Effect of Different Sampling Methodologies on Measured Methane Concentrations in Groundwater Samples

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Abstract

Analysis of dissolved light hydrocarbon gas concentrations (primarily methane and ethane) in water supply wells is commonly used to establish conditions before and after drilling in areas of shale gas and oil extraction. Several methods are currently used to collect samples for dissolved gas analysis from water supply wells; however, the reliability of results obtained from these methods has not been quantified. This study compares dissolved methane and ethane concentrations measured in groundwater samples collected using three sampling methods employed in pre- and post-drill sampling programs in the Appalachian Basin. These include an open-system collection method where 40 mL volatile organic analysis (VOA) vials are filled directly while in contact with the atmosphere (Direct-Fill VOA) and two alternative methods: (1) a semi-closed system method whereby 40 mL VOA vials are filled while inverted under a head of water (Inverted VOA) and (2) a relatively new (2013) closed system method in which the sample is collected without direct contact with purge water or the atmosphere (IsoFlask®). This study reveals that, in the absence of effervescence, the difference in methane concentrations between the three sampling methods was relatively small. However, when methane concentrations equaled or exceeded 20 mg/L (the approximate concentration at which effervescence occurs in the study area), IsoFlask® (closed system) samples yielded significantly higher methane concentrations than Direct-Fill VOA (open system) samples, and Inverted VOA (semi-closed system) samples yielded lower concentrations. These results suggest that open and semi-closed system sample collection methods are adequate for non-effervescing samples. However, the use of a closed system collection method provides the most accurate means for the measurement of dissolved hydrocarbon gases under all conditions.

Introduction

Over the last decade, tens of thousands of samples have been collected from water supply wells by oil and gas operators to establish baseline dissolved hydrocarbon gas concentrations (i.e., primarily methane, but

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also ethane and propane) and to evaluate the presence or absence of impacts after drilling in areas of unconventional oil and gas extraction (e.g., Molofsky et al. 2013; Siegel et al. 2015). Such samples are almost exclusively collected at the surface from a tap or faucet because internal access to the downhole portion of the well is either impractical (e.g., the wellhead is not accessible or the presence of a drop-pipe and permanent submersible pump obstructs access to the wellbore) or because the potential for damaging the well and its contents presents a liability. A number of different sample collection methods have been employed to collect dissolved hydrocarbon gas samples at the surface. However, these methods have not been systematically evaluated to determine the accuracy, precision, and comparability of results obtained using different methods.

The collection of dissolved light hydrocarbon gas samples at the surface can be complicated by effervescence (bubble formation), which occurs when groundwater is supersaturated with dissolved gases. At depth within the aquifer and water supply well, methane concentrations above its solubility limit at the surface can be sustained because the hydrostatic head creates

a pressure greater than one atmosphere. However, as the sample is pumped to the surface, the reduction in pressure decreases the amount of methane that can be maintained in solution, resulting in exsolution.

If methane was the only gas present in groundwater, effervescence at the surface would occur at the saturation concentration of methane ($\sim$25 to 35 mg/L, depending on water temperature and elevation). However, methane commonly occurs with carbon dioxide and other gases, which also exert gas pressure in groundwater. For example, methanogenesis produces equal molar concentrations of methane and carbon dioxide (Drever 1988). As a result, effervescence can occur before any one gas reaches its individual saturation concentration (i.e., at methane concentrations below 25 to 35 mg/L).

Commonly used protocols for collection of dissolved hydrocarbon gas samples have been adapted from the protocols for volatile organic compounds (VOCs) (e.g., BTEX), which are generally more soluble and less volatile than gaseous hydrocarbons (Sander 1999). For many VOCs, concentrations of regulatory concern (i.e., concentrations considered to potentially pose a risk to human health and/or the environment, with a margin of safety) are several orders of magnitude below the solubility limits (Pankow and Cherry 1996; Moran 2006; Cwiertny and Sherer 2010). In contrast, methane is nontoxic; however, it is a potential asphyxiation and explosion hazard. Therefore, methane is of the greatest concern under conditions at which exsolution could result in an oxygen-deficient or explosive atmosphere (Eltschlager et al. 2001). Thus, the accurate measurement of methane in these samples is critical to support appropriate decision making on the need for potential mitigation.

In principle, the use of an "open system" for sample collection may allow dissolved gases to escape to the atmosphere, whereas a "closed system" traps all gases, both dissolved and effervescing. The potential for low bias associated with open systems is well recognized (Beyerle et al. 2000); however, the most common closed-system method utilized historically to collect samples at the surface (e.g., the copper tube method; Beyerle et al. 2000) can be challenging to implement, and commercial laboratories are not typically equipped to process these samples. As a result, open-system collection methods continue to be widely used.

Currently, most oil and gas operators in the Appalachian Basin collect groundwater samples for dissolved hydrocarbon gas analysis using an open-system collection method, in which the samplers fill 40 mL glass volatile organic analysis (VOA) vials directly from tubing or a tap at the surface (i.e., Direct-Fill VOA method). In this study, we compare methane and ethane concentrations measured using the Direct-Fill VOA method with concentrations measured using two alternative collection methods, which are intended to minimize or eliminate contact with the atmosphere during sample collection. The first alternative method, known as the Inverted VOA method, is a semi-closed system that involves the filling of VOA vials while inverted in a bucket of purge water

(Coleman et al. 1988; Aravena et al. 1995; Hirsche and Mayer 2009; Bolton and Pham 2013). The Inverted VOA method is considered a semi-closed system in this paper because, although the sample is not directly exposed to the atmosphere, the liquid in the bucket is still in contact with the atmosphere during sample collection. The second alternative method, the IsoFlask® (Isotech Laboratories, Champaign, Illinois), is a relatively new method made commercially available in 2013. It uses an evacuated 750 mL flexible plastic container filled via an in-line sampling manifold to capture both water and exsolving gases from the sampling point (Isotech 2014). The IsoFlask® is a fully closed sampling system because the sample is completely isolated from the atmosphere during sample collection. In addition, the analytical procedure quantitatively accounts for the volume and composition of exsolved gas in the sample container, thereby allowing for the determination of original dissolved gas concentrations prior to any exsolution. The IsoFlask® is presently only available through Isotech; however, the design of the sampling device and analytical procedures could be replicated by others.

This study does not evaluate the effect of other factors acting on dissolved hydrocarbon gas concentrations prior to the sampling point at the surface (e.g., water level drawdown within the wellbore during pumping, movement through a pressure tank). These factors are important to understand; however, their effect cannot be evaluated without first understanding the precision and accuracy of methods for collecting dissolved hydrocarbon gas samples at the surface. The findings of this study, which is directed toward assessing the effect of sampling methods on dissolved methane and ethane test results, may assist both industry and regulatory agencies in the selection of the sampling methodology best suited for (1) initial predrill and postdrill screening of dissolved hydrocarbon gas concentrations and (2) investigations to evaluate the nature of a potential stray gas impact and the effectiveness of remedial measures.

Methods

Water Supply Wells

Samples were collected from nine residential water supply wells in Northeastern Pennsylvania; eight were located in Susquehanna County and one in Bradford County. The study wells were selected from a larger population of water wells in the region for which dissolved gases had been previously characterized. The selection criteria for this study included:

- The gas composition and carbon and hydrogen stable isotope ratios of methane in the wells were consistent with dissolved gases that occurred naturally in the subsurface aquifers throughout this region (Kappel and Nystrom 2012; Molofsky et al. 2013; Senior 2014; Sloto 2014; Baldassare et al. 2015).
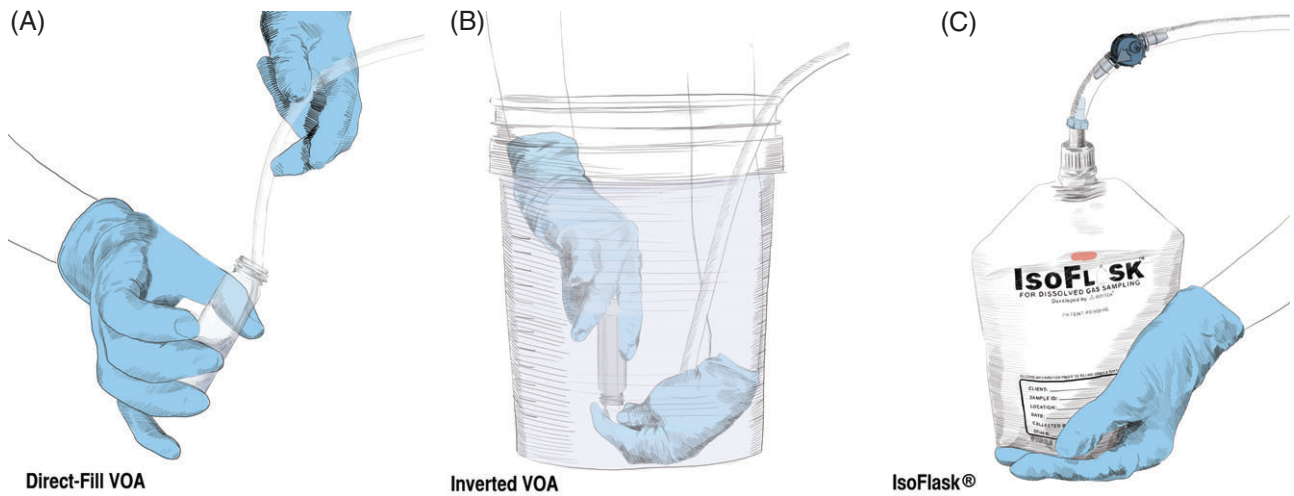
Figure 1. Illustration of three sample collection methods: (A) the Direct-Fill VOA method, (B) the Inverted VOA method, and (C) the IsoFlask® method.

- Eight of the nine wells were located greater than 4000 ft. from the nearest commercially-producing gas well at the time of sampling. The remaining well was investigated by the Pennsylvania Department of Environmental Protection (PaDEP) and determined to contain naturally-elevated methane concentrations (PaDEP 2010).

- Wells were selected to represent a range of methane concentrations including three low concentration wells (i.e., less than the PaDEP action level of 7 mg/L; Pennsylvania Bulletin 2011), four medium concentration wells (7 to 30 mg/L), and two high concentration wells (i.e., greater than the estimated methane solubility of 30 mg/L at ambient conditions in the study area with an average groundwater temperature of ~10 °C and elevation of ~1400 ft. above sea level).

Sampling Procedures

The comparison of sample collection methods was conducted as part of a larger study to evaluate short-term and long-term variability of naturally-occurring methane concentrations in groundwater samples collected from residential water supply wells. Sampling was conducted over four sampling events in February 2014 and September/October 2015. A total of 26–39 samples (including field duplicates) were collected from each of the nine wells. Samples were collected from a faucet at the base of a pressure tank prior to any water treatment devices (e.g., filters and water softeners). This is consistent with the access point most commonly sampled for baseline sampling programs in the Appalachian Basin. Prior to sample collection, the flow rate was reduced from 3 gallons per minute (gpm) to approximately 0.5 gpm to minimize turbulent flow. At a minimum, the samples were collected after the stabilization of field parameters (i.e., specific conductivity, pH, temperature). However, in some cases, additional purging was conducted prior to sample collection as part of a larger and more comprehensive study on short-term variability.

During all sampling events, matched water samples were collected using the Direct-Fill VOA and IsoFlask® collection methods. This resulted in 70 pairs of matched samples collected using both sampling methods. In addition, for 43 of the 70 pairs, an additional sample was collected using the Inverted VOA method. Two variations of the Inverted VOA method were used: a) high-flush Inverted VOA (27 samples) and b) low-flush Inverted VOA (16 samples). Matched samples were collected consecutively immediately after one another. Brief descriptions of the sampling methods are provided below, and the sampling methods are illustrated in Figure 1.

Direct-Fill VOA

For each sample, two clear 40 mL glass VOA vials with Teflon-lined silicone septum were filled directly from the faucet (or via $1/4''$ polyethylene tubing connected to the faucet) at the base of the pressure tank. Fifty-four of the samples were preserved using hydrochloric acid, and 16 samples were unpreserved. The use of preservative had no measurable effect on methane concentration (Supporting Information).

Inverted VOA

For each sample, two 40 mL unpreserved VOA vials (as described above) were inverted and submerged in a 5-gallon bucket filled with purge water and subsequently filled through dedicated $1/4''$ polyethylene tubing attached to the faucet. The Inverted VOA method has been suggested to be an improvement over the Direct-Fill VOA method because it prevents contact between the sample and the atmosphere (Coleman et al. 1988; Aravena et al. 1995; Hirsche and Mayer 2009; Marcellus Shale Coalition (MSC) 2012; Bolton and Pham 2013). Two variants of the Inverted VOA method were tested in this study. These variants differed by both the flushing rate and the volume of water flushed through the inverted VOA vial:

1. *Low-flush:* Water was flushed through the inverted VOA vial at a rate of 0.5 L per minute (lpm) for 10 s (equal to ∼2 VOA vial volumes) prior to capping the submerged vial near the base of the filled bucket. The Marcellus Shale Coalition has recommended this low-flush approach to minimize entrapment of bubbles within the VOA vial (Marcellus Shale Coalition (MSC) 2012).

2. *High-flush:* Water was flushed through the inverted VOA vial at a rate of 0.5 gpm for 1 min (equal to ∼40 VOA volumes) prior to capping the submerged vial near the base of the filled bucket. The high-flush variation was included to evaluate the effect of flush volume on results.

IsoFlask®

For each sample, a single 750 mL IsoFlask® container was filled directly through a sampling line connected to the pressure tank faucet. The IsoFlask® is a flexible, evacuated plastic container preloaded with a benzalkonium chloride bactericide capsule and constructed with a Luer® valve that enables direct connection to a sampling manifold or sample location. In combination, the IsoFlask® and sampling line serve as a closed system, designed to collect bulk samples of water and any exsolving gases (Isotech 2014).

In addition to the collection of matched samples using different sample collection methods, the field sampling program included the collection of 27 field duplicates for each sample collection method. Field duplicate samples were collected consecutively immediately after one another. For 16 sample events, replicate Direct-Fill VOA and Inverted VOA samples were collected for analysis by the Pennsylvania Department of Environmental Protection (PaDEP) Bureau of Laboratories (BOL), as discussed below. For eight of these sample events, replicate IsoFlask® samples were collected for analysis by the PaDEP BOL. The results for these eight samples, which were analyzed using a different procedure from that utilized by Isotech Laboratories, Inc. (Isotech), are presented in the Supporting Information.

Laboratory Analyses

Direct-Fill and Inverted VOA samples were submitted to Eurofins Lancaster Laboratories Environmental, LLC (Lancaster) for analysis of dissolved hydrocarbon gases (methane, ethane, propane, isobutane, *n*-butane). IsoFlask® samples were submitted to Isotech Laboratories, Inc. (Isotech) for analysis of methane, ethane, propane, isobutane, and *n*-butane. In addition, a subset of replicate samples using the Direct-Fill VOA, Inverted VOA, and IsoFlask® methods were submitted to the PaDEP BOL for analysis of dissolved methane and ethane. The type and number of samples analyzed at each laboratory are summarized in Table 1.

Both Lancaster and the PaDEP BOL exclusively report the dissolved phase concentration in VOA vials and/or IsoFlasks® (i.e., the analytical procedure does not account for gases contained in bubbles in the VOA vials or headspace of the IsoFlask®). In contrast, the analytical procedure used by Isotech quantifies the total mass of methane in both the dissolved phase and gas phase in the IsoFlask® container, thus enabling the reporting of a dissolved hydrocarbon gas concentration prior to any exsolution that occurs during sample collection or before sample analysis (Isotech 2014). Sample preparation and analytical procedures for each laboratory are described below.

Eurofins Lancaster Laboratories Environmental, LLC (Lancaster)

Lancaster's procedure is designed to report dissolved gas concentrations within the water portion of a sample (i.e., free gas is noted but not analyzed). Unpreserved and preserved samples were analyzed within 7 and 10 days, respectively. Dissolved gases were analyzed using a modified version of the RSK-175 method (Kampbell and Vandegrift 1998) as follows: 5 mL of water sample was extracted from the 40-mL VOA vial using helium displacement via a gas-tight syringe. The extracted sample was then transferred to a 10-mL headspace vial, which was subsequently agitated at a constant temperature for a specified period of time. Following agitation, an aliquot of the headspace above the water sample was withdrawn and injected into a gas chromatograph equipped with

Table 1
Type and Number of Samples Analyzed at Each Laboratory

Sample Collection Method	Lancaster		PaDEP BOL		Isotech	
	Primary Sample	Field Duplicate	Primary Sample	Field Duplicate	Primary Sample	Field Duplicate
Direct-Fill VOA with preservative	54	27	—	—	—	—
Direct-Fill VOA without preservative	25	9	16	8	—	—
Inverted VOA (high-flush)	27	27	—	—	—	—
Inverted VOA (low-flush)	16	—	16	8	—	—
IsoFlask®	—	—	8 [1]	—	70	26 [2]

Notes: — = No samples collected.
[1] IsoFlask® samples analyzed at the PaDEP BOL are discussed in Supporting Information.
[2] One IsoFlask® field duplicate sample was compromised during shipment; consequently, 26 of 27 field duplicate samples collected were analyzed.

a flame ionization detector (GC-FID). To avoid the calculations associated with the use of Henry's Law, the instrument is calibrated using aqueous calibration solutions. Specifically, known volumes of a gas calibration standard are injected into deionized water in headspace vials. The vials are then treated in an identical manner to water samples (i.e., agitated at a constant temperature for a specified period of time), and aliquots of the headspace above the deionized water are analyzed. Dissolved gas concentrations in water samples are identified by matching the respective retention times and peaks with that of known concentrations of dissolved gases in the aqueous calibration standards.

Pennsylvania Department of Environmental Protection Bureau of Laboratories (PaDEP BOL)

The PaDEP BOL procedure is designed to report dissolved gas concentrations within the water portion of a sample (i.e., free gas is noted but not analyzed). PaDEP BOL VOA vial samples were unpreserved and were analyzed within 7 days of collection. Dissolved hydrocarbon gases were analyzed using an in-house method (PaDEP 3686, Rev. 1) as follows: Working with cold samples (i.e., samples are stored at ~4 °C), each vial was opened, and a 10 mL aliquot was quickly transferred to a 20 mL headspace vial using a volumetric pipet. Headspace vials were immediately capped, and the samples were agitated and heated to a constant temperature for a specified period of time in an automatic headspace sampler. A 1 mL aliquot of the equilibrated headspace was then automatically transferred to a GC-FID for separation and detection of methane and ethane. To avoid the calculations associated with the use of Henry's Law, the instrument is calibrated using aqueous calibration solutions. Specifically, a saturated solution of each gas is prepared in reagent water; then, aliquots are diluted to create a set of aqueous calibration standards at concentrations ranging from 12 ppb to 39 ppm. The saturated solution concentration of each gas at a known temperature was obtained from scientific literature. Eight IsoFlask® samples were also analyzed at the PaDEP BOL. The analytical procedure and results for these samples are discussed in the Supporting Information.

Isotech Laboratories Inc. (Isotech)

Isotech's procedure accounts for gases that are both dissolved in the water portion of a sample and present as free gas in the headspace of a sample container. All IsoFlask® samples were submitted to Isotech and analyzed within their standard turnaround time of 30 days. Dissolved hydrocarbon gases (methane, ethane, and propane) were analyzed by GC-FID, and fixed gases (argon, nitrogen, carbon dioxide, carbon monoxide, hydrogen, helium, and oxygen) were analyzed by a gas chromatograph equipped with a thermal conductivity detector (GC-TCD). If the IsoFlask® sample arrived with a headspace of less than 30 mL, additional headspace was created by injecting 30 to 60 mL of helium into the IsoFlask®. After the headspace volume was verified, the sample was placed on a shaker for a minimum of

2 h for equilibration between the water and headspace gas. An aliquot (5 cc) of the headspace gas sample was then introduced into the GC-FID/TCD, which determined the concentrations of hydrocarbons and fixed gases in the headspace via comparison to free gas standards. Dissolved concentrations of methane, ethane, propane, argon, nitrogen, and oxygen in the water portion of the sample were then determined by Henry's Law based on the water temperature and atmospheric pressure. Dissolved gas concentrations prior to exsolution were calculated using the weight of the sample (by which the volume of water may be determined), the volume of the headspace, and the concentrations of hydrocarbons in the water and headspace, respectively.

Statistical Analyses

The variability in concentration between matched samples was compared using the absolute relative percent difference (RPD) and directional percent difference (DPD):

$$RPD = \left[(X_1 - X_2) \ / \ (X_1 + X_2)/2\right]$$

$$DPD = (X_2 - X_1) \ / \ X_1$$

DPD was calculated relative to the Direct-Fill VOA result (i.e., X_1 was the Direct-Fill VOA result, and X_2 was the result obtained using the alternative sample collection method [Inverted VOA or IsoFlask®]). The Wilcoxon signed-rank test was used to evaluate the significance of differences in methane concentrations between matched samples collected using different sampling methods (with p-value ≤ 0.05 indicating a significant difference between groups of data).

The variability in concentration between field duplicates (i.e., duplicate samples collected using the same sample method) was compared using the RPD. A Mann–Whitney U test was used to determine whether the median value for the RPD of field duplicates was different between sample collection methods.

Results

Results are presented below for VOA and IsoFlask® samples analyzed at Lancaster and Isotech, respectively. A comparison between VOA results reported for Lancaster vs. the PaDEP BOL is discussed later in this paper.

Variability in Field Duplicate Samples for the Three Sampling Methods

For all three methods, the variability associated with field duplicate samples was small. Specifically, 70% (19/27) of Direct-Fill VOA field duplicate pairs, 67% (18/27) of Inverted VOA field duplicate pairs (all collected using the high-flush variant), and 81% (21/26) of IsoFlask® field duplicate pairs had an RPD less than 10%. Out of all 80 pairs of method field duplicates, only six pairs exhibited RPDs greater than 30%, which is the typical laboratory duplicate quality assurance goal.

Four of these pairs were collected using the high-flush Inverted VOA method, which exhibited the highest median duplicate variability of the three sample collection methods (median RPD = 8.7%). This was significantly higher than the median RPD for samples collected using the IsoFlask® method (4.8%, $p = 0.03$) but not significantly different than the median RPD for samples collected using the Direct-Fill VOA method (6.2%, $p = 0.44$). For all sampling methods, there was no clear relationship between RPDs and methane concentrations (i.e., higher RPDs did not necessarily occur in association with higher methane concentrations) (Figure 2).

Comparison of Reported Methane Concentrations Between Methods

All three sample collection methods yield similar methane concentrations for matched samples below 20 mg/L. At or above approximately 20 mg/L, methane concentrations in IsoFlask® samples were notably higher than those reported for matched Direct-Fill VOA samples (Figure 3A), whereas Inverted VOA methane concentrations (both high-flush and low-flush) were generally lower (Figure 3B).

Similar Results Between Sampling Methods at Methane Concentrations Below 20 mg/L

In the lower range of methane concentrations (<20 mg/L), the difference between matched samples from all three sampling methods was relatively small. Specifically, for samples with a Direct-Fill VOA methane concentration less than 20 mg/L, 78% (38/49) of the matched IsoFlask® samples and 93% (28/30) of the matched Inverted VOA samples (high-flush and low-flush combined) yielded concentrations within 30% of the Direct-Fill VOA samples (Figure 4A and 4B). Although overall differences in measured concentrations between methods were small, IsoFlask® results were consistently higher than either Direct-Fill VOA or Inverted VOA results. For 90% (44/49) of sample pairs, the methane concentration in the IsoFlask® sample was higher than the Direct-Fill VOA sample, with a median concentration difference of +16%. This difference in concentration was statistically significant according to the Wilcoxon signed-rank test ($p < 0.001$). In contrast, there was no consistent difference between Direct-Fill VOA and Inverted VOA (high-flush or low-flush) results (i.e., median difference of 0%, $p = 0.74$).

Different Results Between Methods at Methane Concentrations at or Above 20 mg/L

For the population of samples with Direct-Fill VOA methane concentrations at or above 20 mg/L, there were significantly larger differences in methane concentrations between the three sampling methods. For these samples, 52% (11/21) of matched IsoFlask® samples yielded a methane concentration more than 30% higher than the Direct-Fill VOA result, while none of the IsoFlask® samples yielded a methane concentration lower than the Direct-Fill VOA result (Figure 4A). Overall, the median
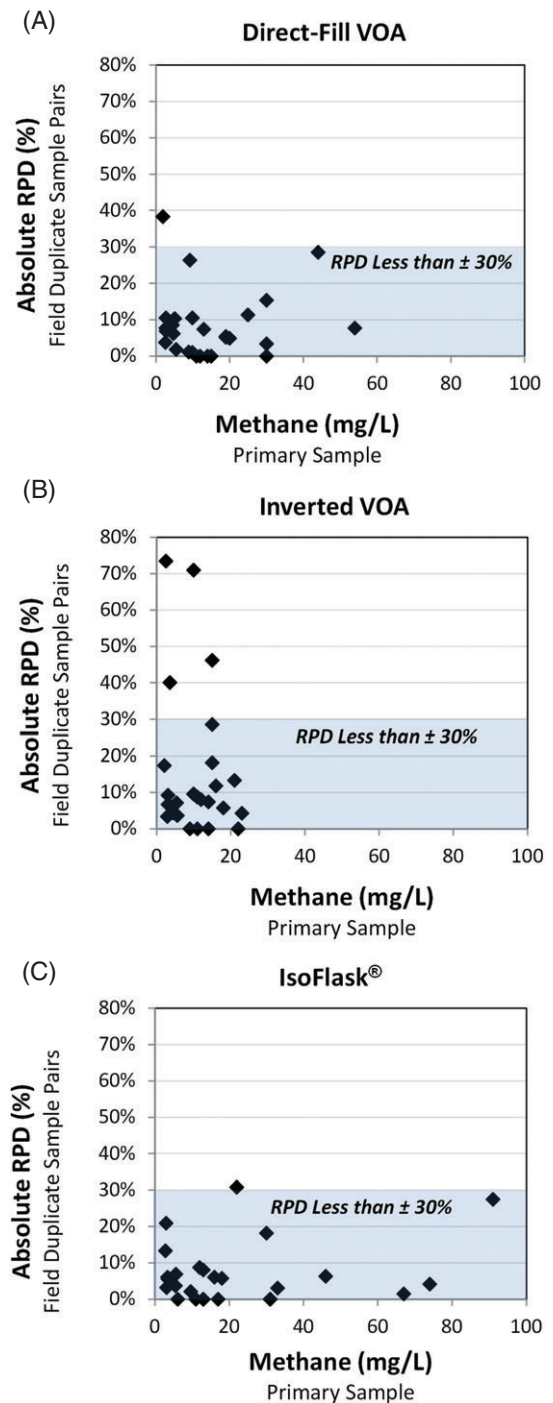

Figure 2. Variability of field duplicate samples collected using each sample collection method. Plots show RPDs for field duplicate samples collected using (A) Direct-Fill VOA method, (B) inverted VOA Method, and (C) IsoFlask® method vs. the methane concentration of the primary sample.

concentration difference between matched IsoFlask® and Direct-Fill VOA samples in this concentration range was +32%. This difference was statistically significant according to the Wilcoxon signed-rank test ($p = <0.001$).

The Inverted VOA method reported lower methane concentrations than the Direct-Fill VOA method when methane concentrations were at or above 20 mg/L. For the
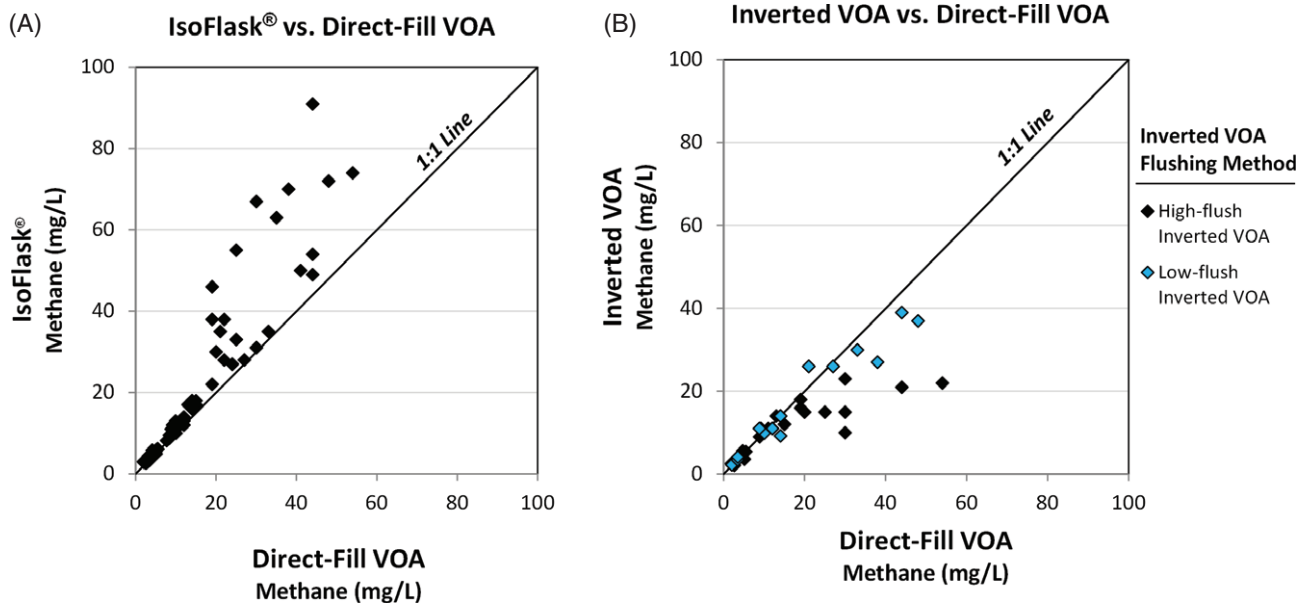
Figure 3. Methane concentrations of matched samples collected using different sample collection methods. At methane concentrations >20 mg/L, IsoFlask® samples yielded higher concentrations than Direct-Fill VOA (A), and Inverted VOA samples yielded lower concentrations than Direct-Fill VOA (B). All values represent those associated with primary (as opposed to duplicate) samples.
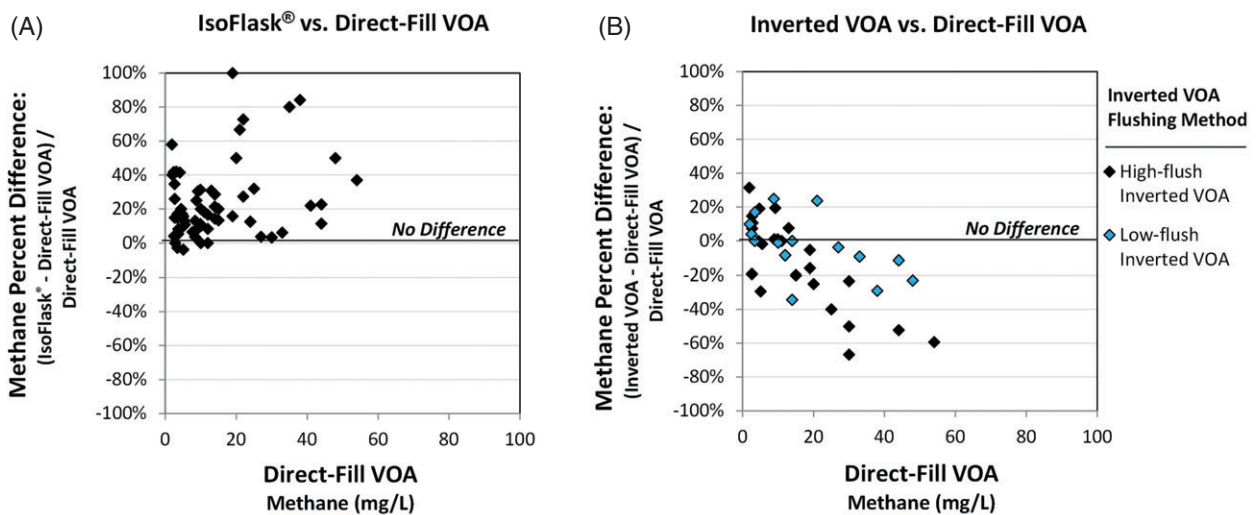

Figure 4. Percent difference between methane concentrations reported for different sample collection methods. Percent difference between methane concentrations reported for (A) IsoFlask® and matched Direct-Fill VOA samples and (B) Inverted VOA and matched Direct-Fill VOA samples. All values represent those associated with primary (as opposed to duplicate) samples.

13 matched samples, 92% (12/13) of the Inverted VOA samples (high-flush and low-flush combined) yielded a lower methane concentration than the Direct-Fill VOA result, with 38% (5/13) of the Inverted VOA samples yielding a methane concentration more than 30% lower than the Direct-Fill VOA result. Conversely, only one Inverted VOA sample yielded a methane concentration higher than the Direct-Fill VOA result. The median concentration difference between matched Inverted VOA and Direct-Fill VOA samples was −25% (Figure 4B). This difference was statistically significant according to the Wilcoxon signed-rank test ($p = 0.006$).

High–Flush Versus Low–Flush Inverted VOA

At methane concentrations at or above 20 mg/L, the high-flush Inverted VOA samples yielded lower methane concentrations than the low-flush samples when compared to Direct-Fill VOA results (Figure 5). Significant differences were noted between the volume of headspace gas in these vials, where several high-flush Inverted VOA samples contained >40% headspace by volume within the container as compared to low-flush Inverted VOA samples, which contained, at most, approximately 10% headspace gas by volume. Regardless of the flushing volume, both variants of the Inverted VOA
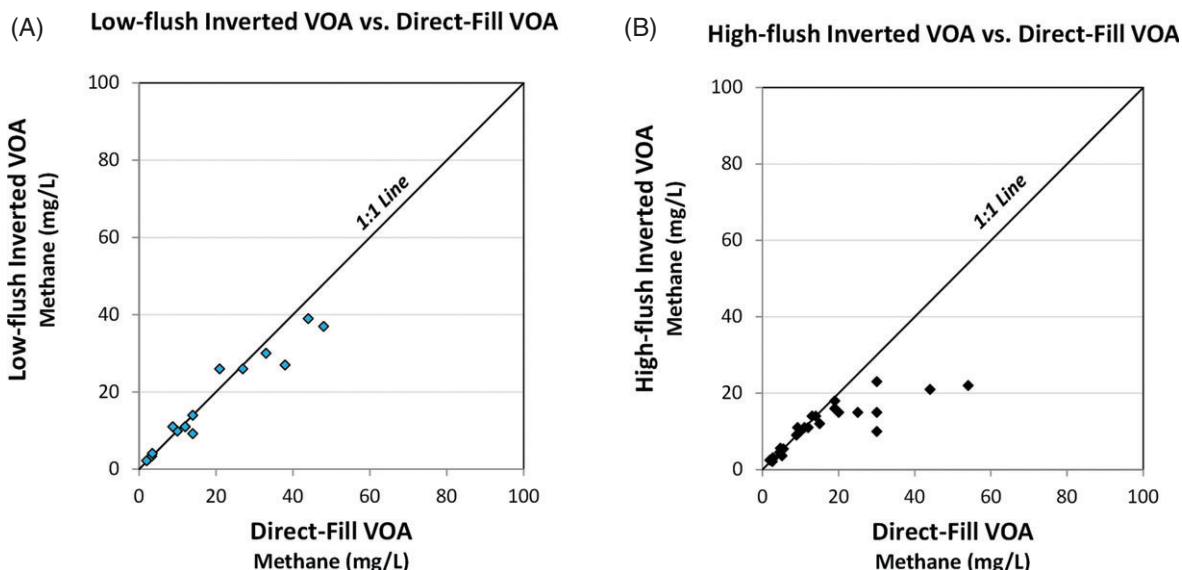
Figure 5. Comparison of low-flush to high-flush Inverted VOA results. Methane concentrations of (A) Low-flush Inverted VOA samples vs. matched Direct-Fill VOA samples and (B) High-flush Inverted VOA samples vs. matched Direct-Fill VOA samples. All values represent those associated with primary (as opposed to duplicate) samples.
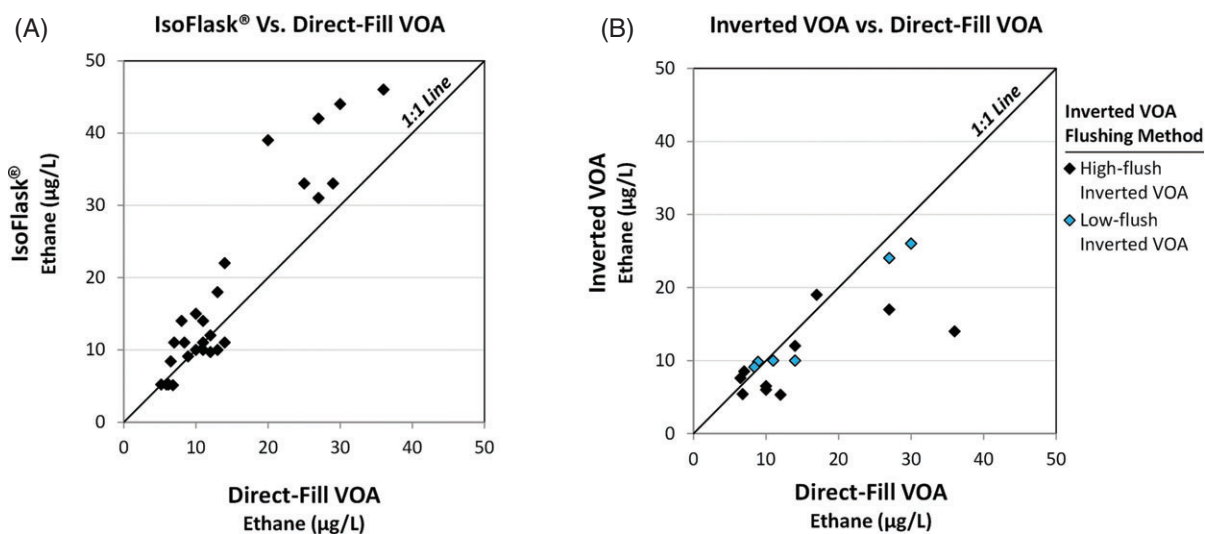

Figure 6. Detected ethane concentrations of matched samples collected using different sample collection methods. Ethane concentrations of (A) IsoFlask® samples vs. matched Direct-Fill VOA samples and (B) Inverted VOA samples vs. matched Direct-Fill VOA samples. All values represent those associated with primary (as opposed to duplicate) samples.

method showed evidence of negative bias relative to the Direct-Fill VOA method.

Comparison of Reported Ethane Concentrations Between Methods

Ethane was detected above 5 µg/L (the ethane reporting limit for Lancaster) in an approximately equal percentage of Direct-Fill VOA samples (40%, 28/70 samples), Inverted VOA samples (40%, 17/43 samples), and IsoFlask® samples (46%, 32/70 samples). For each sampling method, the RPD for ethane measured in field duplicate samples was generally less than 30%.

For the population of Direct-Fill VOA samples with detected ethane, concentrations were compared to those reported for matched IsoFlask® and Inverted VOA samples (Figure 6A). Ethane results were significantly higher in IsoFlask® samples than Direct-Fill VOA samples ($p = 0.003$), with a median difference of +21%. The difference was more pronounced when ethane concentrations in the Direct-Fill VOA sample exceeded 20 µg/L (Figure 6A). These ethane concentrations were universally associated with methane concentrations equal to or greater than 30 mg/L in Direct-Fill VOA samples. The difference between ethane results for the matched IsoFlask® and Direct-Fill VOA samples was observed even though reported ethane concentrations in all VOA and IsoFlask® samples were several orders of magnitude below the respective solubility concentration for ethane
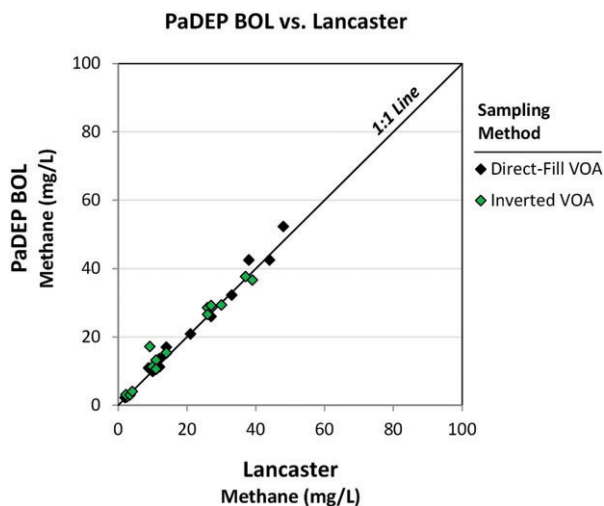
PaDEP BOL vs. Lancaster

Figure 7. Comparison of methane results reported for VOA vial samples analyzed at the PaDEP BOL vs. Lancaster.

($\sim$58 mg/L at standard temperature and pressure). In contrast, ethane results were typically lower in Inverted VOA samples than Direct-Fill VOA samples ($p = 0.04$, with a median difference of -14%, Figure 6B). A comparison of the methane to ethane ratios reported for samples collected using different methods is provided in the Supporting Information (Figure S2).

Comparison of PaDEP BOL to Lancaster Methane Results for VOA Samples

Although the PaDEP BOL and Lancaster laboratories employ different procedures for handling water samples, the methane results reported by the two laboratories for replicate samples were quite similar. Of the 16 matched PaDEP BOL and Lancaster Direct-Fill VOA samples (Figure 7), none exhibited an RPD greater than 30%. Of the 16 matched Inverted VOA samples, only 2 pairs exhibited an RPD greater than 30%. The median RPD for all matched samples analyzed by the two laboratories was 6.5%. This shows that, despite the difference in sample preparation (i.e., opening the vial and removing the water aliquot with a pipette vs. removing it through the septum with a syringe), the difference between PaDEP BOL and Lancaster results was minor.

Discussion

Based on the relative methane and ethane concentrations and duplicate variability associated with each method, we have made the following observations regarding the three sampling methods tested.

Relatively Small Variability Among Field Duplicate Samples

For all field duplicates, the median RPD was 6.3%, showing that the variability among duplicates collected by the same method was minimal relative to differences observed between the three different sampling methods.

Good Agreement Between Lancaster and PaDEP BOL

Similarly, for replicate VOA samples analyzed by Lancaster and the PaDEP BOL, the median RPD was 6.5%. This difference was no larger than the difference between field duplicates analyzed at the same laboratory.

At Dissolved Methane Concentrations Below 20 mg/L, the Three Sample Collection Methods Provide Comparable Results

For samples with a dissolved methane concentration of less than 20 mg/L, there was no statistical difference in concentration for the Inverted VOA method (both high-flush and low-flush variants) compared to Direct-Fill VOA (median difference = 0%), and the concentration for IsoFlask® samples was only moderately higher than Direct-Fill VOA (median difference = +16%). The difference between reported results for VOA samples and IsoFlask® samples in this concentration range is potentially attributable to (1) differences in the calibration and/or analytical procedures between Lancaster and Isotech or (2) a small percentage loss of volatile methane from water in samples collected using the Direct-Fill and Inverted VOA methods. It is not uncommon for different laboratories to report results that differ by as much as 25% (e.g., McHugh et al. 2011). Consequently, a difference between measurements reported by laboratories of 30% or less is not unexpected. Loss of dissolved volatiles has also been reported during the collection of samples into VOA vials. Although the loss of VOCs has been reported to be less than 10% under most sampling conditions (Nadim et al. 2001; Parker and Britt 2012), methane is significantly more volatile than the VOCs evaluated in these studies.

A Fully Closed Sampling System Is Best for Collecting Effervescing Samples

When methane concentrations were at or above 20 mg/L, methane concentrations in IsoFlask® samples were significantly higher (median of +32%) than those collected using Direct-Fill VOA. This finding suggests that, as an open-system collection technique, the Direct-Fill VOA method is prone to loss of exsolving gases, resulting in low-biased methane concentrations associated with the water sample. The fact that the Direct-Fill VOA and IsoFlask® method results diverge at concentrations below theoretical methane saturation (i.e., 25–35 mg/L) is consistent with the expectation that the combined partial pressures of all dissolved gases (including CO_2, N_2, O_2, etc.) is driving effervescence.

Dissolved ethane concentrations were also higher in the samples collected using the IsoFlask® for the water samples with elevated methane concentrations. This finding is consistent with previous literature (e.g., Gvirtzman and Gorelick 1992; Aeschbach-Hertig et al. 2008; Darrah et al. 2014), which shows that effervescence of one gas will strip other gases from the sample, even when the other gases are present at concentrations well below their respective solubility concentrations. These results highlight a potential concern of low-bias due to

effervescence that may be less obvious when the target analytes are constituents typically present below their solubility (e.g., benzene or other VOCs). The effect may be less pronounced for VOCs with lower Henry's law constants; nevertheless, the loss of any VOC during sample collection may still be enhanced by effervescence.

Inverted VOA Sampling Method Provides No Advantage Relative to Direct–Fill VOA Sampling Method in Non–Effervescing Conditions, and Reports Lower Methane Concentrations When Bubbles of Exsolved Gases Are Present

Although the intent of the Inverted VOA method was to prevent gas loss associated with atmospheric exposure during sample collection, the Inverted VOA method performed no better than the Direct-Fill VOA method for samples with methane concentrations less than 20 mg/L. Rather, in this concentration range, the more time consuming and complicated Inverted VOA sampling method provided comparable results to the Direct-Fill VOA method. At or above 20 mg/L methane, the Inverted VOA method (both high-flush and low-flush variants) reported lower methane concentrations than the Direct-Fill VOA method, indicating that in the higher range of methane concentrations, the Inverted VOA method was low-biased.

This difference appears to be related to the presence of bubbles comprised of exsolved gases in the Inverted VOA vials. Most protocols for the collection of VOA samples stipulate that no bubbles be present in the VOA vial at the end of sample collection. Using the Direct-Fill VOA method, exsolving gas from effervescing groundwater is lost to the atmosphere during sample collection, and the VOA vial can be completely filled with water. However, when using the Inverted VOA method with effervescing groundwater, it is not feasible to prevent the accumulation of exsolved gases (e.g., methane and carbon-dioxide) inside the inverted VOA vial. These bubbles cannot be removed from the vial without compromising the sample collection process.

During our study, larger bubbles (i.e., headspace comprising $\geq 5\%$ of the VOA vial) were commonly observed in the Inverted VOA samples when the methane concentrations were high (i.e., Direct-Fill VOA result was at or above 20 mg/L). The largest bubbles were observed in Inverted VOA samples collected using the high-flush Inverted VOA method, many of which contained headspace gas volumes greater than 40% of the vial. As these bubbles originate from both the water captured in the bottle as well as the water flushed through the container prior to capping, it follows that the high-flush variant creates the potential for the greater accumulation of exsolved gases than the low-flush variant.

The gases in the headspace of the Inverted VOA vials are comprised of exsolved gases including both i) gases trapped at the time of sample collection, and ii) gases that continue to exsolve out of solution after the vials are sealed. Specifically, when the Inverted VOA vial is capped, exsolved gases in the headspace are at approximately atmospheric pressure. If the total partial pressures of dissolved gases in the water phase are still greater than atmospheric pressure, then gases will continue to exsolve out of the dissolved phase into the headspace bubble after capping of the vial. This off-gassing will continue until the headspace pressure is equilibrated with the pressure of the dissolved gases. This process is analogous to the re-pressurization of the headspace that occurs in a bottle of soda that has been opened and then resealed.

For the Direct-Fill VOA method, effervescing gases are lost directly to the atmosphere during sampling, and the sample can be filled to the top. The absence of headspace in the sample vial limits the potential for further gas loss after the vial is sealed. However, in the Inverted VOA method, effervescing gases are trapped in the vial as headspace, and gases continue to be lost from the dissolved phase into the headspace after capping of the vial. When these samples arrive at the laboratory, the dissolved methane concentration in the water phase is analyzed without accounting for methane accumulated in the headspace of the vial. Consequently, the dissolved gas concentration reported for the Inverted VOA method can be lower than the dissolved gas concentration reported for the Direct-Fill VOA method. (As a note, with a different analytical procedure (e.g., the helium displacement method), the presence of exsolved gases in Inverted VOA samples could result in higher reported methane concentrations than Direct-Fill VOA samples.) Modifying the Inverted VOA analytical procedure to account for the methane in the vial headspace would only partly correct the deficiencies of the Inverted VOA method because some of the gas collected in the VOA vial originates from water that is flushed though the vial but not retained for analysis. It follows that high-flush Inverted VOA samples, which contained the largest bubbles of the two Inverted VOA variants, reported lower methane concentrations than the low-flush Inverted VOA samples when compared to Direct-Fill VOA samples.

Using the IsoFlask[®] method, gases may also be lost to the headspace within the sample container after sample collection (and in fact, a larger headspace may form due to the flexible nature of the sample container); however, the analytical procedure accounts for the methane in both the water and headspace.

Implications of Findings for Groundwater Sampling Programs

1. In non-effervescing conditions, the open-system, semi-closed system, and closed-system methods tested in this study performed similarly (i.e., sample collection method was observed to have little effect on measured methane concentration) (Table 2).
2. In effervescing water, the use of a closed-sample collection system provides the most accurate means for the measurement of dissolved hydrocarbon gases. In this study, the IsoFlask[®] was tested as a novel embodiment of a closed system. Although the IsoFlask[®]

Table 2
Advantages and Disadvantages of the Three Sample Collection Methods

	Sample Collection Method		
	Direct-Fill VOA (Open System)	**Inverted VOA (Semi-Closed System)**	**IsoFlask® (Closed System)**
Applicability	*Non-effervescing sample:* Results are comparable to closed-system method. *Effervescing sample:* Negative bias (lower methane concentrations) compared to closed-system.	*Non-effervescing sample:* Results are comparable to closed-system method. *Effervescing:* Negative bias (lower methane concentrations) compared to open- and closed-system.	Negative bias not observed under any conditions
Reproducibility	*Good:* Median RPD ~6%	*Good:* Median RPD ~9%	*Good:* Median RPD ~5%
Ease of implementation	*Easy:* directly fill a 40 mL VOA vial.	*Moderate:* fill 5-gallon bucket with purge water, invert VOA vial in bottom of bucket, flush twice at rate of 0.5 liters per minute, cap vial under water.	*Easy:* directly fill an IsoFlask® using in-line tubing and fitting provided with the sample container.
Analytical availability	*Broad:* Many labs analyze dissolved light hydrocarbon gas concentrations in VOA vials.		*Limited:* Analysis of the IsoFlask® is currently only supported by Isotech.

allows a headspace to form, the laboratory analysis accounts for both dissolved and exsolved gases, enabling the reporting of an original dissolved gas concentration (i.e., that prior to exsolution). In contrast, in an open-sample collection system, gases exsolving during sample collection are lost directly to the atmosphere, resulting in a measured methane concentration that is lower than the original dissolved concentration.

3. The Inverted VOA method was intended to prevent the loss of exsolving gases to the atmosphere, thus producing more accurate dissolved gas concentrations than open-sample collection methods. However, in this study, we found that the presence of exsolved gases trapped in the Inverted VOA vials contributed to an even greater loss of dissolved gases than that observed in the Direct-Fill VOA samples, resulting in lower measured dissolved methane concentrations. As described previously, even if methane in the headspace of these vials was accounted for, this would only partially correct the deficiencies of the Inverted VOA method.

4. When gases other than methane are present in groundwater, effervescence can occur when methane is well below its solubility limit (25 to 35 mg/L). Depending on local gas composition, the methane concentrations associated with effervescence could be higher or lower than the 20 mg/L value presented in this study.

5. Dissolved gas concentration data previously obtained using the Direct-Fill VOA or Inverted VOA sample collection methods should be considered valid unless effervescence is known or suspected.

Acknowledgments

Supporting Information

Additional Supporting Information may be found in the online version of this article:

Figure S1. Methane concentrations of preserved vs. unpreserved Direct-Fill VOA samples.
Figure S2. Methane to ethane (C1/C2) ratios reported for matched samples collected using different sample collection methods.
Figure S3. Methane concentrations of replicate IsoFlask® samples analyzed at the PaDEP BOL vs. Isotech.
Table S1. Methane concentrations reported for the Direct-Fill VOA, Inverted VOA, and IsoFlask® matched samples and field duplicates.

Table S2. Ethane concentrations reported for the Direct-Fill VOA, Inverted VOA, and IsoFlask® matched samples and field duplicates.

References

Aeschbach-Hertig, W., H. El-Gamal, M. Wieser, and L. Palcsu. 2008. Modeling excess air and degassing in groundwater by equilibrium partitioning with a gas phase. *Water Resources Research* 44, no. 8: W08449.

Aravena, R., L.I. Wassenaar, and J.F. Barker. 1995. Distribution and isotopic characterization of methane in a confined aquifer in southern Ontario, Canada. *Journal of Hydrology* 173, no. 1–4: 51–70.

Baldassare, F., M.A. McCaffrey, and J.A. Harper. 2015. A geochemical context for stray gas investigations in the N. Appalachian Basin: implications of analysis of natural gases from Neogene-through-Devonian-age strata. *American Association of Petroleum Geologists Bulletin* 98, no. 2: 341–372.

Beyerle, U., W. Aeshbach-Hertig, D.M. Imboden, H. Baur, T. Graf, and R. Kipfer. 2000. A mess spectrometric system for the analysis of noble gases and tritium from water samples. *Environmental Science and Technology* 34: 2042–2050.

Bolton, D., and M.P.T. Pham. 2013. Dissolved-methane concentrations in well water in the Appalachian Plateau Physiographic Province of Maryland. Administrative Report No. 14-02-01. Maryland Department of Natural Resources, Maryland Geological Survey.

Coleman, D.D., C.-L. Liu, and K.M. Riley. 1988. Microbial methane in the shallow Paleozoic sediments and glacial deposits of Illinois, U.S.A. *Chemical Geology* 71: 23–40.

Cwiertny, D.M., and M.M. Scherer. 2010. Chlorinated solvent chemistry: Structures, nomenclature and properties (Chapter 2). In *In Situ Remediation of Chlorinated Solvent Plumes*, ed. H.F. Stroo and C.H. Ward. Springer Science + Business Media LLC.

Darrah, T.H., A. Vengosh, R.B. Jackson, N.R. Warner, and R.J. Poreda. 2014. Noble gases identify the mechanisms of fugitive gas contamination in drinking water wells overlying the Marcellus and Barnett Shales. *Proceedings of the National Academy of Sciences of the United States of America* 111, no. 39: 14076–14081.

Drever, J.I. 1988. *The Geochemistry of Natural Waters*, 2nd ed. Eaglewood Cliffs, New Jersey: Prentice Hall.

Eltschlager, K.K., J.W. Hawkins, W.C. Ehler, and F. Baldassare. 2001. Technical measures for the investigation and mitigation of fugitive methane hazards in areas of coal mining. Pittsburgh, Pennsylvania: Office of Surface Mining Reclamation and Enforcement, 125 p.

Gvirtzman, H., and S.M. Gorelick. 1992. The concept of insitu vapor stripping for removing VOCs from groundwater. *Transport in Porous Media* 8: 71–92.

Hirsche, T., and B. Mayer. 2009. *A Comprehensive Literature Review on the Applicability of Free and Dissolved Gas Sampling for Baseline Water Well Testing, 2007*. Edmonton, Canada: Alberta Environment.

Isotech. 2014. Collection of ground water samples from domestic and municipal water wells for dissolved gas analysis using IsoFlasks. http://www.isotechlabs.com/products/IsoFlask/ISOFLASK_SAMPLING.pdf (accessed May 2015).

Kampbell, D.H., and S.A. Vandegrift. 1998. Analysis of dissolved methane, ethane, and ethylene in ground water by a standard gas chromatographic technique. *Journal of Chromatographic Science* 36: 253–256.

Kappel, W.M., and E.A. Nystrom. 2012. Dissolved methane in New York groundwater, 1999—2011: U.S. Geological Survey Open-File Report 2012–1162. Reston, Virginia: USGS, 6 p. http://pubs.usgs.gov/of/2012/1162.

Marcellus Shale Coalition (MSC). 2012. Pre-drill water supply sampling and analysis plan. Document augments the MSC Recommended practice for pre-drill water supply surveys (MSC RP 2012-3). Pittsburgh, Pennsylvania: Marcellus Shale Coalition.

McHugh, T.E., L.M. Beckley, C.Y. Liu, and C.J. Newell. 2011. Factors influencing variability in groundwater monitoring data sets. *Ground Water Monitoring and Remediation* 31, no. 2: 92–101.

Molofsky, L.J., J.A. Connor, A.S. Wylie, T. Wagner, and S.K. Farhat. 2013. Evaluation of methane sources in groundwater in Northeastern Pennsylvania. *Groundwater* 51, no. 3: 333–349.

Moran, M.J.. 2006. Occurrence and implications of selected chlorinated solvents in ground water and source water in the United States and in drinking water in 12 Northeast and Mid-Atlantic States, 1993–2002. USGS Scientific Investigations Report 2005-5268. Reston, Virginia: USGS.

Nadim, F., S. Liu, and G.E. Hoag. 2001. The effect of air bubbles and headspace on the aqueous concentrations of volatile organic compounds in sampling vials. *Ground Water Monitoring and Remediation* 21, no. 1: 89–96.

PaDEP (Pennsylvania Department of Environmental Protection). 2010. Act 223 Section 208 Determination, Complaint No. 276316, December 23, 2010. Pennsylvania Department of Environmental Protection.

Pankow, J.F., and J.A. Cherry. 1996. *Dense Chlorinated Solvents and Other DNAPLs in Ground-Water*. Portland, Oregon: Waterloo Press.

Parker, L., and S. Britt. 2012. The effect of bottle fill rate and pour technique on the recovery of volatile organics. *Ground Water Monitoring and Remediation* 32, no. 4: 78–86.

Pennsylvania Bulletin. 2011. Title 25—Environmental Protection, Environmental Quality Board [25 PA. CODE CH. 78], Oil and Gas Wells, [41 Pa.B. 805], February 5, 2011. http://www.pabulletin.com/secure/data/vol41/41-6/239.html.

Sander, R. 1999. Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry. http://www.henrys-law.org/henry-3.0.pdf (accessed December 2015).

Senior, L.A. 2014. A reconnaissance spatial and temporal baseline assessment of methane and inorganic constituents in groundwater in Bedrock Aquifers, Pike County, Pennsylvania, 2012–2013. USGS, Scientific Investigations Report 2014-5117. Reston, Virginia: USGS.

Siegel, D.I., N.A. Azzolina, B.J. Smith, A.E. Perry, and R.L. Bothun. 2015. Methane concentrations in water wells unrelated to proximity to existing oil and gas wells in Northeastern Pennsylvania. *Environmental Science and Technology* 49: 4106–4112.

Sloto, R.A. 2014. Baseline groundwater quality from 34 wells in Wayne County, Pennsylvania, 2011 and 2013. USGS Open-File Report 2014-116. Reston, Virginia: USGS.