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Trace metals load on beached microplastics in the anthropogenically influenced estuarine environment - Croatian middle Adriatic

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Marine plastic litter can be a significant vector for ecotoxic trace metals into coastal areas. Eventually, it can be burried in sediment and in accumulated material on the beach with organic and inorganic material on its surface. In order to analyze the trace metal quantities (Cd, Cu, Pb and Zn) on different size particles in an anthropogenically affected environment, microplastics were sampled from the accumulated material on the Mala Martinska natural beach (Šibenik Bay, Croatia) in September 2019. The city of Šibenik and the Šibenik Bay are located in the lower part of the Krka River estuary (middle Adriatic). It is the main Croatian port for the phosphate ore import. Also, it was found earlier that Šibenik Bay was polluted by the ex-ferromanganese industry located in it, and the industrial slag spreading around the factory was the significant supply of trace metals in the Bay. The concentrations of dissolved and total metals in the surface seawater at the same location and at the reference point (coastal surface seawater at Jadrija, ~4 km SE from the sampling site) were determined in February and June 2020.

The collected material was sieved through a metal sieve with a 4 mesh size, resulting in 4 bulk (mixed microplastics) aliquots (> 4mm; 4-2 mm; 2-1 mm; 1-0.250 mm). From each of of the 4 bulk aliquots, subsamples of mixed plastics and polystyrene (PS) particles were isolated, resulting in 8 subsamples in total. The type of plastic particles (> 4mm; 4-2 mm and PS) was determined by FTIR spectroscopy performed on Bruker Tensor 27 in the region from 4000-400 cm^{-1}. Trace metal concentrations on such defined particles and in seawater samples were determined using differential pulse anodic stripping voltammetry (DPASV) by Metrohm Autolab modular potentiostat/galvanostat Autolab PGSTAT204, connected with a three-electrode system Metrohm 663 VA STAND (Utrecht, The Netherlands). Working electrode used was static mercury drop electrode (SMDE).

In general, the amounts of trace metals associated with the plastic particles (Cd 0.02-0.35 µg/g; Pb 1.1-34.1 µg/g; Cu 1.7-32.9 µg/g and Zn 6-147 µg/g) were in the range of unpolluted and moderately affected sediments in the Adriatic Sea. The mass fractions of all tested trace metals increase with decreasing plastic particle size, probably due to the larger specific surface areas on the smaller particles. That was not the case for the plastic particles larger than 4 mm, both in mixed and PS

samples, where the amounts of metal were higher compared to particles of 4-2 mm and 2-1 mm. Furthermore, all metals except cadmium showed a higher affinity for PS in comparison with mixed plastic samples of the same particle sizes (up to order of magnitude higher metal amounts), due to the PS highly developed specific surface area. In order to better understand the mechanism of association of trace metals with microplastics under different environmental conditions, further investigations are needed.

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