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ORIGINAL PAPER

DISTRIBUTION OF PHOSPHORUS IN GRANULOMETRIC FRACTIONS OF CAMBISOL DEVELOPED FROM MORAINIC LOAM*

Zygmunt Brogowski, Józef Chojnicki

Department of Soil Environment Sciences Warsaw University of Life Sciences-SGGW,Poland

Abstract

The purpose of the study was to investigate the total phosphorus content in granulometric fractions isolated from the genetic horizons of arable Cambisol developed from morainic loams of the Middle-Polish (Riss) Glaciation, Wartanian Stadial (central Poland). Isolation of granulometric fractions was achieved with application of the Atterberg method without the use of centrifuging and dispersing agents. The total phosphorus content in granulometric fractions increased with a decreasing fraction diameter, and its average content (mg kg⁻¹) and contribution in particular fractions (%) was: 1-0.5 mm - 120 (1.1%), 0.5-0.25 mm - 72 (0.6%), 0.25-0.1 mm - 62 (0.5%), 0.1-0.05 mm - 276 (2.5%), 0.05-0.02 mm - 317 (2.8%), 0.02-0.01 mm - 396 (3.5%), 0.01-0.005 mm - 807 (7.2%), 0.005-0.002 mm - 3590 (32.2%), and fraction <0.002 mm - 5489 (49.3%). Fractions of the surface humus horizon (A) and some underlying cambic horizon (Bw) had the highest total phosphorus content, but the lowest contribution to the accumulation of total phosphorus in the soil profile. The enrichment of the surface horizon fractions with phosphorus is the result of its bioaccumulation and fertilisation of this soil, intensively used for agriculture. The leaching process in the soil studied caused migration of phosphorus in the finest fractions (with diameter <0.02 mm) from the humus horizon to the cambic horizon located directly below. However, the small migration depth and particularly the fine graining, coupled with high sorption capacity and low water permeability tested soil, point to limited removal of easily-soluble phosphorus forms from the soil to ground- and surface water.

Keywords: phosphorus, granulometric fractions, Cambisol, morainic loam.

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Józef Chojnicki, Prof., Department of Soil Environment Sciences, Faculty of Agriculture and Biology, Warsaw University of Life Sciences-SGGW, 159 Nowoursynowska Str., 02-776 Warsaw, Poland, e-mail: jozef_chojnicki@sggw.pl

INTRODUCTION

Studies on the occurrence, transformation and sorption of various forms of phosphorus in soils are widely performed for elaboration of appropriate fertilisation technologies of crops, for which phosphorus is a vital macroelement (GAJ et al. 2018, POTARZYCKI, GRZEBISZ 2019). Also, numerous studies are focused on the removal process of mobile phosphorus forms from soil, where it can cause environmentally harmful eutrophication of ground- and surface water (Andersson et al. 2015, KLEINMAN et al. 2015, SZARA et al. 2019). It should be emphasised that the phenomenon of excessive removal of phosphorus from soil is largely due to mistakes made during crop fertilisation. Common occurrence of various phosphorus forms in soil, particularly mobile compounds, is used in the study of pedogenic processes (Pokojska 1979, OKTABA, CZERWIŃSKI 2003), and the origin and properties of paleosols (KONECKA--BETLEY et al. 1985, BROGOWSKI, OKOŁOWICZ 1986). Both Polish and international literature supplies numerous reports on the total phosphorus content in the entire soil mass (ANTONKIEWICZ et al. 2019, CHOJNICKI 2002); in turn, there are relatively few studies on its content in particular granulometric fractions (GEISSELER et al. 2011, ZHANG, LI 2016). One of the main reasons of this discrepancy is that isolation of particular granulometric fractions from the soil solid phase is a time-consuming and laborious process, especially when centrifuging and peptizing agents are not applied.

This study focused on analysing the total phosphorus content in particular granulometric fractions isolated from the genetic horizons of Cambisol developed from morainic loams. The soil represents fertile arable soils, constituting about 30% of the surface covered by soils used in Poland for farming. Deeper knowledge of phosphorus sorption in the soil granulometric fractions may be used for improvement of currently applied and elaboration of new techniques of crop fertilization. They may increase the yield effectiveness of phosphorus as a nutrient, and simultaneously decrease its leaching, thereby minimising its negative impact on the natural environment (water eutrophication).

MATERIALS AND METHODS

According to the FAO-WRB classification (IUSS Working Group WRB 2015), the soil studied in this research was determined as a Eutric Cambisol developed from morainic loams of the Middle-Polish (Riss) Glaciation, Wartanian Stadial. It is located in Gabin near Plock (central Poland: 52°23'43.7"N, 19°45'20.4"E).

Fieldwork including measuring and description of the soil profile, and sample collection from particular genetic horizons was carried out according to commonly used soil testing methods. Isolation of granulometric fractions was made with application of the Atterberg method without the use of centrifuging and chemical compounds for peptisation. Peptisation was carried out using thermal-mechanical methods by boiling the soil with redistilled water (0.5 h) and then mixing it in a rotary mixer for about 10 min. Boiling and mixing was performed until the entire <0.002 mm fraction was separated. Similarly, although without boiling, the >0.002 mm fraction was separated, whereas the 1-0.1 mm fractions were sieve-separated after drying. The isolated fractions were first dried on evaporating dishes in a water bath, and then dried completely in a dryer at 80-90°C. After drying and weighing, the percentage content of particular fractions in the studied soil was calculated.

The following properties were determined in the soil: total organic carbon (TOC) using an automatic carbon analyser Shimadzu TOC 5000 A, pH in distilled water and 1 M KCl, using the potentiometric method at a soil:liquid ratio of 1:2.5 (v/v), and the calcium carbonate equivalent using the volumetric method with a Scheibler apparatus. The following properties were determined in the soil: total potential acidity (H) using the Kappen method (extraction using 1 mol·dm⁻³ calcium acetate and titration using 0.1 mol·dm⁻³ NaOH), total exchangeable base cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) using 1 M ammonium acetate at pH = 7 (in samples with carbonates using 1 M ammonium chloride at pH = 8.2) and analysed in an atomic absorption spectrometer (thermoelemental Solaar M6). The cation exchange capacity (CEC) and base saturation (BS) were calculated from the sum of total exchangeable base cations (TEB) and potential acidity (H).

The total phosphorus content in particular fractions was determined in the extracts, after fusion with Na_2CO_3 , by colorimetry using ammonium molybdate and applying tin chloride for reduction, according to the method developed by GIGEL and modified by BROGOWSKI (1966). The modification consists in adding metol to reagent No 2, which eliminates the phosphorus-like silica colour and removes disturbances of phosphorus colouration by iron and manganese due to the previous composition of reagent No. 2. Regression analysis was applied for statistical evaluation of the results.

RESULTS

The surface soil horizons (A and Bw) have the texture of sandy loam with the prevalence of the fine sand fraction (0.25-0.1 mm), and in deeper horizons – clay loam with the prevalence of the clay fraction <0.002 mm (Table 1). Acid reaction in the surface horizons changes into neutral in the deepest part of the soil profile; similarly, saturation of the sorption complex with base cations (BS) increases with depth (Table 2). Cation exchange capacity is the lowest in the surface horizons, whereas its highest values

				Ц	article size	distributi	ion in the se	oil studied	diamaton (m	(
Horizon	Dept				-	Content	of fractions	(%) WIth (diameter (m	m)		
	(cm)		1-0.5	0.5 - 0.25	0.25-0.	1 0.1-	0.05 0.0	5-0.02	0.02 - 0.01	0.01-0.005	0.005 - 0.002	<0.002
A D	0-25		5.7	14.7	35.6	101	5.4	8.6 7.7	4.3 7 6	4.3 7 5	4.2 6 9	7.2
BwC.	20-02		4. –	0.11	10.9	110	c, x	6.7 6.7	0.00	0.0 7 0	7.0	39.4
	75-10		1.3	4.6	16.8		2.7	6.0	7.0	7.7	9.1	33.8
Ck	100-12	25	1.6	4.8	9.5	21	80	3.6	6.4	8.3	10.8	33.2
\mathbf{Ck}	125-15	20	1.8	5.2	14.6	13	.3	6.9	8.8	8.6	8.0	33.8
Average			2,8	7.2	20.8	16	3.2	6.6	6.3	7.1	7.9	25.2
					Physic	ochemical	properties c	of soil				Table 2
	Depth		He			cu	nol(+) kg ⁻¹			BS	TOC	Carbonates
Horizons	(cm)	KCI	H ₂ O	Ca^{2+}	${ m Mg}^{2+}$	\mathbf{K}^+	Na^+	TEB	H ⁺ C	EC	%	
A	0-25	5.1	5.6	2.40	0.16	0.58	0.06	3.20	2.50 5.	.70 56.1	1.82	
$\mathbf{B}\mathbf{w}$	25-50	5.0	5.7	2.17	0.20	0.20	0.09	2.66	2.74 5	.40 49.2	0.41	
BwC	50-75	4.3	5.4	8.50	1.02	0.26	0.22	10.00	3.00 15	3.00 76.9	0.46	·
C	75-100	4.9	5.7	9.20	1.03	0.30	0.26	10.76	2.10 12	2.86 83.7	0.33	
Ck	100-125	.0 1 1	2.3 2.3	21.25	1.45	0.31	0.45	23.46	$1.10 \qquad 24$	L56 95.5	0.29	1.27
CK CK	125-150	-1-9 T-0-0	1 7.6	25.30	1.15 TED +04	0.26	0.48 0.48 0.48 0.000	27.19 DC hoo	1.00 28	8.19 96.4	0.22	3.82
(-) - 1ack 01	carpollates	, 100 -	LULAI UF	ame carbon,	101 - 071	al excitati	seante pase	, Do – Uds	e saturation	Ι		Table 3
				Ph	osphorus c	ontent in g	granulomet	ric fractior	IS			
11	Del	pth				Fract	cions (mg k	g ¹) with d	iameter (mr	u)		
HOTIZON	(<u>c</u>)) (E	1-0.5	0.5-0.25	0.25 - 0.1	0.1 - 0.05	0.05-0.02	0.02-0.01	0.01-0.005	0.005-0.002	<0.002	Sum
A	-0	25	157	83	135	310	371	524	1677	4306	9275	16 840
Bw	25	-50	135	61	70	231	332	454	934	3678	8034	$13 \ 930$
BwC	20	-75	118	78	39	205	354	323	644	3258	4210	9 230
50	-G/	TUU	148 00	220	30 1	266	219	675 902	909	3098	3694	000 6
CK		-120	7 C	93 93	44	310	203	1.62 1.62	463	3624	4017	9 290
UK	.07T	- net	14	40	40	000	÷10	ane	000	41 NG	0010	0 40N

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Table 1

were observed in the deepest parts of the soil profile, where carbonates occur, and this is linked to the soil fine graining. The largest total organic carbon (TOC) content occurs in the humus horizon and gradually decreases with depth.

Fractions with a diameter of 1-0.1 mm were the only group in which the total phosphorus content decreased with a decreasing diameter (Table 3, Figure 1). Particles with a diameter of 1-0.5 mm contained the largest



Fig. 1. Average phosphorus content in particular fractions and their percentage contribution

amounts of phosphorus, whereas the lowest amounts occurred among particles with diameters of 0.25-0.1 mm. The average content of phosphorus in particles with a diameter of 1-0.5 mm was 120 mg kg⁻¹ (in the range of 72-157), in particles with a diameter of 0.5-0.25 mm - 72 mg kg⁻¹ (in the range of 43-93), and in particles with a diameter of 0.25-0.1 mm - 62 mg kg⁻¹ (in the range of 35-135). In the soil profile, the highest phosphorus content was noted in fractions of the humus horizon, except the fraction with a diameter of 0.5-0.25 mm, in which slightly higher contents occur in deeper horizons of the parent material (C, Ck). This phenomenon is attributed to the natural process of bioaccumulation of mineral nutrients in the surface humus horizon and fertilisation of arable soils. Despite the leaching process, no migration of phosphorus to deeper profile horizons was observed. This fraction group had a very small contribution (on average 2.4%) to sorbing phosphorus in the soil studied (Figure 2).

The group of four granulometric fractions with a diameter of 0.1-0.005 mm showed a systematic increase of the total phosphorus content with a decreasing particle diameter (Table 3, Figure 1). The average content of this element and its range (mg kg⁻¹) for these fractions were as follows: 0.1-0.05 mm – 276 (205-338), 0.05-0.02 mm – 317 (253-371), 0.02-0.01 mm – 396 (306-524) and 0.01-0.005 mm – 807 (463-1677). With a diminishing fraction diameter, the dominating phosphorus content increased in all fractions of the surface



Fig. 2. Percentage contribution of granulometric fractions to the sorption of phosphorus in particular soil horizons

humus horizons. The only exception was the highest content of this element in the fraction with a diameter of 0.1-0.05 mm in the deepest horizon of the parent material (Ck). In fractions with diameters of 0.02-0.01 and 0.01-0.005 mm of the sub-surface cambic horizon (Bw), higher contents of phosphorus were noted in comparison with the underlying horizons, which may point to its migration from the fractions of the overlying humus horizon. The contribution of this fraction group to the accumulation of phosphorus was also relatively small, at 8.1% (Figure 2).

Granulometric fractions with a diameter of <0.005 mm showed a rapid increase in the total phosphorus content compared to the other fractions (Table 3, Figure 1). In these fractions, the average content of this element and its range (mg kg⁻¹) were as follows: 0.005-0.002 mm – 3590 (3074-4306) and <0.002 mm – 5489 (3694-9275). Therefore, the contribution of both fractions to the sorption of phosphorus was clearly the highest, and reached 32.2 and 49.3%, respectively (Figure 2). The highest content of phosphorus occurred in both fractions from the humus horizon. However, its content was clearly higher in the clay fraction and about twice as high as in the same fraction in the parent material. Both fractions yielded a considerable content of phosphorus, particularly the clay fraction, in the sub-surface cambic horizon (Bw). The significance of the correlation between the increase of the total phosphorus content in granulometric fractions with a decreasing particle diameter has been confirmed by statistical analysis (Figure 3).

Total phosphorus supply in the granulometric fractions of particular genetic horizons of the entire soil profile depended on the content of a given



Fig. 3. Relationship between phosphorus content in fractions and their diamet

fraction and its ability of sorbing this element (Table 4). Particular fractions were accumulated on a surface of 1 m^2 in the entire soil profile to the depth of 150 cm at phosphorus amount of: 1-0.1 mm – 58.3, 0.1-0.01 mm – 200.5 and <0.01 mm – 3121.3 (g m⁻²). In turn, all fractions combined bound 3380.1 g m⁻² of this element, varying from 408.6 g m⁻² in the humus horizon to 703.6 g m⁻² in the parent rock. The dominant contribution (exceeding 80%) to phosphorus accumulation was achieved by fractions with a diameter of <0.01 mm; a much lower contribution, at 5-10%, was made by the fraction with a diameter of 0.1-0.01 mm, whereas the lowest one, only up to 5%, originated form the fractions with a diameter of 1-0.1 mm (Figure 4). In the soil profile, fractions with a diameter of 1-0.02 mm accumulated the largest amount of phosphorus in the soil humus horizon, while the remaining, smaller fractions bound the largest amounts of this element in the deeper horizons of the soil profile, below 50 cm.

DISCUSSION

The results of this study and similar research by other authors have indicated that occurrence, transformations and mobility of phosphorus in soils and in the environment are complicated and depend on many factors (CZĘPIŃSKA-KAMIŃSKA 1992, GEISSELER et al. 2011, RUBAEK et al. 2013). The main factors include properties of the parent rocks, such as mineral composition, susceptibility to weathering and pH, pedogenic processes, climatic conditions influencing the intensity of weathering processes, formation and transformation of organic matter, and increasing human activity linked with food and nutritional security. The total phosphorus content in the analysed granulometric fractions increases with a decreasing fraction diameter, and clearly the highest content was noted in fractions with a dia-

	Sum		408.6	469.7	622.9	558.8	703.6	616.5	3380.1
Accumulation of phosphorus in soil horizons and in particular fractions (g m ²)		<0.002	250.4	316.7	509.8	468.0	500.1	455.0	2500.0
	ith diameter (mm)	0.005-0.002	67.2	85.2	41.4	41.7	146.8	92.2	474.5
		0.01 - 0.005	27.0	19.2	39.5	16.1	14.4	30.6	146.8
		0.02 - 0.01	8.4	9.5	6.6	9.8	9.5	10.1	53.9
rizons and	mg kg ^{.1}) wi	0.05- 0.02	11.9	9.3	8.9	C 75-100 0.7 1.6 3.0 11.6 6.3 9.8 16.1 41.7 468.0 558.8 C 75-100 0.7 1.6 7.0 7.0 7.0 7.0 7.0 7.0 7.0 7.0 7.0 7.0	3.3	8.1	47.8
s in soil ho	Fractions (1	0.1-0.05	17.4	16.0	11.4	11.6	25.3	16.6	98.8
phosphoru		0.25-0.1	18.0	7.9	3.8	3.0	1.6	2.6	36.9
Accumulation of phos		0.5-0.25	4.6	3.7	0.8	1.6	2.0	0.8	13.5
Accun		1-0.5	3.2	2.2	0.7	0.7	0.6	0.5	7.9
Accu	Depth (cm)		0-25	25-50	50-75	75-100	100-125	125 - 150	m
	Horizon		Α	Bw	BwC	C	\mathbf{Ck}	Ck	S

Table 4

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of phosphorus

meter of <0.005 mm. Similar contents of bound phosphorus were observed also in fractions of some soils from Germany (GEISSELER et al. 2011), the Caucasus (MAKAROV et al. 2004), Canada (HINDS, LOWE 1980), China (ZHANG, LI 2016), and in alluvial soils of the Vistula River in Poland (BROGOWSKI, KWASOWSKI 2014). High contents of phosphorus in the analysed fractions with a diameter of < 0.005 mm, occurring in some soils of the world (SPOHN 2018), result from the fact that they were isolated from soils developed from boulder loams. Numerous studies indicate that loams are characterised by high and very high content of phosphorus (CZEPIŃSKA-KAMIŃSKA 1992, CHOJNICKI 2002), and other macro- and microelements. Also, bioaccumulation had significant participation in the enrichment of all fractions of the humus horizon (Table 3), particularly the fractions with a diameter of <0.005 mm. In this process, phosphorus absorbed by the roots of crops, often by plants with deep root systems from large depths, returns to soil due to the biological cycle and is accumulated in the surface humus horizon (HINDS, LOWE 1980, CZEPIŃSKA-KAMIŃSKA 1992, GEISSELER et al. 2011). Fertilisation, both organic and mineral, of these soils intensively used in farming had some contribution to the enrichment of these fractions in phosphorus.

Leaching taking place in the studied soil, a common process in soils of the world and Poland (ADDISCOTT, WAGENET 1985, CHOJNICKI 1993), had influence on the profile distribution of phosphorus in the fractions studied. The largest content of phosphorus, with a few exceptions, was observed in humus horizon fractions with a diameter of >0.02 mm, whereas in the remaining fractions, their decreasing diameter coincided with a successive increase of the phosphorus content in the subsurface horizon fractions (Table 3). This may point to the migration process of labile phosphorus compounds in the finest fractions from the surface humus horizon to the cambic horizon directly below. However, the small migration depth and especially fine graining related with high sorption capacity and low permeability of the soil studied allows us to conclude that the removal of easily-soluble forms of phosphorus to ground- and surface water does not take place or is very limited. Such conditions of phosphorus removal were also indicated by the results obtained by numerous authors (DE BOLLE et al. 2013, RUBAEK et al. 2013, ANDERSSON et al. 2015).

CONCLUSIONS

1. The total phosphorus content in the granulometric fractions of the soil submitted to our analysis was variable, depending on a decreasing particle diameters: the phosphorus content decreased gradually in fractions with a diameter of 1-0.1 mm, increased slightly in fractions with a diameter of 0.1-0.005 mm, whereas it increased rapidly in fractions with a diameter of <0.005 mm.

2. The total phosphorus content in mg kg⁻¹ and its percentage in particular fractions was: 1-0.5 mm - 120 (1.1%), 0.5-0.25 mm - 72 (0.6%), 0.25-0.1 mm - 62 (0.5%), 0.1-0.05 mm - 276 (2.5%), 0.05-0.02 mm - 317 (2.8%), 0.02-0.01 mm - 396 (3.5%), 0.01-0.005 mm - 807 (7.2%), 0.005-0.002 mm - 3590 (32.2), and diameter <0.002 mm - 5489 (49.3%).

3. Fractions of the surface humus horizon (A) and subsurface cambic horizon (Bw) of the soil studied had the highest total phosphorus content, but at the same time the lowest contribution to the total phosphorus accumulation in the soil profile.

4. Leaching caused migration of phosphorus in the finest fractions from the humus horizon only to the cambic horizon directly below, which indicates limited removal of easily-soluble forms of phosphorus from the analysed soil to ground- and surface water.

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