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Scrubbing Bubbles: The Importance of Sample Collection Method for Measuring Methane in Groundwater

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Background/Objectives. The boom in shale gas development in the United States in the last decade has led to increased public concern over the potential for methane impacts associated with shale gas extraction activities on shallow groundwater. In addition, the use of ethanol in gasoline and the injection of carbon substrate to enhance natural attenuation has led to increased concerns regarding biogenic methane at corrective action sites. The ability to accurately assess methane in groundwater requires a reliable sample collection method. Currently, several methods are used to collect groundwater samples for dissolved hydrocarbon gas analyses. However, the reliability of results obtained from these methods, particularly in the presence of effervescence, has not been quantified. This study compares dissolved methane and ethane concentrations measured in samples collected using three commercially-available sampling methods that are commonly used in sampling programs.

Approach/Activities. We compared methane concentrations measured in domestic water wells using an open system method (40 ml VOA, direct fill) and a closed system method (IsoFlask™). In addition, we evaluated a second open system method (40 ml VOA, inverted bottle) that is often claimed to provide some of the benefits of a closed system method. The sample methods were used for collection of samples from nine domestic water wells over multiple sample events. For each sample event, replicate samples were collected using each of the three sample methods.

Results/Lessons Learned. In the absence of effervescence, the difference in the dissolved methane concentrations measured by the Direct-Fill VOA (open system), Inverted VOA (semi-closed system), and IsoFlask™ (closed system) sampling methods was relatively small (i.e., within 30%). However, when methane concentrations equaled or exceeded the approximate concentration at which effervescence occurs in the study area (i.e., 20 mg/L), IsoFlask™ samples yielded significantly higher methane concentrations than Direct-Fill VOA samples, and Inverted VOA samples yielded lower concentrations than Direct-Fill VOA samples. This field study suggests that the open-system methods are adequate for the collection of samples with low concentrations of dissolved gases. However, for groundwater that is supersaturated with dissolved gases, samples collected using open-system methods are likely to be biased low because exsolving gas can escape during sample collection. Although the inverted bottle method may retain some exsolved gas during sample collection, this method yielded the least accurate result because the analytical procedure does not account for redistribution of methane between the gas and water phases that occurs between sample collection and sample analysis.