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Correlation of microplastic type and metal association: Croatian coast case study (Žirje Island)

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The aim of the study was to determine the correlation of metals on floating marine litter and weathered microplastic samples from the pristine area. Sampled were collected from the accumulated material on the natural beach in Mala Stupica Cove (Žirje Island, Croatia) in June 2020. In addition to weathered microplastic, the concentrations of dissolved metals in the seawater, at the same location were determined. According to these measurements, the sampling site can be considered pristine, with Cd and Pb concentrations as background values and Zn and Cu as elements that have no toxic effect, based on the classification proposed by Bakke et al., (2010). The metals of interest due to their high toxicity were Zn, Cd, Pb, and Cu.

After sampling, the collected material was sieved through a metal sieve with a 4 mesh size, resulting in 4 subsamples (>4 mm; 4-2 mm; 2-1 mm; 1-0.250 mm). The type of plastic particles from subsample >4 mm was determined by FTIR spectroscopy performed on Bruker Tensor 27 in the region from 400-4000 cm^{-1}. On such defined particles and in the seawater sample, trace metal concentrations were determined by the electrochemical method differential pulse anodic stripping voltammetry (DPASV) with standard addition method by Metrohm Autolab modular potentiostat/galvanostat Autolab PGSTAT204. A static mercury drop electrode (SMDE) was used as the working electrode.

Plastic particles were isolated from additional two fractions (2-1 mm and 1-0.250 mm) as bulk samples, but without polystyrene, and the metal concentration was also determined using the same method. Due to the particle size, the type of plastic was not determined. Additional analyzes of metal concentrations on a defined and isolated polystyrene particles (PS) from a subsample (4-2 mm) and (2-1 mm) were also performed.

By analogy with sediment particles, one would expect smaller microplastic particles to have higher metal concentrations due to their larger specific surface area, but this was not observed in this study. The metal concentration varied with the type of plastic, and from the observed results, plastics could be ranked according to their affinity for the analyzed metals, as follows: polystyrene (PS)>Polypropylene (PP)>Low-density polyethylene (LDPE). According to an average concentration of all analyzed samples defined as LDPE, Zn could be single out as an element with around 7-time higher affinity for LDPE than other elements (Cd, Pb, and Cu). For samples defined as PP, the

highest affinity is observed for Pb, even 30 times higher than in LDPE, followed by Zn and Cu, while Cd has similar values as in LDPE. For PS samples affinity of all elements is higher in comparison with the LDPE and PP, as follows: Pb>Cu> Zn>Cd, with a concentration of Pb 2.5 times higher than in PP and even 88 times higher than in LDPE.

A general conclusion could be drawn, but the observed wide ranges indicate the need for additional research to determine the relationship between the degree and type of weathering with the associated metals.

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