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Molecularly imprinted polymers for the pre-concentration of polar organic micropollutants for compound-specific isotope analysis

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Compound-specific isotope analysis (CSIA) is a promising tool for assessing transformations of polar organic micropollutants such as pesticides, pharmaceuticals and consumer chemicals in aquatic systems. There are, however, two major challenges: (1) Polar organic micropollutants occur at very low levels and, as a consequence, large amounts of water are required to achieve analyte enrichment with factors of 50'000 and more, inevitably leading to large interferences from the aqueous matrix. (2) The polarity of these micropollutants impedes the use of typical non-polar sorbates for solid-phase enrichment.

In view of these challenges, the use of molecularly imprinted polymers (MIP) is a promising approach to produce tailor-made materials for highly selective enrichment of polar organic micropollutants with reduced matrix interferences. In this work, we explore the use of MIP to selectively enrich benzotriazoles, an important class of polar aquatic micropollutants. Polymers were synthesized in the presence of 5,6-dimethyl-1H-benzotriazole as a template, which leaves cavities in the polymer matrix with a very high affinity to the template and closely related structures including our main target analyte, 1H-benzotrizole. After extraction of the template, specific recognition of substituted benzotriazoles is expected by the synthesized MIPs. As the MIP has no specific affinity to the matrix, there is also expected to be negligible enrichment of the matrix.

Retention factors of the MIP are compared for different synthetic procedures and to non-imprinted polymers where no specific intermolecular interactions with benzotriazoles are expected. Optimum performance of the MIP is demonstrated in this study in terms of the selectivity of enrichment, recoveries of analytes and the goodness of carbon and nitrogen isotope ratios measured by gas chromatography isotopic ratio mass spectrometry (GC/IRMS). This approach will enable us to enrich large amounts of aqueous samples while minimizing interferences from organic matter and other organic pollutants in the sample matrix and thus offer new perspectives for CSIA of polar organic micropollutants.