

Polar Organic Chemical Integrative Sampler (POCIS) Allows Compound Specific Isotope Analysis of Substituted Chlorobenzenes at Trace Levels

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Background/Objectives. Compound specific isotope analysis (CSIA) is an established tool to demonstrate in situ degradation of traditional groundwater contaminants at heavily contaminated sites, usually at mg/L range aqueous concentrations. Our objective was to develop methods to apply CSIA at low concentrations of two groups of contaminants, NH₂- and NO₂-substituted chlorobenzenes that are used in the production of various chemicals, e.g., dyes, pesticides, and explosives. Currently, an efficient preconcentration method is lacking to expand CSIA to low aqueous concentration environmental samples.

Approach/Activities. We evaluated the potential to combine a type of passive integrative sampler, POCIS, with CSIA. POCIS (i.e., polar organic chemical integrative sampler) are widely used to monitor the presence of trace organic contaminants in water, e.g., pesticides. It consists of a sorbent sandwiched between two polyethersulfone membrane. Contaminants in the water diffuse through the POCIS membrane and adsorb on the sorbent during the deployment period of POCIS in water, i.e., a few weeks. The POCIS retrieved from the water are then extracted in the lab for concentration analysis. In this work, we also tested them for CSIA, to evaluate if the original isotope signatures of target compounds were preserved.

Results/Lessons Learned. We demonstrated the compatibility of POCIS with CSIA of C, H, and N isotopes for four NH₂- and NO₂-substituted chlorobenzenes at low µg/L. Diffusion and sorption showed insignificant carbon isotope fractionation (<0.7‰) in laboratory experiments, except for a reproducible shift of 1.6‰ for 3,4-dichloronitrobenzene. A similar constant reproducible shift of 0.8-2‰ was evident for N-CSIA. The compatibility of POCIS for H-CSIA seems to be analyte specific possibly reflecting the adsorption mechanism to POCIS by H-bonding. The performance of the POCIS-CSIA method was evaluated in a pilot constructed wetland where comparable C- and N-CSIA results were obtained from grab sampling and POCIS. This work allows to obtain reliable stable isotope signatures of contaminants at low concentrations, e.g., after a large fraction of the original contaminant was degraded. This is critical to accurately calculate the extent of transformation. Our results also open the potential of CSIA application to the low concentration polar emerging contaminants in the environment, such as pesticides, pharmaceuticals, and flame-retardants.