**Fingerprinting and marker identification of fracking fluids in contaminated natural waters with ultra-high resolution mass spectrometry.**

Oliver J. Lechtenfeld1,2, Hans H. Richnow2,3, Thorsten Reemtsma1

1 Helmholtz Centre for Environmental Research - UFZ, Department of Analytical Chemistry, Permoserstraße 15, 04318 Leipzig, oliver.lechtenfeld@ufz.de, thorsten.reemtsma@ufz.de

2 ProVIS – Centre for Chemical Microscopy

3 Helmholtz Centre for Environmental Research - UFZ, Department Isotope Biogeochemistry, Permoserstraße 15, 04318 Leipzig, hans.richnow@ufz.de

The exploitation of unconventional gas and oil resources poses major environmental management and regulatory challenges for policy makers and jurisdiction. However, significant research gaps have been recognized and addressed [1]. This comprises the monitoring of chemicals used in fluids for drilling and hydraulic fracturing (fracking fluids), their transformation products as well as geogenic compounds mobilized by the fracturing process. Such compounds have to be monitored in flowback and produced waters but also in treated waters and groundwaters. Potential hydraulic fracturing related contaminations and natural baseline conditions need to be individually assessed in official approval procedures. Existing and planned monitoring programs typically involve isotope and biomarker analysis of gases (methane and n-alkanes), trace metals and radionuclides to track the release from the producing or intermediate zone in conjunction with baseline data prior to the well drilling. Malfunction scenarios of hydraulic fracturing wells include leakages of flowback and produced waters during and after the exploitation or spills of treatment waters that may either affect surface water or groundwater bodies. However, the composition and transformation products of organic chemicals used in fracking fluids and a thorough assessment of their ecosystem toxicity are not adequately reflected in previous research.

Ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is an ideal tool to study the composition of organic molecules in aqueous samples, such as surface and groundwater. Compounds with a wide range of chemical properties, even in highly saline samples, can be analyzed with only little sample pretreatment. The high mass resolution provided by this instrument (1,000,000 at m/z 400) further allows for identification of compounds within a matrix of naturally present organic compounds. Identification and tracking of specific chemical markers for hydraulic fracturing operations, of metabolites and fingerprinting of contamination sources are within the range of application for this technique in future monitoring programs.

We demonstrate the applicability of FT-ICR MS for fingerprinting of fracking fluids in natural waters. These fingerprints may help to track the sources and spill sites of chemicals used in fracking fluids. Biodegradation experiments suggest that native bacterial communities are able to selectively utilize compounds in produced waters [2]. Therefore, degradation experiments need to accompany the high resolution fingerprinting for validation purposes and assessing the potentials of bioremediation and water treatment systems. Potential marker chemicals in fracking fluids may thus be identified and used for further targeted analysis of their (bio-) transformation and toxicity.

1. Vengosh, A., et al., *A Critical Review of the Risks to Water Resources from Unconventional Shale Gas Development and Hydraulic Fracturing in the United States.* Environmental Science & Technology, 2014. **48**(15): p. 8334-8348.

2. Strong, L.C., et al., *Biodegradation in Waters from Hydraulic Fracturing: Chemistry, Microbiology, and Engineering.* Journal of Environmental Engineering, 2014. **140**(5).