DISTRIBUTION, MOBILITY AND BIOAVAILABILITY OF PHOSPHORUS INTO SOILS FROM GLASSHOUSES

DISTRIBUŢIA, MOBILITATEA ŞI BIODISPONIBILITATEA FOSFORULUI ÎN SOLURILE DIN SERE

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Abstract. *The studies performed in Copou-Iaşi glasshouse have evidenced that in these soils the phosphorus has a particularly dynamic,. The occurrence forms of phosphorus are more varied, the ratios between the mobile and fix forms and between organic and inorganic forms respectively, had large variations from one horizon to another and even within the same horizon. The total phosphorus content varied between 94.57–747.15 μg P_2O_5 / g soil, with a profile average of 357.53 μg P_2O_5 / g soil. The maximum contents of P_{total} is observed in Ap1k (2.08 times more that the profile average) and Aho2k(x) (1.84 times more that the profile average). In Ahok(x) horizons, the phosphorus has two particular occurrence forms: (**i**) inorganic form – most probable a polymetaphosphate associated with aluminisilicated gel; (**ii**) complex association forms between humic and fulvic acids, amorphous clay minerals and iron complex phosphates (or other ions) – these having an important role in the formation of frangipane horizons.*

Key words: phosphorus bioavailability, greenhouse soils

Rezumat. *Studiile realizate în sera Copou-Iaşi au evidenţiat faptul că în solurile din sere fosforul are o dinamică particulară. Formele de ocurenţă ale fosforului sunt mai variate, iar raporturile dintre formele mobile şi cele fixe, respectiv dintre formele organice şi cele anorganice, prezintă variaţii largi de la un orizont la altul şi chiar în cadrul aceluiaşi orizont. conţinutul total de fosfor variază între 94,57–747,15 μg P_2O_5 / g sol, cu o medie pe profil de 357,53 μg P_2O_5 / g sol. Conţinuturi maxime ale P_{total} se înregistrează la Ap1k (de 2,08 ori mai mare ca media pe profil) şi Aho2k(x) (de 1,84 ori mai mare ca media pe profil). În orizonturile Ahok(x) fosforul prezintă două forme de ocurenţă particulare: (i) forma anorganică – cel mai probabil un polimetafosfat asociat cu gel aluminosilicatic; (ii) forme de asociere complexe între acizii fulvici sau huminici, minerale argiloase amorfe şi fosfaţi complecşi de fier (sau alţi ioni metalici) – acestea au un rol în formarea orizonturilor fragipanice*

Cuvinte cheie: biodisponibilitate fosfor, sol seră

INTRODUCTION

The phosphorus is a key element for the structural support of organisms and dynamic of fundamental biochemical reactions, which involve the genetic material and energy transfer. In comparison with other nutritive essential elements, phosphorus has a reduced geochemical mobility and is low assimilable by plants, in conditions of most of soils. The phosphorus from parental material of soils is not directly accessible for plants and organisms. The conversion of inaccessible forms in soluble orto-phosphate, which can be directly assimilated, is done by geochemical and biochemical processes, in different steps of pedo-geochemical cycle of phosphorus (S.K. Sanyal & D.K. De Datta, 1991; M.D. Mullen, 2003; K.C. Ruttenberg, 2003; J.T. Sims & P.A. Vadas, 2005). At world level, the total content of phosphorus from soils varied between 0.01–0.15 % P. In soils from Romania, the total content of phosphorus varied between 0.026 % P – 0.093 % P. From total phosphorus content only 0.5–1.0 % is accessible by plants (Z. Borlan & Cr. Hera, 1973; R. Lăcătuşu, 2006).

Due to its importance, in literature are numerous studies which present different agrochemical aspects of phosphorus: various occurrence forms (inorganic and organic) in soils, association way of these with soil components, inter-phases distribution and adsorption mechanisms by plants, etc. For the soils from glasshouses and solariums, these problems are these problems are insufficiently known and studied. Despite the research conducted by now, the current representations on the phosphorus issue in soils from glasshouses require substantially studies. The data from literature concerning the distribution and dynamic of phosphorus in soils from glasshouses are mostly contradictory. In most of cases, the studies present different particular cases, there are no clear indications and generalizations (Z. Borlan & Cr. Hera, 1973; B. Mănescu, 1984; D. Davidescu & V. Davidescu, 1992; I. Avarvarei et al., 1994; V. Voican & V. Lăcătuş, 1998).

Ours studies were performed using soil samples from Copou – Iaşi glasshouse, from two profiles. We follow the variations on profile of total and differential (extractable) contents of phosphorus, the distribution way of occurrence and speciation forms of phosphorus, respectively. The obtained results have show that in soils from glasshouses, the phosphorus has a particularly dynamics, different that those observed in case of unprotected plants soils. The occurrence forms of phosphorus are more varied, ratios between mobile and fix forms, and between the organic and inorganic forms respectively, present large variations from to a horizon to other, and the equilibriums between these are very sensible even at relative low variations of physic-chemical conditions.

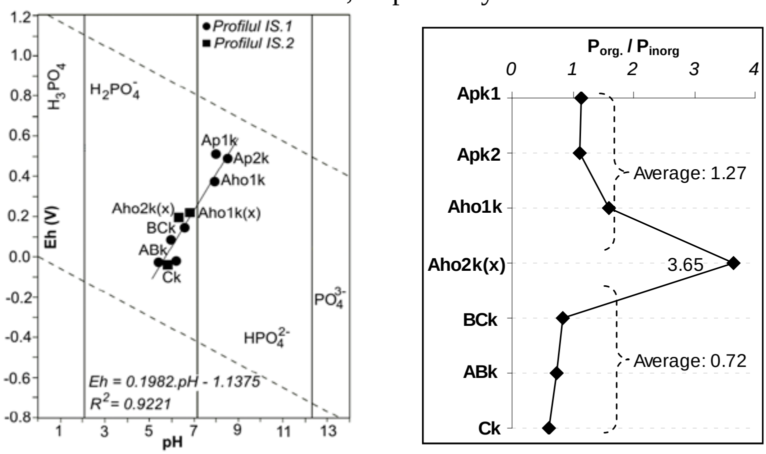
MATERIAL AND METHOD

The studies were performed on soil samples from Copou – Iaşi glasshouse, from two profiles (IS.1 and IS.2 – table 2). The pedo-geochemical and chemical-minerlogical characteristics of studied soils have been presented in a previous study (F. Filipov et al., 2008). The determination of total phosphorus contents and of its extractable fractions was done according with work methodology described by Z. Borlan & C. Răuţă (1981) and N. Florea et al. (1986), respectively. The determination of occurrence forms and the estimation of speciation forms of phosphorus the specific association ways of these with the mineral and organic components of soils respectively, was performed by sequential solid-liquid extractions, chemical analysis, microscopy, spectrometry (IR and Raman) and X-ray diffraction respectively, according with the methodology described by D. Bulgariu et al. (2008).

RESULTS AND DISCUSSIONS

For the studied soil samples, the total phosphorus (P_{total}) varied between 94.57-747.15 µg P_2O_5 / g (0.041-0.326 % P) with an average of 357.53 µg P_2O_5 / g (0.156 % P) on profile, and 374.78 µg P_2O_5 / g for studied perimeter (span no. 16, Copou-Iaşi glasshouse) (table 2). The maximum concentrations of P_{total} were observed in Ap1k and Aho2k(x) horizons, and the minim contents in ABk and Ck horizons. From total phosphorus content point of view, the soisl from Copou glasshouse fall within the normal limits (Z. Borlan & Cr. Hera, 1973; B. Mănescu, 1984; I. Avarvarei et al., 1994; V. Voican & V. Lăcătuş, 1998).

The organic phosphorus ($P_{org.}$) varied between 36.45-563.60 µg P_2O_5 / g with an average of 211.95 µg P_2O_5 / g on profile and 242.52 µg P_2O_5 / g for the studied perimeter. The maximum concentration of $P_{org.}$ is obtained in Aho2k(x) and Ap1k horizons, and the minim contents in ABk and Ck horizons (figure 1.b). The inorganic phosphorus ($P_{inorg.}$) varied between 54.67-350.48 µg P_2O_5 / g with an average of 145.57 µg P_2O_5 / g on profile, and 132.25 µg P_2O_5 / g for the studied perimeter. The maximum concentrations of P_{inorg} are obtained in Ap1k horizon, and the minim concentrations in ABk and Ck horizons, respectively.



(a) (b)

Fig. 1. (a) pH – E_h diagram of P – O – H system at 298,15 K, 10^5 Pa and $\sum[P] = 10^{-10}$ (E_h – redox potential). The diagram evidenced the differentiation of pH and redox potential conditions between superior and inferior horizons of IS.1 profile determined by the formation of Aho2k(x) frangipane horizon. (b) The variation of ratio between organic and inorganic phosphorus in IS.1 profile.

The mobile phosphorus, extractable in acetate-lactate P(AL), varied between 90.09-734.67 µg P_2O_5 / g (88.61-98.71 % from P_{total}) with an average of 338.93 µg P_2O_5 / g on profile and 348.93 µg P_2O_5 / g for the studied perimeter. The maximum concentrations of P(AL) are obtained in Ap1k and Aho2k(x) horizons, and the minim contents in BCk and Ck horizons. The weight of extractable phosphorus forms follow the order: $P(H_2SO_4)$ >> P(NaOH) > $P(NH_4F)$ >> $P(H_2O)$, the higher values being obtained in superior horizons. It was observed that in Aho2k(x) horizon, the concentrations of Ca-P and Al-P are higher that those from other horizons.

The experimental results presented in figure 1.a and in table 2 indicate that the phosphorus from Copou-Iaşi glasshouse is sufficiently mobile for to ensure the necessary for the cultivated plants. However, the bioavailability of phosphorus in these soils is relatively low, which limits the possibility to be assimilated by plants. In our opinion, this is determined by: (i) significant decrease of inorganic phosphates solubility, due to salinization processes, (ii) incorporate appreciable amounts of phosphorus in the composition of the organic-mineral complexes (table 1) and of organic-phosphoric esters (inosito-phosphate, in specially) – in which the phosphorus is hard assimilable, even though partially these forms of occurrence of phosphorus is extracted in acetate-lactate, (iii) the geochemical segregation phenomena induced by Aho2k(x) frangipane horizons, which determined the differential evolution of pedo-geochemical processes in superior horizons (aerobic conditions, CTS = 315.51–675.49 mg / 100 g soil; pH=7.84–8.28; E_h=365,19–521,37 mV, higher humidity and temperature), in comparison with inferior horizons (anaerobic conditions, CTS= 52,95–305.82 mg / 100 g sol; pH=5.41–6.17; E_h=(- 14,71)–96,45 mV; reduced humidity and temperature).

Table 1

Phosphorus content of organic-mineral complexes in soils from Copou-Iaşi glasshouse (profile IS.1)

Horizons	OMC* %, w/w	Composition OMC [%, w / w]					Phosphorus from OCM	
		CM.	OOC.	SiO_2	FeOx	OC.	μg P_2O_5/g#	% din P_{total}
Apk	13.05	71.39	18.47	3.41	4.88	1.85	40.69	7.89
Aho1k	32.87	64.11	24.90	2.63	7.09	1.27	55.55	17.05
Aho2k(x)	48.36	62.08	22.05	5.69	7.36	2.82	357.95	54.37
BCk	29.05	72.53	13.91	4.56	5.83	3.17	12.06	10.72
ABk	37.19	78.86	11.53	2.73	4.15	2.73	11.73	12.41
Ck	11.36	76.45	9.76	3.39	7.61	2.79	10.02	8.05

*Organic-mineral complexes (% towards soil sample). CM. – clay minerals. OOC. – organic compounds. SiO_2 – amorphous silica. FeOx – iron oxides and oxy-hydroxides. AC – other components. # μg P_2O_5 / g sol.

Corroborating data on the distribution of forms of occurrence of phosphorus in the profile with results from microscopic, spectral (in UV-VIS, IR and Raman) and X-ray diffraction studies, result that in Aho2k(x) horizons, the phosphorus from glasshouses has two particular occurrence forms, with a very important role in the formation of frangipane horizons: (**i**) inorganic forms, represented most probable by solid solutions of polymethaphosphates and aluminosilicates gel–crystall-chemical formulas: $0.69K_2O.Al_2O_3.1.59SiO_2.0.38 P_2O_5.2.53H_2O$ and $0.58 Na_2O.Al_2O_3.0.99SiO_2.0.52P_2O_5.3.12H_2O$ in IS.1 profile, and $0.54K_2O.Al_2O_3.1.54SiO_2.0.36P_2O_5.3.82H_2O$ and $Na_2O.Al_2O_3.1.71SiO_2.0.24 P_2O_5.4.32H_2O$ in IS.2 profile; (**ii**) complex association forms between fulvic and huminic acids, amorphous clay minerals, complex phosphates with iron (or other metal ions) and inositol-phosphates – which include cca. 54 % from P_{total} localized at the level of this horizon (table 2).

Table 2

The distribution of phosphorus in soils from Copou-Iaşi glasshouse

Horizons	H, cm	P_{Total};	$P_{org.}$;	$P_{inorg.}$;	Extractable phosphorus; µg P_2O_5 / g					$P_{ocl.}$	$P_{non-ocl}$	$P_{org.}$/ P_{inorg}
	µg P_2O_5 / g				$P(H_2O)$*	$P(NH_4F)$*	P(NaOH)	$P(H_2SO_4)$	P(AL)	µg P_2O_5 / g		
Profile IS.1: Hipohortic Entianthrosol Mixed-Proxicalcaric												
Ap1k	0–10	747.15	396.66	350.48	32.50	24.35	58.95	630.29	734.67	734.67	12.47	1.13
Ap2k	10–18	439.72	231.51	208.20	11.65	17.80	36.54	372.13	426.74	426.74	12.97	1.11
Aho1k	18–28	325.81	200.17	125.63	5.96	21.60	37.89	259.99	308.05	308.05	17.75	1.59
Aho2k(x)	28–40	658.36	516.87	141.48	4.93	75.77	128.64	445.77	583.37	583.37	74.98	3.65
BCk	40–48	112.59	51.60	60.99	1.06	7.93	10.97*	91.99	108.94	108.94	3.64	0.84
ABk	48–70	94.57	39.89	54.67	1.10	5.43	9.67*	78.05	90.09	90.09	4.47	0.72
Ck	70–75	124.55	46.98	77.56	2.75	7.63	8.04*	105.80	120.70	120.70	3.84	0.60
	M1	357.53	211.95	145.57	8.56	22.93	41.53	283.43	338.93	338.94	18.59	1.38
	M2	504.22	276.11	228.10	16.70	21.25	44.46	420.80	489.82	489.82	14.40	1.27
	M3	110.57	46.15	64.41	1.64	7.00	9.56	91.95	106.57	106.58	3.98	0.72
Profile IS.2: Hortic Anthrosol Mixied-Proxicalcaric												
Aho1k(x)	18–28	367.18	219.20	147.97	6.09	36.02*	51.80	270.79	339.05	339.05	28.12	1.48
Aho2k(x)	28–40	703.27	563.60	139.66	3.58	110.06	125.60	461.83	633.50	633.50	69.76	4.03
Ck	70–75	105.63	36.45	69.17	1.46	7.73*	11.69	84.57	104.26	104.26	1.36	0.52
	M1	392.02	273.08	118.94	3.71	51.27	63.03	272.40	358.93	358.94	33.08	2.01
	M4	374.78	242.52	132.25	6.14	37.10	52.28	277.92	348.93	348.94	25.83	1.69

H – depth. M1 – average on profile. M2 – average for superior horizons – above Aho2k(x) horizon: Ap1k, Ap2k and Aho1k. M3 – average for inferior horizons – below Aho2k(x) horizon: BCk, ABk and Ck. M.4 – average for span (no. 16, Copou – Iaşi glasshouse) where was done the two profiles. $P(H_2O)$ – phosphorus extractable in water (NH_4Cl solution): non-occluded phosphorus; easy soluble phosphates. $P(NH_4F)$ – phosphorus extractable in ammonia fluoride: non-occluded aluminium phosphates. P(NaOH) – phosphorus extractable in NaOH: non-occluded iron phosphates. $P(H_2SO_4)$ – phosphorus extractable in sulphuric acid: non-occluded Ca phosphates (partially occuded Al and Fe phosphates). P(AL) – phosphorus extractable in buffered ammonia acetate-lactate acid solution (pH=3.7): the sum of non-occluded Fe, Al and Ca phosphates (soluble phosphates). *Determination in extract, after pre-concentration.

CONCLUSIONS

For studied soil samples, the total phosphorus (P_{total}) varied between 94.57-747.15 μg P_2O_5 / g (0.041-0.326 % P), organic phosphorus ($P_{org.}$) varied between 36.45-563.60 μg P_2O_5 / g, and the inorganic phosphorus between 36.45-563.60 μg P_2O_5 / g. Even P(AL) has high values (90.09-734.67 μg P_2O_5 / g, 88.61-98.71 % from P_{total}, respectively), the phosphorus biodisponibility from these soils is relatively reduced. This fact is determined by: (**i**) significant decreasing of inorganic phosphates solubility due to the salinization processes; (**ii**) incorporate appreciable amounts of phosphorus in the composition of the organic-mineral complexes and of organic-phosphoric esters (inosito-phosphate, in specially) – in which the phosphorus is hard assimilable, (**iii**) the geochemical segregation phenomena induced by Aho2k(x) frangipane horizons, which determined the differential evolution of pedo-geochemical processes.

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