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REGULAR ARTICLE

Rock-type control of Ni, Cr, and Co phytoavailability in ultramafic soils

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Abstract

Background and aims Ultramafic soils constitute an extreme environment for plants because of specific physico-chemical properties and the presence of Ni, Cr, and Co. We hypothesized that type of ultramafic parent rock depending on their origin affects the composition of soils and plants. Therefore, phytoavailability of metals would be higher in soil derived from serpentinized peridotite compared to serpentinite because of differences in susceptibility of minerals to weathering.

Results Based on DTPA-$CaCl_2$ extractions, we noted that soil derived from the serpentinized peridotite is characterized by a higher phytoavailability of Ni compared to soil derived from the serpentinite. On the contrary, plant species growing on soil derived from the serpentinite contain higher concentrations of metals.

Conclusions Our study suggests that the metal uptake by plants is controlled by the mineral composition of parent rocks, which results from both their original magmatic composition and later metamorphic processes. Chemical extractions show that the phytoavailability of Ni and Co is higher in soil derived from the serpentinized peridotite than the serpentinite. Surprisingly, plants growing on the soil derived from the serpentinite contain higher levels of metals compared to these from the serpentinized peridotite derived soil. This contrasting behavior is due to higher abundances of Ca and Mg, not only Ni and Co, in soil derived from the serpentinized peridotite as compared to those in the soil derived from the serpentinite. Calcium and Mg are favored by plants and preferably fill the available sites, resulting in low Ni and Co intake despite their higher abundances.

Keywords Peridotite · Serpentinite · Excluders · Ni isotopes · Ca/mg ratio

Abbreviations

Mdn_A	Median of aboveground parts
Mdn_U	Median of underground parts
α	Significance level

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p	Probability level
r	Effect size for U-Mann Whitney test
r_s	Rank Spearman correlation coefficient
TF	Translocation factor

Introduction

Ultramafic soils refer to specific soils derived from weathering of peridotites and/or serpentinites. Peridotite is an igneous rock composed mostly of olivine, whereas serpentinite is formed during serpentinization and consists of hydrous silicates, e.g. serpentine (Coleman and Jove 1992). Other minerals such as magnetite are minor in both above mentioned rocks. Ultramafic soils are characterized by several specific traits: (a) low Ca/Mg ratio; (b) deficiency of nutrients such as: N, P and K and (c) high contents of Ni, Cr, and Co (Whittaker 1954; Kruckeberg 2004; O'Dell and Claassen 2006; Kazakou et al. 2008; Oze et al. 2008). All these characteristics cause ultramafic soils to be low productivity soils. The response of vegetation to such stressful conditions was named "serpentine syndrome" by Jenny in 1980 (after Kruckeberg 2004).

One of the major challenges for plants growing on ultramafic soils is the high content of Mg at deficiency levels of Ca (Proctor 1970). Based on experiments with *Agrostis* genus the author proved that Mg can be toxic for plants (i.e. reduction in root growth). However, species growing on ultramafic soils are characterized by greater tolerance to high contents of Mg in soils compared with species from non-ultramafic soils. The previous research indicates that adaptation of plants for low Ca/Mg status of ultramafic soils is associated with several mechanisms: (a) selectivity, (b) tolerance to low content of Ca and high content of Mg and (c) luxury consumption of Mg (reviewed in Kazakou et al. 2008). Studies with *Arctostaphylos viscida* showed that selectivity in species from ultramafic soils lies in higher ability to translocation of Ca than Mg from roots to aboveground parts compared with non-ultramafic species (O'Dell et al. 2006). Furthermore, tolerance to deficiency of Ca and excess of Mg was observed in *Agrostis stolonifera* (Marrs and Proctor 1976). The latter mechanism, called luxury consumption, involves uptake and storage of Mg for later use (i.e. *Helianthus bolanderi ssp. exilis*; Madhok and Walker 1969). The first two mechanisms are likely not independent from each other (Kazakou et al. 2008). An example of plant adaptation from ultramafic areas to low content of Ca and high content of Mg is *Achillea millefolium*. O'Dell and Claassen (2006) collected seeds of this species from two various substrates (ultramafic soils, granites) and from a commercial source. Seeds were sown in pots with ultramafic soils. The accession of *Achillea millefolium* from granites and commercial source had necrosis in the root system when exposed to high Mg and low Ca contents of ultramafic soils. The accession from ultramafic areas had healthy roots.

Another factor causing serpentine syndrome is the low content of N, P, and K. Nagy and Proctor (1997) pointed out that plant growth in ultramafic areas at Meikle Kilrannoch (Scotland) is limited rather by the low content of P than N or K without affecting the phytoavailability of Ni and Mg. On the other hand, O'Dell et al. (2006) showed that vegetation in California (USA) is limited rather by N than by P. Moreover, in the study of *Achillea millefolium,* it was demonstrated that adverse conditions of ultramafic soils can be ameliorated by adding compost, and before compost decomposition, by fertilizer containing N, P, and K (O'Dell and Claassen 2006).

The growth of plants in ultramafic areas is also controlled by metal phytoavailability (Ni, Cr, Co, Mn). Nickel is the metal that is the most studied in plants because of its relatively higher phytoavailability compared to Cr and Co. Nickel is required in relatively low quantities in plants i.e. for urea metabolism (Uren 1992; Yusuf et al. 2011). However, elevated contents of Ni (> 10 mg kg^{-1}) can cause nutrient imbalance, disruption of cell membrane functions, chlorosis, and necrosis (Yadav 2010; Yusuf et al. 2011). Plants colonizing ultramafic soils or other metalliferous soils display three strategies of metal transport: (a) exclusion, (b) indication and (c) accumulation (Baker 1981; Kazakou et al. 2008). To determine which strategy is used by a plant species, translocation factor (TF, see below) is helpful. The TF indicates the ability to translocate metals from roots to aboveground parts. Currently, research aiming plant communities in ultramafic areas are focused mostly on Ni-hyperaccumulators referred as species with Ni content of at least 1000 mg kg^{-1} in the dry matter of leaves i.e. *Pycnandra acuminata* (Reeves 1992; Reeves and Baker 2000; Reeves et al. 2007a; Van der Ent et al. 2013a; Gałuszka et al. 2015; Van der Ent et al. 2015). Furthermore, some Ni-hyperaccumulators give opportunity in phytomining operations because of high content of Ni and relatively high biomass (Nkrumah et al. 2016). The process involves cultivation of Ni-hyperaccumulators in large ultramafic massifs or contaminated areas. Afterwards, plants are harvested, combusted, thus giving "bio-ore", and Ni is recovered as Ni salts or metallic Ni. Chaney et al. (2007) suggested that costs of phytomining are similar to the costs of food crops production, thus it gives economic opportunities for developing countries (i.e. Indonesia, Van der Ent et al. 2013b).

Very recently, several studies dealing with Ni isotopes composition of ultramafic rocks, soils derived from them and plants have been published (Ratié et al. 2015; Estrade et al. 2015; Ratié et al. 2016). The range of δ^{60}Ni in ultramafic soils in Brazil (Barro Alto and Niquelândia) is from – 0.30 to 0.11 ‰ and in Albania (Qaftë Shtamë, Gjegjan, Prrenjas, Pojskë) from – 0.33 to 0.38 ‰ (Estrade et al. 2015; Ratié et al. 2016). Soils derived from ultramafic rocks are depleted in heavier Ni isotopes compared to the parent rock (Δ^{60}Ni$_{\text{soil-rock}}$ was - 0.47 ‰ in Ratié et al. 2015 and Δ^{60}Ni$_{\text{soil-rock}}$ was up to – 0.63 ‰ in Estrade et al. 2015). Authors suggested that secondary minerals (clay minerals and Fe-oxides) were responsible for the depletion in heavier isotopes. Fractionation of Ni in soils containing Fe-oxides as a main secondary mineral was higher (Δ^{60}Ni $_{\text{soil-rock}}$ was - 0.60 ‰) than in soils containing smectite as a main secondary mineral (Δ^{60}Ni $_{\text{soil-rock}}$ was - 0.20 ‰; Estrade et al. 2015). This was supported by isotope analysis of both exchangeable and phytoavailable pools that show heavier Ni signature than the solid. Nickel contained in whole plants growing in Albanian ultramafic area was isotopically heavier than that in the soil (Δ^{60}Ni $_{\text{wholeplant-soil}}$ up to 0.40%; Estrade et al. 2015). Furthermore, non-hyperaccumulators translocated light Ni isotopes from roots to leaves (Δ^{60}Ni $_{\text{leaves-roots}}$ up to - 0.60 ‰). In the case of hyperaccumulators, fractionation was observed only during early growth stage (Estrade et al. 2015). In other studies, Deng et al. (2014) cultivated the Ni - hyperaccumulator (*Alyssum murale*), the Ni, Zn - hyperaccumulator (*Noccaea caerulescens*) and a non - accumulator (*Noccaea arvense*) in hydroponic culture with low and high concentrations of metals in order to determine fractionation during accumulation. The isotopically light Ni was generally taken up by plants due to low-affinity transport system in cell membrane. However, the magnitude of fractionation was higher in hyperaccumulators (Δ^{60}Ni $_{\text{plant-solution}}$ from - 0.63 ‰ to - 0.90 ‰) than non-hyperaccumulators (Δ^{60}Ni $_{\text{plant-solution}}$ was - 0.21 ‰) growing in hydroponic culture.

The aim of the present paper is to determine how different types of parent ultramafic rocks, which results from their metamorphic transformations, affect the metal phytoavailability and the metal content in plants under temperate climate. To achieve this objective, we compared results of the DTPA-CaCl$_2$ extraction with Ni isotopes of parent rocks and soils. Furthermore, we analyzed chemical composition of plants.

Materials and methods

Outline of climate, soils, and vegetation in lower Silesia

The climate of Lower Silesia belongs to temperate climates with the characteristics of a oceanic and continental climate (Głowicki et al. 2005 and references therein). Occasionally, the arctic and tropical air arrives to the studied area. Lower Silesia is characterized by a wide range of altitudes (from 70 m a. s. l. to 1603 m a. s. l.) with high diversified topography thus meteorological elements change rapidly in a small space. Long-term temperature and rainfall are not known precisely for study areas because of lack of the meteorological stations.

Distribution of soil cover in Lower Silesia is strongly influenced by variability of geological bedrock. Moreover, the whole region was overprinted in the Pleistocene with glacial sediments, therefore loess material, tills, and glaciofluvial sands significantly control soil evolution and classification (Kabała et al. 2015). Approximately 35% of the total region area is represented by Luvisols/Planosols derived from (1) aeolian silt or (2) stratified materials, layer of sand over loam (Musztyfaga and Kabała 2015; Kabała et al. 2015). Cambisols cover approximately 18% of Lower Silesia, Fluvisols/Fluvic Cambisols near 13%, Brunic Arenosols contribute with around 12%, whereas Chernozems, Mollic Gleysols, and Gleyic Pheozems cover 8% (Łabaz and Kabała 2014; Kabała et al. 2015). Podzols are less widespread (4%), their presence is limited to mountain regions (Waroszewski et al. 2016) and large sand plains. Overall, soils derived from ultramafic rocks in Poland are classified as Leptosols and Cambisols (Weber 1980). Parent rocks are represented by serpentinites with different stages of metamorphism. Ultramafic soils in Poland are generally shallow (up to 50 cm) with high amounts of rock fragments, which increase downwards the profiles. Kierczak et al. (2007) showed that Ni is less mobile in Polish ultramafic soils compared to other soils in Europe because climate in Poland represents colder and dryer variety of a temperate climate. Furthermore, in

Polish soils, olivine is still observed even in surface horizons due to specific climate conditions and previous hydrothermal alteration of parent rocks.

Lower Silesia is characterized by highly diversified vegetation. The flora contains 1890 species which represent 76% of the whole Polish flora (Kącki et al. 2005 and references therein). Almost 34% of plants in Lower Silesia are threatened or rare. Postglacial characteristics of the flora and low isolation of the region are responsible for a small number of endemites emphasizing uniqueness of vegetation. The endemites mostly grow in mountainous part of Lower Silesia, i.e. *Pedicularis sudetica*. Plant communities are represented by forests both in mountains and in lowlands (i.e. *Tilio platyphhyllis-Acerion pseudoplatani*). Furthermore, meadow communities (i.e. *Calthion palustris*) are refuge for rare and protected species. Xerothermic, psammophilous and on the rock grasslands (i.e. *Festucetalia valesiacae*) occupy small areas (Kącki et al. 2005 and references therein). Moreover, 13 species in Lower Silesia are protected according to habitat directive of the European Union. One of the species listed in the habitat directive (*Asplenium adulterinum*) grows only in gaps of ultramafic rocks cropping out i.e. on Żmijowiec (Pędziwiatr 2015). The chemical composition of plants occurring in ultramafic areas in Poland was the subject of several studies (Brej and Fabiszewski 2006; Kasowska 2007; Żołnierz 2007; Samecka-Cymerman et al. 2008; Kubicka et al. 2015). The metallophytic flora is represented by *Asplenium onopteris* var. *silesiaca* and *Noccaea caerulescens* (Brej and Fabiszewski 2006). The highest content of Ni was found in *Noccaea caerulescens* from Mikołajów (3100 mg kg^{-1}) while metal contents in other species were much lower. For example, the Ni, Cr, and Co contents in *Asplenium onopteris* var. *silesiaca* were 101 mg kg^{-1}, 61 mg kg^{-1}, and 21 mg kg^{-1} respectively; Brej and Fabiszewski 2006).

Study area and soil characteristics

Studied materials (parent rocks, soils, and plants) were collected from two ultramafic sites previously described by Kierczak et al. (2016). We chose the Szklary Massif (site 1) and Jordanów (site 2) located in Lower Silesia (southwestern Poland; Fig. 1) because of the same position in the geomorphological sequence but differing in terms of parent rocks.

The Szklary Massif is located in the Fore Sudetic Block (Fig. 1). Soil from this locality is derived from partially serpentinized peridotite under lower range of greenschist facies (serpentine group minerals; olivine; amphibole; magnetite, Cr-magnetite, chlorite and orthopyroxene) and there is classified as Eutric Leptosol (Humic, Magnesic; Fig. 2; Gunia 2000; Kierczak et al. 2016). From a mineralogical point of view, soil contains (a) minerals inherited from parent rock or derived from weathering (serpentine, olivine, chlorite, talc) and (b) quartz as an allogenic mineral. Clay minerals are represented by smectite.

Jordanów (site 2) is located also in the Fore Sudetic Block (Fig. 1). The parent rock is represented by serpentinite (>90 vol.% of serpentine group minerals; Kierczak et al. 2016). Soil from site 2 correspond to Eutric Skeletic Cambisol (Loamic), Fig. 2, with serpentine and quartz in mineral composition. Swelling phases are represented by smectite similarly to site 1. Details of chemical composition of parent rocks and soils are presented in Table 1. In both studied sites, the SiO_2 contents increase upward the profile (up to 58% in ABw horizon in site 2), whereas MgO contents increase downwards the profiles (up to 27% in BwC horizon in site 2). The highest contents of Ni are noted in site 1 in ABw horizon (2341 mg kg^{-1}), whereas Cr contents in surface horizon (3503 mg kg^{-1}). In site 2, the highest contents of Ni and Cr are noted in horizon above parent rock. The Co contents do not exceed 170 mg kg^{-1} in both sites.

Plant sampling and analysis

Plants from 56 species belonging to 22 families have been collected. Names of species are given after Flora Europaea (Tutin et al. 1968; Tutin et al. 1972; Tutin et al. 1976; Tutin et al. 1980; Tutin et al. 1993) and phytosociological affiliation is based on Mucina (1997). At least three specimens of single species of plants were collected in order to obtain an averaged sample and sufficient biomass for analysis. Plants were collected randomly in the distance of several meters from the soil profiles during efflorescence in 2014 and 2015. Underground and aboveground parts of plants were analyzed separately. Firstly, samples were rinsed in fresh water and next washed in distilled water avoiding contamination by soil and dust particles. Subsequently, samples were air dried and milled. Aliquot of the sample (1 g) was digested in concentrated HNO_3

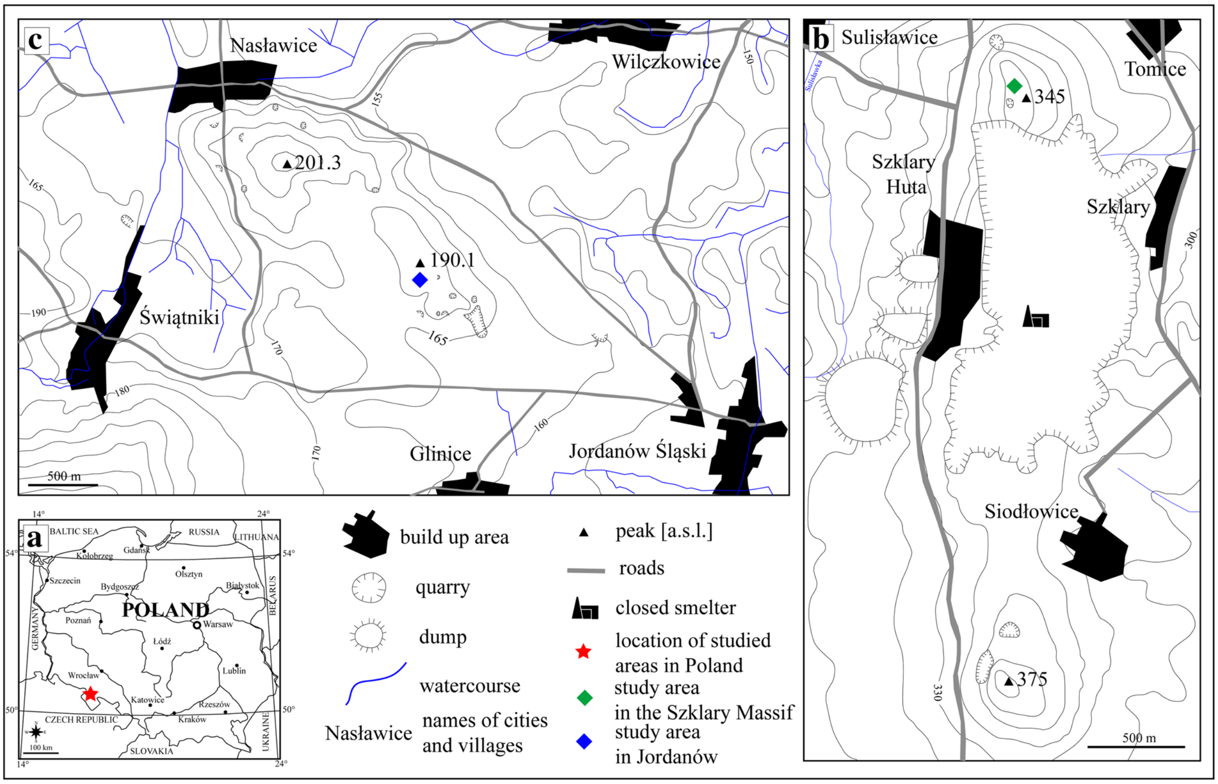


Fig. 1 Sketch maps of studied area: (**a**) location in Poland, (**b**) location of soil profile in the Szklary Massif (site 1, simplified after Badura and Dziemiańczuk 1981), (c) location of soil profile in Jordanów (site 2, simplified after Trepka and Mierzejewski 1957)

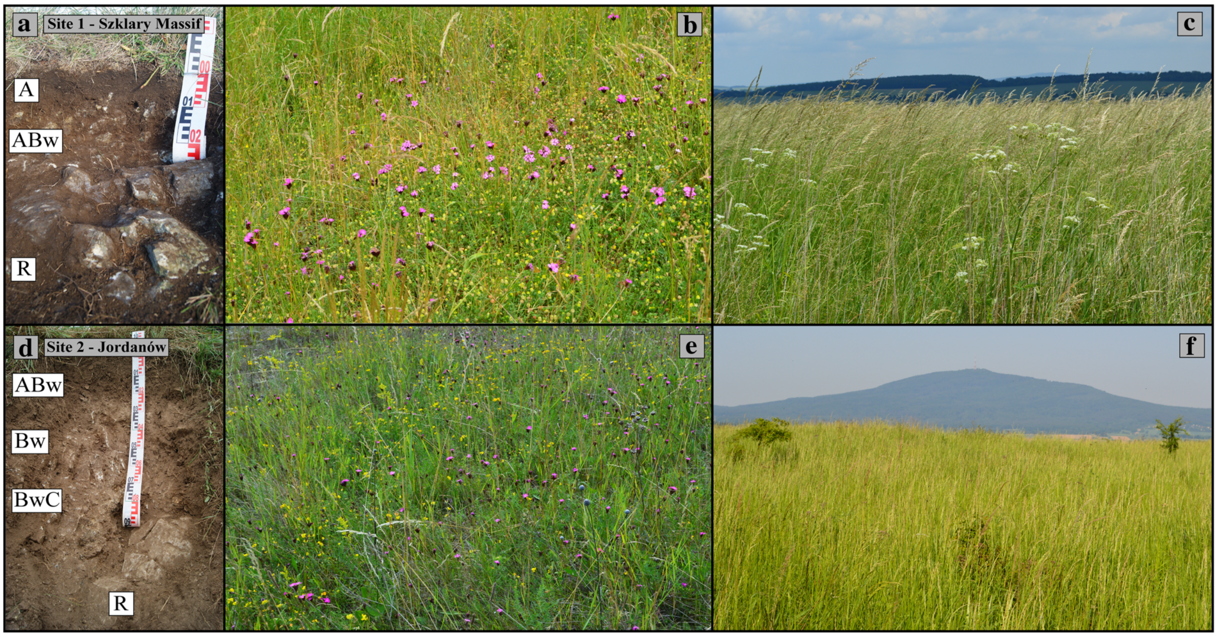


Fig. 2 Studied areas: (**a-c**) the Szklary Massif (site 1): (a) soil profile, (b) xerothermic grassland, (c) expansion of *Calamagrostis epigejos* and *Arrhenatherum elatius*; (**d-f**) Jordanów (site 2): (d) soil profile, (e) xerothermic grassland, (f) expansion of *Calamagrostis epigejos* and *Arrhenatherum elatius*

Table 1 Basic physicochemical composition of soils and rocks from the Szklary Massif (site 1) and Jordanów (site 2; after Kierczak et al. 2016)

Horizon	Depth	pH		CEC	Exchangeable cations		C_{org}	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Ni	Cr	Co	Mn
					Mg	Ca										
	[cm]	H_2O	KCl	[cmol(+) kg^{-1}]			[wt%]	[wt%]					[mg kg^{-1}]			
Site 1: Szklary Massif (N 50°39′09.1″ E 16°49′49.9″; 342 m a. s. l.)																
A	0–8	7.0	5.9	60.6	36.8	20.8	4.4	48.4	4.6	10.5	14.0	1.4	2117	3503	164	1781
ABw	8–20	7.2	6.4	77.7	59.9	16.0	2.2	42.0	4.1	11.4	21.6	0.7	2341	2915	155	1394
R	>20	–	–	–	–	–	–	42.5	3.1	8.4	31.1	0.3	2232	2730	98	620
Site 2: Jordanów (N 50°52′19.1″ E 16°49′55.3″; 182 m a .s. l)																
ABw	0–20	6.3	5.5	14.6	5.3	6.3	2.18	58.3	3.7	7.2	15.8	0.5	817	2251	83	774
Bw	20–40	6.7	5.7	16.4	8.7	5.7	0.7	55.8	3.8	7.7	19.3	0.3	1567	2005	113	542
BwC	40–110	6.8	5.7	17.7	9.1	7.0	0.4	43.3	3.1	9.4	26.8	0.1	3944	2751	168	620
R	>110	–	–	–	–	–	–	44.1	0.7	8.2	33.8	0.02	1577	2196	99	465

and then in aqua regia. Plants were analyzed by means of ICP-MS PerkinElmer NexION300 in Bureau Veritas Mineral Laboratories (Canada).

Chemical extraction

The DTPA-$CaCl_2$ extraction was applied in assessment of phytoavailability of Ni, as it was used extensively for estimating the worst scenario of phytoavailable pool of metals (Lombini et al. 1998; Echevarria et al. 2006). The extraction was made in 0.005 DTPA and 0.01 M $CaCl_2$ solution at pH = 5.3 in 1: 5 soil or pulverized rock to solution ratio (Quantin et al. 2008). The mixture was shaken for 2 h. Afterwards, suspension was centrifuged and filtered by 0.45 μm syringe filters (cellulose acetate membrane, VWR International®). All samples were prepared in duplicates with reagent blank samples. Nickel concentrations were measured by Flame Atomic Absorption Spectroscopy – VARIAN AA240FS at GEOPS laboratory. Phytoavailability of Ni extracted with the DTPA-$CaCl_2$ solution was calculated as phytoavailable fraction relative to total content in soil or parent rock.

Isotope analysis

Preparation of samples for Ni isotope analyses consisted in digestion of rocks and soils followed by purification using two types of resins. Approximately 100 mg of crushed and homogenized sample was transferred to Teflon® beakers and digested with 5 mL of concentrated HF and 1.5 mL $HClO_4$. After digestion, solutions were evaporated to dryness. In the next step mixture of concentrated HCl (3.75 mL) and HNO_3 (1.25 mL) was added to residuum and evaporated. Afterwards, samples were treated with 3 mL of HNO_3 and evaporated. This step was repeated. The residuum was taken with 2 mL of HNO_3 and transferred to volumetric flasks and diluted with Mili-Q® water to 50 mL.

The chemical separation of Ni was performed according to protocol adopted by Gueguen et al. (2013). The aliquot of solutions (digested rocks and soils) and the DTPA-$CaCl_2$ leachates were evaporated to dryness and conditioned in 6 M HCl. The Ni chemical purification of samples was based on a two-step chromatography separation. A first set ion-exchange chromatography columns was filled with 2 mL (wet volume) of anionic resin AG1-X8 in 6 M HCl (BioRad® 100–200 mesh). This resin retained Fe, Zn, and a high amount of Co and Cu (Moynier et al. 2007), while Ni remained in solution. Before the second chromatography column, a Ni double spike was added to the samples with a spike/natural ratio of 1 (Gueguen et al. 2013). The second set of ion-exchange chromatography columns use a specific Ni-resin (O.5 mL, wet volume) composed of polymethacrylate containing a dimethylglyoxime (DMG) molecule that retained Ni onto the resin as an insoluble Ni-DMG complex at pH 8–9, while the other elements were removed in solution. The eluted Ni solution was evaporated and taken up in 0.28 M HNO_3 for measurement. Ni purification was performed at GEOPS laboratory and the Ni isotope ratios were measured with a Neptune (Thermo-electron) MC-ICP-MS at the Pôle Spectrométrie Océan (PSO), of IFREMER (Centre de Brest, France). The samples and standards were introduced via an ApexQ (50–75 V per μg/mL). A single "run" consisted of one block of 40 measurements. During the measurement, the Ni concentration (spike + natural) in the sample is 400 μg/L. The double spike is a mixture of ^{61}Ni and ^{62}Ni with a ratio of 1.1004. Application of a three-dimensional data reduction procedure was used to determine the true isotope ratios of the samples (Siebert et al. 2001). In addition, each sample analysis was bracketed by the measurements of the spiked standard Ni NIST SRM 986 solutions at the same concentration and same spike/standard ratio as the samples. The ratios of δ^{60}Ni were expressed in per mil and normalized with the average value of the bracketing standard SRM-986 (Eq. 1; Gramlich et al. 1989).

$$\delta^{60}Ni = \left(\frac{\left(\frac{^{60}Ni}{^{58}Ni}\right)_{sple}}{\left(\frac{^{60}Ni}{^{58}Ni}\right)_{std}} - 1 \right) \times 1000 \qquad (1)$$

The long-term analytical reproducibility (2SD) of the standard Ni NIST SRM 986 was typically comprised between 0.03 and 0.05 ‰.

The magnitude of fractionation between soils and rocks is estimated as $\Delta^{60}\mathrm{Ni}_{\mathrm{soil\text{-}rock}} = \delta^{60}\mathrm{Ni}_{\mathrm{soil}} - \delta^{60}\mathrm{Ni}_{\mathrm{rock}}$ and between phytoavailable fraction (DTPA-$CaCl_2$) and soils is estimated based on $\Delta^{60}\mathrm{Ni}_{\mathrm{DTPA/CaCl2\text{-}soil}} = \delta_{60}\mathrm{Ni}_{\mathrm{DTPA\text{-}CaCl2}} - \delta^{60}\mathrm{Ni}_{\mathrm{soil}}$.

Translocation factor

The Translocation Factor (TF) is a widely used parameter showing ability to transferring metals from roots to aboveground parts of plants. The TF was calculated using equation (Eq. 2) given below:

$$\mathrm{TF} = \mathrm{C}_{\mathrm{shoot}}/\mathrm{C}_{\mathrm{root}} \qquad (2)$$

where C_{shoot} and C_{root} is content of metals (mg kg^{-1}) in aboveground and underground parts respectively.

Quality control and statistical analysis

The analytical reproducibility (2σ/2SD), as estimated from replicate analyses of composite samples *Euphorbia cyparissias* (aboveground part), *Hieracium pilosella* (aboveground part), *Dianthus caarthusianorum* (underground part), *Achillea pannonica* (underground part), *Helianthemum nummularium* (underground part) and *Lepidium campestre* (underground part) ranges from 0% (Ca) to 20% (Cr) at 95% confidence limits. Analytical accuracy (2σ), as estimated from 6 measurements of standard CDV-1 is from 0.2% (Ca) to 5% (Ni) at 95% confidence limits. Furthermore, analytical accuracy (2σ), as estimated from 7 measurements of standard V16 is from 1.4% (Cr) to 6.7% (Ca).

We compare chemical composition of plant populations from the serpentinized peridotite (site 1) and from the serpentinite (site 2) using the U-Mann Whitney test and the Cochran-Cox test. The normality of results was verified by the Kolmogorov – Smirnov test with Lillefors correction and homogeneity of variance by the Levene and Brown-Forsythe test. Effect size for the U-Mann Whitney test was calculated after Fritz et al. (2012). Relationships between elements in plants were analyzed by rank Spearman correlation (data with non-normal distribution) and Pearson linear correlation (data with normal distribution). Significance level (α) in this study is 0.05. For statistical analysis Statistica ver. 10. (StatSoft 2011) was applied. Results of statistical analysis are presented in supplementary materials (Online Resource 3–4) and selected results in appropriate figures.

Results

Chemical extraction

The chemical extraction of soils with the DTPA-$CaCl_2$ demonstrates that Ni is more phytoavailable in soil derived from the serpentinized peridotite (site 1) compared with soil derived from the serpentinite (site 2;

Fig. 3; Online Resource 1). The similarity of studied sites lies in the highest phytoavailability of Ni in surface horizons. In detail, the quantity and proportion of phytoavailable Ni in surface horizon in site is 138 mg kg^{-1} (6.5%), whereas in site 2 is 33 mg kg $^{-1}$ (4%).

Vegetation

Plant species from *Leguminosae*, *Graminae,* and *Compositae* families have been most frequently collected in site 1 (8, 6 and 5 species respectively) and in site 2 from *Compositae* and *Graminae* (6 and 5 species respectively). However, it is not whole floristic compositions because not all species are analyzed and plants were collected randomly in this study. Details of floristic composition and community structure of vegetation occurring on Polish ultramafic soils are presented in the study of Żołnierz (2007). Nevertheless, it is worth to note that according to phytosociological affiliation of plants, the largest number of collected species (10 from site 1 and 15 species from site 2) is associated with the *Festuco-Brometea* class (xerothermic grassland; Online Resource 2) and is divided in Poland in two orders: *Brometalia erecti* and *Festucetalia valesiacae* (Szczęśniak 2003). In general, xerothermic grasslands are highly insolated and rich floristically. The phytosociological affiliation of Polish

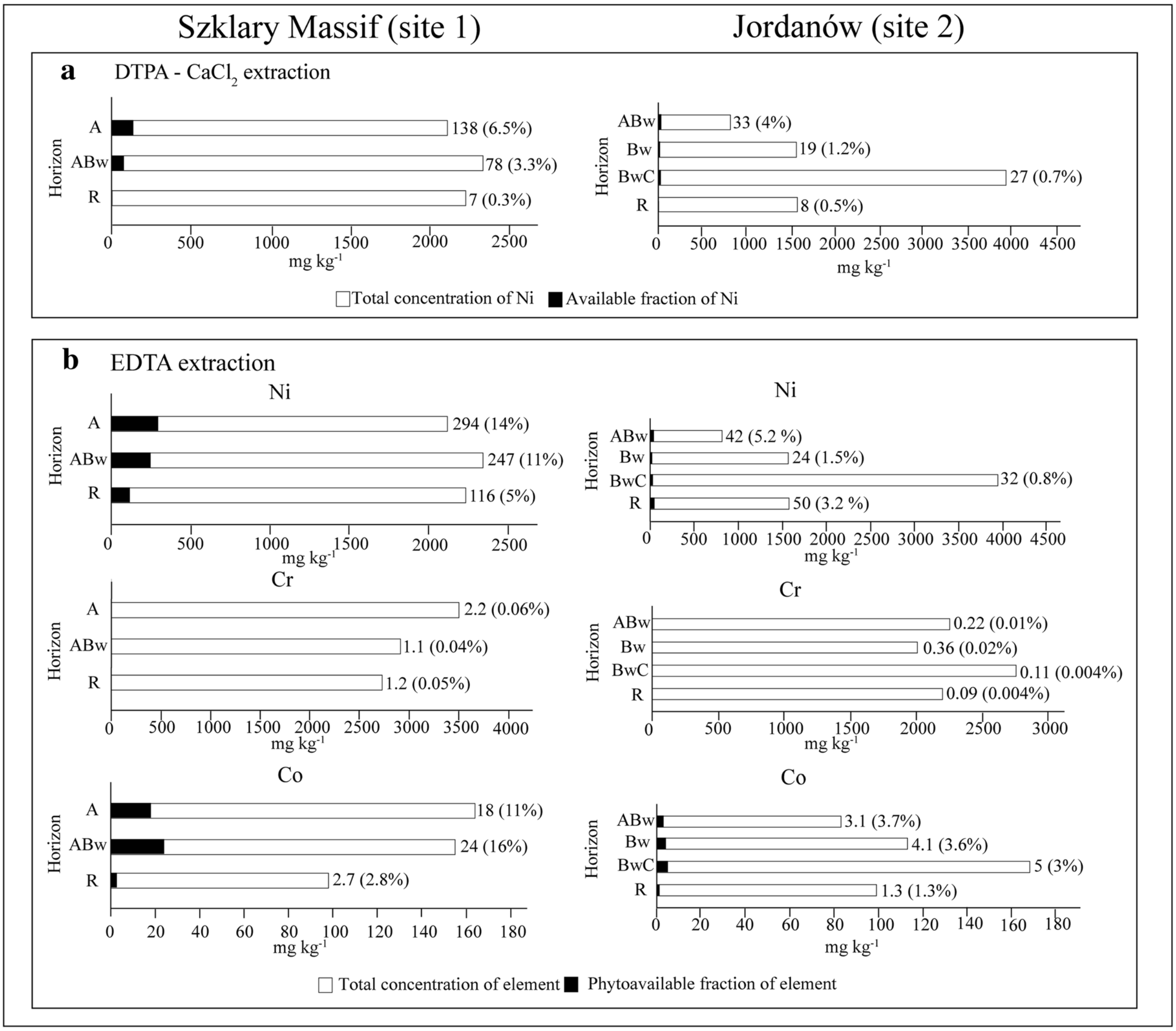


Fig. 3 Diagrams presenting phytoavailability of Ni, Cr and Co obtained from chemical extractions with (**a**) 0.005 M DTPA - 0.01 M $CaCl_2$ and (**b**) 0.05 M EDTA (the numbers in brackets show proportion of extracted elements with respect to the total contents in rock or soil)

xerothermic grasslands developed on ultramafic rocks is discussed. According to Szczęśniak (2003), xerothermic grasslands in ultramafic areas belong to *Brometalia erecti*. However, in other studies, there are classified to *Festucetalia valesiacae* (Matuszkiewicz 2012). Furthermore, we observe that two grasses (*Calamagrostis epigejos* and *Arrhenatherum elatius*) compete for space with species representing *Festuco-Brometea* class (Fig. 2). Żołnierz (2007) called areas with these grasses as degraded xerothermic grasslands. It is noteworthy that among studied plants, *Avenula pratensis*, *Achillea pannonica,* and *Salvia pratensis* are listed on the local Red List (Lower Silesia; Kącki et al. 2003).

The chemical composition of plants is presented in Tables 2 and 3. In general, most of species from both localities is characterized by Ca/Mg ratio higher than 1. For example, the highest Ca/Mg ratio in site 1 is noted in aboveground parts of *Plantago media*. However, some species maintain relatively low Ca/Mg ratio i.e. *Calamagrostis epigejos* from site 2 represents species with low Ca/Mg ratio which is 0.3. On the other hand, this plant is characterized by the highest contents of Ni, Cr, and Co in both sites. The roots of *Calamagrostis epigejos* from site 1 contain 642 mg kg^{-1} of Ni and from site 2 content of this element is two times lower. The Cr content is higher in roots of *Calamagrostis epigejos* from site 2 (165 mg kg^{-1}) compared with site 1 (97 mg kg^{-1}), whereas Co content is similar in both areas. In both localities, the Ni, Cr, and Co are absorbed in greater amounts in roots compared with aboveground parts, thus TF of almost all species is lower than 1. Nevertheless, several species translocate effectively metals from roots to aboveground parts (i.e. TF_{Co} in *Sedum maximum* from Jordanów is 1.31). Furthermore, species belonging to *Graminae* (i.e. *Avenula pratensis*, *Calamagrostis epigejos*) stand out generally by the lowest ability to metals translocation.

Ni isotopic composition

The isotopic signature (δ^{60}Ni) of the serpentinized peridotite from the Szklary Massif (site 1) is 0.13 ± 0.06 ‰ and in the serpentinite from Jordanów (site 2) is 0.20 ± 0.06 ‰ (Table 4). The soil horizons from site 1 are isotopically lighter relative to the parent material: δ^{60}Ni of uppermost horizon (A) is – 0.09 ± 0.06 ‰ and in ABw horizon 0.07 ± 0.07 ‰. The range of δ^{60}Ni values of soil from site 2 is larger, from 0.01 ± 0.06 ‰ (BwC horizon) to 0.32 ± 0.07 ‰ (ABw horizon). Furthermore, the DTPA-$CaCl_2$ extractable Ni displays heavy isotope composition in all horizons in site 1, with a $\Delta^{60}Ni_{DTPA/CaCl2\text{-}soil}$ of +0.63 to +0.74 ‰ (Table 4). For site 2, the $\Delta^{60}Ni_{DTPA/CaCl2\text{-}soil}$ is more variable, ranging from −0.56 to +0.12 ‰.

Discussion

Phytoavailability of metals in soils and Ni isotopic fractionation

The results of the chemical extraction with the DTPA-$CaCl_2$ show that type of ultramafic parent material appears to affect the Ni phytoavailability. Kierczak et al. (2016) have explained higher phytoavailability of Ni in soils derived from the partially serpentinized peridotite (the EDTA extraction) compared to the soils derived from the serpentinite due to fact that olivines (Ni-bearing phase in site 1) are more susceptible to weathering than serpentine group minerals (Ni-bearing phase in site 2). Furthermore, the authors have shown that the Ni phytoavailability is higher than Co and Cr. Phytoavailability of Cr has been low in soils due to fact that this element is bound in the spinel group of minerals characterized by low susceptibility to weathering. The phytoavailability of metals can be controlled also by organic matter. The soil from site 1 is characterized by higher content of organic carbon (up to 4% in A horizon) compared to the soil from site 2 (up to 2% in ABw horizon). The organic matter in the soil from site 1 is able to retain more Ni on exchangeable positions compared to site 2 thereby, higher phytoavailability of Ni is observed in site 1 than site 2 (Echevarria et al. 2006). The phytoavailability of metals can be regulated by clay minerals. In the study of Echevarria et al. (2006), the Ni was more phytoavailable in soils, which were richer in smectite, as a result of presence exchangeable positions similarly to the organic matter. The smectite is present in both studied soils but it is difficult to determine proportion of this mineral in soils based on XRD observations. Moreover, the phytoavailability of metals can be controlled by crystalline Fe-oxides that can be considered as stable sink of metals under oxic conditions. In contrast, the amorphous Fe-oxides are considered as available source of Ni because of the sorption of Ni on the surface rather than incorporation within crystal lattice observed in crystalline Fe-oxides (Massoura et al. 2006; Chardot et al. 2007). However, the Fe-oxides were not identified

Table 2 Chemical composition of studied plants from the Szklary Massif (site 1)

Latin name	Family	Part[a]	Mg [%]	Ca [%]	Ni [mg kg^{-1}]	Cr [mg kg^{-1}]	Co [mg kg^{-1}]	Mn [mg kg^{-1}]	Ca:Mg[b]	$\mathrm{TF_{Ni}}$[c]	$\mathrm{TF_{Cr}}$[c]	$\mathrm{TF_{Co}}$[c]
Plantago media L.	*Plantaginaceae*	A	0.40	2.22	17.2	2.6	0.58	12	5.55	0.24	0.31	0.25
		U	0.36	0.99	72.9	8.4	2.36	36	2.75			
Fragaria vesca L.	*Rosaceae*	A	0.51	1.02	16.4	3.5	0.48	34	2.0	0.32	0.43	0.28
		U	0.32	1.12	51.6	8.2	1.72	55	3.50			
Silene vulgaris (Moench) Garcke	*Caryophyllaceae*	A	0.21	0.44	5.4	1.9	0.20	22	2.10	0.06	0.16	0.06
		U	0.31	0.86	89.6	11.8	3.17	79	2.77			
Melandrium album (Miller) Garcke	*Caryophyllaceae*	A	0.68	0.99	21.4	4.0	0.86	41	1.46	0.27	0.37	0.29
		U	0.38	1.88	80.4	10.8	2.93	54	4.95			
Lychnis viscaria L.	*Caryophyllaceae*	A	0.34	0.62	12.2	2.8	0.48	67	1.82	0.24	0.31	0.19
		U	0.29	0.73	51.2	9.1	2.51	98	2.52			
Lupinus polyphyllus Lindley	*Leguminosae*	A	1.17	1.26	33.3	1.8	0.75	90	1.08	0.75	0.46	0.73
		U	0.91	0.25	44.5	3.9	1.03	45	0.27			
Dianthus carthusianorum L.	*Caryophyllaceae*	A	0.38	0.93	10.4	2.5	0.37	33	2.45	0.30	0.50	0.33
		U	0.37	0.49	34.7	5.0	1.13	38	1.32			
Ranunculus polyanthemos L.	*Ranunculaceae*	A	0.45	0.97	28.9	2.4	0.44	39	2.16	0.31	0.30	0.17
		U	0.50	0.91	91.9	8.1	2.59	70	1.82			
Hieracium caespitosum Dumort.	*Compositae*	A	0.46	0.49	13.0	2.2	0.97	23	1.07	0.13	0.17	0.20
		U	0.44	0.65	102.5	12.7	4.94	74	1.48			
Genista tinctoria L.	*Leguminosae*	A	0.29	0.22	12.3	1.8	0.08	28	0.76	0.48	0.41	0.11
		U	0.22	0.14	25.4	4.4	0.70	32	0.64			
Scabiosa ochroleuca L.	*Dipsacaceae*	A	0.30	0.71	13.4	1.8	0.10	7	2.37	0.32	0.25	0.06
		U	0.26	0.55	42.0	7.3	1.64	31	2.12			
Lotus corniculatus L.	*Leguminosae*	A	0.61	0.50	17.5	2.5	0.21	21	0.82	0.25	0.34	0.12
		U	0.31	0.38	70.3	7.4	1.72	26	1.23			
Galium verum L.	*Rubiaceae*	A	0.25	0.59	3.9	1.9	0.16	22	2.36	0.11	0.42	0.13
		U	0.19	0.78	35.8	4.5	1.28	25	4.11			
Trifolium montanum L.	*Leguminosae*	A	0.49	0.82	21.2	2.0	0.23	20	1.67	0.31	0.28	0.16
		U	0.23	0.37	67.5	7.2	1.48	27	1.61			
Centaurium erythraea Rafn	*Gentianaceae*	A	0.25	0.23	15.0	1.9	0.22	20	0.92	0.87	0.46	0.29
		U	0.12	0.19	17.2	4.1	0.77	16	1.58			
Phleum phleoides (L.) Karsten	*Graminae*	A	0.08	0.15	7.8	1.8	0.06	13	1.88	0.13	0.30	0.04
		U	0.10	0.16	59.1	6.1	1.47	23	1.60			
Sedum acre L.	*Crassulaceae*	A	0.49	1.97	14.0	3.3	0.48	12	4.02	0.24	0.37	0.22
		U	0.55	1.24	58.5	8.9	2.16	32	2.25			
Senecio jacobaea L.	*Compositae*	A	0.20	0.76	25.8	1.8	0.32	10	3.80	0.50	0.45	0.28
		U	0.11	0.47	51.3	4.0	1.14	29	4.27			
Allium oleraceum L.	*Liliaceae*	A	0.12	0.43	4.9	2.1	0.13	15	3.58	0.24	0.91	0.37
		U	0.09	0.20	20.8	2.3	0.35	9	2.22			
Hypericum perforatum L.	*Guttiferae*	A	0.17	0.28	8.9	1.8	0.24	23	1.65	0.33	0.47	0.24
		U	0.09	0.14	27.2	3.8	0.98	22	1.56			
Artemisia vulgaris L.	*Compositae*	A	0.34	0.6	16.8	1.9	0.32	71	1.76	0.48	0.59	0.43
		U	0.13	0.24	35.0	3.2	0.75	34	1.85			

Table 2 (continued)

Latin name	Family	Part[a]	Mg [%]	Ca [%]	Ni [mg kg^{-1}]	Cr [mg kg^{-1}]	Co [mg kg^{-1}]	Mn [mg kg^{-1}]	Ca:Mg[b]	TF$_{Ni}$[c]	TF$_{Cr}$[c]	TF$_{Co}$[c]
Melilotus alba Medicus	*Leguminosae*	A	0.59	1.09	21.7	1.8	0.44	30	1.85	0.87	0.38	0.49
		U	0.47	0.25	25.0	4.8	0.89	15	0.53			
Sedum maximum (L.) Suter	*Crassulaceae*	A	0.55	1.86	22.6	3.9	1.11	35	3.38	0.41	0.49	0.62
		U	0.44	0.40	54.5	7.9	1.79	21	0.91			
Achillea pannonica Scheele	*Compositae*	A	0.26	0.57	8.3	1.7	0.39	27	2.19	0.47	0.65	0.41
		U	0.17	0.37	17.5	2.6	0.95	29	2.18			
Trifolium arvense L.	*Leguminosae*	A	0.34	0.53	8.6	2.0	0.25	16	1.56	0.33	0.44	0.28
		U	0.21	0.14	26.4	4.5	0.90	18	0.67			
Tanacetum vulgare L.	*Compositae*	A	0.23	0.41	9.1	1.6	0.24	25	1.78	0.31	0.44	0.33
		U	0.10	0.31	29.1	3.6	0.72	29	3.10			
Trifolium campestre Schreber	*Leguminosae*	A	0.31	0.69	11.3	1.8	0.32	29	2.23	0.50	0.51	0.35
		U	0.22	0.37	22.5	3.5	0.92	29	1.68			
Daucus carota L.	*Umbelliferae*	A	0.43	1.57	17.5	1.6	0.11	17	3.65	0.29	0.16	0.08
		U	0.40	0.47	60.9	10.1	1.33	25	1.18			
Thymus pulegioides L.	*Labiatae*	A	0.52	0.53	15.0	3.0	0.61	30	1.02	0.37	0.55	0.36
		U	0.39	0.27	40.1	5.5	1.69	37	0.69			
Potentilla heptaphylla L.	*Rosaceae*	A	0.46	1.44	18.1	3.2	0.84	40	3.13	0.31	0.68	0.39
		U	0.59	2.42	58.1	4.7	2.15	53	4.10			
Anthyllis vulneraria L.	*Leguminosae*	A	1.71	1.32	21.3	2.9	0.57	53	0.77	0.26	0.28	0.33
		U	0.72	0.45	80.5	10.4	1.72	38	0.63			
Festuca ovina agg. L.	*Graminae*	A	0.11	0.28	12.6	3.6	0.42	30	2.55	0.04	0.11	0.04
		U	0.50	0.88	308.1	32.4	9.78	181	1.76			
Rumexa cetosa L.	*Polygonaceae*	A	0.56	0.23	12.7	2.8	0.29	24	0.41	0.74	1.12	1.04
		U	0.42	0.16	17.2	2.5	0.28	12	0.38			
Briza media L.	*Graminae*	A	0.19	0.22	9.8	2.4	0.08	30	1.16	0.06	0.13	0.01
		U	0.32	0.87	177.2	18.5	6.27	128	2.72			
Calamagrostis epigejos (L.) Roth	*Graminae*	A	0.14	0.27	20.9	4.5	0.72	49	1.93	0.03	0.05	0.03
		U	1.12	0.72	642.4	96.9	24.96	274	0.64			
Arrhenatherum elatius (L.) P. Beauv. ex J. Presl& C. Presl	*Graminae*	A	0.26	0.26	6.8	2	0.11	28	1.00	0.03	0.07	0.01
		U	0.31	0.75	211.8	30.6	7.51	134	2.42			
Avenula pratensis (L.) Dumort.	*Graminae*	A	0.13	0.25	7.9	1.9	0.14	78	1.92	0.03	0.05	0.01
		U	0.22	0.38	260.0	35.2	10.80	97	1.73			

[a] *A*, aboveground parts; *U*, underground parts

[b] on a weight basis

[c] TF$_{Ni}$,TF$_{Cr}$,TF$_{Co}$ – translocation factor for nickel, chromium, and cobalt respectively

Table 3 Chemical composition of studied plants from Jordanów (site 2)

Latin name	Family	Part[a]	Mg [%]	Ca [%]	Ni [mg kg^{-1}]	Cr [mg kg^{-1}]	Co [mg kg^{-1}]	Mn [mg kg^{-1}]	Ca:Mg[b]	TF$_{Ni}$[c]	TF$_{Cr}$[c]	TF$_{Co}$[c]
Hieracium pilosella L.	*Compositae*	A	0.49	0.65	72.5	14.3	2.65	47	1.33	0.36	0.33	0.40
		U	0.45	0.68	202.7	43.3	6.65	77	1.51			
Ranunculus polyanthemos L.	*Ranunculaceae*	A	0.35	0.78	23.3	3.6	0.49	97	2.23	0.42	0.25	0.20
		U	0.46	0.70	55.1	14.4	2.46	222	1.52			
Trifolium montanum L.	*Leguminosae*	A	0.47	1.07	45.3	4.6	0.72	37	2.28	0.35	0.19	0.19
		U	0.38	0.51	127.9	24.5	3.75	46	1.34			
Anchusa officinalis L.	*Boraginaceae*	A	0.50	0.91	29.8	2.6	0.32	31	1.82	0.25	0.09	0.08
		U	0.43	1.12	120.8	28.3	3.98	92	2.60			
Salvia pratensis L.	*Labiatae*	A	0.72	0.72	27.6	3.4	0.30	19	1.00	0.12	0.03	0.03
		U	0.85	0.75	236.6	100.0	9.53	114	0.88			
Lychnis viscaria L.	*Caryophyllaceae*	A	0.42	0.62	17.0	3.1	0.36	189	1.48	0.23	0.25	0.16
		U	0.33	0.57	73.4	12.4	2.30	256	1.73			
Euphorbia cyparissias L.	*Euphorbiaceae*	A	0.45	0.71	65.2	1.8	1.65	39	1.58	0.64	0.07	0.46
		U	0.34	0.50	101.1	24.1	3.60	109	1.47			
Polygala vulgaris L.	*Polygalaceae*	A	0.25	0.46	31.4	6.2	0.62	22	1.84	0.25	0.22	0.20
		U	0.14	0.18	125.7	28.8	3.13	25	1.29			
Dactylis glomerata L.	*Graminae*	A	0.13	0.13	13.8	2.0	0.16	122	1.00	0.09	0.04	0.02
		U	0.33	0.37	148.0	52.0	8.15	155	1.12			
Scabiosa ochroleuca L.	*Dipsacaceae*	A	0.56	0.29	66.4	14.5	1.94	17	0.52	0.34	0.49	0.37
		U	0.41	0.32	194.3	29.8	5.25	29	0.78			
Dianthus carthusianorum L.	*Caryophyllaceae*	A	0.42	0.38	21.1	2.3	0.51	46	0.90	0.27	0.11	0.13
		U	0.36	0.37	78.7	21.5	3.90	94	1.03			
Centaurea stoebe L.	*Compositae*	A	0.29	0.27	15.0	4.3	0.44	17	0.93	0.19	0.20	0.13
		U	0.30	0.30	78.1	21.2	3.43	55	1.00			
Centaurea scabiosa L.	*Compositae*	A	0.31	0.45	14.0	2.5	0.33	27	1.45	0.38	0.40	0.43
		U	0.28	0.43	36.9	6.2	0.76	51	1.54			
Trifolium arvense L.	*Leguminosae*	A	0.26	0.47	15.5	3.3	0.38	28	1.81	0.60	0.51	0.37
		U	0.18	0.16	26.0	6.5	1.02	22	0.89			
Galium verum L.	*Rubiaceae*	A	0.31	0.57	27.1	2.3	0.29	37	1.84	0.23	0.15	0.07
		U	0.28	0.70	115.4	15.5	4.33	47	2.50			
Thymus pulegioides L.	*Labiatae*	A	0.60	0.34	74.0	4.8	0.68	42	0.57	0.45	0.21	0.15
		U	0.44	0.27	164.8	23.0	4.60	137	0.61			
Achillea pannonica Scheele	*Compositae*	A	0.32	0.44	25.4	2.7	0.37	47	1.38	1.01	0.42	0.33
		U	0.18	0.44	25.2	6.5	1.12	77	2.44			
Veronica spicata L.	*Scrophulariaceae*	A	0.33	0.43	15.5	3.7	0.70	28	1.30	0.56	0.46	0.53
		U	0.19	0.32	27.5	8.0	1.33	59	1.68			
Rhinanthus minor L.	*Scrophulariaceae*	A	0.29	0.45	18.4	1.9	0.32	29	1.55	0.74	0.59	0.53
		U	0.19	0.26	24.9	3.2	0.60	53	1.37			

Table 3 (continued)

Latin name	Family	Part[a]	Mg [%]	Ca [%]	Ni [mg kg^{-1}]	Cr [mg kg^{-1}]	Co [mg kg^{-1}]	Mn [mg kg^{-1}]	Ca:Mg[b]	TF$_{Ni}$[c]	TF$_{Cr}$[c]	TF$_{Co}$[c]
Tanacetum vulgare L.	*Compositae*	A	0.37	0.40	16.6	1.8	0.41	90	1.08	0.65	0.27	0.46
		U	0.14	0.20	25.6	6.6	0.90	49	1.43			
Knautia arvensis (L.) Coulter	*Dipsacaceae*	A	0.40	0.48	29.2	2.6	0.26	25	1.20	0.85	0.47	0.24
		U	0.41	0.81	34.5	5.5	1.07	174	1.98			
Sedum maximum (L.) Suter	*Crassulaceae*	A	0.92	1.46	28.8	2.8	1.64	57	1.59	0.57	0.42	1.31
		U	0.45	0.35	50.7	6.7	1.25	35	0.78			
Euphrasia stricta D. Wolff ex J. F. Lehm.	*Scrophulariaceae*	A	0.38	0.37	41.3	2.2	0.25	84	0.97	0.74	0.51	0.42
		U	0.21	0.26	55.7	4.3	0.59	137	1.24			
Daucus carota L.	*Umbelliferae*	A	0.27	0.69	15.3	1.9	0.13	32	2.56	0.32	0.17	0.10
		U	0.28	0.58	47.5	11.2	1.33	41	2.07			
Asparagus officinalis L.	*Liliaceae*	A	0.21	0.20	5.9	2.0	0.06	23	0.95	0.13	0.19	0.03
		U	0.11	0.13	44.0	10.5	1.97	19	1.18			
Helianthemum nummularium (L.) Miller	*Cistaceae*	A	0.40	0.42	35.1	2.2	0.23	89	1.05	0.58	0.50	0.34
		U	0.22	0.74	60.7	4.4	0.68	122	3.36			
Geranium pratense L.	*Geraniaceae*	A	0.40	1.30	16.1	2.6	0.89	64	3.25	0.66	0.19	0.50
		U	0.29	0.38	24.4	13.5	1.79	24	1.31			
Carlina vulgaris L.	*Compositae*	A	0.39	0.53	26.8	2.2	0.41	20	1.36	0.46	0.21	0.25
		U	0.22	0.35	58.9	10.5	1.62	21	1.59			
Verbascum densiflorum Bertol.	*Scrophulariaceae*	A	0.34	0.47	13.7	2.4	0.16	29	1.38	0.46	0.23	0.07
		U	0.27	0.28	29.9	10.4	2.40	75	1.04			
Plantago media L.	*Plantaginaceae*	A	0.74	1.38	61.4	4.6	1.12	38	1.86	0.59	0.40	0.43
		U	0.44	0.63	104.0	11.6	2.63	66	1.43			
Arrhenatherum elatius (L.) P. Beauv. ex J. Presl & C. Presl	*Graminae*	A	0.17	0.10	7.8	2.7	0.09	48	0.59	0.11	0.12	0.01
		U	0.22	0.30	68.6	23.3	9.69	169	1.36			
Filipendula vulgaris Moench	*Rosaceae*	A	0.62	0.51	36.7	5.2	0.64	63	0.82	0.52	0.51	0.26
		U	0.59	1.45	70.2	10.1	2.49	168	2.46			
Lepidium campestre (L.) R. Br.	*Cruciferae*	A	0.71	0.85	45.7	13.4	1.59	45	1.20	0.71	0.84	0.75
		U	0.29	0.49	64.7	16.0	2.13	33	1.69			
Festuca ovina agg. L.	*Graminae*	A	0.20	0.26	17.6	6.1	0.41	108	1.30	0.10	0.08	0.03
		U	0.49	0.50	172.2	75.4	13.88	161	1.02			
Avenula pratensis (L.) Dumort.	*Graminae*	A	0.22	0.27	12.5	2.2	0.18	122	1.23	0.08	0.03	0.01
		U	0.46	0.33	153.2	64.1	14.95	93	0.72			
Calamagrostis epigejos (L.) Roth	*Graminae*	A	0.12	0.13	10.6	3.9	0.56	118	1.08	0.04	0.02	0.03
		U	1.03	0.32	262.6	164.7	20.78	194	0.31			

[a] *A*, aboveground parts; *U*, underground parts

[b] on a weight basis

[c] TF$_{Ni}$, TF$_{Cr}$, TF$_{Co}$ – translocation factor for nickel, chromium, and cobalt respectively

Table 4 Isotopic composition of studied rocks and soils

Horizon	Depth [cm]	δ^{60}Ni [‰]	2σ	Δ^{60}Ni$_{\text{soil-rock}}$ [‰]	δ^{60}Ni$_{\text{DTPA/CaCl2}}$ [‰]	2σ	Δ^{60}Ni$_{\text{DTPA/CaCl2-soil}}$ [‰]	[Ni/Al]$_{\text{soil}}$/[Ni/Al]$_{\text{rock}}$
Site 1 (Szklary Massif)								
A	0–8	−0.09	0.06	−0.22	0.65	0.04	0.74	0.64
ABw	8–20	0.07	0.07	- 0.06	0.70	0.03	0.63	0.79
R	> 20	0.13	0.06	–	–	–	–	–
Site 2 (Jordanów)								
ABw	0–20	0.32	0.07	0.12	- 0.24	0.06	−0.56	0.10
Bw	20–40	0.16	0.06	- 0.04	0.28	0.03	0.12	0.18
BwC	40–110	0.01	0.06	- 0.19	- 0.17	0.03	- 0.18	0.56
R	> 110	0.20	0.06	–	–	–	–	–

during XRD studies, even, if Kierczak et al. (2007) previously observed oxy-hydroxides - clayous mixture in soil from site 1 by SEM and EMPA.

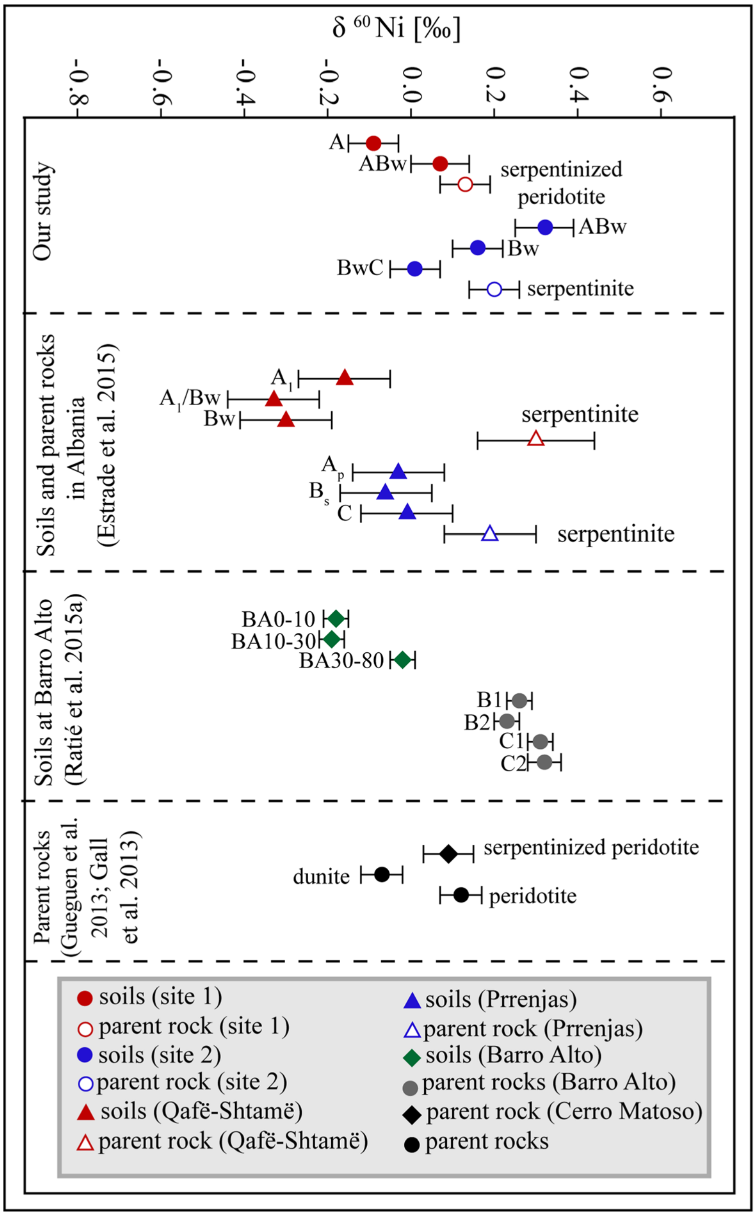
The Ni isotopic composition of the partially serpentinized peridotite and serpentinite is close to the parent rocks presented in other studies (Fig. 4; Gueguen et al. 2013; Estrade et al. 2015). The slight differences in Ni isotopic composition of parent rocks from various ultramafic massifs can be explained by variabilities of parent magma and degree of serpentinization causing a possible isotopic fractionation (Ratié et al. 2015; Estrade et al. 2015). In the last studies, Gall et al. (2017) have suggested that serpentinization probably does not affect δ^{60}Ni. Our results support this finding to some extent because δ^{60}Ni for both parent rocks is in the range noted for unweathered peridotite xenoliths (from 0.09 ‰ to 0.32 ‰; Gall et al. 2017). Furthermore, the authors have explained differences in δ^{60}Ni of ultramafic rocks by proportion of clinopyroxene that represents heavy Ni isotope composition (up to 2.83 ± 0.11 ‰) compared to olivine (up to 0.17 ± 0.05 ‰) or orthopyroxene (up to – 0.04 ± 0.04 ‰).

Isotopic composition of the Leptosol in site 1 shows that soil is lighter than parent material i.e. Δ^{60}Ni$_{\text{soil-rock}}$ for A horizon is – 0.22 ‰. This trend is previously reported in Albania (Δ^{60}Ni$_{\text{soil-rock}}$ is up to - 0.63 ‰) and at Barro Alto (Estrade et al. 2015; Ratié et al. 2015). The Ni isotope composition of phytoavailable fraction estimated using the DTPA-CaCl$_2$ solution shows that heavier Ni isotope pool is released during weathering of ultramafic rocks. In detail, the Δ^{60}Ni$_{\text{DTPA/CaCl2-soil}}$ for A and ABw horizon is 0.74 ‰ and 0.63 ‰ respectively. The magnitude of fractionation (Δ^{60}Ni$_{\text{DTPA/CaCl2-soil}}$) in Albanian's ultramafic soils was up to 0.89 ‰. Our results for soil from site 1 support to some extent findings that pedogenesis leads to removal isotopically heavy phytoavailable pool of Ni.

The Ni isotope composition of the Cambisol from site 2 is more diverse. The Bw and BwC horizons are lighter than parent material confirming previous results. On the contrary, the surface horizon (ABw) has heavy isotopic composition. We suggest that decomposition of aboveground parts of plants can explain to some extent heavy isotope composition of soil in the surface horizon from this locality. Studies in ultramafic areas in Albania demonstrated that the litter was isotopically heavier than rhizospheric soil thus, decomposition of litter can deliver heavy isotopes to the surface horizon. Very recently, Šillerová et al. (2017) suggested that biological and biochemical fractionation is responsible for heavy isotope composition of topsoil from Norway (δ^{60}Ni up to 1.71 ‰). Furthermore, experiments simulating litter decomposition on the *Rinorea bengalensis* (Ni-hyperaccumulator) showed that 80% of Ni was released during first 10 days of the experiment. The released pool of Ni was enriched in heavy isotopes (Δ^{60}Ni$_{\text{leached10days-leached30days}}$ = 0.20 ‰; Zelano et al. 2017).

The phytoavailable fraction from Bw horizon of the Cambisol in site 2 presents only heavy isotope composition. It is difficult to clearly explain light isotopic composition of phytoavailable fraction in ABw and BwC horizons. Estrade et al. (2015) pointed out that differences in isotope composition between various soils (Cambisol and Vertisol) can be explained by functions and pedogenesis of these soils. We study the Leptosol (site 1) and the Cambisol (site 2) thus, differences between these soils can result from pedogenesis. The slight distinction between these soils is reflected in the spatial distribution of the elements. The Ni content in soil relative to the parent rock is rather stable in site 1 (Fig. 5).

Fig. 4 Comparison of Ni isotope composition between soils and rocks in this study with samples from other localities (Gall et al. 2013; Gueguen et al. 2013; Ratié et al. 2015; Estrade et al. 2015)



On the other hand, the enrichment of Ni is observed in BwC horizon and depletion in ABw horizon in site 2. Chromium is stable in both sites (except the surface horizon in site 1) and Co is enriched in site 1 compared to site 2. Calcium and Mg are similarly distributed in both soil profiles relative to the parent rocks. The relevant difference between studied soils is noticeable in normalization of the Ni content between soils and rocks to the immobile Al. The $[Ni/Al]_{soil}/[Ni/Al]_{rock}$ demonstrates that weathering process is more advanced in site 2 than site 1 (Table 4; calculated after Estrade et al. 2015). The comparison of the $[Ni/Al]_{soil}/[Ni/Al]_{rock}$ relative to the δ^{60}Ni of soils shows surprisingly that the more advanced weathering, the heavier isotopic composition of soils (Fig. 5). It suggests that light pool of Ni could have leached out during pedogenesis in Polish soils. However, this is not reflected in the δ^{60}Ni of the DTPA-$CaCl_2$ fraction of the soils. The DTPA extraction of the soils is considered as efficient to assess phytoavailability of metals (Estrade et al. 2015 and references therein). On the other hand, it is possible that during 2 h of the extraction the entire pool of

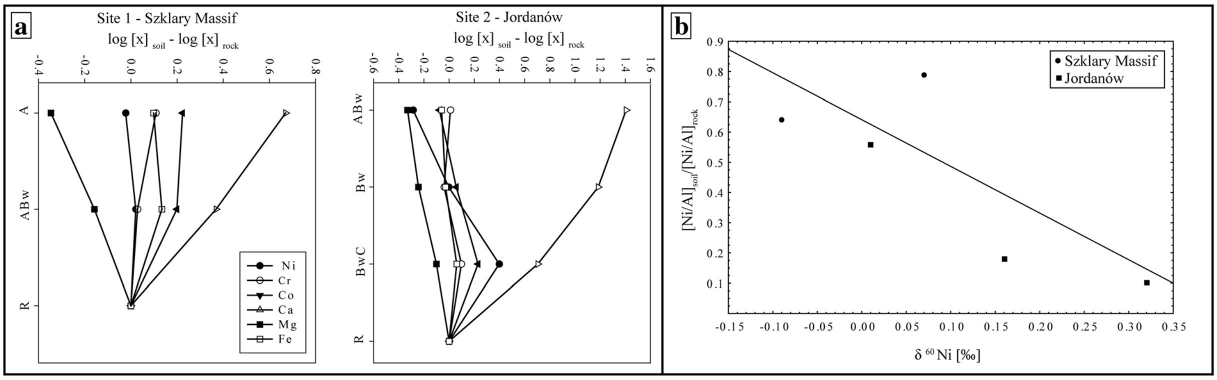


Fig. 5 Distribution of elements in soil horizons relative to the parent rocks (**a**) and the relationship between $[Ni/Al]_{soil}/[Ni/Al]_{rock}$ and $\delta^{60}Ni$ in soils (**b**)

phytoavailable Ni is not extracted because of diffusion controlled processes that may affect Ni isotopic signature.

Accumulation of metals by plants

The ecological peculiarity of ultramafic areas is related to the excess of Mg^{2+} at deficiency of Ca^{2+} in soils (Proctor 1970; Becquer et al. 2010). The imbalance between these cations in soils (Ca/Mg ratio < 1) together with presence of metals are responsible for toxicity for plants. Our results support hypothesis that imbalance between exchangeable Ca and Mg in soils is an important factor controlling vegetation because Ca/Mg ratio in most horizons is lower than one (from 0.27 to 0.77) except for the surface horizon in site 2 (1.19). Furthermore, metal contents in soils are in the range published in other studies.

The results of chemical composition of studied plants are generally consistent with previous results for plants from grasslands developed on ultramafic rocks and spontaneous vegetation on waste dumps in Poland (Żołnierz 2007; Koszelnik-Leszek and Kasowska 2009). All species, both in above- underground parts are characterized by the highest contents of Ni followed by Cr and Co. The same tendency was observed in other studies independently the climate conditions (Kataeva et al. 2004; Reeves et al. 2007a; Reeves et al. 2007b; Lago-Vila et al. 2015). For example, leaves of *Bonamia mexicana* from Santa Elena peninsula (Costa Rica) accumulated 12 mg kg^{-1} of Ni followed by 0.5 mg kg^{-1} of Cr and 0.1 mg kg^{-1} of Co. Most of the species is characterized by the TF for Ni, Cr, and Co lower than 1 suggesting strategy for exclusion in Polish ultramafic vegetation. It was reported also for plants from Spain, USA, and Taiwan (Oze et al. 2008; Lago-Vila et al. 2015; Gonneau et al. 2017; Hseu and Lai 2017). The exclusion can be explain by sequestration of metals in the vacuoles of roots or binding to the exchange sites of cell walls in xylem (Seregin and Kozhevnikova 2006; Yusuf et al. 2011).

Taking into account higher phytoavailability of metals in soils from site 1 compared to site 2 we expected similarly higher contents of these elements in plants from site 1. However, we observed another tendency especially with regard to aboveground parts (Online Resource 3). Aboveground parts of plants from site 2 have significantly higher content of Ni (i.e. $Mdn_A = 24.35$ mg kg^{-1}) than plants from site 1 (i.e. $Mdn_A = 13.40$ mg kg^{-1}; $Z = -3.88$, $p < 0.05$, $r = -0.45$). Studied species from site 2 have also significantly higher content of Cr both in aboveground parts ($Z = -3.31$, $p < 0.05$, $r = -0.39$) and underground parts ($Z = -3.69$, $p < 0.05$, $r = -0.43$). For Co difference is noted only in underground parts ($Z = -1.98$, $p < 0.05$, $r = -0.23$). On the contrary, aboveground parts of plants from site 1 are characterized by higher Ca/Mg ratio than plants from site 2 ($t = 3.22$, $p < 0.05$; Online Resource 3). The results of statistical analysis can partly indicate alleviating role of Ca and/or Mg in the case of high content of metals in soils. One way to confirm this hypothesis is to look at the difference in physicochemical composition of studied soils. In detail, the Leptosol from site 1 derived from the serpentinized peridotite has higher contents of exchangeable Ca (up to 20.8 cmol (+) kg^{-1} in A horizon) and Mg (up to 59.9 cmol (+) kg^{-1} in ABw horizon) than the Cambisol from site 2 derived from the serpentinite (exchangeable Ca and Mg do not exceed 7.0 cmol (+) kg^{-1} and 9.1 cmol (+) kg^{-1} respectively in BwC horizon). Therefore, it is possible that exchangeable Ca can compete with metals in plants from site 1. The competition between Ca and metals was observed by other authors (Li et al. 2009; Wang et al. 2010; Yusuf et al. 2011; Lago-Vila et al. 2015; Aziz et al. 2015). For example, Li et al. (2009) and Lago-Vila et al. (2015) suggested that exchangeable Ca can decrease Ni and Co accumulation by plants because of competition for binding sites in root cells. Furthermore, Wang et al. (2010) studied relationships between Ca^{2+} and Cu^{2+}, Cd^{2+}, Ni^{2+} in *Triticum aestivum* and *Pisum sativum*. In detail, after Ca^{2+} was added to the growth medium, electric potential in the outer surface of cell membrane decreased. Consequently, activity of metals was lower and toxicity was alleviated. Aziz et al. (2015) used rice for studying interactions between Ca and Ni. The presence of Ca in tested soils caused decrease in Ni content in plants due to improvement metabolic functions of cell membrane and maintaining its integrity. Furthermore, the Ca caused increase in chlorophyll content and increase in the rate of transpiration.

High contents of Mg in ultramafic soils are known as toxic for plants (Proctor 1970). Most of the plants from both localities have Ca/Mg ratio higher than 1 suggesting that plants overcome high content of Mg and low of Ca in soils due to adaptation mechanisms. This is in agreement with other studies (Pandolfini and Pancaro 1992; Lombini et al. 1998; Oze et al. 2008). Despite the toxic role of Mg for plants, it is possible that this element is also able for limiting accumulation of metals. Studies of surface potential of plasma membrane in plants (not from ultramafic areas) revealed that Mg can compete with metals because of decrease negativity of the plasma membrane surface electrical potential (Kinraide 2006). Furthermore, important insight into the alleviating role of Ca and Mg comes from studies of ion channels. For instance, the Ca^{2+} channel "*rca*" is able to transport monovalent (i.e. Na^{+}) and divalent cations (i.e. Ni^{2+}, Cu^{2+}, Mg^{2+}) if there is no Ca^{2+} (White 2000). It suggests that competition between Ca^{2+}, Mg^{2+}, and Ni^{2+} seems possible. Studies with *Berkheya coddii* demonstrated also that Ni accumulation can be inhibited by both Ca and Mg (Robinson et al. 1999). Correlation analysis of species in our study supports alleviating role of Ca^{2+} and Mg^{2+} (Fig. 6; Online Resource 4). For instance, rank Spearman correlation coefficient between Ni and Mg of aboveground parts in site 1 is 0.65 ($p < 0.05$). Similarly to our results, Ater et al. (2000) found significant positive correlation between Mg and Ni in plants from North Morocco suggesting that plants growing on ultramafic soils cope with high content of Ni and Mg in soils by the same mechanisms (exclusion and accumulation). Similar observations were also reported in the study of plants growing in Europe (Shewry and Peterson 1971).

The differences in chemical composition of plants indicate that type of ultramafic parent material affects metals accumulation by plants. The main Mg-bearing phase in the serpentinized peridotite is olivine and serpentine and only serpentine in the serpentinite. We observe higher content of exchangeable Mg in soils derived from the serpentinized peridotite because olivine is more extensively weathered than serpentine. Higher content of exchangeable Ca in site 1 is related to the presence of amphibole (tremolite – a Ca bearing mineral, Kierczak et al. 2007) which does not occur in site 2.

Another explanation of differences in the accumulation of Ni, Cr, and Co in studied plants can be attributed to changes in pH. Mobility of metals increases when pH of soil decreases (Greger 1999). Soil from site 2 has slightly lower pH (6.3 in uppermost horizon) compared to soil from site 1 ($pH = 7$ in uppermost horizon; Kierczak et al. 2016). Lower pH of soil from site 2 could promote Ni, Cr, and Co accumulation by plants from this locality.

Broadhurst et al. (2009) studied interactions between Mn and Ni in two hyperaccumulators (*Alyssum murale* and *Alyssum corsicum*). Authors observed that phytoextraction of Ni by *Alyssum* species can be reduced by more available Mn. Our results showed that soil from site 1 contain higher content of Mn (up to 1781 $mg\ kg^{-1}$ in A horizon) compared to soil from site 2 (up to 774 $mg\ kg^{-1}$ in ABw horizon; Kierczak et al. 2016). Higher content of Mn in ultramafic soils from site 1 and significant correlation between Ni, Cr, Co, and Mn in plants support hypothesis that Mn reduces metal accumulation by plants (Fig. 7; Online Resource 4). Furthermore, these results demonstrate that type of ultramafic rocks affects metal accumulation by plants. Olivine and pyroxene in the serpentinized peridotite from site 1 are the most enriched in Mn (average 929 $mg\ kg^{-1}$ and 1936 $mg\ kg^{-1}$ respectively; Kierczak et al. 2016), whereas serpentine in the serpentinite from site 2 contain with an average of 542 $mg\ kg^{-1}$ of Mn. Olivines are easily weatherable thus they could release Mn which possibly reduces accumulation of other metals by plants. Similarly to olivines, pyroxenes weather to hydrous layer silicates (Wilson 2004) supplying soils also in Mn. The significant positive correlation between Cr and Mn in plants was found also in

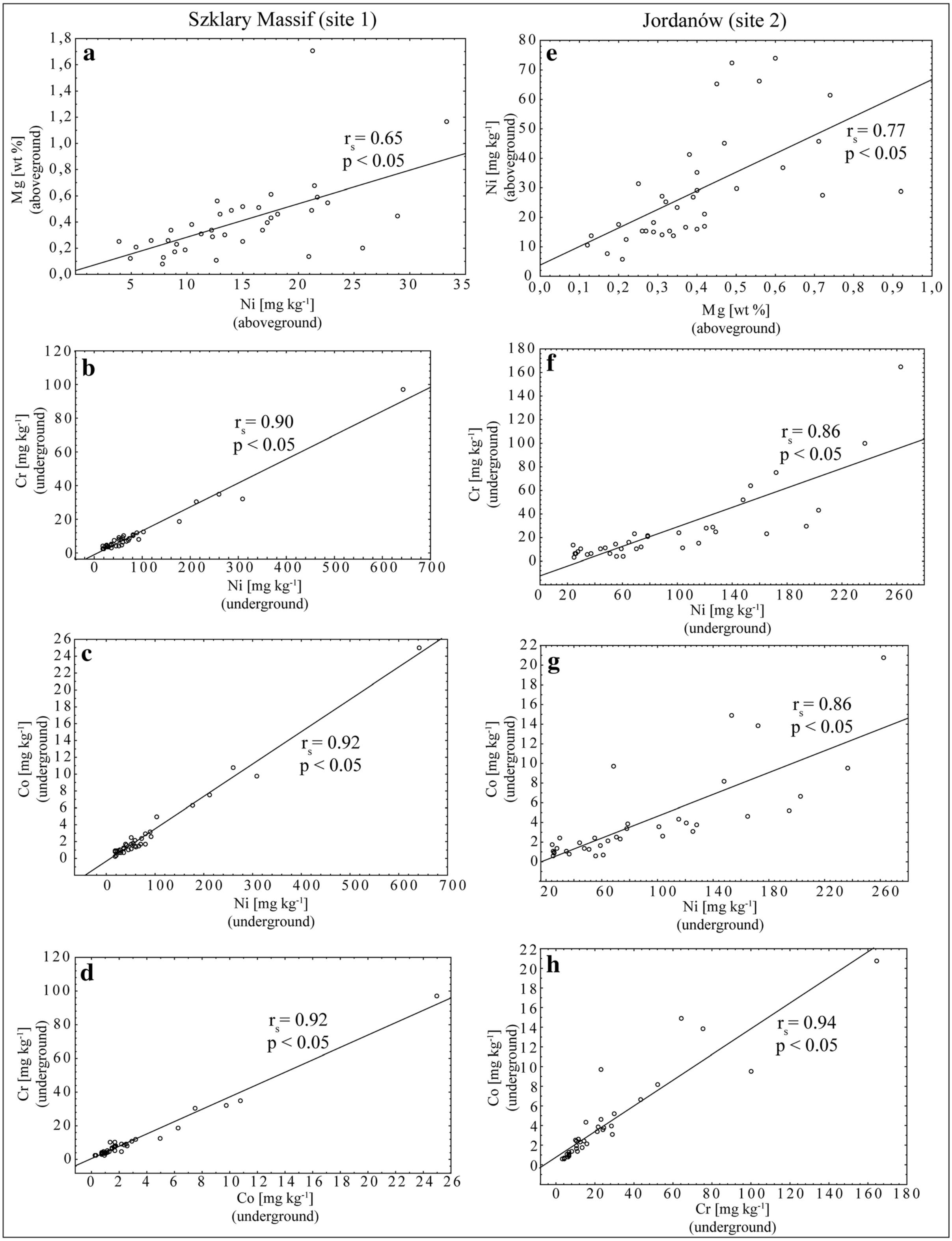


Fig. 6 Diagrams presenting relationships between Mg and Ni in aboveground parts of plants (**a**, **e**) and relationships between Ni, Cr and Co in underground parts of plants (**b-d**; **f-h**)

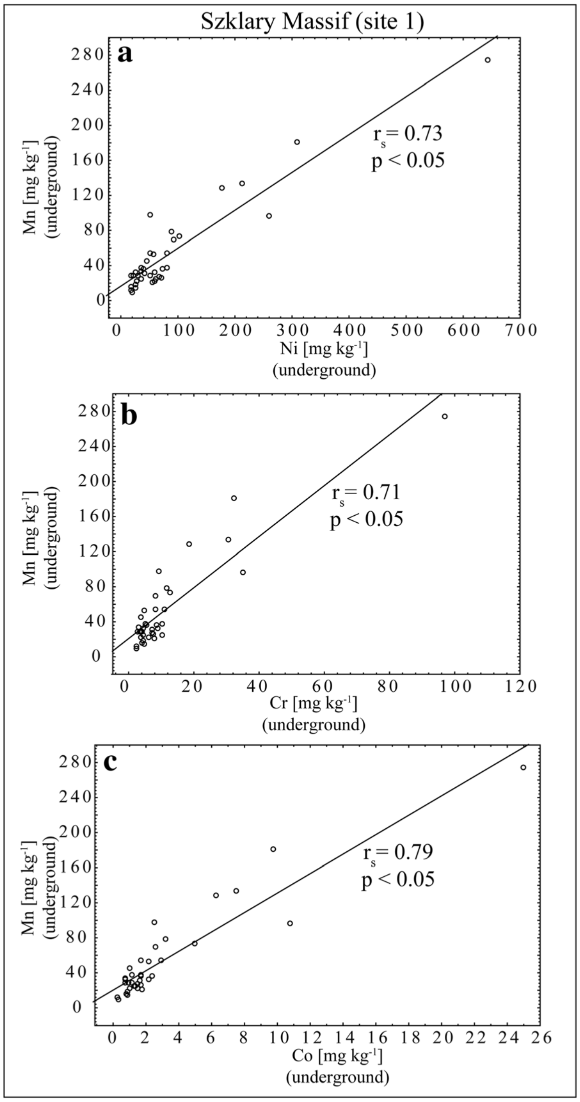


Fig. 7 Diagrams presenting relationships between Mn, Ni, Cr and Co in underground parts of plants in site 1

the study of Megremi (2010) suggesting strong relationships between both elements. The U-Mann Whitney test revealed surprisingly significant higher content of Mn in plants from site 2 than site 1 although the fact that soil from site 1 contains higher content of Mn. Soil from site 2 is characterized by higher content of clay fraction compared to site 1 hence possibly less drained. Therefore, higher moister of soils in site 2 can induce reduction of Mn oxides and release available Mn.

We found also positive significant correlation between Ni, Cr, and Co in plants regardless of the study area (Fig. 6; Online Resource 4). Rencz and Shilts (1990) suggested that correlations between these elements reveal strong interrelationships between metals. Moreover, Megremi (2010) found a significant positive correlation between Ni and Cr, similarly to our study.

The complexity in the study of plants from ultramafic soils

Species growing in ultramafic soils are extensively studied for many years (i.e. Whittaker 1954; Main 1974; Main 1981; Galey et al. 2017; Gonneau et al. 2017; Van der Ent et al. 2017; Van der Ent et al. 2018). Although knowledge about relationships between metals with other elements or factors in plants is broad, it is still difficult to final identify the causes of differences in Ni, Cr, and Co content in plants from Polish ultramafic soils. Some authors suggested that accumulation of metals depends on the nature of plants (i.e. differences in genetic composition between species or specimens; Greger 1999). Another factor affecting accumulation of metals can be attributed to anthropogenic pollution. According to Becquer et al. (1992), acid rain (containing NO_3^- and SO_4^{2-}) modifies pH of soils and Al toxicity. It was observed that during vegetation season coniferous trees from Vosges Mountains (France) are able to take up NO_3^- ions. At the same time, Ca^{2+}, Mg^{2+}, and K^+ are extracted from plants by acid rains leading to alkalinization and decreasing Al toxicity. The Szklary Massif and Jordanów are covered mainly by xerothermic grassland. However, it is possible that NO_3^- in rain can affect the pH of soils and metals contents in plants.

The variation in the chemical composition of plants can be explained also by presence of glacial material in ultramafic soils. Rencz and Shilts (1990) consider that glaciation affects species composition, vigor of plant communities, and change of the cation exchange capacity in the soil-roots system. Glacial material could deliver additional amount of Si which is considered as an element alleviating toxicity of metals when is absorbed by plants (Adrees et al. 2015).

Our field observations and results of chemical composition of plants do not show presence of endemites and Ni-hyeraccumulators. In our opinion, presence of glacial material in Polish soils can be responsible for the lack of these species in studied communities. Furthermore, it was also demonstrated that age of ultramafic area affects the number of endemites (reviewed in Proctor and Nagy 1991) thus relatively young age of Polish ultramafic soils can be responsible for lack of these species. On the other hand, plant growth in ultramafic soils can lead to the formation ecotypes and afterwards endemites (Anacker 2014), thus it is possible that Polish flora in ultramafic areas move towards endemism.

Conclusions

The chemistry of soils and plants is controlled by the mineral composition of parent rocks, which results from both their original magmatic composition and later metamorphic processes. Soil derived from the serpentinized peridotite (Leptosol) is shallower compared to soil formed from the serpentinite (Cambisol). Chemical extractions show that the phytoavailability of Ni and Co is higher in soil developed from the serpentinized peridotite than the serpentinite. Surprisingly, plants growing on the soils derived from the serpentinite contain higher levels of metals compared to these from the serpentinized peridotite derived soils. This contrasting behavior is due to higher abundances of Ca and Mg, not only Ni and Co, in soils developed from the serpentinized peridotite as compared to those in the soils derived from the serpentinite. Calcium and Mg are favored by plants and preferably fill the available sites, resulting in low Ni and Co intake despite their higher abundances. Differences between studied soils are also reflected in the isotopic composition. The isotopic signature of surface horizon in the Leptosol is lighter relative to the parent rock. On the other hand, enrichment in heavy isotopes is observed in surface horizon in the Cambisol. Furthermore, the phytoavailable pool of Ni extracted with the DTPA-$CaCl_2$ in the Leptosol presents heavy isotopic signature, whereas in the Cambisol only in the middle part of the profile. Our results are only to some extent consistent with observations in soils derived from peridotites and serpentinites (Alexander 2009; Alexander and DuShey 2011). Soil derived from the serpentinized peridotite is not redder compared to soil developed from the serpentinite. The topographic differences are not visible because both sites are characterized by similar topography. However, our study is in agreement with observations that vegetation cover on soils derived from both types of rocks is generally similar. These observations are characteristics for temperate climate. The high degree of endemism sensu Whittaker (1954) is not visible in Polish ultramafic sites. In tropical zone, the vegetation growing in serpentinite derived soils (Cambisols, Leptosols) is characterized by high level of endemism (Van der Ent et al. 2018). Soils developed on peridotites (Ferralsols) are covered by rainforests, not so different from that on non-ultramafic soils. Furthermore, the vegetation cover in the Szklary Massif and Jordanów distinguishes from neighboring areas.

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