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**ACCUMULATION AND MIGRATION
OF SELECTED FORMS
OF ARSENIC AND PHOSPHORUS
IN VARIOUSLY UTILIZED LESSIVE SOILS OF LUBLIN**

**AKUMULACJA I MIGRACJA
WYBRANYCH FORM ARSENU I FOSFORU W GLEBACH PŁOWYCH
RÓŻNIE UŻYTKOWANYCH MIASTA LUBLINA**

Abstract: The results of total arsenic and phosphorus contents as well as selected forms of these elements, in lessive (gray-brown podsolic) soils derived from loess, located in forests and in arable fields in the area of the city of Lublin were presented. An attempt was also made to assess land-use form influence on both elements behaviour. The sequential analysis used for arsenic and phosphorus is based on the scheme proposed by Chang and Jackson, which takes into account the anionic character of arsenic and phosphorus compounds present in soil.

Lessive soils contained from 1.87 up to 12.24 mg · kg⁻¹ of arsenic and from 0.16 up to 0.99 g · kg⁻¹ of phosphorus. The influence of land use method was observed. Arsenic and phosphorus contents were higher in surface as well as in illuvial horizons of soils located in arable field as compared with forest ones. Fractions of arsenic and phosphorus obtained during analysis showed strong differentiation. Amorphous and crystalline fractions of arsenic bound with iron oxides have the highest share in total arsenic pool. The same situation was noted in the case of phosphorus.

Keywords: arsenic, phosphorus, lessive soils, sequential extraction

A significant source of phosphorus and arsenic in soils, especially in their surface horizons, are mineral fertilizers and pesticides. The behaviour of these two elements in soils depends on their chemical form as well as the composition and physical and chemical properties of soils. The distribution of arsenic and phosphorus, elements that display chemical similarity in soils is characterized by high variability. The occurrence of competition between ions of phosphorus and arsenic sorption on various soil components was described in the literature [1–3]. It mostly results from different sizes

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of both anions as well as the different density of the electrical charge distribution. Both ions are subject to sorption by iron and aluminium hydroxides, as well as organic matter [4, 5]. Arsenic and phosphorus are bound by many soil components, so, profile distribution of both elements showed characteristic maximums in surface horizons abundant in humus, as well as in illuvial horizons rich in iron compounds colloidal clay fractions. Phosphorus present in soils in different shapes may successively compete with arsenic ions AsO_4^{3-} in sorption at various soil components. This especially occurs in farming soils fertilized among others with phosphorus compounds, where arsenic specifically fixed to iron and aluminium oxides may be dislodge in certain conditions. The consequence of such procedures is an increase in dissolvable and easily available forms of arsenic in the soil [6]. The effective analysis of both elements is conducted through sequential extraction during which arsenic and phosphorus fractions bound with various soil components are removed. The total content of arsenic and phosphorus in investigated soils does not fully reflect the content form of these elements, but is a very significant environment quality evaluation indicator. The applied sequential extraction of both arsenic and phosphorus is based on an analytical model suggested by Chang and Jackson [7] and differentiating the anion characteristics of arsenic and phosphorus compounds present in the soil [8, 9].

The aim of the study was the determination of total arsenic and phosphorus contents and selected forms of these elements in lessive (grey-brown podsollic) soils derived from loess, gathered in forests and arable fields in Lublin. The evaluation of the influence of soils utilization on the behaviour of both elements was additionally made.

Material and methods

The material under examination represents lessive soils, typical, formed from loess, collected from arable fields and forests. The soil pits were located within Lublin and outside of the Lublin agglomeration influence, in Czeslawice near Naleczow. The following parameters were determined: granulometric composition with the Bouyoucos method modified by Casagrande and Proszynski, sand fraction were separated on sieve with mesh of \varnothing 0.1 mm, pH in water and 1 mol $\text{KCl} \cdot \text{dm}^{-3}$ potentiometrically, organic carbon (organic C) with the Tiurin method, exchangeable cations in 1 mol $\text{NH}_4\text{Cl} \cdot \text{dm}^{-3}$, and cation exchange capacity (T) [10, 11].

The collected samples were sequentially analysed for arsenic according to the Wenzel method [8], and for phosphorus according to Chang-Jackson, modified by Hieltjes-Lijklema [12] (Table 1).

The residue was mineralized by *aqua regia*. The determination of arsenic in all sequential extracts was conducted through generation of hydrides on the AAS 3300 Perkin Elmer spectrometer with the FIAS 400 support, while that of phosphorus with the ascorbic acid method, spectrophotometrically on the Perkin Elmer Lambda 12 spectrophotometer.

Table 1
Sequential analysis model of arsenic and phosphorus extraction in investigated soils

Arsenic fraction	Arsenic extraction conditions	Phosphorus fractions	Phosphorus extraction conditions
As-sol. – arsenic forms not specifically fixed with soil components	0.05 mol · dm ⁻³ (NH ₄) ₂ SO ₄ , shaking 4 hours, centrifuging, decantation	P-sol. – phosphorus forms not specifically fixed with soil components	1 mol NH ₄ Cl · dm ⁻³ , shaking 2 hours (twice), centrifuging, decantation
As-ex. – arsenic forms specifically fixed with soil components	0.05 mol · dm ⁻³ (NH ₄) ₂ PO ₄ , shaking 16 hours, centrifuging, decantation	P-nap. – phosphorus forms fixed with oxides and hydroxides of iron, aluminium and manganese (non-organic “non-apatite” phosphorus)	0.1 mol · dm ⁻³ NaOH, shaking 17 hours, centrifuging, decantation
As-am. – arsenic forms fixed with amorphous, hydrated oxides	0.2 mol · dm ⁻³ oxalate buffer, pH = 3.25; shaking 4 hours in dark, centrifuging, decantation, cleaning with oxalate buffer through shaking in dark through 10 min	P-ap. – phosphorus forms fixed with calcium (non-organic “apatite” phosphorus)	0.5 mol HCl · dm ⁻³ , shaking 24 hours, centrifuging, decantation
As-cr. – arsenic forms fixed with crystalline oxides	0.2 mol · dm ⁻³ oxalate buffer + 0.1 mol · dm ⁻³ ascorbic acid, pH = 3.25; in temp. 96 °C, centrifuging, decantation, cleaning with oxalate buffer through shaking in dark through 10 min	P-org. – phosphorus forms fixed with organic matter	P-org = P-tot. – (P-sol. + P-nap. + P-ap.)
As-res. – arsenic residue	<i>Aqua regia</i> (16 hours in room temperature + 2 hours in temp. 130 °C, under manoeuvrable radiator)	P-tot. – total phosphorus content	<i>Aqua regia</i> (16 hours in room temperature + 2 hours in temp. 130 °C)

Results and discussion

The profiles of investigated lessive soils, which parent material is loess, are created by silty formations. Clearly distinguished is the lessivage process, which resulted in the Bt illuvial horizon development (Table 2).

The pH is mostly strongly acid and acid, while in horizons of the parent material, where there are present carbonates, the pH is above 7.25. Highest content of organic carbon of lessive soils collected in forests and fields was observed in surface horizons, and these values usually decrease with depth. Investigated lessive soils contained from 1.87 to 12.24 mg · kg⁻¹ of arsenic and its content did not exceed the limit defined in the Decree of the Polish Minister of Environment on soil and ground quality standards. Arsenic content ranges in forest soils as well as in soils located on arable fields within Lublin boundaries, stay on similar level, when compared with samples taken in Czeslawice near Naleczow. Anthropogenic factors, such as location between dense buildings, roads vicinity, car pollution and recreational utilisation of this area have not decisive influence on arsenic content in soil samples taken in Lublin. The accumulation of this element has primarily been confirmed in illuvial horizons (Bt). The phosphorus content in investigated soils was between 0.16 and 0.99 g · kg⁻¹, with characteristic increase in surface (A) and illuvial horizons (Bt). Therefore the profile distribution of total content of both elements shows much similarity. At the same time it is possible to declare that the strongest influence on phosphorus and arsenic accumulation by the content of organic matter and soil mineral colloids is characteristic for lessive soils. Both elements show strong relationship with the fine soil fractions, which high concentration was observed in Bt horizons. The amounts of phosphates absorbed in soils are higher than those of arsenates. The phosphates are fixed mainly by soil colloids and hydrated oxides of aluminium and iron, while arsenates mainly by oxides and hydroxides of iron [13].

The influence of soil utilization on the profile distribution of arsenic and phosphorus was also observed. Concentration of both elements was higher in surface and illuvial soil horizons located in fields as compared with samples collected in forests.

The fractions of arsenic and phosphorus separated during the sequential extraction showed high diversity (Fig. 1).

The largest share of arsenic in the overall pool belonged to fractions fixed with amorphous and crystalline iron oxides and was as high as over 70 %. The share of analogous fraction of phosphorus counted up to 50 %. For the total pool of arsenic and phosphorus fractions extracted from investigated soils, the amount of mobile fractions and simultaneously available to plants does not exceed 10 %. The share of dissolvable phosphorus fractions, in both forest and farming soils decreases with depth with simultaneous increase of mobile arsenic form (*As-sol* + *As-ex*). There is higher concentration of mobile arsenic forms (*As-sol* + *As-ex*) in lessive soils, and smaller of phosphorus forms in relation to forest soils, which may indicate of sorptive competition of both elements in soil components. The consequence of high affinity of phosphates to soil colloids and hydrated iron and aluminium oxides may be the increase in available arsenic content in the case of soils rich in phosphorus [6].

Table 2

Selected characteristics of lessive soils of Lublin

Profile No.	Location/ Utilisation	Horizon	Depth [cm]	CaCO ₃ [%]	pH		Organic C [g · kg ⁻¹]	T [mmol(+) · kg ⁻¹]	Share of fraction [Ø mm]			
					H ₂ O	1 M KCl			1-0.1	0.1-0.02	<0.02	<0.002
1.	Lublin, Stary Gaj Reserve (forest)	O	3-0	—	5.52	4.92	245.5*	371.9	—	—	—	—
		A	0-23	—	4.69	3.73	8.8	74.0	0.4	59.6	40	9
		Eet	23-48	—	4.52	3.82	4.0	50.2	0.5	58.5	41	7
		EetBt	48-62	—	5.05	3.87	1.1	55.7	0.6	56.4	43	11
		Bt	62-93	—	5.26	3.87	0.9	110.2	0.3	55.7	44	21
		BtC	93-160	—	5.22	3.97	0.6	100.3	0.5	61.5	38	15
		C	> 160	—	5.18	3.96	0.5	85.9	0.6	63.4	36	13
2.	Lublin, Stary Gaj (arable field)	Ap	0-33	—	5.24	3.88	7.7	100.6	0.8	58.2	41	11
		Bt	33-66	—	5.44	3.95	1.6	120.8	0.4	51.6	48	25
		BtC	66-82	—	5.64	4.05	0.8	69.0	0.8	65.2	34	13
		C	82-146	—	5.72	4.09	0.6	81.1	0.5	61.5	38	15
		Cca	< 146	4.32	8.15	7.25	0.7	496.8	0.6	63.4	36	13

Table 2. contd.

Profile No.	Location/ Utilisation	Horizon	Depth [cm]	CaCO ₃ [%]	pH		Organic C [g · kg ⁻¹]	T [mmol(+) · kg ⁻¹]	Share of fraction [Ø mm]				
					H ₂ O	1 M KCl			1-0.1	0.1-0.02	<0.02	<0.002	
													[%]
3.	Czeslawice near Naleczow (forest)	O	1-0	—	5.55	4.98	694.1*	745.5	—	—	—	—	—
		A	0-7	—	4.17	3.41	32.5	165.8	0.4	60.6	39	13	13
		AEt	7-16	—	4.95	3.75	7.9	382.2	0.4	59.6	40	12	12
		Bt	16-50	—	5.31	3.66	1.8	98.7	0.3	52.7	47	25	25
		BtC	50-70	—	5.63	3.83	1.4	75.4	0.3	59.7	40	20	20
		C	70-129	—	6.05	4.12	0.8	60.8	0.3	68.7	31	14	14
		Cca	<129	10.04	8.69	7.85	0.6	628.2	0.6	61.4	38	14	14
4.	Czeslawice near Naleczow (field)	ApBt	0-15	—	5.23	4.66	7.8	112.5	0.2	57.8	42	13	13
		B1t	15-40	—	5.18	4.59	1.3	92.2	0.2	45.8	54	27	27
		B2t	40-65	—	5.11	4.43	0.8	82.0	0.1	42.9	57	31	31
		B2tC	65-90	—	5.09	4.42	0.4	69.3	0.1	43.9	56	26	26
		C	90-150	—	4.20	4.53	0.4	87.0	0.2	48.8	51	21	21
		Cca	<150	7.97	8.32	7.64	0.2	509.8	0.1	59.9	40	14	14

* Organic matter.

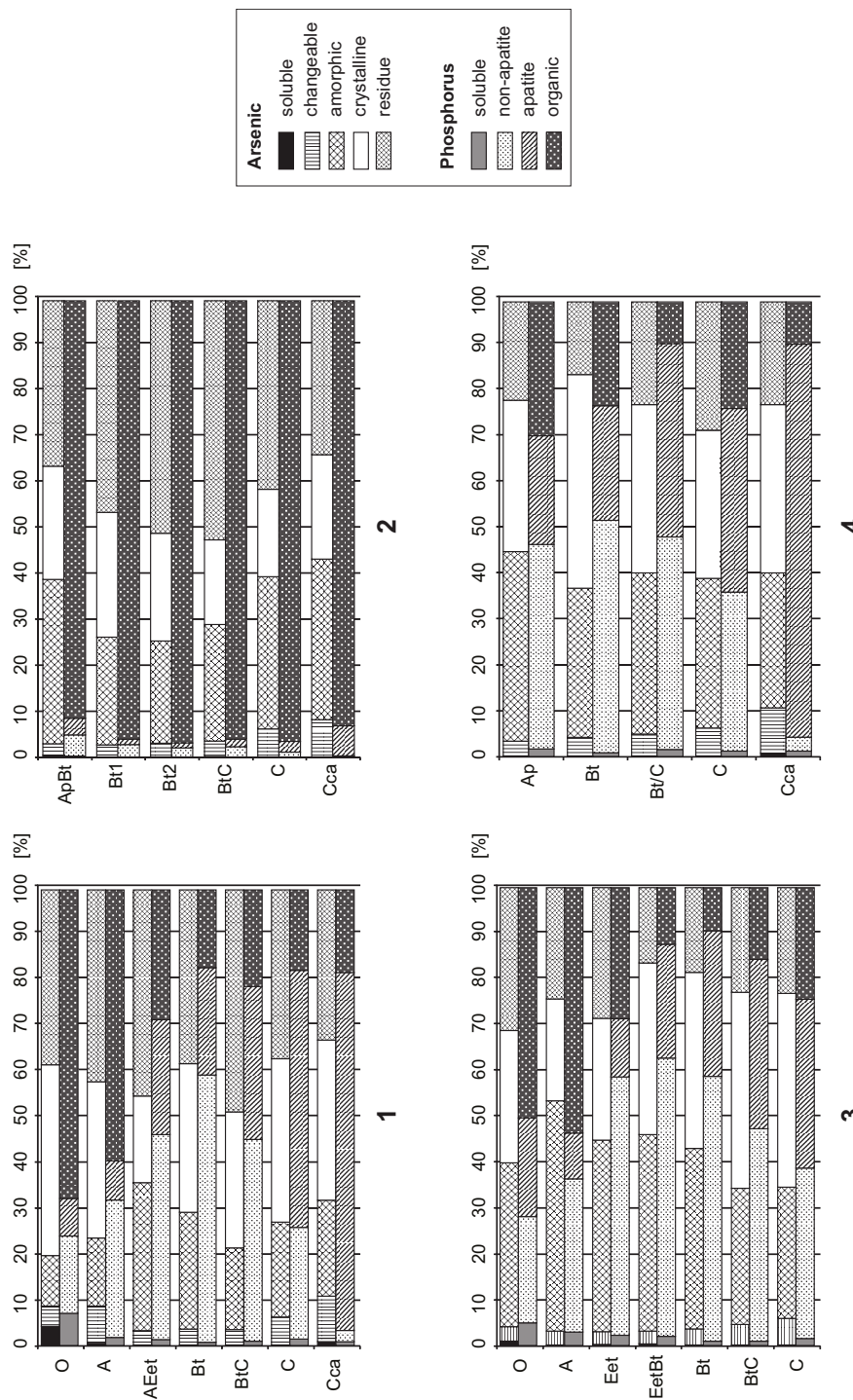


Fig. 1. Share [%] of determined As and P fractions in lessive soils of different utilization. 1 and 2: profiles beyond agglomeration influence (1 – forest, 2 – field); 3 and 4: profiles located within the city boundaries (3 – forest, 4 – field)

A regularity is also recognized that the higher phosphorus content in A horizons of lessive soils collected from fields was connected with the higher share of mobile arsenic forms. Fixation of arsenic and phosphorus by many soil components causes their gathering in surface horizons. It was especially observed in places subject to strong anthropopression (eg cities) what is connected with accumulation of various pollutants as well as fertilization. However the comparison of both elements content in soils located within Lublin as well as in Czeslawice near Naleczow shows small influence of the Lublin agglomeration. The profile distribution of arsenic and phosphorus content has a similar pattern.

Conclusions

1. The influence of land utilization on the content of arsenic and phosphorus is observed. The content of both elements was higher in soils located in fields than in forests ones.
2. The influence of the Lublin agglomeration on the content of both elements is slight. The contents of arsenic and phosphorus are at similar levels in lessive soils collected both in Lublin and outside of the Lublin agglomeration.
3. The highest share in the total pool of arsenic and phosphorus is held by fractions of limited mobility (associated with iron, aluminium, manganese oxides or calcium compounds).
4. Lessive soils utilized agriculturally have a higher share of mobile arsenic fractions (*As-sol* + *As-ex*), and lower of phosphorus fractions (*P-sol*) as compared with the investigated forest soils.

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**AKUMULACJA I MIGRACJA WYBRANYCH FORM ARSENU I FOSFORU
W GLEBACH PŁOWYCH RÓŻNIE UŻYTKOWANYCH MIASTA LUBLINA**

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Abstrakt: Przedstawiono wyniki oznaczeń całkowitych zawartości arsenu i fosforu oraz wybranych frakcji tych pierwiastków w glebach płowych wytworzonych z lessu, pobranych w lesie i na polu uprawnym na terenie miasta Lublina. Podjęto także próbę oceny wpływu użytkowania na zachowanie się obu pierwiastków. Zastosowana sekwencyjna ekstrakcja zarówno arsenu, jak i fosforu korzysta ze schematu analitycznego zaproponowanego przez Changa i Jacksona, uwzględniającego anionowy charakter występujących w glebie związków arsenu i fosforu.

Badane gleby płowe typowe zawierały od 1.87 do 12.24 mg arsenu \cdot kg⁻¹, a zawartość fosforu wahała się od 0.16 do 0.99 g \cdot kg⁻¹. Jednocześnie zaznaczył się także wpływ sposobu użytkowania gleb. Zawartości arsenu i fosforu były większe w poziomach powierzchniowych. Obserwowano też wzbogacenie w te pierwiastki gleb z pola uprawnego w stosunku do próbek glebowych pobranych w lesie. Zawartość frakcji arsenu i fosforu wydzielonych w analizie specjacyjnej wykazywała duże zróżnicowanie. Największy udział arsenu w ogólnej puli tego składnika miały frakcje związane z amorficznymi i krystalicznymi tlenkami żelaza. Analogiczne zależności stwierdzono też w przypadku fosforu.

Słowa kluczowe: arsen, fosfor, gleby płowe, sekwencyjna ekstrakcja