaOH–Fe	0.241	**0.915**	0.303	–0.016	–0.069	0.991
NaOH–Mn	0.270	**0.909**	0.291	–0.014	–0.104	0.996
pH	–0.546	**–0.704**	0.127	–0.079	–0.324	0.921
NH_4F–Mn	0.360	0.225	**0.838**	0.169	0.113	0.925
TCa	–0.395	–0.378	–0.644	–0.245	–0.418	0.947
NH_4F–Fe	0.561	0.242	0.599	0.421	0.180	0.941
TMg	–0.287	0.067	–0.224	**–0.921**	–0.104	0.996
C_{org}	–0.050	–0.006	0.147	0.074	**0.976**	0.987

Factor 1 is composed of three groups of parameters (Table VI): group 1, with TMn, TFe and TA1, which represent the hydroxide–oxide–clay associations group II, with NH_4F–Al, which is significantly correlated with each component of group I, and group III, the carbonates – C_{carb} (–0.748). Detailed analysis of all correlation diagrams of NH_4F–Al (not shown) did however demonstrate that the significance of the NH_4F–Al correlations is artificial because it is the result of two relatively compact and very distant groups of data points. Hence, Factor 1 represent the status of the oxide–hydroxide–clay association and the complementary carbonate group.

Factor 2 is composed of two negatively correlated groups of parameters: (*i*) NaOH–Fe and NaOH–Mn and (*ii*) soil pH (–0.704) (Table VI). The NaOH–metals correlate positively with the TFe and TMn, suggesting a relationship with the native Fe and Mn complexes of the humic substance, as in the Aerodrom-soil. The significant negative correlation of NaOH–Fe and NaOH–Mn with pH ($p = 0.030$ and 0.027, respectively), could have several explanations: (*i*) the consequence of complementarity of the oxide–hydroxide–clay group and the carbonate group, which is mainly responsible for the pH value; (*ii*) the result of the pH-mediated higher mobility of humic substance complexes,[32,33] (*iii*) a pH-mediated reduced availability of Fe-and Mn-ions for complex formation, and (*iv*) the competitive action of hydroxyl ions on the ligands of bridge-forming metals.[19] Considering all these, Factor 2 is likely to represent the status of Fe–and Mn–humic substance complexes and the pH-status of the soil.

Factor 3 defines the Šipčanik-soil through the NH_4F–Mn fraction. As with the discussion relating to this fraction in the Aerodrom-soil (Factor 5), the NH_4F–Mn, most probably, represents the status of manganese in this soil.

Factor 4 defines the soil by its acid-extractable magnesium content, TMg (–0.21). The diverse associations of Mg in these soils have been discussed above. Thus, Factor 4 is most likely to represent the status of magnesium.

Factor 5 is represented by C_{org} (Table VI). The organic carbon content does not correlate with any other parameter, hence it is a manly independent soil characteristic. Therefore, Factor 5 was defined as representing the organic matter status.

The relations between the phosphorus fractions in the Šipčanik-soil with the Factor scores representing the soil characteristics are shown in Table VII.

TABLE VII. Šipčanik-soil: Factor scores and correlation matrix for TP, NH_4F–P, NaOH–P and (n=8). F1: oxide–hydroxide–clay group + carbonate-status; F2: status of Fe– and Mn– humic substance complex + pH-status of soil; F3: Mn-status; F4: Mg-status; F5: organic matter status (statistically significant correlation coefficient are shown in bold)

		F1 score	F2 score	F3 score	F4 score	F5 score	TP	NH_4F–P
TP	*R*	0.471	**0.624***	0.237	0.500	– 0.035		
	p	0.119	**0.049**	0.286	0.103	0.467		
NH_4F–P	*R*	**0.666***	– 0.287	0.445	0.044	– 0.465	0.265	
	p	**0.036**	0.245	0.135	0.459	0.123	0.263	
NaOH–P	*R*	**0.627***	**0.702***	0.094	0.103	0.279	**0.835****	0.124
	p	**0.048**	**0.026**	0.412	0.404	0.252	**0.005**	0.385

*, ** Significant at the 0.05 and 0.01 probability levels (1-tailed), respectively

The content of TP is defined by the status of the Fe– and Mn–humic substance complexes and the pH-status (Table VII; Factor 2 scores). This direct proportionality between TP and Fe–HSc and Mn–HSc, respectively, suggests that they play a significant role in the fixation mechanism of phosphorus. The inverse proportionality of TP

with soil pH can therefore be explained by the increased mobility of humic substances with increasing pH.[33,37] There is ample evidence for the fixation of inorganic and organic phosphorus on humic and other organic substances.[4,9,39,41,42] The main part of the TP in the Šipčanik-soil, which is related to Fe– and Mn–HSc, is defined as ΔP_{SIP} (Eq. (3)) and it is also related to the NaOH–P fraction, as will be shown below:

$$\Delta P_{SIP} = TP - NH_4F-P = 27.85 - 1.53 = 26.32 \text{ mmol/kg (or 94.5 \%)} \qquad (3)$$

The contents of NH_4F–P (defined as the Al–P), as well as of the NaOH–P fraction (defined as the Fe–P) are both defined by the status of the oxide–hydroxide–clay group and by the status of C_{carb} (Table VII; scores of Factor 1). In addition, the NaOH–P fraction is simultaneously defined by the status of the Fe– and Mn–humic substance complexes (Table VII, Factor 2 scores), *i.e.*, the same Factor score which defines TP. At the same time, NaOH–P and TP are highly significantly correlated (Table VII). Hence, in contrast to the Aerodrom- and Centar-soils, this points to the occurrence of an equilibrated partition of phosphorus between the constituents of the oxide–hydroxide–clay group.

A comparative consideration of Factor defining the P-fractions

The conent of TP in the Centar- and Šipčanik-soils is defined by the status of Mn– and Fe–humic substance complexes (Table V, Table VII), Consequently, these HSc are, directly or indirectly, a significant factor in the accumulation of the main part of P: for the Centar-soils (Eq. (2)) and for the Šipčanik-soils (Eq. (3)). The score of Factor 2 for the Šipčanik soil additionally includes pH, as an inversely proportional Factor (Table VI, Table VII), which points to a different nature of binding of ΔP_{SIP} on the humic complexes. In the Centar-soil, it is proposed that ΔP forms more stable bonds to the substates whereas in the Šipčanik-soil, these bonds or the substrates are obviously susceptible to the action of hydroxyl ions. This action of hydroxyl ions could be the consequence of either, (*i*) competition with the phosphate ions for binding sites, or (*ii*), a gradual charge-changing effect on those soil components, the pH_{zpc} of which are on the border of the actual pH-range, such as amorphous FeOOH (pH_{zpc} 8.2) and γ-AlOOH (pH_{zpc} 8.1).[20] This would decrease the capacity of constituents of the soil to directly bind phosphate ions. In contrasts with these two soils, in the Aerodrom-soil, ΔP_{AER} (Eq. (1)) is defined by only one Factor (pH) and this feature can be explained as for the Šipčanik-soil. However, the absence of substrate-representing parameters in the Factor-score which defines TP, *i.e.,* ΔP_{AER}, leads to the assumption that the P-mobilizing effect of hydroxyl ions in the Aerodrom-soil is not substrate-species.

The NH_4F–P (Al–associated P) is only defined in the Aerodrom-soil by the status of manganese, which was shown to be closely related to the *E*h of a soil.[35] In fact, the ratio, "potential reductants"/"potential oxidates", *i.e.,* C_{org} (TFe + TMn) which may be critical in determining redox equilibria, is highest in the Aerodrom-soil, 7.1 (whereas this ratio for the Centar-and the Šipčanik-soil is 6.5 and 4.9, respectively). In the latter

two soils, NH$_4$F–P is defined by the status of the oxide–hydroxide–clay group and by the status of the carbonates. It should be emphasized that among the constituents of the oxide–hydroxide–clay group, Al-species may play a significant role considering the *p*-values obtained by simple correlation analysis: for the Centar-soil, the *p*-values for the correlations of NH$_4$F–P with TA1, TFe and TMn were 0.028, 0.025 and 0.034, respectively; for the Šipčanik-soil: 0.022, 0.120 and 0.107, respectively. It remains, however, unclear whether the above shown good correlation of NH$_4$F–P also with TFe is the consequence of the unsatisfactory selectivity of the NH$_4$F-reagent, characterized by a contribution of Fe–phosphorus,[11,14,16,17] or a result of the highly significant correlation between TA1 and TFe (for the Centar-soil, *p* = 0.000 and for the Šipčanik soil *p* = 0.002). According to Vig *et al.*,[22] the NH$_4$F–P fraction in calcareous soil is positively correlated with the Morgan-phosphorus (acetic acid extractable P) and belongs to the plant-available P pool. Similarly, Blagojević *et al.*[21] obtained a significant correlation between Al–P and plant-available P.

As shown in Table III, Table V and Table VII, the most striking difference between the three soils is expressed by the nature of the Factors which define the content of the NaOH–P fraction (Fe–associated phosphorus) and no consistent generalization is possible. The high degree of proportionality between NaOH–P and TP in the Šipčanik-soil is probably due to the high competitive capacity of the constituents of the oxide–hydroxide–clay group for binding P-species, as shown by the high value of the ratio (TA1 + TFe + TMn)/TP = 60.8 (this ratio for the Aerodrom- and the Centar-soil is significantly lower, 35.3 and 43.7, respectively). The inverse relationship of NaOH–P with pH (Centar- and Šipčanik-soils) emphasizes the competitive effect of hydroxyl ions on the binding sites of phosphorus or the pH$_{zpc}$-related effect,[19,20] as was previously discussed. The relative stoichiometric closeness of the values for the contents of NaOH–P and NaOH–Fe in the three soils (Aerodrom: 1.44 *vs*. 1.14; Centar: 1.68 *vs*. 1.64 and Šipčanik: 1.29 *vs*. 1.24 mmol/kg, respectively) demonstrates a possible bridge-forming role of this iron-fraction, most likely as humic substances–Fe–P, as was proposed by Boers and DeBles.[9] However, for the Centar-soil this is not very likely because of the not significant correlation between NaOH–P and NaOH–Fe (not shown) and the existence of much better correlations of NaOH–P with organic carbon, TMg and NaOH–Al, indicating a different association feature characterized by the participation of organic matter, as well as Mg- and Al-species.

CONCLUSION

In the three highly calcareous soils, the significantly differing contents of C$_{org}$, TMg and TP, supplemented by the influence of the existing slight differences in the contents of main soil-constituents (TCa, TA1, TFe) causes, to a certain degree, differing chemodynamics of phosphorus. These difference are reflected in the nature of the Factors which define the contents of particular P-fractions, as well as the characteristics of P/substrate associations.

The content of the exchangeable-bound P-fraction, extracted with KCl in all three soils, was found to be below 0.02 mmol/kg, reflecting either a low concentration or the effect of subsequent removal from the solution by reactions with other active species during the extraction procedure, due to the high pH of the suspension.

The NH_4F–P fraction (assigned as the Al–associated P) amounted, on average, to 2.16, 1.43 and 1.53 mmol/kg or 5.35, 4.29 and 5.49 % of TP, in the three soils, Aerodrom, Centar and Šipčanik, respectively, This P-fraction is defined by the constituents of the oxide–hydroxide–clay group (Centar- and Šipčanik-soils) and among these constituents there is a slight dominance of Al-species, but the status of this group as a whole seems to be the key-Factor. In other words, despite the high atomic ratio of reactive Al *versus* reactive Fe (Al/Fe = 2.9), no unambiguous indication for the selectivity of the NH_4F-reagent was obtained. In soils with the lowest probable oxidation potential, *i.e.,* those having the highest ratio (potential reductants)/(potential oxidants) = C_{org}/(TFe + TMn), as in the Aerodrom-soil, NH_4F–P is defined by the status of manganese, which is closely related to the Eh of the soil. Generally, it can be concluded that the content of the NH_4F–P fraction is defined by the contents of the main metals of the oxide–hydroxide–clay association (Al, Fe, Mn) or by the Eh-expressing status of manganese, and this P-fraction does not depend on pH in the observed range of values, 8.0 – 8.2.

The NaOH–P fraction (the Fe–P) amounted on average to 1.44, 1.69 and 1.29 mmol/kg or 3.56, 5.08 and 4.63 % of TP, in the three soils, Aerodrom, Centar and Šipčanik, respectively. The differences in the composition of these three calcareous soils are most remarkably reflected by the nature of the Factors which define the content of NaOH–P, and no generalization can be made.

The high degree of proportionality between NaOH–P and TP in the Šipčanik-soil is probably a consequence of the high competitive activity of the constituents of the oxide–hydroxide–clay association for binding P-species, as shown by the high value of the (TA1 + TFe + TMn)/TP ratio = 60.8 (the values of this ratio for the Aerodrom- and the Centar-soils are 35.3 and 43.7, respectively). The binding sites of NaOH–P (Centar- and Šipčanik-soil) are susceptible to the action of hydroxyl ions, which indicates either (*i*) the hydroxyl ions are directly competitive with the P-ions for the binding sites, or (*ii*) they affect the pH_{zpc}.

In the Aerodrom-soil, the content of NaOH–P is defined by the constituents of the oxide–hydroxide–clay association and the status of humic substances. The content of NaOH–P is apparently independent of pH, which suggests the existence of a relatively strong, perhaps coordinative bonding of the bridge-forming Fe.

In the Centar-soil, a partitioning of NaOH–P between several substrates, with the participation of organic matter, Mg- and Al-species in the binding of NaOH–P, is proposed and the P/substrate bonds are susceptible to the influence of hydroxyl ions.

As a common feature of the soils Aerodrom, Šipčanik, in which the content of NaOH–P is defined by the oxide–hydroxide–clay association, the participation of

NaOH–Fe as a bridge-forming metal in structures such as humic substance–Fe–P is indicated and no dependence on pH is observed.

The soil characteristic, which defines the retention of the main part of the total P (*i.e.*, TP – NH_4F–P and/or NaOH–P; amounting for the Centar-soils to 90.6% and for the Šipčanik-soils to 94.5 %) – is the status of the Mn– and Fe–humic complexes. In the Aerodrom-soil, the main of the TP, *i.e.,* 91.1 %, is inversely related to the pH, which demonstrates a non-selective P mobilization or the limiting action of the hydroxyl ions.

ИЗВОД

ХЕМИЈСКЕ КАРАКТЕРИСТИКЕ ВИСОКО-КРЕЧЊАЧКИХ ЗЕМЉИШТА КОЈЕ ОДРЕЂУЈУ РАСПОДЕЛУ ФОСФОРА

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Из три високо-кречњачка земљишта (просечни садржај CO_3^{2-} 24.9 ± 4.8%, pH 8.0 – 8.2), са локација са средоземном климом, изоловане су фракције фосфора секвенцијалном екстракцијом. У циљу обезбеђивања поузданије основе за дефинисање добијених фракција фосфора (P-фракција), примењена је анализа принципалне компоненте (PC-анализа). Међу 14 хемијских карактеристика земљишта, издвојене су оне које дефинишу садржај појединих P-фракција и природу њихове асоцијације са састојцима земљишта. Фракција NH_4–P (изолована са 0,5M NH_4F, pH = 8,2) дефинисана је садржајем главних метала оксидне–хидроксидне–глинене асоцијације (Al, Fe, Mn) или *E*h-статусом израженим садржајем Mn. Акумулација NaOH–P (екстрахованог са 0,1 M NaOH) зависила је од састојака оксидне–хидроксидне–глинене асоцијације, од хуминских супстанци и од фактора који стоје у вези са *E*h. У оним земљиштима у којима је NaOH–P дефинисана састојцима оксидне–хидроксидне–глинене асоцијације, претпостављено је везивање фосфора преко Fe-мостова. Главна количина фосфора ΔP = TP – (NH_4F–P + NaOH–P), у појединим земљиштима дефинисана је или статусом Mn– и Fe–хуминских комплекса, или pH-вредношћу.

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