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Point source attribution of ambient contamination events near unconventional oil and gas development

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HIGHLIGHTS

- Air quality characterized *in situ* with mobile mass spectrometry
- Episodic BTEX contaminated events attributed to specific anthropogenic processes
- Emissions from unconventional oil and gas development influence regional air quality

GRAPHICAL ABSTRACT

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ABSTRACT

We present an analysis of ambient benzene, toluene, and xylene isomers in the Eagle Ford shale region of southern Texas. *In situ* air quality measurements using membrane inlet mobile mass spectrometry revealed ambient benzene and toluene concentrations as high as 1000 and 5000 parts-per-billion, respectively, originating from specific sub-processes on unconventional oil and gas well pad sites. The detection of highly variant contamination events attributable to natural gas flaring units, condensate tanks, compressor units, and hydrogen sulfide scavengers indicates that mechanical inefficiencies, and not necessarily the inherent nature of the extraction process as a whole, result in the release of these compounds into the environment. This awareness of ongoing

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contamination events contributes to an enhanced knowledge of ambient volatile organic compounds on a regional scale. While these reconnaissance measurements on their own do not fully characterize the fluctuations of ambient BTEX concentrations that likely exist in the atmosphere of the Eagle Ford Shale region, they do suggest that contamination events from unconventional oil and gas development can be monitored, controlled, and reduced.

1. Introduction

There is a growing societal concern regarding the relationship between unconventional oil and gas development (UD) and environmental quality in petroliferous shale energy basins. Recent investigations have reported the migration of methane gas in shallow groundwater (Jackson et al., 2013; Osborn et al., 2011), the leaching of harmful chemical compounds into the soil and water (Drollette et al., 2015; Hildenbrand et al., 2015; Hildenbrand et al., 2016; Lauer et al., 2016; Llewellyn et al., 2015; Thacker et al., 2015), and the mishandling of produced fluids (Lauer et al., 2016) each of which can have a deleterious effect on the quality of surface and sub-surface water resources.

The majority of the air quality studies performed near UD have focused primarily on the detection and quantification of methane emissions (Allen et al., 2013; Harriss et al., 2015; Yacovitch et al., 2015). A recent review of the literature by Moore et al. attributed rogue hydrocarbon emissions to unconventional drilling and hydrocarbon processing (Moore et al., 2014). Air quality measurements in both the Bakken and Marcellus shale regions have also detected methane emissions from non-sputtering flares, which exhibited a 98% destruction removal efficiency (Caulton et al., 2014a). In these regions the greatest methane emissions were attributed to unidentified venting practices (Caulton et al., 2014a). These particular findings corroborate data collected in the Barnett, Denver-Julesburg, Pinedale, and Western Gulf basins where a weak correlation between emission and production rates was observed, indicating that maintenance-related stochastic processes and the design of production/control equipment are factors determining emission levels (Brantley et al., 2014).

Methane emissions have also been quantified in parts of southwestern Pennsylvania *via* an instrumented aircraft platform. These measurements revealed an average of 34 g of CH_4/s per well from seven well pad sites that were determined to be in the drilling phase, which accounted for up to 30% of the observed regional flux (Caulton et al., 2014b). While a potent greenhouse gas, rogue methane emissions of these proportions likely do not have an immediate effect on human health, as these concentrations are orders of magnitude below what would be required for human asphyxiation. In the Barnett Shale region of northern Texas, several point sources have been identified as potential contributors to the emission of NO_x and volatile organic compounds (VOCs), chemicals that can negatively impact human health. These include compression units (upstream), engine exhausts and condensate and oil tanks, in addition to production, well drilling, hydraulic fracturing, well completions, natural gas processing and transmission lines (midstream), each of which can contribute fugitive emissions intermittently (Armendariz, 2009). Two recent investigations in the Barnett shale region reported the emission of various chemical species from gas production sources, particularly lower molecular weight alkanes (<C6) (Zielinska et al., 2014) and aromatics (Bunch et al., 2014). However, these detections were not detectable beyond a distance of ~100 m in the downwind direction of the source in question, and all ambient

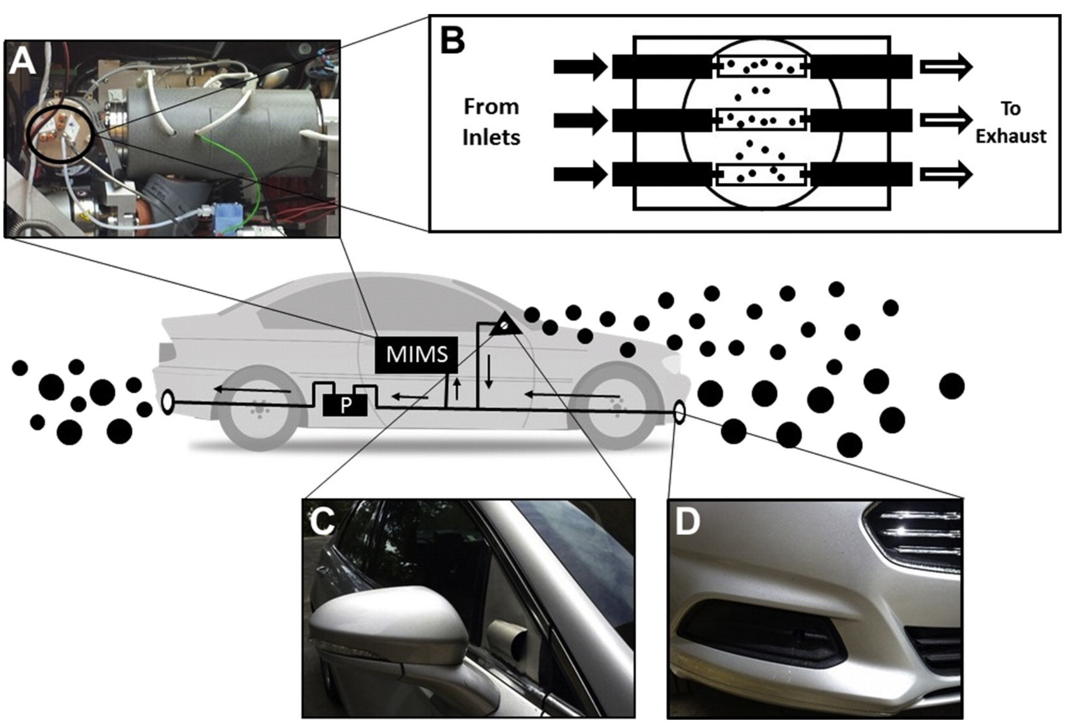

Fig. 1. Anatomy of the MIMS system. (A) Membrane inlet and linear quadrupole housing, (B) membrane inlet schematic, (C) quarter glass inlet, and (D) fog lamp inlet. Sampling of target atmosphere is provided by one of two inlets, either in a custom 'quarter glass' inlet or through a modified foglamp inlet. Atmosphere is subsequently metered for constant flow. Air is then directed into a membrane inlet of the installed mass spectrometer. All gases then exit *via* an exhaust port. Plots are created by associating mass spectra obtained with the GPS location at point of sample.