Application of CSIA in 1,4-Dioxane Studies: Latest Developments

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Background/Objectives. Given the widespread occurrence of 1,4-dioxane in groundwater and its reputation for recalcitrance, compelling evidence for 1,4-dioxane degradation is needed, and in areas with multiple sources, forensic tools can be important. Compound-specific isotope analysis (CSIA) is a powerful method for demonstrating the degradation of many chemicals of concern (COC) and for discerning COC sources. However, application of CSIA towards 1,4-dioxane has not been widely applied because of the following limitations:

1. Most 1,4-dioxane plumes are relatively dilute (e.g. 10 micrograms per liter; µg/L) with concentrations too low for CSIA.
2. The enrichment factors for carbon and hydrogen isotopes are not well known for aerobic biodegradation.
3. To our knowledge, the range in carbon- and hydrogen-isotopic composition of "undegraded" 1,4-dioxane (as manufactured solvent and in groundwater) has not been well defined (one paper published to date), making interpretation of carbon and hydrogen isotopic composition of 1,4-dioxane difficult.

The objective of this work is to solve the limitations described above.

Approach/Activities. The three limitations discussed above were addressed by:

1. Developing a method to provide reliable CSIA of 1,4-dioxane at concentrations as low as 1 µg/L. This was accomplished by using a synthetic carbonaceous adsorbent to concentrate 1,4-dioxane from dilute aqueous solutions onto the sorbent, followed by thermal desorption and gas chromatography – isotope ratio mass spectrometry for analysis carbon and hydrogen isotope ratios.
2. Determining the enrichment factors for carbon and hydrogen isotope ratios during aerobic cometabolic degradation of 1,4-dioxane in reactions using pure cultures of *Rhodococcus rhodochrous* ATCC 21198 grown on either propane or isobutane or a culture of *Pseudonocardia tetrahydrofuranoxidans* K1 grown on tetrahydrofuran.

Analyzing groundwater samples from 5 different sites; two of the sites have active 1,4-dioxane bioremediation systems (propane and oxygen addition).

Results/Lessons Learned. The three different cultures all degraded 1,4-dioxane with enrichment in heavier carbon and hydrogen isotopes that closely followed the Rayleigh model. The enrichment factors for the three different cultures were different, although deuterium enrichment was consistently much higher than carbon-13 enrichment. The culture grown on THF demonstrated the strongest deuterium enrichment. The results demonstrate the importance in analyzing carbon and hydrogen isotope ratios for demonstrating biodegradation, as it is more difficult to conclusively demonstrate biodegradation with carbon isotope ratios alone. Groundwater samples from five sites were analyzed using the new CSIA method. At four of the five sites, the isotopic composition of 1,4-dioxane in groundwater samples was "more enriched" than the published range for undegraded 1,4-dioxane; this includes the two sites undergoing aerobic cometabolic bioremediation of 1,4-dioxane. This research, funded by the Strategic Environmental Research and Development Program (SERDP), has greatly advanced the applicability of CSIA to 1,4-dioxane for demonstrating biodegradation and for forensic purposes.