Minimizing influences of adsorption/desorption processes of analytical systems on isotope ratio measurements

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Measurements of carbon and oxygen isotopes of CO_2 by continuous flow IRMS (isotopes ratio mass spectrometry) is widely used in environmental studies and climate change research, e.g. we are measuring $\delta^{13}C$ on CO_2 in air from the Dome C ice core. Yet there are problems associated with the reproducibility, in particular for small sample sizes. Namely, potential fractionations in the open-split and difficulties in understanding the non-linearity effect are affecting the results. A method is presented how these fractionations in the open-split can be eliminated. The non-linearity effect is explained by adsorption/desorption processes in the ionisation chamber or its vicinity and is independent on the open-split settings and on the ion source settings. It is just dependent on the amount of CO_2 entering the ion source. The non-linearity can be eliminated by a small additional flux of a specific conditioning gas. For the adsorption process in the mass spectrometer we found a fractionation factor of 0.982 ± 0.005 for $\delta^{13}C$ and 1.002 ± 0.004 for $\delta^{18}O$, respectively.

Tracing transformation of organic groundwater contaminants by stable isotope fractionation

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Isotope methods are indispensible for sustainable use of groundwater. Traditional analysis of ^2H, ^{18}O and ^3H in water serves to assess groundwater infiltration. The advent of gas chromatography – isotope ratio mass spectrometry (GC-IRMS) has made it possible to trace origin and degradation of single organic groundwater contaminants at low concentrations. A recent US-EPA guide details how isotope ratios of the contaminants may serve as fingerprints to allocate different sources, and how increasingly positive isotope values downstream of a contamination source can show how much of the contaminant has been degraded [1].

Enrichment of heavy isotopes (^{13}O ^2H, ^{15}N) in the remaining compound depends on underlying characteristic kinetic isotope effects during (bio)chemical transformations. My work has shown how such enrichment trends may be used to identify also degradation pathways and mechanisms by which a contaminant is transformed [2]. In particular, if changes in isotope ratios are measured for more than one element and drawn in a dual isotope plot, characteristic trends can make different transformation pathways visible [3, 4].

While past studies have focussed on point source pollutants, future challenges lie in addressing also diffuse contaminants like pesticides. For these new compounds, precise and accurate GC-IRMS methods need to be established [5]. Also, natural concentrations are lower so that non-fractionating enrichment and purification methods are warranted. Finally, source-related isotope patterns need to be distinguished from degradation-related trends. To this end, information from one isotope is generally not sufficient. For isoproturon we show that multi-element (^{13}C, ^{15}N) as well as intramolecular isotope analysis of different molecular fragments provides enhanced information that enables a detailed mechanistic study of transformation reactions [6].

[1] Hunkeler *et al.* (2008) *EPA 600/R-08/148*. [2] Elsner *et al.* (2005) *Environ. Sci. Technol.* **39**, 6896-6916. [3] Zwank *et al.* (2005) *Environ. Sci. Technol.* **39**, 1018-1029. [4] Elsner *et al.* (2007) *Environ. Sci. Technol.* **41**, 5693-5700. [5] Meyer *et al.* (2008) *Environ. Sci. Technol.* **42**, 7757-7763. [6] Penning *et al.* (2008) *Environ. Sci. Technol.* **42**, 7764-7771.