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GEOCHEMICAL STUDIES ON PODZOLIZATION

PART III. PHOSPHORUS IN PODZOLIZATION

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INTRODUCTION

One of the few writers who have noted the part of phosphorus in podzolization is Kundler [1]. The eluvial-illuvial differentiation of P content is, according to him, a very good indicator of soil podzolization. However, the only explanation of this sort of distribution of phosphorus in soil profiles he gives is that it closely coincides with that of sesquioxides, with which phosphoric acid forms low solubility phosphates.

The phenomenon of binding phosphates by sesquioxides has been for a long time one of the most important problems in soil chemistry. Recent studies [6, 9] have confirmed the assumption that it is of the nature of chemisorption.

Chemisorption, however, can only account for immobilizing phosphorus in soil. In studies on podzolization it is of even greater importance to account for the causes of mobilizing phosphorus in the upper portion of the profile. Studies on the combinations of phosphate ions with humic substances have to a certain extent contributed to the elucidation of this problem.

Misterski and Łoginow [5] studied how reactions proceeded in systems containing humic acids (from compost extracts), soluble phosphates and Ca^{2+} , Fe^{3+} and Al^{3+} ions. These authors have found that the presence of humic acids prevents to a large extent the precipitation of inorganic phosphates, while on the other hand, the presence of phosphates inhibits the process of coagulation of humic acid by the above-mentioned ions. According to them, the interaction of these compounds bringing about an increase in their solubility is due in the

first place to the formation of humic acids-phosphates complexes bridged by metal ions. The results obtained by Misterski and Łoginow have been supported by later works by Levesque and Schnitzer [3], Levesque [2] and Sinha [10]. In the latter works were used humic and fulvic acids extracted from podzol humus. It has been found that ash-free or low-ash humic and fulvic acid preparations do not form stable compounds with phosphates. In the presence of Fe^{3+} or Al^{3+} ions, however, stable complex organometallic phosphates are formed. According to Sinha [10], such complexes may form in soil as a result of reactions of soluble phosphates with Fe- and Al-humic and fulvic acids complexes or of insoluble Fe- and Al-phosphates with humic and fulvic acids occurring in soil solution. The actual role of complex organo-metallic phosphates in phosphorus migration needs further studies.

Studies on transformations of phosphorus compounds in soil chronosequences have provided interesting results [12]. In unweathered bedrock the prevailing form of phosphorus is apatite. According to Walker and Syers [12], with the development of the pedogenic process the amount of calcium phosphates, comparatively easily available for plants, gradually decreases, while the amount of organic phosphorus and of inorganic low-solubility forms increases. After the calcium phosphate supplies have been exhausted, there is a decrease in organic phosphorus content due to the low amount of phosphorus taken in by plants. The whole of inorganic phosphorus passes into forms inaccessible to plants (iron and aluminium phosphates occluded by sesquioxides).

The present work reports the results of studies on the distribution of phosphorus in profiles of ferro-humic podzols and describes the geochemical conditions under which phosphorus migrates in these soils. An attempt has been also made at determining the degree of advancement of transformation of phosphorus compounds in the particular genetic horizons of podzols.

MATERIAL AND METHODS

The present studies have been made on the same podzol profiles that were analyzed earlier for the participation of Fe, Al and Si in podzolization [7, 8].

The total phosphorus content (P_t) in raw humus was determined after mineralization in conc. H_2SO_4 with an addition of 30% H_2O_2 , and in the mineral portion of the profile after melting the samples with Na_2CO_3 . Moreover, the dithionite extracted phosphorus fraction (P_d) was determined by Mehra-Jackson's method. Subject to this extraction are mainly combinations of phosphorus with sesquioxides. The quantitative analysis of phosphorus was made by the colorimetric method with molybdenic blue.

RESULTS AND DISCUSSION

Among the ash constituents of podzol raw humus phosphorus occupies a specific position. In the successive A_0 subhorizons it does not become so strongly concentrated as Si, Al and Fe, or so rapidly reduced as the basic elements, particularly Ca [cf. 7, 8]. In the initial stages of mineralization and humification of the plant litter fall there is usually a certain increase in phosphorus concentration. This increase is probably due to the fact that the rate at which P is released from its organic compounds is comparatively slow, while the total mass of plant remains decreases at a quick rate. At the following stage of organic matter transformation (in A_0F or A_0H) a decrease in phosphorus content is observed, probably due to its being taken in by plants and possibly also partially washed down to the mineral portion of the profile.

In the mineral horizons of the podzols under study there is a great deal of variation in phosphorus content (Table 2). The total phosphorus content (P_2O_{5t}) in the bedrock amounts to only some hundredths of one per cent (except in Profile 3, where it is slightly higher). The eluvial

Table 1

Average content of P_2O_5 in the particular raw humus subhorizons of 6 profiles
/in % of organic matter mass without mineral grains/

Subhorizon	Profile No.					
	1	2	3	4	5	7
AoLo	-	-	0,151	0,095	-	-
AoL	0,230	0,300	-	-	0,156	0,125
AoF	0,196	0,224	0,239	0,183	0,230	0,225
AoH	0,140	0,161	0,209	0,107	0,184	0,182
AoH''	0,126	0,104	0,182	0,106	0,145	

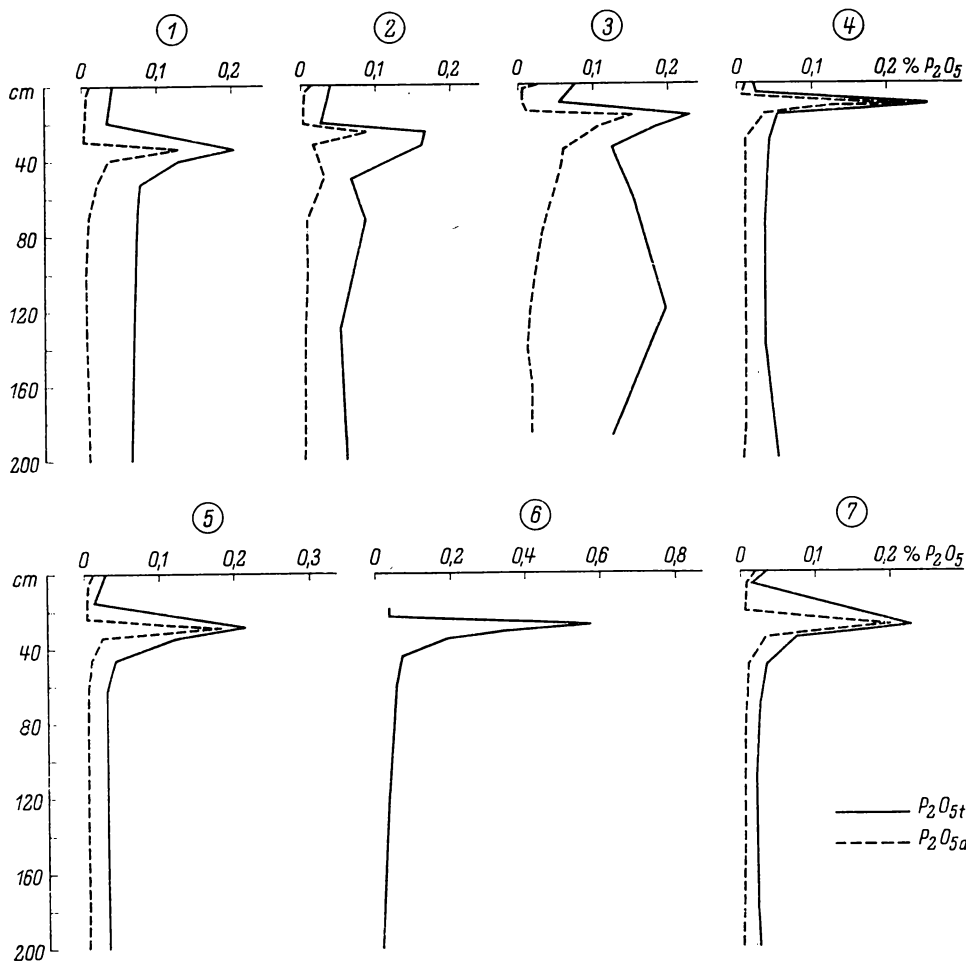
horizons are even poorer than the bedrock, whereas in the illuvial horizons the phosphorus concentration is several times that in the bedrock. The maximum P_2O_{5t} content in all the profiles in question occurs in subhorizon Bh and amounts to 0.17–0.25%. The phosphorus fraction subject to extraction in dithionite together with the sesquioxides (P_2O_{5d}) also shows eluvio-illuvial differentiation — Fig. 1.

The question arises whether the phosphorus migration from horizons A_0 and A_e to horizon B goes on in the form of free phosphate ions or in combinations with other constituents of the soil solution. Studies carried out by Misterski and Łoginow [5], Levesque [2] and Sinha [10] have revealed the possibility of forming organo-metal-phosphate complexes, in which the phosphate ions are linked to the

Total P_2O_5 and dithionite-extractable P_2O_5 content in podzols under study

Profile No.	Horizon	Depth cm	P_2O_5t %	P_2O_5d %	P_d/P_t
1	Ao/Ae	1-0-1	0,041	0,012	0,29
	Ae	12-28	0,033	0,003	0,09
	Bh	33-35	0,201	0,126	0,63
	Bhs	35-45	0,128	0,036	0,28
	Bs	60-75	0,075	0,011	0,15
	C	110-145	0,070	0,006	0,08
2	Ao/Ae	1-0-0,5	0,040	0,014	0,35
	Ae	16-23,5	0,027	0,003	0,11
	Bh	23,5-26	0,166	0,086	0,52
	Bhs	26-38	0,162	0,014	0,08
	Bs	60-85	0,085	0,009	0,10
	C	115-145	0,054	0,005	0,09
3	Ao/Ae	0,5-0-0,5	0,075	0,024	0,32
	Ae	4-12	0,054	0,006	0,11
	Bh	16-18	0,229	0,150	0,66
	Bhs	18-28	0,183	0,106	0,58
	Bs	40-50	0,136	0,055	0,40
	C	110-130	0,196	0,014	0,07
4	Ao/Ae	0,3-0-0,5	0,022	0,010	0,45
	Ae	0,5-10	0,025	0,004	0,16
	Bh	10-11,5	0,251	0,238	0,95
	Bhs ₁	11,5-13	0,184	0,132	0,72
	Bhs ₂	13-20	0,064	0,036	0,56
	Bs	20-40	0,043	0,012	0,28
	C	120-140	0,037	0,010	0,27
5	Ao/Ae	0,5-0-1	0,027	0,012	0,44
	Ae	10-20	0,014	0,003	0,21
	Bh	28,5-30	0,216	0,182	0,84
	Bhs	30-38	0,125	0,024	0,19
	Bs	38-55	0,042	0,010	0,24
	C	110-130	0,030	0,004	0,13
7	Ao/Ae	0,2-0-0,5	0,036	0,023	0,64
	Ae	0,5-14	0,015	0,007	0,47
	Bh	28-29,5	0,229	0,200	0,87
	Bhs	29,5-40	0,073	0,033	0,45
	Bs	40-60	0,036	0,010	0,28
	C	100-120	0,020	0,003	0,15

fulvic acids by Fe and Al ions. The results of the present studies indicate that this form of phosphorus migration plays an important part in podzols. Soluble organo-metal-phosphate complexes may form already in raw humus, where all the necessary components are present. Fulvic acids forming in the course of decomposition of plant remains may, in the presence of Fe and Al ions, react with the liberated phosphate ions. Also in the eluvial horizons adequate conditions exist for the formation



Diagrams of profile distribution of P_2O_{5d} and P_2O_{5t} in podzols under study

of the complexes in question. Indirect evidence of the common migration of fulvic acids, sesquioxides and phosphates is provided by their common accumulation in the illuvial horizon. Since the maximum phosphorus content occurs in subhorizon *Bh* together with free Fe maximum, it may be inferred that in binding phosphates Fe is more important than Al.

The varying value of the ratio P_d/P_t in the profile (Table 2) deserves some attention. It determines the percentage of the phosphorus fraction bound with R_2O_3 in total phosphorus, and indirectly permits to estimate the percentage of other forms of phosphorus. Phosphates combined with R_2O_3 constitute the major part of soil phosphorus in illuvial horizons, particularly in subhorizon *Bh*, where the P_d/P_t ratio

reaches values ranging from 0.52 to 0.95. Below subhorizon *B_{hs}* this fraction gradually decreases, and in the bedrock its percentage is negligible (P_d/P_t in horizon *C* ranges from 0.03 to 0.13). Since horizons *B_s/C* and *C* essentially lack organic phosphorus compounds, the low values of P_d/P_t are evidence of a clear predominance in these horizons of the calcium phosphate fraction. In the eluvial horizon, on the other hand, where, considering the fairly rapid decomposition of apatite [7, 11], no considerable percentage of calcium phosphates is to be expected, the low P_d/P_t values point to a higher content of organic phosphorus compounds.

The picture of profile differentiation of the principal phosphorus fractions in podzols obtained in the present study is essentially in agreement with the data reported by MacLean and coworkers [4] except for the illuvial horizon, where they found a lower content of the phosphate fraction combined with Fe and Al and a higher one of the organic phosphorus fraction. The differences are due to unequal extraction capacities of the reagents used and to the difficulty in drawing a precise borderline between organic and inorganic phosphorus in soil. Moreover, MacLean's and coworkers' data suggest that the Fe- and Al-phosphate combinations accumulated in horizon *B* become to a large extent occluded by amorphous Fe oxides.

When comparing the qualitative and quantitative differentiation of phosphorus compounds in podzol profiles with the general scheme of transformations of these compounds in soil elaborated by Walker and Syers [12], it is seen that the former corresponds fairly well with the latter. The podzol bedrock, in which the most important fraction of phosphorus is calcium phosphates corresponds to the initial stage of transformations of phosphorus compounds in Walker and Syers' scheme. The illuvial horizon, on the other hand, in which alongside with organic forms of phosphorus occur nearly exclusively combinations of phosphorus with R_2O_3 occluded to a large extent by Fe oxides, corresponds to the final stage of phosphorus compounds transformations in soil.

CONCLUSIONS

1. The transformations and the migration of phosphorus compounds constitute important elements of podzolization.

2. The primary form of phosphorus in podzols is in the first place calcium phosphates (apatite). The high acidity of the upper portion of the podzol profile causes a comparatively rapid (compared with other soils) decomposition of these phosphates.

3. Biological accumulation in horizon A_0 involves an accumulation of organic phosphorus compound. Mineralization of these compounds is

associated with secondary taking in of phosphorus by plants and with partial washing it down the profile.

4. In the illuvial horizon of podzols a considerable accumulation of phosphorus is observed, and its maximum content occurs in subhorizon *Bh*. The most likely form of phosphorus migration from horizons *A₀* and *A_e* to horizon *B* is organo-metal-phosphate complexes composed of fulvic acids, Fe and Al ions and phosphate ions.

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У. ПОКОЙСКА

ГЕОХИМИЧЕСКИЕ ИССЛЕДОВАНИЯ ПОДЗОЛООБРАЗОВАТЕЛЬНОГО ПРОЦЕССА

ЧАСТЬ 3-Я. ФОСФОР В ПРОЦЕССЕ ПОПДОЛИВАНИЯ

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Резюме

Целью статьи было предъявление результатов исследований по размещению фосфора в профиле железисто-гумусовых подзолов и обсуждение геохимических условий, в каких происходит миграция фосфора в этих почвах. Предпринята тоже была попытка определения степени превращения фосфорных соединений в отдельных генетических горизонтах подзолов.

В почвенных образцах определяли общий фосфор (P_t) и фракцию фосфора извлекаемого дитионитовой вытяжкой (P_d) согласно методу Мэра-Джексона. Эту фракцию составляют в главном соединения фосфора с полуторными оксидами. Во всех испытанных профилях количественная дифференциация одинаково как P_t так и P_d изображает характерную картину элювиально-иллювиальной дислокации (рис. 1). Кажется, что существенную роль в транслокации фосфора играют комплексные органо-металлофосфатные соединения, в которых фосфатные ионы связаны с подвижными гумусовыми кислотами посредством ионов Fe и Al. Возможность образования таких соединений в почве доказана многими авторами [2, 5, 10]. В подзолах растворимые Fe- и Al-гумусовые комплексные соединения с фосфатами могут образоваться уже в сыром перегное, где находятся все имеющие существенное значение компоненты. Выпадение в осадок этих сложных комплексов в горизонте B протекает вероятно согласно подобному механизму, как тот который влечет за собой утрату растворимости в соединениях гумусовых кислот с полуторными оксидами.

Заслуживает внимания изменяющаяся в профиле величина соотношения $P_d:P_t$ (табл. 2). Фосфаты связанные с R_2O_3 составляют наибольшую часть почвенного фосфора в иллювиальных горизонтах (в Bh соотношение $P_d:P_t$ достигает величины 0,52-0,95). Ниже подгоризонта Bhs названная фракция играет все меньшую роль и в материнской породе участие ее совсем ничтожно. Свидетельствует это о подавляющем преобладании в горизонте C кальциевых фосфатов. В элювиальном горизонте, где вследствие довольно интенсивного разложения апатита нельзя ожидать большего накопления кальциевых фосфатов, низкие значения $P_d:P_t$ указывают на наличие высшего содержания органических фосфорных соединений. Сравнивая количественную дифференцированность фосфорных соединений в профиле подзолов с предложенной Уолкера и Сьерсом [12] общей схемой превращения этих соединений в почве нетрудно обнаружить далеко идущие аналогии. Материнская порода подзолов с доминирующей фракцией фосфатов кальция соответствует начальной стадии; иллювиальный-же горизонт с накоплением фосфатов связанных с R_2O_3 соответствует конечной стадии превращения фосфорных соединений в схема Уолкера и Сьерса.

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GEOCHEMICZNE BADANIA NAD PROCESEM BIELICOWANIA

CZĘŚĆ. III FOSFOR W PROCESIE BIELICOWANIA

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w Toruniu

Streszczenie

Celem niniejszej publikacji było przedstawienie wyników badań nad rozmieszczeniem fosforu w profilach biellic żelazisto-humusowych oraz przedyskutowanie geochemicznych warunków, w jakich odbywa się migracja fosforu w tych glebach. Podjęto również próbę określenia stopnia zaawansowania przemian związków fosforowych w poszczególnych poziomach genetycznych biellic.

W gęsto pobranych próbkach glebowych oznaczono fosfor ogółem P_t oraz frakcję fosforu ekstrahującego się w wyciągu dithionitowym P_d według Mehra-Jacksona. Frakcję tę stanowią głównie połączenia fosforu z półtoratlenkami. We wszystkich badanych profilach ilościowe zróżnicowanie zarówno P_t jak i P_d przedstawia charakterystyczny obraz eluwalno-iluwalnego przemieszczenia (rys. 1). Wydaje się, że istotną rolę w przemieszczaniu fosforu odgrywają połączenia kompleksowe organiczno-metalofosforanowe, w których jony fosforanowe połączone są z ruchliwymi kwasami próchnicznymi za pośrednictwem jonów Fe i Al. Możliwość tworzenia się takich połączeń w glebie wykazali liczni autorzy [2, 5, 10]. W biellicach rozpuszczalne kompleksy Fe- i Al-humusowe z fosforanami mogą powstawać już w próchnicy nadkładowej, gdzie znajdują się wszystkie istotne komponenty. Wytrącanie tych złożonych kompleksów w poziomie B odbywa się zapewne według tego samego mechanizmu, jaki powoduje utratę rozpuszczalności połączeń kwasów humusowych z R_2O_3 .

Na uwagę zasługuje zmieniająca się w profilu wartość stosunku P_d/P_t (tab. 2). Fosforany związane z R_2O_3 stanowią największą część fosforu glebowego w poziomach iluwalnych (w *Bh* stosunek P_d/P_t osiąga wartość 0,52–0,95). Poniżej poziomu *Bhs* frakcja ta odgrywa coraz mniejszą rolę, a w skale macierzystej jej udział jest zupełnie znikomy. Świadczy to o wyraźnej dominacji w poziomie C fosforanów wapniowych. W poziomie eluwalnym, w którym ze względu na dość intensywny rozkład apatytu nie należy się spodziewać większego udziału fosforanów wapniowych, niskie wartości P_d/P_t wskazują na większą zawartość organicznych związków fosforu. Porównując jakościowe zróżnicowanie związków fosforowych w profilach biellic z ogólnym schematem przemian tych związków w glebie opracowanym przez Walkera i Syersa [12], łatwo dostrzec daleko idące analogie. Skala macierzysta biellic z dominującą frakcją fosforanów Ca odpowiada stadium początkowemu, zaś poziom iluwalny z nagromadzeniem fosforanów związanych z R_2O_3 odpowiada stadium końcowemu przemian związków fosforowych w schemacie Walkera i Syersa.

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