



A new method for stable carbon isotope analysis of chlorofluorocarbons in contaminated groundwater

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Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) have been widely used as refrigerants, propellants, solvents, foaming agents and are important intermediates in the production of anesthetics and other fluorinated compounds. Due to their ozone depletion potential, production was banned for most uses under the Montreal Protocol (1987) and its amendments and atmospheric mixing ratios have started to decrease. In addition to the atmosphere, CFCs and HCFCs have been detected in groundwater, and emissions from various sources such as landfill sites are still ongoing.

Previous studies have shown that both abiotic and biotic transformation of CFCs may occur under certain conditions. To investigate degradation that may take place in soils and groundwaters, a purge and trap method (P&T) has been developed to measure the stable carbon isotopic composition of CFCs and HCFCs extracted from waters. A set of pure phase working standards (HCFC-22, CFC-11, CFC-113) has been prepared offline and characterized by sealed tube combustion dual inlet mass spectrometry. Comparison between isotopic standards and CFCs extracted by our method demonstrates the sample P&T extraction steps do not induce significant $\delta^{13}\text{C}$ fractionation (<0.5 per mill). Standards characterized by continuous flow CSIA (compound specific isotope analysis) after extraction agree with offline characterized values.

Evaporation experiments were carried out to investigate any isotope effects due to volatile loss that might occur either due to sampling methods or sample handling in the lab. Monitoring $\delta^{13}\text{C}$ values during progressive evaporation showed small isotopic fractionation associated with evaporation. Enrichment factors, obtained from Rayleigh plots, showed inverse isotope fractionation i.e depletion in ^{13}C in the remaining compound. Notably, this effect is in the opposite direction to the fractionation (^{13}C enrichment) that is likely to be associated with abiotic or biotic transformation effects. This bodes well for the use of CSIA to identify and monitor transformation in the field as any isotopic effects due to volatile loss would only result in a conservative estimate of transformation but not confuse the degradation signal. As a result, enrichment factors in field samples might be underestimated and lead to a more conservative estimate of degradation at contaminated sites.

CFCs from several suppliers were characterized to investigate $\delta^{13}\text{C}$ variation between sources and between different CFC compounds. Significant differences were observed between all measured compounds. However for each compound, $\delta^{13}\text{C}$ values determined in this study were similar to ranges reported previously for other pure phase CFCs – suggesting a consistent range of source signatures may exist for each compound. As a last step of method evaluation, water samples from a contaminated industrial site were measured. This first preliminary field data will be discussed in comparison to pure phase compounds and with respect to potential degradation.