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TRACE ELEMENTS IN THE TANNERIES ENVIRONMENT

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Abstract. Two tanneries “Elnias” and “Stumbras” have been functioning in Šiauliai (Lithuania) since XIX century. They have created heavy metal anomalies in their environment: topsoil, Talša lake, and even Kulpė river. The aim of the research was to recognise the extent of tanning influence on the surrounding environment and its changes since 1989. The repeated sampling of the topsoil was carried out in 2003 at the same 55 investigation sites as before (on the territories of the tanneries and in their nearest surroundings). Talša sediments were sampled in 1989, 1991, and 2002. All samples were analysed for total contents of a large group of elements, including Ag, B, Ba, Co, Cr, Cu, Mo, Mn, Ni, Pb, Sn, V, and Zn. Accumulated associations in topsoil of tanneries included at different time Cr>>Zn, Cu, Pb, Mo, Ni, and Sn. Associations accumulated in various time in Talša sediments were also similar, but except for the above mentioned elements they contained also Ag, Ba, Co, and V. Median additive contamination has increased in topsoil of “Stumbras” territory and in the nearest surroundings of “Elnias”. It has increased also in Talša but mainly due to essential growth of Zn and Pb pollution.

Key words: tanneries, heavy metals, topsoil, lake sediments.

Abstrakt. Dwie garbarnie „Elnias” i „Stumbras”, które funkcjonowały w Šiauliai (Litwa) od dziewiętnastego wieku, spowodowały anomalię metali ciężkich w środowisku: w powierzchniowym poziomie gleb, w jeziorze Talša i w rzece Kulpė. Celem badań było określenie zakresu wpływu garbarni na otaczające środowisko i zaobserwowanie zachodzących zmian w porównaniu do roku 1989. Powtórne opróbowanie gleb zostało wykonane w 2003 r. w tych samych 55 punktach obserwacyjnych (na obszarze garbarni oraz w ich najbliższym sąsiedztwie). Osady jeziora Talša zostały opróbowane w latach 1989, 1991 i w 2002. We wszystkich próbkach oznaczono zawartość Ag, B, Ba, Co, Cr, Cu, Mo, Mn, Ni, Pb, Sn, V i Zn. Akumulacja metali ciężkich w górnej warstwie glebowej na terenie garbarni w obu okresach badawczych obejmowała Cr>>Zn, Cu, Pb, Mo, Ni i Sn. Akumulacja w osadach jeziora Talša była podobna, jednakże oprócz wymienionych poprzednio pierwiastków obejmowała także Ag, Ba, Co i V. Zaobserwowano, że średni poziom zanieczyszczeń w glebach wzrósł w tym czasie na terenie garbarni „Stumbras” i w sąsiedztwie garbarni „Elnias”. Odnotowano także wzrost zanieczyszczenia w osadach jeziora Talša; był on spowodowany głównie wzrostem zawartości Zn i Pb.

Słowa kluczowe: garbarnie, metale ciężkie, gleby, osady jeziorne.

INTRODUCTION

The tanning industry is a potentially pollution-intensive industry: its environmental impacts originate from different waste streams (liquid, solid, and gaseous), which are produced during the hide and skin storage, and the beamhouse, tanyard, post-tanning, and finishing operations (IPPC, 2003). Therefore, it is an iłmportant pollution source of rivers, lakes, air, and soil. Tanneries in Europe usually discharge their wastewater effluents to large wastewater treatment plants, only few of them — directly to the surface water. Most of them have some form of on-site effluent treatment installed (IPPC, 2003). Of world tanneries, 80–90% use Cr (III) salts in their tanning processes and are important sources of Cr pollution. In Finland consumption of Cr compounds is as follows: stainless steel>leather tanning>metal plating>chemicals (Mukherjee,

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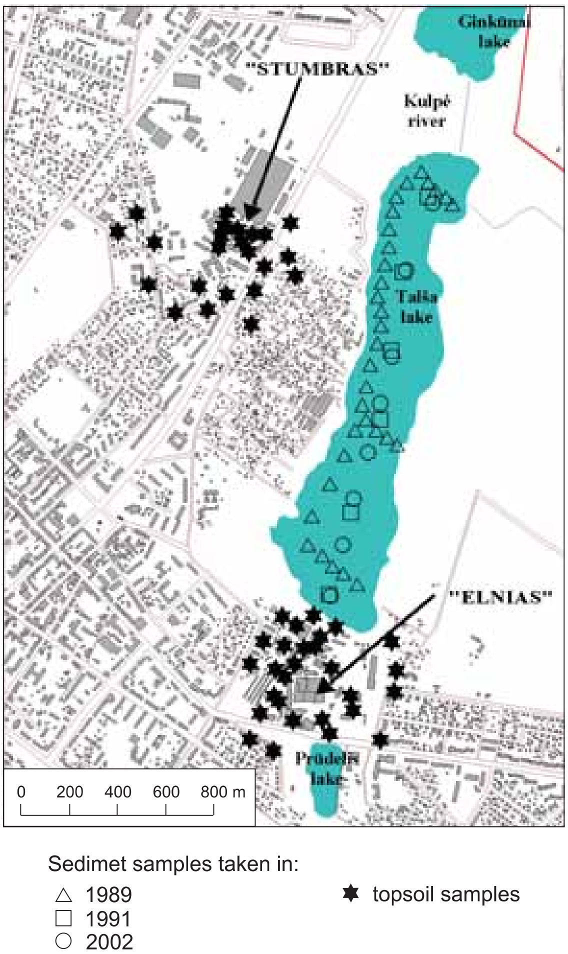

Fig. 1. Scheme of the study area

1998). Tanneries also use certain chemicals, e.g. biocides, surfactants, and organic solvents (IPPC, 2003).

Tanneries are the second largest hazardous waste generator in Lithuania, and two of them in Šiauliai generate 98.7 per cent (9,020 t) of tannery waste containing Cr (EPR, 1998). Both tanneries are near Talša (Fig. 1) which is the most heavy metal polluted lake in Lithuania (Budavičius, 2003). The same concerns the Kulpė river (Kadūnas *et al.*, 1999) which crosses Prūdelis, Talša, and Ginkūnai lakes, and falls into the Mūša river. Talša lake could have been polluted in different pathways: through industrial and municipal wastewater or rainwater discharge, surface runoff from contaminated banks of the lake or even through contaminated water inflow from Prūdelis. Industrial wastewater discharge to Talša must have decreased after construction of wastewater treatment plant in 1963. However, both tanneries could have polluted Talša since the end of the XIX century: “Elnias” was founded in 1879, and “Stumbras” in 1898. There are some more possible pathways of pollutants from “Elnias”, which is very close to the southern bank of Talša, but the rainwater from “Stumbras” territory could have also reached this lake earlier through a system of ditches. Now the impact of “Stumbras” on Talša must have decreased, because since 1986 the rainwater from its territory has been discharged to Ginkūnai lake, and because the modern water cleaning equipment was installed after 1994.

The aim of this research was to find out the extent of tanning influence on the surrounding environment (Talša lake and topsoil of the territories of tanneries and around them) and to reveal its changes since 1989, when geochemical investigations in Šiauliai started (Taraškevičius, 1994).

METHODS

Complex topsoil samples consisting of several sub-samples were taken in 2003 on the territories of the tanneries and in the nearest surroundings at the same 55 sites as in 1989 (Fig. 1). Samples of Talša sediments were taken at different sites in 1989 (32 samples), 1991 (6 samples), and 2002 (8 samples). All samples were air-dried, sieved through nylon sieves (fraction <1mm). After burning to ash at 450°C and grinding, they were analysed by DC arc emission spectrophotometry in the laboratory of the Institute of Geology and Geography for total contents of Li, B, Ga, P, Mn, Ti, V, Cr, Co, Ni, Cu, Zn, Pb, Mo, Ag, Sn, Zr, Y, Yb, Sc, Sr, and Ba. Analytical quality control of this laboratory is assured by international reference materials and participation in “International Soil Analytical Exchange” (Taraškevičius, Zinkutė, 1999).

Two additive contamination indices were calculated for both topsoil and lake sediments: Z(13) in relation to Ag, B, Ba, Co, Cr, Cu, Mo, Mn, Ni, Pb, Sn, V and Zn, and Z(7) in relation to the main pollutants (Cr, Mo, Ni, Pb, Cu, Zn, and Sn). When computing element enrichment factors in topsoil, background values of Middle Venta soil region were used (Kadūnas *et al.*, 1999), and for the lake sediments different background values were used on the base of the organic matter content (Budavičius, 2003). Data processing included computing of statistical parameters and applying Mann-Whitney U-test, and for data logarithms — cluster analysis and principal component analysis (PCA) were used. Maps were generated using Surfer surface mapping system.

RESULTS AND DISCUSSION

Increase of Z(13) median in topsoil of "Stumbras" territory as well as in "Elnias" surroundings indicates that tanneries are still hazardous pollution sources (Table 1). The growth of topsoil additive pollution on "Stumbras" territory in 2003 can be explained by the increase of production volume and involvement not only of chrome tanning but also of leather finishing.

Accumulating associations contain the same main pollutants: Cr>>Zn, Cu, Pb, Mo, Ni and Sn, which predetermine Z(13), though presently this group in topsoil of "Stumbras" has become even broader (with Mn and Co). Correlation among the most of the main pollutants, except for Ni, existed already in 1989 (Fig. 2) when they were related to organic matter, carbonates, and Mn, and were associated with Sr, Ba, Ag, and P. Correlation grew up in 2002 when the main pollutants formed obvious group in the dendrogram, indicating their common origin. The group was related to organic matter.

Close correlation between Cr and Mo in topsoil, revealed by cluster analysis (Fig. 2) and PCA, indicated that they are typical pollutants of tanneries. Other main pollutants (Pb, Zn, Cu, Sn, and Ni) are auxiliary and can be related either to technological peculiarities of tanneries (e.g. Pb to some kind of dyes) or to transport activity and weathering of building materials. Typical pollutants of tanning process have always greater (often essentially grater) median content on the territory of the enterprise compared to its surroundings, but the role of auxiliary pollutants also grows up (Table 2).

Though essentially greater content of Mo and Zn in "Elnias" territory compared to "Stumbras" was observed in 1989, but in 2003 the differences vanished indicating similarity of the pollution type. The contents of the main pollutants, except for Cr in "Elnias", and also for Cr and Pb in "Stumbras", have increased on the territories of the enterprises (Table 1). Decrease of chromium tanning volume ("Elnias") or lower emissions after installation of more effective filters in the ventilation system ("Stumbras"), as well as intensive washout from the territories of the plants could be the reasons of lower accumulation of Cr in tanneries. However, everywhere the changes in Cr accumulation are not significant.

The same concerns Mo. Accumulation of Mo, which is probably related to dyes, has increased more in "Stumbras" which is involved in the leather finishing, and less in the "Elnias" territory. Due to the growth of production volume in "Stumbras", more auxiliary pollutants (Zn, Cu, Ni) or other elements (Mn, Co) with significant increase of accumulation were revealed in the topsoil of their terri-

Table 1

Temporal variability of median enrichment factors and additive pollution indices in topsoil of the tanneries and in their nearest surroundings

	Z(13)	Z(7)	**Cr**	**Zn**	**Cu**	**Pb**	**Mo**	**Ni**	**Sn**	Mn	Co	Ag	V	Ba	B
ET1	40.04	39.56	**21.06**	**3.57**	**1.88**	**2.10**	**2.15**	**1.30**	**1.63**	0.98	0.89	1.01	0.53	1.24	0.90
ET2	40.24	38.54	**14.57**	**8.39**	**5.66**	**4.83**	**2.60**	**2.31**	**2.22**	1.14	1.10	1.08	0.99	0.98	0.90
R	1.00	0.97	0.69	2.35	**3.02**	2.30	1.21	**1.78**	1.36						
			Zn	**Cu**	**Pb**	**Cr**	**Sn**	Ag	**Ni**	**Mo**	Mn	Ba	Co	B	V
ES1	13.54	12.26	**3.56**	**2.76**	**1.91**	**3.05**	**2.12**	**1.60**	1.28	**1.45**	1.26	**1.82**	0.95	1.29	0.67
ES2	19.88	16.69	**6.87**	**3.78**	**2.67**	**1.93**	**1.78**	**1.76**	**1.66**	**1.64**	**1.36**	1.23	1.18	0.95	0.94
R	1.47	1.36	1.93	**1.37**	1.40	0.63	0.84		**1.29**	1.14					
			Cr	**Zn**	**Cu**	**Pb**	**Mo**	**Sn**	**Ni**	Mn	Co	B	Ba	Ag	V
ST1	23.28	22.10	**16.28**	**1.83**	**2.37**	**3.65**	**1.66**	**1.37**	1.27	1.00	0.83	1.04	1.18	1.17	0.73
ST2	37.09	36.28	**14.49**	**4.73**	**4.37**	**3.47**	**2.38**	**2.25**	**1.83**	**1.33**	**1.32**	0.93	0.88	0.86	0.70
R	1.59	1.64	0.89	**2.59**	**1.84**	0.95	1.43	1.65	**1.44**						
			Zn	Ag	**Pb**	**Sn**	**Cr**	**Cu**	**Mo**	**Ni**	Mn	Ba	B	Co	V
SS1	18.15	14.01	**4.69**	**2.72**	**3.32**	**2.40**	**2.72**	**2.70**	**1.62**	**1.42**	**1.30**	**1.61**	1.19	0.99	0.56
SS2	17.78	14.39	**6.65**	**3.34**	**2.44**	**2.16**	**2.11**	**1.89**	**1.73**	**1.35**	**1.30**	1.25	1.19	1.14	0.97
R	0.98	1.03	1.42		0.74	0.90	0.78	0.70	1.07	0.95					

ET1 and ET2 – "Elnias" territory in 1989 and 2003, respectively, ES1 and ES2 – "Elnias" nearest surroundings in 1989 and 2003, respectively; ST1 and ST2 – "Stumbras" territory in 1989 and 2003, respectively; SS1 and SS2 – "Stumbras" nearest surroundings in 1989 and 2003, respectively. Main pollutants of tanneries are in bold. Enrichment factors greater than 1.3 are in bold (corresponding elements belong to accumulating associations). Z(13) – additive contamination index calculated according to all 13 elements in the table, Z(7) – additive contamination index calculated according to the main pollutants, R – indices of the main pollutants observed in 2003 divided by corresponding indices observed in 1989. The values of R are in bold, when the index according to U-test has essentially ($p < 0.05$) grown up in 2003 compared to 1989.

Table 2

Temporal variability of the main pollutants of tanneries

Greater median content in:	1989	2003
“Elnias” territory than in surroundings	Cr*, Mo*, Pb, Ni, Zn	Cr*, Pb, Mo, Cu*, Ni*, Sn, Zn
“Elnias” surroundings than on its territory	Cu, Sn	—
“Stumbras" territory than in surroundings	Cr*, Pb, Mo	Cr*, Mo*, Cu*, Ni, Pb, Sn
“Stumbras” surroundings than on its territory	Zn*, Sn*, Cu, Ni	Zn

* indicates that according to U-test ($p <0.05$) the content of element is essentially greater on the study territory

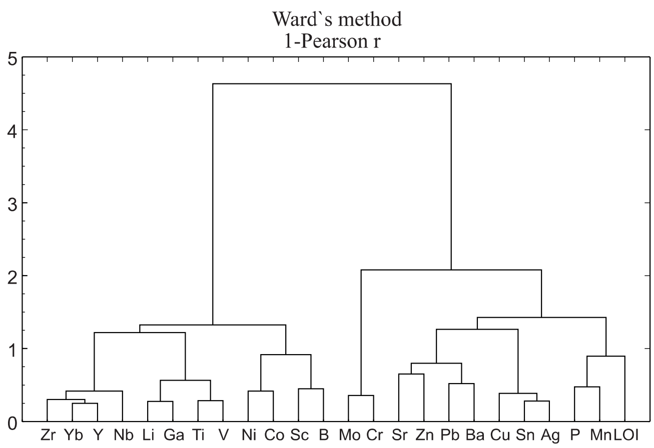

Fig. 2. Associations of trace elements and loss on ignition (LOI) in topsoil of the tanneries and their nearest surroundings in 1989

tory. Is those sites, where Z(7) grows up, very often, but not always, contamination of typical pollutants increases (Fig. 3). Increase of Z(13) in “Elnias” surroundings, in comparison with decrease of Z(13) in “Stumbras” surroundings, indicates that the first territory is affected also by other pollution sources, mostly by motor transport.

Except for the main pollutants, accumulating associations in the nearest surroundings of the tanneries contain Ag, Mn, and Ba. The contents of some main pollutants have grown up in the surroundings of tanneries. However, Cr accumulation has decreased indicating the efficacy of the environmental protection measures in enterprises.

Tanneries have obviously polluted Talša sediments because Cr is characterised by the greatest enrichment factor (Table 3) and, regarding to its content, most of the samples can be attributed to category III or II of the sewage sludge. Great part of samples belongs to category II of sewage sludge according to Ni, and presently also to Zn and Pb, which are also the main pollutants of tanneries. However, also other

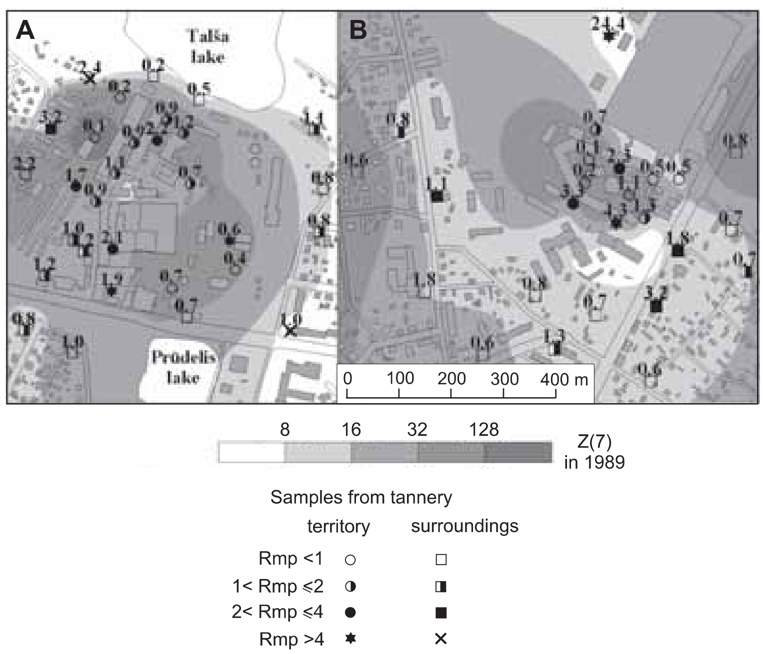

Fig. 3. Temporal change of topsoil pollution on the territories of the tanneries and in their nearest surroundings:

A – “Elnias”, B – “Stumbras”

Rmp – additive contamination index Z(7) calculated according to the main pollutants in 2003, divided by the same index in 1989. Label indicates Cr and Mo additive contamination index in 2003, divided by the same index in 1989.

Table 3

Temporal variability of median enrichment factors and additive pollution indices in Talša lake sediments

Year	Z(13)	Z(7)	**Cr**	Ag	**Zn**	**Pb**	**Ni**	**Cu**	**Sn**	V	Ba	**Mo**	Co	Mn	B
1989	47.5	37.3	**26.4**	**10.7**	3.16	**2.56**	**3.09**	**3.36**	**1.59**	0.61	1.17	**1.78**	1.09	0.94	0.71
1991	40.2	30.4	**20.3**	**9.4**	**3.06**	**1.95**	**4.14**	**2.64**	**2.70**	**1.61**	0.74	**1.83**	**1.39**	0.80	0.87
2002	60.6	40.8	**23.9**	**19.5**	**7.60**	**4.87**	**3.85**	**2.34**	**1.95**	**1.68**	**1.54**	1.11	0.90	0.66	0.57
R	1.28	1.10	0.90		**2.41**	**1.90**	1.25	0.70	1.22			0.62			

Main pollutants of tanneries are in bold. Enrichment factors greater than 1.3 are in bold (corresponding elements belong to accumulating associations). Z(13) – additive contamination index calculated according to all 13 elements in the table, Z(7) – additive contamination index calculated according to the main pollutants, R – indices of the main pollutants observed in 2002 divided by corresponding indices observed in 1989. The values of R are in bold, when the index according to U-test has essentially ($p < 0.05$) grown up in 2002 compared to 1989.

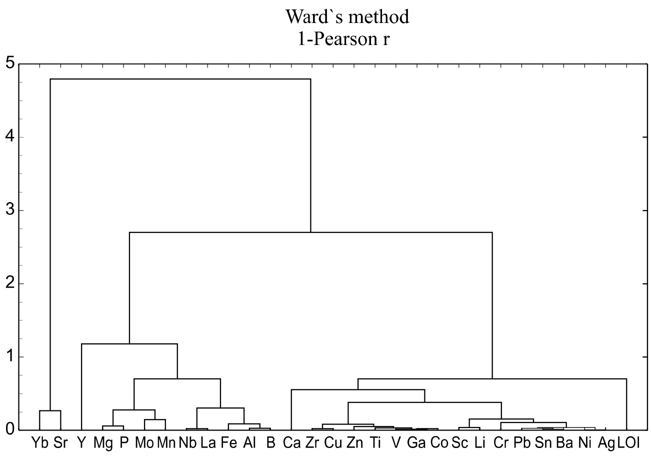

Fig. 4. Associations of the trace and major elements, and loss on ignition (LOI) in Talša lake sediments, in 2002

sources have polluted Talša because accumulating associations contain Ag, Ba, Co, and V. Due to this, and also to the different modes of their occurrence and geochemical peculiarities, the main pollutants of tanneries are not so well correlated (Fig. 4). In 2002 their greatest part, except for Mo, was related to allogenic and allogenic-accessory elements (Budavičius, 2003), less to carbonates (Ca) and to organic matter (LOI). Four elements (Cr, Ni, Pb, Sn) were associated with Ba and Ag, and could have come also with surface runoff from territories affected by transport and household pollution.

Mo is related to Mn–Fe oxides and hydroxides, and to Al. According to Z(7) median, the sediments in Talša belong to the dangerous pollution category. In 2002, both additive pollution indices have increased compared to 1989, though the contents of typical pollutants of tanneries have decreased (Fig. 5), however insignificantly, indicating that self-purification processes are not very intensive yet (greater for Mo and smaller for Cr). The same concerns Cu. Meanwhile, the contents of the most auxiliary pollutants have increased there, indicating that pollution level of Talša sediments has grown up mainly due to Zn and Pb, which

Fig. 5. Temporal change of Talša sediment contamination by main pollutants of tanneries

The label indicates additive contamination index of typical pollutants Cr and Mo divided by additive contamination index of auxiliary (Ni, Pb, Cu, Zn, Sn) pollutants of tanneries might have come with rainwater both from tanneries and from other territories, i.e. residential districts to the west of Talša.

In 2002, compared with 1989, the median enrichment factors of all the main pollutants have increased more in the southern part of the lake than in the central or northern parts, suggesting that "Elnias" still can influence it. However, in the very southern part pollution has already decreased, possibly due to the relatively clean water inflow from the Prēdelis lake. Constant maximum accumulation of Cr in the northern part of the lake is related to elevated organic matter content there.

CONCLUSIONS

The main topsoil pollutants of two old tanneries in Šiauliai are Cr>>Zn, Cu, Pb, Mo, Ni, and Sn, but only Cr and Mo are their typical pollutants; the other are auxiliary and are related either to leather finishing processes or to transport activity and weathering of the building materials. Talša lake sediments were obviously contaminated by tanneries, but also by other anthropogenic activity. The efficacy of the environmental protection measures in chromium tanning in "Stumbras" as well as decrease of the production volume in "Elnias" have lead to the slight decrease of the topsoil and lake sediment contamination by Cr, although they are still heavily polluted. Due to the finishing operations or transport activity, Mo content still increases in topsoil, but not significantly. Therefore, self-purification processes from Mo in Talša lake sediments are already taking place.

Essential increase of the Cu and Ni pollution is observed in both tanneries, also in the "Elnias" surroundings, but their changes in Talša lake sediments are not significant. The changes of Sn both in topsoil and lake sediments are insignificant. Only the contents of Zn and Pb have increased essentially in the Talša lake sediments. The content of Zn has grown up in both tanneries and their surroundings, and Pb only in "Elnias". Therefore, "Elnias" can be partly responsible for the increase of sediment contamination in the southern part of Talša, though surface runoff from other territories, i.e. residential districts to the west of Talša, might have influenced the present growth of Pb and Zn even much more.

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