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Original Research

Chemical Composition of Soil Solutions from Forest Lands under Anthropogenic Pressure: Comparing Two Extract Recovery Methods

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Abstract

Investigations were carried out on sandy forest soils from Wielkopolski National Park (west-central Poland), which have been exposed for a long time to anthropogenic pressure. Two comparative extract recovery methods were performed for aqueous soil extracts (ME) at ratios 1:1, and those obtained from so-called saturated paste (MP). Recovered extracts were analyzed for sodium, potassium, magnesium, calcium, aluminium, chloride, fluoride, nitrate and sulphate concentrations, at various depths of two slightly different soil profiles. Higher levels of alkaline cations were obtained in extracts recovered at ratios 1:1, in the case of sandy soils along the entire profile, whereas in profiles with variable lithology, the granulometric composition clearly affected the mechanism of ion release. The patterns of changes in the contents of chlorides and sulphates were similar to those of calcium and magnesium, while fluoride levels in the topsoil differed significantly, depending on the method applied. Differences between the two methods were also significant in the case of aluminium content. The elaboration of aluminium toxicity indices should consider such approaches.

Keywords: saturated paste, soil extracts, ionic species, Wielkopolski National Park

Introduction

Atmospheric deposition of strong acids produces many detrimental changes in the soil, such as an increase in alkaline cation leaching, a decrease in soil pH and base saturation, a change in mineral weathering rates, and a modification of soil biology. Soils develop several buffering capacities aimed at counteracting acidification processes [1, 2]. Detailed information on the composition and changes within soils affected by acid deposition is highly relevant to an assessment of risks of acidification-related forest damage. Soil solution chemistry provides insight into element cycle, nutrient uptake and availability, mineral transformation, and pollutant transport processes within the subsurface environment [3-5]. Forest decline is believed to result largely from disturbed relationships among the elements of soil solutions [6, 7].

The matter of concern is, however, how to recover soil extracts. There is no doubt that data from the chemical analysis of soil extracts are affected by the way they are obtained. Several methods are described in the literature, including *in situ* sampling with the use of pans or suction lysimeters, among others [8], but also suitable procedures of displacement or extraction under laboratory conditions (ethyl alcohol, acetone, KSCN, $SrCl_2$) [9]. The use of

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lysimeters is the recommended method [10], where soil water is sucked from a variety of depths as a result of the vacuum produced. This method is widely applied in studies on the balance of ionic flows in catchments [11], a complicated research method, since it requires not only suitable technical equipment, but also soil and precipitation conditions making this technique of soil solutions sampling possible. Sandy soils and low rainfall preclude obtaining soil solutions in this way.

In studies concerning the assessment of changes in the composition of soil extracts, the separation of the liquid phase by centrifugation or squeezing is one of the frequently applied methods. However, this procedure can be performed exclusively on fresh solutions, which in turn restricts the number of analyses [12]. That is why other techniques have been used for extract recovery from air-dried soils, an approach which greatly increases the number of soil samples. Two methods are generally suggested: water extraction (ME), where the ratios of soil and distilled water, as well as the shaking time, are strictly specified [13]. The other method is based on imitating natural process, and involves a recovery of extracts from air-dried soils by moistening them to a field water-holding capacity or to form a saturated paste (MP). Next, the samples undergo incubation for a strictly specified time and finally the extracts are filtered off [9, 14, 15]. This procedure creates an equilibrium between the phases and helps release a specified pool of elements characteristic to a given soil (and method). Each of the methods has its advantages and limitations.

The aim of the study was to compare the chemical composition of aqueous extracts of forest soils exposed for many years to anthropogenic pressure. Two methods of extracts recovery were applied for this purpose. The comparison was intended to determine the better method and to point out the possibility and sources of mistakes.

Materials and Methods

Soil samples were collected in fall 2006, within Wielkopolski National Park (west-central Poland), at two sites (Wiry and Jeziory). The study of the soil properties was carried out in soil layers, where the main root biomass can be found. The age of the tree stands (pines and maples) was similar for the two sites: about 60-80 years. After digging an exposure of 1.2 m depth, samples were extracted from individual genetic horizons and placed in plastic bags. Three independent samples were taken from each horizon and analyzed separately, with the average used in further research. Soil samples were air-dried, crushed in a mortar and passed through a 2-mm mesh sieve in order to separate framework particles (stones, gravel) from fine fractions (sand, silt, clay). The following physical and chemical analyses were carried out for the <2 mm fraction:

- Granulometric analysis, using the areometric method after Casagrande modified by Prószyński (supplemented with the sieve method to determine the grain-size distribution of the sand fraction).
- Soil reaction (pH), potentiometrically – in H_2O and 1mol KCl at 1:2.5 ratio by weight. The method consisted in measuring the pH of the suspension after 30 min. in the aqueous suspension, and after 60 min. in the KCl-electrolyte.
- Cation exchange capacity (CEC): summation of alkaline cations *via* extraction with ammonium acetate, and acidity, with sodium acetate [14].

Two methods were applied for recovering soil extracts:

- The extraction method (ME): 60 g of an air-dried sample were mixed with 60 ml of de-ionised water. The mixture was shaken in a rotary shaker for an hour, then centrifuged for 30 min. at 4,500 rotations. The extract was passed through a 0.45-µm filter and stored at 4°C for analysis. This ratio (60 g: 60 ml) makes easier the conversion of the data from $mg\cdot dm^{-3}$ into $mg\cdot kg^{-1}$ of soil.
- The saturated paste method (MP): the paste is prepared by adding de-ionized water to 1 kg of soil sample while stirring the mixture until the soil paste meets the saturation criteria, i.e. the soil paste glistens as it reflects light and flows slightly when the container is tipped. The mixture is covered and allowed to stand overnight. The saturation criteria are then re-checked. If the mixture fails to meet them, more water or more soil is added until the criteria are met again. A saturated paste subsample is used to determine the moisture content [10]. The aqueous extracts are recovered from the saturated paste using a Büchner funnel and a vacuum pump with manometer control.

The chemical composition of the extracts (K^+, Na^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, and F^-) was determined *via* ion chromatography using a DIONEX 120 ion chromatograph. For anion analysis the eluent employed was a mixture of 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ (Merck), with an IonPac AG14 guard and an IonPac AS14 analytical column. For cation analysis the eluent was 20 mM methanesulphonic acid (Fluka), with an IonPac CG12A guard and an IonPac CS12A analytical column. For both analyses two self-regenerating suppressors and a CDM 3 conductivity detector were employed. An injection volume of 25 mL and a flow rate of 1.2 mL/ min were used. The basic standard solutions for the ions to be determined were Merck solutions at a concentration of 1.000 $mg\cdot dm^{-3}$. Atomic absorption spectrometry (Varian Spectra 220 FS) with atomization in a flame of acetylene/nitrous oxide was the method used for aluminium determination in all extracts. The accuracy of data was additionally tested by incorporating reference material RTH 907 (WEPAL). The method error is below 8% ($c < 1\ mg\cdot dm^{-3}$) and does not exceed 4% ($c > 1\ mg\cdot dm^{-3}$) for chromatographic analysis, and for the aluminium determination it is below 20% ($c<3\ mg\cdot dm^{-3}$) and below <5% ($c > 3\ mg\cdot dm^{-3}$). A detailed description of the analytical methods, their calibration and validation is reported by Walna et al. [16].

The comparison of results reported in figures was made after converting concentrations (mg·dm^{-3}) of the particular elements from the saturated paste method into mg·kg^{-1} dry mass, as shown below:

$$X = c \cdot w / (100 - w)$$

where:
X – element content, (mg·kg^{-1}),
c – element concentration of the extract from the saturated paste (mg·dm^{-3})
w – moisture content of the saturated paste (%).

Results and Discussion

The geochemistry of chemical species in soil extracts depends on several soil factors, of which the granulometric composition and moisture levels play an important role. Table 1 lists data of some selected physical and chemical properties of investigated soils. The Wiry profiles are sandy, hence their grainsize and granulometric composition differ slightly from the loamy sands and sandy loams occurring in the Jeziory profiles. Differences in the granulometric composition of soils from the two sites resulted in a higher content of the 2.0-0.1 mm fraction in the Wiry samples (77-91%) as compared to the Jeziory samples (48-59%). An analysis of the < 0.002 mm fraction at the lower layers of the Jeziory profile showed a significant share (14-15%) of clay minerals. Their presence certainly altered the mechanism of ion release from the sorptive complex into the soil solution. Data dealing with the base saturation of the sorptive complex were reported in Table 1 and outlined differences between soils from both profiles.

The sandy profiles have exhibited strongly acidic conditions with pH varying between 3.34 and 4.46, leading to the occurrence of markedly low buffering capacities (i.e., low CEC). A substantial deposition of H$^+$ with precipitation will initiate buffering processes involving the dissolution of aluminium in order to prevent a decrease in the pH of soil water [17-20]. The soils also differ in their humus content, which could influence the pool of organically bound elements and the amount of individual components released to the soil solution [21].

Fig. 1 elaborates on the basis of results obtained from paste-based extracts (MP) and shows that aluminium levels were higher in the Wiry site as compared to Jeziory: they declined down the profile from 6.6 mg·dm^{-3} (A) and 6.8 mg·dm^{-3} (Bv) to 1.88 mg·dm^{-3} (C2) as the soil pH$_{H2O}$ rises from 3.49 to 4.67. Aluminium contents determined by the MP method were also low for the Jeziory profile: they varied from 1.47 mg·dm^{-3} in the upper horizon characterized by a pH of 4.0, similarly in the adjacent horizons and down to a depth of 60 cm at pH 4.73. Contrary to the lower horizons, where pH was higher (i.e. from 5.26 to 5.31), aluminium content decreased drastically to 0.18-0.16 mg·dm^{-3}. For compar-

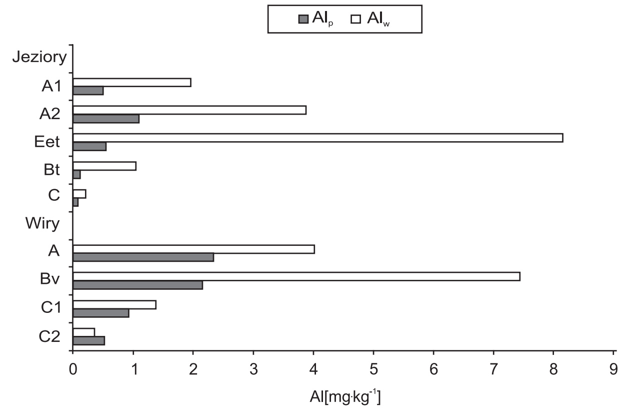

Fig. 1. Comparison of aluminium contents determined by the two methods (Al$_w$ – extraction method, Al$_p$ – saturated paste method).

Table 1. Basic properties of the investigated soils (CEC – Cation Exchange Capacity; BS – Base Saturation).

Profile/ Site	Depth	Horizon	Sand	Silt	Clay	Group acc. FAO/USDA	Ignition loss	pH $_{H2O}$	1 mol pH $_{KCl}$	CEC	BS
	cm		%				%			cmol(+) kg^{-1}	%
Jeziory	0-5	A$_1$	75	22	3	Loamy sand	4.6	4.00	3.36	10.12	14.8
	5-10	A$_2$	77	19	4	Loamy sand	3.2	4.11	3.43	6.96	12.7
	10-60	E	79	16	5	Loamy sand	0.6	4.73	3.97	3.45	19.5
	60-100	Bt	70	16	14	Sandy loam	0.3	5.26	3.81	7.42	55.5
	100-120	C	71	14	15	Sandy loam	0.9	5.31	3.81	8.55	63.1
Wiry	0-6	A/E	89	8	3	Sand	2.4	3.49	3.35	10.24	13.9
	6-20	Bv	91	5	4	Sand	1.1	4.17	3.59	5.27	13.2
	20-50	C$_1$	93	3	4	Sand	0.5	4.69	4.13	3.39	17.0
	50-100	C$_2$	94	2	2	Sand	0.1	4.67	4.47	2.65	16.5

ison, aluminium contents in the aqueous extract (ME) were also plotted jointly with those of the MP method. It could be observed that the ME-based results were much higher than the paste-based ones. The use of a greater volume of water to recover the extract and the intensity of shaking have resulted in the dissolution of much greater amounts of aluminium compounds. This especially concerns soil samples characterized by a higher share of the clay fraction, basically from the lower layers of the Jeziory profile. In the case of the loose sands from the Wiry profile, it was found that Al contents in the ME extracts were only slightly higher, whereas for the Jeziory profiles, Al levels in Eet and Bt horizons were higher *ca* 15 and 9 times, respectively, (Table 2). For low aluminium concentrations the differences between the ME and MP methods may result from method error (Jeziory – C, Wiry – C1, C2), as has been mentioned above in Methods.

When analyzing results obtained for the remaining cations, no great disparities were observed between both methods. Amounts of calcium obtained from ME extracts were higher than for the paste method (MP), which showed amounts of dissolved calcium compounds to increase along with the volume of the extractant applied (Table 2). The situation was different in the lower layers of the Jeziory profiles, where Ca levels were somewhat higher for the paste (Fig. 2). The clayey character of those samples may trigger a different mode of calcium release and give the paste extracts (MP) a higher calcium content, while in the case of the ME extracts, greater amounts of water only dilute the extracts.

Similar processes have shaped magnesium levels (Fig. 3), and the ratios ME:MP obtained by the two methods are lower (1.3 to 1.7), as compared to ratios established for calcium, with the exception of soils from the two lower soil horizons in the Jeziory profile (Table 2), where Mg content in the paste (MP) exceeded that assayed in the ME extract.

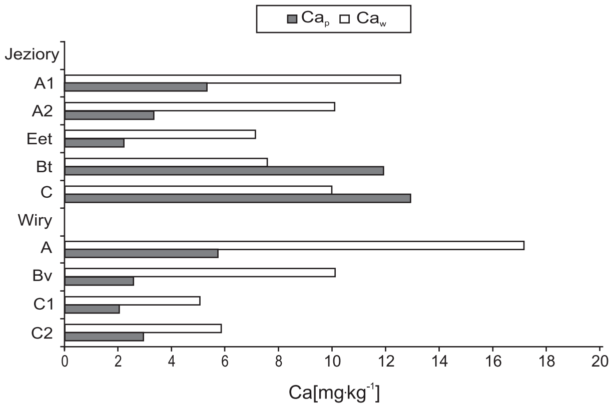

Fig. 2. Comparison of calcium contents determined by the two methods (Ca$_w$ – extraction method, Ca$_p$ – saturated paste method).

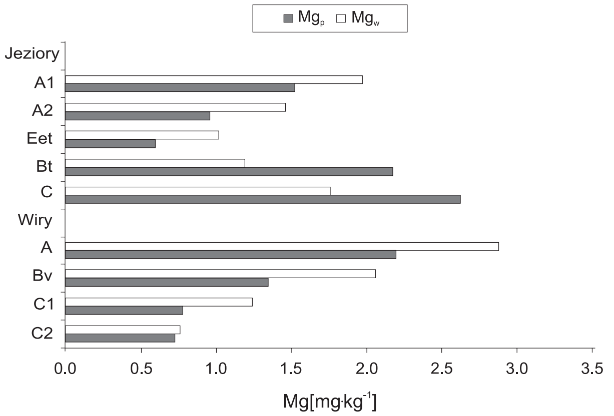

Fig. 3. Comparison of magnesium contents determined by the two methods (Mg$_w$ – extraction method, Mg$_p$ – saturated paste method).

Table 2. Ratio of the concentration determined by the two methods: X$_w$ – the extraction method (ME), X$_p$ – the saturated paste method (MP).

Profile/ Site	Horizon	Depth [cm]	Ca$_w$/Ca$_p$	Mg$_w$/Mg$_p$	K$_w$/K$_p$	Na$_w$/Na$_p$	Al$_w$/Al$_p$	SO$_{4w}$/SO$_{4p}$	Cl$_w$/Cl$_p$	NO$_{3w}$/NO$_{3p}$	F$_w$/F$_p$
Jeziory	A1	0-5	2.4	1.3	1.4	5.9	3.9	2.2	2.1	1.5	36.4
	A2	5-10	3.0	1.5	1.3	1.7	3.5	0.9	1.7	2.9	15.6
	Eet	10-60	3.2	1.7	3.2	2.4	14.9	1.6	2.2	1.0	0.5
	Bt	60-100	0.6	0.5	1.1	0.8	8.5	0.5	0.4	1.5	0.5
	C	100-120	0.8	0.7	1.5	1.3	2.6	1.0	0.8	1.6	1.1
Wiry	A	0-6	3.0	1.3	1.7	2.9	1.7	1.1	1.3	2.1	1.3
	Bv	6-20	3.9	1.5	1.8	2.0	3.4	1.1	1.4	2.4	0.9
	C1	20-50	2.5	1.6	1.5	2.1	1.5	1.8	1.2	3.1	1.5
	C2	50-100	2.0	1.0	2.3	0.9	0.7	1.2	1.3	2.7	1.2

For potassium (Fig. 4) it was found that in all cases, K contents in the ME extracts were higher than in the paste method (MP). Most often, differences were slight, i.e., in horizon Bt of the Jeziory profile, K contents amounted to 1.82 and 1.72 $mg\cdot kg^{-1}$, respectively.

When comparing differences in the sodium levels (Fig. 5), significant differences were found between upper horizons of the two profiles. This could be related to the dissolution of readily soluble sodium salts accumulated in those horizons. Furthermore, the highest ratios were found for horizons Eet, which implies an easier dissolution and next release of cations from this horizon when applying the extraction method (ME).

The Ca/Al molar ratio (or basic cations/Al ratio) is often used as an acidification indicator in forest ecosystem analysis [22, 23]. It should be noted that, because of the wide discrepancies between the two methods (especially in aluminium content), there will also be differences in the values of the toxicity coefficient. For instance, for the Eet horizon in the Jeziory profile, this coefficient equals 0.59 for the extraction method (ME), and 2.73 for the saturated paste method (MP). Thus, the ME-derived coefficient (<1) indicates conditions inhibiting the growth of the root system, while the MP-derived shows no threat because the concentration of calcium exceeds that of aluminium almost three times. Moreover, one should keep in mind that Al toxicity is low when it forms complexes with fluoride and sulphate ions [24], while the toxicity of AlF and $AlSO_4$ complexes is none, or low. Only free Al^{3+} forms provide a basis for determining the toxicity of the soil solution. Great caution seems advisable when calculating the toxicity coefficient; rather, it is recommended to use suitable mathematical models, e.g. ALCHEM.

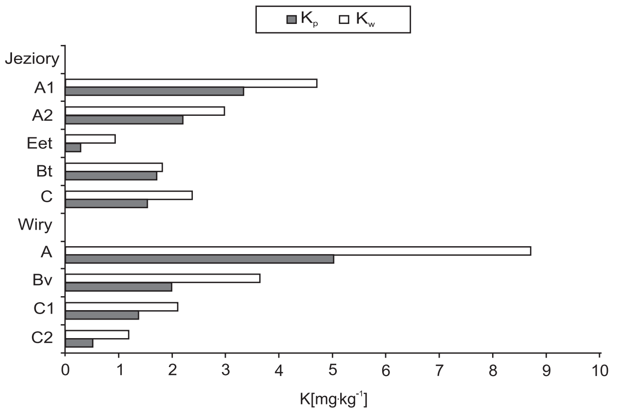

Fig. 4. Comparison of potassium contents determined by the two methods (K_w – extraction method, K_p – saturated paste method).

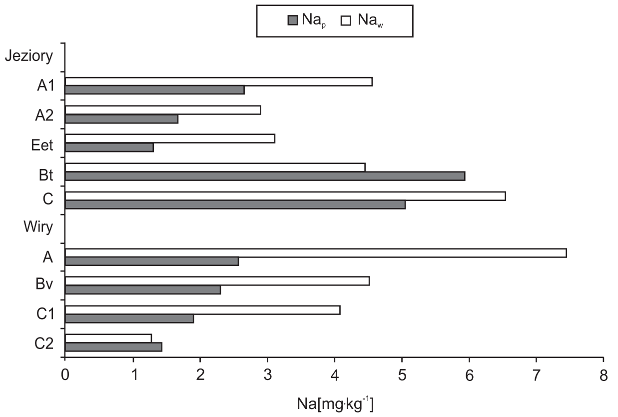

Fig. 5. Comparison of sodium contents determined by the two methods (Na_w – extraction method, Na_p – saturated paste method).

The contents of nitrates tended to decline with depth and were higher when the extraction method (ME) was applied (Fig. 6). The differences in their levels between the two methods were greater for the Wiry profile (ratio 2.1-3.1) than for Jeziory, where only in the case of horizon A2 was the content obtained by the ME method almost triple that obtained by MP.

The contribution of sulphates to forest floors is primarily of anthropogenic origin, in the form of deposition with precipitation. It is quite substantial in the study area and can reach 2,120 $mg\cdot m^{-2}\cdot year^{-1}$ [25]. A significant role in sulphate retention is played by reactions of surface adsorption, hence an important parameter is the specific surface area of the soil. Due to their adsorption properties, sulphates are retained in the soil and migrate rather slowly. That is why differences in the contents of sulphates (Fig. 7), especially in the Wiry profile, were not great and the values yielded by the two methods are rather similar. In the case of the Jeziory profile there is a sudden jump in sulphate levels for the lithologically different horizons Bt and C. Such a drastic rise occurring in both methods seems to indicate a release of sulphates adsorbed on the surface of clay minerals. Another crucial factor is that as pH declines, the adsorption of sulphate ions tends to grow [26], thus ameliorating the effect of the increased immission. Continued high inputs of H^+ and SO_4^{2-} from atmospheric deposition coupled with a slow rate of alkaline cation supply from weathering have resulted in highly acidic soil water and the mobilization

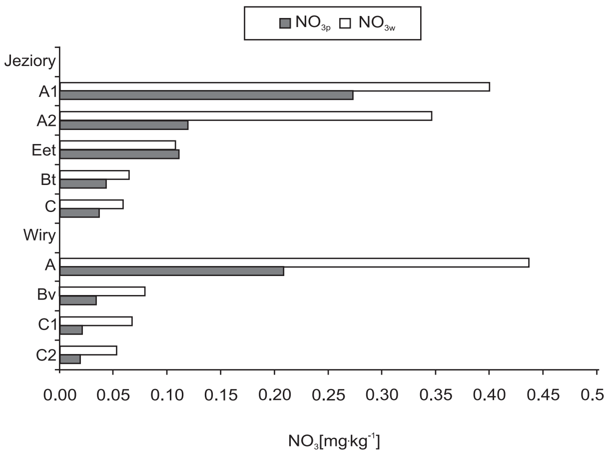

Fig. 6. Comparison of nitrate contents determined by the two methods (NO_{3w} – extraction method, NO_{3p} – saturated paste method).

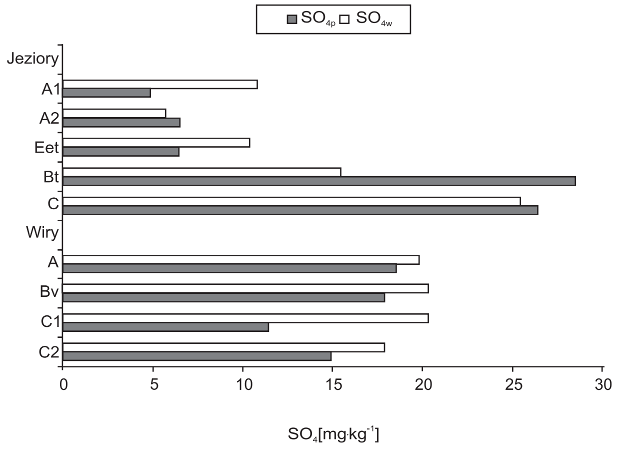

Fig. 7. Comparison of sulphate contents determined by the two methods (SO_{4w} – extraction method, SO_{4p} – saturated paste method).

of available soil aluminium. Studies of soils exposed to considerable deposition of acids showed sulphates to be the principal anions accompanying dissolved inorganic Al [19, 27].

The pattern of variability of chloride concentrations is presented in Fig. 8. In the Wiry profile, the differences in their content determined by the two methods decreased with depth (Table 2). For the Jeziory profile, however, a sudden jump connected with the granulometric composition could be observed – the concentration in solutions from the paste (MP) exceeded that obtained from extracts (ME).

The variability in the levels of calcium and magnesium cations (partly also sodium) for the Jeziory profile was similar to that of chloride and sulphate anions. There was a marked rise for horizons Bt and C (60-120 cm) corresponding to a lithological change and an increase in the saturation of the sorptive complex with alkaline cations (Table 1).

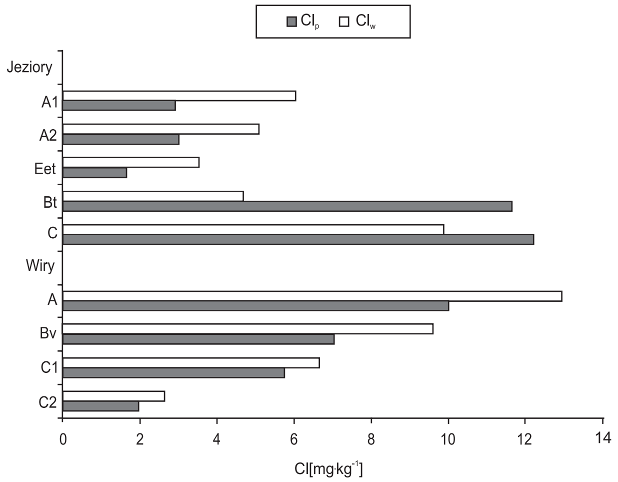

Fig. 8. Comparison of chloride contents determined by the two methods (Cl_w – extraction method, Cl_p – saturated paste method).

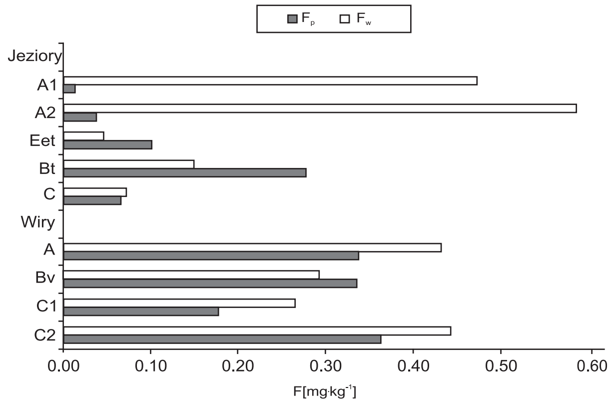

Fig. 9. Comparison of fluoride contents determined by the two methods (F_w – extraction method, F_p – saturated paste method).

Fluorides are a typical pollutant occurring in the study area. Although F^- is a secondary component of anions in soil water, it has a significant impact on the presence of dissolved forms of aluminium even at very low concentrations, especially in an acid environment [29-31]. For soil extracts from the Wiry profile, the fluoride content hardly varies with method and depth, and stays at a level of 0.2-0.4 mg·kg^{-1} (Fig. 9). In the Jeziory profile, in turn, fluoride content in the upper soil horizons (A1, A2) as determined by the extraction method (ME) greatly exceeded those in the lower horizons and are several times higher than those obtained from paste (MP). Fluorides are probably released from humus with increasing amounts of the extractant.

Conclusions

- The application of the two extract-recovering methods (MP and ME) revealed that the contents of elements of soil extracts, whether expressed in mg·dm^{-3} or converted into kg dry mass, differed significantly.
- Differences resulted not only from the volume of the extractant used, but also from the granulometric (mineralogical) composition of the soil samples.
- Differences were especially wide in the case of aluminium contents. This disabled the calculation and assessment of its toxicity on the basis of the Ca/Al ratios.

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