2014 ASMS Workshop Report

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

Workshop Title: **Environmental Impacts and Implications of Hydrocarbon Extraction and Processing – The Role of Mass Spectrometry**

Presiding: **Kerry M. Peru (Environment Canada), Chris Gill (Vancouver Island University)**

Date: **June 17, 2014 5:45-7:00 pm**

Estimate Attendance: **115**

Summary of Program and Discussion

The 2014 Environmental Interest Group Workshop discussed:

The rapid expansion of hydrocarbon extraction, production and processing from nonconventional sources such as shale gas and oil sands has led to the need of determining the industry's impact on the environment by characterizing and monitoring associated contaminants. This year's Workshop was a continuation of last year's topic which drew considerable interest. Updates on analytical methodologies used for monitoring, identification and characterization of contaminants were discussed along with an update of the state of the industry from an environmental perspective. Three invited speakers gave short presentations that acted as catalysts for further discussion.

Frank Dorman (Penn State University) presented am excellent environmental forensics review relating to the range of potential contaminants specifically associated with hydraulic fracturing for natural gas extraction in the state of Pennsylvania. Discussions followed regarding the environmental concerns and impact of this industrial process and how mass spectrometry plays a critical role.

Tammy Jones-Lepp (USEPA) gave a short presentation entitled "Environmental Forensic Research Directed towards Emerging Contaminants. Her presentation encompassed the story of two different environmental emergency response situations, and the use of mass spectrometry to help resolve relevant unknowns present. The first example pertained to 2010 Gulf Oil Spill, and how many different types of mass spectrometric techniques were used to reverse engineer the major chemical used to control the spill (dispersants) within a 24-hour time-frame. This quick determination was only possible through the use of various mass spectrometric techniques, i.e., gas chromatography, liquid chromatography, low resolution and high resolution/accurate mass - mass spectrometers. All mass spectrometric techniques were necessary in order to ensure an accurate understanding of the chemical(s) used to control the oil spill. The second example examined four major fish kills events in the Oklahoma Red River. In this emergency response situation, low resolution LC-ion trap mass spectrometry technology was used to prescreen and then perform MS/MS experiments on the most significant chromatographic peak(s). However, a high-resolution time-of-flight mass spectrometry (TOFMS) had to be used to obtain a more accurate formula and hypothesized structure for the major chromatographic unknown. Ultimately though, it took the use of a Fourier transform ion cyclotron resonance mass spectrometer to determine accurately the structure of the major unknown contaminant.

Nicola Watson (Markes International) gave a short presentation entitled "Scratching beneath the surface of hydraulic fracturing". Her presentation discussed the widespread surge in shale hydraulic fracturing to make available natural gas deposits in shale deposits, resulting in increased concern over its impact on the environment and public health. Watson discussed a number of challenges associated with assessing the impact of hydraulic fracturing:

a) ground water monitoring challenges:
   - Complex mixtures. Fracturing fluids are a closely guarded secret, but many chemicals are employed. (2500 additives of which 650 are known or possible carcinogens*)
   - Complicated identification, No/weak molecular ion and there are VOCs present with ions in common with background (e.g. *m/z* 44 CO_2)

Given these challenges a potential tool for identifying compounds in complex mixtures was discussed. GCxGC-TOF-MS, is a viable method for untargeted screening. However, compounds at trace levels or in

heavy matrix/background may still be overlooked, as well as those that are challenging to analyze & identify (e.g. with weak/no molecular ion). A new technology was discussed to overcome this limitation: soft ionization using low energy electrons. This method reduces fragmentation due to the low electron energies used, which in turn can give higher selectivity because of lower baseline and greater signal-to-noise for target peaks, improving detection limits.

b) Potential emissions in to the air associated with fracking are of more than just methane – other volatile organic compounds (VOCs) can also be released. These include members of the groups known as 'air toxics' (also known as 'hazardous air pollutants') and 'ozone precursors', both of which have for many years been the subject of legislation. The areas of concern for monitoring emissions to air are:
   - Worker exposure to chemicals used in fracturing fluid
   - Worker exposure to VOCs from flow-back ponds
   - Diesel emissions from on-site operations
   - Increased road traffic
   - Local Air Quality impacts from operations.
   -

Potential solutions to the challenges include:
For monitoring impacts on workers, assessments utilizing diffusive monitoring can be employed, The process involves sorbent tubes that are clipped to the worker's clothing to collect information on VOCs the worker is exposed to. They provide information to companies about the average exposure of the worker to the VOCs during the shift period.

For looking at emission impacts on the local community, perimeter monitoring may be a potential solution and has long been used to assess the effect of industrial operations on the surrounding environment. This is particularly relevant to fracking, as many new sites are in rural areas. With the implementation of Method 325 planned in 2015 for refineries, Watson asks if these regulations will be applied to fracturing sites, during production and completion.

For assessing regional/national impacts on air quality from hydraulic fracturing, the issue of determining if an increase in VOCs is due to the well(s) and not some other industrial activity. Source apportionment can be used for identifying sources of VOCs, since the ratio's between certain Hydrocarbons can indicate a particular source. More research is needed in to source apportionment for hydraulic fracturing.
Watson closed her discussion by summarizing that the main theme throughout is that whatever technique is used to monitor the environmental impacts, the common denominator is mass spectrometry. It provides the identification of the widest range of potential contaminants and is used in the majority of standard methods for water and air monitoring. But she challenged the group to also think about the techniques that are currently employed, do they give us the answers we need? Are their better techniques out there? Are there any techniques that we may be missing, either from oversight or techniques which don't currently exist? These are all valid questions and in order to full understand the environmental impacts of hydraulic fracturing, we have to fully define the potential problems, before finding the solutions.

In summary, much discussion ensued between the group members regarding both potential sources of the various cases studied, and it became clear in numerous instances that high resolution mass spectrometry is becoming increasingly important for both the identification of 'new' environmental contaminants as well as their quantitative measurement. Novel ionization modes were also a topic of discussion, including both atmospheric pressure ionization as well as low energy electron ionization. At the completion of the workshop, a large sub-group of the interest group attended an informal dinner at a local area restaurant for continued discussions.