Vasileios Antoniadis, Revekka Koliniati, Evaggelia Golia, Spyridon Petropoulos EFFECT OF SOIL PROPERTIES ON PHOSPHORUS SORPTION IN 13 SOILS WITH VARYING DEGREE OF WEATHERING

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Abstract. Phosphorus sorption by soils depends on a series of soil properties, most important of which are pH, clay, organic matter, cation exchange capacity (CEC), amorphous Fe, Al and Mn oxides, as well as CaCO₃. However, such properties may vary in soils of different degree of weathering. The aim of this work was to examine the soil properties that affect P sorption in 13 soils of Central Greece, evaluating the effect soil taxonomy may have on P sorption. We chose soils that differed considerably in pH (4 acidic and 9 alkaline) and in taxonomy (4 Alfisols, 4 Entisols, and 5 Inceptisols), and we conducted batch sorption tests with initial added element concentrations of C_0 =0-100 mg L^{-1} at 1-to-10 soil-to-solution ratio. We measured sorption at C_0 =100 mg $L^{-1}(q_{100})$ and the distribution coefficient, K_{d-100} (equal to q/C at $C_0=100$ mg L^{-1}). We also measured important soil physico-chemical properties, and the sorption indices were correlated with the measured soil properties. When soils were divided according to taxonomy, we found that Alfisols had significantly higher CEC, amorphous Fe and Mn oxides, and q100, but also significantly lower P extractability (water soluble-P and Mehlich-3-P). The other two soil orders did not have different soil properties. When soils were divided according to pH, exchangeable Ca, and the two above mentioned P extractability indices were lower in the acidic group of soils than in the alkaline. These results suggest that although differences in exchangeable Ca are entirely pH-related, differences in extractable P, as well as CEC, Fe and Mn oxides and q100 are taxonomyrelated. We also found that $K_{4.100}$ was significantly correlated only with exchangeable Ca (R^2 =0.304, p<0.05). Extractable P decreased with increasing sand, while organic C increased extractable P. We conclude that soil taxonomy is a key factor in understanding P sorption/extractability in soils, because highly weathered soils (here, Alfisols) have higher amorphous oxides content and this tends to enhance P retention by soils.

Keywords: Extractable phosphorus; Alfisols; amorphous oxides.

INTRODUCTION

Phosphorus is one of the most important nutrients, and its availability to plants depends on various soil properties, most important of which are pH, CaCO₃, organic matter, and Al, Fe, and Mn oxides (Al-Rohily et al., 2013). There are two types of studies typically employed for estimating P availability: sorption studies and the use of P extractants. From such studies it has been reported that P tends to be strongly retained by soils in alkaline, as well as in acidic pH, for different reasons. In alkaline pH values, P is bound by CaCO₃ (Naeem et al., 2013), while in acidic pH it is bound by soil oxides (Arai and Livi, 2013). Thus P availability is dramatically reduced in soil pH values that significantly depart from neutrality. Especially the role of oxides in P availability becomes more complicated because in weathered soils, oxides are of greater content but of higher crystallinity, and thus of lower reactivity. Thus there is a void in knowledge concerning the role of oxides from soils with variable degree of weathering. This is even more evident in areas with low organic matter content (such as those in the southeast Mediterranean region), because in such soils one of the key factors controlling P availability is expected to have no significant effect. Thus the aim of this work was to study soil P mobility by using a series of soil extractants and batch sorption tests, in order to examine the role of various soil parameters in low organic matter soils with variability in the degree of soil weathering.

MATERIAL AND METHODS

We obtained 13 soil samples from Central Greece, so that they may represent the three major taxonomic orders of different progress in weathering: 4 Entisols (newly developed soils, without a B horizon), 5 Inceptisols (with intermediate level of weathering), and 4 Alfisols (highly weathered). The soils were purposefully obtained from cultivated areas so that they may be of low organic matter. The soils were air-dried, passed through a 2-mm sieve, and analysed for some selected

physico-chemical properties (according to Rowell, 1994): pH (1:2.5 H₂O), particle size distribution (Bouyoucos hydrometer), organic C (wet oxidation), CaCO₃ (calcimeter), exchangeable Ca (1 M CH₃COONH₄), cation exchange capacity (CEC, 1 M CH₃COONa), and Fe and Mn oxides (ammonium oxalate) (table 1). We also conducted four P extractions: Water soluble (10

mM CaCl₂, thereafter, WS-P), ammonium oxalate (thereafter, AO-P), Mehlich-3 (thereafter, M_3 -P), and Olsen (0.5 M NaHCO₃, thereafter, Olsen-P). Then we also conducted batch sorption tests at 1-to-10 soil-to-solution ratio with added phosphorus concentrations of C_0 =1-100 mg L-1. We measured P sorption, q, and P in the equilibrium solution, C. From these we

Table 1 - Selected physicochemical properties of the 13 studied soils

Soils	Sand	Clay	pН	Org. C	CaCO ₃	Exch.Ca	CEC	Fe-ox	Mn-ox
								mg kg	
	%	%		%	%	mg kg¹	cmol _e kg ⁻¹	1	${ m mg~kg^1}$
A1	37.2	30.4	6.80	0.76		933.77	16.41	3217	1077
A2	28.4	38.4	6.73	0.62		640.00	23.10	1986	599
A3	18.4	42.4	7.21	1.01	0.24	947.37	32.30	1699	594
A4	22.4	38	7.46	0.77	0.30	804.64	25.61	1729	557
E1	68.4	24.4	6.67	0.70		180.00	5.14	750	228
E2	12.4	38.4	7.53	0.84	3.88	2000.00	40.67	1919	422
E3	54.4	24.4	7.62	0.99	1.42	803.92	11.58	398	345
E4	58.4	28.4	7.75	1.23	0.45	1082.78	17.86	1064	228
I1	56.4	14.4	7.83	1.19	2.18	1490.07	10.55	472	335
12	36.4	20.4	6.55	1.18		450.00	6.37	1095	272
13	31.6	22.4	7.07	0.68	0.26	570.00	7.21	1025	329
I4	64.4	26.4	7.64	0.88	0.37	631.58	3.86	435	297
15	32	28.4	7.82	0.27	0.36	996.71	13.90	1005	474
A	A: Alfisols;	E: Entisols;	I: Incept	isols					

Table 2 - Extractability and sorption indices of P in the 13 studied soils

Soils	WS-P	AO-P	М3-Р	Olsen-P	K_{d-100}	q_{100}
	μg kg ⁻¹	mg kg¹	${ m mg}~{ m kg}^{ m 1}$	${ m mg~kg^1}$	$kg L^{-1}$	$mg kg^1$
A1	387.3	318.71	77.14	60.92	3.18	241
A2	360.8	339.73	60.89	51.47	3.56	282
A3	350.2	326.84	52.62	53.75	3.34	250
A4	379.9	318.36	63.05	53.17	2.81	218
E1	444.1	295.62	85.96	54.31	2.10	173
E2	398.0	328.62	59.34	41.44	3.33	246
E3	776.8	323.67	172.76	63.32	0.67	62
E4	450.0	339.73	159.88	73.72	3.12	237
I1	610.9	368.24	333.71	90.24	4.31	301
I2	410.3	321.19	82.55	54.93	0.81	75
13	586.3	334.57	49.74	35.17	0.81	75
I4	1135.9	357.79	113.91	67.64	2.97	227
I5	353.0	326.14	71.10	48.21	3.08	235

A: Alfisols; E: Entisols; I: Inceptisols; WS -P: Water soluble-extractable P; AO -P: Ammonium oxalate-extractable

P; M3-P: Mehlich-3-extractable P; Olsen-P: Olsen-extractable P;

 K_{d-100} : Distribution coefficient of P sorption at C_0 =100 mg L^1 ; q_{100} : P sorption at C_0 =100 mg L^1

Table 3. Average values of solls properties, of P extractability and of P sorption in soils divided according to their taxonomy (Entisols, Inceptisols, and Alfisols), and according to their pH (acidic and alkaline).

	Sand	Clay	ЬH	Org. C	Caco	EXCH.Ca	CEC	Fe-ox	Mn-ox	MAN	AC-P	M3-P	Olsen-P	K4100	9100
	36	36		96	3-6	mg kg	cmol. kg1	mg kg '	mg kg	ug kg	mg kg1	mg kg '	mg kg1	kg L'	mg kg1
Soils divided according to taxonomy	according to	taxonom	AL.												
Alfisols	26.6 a	37.3 b	7.05	62.0	0.13	831	24.4 b	2157 b	707 b	369.5 a	325.9	63.4 a	54.8	3.22	248 b
Inceptisols	44.2 b	22.4 a	7.38	0.84	69.0	828	8.4 a	806 a	341a	619.3 b	340.6	130.2 b	59.2	2.40	183 a
Entisols	48.34 b	28.9 a	7.39	0.94	1.44	1017	18.8 ab	1033 a	306 a	517.2 b	321.9	119.5 b	58.2	3.31	180 a
Significance	*	*	NS	NS	NS	NS	*	**	*	*	NS	*	NS	NS	*
Soils divided according to pH	according to	Hdc													
Acidic	42.6	28.4	6.69 a	0.82	0.9	551 a	12.76	1762	544	400.6 a	318.8	76.6 a	55.4	2.41	193
Alkaline	38.9	2.62	7.54 b	0.87	1.05 b	1034 b	18.17	1083	398	560.1b	336.0	119.6 b	58.5	2.72	506
Significance	NS	NS	*	NS	***	安安安	NS	NS	NS	*	NS	*	NS	NS	NS

sorption at Co=100 mg L'; q_{00} : P sorption at Co=100 mg L'; *Significant at the level of $p_{<0.05}$: **Significant at the level of $p_{<0.001}$; NS: Non-significant. calculated the distribution coefficient at $C_0=100~\text{mg}~\text{L}^{-1}~(\text{K}_{\text{d-}100})$. This sorption index, along with q100 (sorption at $C_0=100~\text{mg}~\text{L}^{-1}$) were further used in this work for studying P (they, along with the P extraction, are reported in table 2).

We then performed correlation analyses between soil properties versus P extractability and P sorption indices. Also average values in various soil divisions were compared for their significance at the level of p<0.05. All such analyses were conducted with the use of the statistical package Statgraphics.

RESULTS AND DISCUSSION

Soils varied considerably in their physico-chemical properties (table 1) and in their P extractability and P sorption (table 2). In an attempt to study these data according to soil taxonomy and to soil pH, we divided them and compared them statistically (table 3). We found that in Alfisols, clay content was significantly higher and sand significantly lower than the other two orders (Inceptisols and Entisols). This has also seemed to have affected CEC, which was significantly higher in Alfisols than in the other soils.

These differences in sand, clay and CEC may be incidental, but may also be a reflection of soil development conditions. This could be the case, should Entisols were recently developed in alluvial plains in short distance from the river-source or in sandstone and igneous felsic rock deposits (Fanning and Fanning, 1989). This hypothesis, although we can not support it in a definite manner, can not be ruled out. Alfisols also had a significantly lower WS-P and M₃-P than the other soils, as well as significantly higher Fe and Mn oxides contents. The higher oxides content is connected with higher retention ability of soils for P (Igwe et al., 2010), and this was also observed here, with Alfisols having a significantly higher q₁₀₀ average value relative to the other soils.

When soils were divided according to their pH (acidic vs. alkaline), we found that in

acidic soils pH was significantly lower (by the definition of this soil differentiation), as well as lower WS-P, M₃-P, and exchangeable Ca. This seems to suggest that differences in exchangeable Ca is pH-affected only, as would rather be expected (i.e., acidic soils have a lower base saturation, and thus lower exchangeable Ca). However, the two P extractability indices (WS-P and M₃-P) were affected within this soil division due to both pH and taxonomy. Indeed, highly weathered soils typically have lower pH (this was not evident in our case, due to the fact that our "highly weathered soil—Alfisols—included two alkaline soils, A₃ and A₄), and also of higher

oxides content, which in turn are the colloidal phases mostly responsible for Pretention.

These findings were also confirmed in our correlation analysis, where we compared soil properties against P extractability and sorption indices (table 4). Sand was proportionally and significantly correlated with WS-P, M₃-P, and Olsen-P, meaning that light-textured soils are likely to extract more P. As expected by the sand effect, clay was inversely and significantly correlated with M₃-P. Also Fe oxides affected WS-P, but no other significant correlation between Fe oxides and Pindices was generated.

Table 4 - Coefficients of determination, R², of extractable P and sorption indices versus soil properties. A positive sign denotes a proportional relationship, and a negative sign denotes an inversely proportional relationship

	WS-P	AO-P	М3-Р	Olsen-P	$K_{ ext{d-}100}$	q_{100}
Sand	0.355*	0.027	0.329*	0.413*	0.014	0.164
Clay	-0.178	0.071	-0.411*	0.206	0.122	0.157
pН	0.128	0.291	0.249	0.159	0.119	0.089
Org. C	0.044	0.109	0.307*	0.379*	0.001	0.001
$CaCO_3$	0.001	0.084	0.125	0.0012	0.061	0.036
Exch.Ca	-0.019	0.161	0.097	0.028	0.304*	0.249
CEC	0.222	0.017	0.133	0.156	0.157	0.160
Fe-ox	0.356*	0.093	0.255	0.108	0.097	0.117
Mn-ox	0.141	0.003	0.096	0.017	0.017	0.130

WS-P: Water soluble -extractable P; AO -P: Ammonium oxalate -extractable P; M3 -P: Mehlich-3-extractable P; Olsen -P: Olsen -extractable P; K_{d-100} : Distribution coefficient of P sorption at C_0 =100 mg L¹; q_{100} : P sorption at C_0 =100 mg L¹; *Significant at the level of p<0.05.

CONCLUSION

Soil taxonomy is a key factor for understanding P mobility (recorded in this study as extractability and sorption): Soils with more progressed development (even Alfisols, which, typical to soils in the Mediterranean region, are not highly weathered compared to other soils, e.g., in the tropics), are of higher ability to retain P compared to newly developed (here, Entisols) and of intermediate weathering (here, Inceptisols) soils.

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РЕЗЮМЕ

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ВЛИЯНИЕ СВОЙСТВ ПОЧВЫ НА ПОГЛОЩЕНИЕ ФОСФОРА В 13 ТИПАХ ПОЧВ ПРИ РАЗЛИЧНЫХ УСЛОВИЯХ ВЫВЕТРИВАНИЯ

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Поглощение фосфора почвами зависит от ряда свойств почв, наиболее важными из которых являются рН, глина, органическое вещество, мощностемкость катионного обмена (СЕС), аморфные Fe, Al и Mn, оксиды, а также $CaCO_3$. Однако такие свойства могут варьироваться в почвах в условиях разных атмосферных воздействий. Целью данной работы было изучение свойств почв, которые влияют на поглощение фосфора в 13 типах почв Центральной Греции, с учетом влияния таксономии. Мы выбрали почвы, значительно отличающиеся значением рН (4 кислые и 9 щелочные) и таксономии (4 Альфисоли, 4 Энтисоли и 5 Инсептисоли). Проведен ряд испытаний на поглощение с исходными концентрациями элементов C0=0-100 mg L^{-1} в соотношении почва-раствор 1 к 10. Были измерены поглощения при $C_0=100$ mg L-1 (\mathbf{q}_{100}) и коэффициенте распределения, \mathbf{K}_{d-100} , (равной (\mathbf{q}/\mathbf{C} at $\mathbf{C}_0=100$ mg $\mathbf{L}-1$).

Мы также измеряли важные физико-химические свойства почвы и показатели сорбнии были соотнесены с измеренными свойствами почв. Когда почвы были разделены по признакам таксономии, мы обнаружили, что Альфисоли имели значительно более высокий СЕС, аморфные Fe и Mn оксиды, и q100, но также имели значительно более низкую экстрагируемость фосфора (водорастворимый-P и Mehlich-3-P). Два других ряда не имели различий в свойствах почвы. Когда почвы были разделены в соответствии с pH, то обменный Са, и два вышеупомянутых показателя выделяемости фосфора были в кислотной группы почв ниже, чем в щелочной. Эти результаты свидетельствуют о том, что, хотя различия в обменном Са полностью связаны с pH, различия по экстрагируемому фосфору, а также СЕС, Fe и Mn, оксидам и q_{100} связаны с таксономией. Мы также обнаружили, что $K_{\pm 100}$. достоверно коррелирует только с обменным Са (R^2 =0.304, p<0.05). Экстрагируемый фосфор уменьшается с увеличением песка, в то время как органический С увеличивал извлекаемый фосфор. Мы пришли к выводу, что таксономия почв является ключевым фактором в понимании фосфорной сорбңии / экстрагируемости в почвах, так как крайняя эрозия почвы (здесь альфисоли) имеют наивысшее содержание аморфных оксидов, и это, как правило, способствует сохранению фосфора в почвах.

Ключевые слова: экстрагируемый фосфор; альфисоли; аморфные оксиды.

ТҮЙІН

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ТҮРЛІ АЗУ (ЭРОЗИЯ) ЖАГДАЙЫНДА 13 ЖЕРДІҢ ТОПЫРАГЫНА ФОСФОРДЫҢ СІҢІРІЛУІНЕ ТОПЫРАҚ ҚАСИЕТТЕРІНІҢ ӘСЕР ЕТУІ

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Топырақтың фосфорды сіңіруі топырақтың бірқатар қасиеттеріне байланысты, олардың ең маңыздылары рН, сазбалшық, органикалық заттектер, катиондық айырбас қуаттылығы (СЕС), аморфтық Fe, Al және Mn тотықтары, сондай-ақ CaCO₃. Алайда мұндай қасиеттер түрлі атмосфералық ықпалдар жағдайында топырақта түрліше болуы мүмкін.

Бұл жұмыстың мақсаты топырақтың Р сіңіруіне таксономияның әсер етуін ескере отырып, Орталық Грекияның 13 жерінің топырағында Р сіңіруге ықпал ететін топырақ қасиеттерін зерттеу болды. Біз рН (4 қышқыл және 9 сілті) және таксондардардың (4 Alfisols, 4 Entisols және 5

Инсептисоли) болуымен біршама ерекшеленетін топырақтарды таңдап алдық, және біз C_0 =0-100 mg L^{-1} элементтердің бастапқы шоғырлануының топырақ-ерітінді 1ден 10 қатынасында сіңірілуіне бірнеше сынақ жүргіздік. C_0 =100 mg L^{-1} (q_{100}) және бөлу коэффициенті K_{d-100} , (q/C at C_0 =100 mg L^{-1} тең) кезіндегі сіңірулер өлшенді. Сонымен қатар, біз топырақтың физикалық-химиялық қасиеттерін де өлшедік және сіңіру көрсеткіштері топырақтың өлшеулі қасиеттерімен арақатынасы белгіленді. Топырақтар таксономия белгілері бойынша бөлінген кезде Альфисолиде айтарлықтай жоғары СЕС, аморфты Fe және Мn тотықтар, и q100 бар екені, бірақ бөліну P (суға ерігіш-P және Mehlich-3-P) төмен екенін анықтадық. Басқа екі топырақ қатарынан топырақтың түрлі қасиеттері табылмады. Топырақ рН-қа сәйкес бөлінген кезде, айырбас Са және жоғарыда аталған екі P бөлінушілік көрсеткіші топырақтың сілтілі тобына қарағанда, қышқылды тобында төмен болды.

Бұл нәтижелер айырбас Са-да айырмашылық рН-пен толық байланысты болғанымен, бөлінетін Р, сондай-ақ СЕС, Fе және Мп тотықтар және $q_{\tiny 100}$ бойынша айырмашылықтар таксономиямен байланысты. Сонымен бірге, $K_{\tiny d-100}$ тек айырбас Са-мен (R^2 =0.304, p<0.05) ғана анық арақатынас орнататынын анықтадық. Құм көбейген сайын бөлінетін Р азаяды, ал органикалық С алынатын Р-ны арттырды. Топырақ таксономиясы топырақтағы Р сіңіру/бөліну түсінігінде маңызды фактор болып табылады, өйткені топырақтың тым азуы (мұнда Альфисоли) көп мөлшердегі аморфты тотықты қамтиды, бұл әдетте, топырақта Р сақталуына ықпал етеді.

Кілтті сөздер: бөлінетін фосфор; Альфисоли; аморфты тотық