## Validating sampling techinques for robust measurements of natural gas levels in groundwater

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Currently there are many methods utilized to collect dissolved hydrocarbon and noble gas samples from water wells to investigate groundwater contamination associated with hydraulic fracturing. Here, we compare the three most popular sampling vessels: VOA exetainers, Isoflasks®, and copper tubes. Despite the long-standing utilization of copper tubes, hydrocarbon gas contamination related to hydraulic fracturing has led to a lack of consensus about the reliability and reproducibility of each method, as a comprehensive study needs to be conducted. Major, hydrocarbon, and noble gas molecular, elemental, and isotopic analyses provide a valuable insight to many of the factors that are used to assess groundwater quality. When sampling a water well for major, hydrocarbon, or noble gas analyses, fractionation and atmospheric contamination of the sample are a serious concern, specifically for noble gases that are present in trace abundances. Using a set of water well samples the compare relative effectiveness of each sampling method was examined by testing for different dissolved hydrocarbon and noble gas abundances via mass spectrometry, gas chromatography, headspace analyses, and traditional gas extraction/exsolution methods. Preliminary data suggests that of the three sampling methods, the copper tube method is the least prone to atmospheric contamination or changes in gas composition due to the inherent lack of opportunity for air contamination. Copper tubes and IsoFlasks have trade-offs when it comes to total hydrocarbon composition and appear comparable for hydrocarbon isotopic work, which is the primary focus of many investigations. Herein, we demonstrate the appropriate usage for each technique and develop a workflow chart that can be used to conduct cross-laboratory calibrations and to produce comparable datasets.