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BUFFER PROPERTIES OF FOREST SOILS
IN SELECTED PROTECTED AREAS

WŁAŚCIWOŚCI BUFOROWE GLEB LEŚNYCH
WYBRANYCH OBSZARÓW CHRONIONYCH

Abstract: The paper presents the results of research on forest soil buffer capacity in selected protected areas. The soil buffer capacity was determined for each soil horizon using modified Arrhenius method. Buffer curves were sketched and soil buffer areas were measured with computer techniques. The date obtained were compared with some soil physical and chemical properties using statistical method. Organic (O) and humus (A) horizons of forest soils demonstrate a greater abilities of buffering alkalines than acids whereas buffer capacity of deeper-lying horizons changes as their physical and chemical properties change. Of the examined types of forest soils, the greatest buffer capacity was found for river alluvial soils. The results of the study indicate that the buffer areas are significantly correlated with pH, hydrolytic acidity, content of organic C, clay fractions, sum of exchangeable bases and cation exchangeable capacity.

Keywords: forest soil, buffer capacity, soil physical and chemical properties

Soils are capable of resisting factors due to a set of physical, chemical and biological properties [1]. The extent of changes in the soil environment depends not only on toxicity of substances introduced to the soil but also soil buffer properties.

The pH value is an indicator of nutrient availability in soils, nitrification properties, an occurrence of aluminium ions and heavy metals, as well as conditions of soil life [2]. Also soil buffer properties are associated with soil pH.

Soil buffer properties are understood and defined as the ability of a soil to maintain a relatively stable pH in spite of an effect of acidifying or alkalising factors [3]. Various buffering processes may take place in one and the same soil depending on the parent rock geological origins and mineralogical composition as well as weathering intensity.

The soil is a mixture of buffer systems. It contains components some of which are able to neutralize acids by means of H^+ ion fixation whereas others neutralize alkalis as

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a result of releasing H$^+$ ions [3–5]. Numerous studies [6–17] have shown that soil buffer capacity depends on physical, chemical and biological properties of the soil, soil--forming processes, habitat type and nature, climatic conditions as well as an effect of anthropogenic factors. Examination of soil buffer properties enables an assessment of an influence of degrading factors and makes it possible to predict the extent of degradation of the soil environment over time [3,13].

The purpose of the study was to estimate the buffer abilities of forest soils in selected protected areas, with regard to their typology and physical and chemical properties.

Material and methods

Studies were conducted on 7 profiles of forest soils which were different typologically and located in protected areas:

– profile 1 – brown river alluvial soil (acc. to "Klasyfikacja gleb leśnych Polski" [18]), (*Fluvisols* acc. to WRB [19]), developed from alluvial sands, covered by the *Ficario-Ulmetum* plants association, the reserve "Leg Debowy", the landscape park "Podlaski Przelom Bugu", the Lublin province;

– profile 2 – humus river alluvial soil (*Fluvisols*), developed from alluvial silts, covered by the *Fraxino-Alnetum* plant association the reserve "Leg Dębowy", the landscape park "Podlaski Przelom Bugu";

– profile 3 – glossic soil lessive (*Albeluvisols*), developed from fluvioglacial silts, covered by the *Tilio-Carpinetum* plants association, the reserve "Stary Las", the landscape park "Podlaski Przelom Bugu";

– profile 4 – brownish rusty soil (*Arenosols*), developed from moraine sands, covered by the *Carpinion-betuli* plants association, the reserve "Stary Las", the landscape park "Podlaski Przelom Bugu";

– profile 5 – proper rusty soil (*Arenosols*), developed from fluvioglacial sands, covered by the *Pino-Quercetum* plants association, "Uroczysko Ceranow", "Nadburzanski Park Krajobrazowy", the Mazovia province;

– profile 6 – proper rusty soil (*Arenosols*), developed from fluvioglacial sands, covered by the *Pino-Quercetum* plants association, the reserve "Pionki", "Kozienicki Park Karjobrazowy", the Mazovia province;

– profile 7 – proper podzol soil (*Podzols*) developed from fluvioglacial sands, covered by the *Pino-Quercetum* plants association, the reserve "Stawy Broszkowskie", the county of Siedlce, the Mazovia province.

Soil samples were taken from selected horizons of the soil profiles researched and dried under laboratory conditions. Sample from raw horizons were ground while samples from the mineral horizons were crushed in a mortar and sieved through 2 mm sieve.

Buffer curves were drawn according to Arrhenius with Brenner and Kappen modification [20] adding increasing amounts of 0.1 mol HCl · dm^{-3} and 0.1 mol NaOH · dm^{-3} to soil, with after 24 h was followed by solution pH measurement. Areas between standard curve and buffer curve drawn for particular genetic horizons were measured with the computer techniques. Similarly there were defined the granulometric

composition according to Bouyoucos method with Cassagrande and Proszynski modifications, carbon in organic compounds – the Tiurin method, H (*hydrolytic acidity*) and TEB (*sum of exchangeable bases*) with the Kappen method, pH in H_2O and 1 mol $KCl \cdot dm^{-3}$ with the potentiometric method (the soil : solution ratio 1 : 2.5). CEC (*cation exchange capacity*) was calculated using to the following equation: CEC = = TEB + H_h, BS (*the degree of base saturation of soil sorption complex*) was definite with % BS = TEB $\cdot$ 100/CEC.

Using the statistical package Statistica 9.0 PL Pearson correlation coefficients (r) were calculated between the buffer area in acidic and alkaline range and physical and chemical properties of soil mineral horizons.

Results and discussion

The forest soils examined were characterised by varying physical and chemical properties. The parent rocks of the examined soils differed as to the geological origins and granulometric composition The content of clay fractions (< 0.002 mm) in the soils ranged between 0 and 13 % (Table 1). The pH of the soils ranged from very acid to neutral (pH in 1 mol $KCl \cdot dm^{-3}$ from 3.1 to 7.0). A very acid pH (3.1–4.4) was determined in the organic horizons – O and humus horizons – A of the examined soils (Table 2). The neutral pH was measured in the deeper horizons of river alluvial soils. Calcium carbonate was not detected in the studied soils.

Table 1

Some physical and chemical properties of the soil investigated

Taxonomic Unit	Fraction < 0.002 mm [%]	$C_{org.}$ [g $\cdot$ kg^{-1}]	H	TEB	CEC	BS [%]
			[mmol(+) $\cdot$ kg^{-1}]			
Ranges of values						
River alluvial soil (*Fluvisols*) profile 1, 2	0–13	1.0–337.2	10–712	90–3240	100–3911	65.3–96.7
Soil lessive (*Albeluvisols*), profile 3	1–12	0.4–358.5	202–1168	30–340	276–1498	8.6–60.2
Rusty soils (*Arenosols*), profile 4, 5, 6	1–5	0.4–438.4	120–975	10–521	132–1204	5.9–43.3
Podzolic soil (*Podzols*), profile 7	1–3	0.8–473.2	259–846	13–41	272–887	3.0–6.3

H – hydrolytic acidity, TEB – sum of exchangeable bases, CEC – cation exchange capacity, BS – base saturation.

Organic carbon content in the humus layers of the analysed soils ranged between 20.2 and 57.2 g $\cdot$ kg^{-1}. Most organic C – from 287.4 to 473.2 g $\cdot$ kg^{-1} – was determined

in organic horizons (Table 1). The content of organic carbon decreased with the depth of soil horizons.

The soils analysed had different exchangeable capacity. The greatest cation exchangeable capacity (887–3911mmol(+) · kg^{-1}) was found in the humus horizons of the examined soils. The saturation degree of the sorption complex with exchangeable bases ranged from BS = 3.0 % in the eluvial horizon Ees of the proper podzol soil to BS = 96.7 % in the horizon Gor of the humus river alluvial soil (Table 1).

The analyses showed that the very acid and acid reaction of the soils is the result of natural soil-forming processes, such as relations between parent rock and plant cover (low pH, high value of hydrolytic acidity and low degree of saturation of the sorption complex with bases).

The buffer capacity of the soil profiles analysed was assessed based on the area of buffer surfaces in acidic (P_{HCl}) and alkaline (P_{NaOH}) range, drawn for soil samples taken from individual genetic horizons. Data presented in Table 1 demonstrate that the buffer capacities of genetic horizons of the examined forest soils were clearly different. The buffer area in acidic range was between 0.25 and 11.95 cm^2 and, in alkaline range, between 0.77 and 37.90 cm^2 (Table 2).

There was determined greater capacity of buffering alkalines than acids in the genetic horizons of the brownish rusty soil (profile 4), proper rusty soils (profile 5, 6), proper podzol soil (profile 7) and in almost all horizons of the glossic soil lessive (profile 3), as indicated by the ratio of $P_{NaOH} : P_{HCl}$ buffer areas which ranged between 1.30 to 64.64 (Table 2). In the profile of the glossic soil lessive, the horizons IIBt and IIIC2 were an exception as they revealed a greater capacity of buffering acids than alkalines.

Of the examined forest soils, river alluvial soils had the greatest buffer capacity. The surface horizons of these soils display a greater capacity of buffering alkalines than acids although their buffer area in the acid range is greater compared with the remaining soils. The buffering capacity of samples rich in organic matter are higher than soils with low humus, which are usually poor-buffered. In the horizons of deeper-lying river alluvial soils, there was found a greater capacity of buffering acids than alkalines, which is associated with their pH. The buffer capacity of river alluvial soils is also associated with their granulometric composition (loamy sand, loamy silt, clayey silt), and the content of mineral and organic colloids. The buffer curve of the eluvial horizon Ees of the podzol soil the closest resembled the standard curve in acidic range, which was affected by the process of podzolization by limiting the buffer area P_{HCl} for this horizon to 0.25 cm^2 (Table 2).

In order to find an association between the buffer area in acidic (P_{HCl}) and alkaline (P_{NaOH}) range and physical and chemical properties of the soils, coefficients of Pearson linear correlation (r) were calculated. Statistical analysis showed that the buffer area in the acid range was significantly positively correlated with pH in H$_2$O (r = 0.610***) and in 1 mol KCl · dm^{-3} (r = 0.560***), clay fraction (r = 0.746***) and organic C content (r = 0.373*). The strongest correlation (r = 0.859***) was found between P_{HCl} and cation exchangeable bases (TEB) in the mineral horizons of the examined soils. However, there was found no significant effect of cation exchangeable capacity and hydrolytic acidity (H) on the buffer area in acidic range.

Table 2

Buffering areas in acid range and alkaline range of soil investigated

Profile No.	Genetic horizon	Depth [cm]	pH		P_{NaOH} [cm²]	P_{HCl} [cm²]	P_{NaOH}/P_{HCl}	P_{HCl}/P_{NaOH}
			H_2O	KCl				
1	O	0–2	5.3	4.7	21.45	7.91	2.71	0.37
	A1	2–9	5.2	4.5	24.31	7.32	3.32	0.30
	A2	9–16	5.6	4.8	18.01	8.95	2.01	0.50
	Bbr1	16–41	6.0	5.8	9.92	7.35	1.35	0.74
	Bbr2	41–84	6.9	6.7	5.57	7.53	0.74	1.35
	Cgg	84–180	7.6	6.9	1.10	4.28	0.25	3.89
2	O	0–1	5.7	5.2	24.32	10.82	2.24	0.44
	A	1–20	5.6	4.9	26.11	10.24	2.55	0.39
	ACgg	20–46	6.4	6.0	11.06	11.95	0.93	1.08
	Gor	46–81	7.2	7.0	1.86	6.63	0.28	3.56
	Gr	81–112	7.1	6.9	5.09	9.93	0.51	1.95
	DG	112–180	7.2	7.0	0.77	1.33	0.58	1.73
3	O	0–3	4.1	3.3	15.97	4.03	3.96	0.25
	A	3–7	4.0	3.1	12.36	3.73	3.31	0.30
	AEet	7–22	4.2	3.5	9.23	3.92	2.35	0.42
	Eet	22–43	4.5	3.9	6.28	4.22	1.49	0.67
	Eet/Bt	43–64	4.7	4.0	3.81	2.27	1.67	0.60
	IIBt	64–98	5.3	4.2	3.02	4.52	0.67	1.50
	IIIC1	104–126	4.3	3.7	3.50	2.55	1.37	0.73
	IIIC2	126–150	4.6	3.8	4.60	5.20	0.88	1.13
4	O	0–2	5.6	4.9	16.42	5.34	3.07	0.33
	A	2–7.5	5.4	4.7	11.54	5.16	2.24	0.45
	ABbr	7.5–28	4.7	4.1	10.72	4.30	2.49	0.40
	BbrBv	28–54	4.9	4.3	8.38	3.82	2.19	0.46
	C1	54–89	5.0	4.2	6.08	2.20	2.76	0.36
	C2	89–150	5.1	4.4	2.60	2.00	1.30	0.77
5	O	0–3	3.8	3.4	24.93	1.09	22.87	0.04
	A	3–11	3.6	3.1	22.66	0.88	25.73	0.04
	Bv	11–42	4.5	4.3	8.98	2.92	3.08	0.33
	C	> 42	4.9	4.5	3.30	2.33	1.42	0.71
6	O	0–5	3.7	3.3	25.75	1.15	22.39	0.04
	A	5–15	3.6	3.1	24.02	0.99	24.26	0.04
	Bv1	15–35	4.5	4.3	11.07	4.96	2.23	0.45
	Bv2	35–50	4.6	4.4	10.73	5.09	2.10	0.47
	C	> 50	4.8	4.6	3.59	2.73	1.31	0.76
7	O	0–10	3.4	3.0	37.90	0.89	49.22	0.02
	A	10–19	3.8	3.2	24.69	0.67	36.85	0.03
	Ees	19–30	4.1	3.5	16.16	0.25	64.64	0.02
	Bhfe	30–40	4.5	4.3	17.17	2.50	6.87	0.19
	Bfe1	40–46	4.7	4.5	13.63	2.11	6.46	0.22
	Bfe2	46–60	4.5	4.4	12.45	2.05	6.07	0.24
	C	> 60	4.8	4.8	5.35	1.95	2.74	0.43

High values of correlation coefficients indicate a strong association between the buffer area in alkaline range and hydrolytic acidity (r = 0.763***) and organic C content (r = 0.738***). A weaker yet significant association was found between P_{NaOH} and cation exchangeable capacity (CEC) (r = 0.396*). The buffer area in alkaline range was significantly and negatively associated with pH in H_2O (r = –0.478***) and pH in 1 mol $KCl \cdot dm^{-3}$ (r = –0.473***). There was found no significant association between the buffer area P_{NaOH} and the clay fraction content.

Of the examined forest soil horizons, the organic horizons O and humus horizons A were most resistant to alkalisation, which has also been reported by other authors [2, 5, 6, 8, 10, 11, 17] who examined forest soils. Statistical analysis demonstrated a stronger association between organic C content and the buffer area in alkaline range (P_{NaOH}) compared with the buffer area in acidic range (P_{HCl}). It is most probable the result of unsaturated character of forest litter where acid cations predominate. Hydrogen bound with acid groups and exchangeable aluminium in forest soils may neutralize marked amounts of bases. Many works [2, 5, 6, 9, 10, 13–16] stress the important role of humus and clay minerals as buffer systems. When soil pH is alkaline, hydrogen ions are bound by negatively charges of clay minerals and humus. The H^+ ions is weakly adsorbed onto clay (ionic bonding) and it is strongly adsorbed to carboxyl groups of humus (covalent bonding) [21]. When pH changes into neutral or alkaline, the hydrogen bound is deionised and becomes changeable.

The forest soil types analysed and their genetic horizons varied in their buffer capacity between one another which, as indicated by literature [3, 10–14, 21], is associated with distribution of various buffer systems in soil profiles (silicate, aluminium, iron, ion exchange, carbonate buffers). Urlich [22] defined pH ranges in which individual buffers play the main role. The effectiveness of individual buffer systems depends on physical, chemical and biological soil properties.

Conclusions

1. Organic and humus horizons of forest soils demonstrate a greater abilities of buffering alkalines than acids whereas buffer capacity of deeper-lying horizons changes as their physical and chemical properties change.

2. Of the examined types of forest soils, the greatest buffer capacity was found for river alluvial soils.

3. The statistical analysis showed that the soil resistance to acid activity defined with correlation coefficient was significantly correlated with colloidal clay fractions content, sum of exchangeable basis (TEB), pH value in H_2O and 1 mol $KCl \cdot dm^{-3}$ and with organic C content.

4. The resistance of the forest soils to alkaline activity was significantly correlated with hydrolytic acidity (H), organic C content, pH value in H_2O and in 1 mol $KCl \cdot dm^{-3}$ and with cation exchangeable capacity (CEC).

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WŁAŚCIWOŚCI BUFOROWE GLEB LEŚNYCH WYBRANYCH OBSZARÓW CHRONIONYCH

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Abstrakt: W pracy przedstawiono wyniki badań nad zdolnościami buforowymi gleb wybranych obszarów chronionych. Analizie poddano 7 profili gleb leśnych reprezentujących następujące podtypy gleb: mady rzeczne brunatne, mady rzeczne próchnicze, gleby płowe zaciekowe, gleby rdzawe brunatne, gleby rdzawe właściwe oraz gleby bielicowe właściwe. Wykreślono dla nich krzywe buforowe zmodyfikowaną metodą Arrheniusa i zmierzono techniką komputerową powierzchnie buforowe gleb. Uzyskane dane porównano statystycznie z niektórymi właściwościami fizyczno-chemicznymi gleb. Poziomy organiczne (O) i próchniczne (A) gleb leśnych wykazują większe zdolności buforowania zasad niż kwasów, natomiast zdolności buforowe poziomów głębiej zalegających zmieniają się wraz z ich właściwościami fizyczno-chemicznymi. Wśród badanych typów gleb leśnych największe zdolności buforowe wykazują mady rzeczne. Wyniki badań wskazują, że powierzchnie buforowe badanych gleb są istotnie skorelowane z pH, kwasowością hydrolityczną, zawartością węgla związków organicznych, frakcją iłu, sumą zasad wymiennych oraz z kationową pojemnością sorpcyjną.

Słowa kluczowe: gleby leśne, buforowość gleb, właściwości fizyczno-chemiczne gleb