



Potential of isotope analysis (C, Cl) to identify dechlorination mechanisms

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Chloroethenes are commonly used in industrial applications, and detected as carcinogenic contaminants in the environment. Their dehalogenation is of environmental importance in remediation processes. However, a detailed understanding frequently accounted problem is the accumulation of toxic degradation products such as cis-dichloroethylene (cis-DCE) at contaminated sites. Several studies have addressed the reductive dehalogenation reactions using biotic and abiotic model systems, but a crucial question in this context has remained open: Do environmental transformations occur by the same mechanism as in their corresponding *in vitro* model systems? The presented study shows the potential to close this research gap using the latest developments in compound specific chlorine isotope analysis, which make it possible to routinely measure chlorine isotope fractionation of chloroethenes in environmental samples and complex reaction mixtures.^{1,2} In particular, such chlorine isotope analysis enables the measurement of isotope fractionation for two elements (i.e. C and Cl) in chloroethenes. When isotope values of both elements are plotted against each other, different slopes reflect different underlying mechanisms and are remarkably insensitive towards masking.

Our results suggest that different microbial strains (*G. lovleyi* strain SZ, *D. hafniense* Y51) and the isolated cofactor cobalamin employ similar mechanisms of reductive dechlorination of TCE. In contrast, evidence for a different mechanism was obtained with cobaloxime cautioning its use as a model for biodegradation. The study shows the potential of the dual isotope approach as a tool to directly compare transformation mechanisms of environmental scenarios, biotic transformations, and their putative chemical lab scale systems. Furthermore, it serves as an essential reference when using the dual isotope approach to assess the fate of chlorinated compounds in the environment.