Ekológia (Bratislava) Vol. 32, No. 2, p. 211–219, 2013
doi:10.2478/eko-2013-0018

TRANSFER OF RISK ELEMENTS IN SOIL–BILBERRY SYSTEM

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Abstract

Kuklová M., Kukla J.: Transfer of risk elements in soil–bilberry system. Ekológia (Bratislava), Vol. 32, No. 2, p. 211–219, 2013.

Transfer of Al, Cr and Ni in the soil–plant (*Vaccinium myrtillus* L.) system was examined in four forest ecosystems in the localities Muráň (skeli-humic podzols) and Hliníky (dystric cambisols) in the protected zone of the NP Slovenský raj. In case of Al, the transfer coefficients were low, exceeding 1 only in the litter horizon on the damaged plot in the locality Muráň. The Al content in soils was the highest at a depth of 60–70 cm (10 249 mg kg^{-1}) on the undamaged plot in Hliníky. The amounts of Al accumulated in bilberries were higher than the background value in plants, and they made 11–22% of the maximum Al contents detected in Ooh horizons of the studied soils. Cr on the damaged plot in the locality Muráň displayed higher transfer coefficients (range 1.09–11.3) in comparison with the other plots (0.03–0.59). Considering the value representing the maximum Cr amount detected in Ooh horizon in the corresponding locality as 100%, the content of Cr in bilberries growing on the damaged plot in Muráň was 109%, in contrast to 2% on the damaged plot in Hliníky. The concentrations of Ni in soils exceeded limit values in the surface humus horizons on all studied plots. Ni displayed higher transfer coefficients, exceeding 1 only on the damaged plot in the locality Muráň. Bilberries had accumulated 6–28% Ni in the locality Muráň, and 2–6% in the locality Hliníky of the maximum amounts detected in Ooh horizons of soils. The differences in mean values of transfer coefficients for Al, Ni and Cr were statistically significant ($p < 0.05$).

Key words: forest ecosystems, acid soils, *Vaccinium myrtillus* L., risk elements, transfer.

Introduction

From Slovak regions, Central Spiš is exposed to the most severe impact of toxic and risk elements. Effects of a wide range of pollutants result in reduction of forest and agricultural production and in contamination of food chain with alien substances (Rajčáková et al., 2003; Jamnická et al., 2007; Takáč et al., 2008). Toxic and risk elements belong to the primary environmental contaminants. They are present in all components of the living environment (Píš, Nováková, 2002; Pichler et al., 2006; Janík, 2010). Unlike organic substances, they avoid chemical degradation and accumulate in soil surface layers. Their main sources are waste, fossil fuels and metallurgy. These materials may also be released from natural sources (Komanická, 2009). Their uptake into plants works through stomata or together with uptake of soil nutrients. The amount of toxic and risk elements penetrated in plants from soil is dependent on the degree of soil contamination (concentrations and forms of heavy metals), character of soil-ecological conditions, especially soil reaction values, humus content, redox state in neighbourhood of root systems in the presence of microbial decomposition of organic matter, water dynamics, temperature etc. (Makovníková et al., 2006; Kuklová, Kukla, 2006).

In this work, the extent of soil contamination induced by human activities in damaged and undamaged forest stands is evaluated. Concerned are selected risk elements and their transfer in aboveground phytomass in bilberry (*Vaccinium myrtillus* L.).

Material and methods

The research ran in four forest ecosystems on two undamaged (B, D) and two damaged (A, C) plots situated in localities Muráň (1080–1110 m asl, skeli-humic podzols) and Hliníky (950–960 m asl, dystric cambisols) in the protected zone of the National Park Slovenský raj (Kukla, Kuklová, 2008). Hemi-oligotrophic geobiocoenoses in the locality Hliníky belong to the 5-th fir-beech forest vegetation tier (fvt), geobioceone type group (gtg) *Abieti-Fageta inferiora*. The active reaction values pH_{H_2O} in this site in the surface humus layer range between 3.65 and 4.11, in mineral soil layers between pH_{H_2O} 3.55 and 4.50. The geobiocoenoses in the locality Muráň belong to the 6-th spruce-beech-fir fvt, gtg *Fageta abietino-piceosa*. The active soil reaction values pH_{H_2O} in the surface humus layer in this locality range from 3.61 to 4.52, in mineral soil layers between 3.22 and 3.75. The values of C/N ratio in separate horizons of the studied soils are in the cover humus from 33.9 to 50.7, in the surface soil horizons (2–6 cm) from 17.02 to 38.79 and in the lower situated horizons from 9.2 to 15.8. Šály (1978) reports for forest soil humus C/N values ranging between 8 and 20, with higher values indicating poorer humus quality.

There were sampled soil surface humus layers and mineral layers. The samples were air-dried and sieved with a mesh of 2×2 mm. Risk elements (Al, Cr, Ni) were evaluated according to guidelines set by the MA SR (1994) in 2M extract of HNO_3 (ratio of fine earth to 2M HNO_3 1:10, stirring for 2 hours and filtering) using an appliance Varian Spectr. AA 300/400.

Plant material was sampled randomly from 400 m^2 phytocoenological relevé plots. Green twigs growing out from creeping stems of *Vaccinium myrtillus* L. were collected. The contents of Cr and Ni in bilberry shoots were determined by microwave decomposition of plant material in AAS ETA, the content of Al with ICP AES. The input of the studied elements (Al, Cr, Ni) from soil to plant (the plant/soil transfer coefficient, TC) was calculated as the ratio between mean concentration value in plant dry mass and in soil.

Results and discussion

Amounts of risk elements in studied soils are presented in Tables 1–4. **Aluminium** is the third most abundant element in the Earth's crust, occurring at about 8% (Delhaize, Ryan, 1995). Al is either a main or secondary component of many minerals, especially of all silicates (Kabata-Pendias, 2011). This element is released from acid fallout and therefore may damage forests (Maňkovská, Oszlányi, 2010). Most aluminium is present in the crust surface, in plants it occurs in lower concentrations. Increased concentration of Al in soils with acidic or very acidic

Table 1. Content of risk elements in skeli-humic podzol in locality Muráň (damaged stand A).

Horizon	**Layer (cm)**	**Al**	**Ni**	**Cr**
		(mg kg^{-1})		
Ool	1–2	225.0	5.27	0.48
Oof	1–2	421.0	8.94	0.52
Ooh	7–8	2 482.0	18.24	1.04
Aop	2–6	862.7	1.37	0.31
E/C1	20–40	629.9	0.64	0.10

T a b l e 2. Content of risk elements in skeli-humic podzol in locality Muráň (undamaged stand B).

Horizon	Layer (cm)	Al	Ni	Cr
		(mg kg^{-1})		
Ool	1–2	473.0	10.11	0.66
Oof	1–2	1 024.0	8.80	0.88
Ooh	7–8	1 662.0	10.74	0.97
Aop	2–6	471.8	0.81	0.20
E/C1	20–40	386.6	0.53	0.02

T a b l e 3. Content of risk elements in dystric cambisol in locality Hliníky (damaged stand C).

Horizon	Layer (cm)	Al	Ni	Cr
		(mg kg^{-1} d.m.)		
Ool + Oof	2–3	374.0	10.23	0.38
Ooh	2	1 789.0	8.97	2.18
Aop	2–6	3 467.6	3.75	3.16
Bvs_1	10–20	4 825.7	2.75	3.68
Bvs_2	25–35	6 062.8	3.31	4.02
Bvs_3	40–50	6 806.8	2.27	3.38
Bvs_4	60–80	9 363.2	2.62	3.97

T a b l e 4. Content of risk elements in dystric cambisol in locality Hliníky (undamaged stand D).

Horizon	Layer (cm)	Al	Ni	Cr
		(mg kg^{-1})		
Ool + Oof	3	597.0	22.41	0.91
Ooh	2	1 588.0	9.97	1.81
Aop	2–6	3 469.2	2.19	2.02
Bvs_1	10–20	4 763.5	2.17	3.12
Bvs_2	30–50	7 109.2	2.20	4.53
Bvs_3	60–70	10 249.2	2.03	5.81
Bvs_4	60–80	9 363.2	2.62	3.97

reaction represents a serious harmful factor for plant growth (Mossor-Pietraszewska, 2001). The toxic impact of active aluminium on plants may be either direct or indirect. Aluminium causes changes to morphology of plant root system, changes in root hardness and reduction of amount of hair roots. Accumulated aluminium does not allow intake of other metals, primarily phosphorus – causing their deficit by fixing them. Contents of this element in plants vary greatly, depending on soil and plant factors. Some species of Al-accumulating plants may contain more than 1 000 mg Al kg^{-1} (Kabata-Pendias, 2011).

Aluminium content in surface humus in the studied soils was 225–2 482 mg kg^{-1} of dry matter, being somewhat higher in podzols with amounts increasing downwards – from the litter layer to horizon of humification. Maximum Al values were observed in the 7–8-cm-thick Ooh horizon of podzol on the damaged plot at the locality Muráň (Table 1). Substantially lower amounts were found in the mineral layers of podzols (387–863 mg kg^{-1}) than in less acid cambisols (3 468–10 249 mg kg^{-1}). This fact seemed connected with a very high proportion of sandy fraction in podzols (62–71%) compared to cambisols (20–42%). The Al content was the highest at a depth of 60–70 cm on the undamaged plot D (10 249 mg kg^{-1}) in locality Hliníky (Table 4) and it was substantially lower, as states for soil Al values McLean, Bledsoe (1992).

In plants Al is present in lower amounts. Plant species and even cultivars of the same species differ considerably in their ability to take up and transport aluminium, depending on plant tolerance to the Al excesses. For example, Chinese tea contains Al at levels from 676 to 1875 mg kg^{-1} (Kabata-Pendias, 2011). According to Maňkovská (1996), limit concentrations of Al in plants range between 90 and 530 mg kg^{-1} of dry matter. Uptake by plants is only possible from acid environment. Average aluminium contents in bilberries growing on studied plots ranged as follows [mg kg^{-1}]: 194 (C-plot) < 287 (A-plot) < 300 (D-plot) < 352 (B-plot) and they were 2.4 to 4.4 times higher than the background values in plant reported by Markert (1995).

Transfer coefficients can serve as indicators for element uptake by plants. In case of aluminium lower transfer coefficients were obtained, exceeding 1 only in the litter horizon on the damaged plot A, Fig. 1. The amounts of Al accumulated by bilberries made 12–22% and 11–19% in Muráň and Hliníky, respectively, of the maximum Al amounts detected in Ooh soil horizons. The values of Al transfer coefficients indicate that the element is relatively poor absorbed by *V. myrtillus* species.

Chromium and nickel are primary important trace elements. Present in excessive amounts in air, water and soil, they can lower the soil quality. Their toxicity depends on solubility, absorbance, way of transport and chemical reactivity. Present in plants, the two elements induce conspicuous toxic symptoms (inhibition of growth, altered conformation of bio-molecules, al-

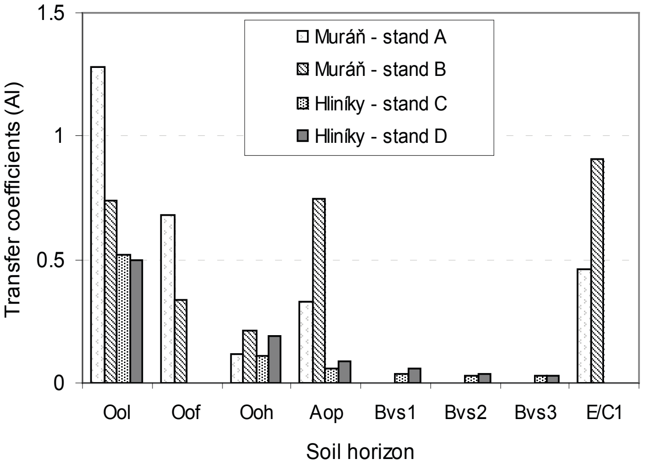

Fig. 1. Transfer coefficients for Al in the soil–bilberry system.

tered cell ultrastructure, DNA damage, disturbed metabolisms and impaired overall vitality). Chromium toxicity is dependent on oxidation grade. Especially toxic is Cr^{6+}, the transfer of which in the food chain may be considerable.

The abundance of Cr in the Earth's upper crust is about 100 mg Cr kg^{-1}. The world soil average content of Cr in soils has been established as 60 mg Cr kg^{-1}. Soil Cr is released from parent rocks, higher contents are generally found in soils derived from argillaceous sediments (Kabata-Pendias, 2011). The Report on State of the Environment in SR (ME SR, 2008) presents 24.5 mg Cr kg^{-1} at 10-cm depth for arable soils (group cambisols) in Slovakia. By Decision MA SR (1994), soils are considered contaminated if exceeding 130 mg Cr kg^{-1} of dry matter. The reference value set for chromium in 2M HNO_3 leachate is 10 mg Cr kg^{-1}. By Act No.220/2004, limit values for chromium in agricultural soil represent 50–90 mg kg^{-1}, dependent on the soil type (determined with aqua regia).

Chromium content in surface humus of the studied soils ranged 0.38–2.18 mg kg^{-1} of dry matter. Its contents in both soil subtypes increased downwards from the litter layer to the horizon of humification (Tables 1–4). In Ooh horizons of cambisols, it was higher by 50% than in Ooh horizons in podzols. Considerably higher chromium amounts were observed in mineral layers of cambisols (3.12–5.81 mg kg^{-1}) than in acid podzols (0.02–0.10 mg kg^{-1}). The soil sampled from our study plots did not display limit-exceeding chromium values. Al-Khashman, Shawabkeh (2006) observed relatively high concentrations of metals in the soil samples in an area close to a cement factory (south Jordan), while the concentration of chromium was low (6–22 mg kg^{-1}). The authors observed that Cr was mostly accumulated on the soil surface (0–10 cm); the amount found in the soil layer of 10–20 cm was much lower. This fact is not in accordance with our observations in Hliníky where the Cr contents in Dystric cambisol increased downwards to the mineral soil layers.

The most available to plants is Cr^{6+}, which is the very unstable form under normal soil condition and its availability depends on soils properties, especially on soil texture and pH. Also, Cr^{3+} and several complex Cr anions may be easily available to plants. Mean contents of Cr in cereal grains fluctuated from 0.01 mg kg^{-1} to 0.09 mg Cr kg^{-1}. Relatively high contents of Cr are accumulated in carrot (0.13 mg kg^{-1}), onion (0.16 mg kg^{-1}) and cabbage (0.13 mg kg^{-1}) (Kabata-Pendias, 2011). Cr is not essential element for plants, but plant concentrations above 5 mg kg^{-1} are according to Maciejewska-Rutkowska et al. (2007) considered toxic to plants. Maňkovská (1996) sets limit concentrations for chromium in plants 0.03–10 mg kg^{-1}. Average Cr content in bilberries growing on studied plots ranged as follows [mg kg^{-1}]: 0.05 (B-plot, C-plot) < 0.29 (D-plot) < 1.13 (A-plot). The least amounts of chromium were observed in aboveground phytomass of bilberries growing on plots B and C, the highest on damaged plot A (Muráň).

Cr on the damaged plot A (Fig. 2) displayed higher transfer coefficients (1.09–11.3), which means that it was more abundant in the aboveground bilberry biomass than in the soil. The transfer coefficients on the other plots were comparatively low. The content of Cr accumulated in bilberries made 109% on the damaged plot A (Muráň), in contrast to 6% on the undamaged plot B of the maximum Cr amounts found in Ooh horizons of podzols. The Cr amounts accumulated in bilberries growing at the locality Hliníky ranged from 2 to 16% of the maximum Cr content detected in Ooh horizons of cambisols. The values of Cr transfer coefficients in the locality Hliníky were distinctly lower than the value of 1, which indicated that Cr was relatively poorly absorbed by *V. myrtillus* species. Better ability to accumulate Cr was showed by this

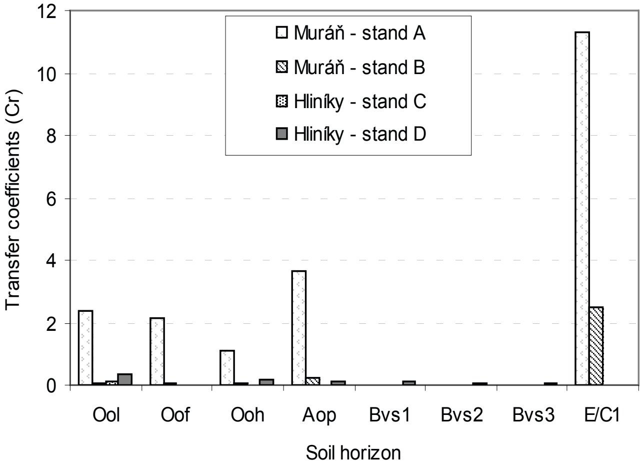

Fig. 2. Transfer coefficients for Cr in the soil–bilberry system.

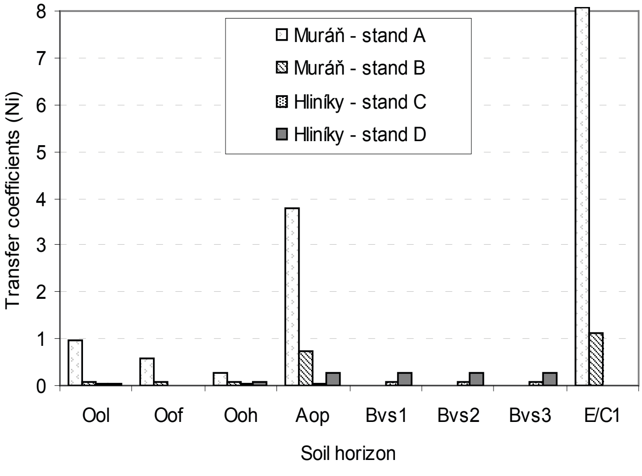

Fig. 3. Transfer coefficients for Ni in the soil–bilberry system.

plant species on the damaged plot in Muráň where the value of transfer coefficients exceeded far beyond the value of 1.

In the Earth's crust, the mean **nickel** abundance has been estimated around 20 mg kg^{-1}. The concentration of Ni in surface soils reflects the additional impact of both soil-forming processes and anthropogenic activities. Ni is quite abundant in all soil groups, with more abundant accumulation observed in cambisols and calcisols (Kabata-Pendias, 2011). The most accessible Ni forms occur in soils with pH 6.5–7.0. The Report on the State of the Environment SR (ME

SR, 2008) declares for arable soils in Slovakia (group of cambisols) at depth of 10 cm on average 9.2 mg of the total Ni kg^{-1}. The Decision by MA SR (1994) declares soil contamination at levels exceeding 35 mg Ni kg^{-1}. The reference value in determining Ni in 2M HNO_3 leachate represents 10 mg Ni kg^{-1} of dry matter. According to the Act No. 220/2004, limit values for Ni in agricultural soil in dependence on the soil type (decomposition in aqua regia) are 40–60 mg kg^{-1}. The limit (critical) value set for Ni in relation to soil and plants (leachate 1 mol L^{-1} ammonium nitrate) is 1.5 mg Ni kg^{-1}.

Ni content in surface humus of the studied soils ranged between 5 and 22 mg kg^{-1} of dry matter. (Table 1–4), being substantially higher than in the mineral layer (0.5–3.8 mg kg^{-1}). A steeper increase in Ni content (by 70%) from horizon Ool to Ooh was observed on the damaged plot A (Muráň). On undamaged plot B, Ni distribution patterns in surface humus layers were fairly uniform; on the other hand, in case of cambisols Ni content in the horizons Ool and Oof was higher than in Ooh horizon. The soil samples were compared with the reference value set for determining Ni in 2M HNO_3 leachate (MA SR, 1994). Beyond-limit Ni amounts were recorded in the surface humus horizons of the study plots. High concentrations of Ni in the organic material (5–190 mg kg^{-1}) were also observed by Uhlig, Junttila (2001) in the north-eastern part of Sør-Varanger, Norway. In general, the major proportion of heavy metals from anthropogenic sources occurs in the upper organic layer (Hazlett et al. 1984; Uhlig, Junttila, 2001) in form of salts or bound in metal–organo complexes.

Ni present in high amounts limits plant growth and suppresses its photosynthesis and transpiration. Ni limit content in plants ranges between 0.1 and 5.0 mg kg^{-1} of dry matter (Maňkovská, 1996). Markert (1995) states the upper limit of the natural range as 1.5 mg kg^{-1}. In food plants, Ni content varies from 0.06 to 2 mg kg^{-1}, with the lowest value in apples and the highest in cucumber. Average Ni contents in cereal grains from different countries vary from 0.34 to 1.28 mg kg^{-1} (Kabata-Pendias, 2011). Average Ni contents in bilberries growing on studied plots ranged as follows (mg kg^{-1}): 0.20 (C-plot) < 0.57 (D-plot) < 0.60 (B-plot) < 5.16 (A-plot).

Ni displayed higher transfer coefficients (3.7–8.1), exceeding 1 only on the damaged plot A (depth 2–40 cm) in the locality Muráň (Fig. 3). The mean values obtained on the other plots were relatively low (<0.41). Bilberry had accumulated 28% Ni on the damaged plot A (Muráň), and 6% on the parallel undamaged plot B of the maximum Ni amounts found in Ooh horizons of podzols. The Ni amounts accumulated in bilberries growing at the locality Hliníky made 2–6% of the maximum Ni content detected in Ooh horizons of cambisols. Plant/soil transfer coefficients in the locality Hliníky indicate that Ni is relatively poorly absorbed by *V. myrtillus* species. Better ability to accumulate Ni by this plant species was observed on the damaged plot in Muráň with the transfer coefficients values beyond the value of 1.

Zeidler (2005) investigated the contents of Ni in soils and plants in the alluvial plain of the Morava river. The mean values of TC for Ni in *Urtica dioica* species varied from 1.2 (root) to 2.9 (leaves), in *Taraxacum* sp. from 1.2 (leaves) to 0.6 (root), and these results were similar to ours obtained by investigation of *Vaccinium myrtillus* species growing in damaged stand at locality Muráň, where Ni displayed higher transfer coefficients, exceeding value 1.

The values of mean transfer coefficients are presented in Table 5. The differences in mean values of transfer coefficients for Al, Ni and Cr were statistically significant ($p < 0.05$). Aluminium was better accumulated by bilberry growing in locality Muráň (both stands A, B) than in the locality Hliníky ($F_{(3, 18)} = 4.2562$, $p = 0.0194$); nickel and chromium were better accumulated by bilberry in locality Muráň (stand A) than in the other stands ($F_{(3, 18)} = 3.3947$, $p = 0.0405$ nickel; and $F_{(3, 18)} = 4.8847$, $p = 0.01174$ chromium).

Table 5. Differences in mean transfer coefficients in the soil–bilberry system between forest stands (ANOVA, LSD test).

Locality	**Muráň**		**Hliníky**		**Sample size**	**Significance level (α)**
Soil	**Podzol**		**Cambisol**			
Forest stand/ risk elements	**A**	**B**	**C**	**D**		
Al min–max	0.57 ± 0.44 0.12–1.28	0.59 ± 0.30 0.21–0.91	0.13 ± 0.19 0.03–0.52	0.15 ± 0.18 0.03–0.50	22	p < 0.05 (A–C,D) (B–C,D)
Ni min–max	2.73 ± 3.29 0.28–8.06	0.41 ± 0.49 0.06–1.13	0.05 ± 0.03 0.02–0.09	0.19 ± 0.11 0.03–0.28	22	p < 0.05 (A–B,C,D)
Cr min–max	4.11 ± 4.11 1.09–11.30	0.59 ± 1.07 0.05–2.50	0.03 ± 0.04 0.01–0.13	0.14 ± 0.09 0.05–0.32	22	p < 0.05 (A–B,C,D)

Conclusion

Transfer of risk elements between soil and plants is an important component of the elements cycle in the nature. It is a process driven by a number of natural and anthropogenic factors. The final values of transfer coefficients for Cr and Ni resulted in finding that the highest average transfer coefficients (TC 4.1 and 2.7, respectively) were on the damaged plot A – Muráň. The research results allowed concluding about a strong influence of physical and chemical properties of very acidic skeli-humic podzols in the locality Muráň on input of Cr and Ni into the aboveground biomass in bilberry. On the other hand, mean transfer coefficients for Al were low on all the analysed plots (TC 0.13–0.59). In the soil samples, beyond-limit values were observed only in case of Ni in the surface humus horizons. Our research results have confirmed that the studied species accumulated risk elements, and that these elements could circulate in the soil–plant system.

Acknowledgements

We appreciate the support from the Science Grant Agency of the Ministry of Education of SR and the Slovak Academy of Sciences (project No. 2/0027/13) and by the project implementation: Extension of the centre of Excellence „Adaptive Forest Ecosystems“, ITMS: 26220120049, supported by the Research & Development Operational Programme funded by the ERDF.

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