2013 ASMS Workshop Report

Interest Group Name: **Environmental MS Interest Group**

Workshop Title: **Emerging Contaminants in Environmental Research: Hydraulic Fracturing Fluids and Shale Gas Produced Waters - Advances, Challenges and Opportunities using Mass Spectrometry**

Presiding**: Kerry M. Peru (Environment Canada), Susan Richardson (US EPA) and Xing-Fang Li (University of Alberta)**

Date: **June 12, 5:45-7:00 pm**

Estimate Attendance: **150**

Summary of Program and Discussion

The 2013 Environmental Interest Group Workshop discussed the challenges facing the environmental laboratory with emphasis on mass spectrometry analysis of emerging contaminants. The objective of the Workshop was to discuss new contaminants, analytical strategies and research opportunities. This year's workshop focused on emerging contaminants relating to hydrofracking, shale gas produced waters and oilsands related environmental analysis all of which are in the forefront of environmental concern and political spotlights. Discussions were centered on how mass spectrometry can be used to fill the need of identifying and monitoring these contaminants.

The Workshop highlighted two areas of water issues and research opportunities, including (1) emerging contaminates associated with hydraulic fracturing of natural gas wells and their analysis by mass spectrometry, (2) feasibility of using membrane introduction mass spectrometry (MIMS) for the rapid analysis of oil sand produced water and shale gas produced waters. The workshop was a success with approximately 150 participants who had extensive discussions and provided suggestions and comments for the future research relating to this significant environmental challenge.

Kerry Peru opened the Workshop be giving a quick overview of the environmental significance and concerns relating to hydrofracking operations. Significant amounts of water which includes a mixture of additives that make up ~10% of the fracture fluid composition are used during the gas well fracturing process. It is these additives that require further investigation to determine their fate, transport and impact on the environment.

Patrick DeArmond (US EPA ORD/NERL/ESD, Las Vegas, NV), presented background information on hydrofracking along with a overview of the research done to date on this subject by his lab.

In his overview presentation entitled "Analytical Methods for the Determination of Analytes in Hydraulic Fracturing Fluids" Patrick introduced EPA's approach to analytical method development within the scope of the EPA's Study of Hydraulic Fracturing and Its Potential Impact on Drinking Water Resources. A brief introduction of the hydraulic fracturing process, provided an overview of the research questions asked within the study as they relate to analytical methods development, and provided insight into some of the analytical challenges faced for the determination of certain chemicals used during the process of hydraulic fracturing. Specific examples of techniques and method development from the EPA's Environmental Sciences Division in Las Vegas were also briefly introduced. Mass spectrometry-based methods include work performed on chemicals such as glycols, ethoxylated alcohols, and acrylamide.

The described work with glycols gave insight into the combination of different standard methods to produce a new method for the analysis of di-, tri-, and tetraethylene glycol, in addition to 2-methoxyethanol and 2-butoxyethanol, and the efforts of a multi-laboratory study to verify the method. Work with ethylene glycol and poly(ethylene glycol) was discussed. A new method for the determination and quantitation of acrylamide, a friction reducer used during hydraulic fracturing was also introduced. Last, work with ethoxylated alcohols and ethoxylated alkylphenols, common surfactant molecules, were described. Common analytical challenges for ethoxylates include contamination issues, i.e., the ubiquitousness of ethoxylates, the stabilities of the ethoxylated compounds, and the lack of certified standards, and workarounds of these challenges were further discussed by the group.

Chris Gill, (Applied Environmental Research Laboratories (AERL), Vancouver Island University) presented an overview entitled “Membrane Introduction Mass Spectrometry” and its applications in the area of fracking fluids and oil sands processing water analysis. Membrane introduction mass spectrometry (MIMS) uses a semi-permeable membrane to transfer analyte mixtures directly to a mass spectrometer from complex samples. Analytes are transported from membrane interface by an acceptor phase which can be either gaseous or condensed (liquid), allowing the implementation of the full range of mass spectrometer types as well as ionization methods. With MIMS, sample preparation and chromatography steps are obviated, and potential problems observed with flow injection (e.g. dilute & shoot) such as ionization suppression are mitigated. Analytes are directly detected and quantified at ppb-ppt levels based on their unique m/z or by tandem mass spectrometric methods. Samples can be gaseous, liquid or slurry, as long as they can be brought in contact with the membrane interface of the MIMS system. Additionally, the transfer of analytes across the membrane is continuous, and therefore MIMS is ideally suited to on-line, real time monitoring scenarios. If a MIMS system is operated with a portable mass spectrometer, the ability to achieve geo-spatially and temporally resolved data is achievable.

The methods of both gaseous acceptor phase MIMS (GP-MIMS) and condensed (liquid) acceptor phase MIMS (CP-MIMS) were presented with examples. In work by the AERL, GP-MIMS has been implemented as a real-time, geospatially resolved monitoring approach for trace atmospheric contaminants. Examples include the real time, in-field detection of VOC and SVOC molecules associated with industrial activities related to oil extraction and processing in Alberta, Canada. The applicability of GP-MIMS for in-field monitoring of VOC/SVOC atmospheric emissions and water measurements associated with hydraulic fracturing hydrocarbon extraction was discussed, as there are many possible point source emissions associated with this methodology. In addition, a mobile, real-time GP-MIMS system was used in the field to inform intelligent, adaptive sampling for a field sampling campaign utilizing off-line, canister sampling and subsequent GC-MS analysis at ppt levels.

Mobile MIMS measurements have been successfully employed to target when and where to collect discrete grab samples and improve data coverage and sampling efficiency. The direct comparison of the MIMS and canister measurement studies was favorable, although the canister – MIMS results showed variations at times, consistent with the high degree of analyte concentration variability measured in real time by the MIMS system. Future work by Chris’s group will include field monitoring studies associated with fracking operations, which typically display a high degree of spatial and temporal variability.

In addition to the GP-MIMS atmospheric monitoring work presented, CP-MIMS was presented and examples given for the direct detection of low volatility aqueous contaminants. In particular, the detection and direct, on-line, quantitative measurement of naphthenic acids in aqueous samples was presented. These species are part of the complex suite of aqueous contaminants associated with oil sands process waters, and are emerging as an important environmental concern. Discussions in the workshop included the detection of a wide range of low volatility analytes in ‘produced’ fracking waters. Because CP-MIMS

is capable of performing direct measurements in highly complex matrices (e.g. high salt content, high DOC etc.) without sample work up and handling, the extension of CP-MIMS to the characterization of other low volatility analytes in aqueous samples associated with fracking is anticipated. Chris is interested in exploring the continued development and application of MIMS related to environmental and process monitoring related to hydraulic fracturing, heavy oil extraction and hydrocarbon processing/transportation.

Discussions continued immediately following the Workshop at The Local restaurant with 35 Interest Group participants attending.