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RESEARCH ARTICLE

Heavy metal distributions of macroalgal species from the Mersin inner bay, Türkiye

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ABSTRACT

The bio-accumulation of heavy metals in macroalgae poses significant risks to marine ecosystems and human health. In this study, heavy metal distributions of macroalgae and potential health risk assessment in the Mersin inner Bay were determined from macroalgae (Stypopodium schimperi, Padina pavonica, Laurencia obtusa, Dictyota sp., Sargassum vulgare, Jania rubens, Halopithys sp., Osmundea sp., Halopithys incurve, Ulva intestinalis, Entromorpha flexuosa, Ulva linza) samples collected between February and September 2021. The levels of heavy metals were found as 1.24-5.93 g/kg for aluminum, 0.61-5.26 g/kg for iron, 1.17-7.61 mg/kg for cobalt, 0.03-0.21 mg/kg for cadmium, 4.26-43.10 mg/kg for chromium, 0.28-437.52 mg/kg for cupper, 17.90-139.08 mg/kg for manganese, 2.78-79.25 mg/kg for nickel, 0.75-3.49 mg/kg for lead and 1.71-70.34 mg/kg for zinc, respectively. The potential risk assessment of macroalgal species using the calculated total cancer risk (TCR) suggested high carcinogenic risk from the carcinogenic chromium, copper and nickel (TCR>1.00E-04).

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Introduction

Coastal marine regions are adversely affected by humaninduced pressures. The development of cities along the coasts and industrialization are the main causes of anthropogenic contaminants in these ecosystems (Bouri et al., 2021; Rahhou et al., 2023). Heavy metals, one of the certain kinds of contaminants, are naturally available in aquatic ecosystems. In

order to assess heavy metal pollution in aquatic ecosystems, it is important to distinguish between anthropogenic heavy metal pollution and background levels (Akcali & Kucuksezgin, 2011). It is well known that anthropogenic and non-anthropogenic inputs into the aquatic environments will eventually accumulate in water column, sediments and organisms (Bibak et al., 2020).

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Heavy metals that accumulate in marine organisms are strongly link to metal contamination (Alkan et al., 2016; Jeong & Ra, 2022). Many marine organisms are widely used for biomonitoring studies to assess the degree of contamination due to anthropogenic pressures (Akcali & Kucuksezgin, 2011; Hao et al., 2019; Rakib et al., 2021; Jeong & Ra, 2022). Additionally, bio-monitoring studies are of critical importance since some marine organisms are used as food resources for humans due to their high content of polysaccharides, polyunsaturated fatty acids, minerals and vitamins (Jeong & Ra, 2022). It was estimated that there are 150 macroalgal species which are consumed as human food (Barrow, 2007; Mohamed & Hasan, 2023).

Mersin Bay is located at the Northeastern (NE) Mediterranean (Figure 1). Previous studies showed the development of eutrophication and sedimentary heavy metal pollution in the Mersin inner bay due to anthropogenic pressures (Akcay et al., 2022; Özbay & Akçay, 2023; Akçay, 2023; Özbay, 2024). However, only a few studies have been conducted on the distributions of heavy metals in the most common macroalgal species along the coastal areas of the Mersin Bay (Alp et al., 2012; Börekçi et al., 2021). Therefore, this study focuses on the heavy metal levels of the collected macroalgal species in the Mersin Bay.

Heavy metal pollution poses a significant threat to macroalgae and the broader marine environment. By understanding the sources and effects of heavy metals, and implementing effective monitoring and mitigation strategies, it is possible to protect marine ecosystems for ensuring the health and sustainability of our seas. The main objective of this study was to determine concentrations of heavy metals in the macroalgae samples collected from the Mersin Bay, located at the NE Mediterranean Sea. Due to the adverse health effects of heavy metals for humans (Doshi et al., 2008; Cheng et al., 2019), assessment of potential health risk due to consumption of the collected species as human food was also determined in the present study.

Material and Methods

In order to determine distributions of heavy metals [aluminum (Al), iron (Fe), cobalt (Co), cadmium (Cd), chromium (Cr), cupper (Cu), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn)] for the collected macroalgal species, 6 stations were visited along the coastal regions of the Mersin inner Bay (Figure 1). The list of macroalgal species was presented in Table 1.

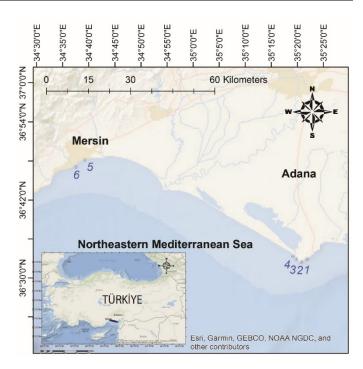


Figure 1. Study area

Table 1. The macroalgal species collected from the Mersin inner bay

Station	Macroalgae	
1	Stypopodium schimperi	
	Padina pavonica	
	Laurencia obtusa	
2	Dictyota sp.	
	Sargassum vulgare	
	Jania rubens	
3	Halopithys sp.	
4	Osmundea sp.	
	Halopithys incurva	
5	Ulva intestinalis	
6	Entromorpha flexuosa	
	Ulva linza	

Macroalgal species, obtained between February and September 2021, were collected by hand and washed by seawater. The obtained samples were put in the polyethylene bags and stored at -20°C till the analysis of heavy metals. In the laboratory, the collected macroalgae samples were dried and homogenized. Then, concentrations of heavy metals were by using Inductively Coupled Plasma Mass Spectrometer (ICP-MS -AGILENT 7850 Model) according to method described by the study of Alp et al. (2012).





Health risk of heavy metals was assessed by the calculation of Hazard Quotient through ingestion pathway (HQ_{ing}) and Total Cancer Risk (TCR) (USEPA, 2002, 2014; Magni et al., 2021; Özbay & Akçay, 2023).

Results and Discussion

Macroalgal species are good bio-indicators for the assessment of heavy metal pollution due to their high capacity for bioaccumulation (Akcali & Kucuksezgin, 2011; Hao et al., 2019; Rakib et al., 2021; Jeong & Ra, 2022; El-Mahrouk et al., 2023). There were some studies carried out to determine heavy metals contents in macroalgae of the Mediterranean coasts. However, studies performed in the Mersin inner Bay are very limited. Previous studies performed in the study region showed that concentrations of heavy metals displayed spatio-temporal variability (Alp et al., 2012; Börekçi et al., 2021). The heavy metal concentrations of the collected macroalgae samples varied between 1.24-5.93 g/kg for Al, 0.61-5.26 g/kg for Fe, 1.17-7.61 mg/kg for Co, 0.03-0.21 mg/kg for Cd, 4.26-43.10 mg/kg for Cr, 0.28-437.52 mg/kg for Cu, 17.90-139.08 mg/kg for Mn, 2.78-79.25 mg/kg for Ni, 0.75-3.49 mg/kg for Pb and 1.71-70.34 mg/kg for Zn, respectively (Table 2). It should be noted that maximum concentrations of heavy metals Co, Cr, Fe, Mn and Ni were recorded in the eastern section of the Mersin Bay for the macroalgae Stypopodium schimperi whilst the Cd, Cu and Zn contents were higher for the macroalgae Halopithys incurva, strongly suggested high bioaccumulation capacity of these macroalgal species for heavy metals.

Previous studies showed heavy metal pollution in sediments and macroalgae of the Mersin inner bay due to natural processes and anthropogenic pressures (Yalçın et al., 2013; Özbay & Akçay, 2023; Özbay, 2024; Akçay, 2023, 2024). The Ni enrichment in the Mersin inner bay is probably due to natural weathering and erosion of rocks (Yalcın et al., 2013; Akçay, 2024). It was also reported that large Cr mineral deposits and the use of pesticide and fertilizer with high Cr, Ni and Mn contents in the study region enhanced heavy metals pollution in the coastal sites of the Mersin Bay (Tuncel et al., 2007; Alp et al., 2012; Özbay, 2024). All these natural and human-induced pressures increased the concentration of heavy metals in the collected macroalgal samples from the Mersin inner bay. Furthermore, comparison of heavy metal concentrations in macroalgae along different coastal regions in the Mediterranean Sea showed that the concentrations of heavy metals Al, Cr, Cu, Fe and Mn were higher along the coastal areas of the Mersin Bay (Table 2). In the recent studies

performed in the Mersin Bay also showed that the macroalgae species has high metal contents due to anthropogenic inputs (Alp et al., 2012; Börekçi et al., 2021).

It was reported that there are 150 macroalgal species which are consumed as food resources for humans due to their high content of polysaccharides, polyunsaturated fatty acids, minerals and vitamins (Barrow, 2007; Jeong & Ra, 2022; Mohamed & Hasan, 2023). Furthermore, about 15-20 edible algae strains are marketed for food consumption in Europe (Polat & Ozogul, 2013; Ozgun & Turan, 2015). Previous studies indicated that though some macroalgal species, (Ulva sp., Entromorpha sp., Laurencia obtusa) are edible, Padina pavonica species are non-edible (Çolakoğlu & Ak, 2017; Caf et al., 2019; Tuzen et al., 2009). The studied macroalgal species collected from the Mersin inner bay is of great importance for their edibility. In the present study, therefore, health risk assessment of heavy metals for the collected macroalgae samples was determined by the calculation of HQing. and TCR. The calculated HQing. values, less than 1 indicated non-carcinogenic risk (safe for human health), while the values, greater than 1, showed carcinogenic risk. For the TCR values, a TCR value, less than 1.00E-06, indicates no significant health hazards, but a TCR value, higher than 1.00E-04, indicates high carcinogenic risk. A TCR values, varied between 1.00E-06 and 1.00E-04, suggests tolerable carcinogenic risk (Magni et al., 2021; Özbay & Akçay, 2023). The calculated values were presented in Table 3. The study findings showed that though all the calculated HQing. values were less than 1, the calculated TCR values ranged from 7.64E-09 for adults to 9.51E-03 for children (Table 3). The high values calculated for the heavy metals Cu and Ni for adults, and Cr, Cu and Ni for children (TCR>1.00E-04) strongly suggested high carcinogenic risk for adults and children. In a recent study, Akçay (2024) reported health hazards for Cr and Ni by studying heavy metals content of *Enteromorpha* sp. in the Mersin inner Bay. Therefore, all these findings suggested that the consumption of these macroalgae species from the coastal regions as human food or animal feed may cause health hazards.

Human-induced metal contamination has been experienced in the Mersin Bay with levels and sources potentially changing over time. This study revealed that regular monitoring is necessary to track these changes and assess the effectiveness of mitigation measures. Establishing a regular monitoring schedule, comparing current data with historical records, and implementing recommended measures based on the findings ensure ongoing protection of the marine environment.





Table 2. Heavy metal contents in macroalgae from the Mersin inner bay (mg/kg)

Table 2. Hea	Table 2. Heavy metal contents in macroalgae trom the Mersin inner bay (mg/kg)	trom the M	ersın ır	ner bay ((mg/kg)							
Region	Macroalgae	Al^*	Fe*	Co	рЭ	Cr	Cu	Mn	Ni	Ьb	Zn	Reference
Mersin Bay	Stypopodium schimperi	5.92	5.26	7.61	0.11	43.10	303.52	139.08	79.25	1.57	30.66	This study
coastal regions,	Padina pavonica	3.86	2.84	3.21	0.10	16.62	5.34	89.07	33.58	2.88	12.82	
Türkiye	Laurencia obtusa	3.26	2.75	2.52	0.14	16.81	4.35	82.76	13.70	2.27	8.93	
	Dictyota sp.	3.19	1.45	2.04	20.0	10.35	4.19	62.12	5.30	1.68	6.16	
	Sargassum vulgare	1.34	0.61	1.32	0.04	4.26	2.05	17.90	4.48	0.75	4.85	
	Jania rubens	1.24	0.77	1.17	0.04	5.30	0.28	28.22	2.78	1.13	1.71	
	Halopithys sp.	1.69	0.87	1.49	0.03	4.95	18.96	58.33	4.92	1.39	6.40	
	Osmundea sp.	3.40	2.15	2.12	0.14	14.30	3.01	51.72	60.6	1.77	7.98	
	Halopithys incurva	4.67	3.87	4.29	0.21	14.93	437.52	62'86	21.29	3.28	70.34	
	Ulva intestinalis	4.28	1.95	1.72	0.13	12.94	5.30	45.23	12.81	2.16	22.92	
	Entromorpha flexuosa	5.93	3.09	3.06	0.14	20.19	6.38	50.11	19.90	1.53	15.92	
	Ulva linza	5.44	2.70	2.46	0.15	17.25	8.36	64.39	20.70	3.49	59.80	
South Adriatic Sea, Italy	Ulva lactuca	1	0.34	1	0.20	1	12.07	1	1	0.84	127.27	Storelli et al. (2001)
	Entromorpha prolifera	1	0.39	1	0.72		10.33		1	1.15	58.79	
Eastern Aegean coastal regions,	Ulva sp.	1	0.128-	1	0.015-0.057	0.78 -4.78	6.49-13.90	1	1	0.001-	1	Akcali and Kucuksezgin
Türkiye	Enterophmorpha sp.	1	0.205-	1	0.013 -0.044	3.15 -9.63	4.43-13.20	1	1	0.001-	1	(2011)
	Padina pavonica	1	0.039-	1	0.018-0.148	0.73 -3.19	3.73 - 8.22	1	1	0.001-	1	
Mediterranean Sea, Mersin,	Ulva sp.	0.05	0.20	1	0.03	3.07	1.02	7.84	7.58	0.81	4.59	Alp et al. (2012)
Türkiye	Enterophmorpha sp.	0.18	0.65	1	0.03	4.02	1.65	14.62	16.77	1.04	6.42	
Mediterranean	Entromorpha prolifera	1	98.0	4.60	60.0	1.02	4.09	15.55	5.70	5.61	102.82	El Zokm et al.
Sea, Egypt	Ulva linza	_	1.54	7.83	1.04	0.85	0.28	23.34	9.16	10.82	88.19	(2021)
	Jania rubens	1	1.36	29.30	3.10	0.84	3.30	56.25	30.00	35.60	48.80	
	Sargassum vulgare	1	0.26	6.70	1.85	1.64	18.00	15.00	14.80	9.00	129.05	
	Padina pavonica	1	0.94	10.52	1.35	0.95	89.9	89.65	12.64	13.36	109.79	
Mediterranean Sea, Mersin, Türkive	Ulva rigada	0.66-1.65	,	1	1	95.96-195.65	1	88.61-224.08	1	1	- 1	Börekçi et al. (2021)
Mediterranean	Ulva lactuca	ı	0.12-	1	1	0.90-1.00	1.90-7.40	25.50-164	4.00-4.50	2.70-	8.52-	Rahhou et al.
Sea, Morocco			0.42							4.80	10.20	(2023)
Note: *I he u	Note: *The units of Al and Fe concentrations are g/kg	are o/ko										

Note: *The units of Al and Fe concentrations are g/kg





Table 3. Health risk assessment for the macroalgae from the Mersin inner Bay

HO		ADIUT									Снпр								
Station	Macroalgae	Co	Cd	Cr	Cu	Fe	Mn	ï	Pb	Zn	3	Cd	Cr	Cu	Fe	Mn	ï	Pb	Zn
1	Stypopodium schimperi	3.04E-02	1.32E-04	1.72E-02	1.82E-02	9.01E-03	1.19E-03	4.75E-03	1.34E-02	1.23E-04	3.24E-01	1 1.41E-03	1.84E-01	1.94E-01	9.61E-02	1.27E-02	5.07E-02	1.43E-01 1	1.31E-03
1	Padina pavonica	1.28E-02	1.20E-04	6.64E-03	3.20E-04	4.86E-03	7.63E-04	2.01E-03	2.47E-02	5.12E-05	1.37E-01	1.28E-03	7.08E-02	3.41E-03	5.19E-02	8.13E-03	2.15E-02	2.63E-01 5	5.46E-04
1	Laurencia obtusa	1.01E-02	1.68E-04	6.72E-03	2.61E-04	4.71E-03	7.09E-04	8.21E-04	1.94E-02	3.57E-05	1.07E-01	1.79E-03	7.16E-02	2.78E-03	5.02E-02	7.56E-03	8.76E-03	2.07E-01	3.81E-04
2	Dictyota sp.	8.15E-03	8.39E-05	4.14E-03	2.51E-04	2.48E-03	5.32E-04	3.18E-04	1.44E-02	2.46E-05	8.69E-02	2 8.95E-04	4.41E-02	2.68E-03	2.65E-02	5.67E-03	3.39E-03	1.53E-01 2	2.63E-04
2	Sargassum vulgare	5.27E-03	4.79E-05	1.70E-03	1.23E-04	1.04E-03	1.53E-04	2.68E-04	6.42E-03	1.94E-05	5.63E-02	2 5.11E-04	1.82E-02	1.31E-03	1.11E-02	1.63E-03	2.86E-03	6.85E-02 2	2.07E-04
2	Jania rubens	4.67E-03	4.79E-05	2.12E-03	1.68E-05	1.32E-03	2.42E-04	1.67E-04	9.67E-03	6.83E-06	4.99E-02	5.11E-04	2.26E-02	1.79E-04	1.41E-02	2.58E-03	1.78E-03	1.03E-01 7	7.29E-05
3	Halopithys sp.	5.95E-03	3.60E-05	1.98E-03	1.14E-03	1.49E-03	4.99E-04	2.95E-04	1.19E-02	2.56E-05	6.35E-02	2 3.84E-04	2.11E-02	1.21E-02	1.59E-02	5.33E-03	3.15E-03	1.27E-01 2	2.73E-04
4	Osmundea sp.	8.47E-03	1.68E-04	5.71E-03	1.80E-04	3.68E-03	4.43E-04	5.45E-04	1.52E-02	3.19E-05	9.04E-02	2 1.79E-03	6.09E-02	1.92E-03	3.93E-02	4.72E-03	5.81E-03	1.62E-01	3.40E-04
4	Halopithys incurva	1.71E-02	2.52E-04	5.97E-03	2.62E-02	6.63E-03	8.46E-04	1.28E-03	2.81E-02	2.81E-04	1.83E-01	1 2.68E-03	6.36E-02	2.80E-01	7.07E-02	9.02E-03	1.36E-02	3.00E-01	3.00E-03
ı,	Ulva intestinalis	6.87E-03	1.56E-04	5.17E-03	3.18E-04	3.34E-03	3.87E-04	7.68E-04	1.85E-02	9.16E-05	7.33E-02	2 1.66E-03	5.51E-02	3.39E-03	3.56E-02	4.13E-03	8.19E-03	1.97E-01 5	9.77E-04
9	Entromorpha flexuosa	1.22E-02	1.68E-04	8.07E-03	3.82E-04	5.29E-03	4.29E-04	1.19E-03	1.31E-02	6.36E-05	1.30E-01	1.79E-03	8.60E-02	4.08E-03	5.64E-02	4.58E-03	1.27E-02	1.40E-01	6.78E-04
9	Ulva linza	9.83E-03	1.80E-04	6.89E-03	5.01E-04	4.62E-03	5.51E-04	1.24E-03	2.99E-02	2.39E-04	1.05E-01	1.92E-03	7.35E-02	5.34E-03	4.93E-02	5.88E-03	1.32E-02	3.19E-01 2	2.55E-03
TCR		ADULT									CHILD								
Station	Macroalgae	Co	рЭ	·Cr	Cu	Fe	Mn	Ni	Pb	Zn	Co	Cd	\mathbf{Cr}	Cu	Fe	Mn	Ni	Pb	Zn
1	Stypopodium schimperi		6.61E-08	2.59E-05	6.18E-04			1.61E-04	1.60E-08			7.05E-07	2.76E-04	6.60E-03			1.72E-03	1.71E-07	
1	Padina pavonica		6.01E-08	90-386-06	1.09E-05			6.84E-05	2.93E-08			6.41E-07	1.06E-04	1.16E-04			7.30E-04	3.13E-07	
1	Laurencia obtusa		8.41E-08	1.01E-05	8.86E-06			2.79E-05	2.31E-08			8.97E-07	1.08E-04	9.45E-05			2.98E-04	2.47E-07	
2	Dictyota sp.		4.20E-08	6.22E-06	8.54E-06			1.08E-05	1.71E-08			4.48E-07	6.63E-05	9.11E-05			1.15E-04	1.83E-07	
2	Sargassum vulgare		2.40E-08	2.56E-06	4.18E-06			9.13E-06	7.64E-09			2.56E-07	2.73E-05	4.46E-05			9.74E-05	8.15E-08	
2	Jania rubens		2.40E-08	3.18E-06	5.71E-07			5.66E-06	1.15E-08			2.56E-07	3.39E-05	6.09E-06			6.04E-05	1.23E-07	
3	Halopithys sp.		1.80E-08	2.97E-06	3.86E-05			1.00E-05	1.42E-08			1.92E-07	3.17E-05	4.12E-04			1.07E-04	1.51E-07	
4	Osmundea sp.		8.41E-08	8.59E-06	6.13E-06			1.85E-05	1.80E-08			8.97E-07	9.16E-05	6.54E-05			1.98E-04	1.92E-07	
4	Halopithys incurva		1.26E-07	8.97E-06	8.92E-04			4.34E-05	3.34E-08			1.35E-06	9.56E-05	9.51E-03			4.63E-04	3.56E-07	
5	Ulva intestinalis		7.81E-08	7.77E-06	1.08E-05			2.61E-05	2.20E-08			8.33E-07	8.29E-05	1.15E-04			2.78E-04	2.35E-07	
9	Entromorpha flexuosa		8.41E-08	1.21E-05	1.30E-05			4.05E-05	1.56E-08			8.97E-07	1.29E-04	1.39E-04			4.33E-04	1.66E-07	
9	Ulva linza		9.01E-08	1.04E-05	1.70E-05			4.22E-05	3.56E-08			9.61E-07	1.10E-04	1.82E-04			4.50E-04	3.79E-07	
HQing.	HQ _{ing} < 1; non- HQ _{ing} ≥ 1; po carcinogenic risk carcinogenic	HQ _{ing} ≥ 1; potential carcinogenic	le	TCR<1	TCR<1.00E-06; No significant health hazards	o significa	nt health h	azards		1.00E-06 <tcr< carcinogenic="" risk<="" th=""><th><tcr< 1.0<="" th=""><th>1.00E-06 <tcr< 1.00e-04;="" acceptable="" carcinogenic="" risk<="" th=""><th>eptable</th><th>T</th><th>TCR>1.00E-04; High risk of carcinogenesis</th><th>04; High ri</th><th>sk of carcin</th><th>ogenesis</th><th></th></tcr<></th></tcr<></th></tcr<>	<tcr< 1.0<="" th=""><th>1.00E-06 <tcr< 1.00e-04;="" acceptable="" carcinogenic="" risk<="" th=""><th>eptable</th><th>T</th><th>TCR>1.00E-04; High risk of carcinogenesis</th><th>04; High ri</th><th>sk of carcin</th><th>ogenesis</th><th></th></tcr<></th></tcr<>	1.00E-06 <tcr< 1.00e-04;="" acceptable="" carcinogenic="" risk<="" th=""><th>eptable</th><th>T</th><th>TCR>1.00E-04; High risk of carcinogenesis</th><th>04; High ri</th><th>sk of carcin</th><th>ogenesis</th><th></th></tcr<>	eptable	T	TCR>1.00E-04; High risk of carcinogenesis	04; High ri	sk of carcin	ogenesis	



Conclusion

In the present study, heavy metal distributions of macroalgae and potential health risk assessment along the coastal regions of the Mersin Bay were determined. The finding of this study showed that the concentrations of Al, Cr, Cu, Fe and Mn were higher in macroalgal species in the Mersin Bay, showing high bioaccumulation of these heavy metals. Furthermore, the high TCR values for the adults and children living in the study region showed potential carcinogenic risk from the carcinogenic Cr, Cu and Ni. Continuous biomonitoring and proactive measures based on these studies are essential for safeguarding marine ecosystems and human health from the adverse effects of metal pollution.

Compliance With Ethical Standards

Authors' Contributions

- ÖÖ: Writing original draft, Formal analysis, Writing review and editing
- İA: Writing original draft, Formal analysis, Writing review and editing
- All authors read and approved the final manuscript.

Conflict of Interest

The authors declare that there is no conflict of interest.

Ethical Approval

For this type of study, formal consent is not required.

Funding

Not applicable.

Data Availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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