

Factors affecting the variability of stray gas concentration and composition in groundwater

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ABSTRACT

Identifying the source of stray gas in drinking water supplies principally relies on comparing the gas composition in affected water supplies with gas samples collected in shows while drilling, produced gases, casing head gases, pipeline gases, and other potential point sources. However, transport dynamics of free and dissolved gas migration in groundwater aquifers can modify both the concentration and the composition of point source stray gases flowing to aquifers and occurring in the groundwater environment. Accordingly, baseline and forensic investigations related to stray gas sources need to address the effects of mixing, dilution, and oxidation reactions in the context of regional and local hydrology. Understanding and interpreting such effects are best addressed by collecting and analyzing multiple samples from baseline groundwater investigations, potential point sources, and impacted water resources.

Several case studies presented here illustrate examples of the natural variability in gas composition and concentration data evident when multiple samples are collected from produced gases, casing head gases, and baseline groundwater investigations. Results show that analyses of single samples from either potential contaminant point sources or groundwater and surface water resources may not always be sufficient to document site-specific baseline conditions. Results also demonstrate the need to consistently sample and analyze a variety of baseline groundwater and gas composition screening parameters. A multidisciplinary approach is the best practice for differentiating among the effects of fluid and gas mixing, dilution, and natural attenuation.

INTRODUCTION

Most complaints of changing water quality reported in the vicinity of active oil and gas well operations share common traits when caused by the invasion of stray gas into domestic water wells. Gas

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bubbling causes oxygen-deprived colloidal complexes and fine-grained sediments that accumulate at the bottom of water wells to rapidly become suspended throughout the water column. Once such suspensions are introduced into the well pump intake port, normally clear water in homes suddenly becomes colored, turbid, slimy, and smelly. Effervescing hydrocarbon gases are immediately noticeable at the tap and pose a potential threat to safety. Gases bubbling through the water column in a well also transform a transitional aerobic to anaerobic redox environment to dominantly strong reducing conditions. Such effects excite the growth rate of strict anaerobes, such as sulfate-reducing bacteria. These in turn readily convert dissolved sulfate into odiferous, noxious, and toxic sulfides that can negatively impact air quality in homes.

Rapidly identifying and mitigating the source of stray gases depends on having readily available background and environmental baseline information. Hydrogeologic data provide the requisite information for addressing local factors governing gas transport. For example, gas bubbling can be caused either by a free gas phase migrating through the shallow groundwater environment or by gas exsolving from a migrating gas-saturated contaminant plume. Gas transport vectors from a potential point source will likely differ depending on the gas phase being transported. The Gas Migration section in this article addresses the factors that control the direction of free and dissolved gas transport in groundwater resources.

Forensic analysis of gas composition in samples from impacted water wells or surface water resources relies on comparisons with a baseline database of potential source gases. Point sources can include hydrocarbon gas migrating from targeted production intervals intersected while drilling, gas migrating from gas-bearing intervals intersected while drilling above a targeted producing horizon, and other natural and anthropogenic sources unrelated to oil- and gas-drilling operations.

In most forensic investigations related to finding and mitigating point gas sources from commercial gas production wells, the assumption is made that a single sample from a producing horizon or from a casing head is sufficient to adequately represent the gas composition at those sources. Case studies presented here show that such assumptions may be unwarranted and need to be tested, particularly when investigating gas wells as potential point sources for groundwater contamination.

Similar assumptions are made regarding the significance of single analyses of gas concentration and com-

position data from water well samples collected for pre-drill baseline investigations. Case study results presented here illustrate the importance of collecting groundwater quality parameter data when interpreting the significance of dissolved gas concentration and composition data. Multiple samples are required to satisfactorily demonstrate that declining dissolved gas concentrations in contaminated groundwater are the result of natural attenuation and not the result of groundwater mixing dynamics.

GAS MIGRATION

Free Gas Phase

The most common cause for stray gas migration arising from drilling operations is annular buildup of gas pressure in and around casing cements (Cheung and Beirut, 1985; Sepos and Cart, 1985; Schmitz et al., 1996; Brooks et al., 2008). Water well complaints related to such stray gas origins are commonly reported during or shortly after commercial gas wells are drilled and completed. The relatively short lag times between the time drilling commences and the time stray gas impacts are perceived imply that gas preferentially invades a low-volume interconnected network of large pores all the way to the surface. This will occur when gas pressure gradients near the source of stray gas and are high enough to exceed both the local potentiometric groundwater gradient, hydrodynamic forces, and minimum threshold capillary entry pressures. Gas expansion drive further serves to accelerate free gas plume migration rates toward the surface.

The path taken by pressurized gas to migrate to the surface from a given point source is generally directed by the shortest distance to the surface across equipotential lines established within the local groundwater regime (Hubbert, 1953; Tóth, 1995). Gas migration and breakthrough near the surface is ultimately driven toward areas of lowest hydrostatic pressures such as groundwater discharge zones, springs, topographic lows or valleys, and cones of depression locally generated around productive water wells. But because natural hydrocarbon gases are mostly insoluble in water, the specific path through rock matrix taken by a migrating free gas plume is locally governed by two-phase flow criteria (Judd and Sim, 1998).

Advective free gas migration from a point source to the surface can only occur when a continuous free gas

phase path is established through an otherwise water-saturated rock matrix. Accordingly, the largest pore spaces with the lowest threshold capillary entry pressures are preferentially invaded (Katz and Coats, 1968). Free gas phase access to permeable horizontal bedding planes greatly facilitates linking the large pore network necessary for stray gas to migrate both laterally and vertically toward the surface. Bedding planes provide the preferred lateral path, which is generally up-dip; vertical or highly inclined fractures provide the preferred vertical path.

The local stress regime plays a role in directing stray gas toward the surface. When the vertical overburden stress is less than horizontal stresses, gas migration through the bedding planes is more favorable. The transition zone where overburden stresses shift from the least to the intermediate principal stress direction can be anywhere between 1000 to more than 2500 ft (305 to >762 m) below the surface. This transition depth varies depending on mean overburden rock density and local structural controls such as folding and faulting (Zoback et al., 2003; Colmenares and Zoback, 2007). Mitigation strategies for sealing off potential stray gas sources from either reaching or breaching this zone have yet to be fully investigated.

Pulsed migration is a characteristic of the constant competition between capillary forces and gas migrating under pressure through the subsurface. Such behavior manifests at the surface in both seeps and affected water well headspace gas concentrations after breakthrough. Gas breakthrough temporarily releases pressure along the migration path, allowing water to imbibe the migration path and shut off gas flow. Subsequent pressure buildup at the source then acts to drive water back out of the capillary spaces, reestablishing flow to the surface. Such dynamics, similar to those driving steam pressure at the Old Faithful geyser in Yellowstone National Park, Wyoming, in large part account for the highly variable headspace concentrations of combustible gas detected when affected water wells are repeatedly sampled during short periods. Pulsing manifests either as on again-off again detections of headspace gas concentrations or as continuous headspace gas readings commonly varying by more than 50% of the maximum headspace concentrations detected at any given well. Once the source of gas pressure is mitigated, maximum headspace gas concentration also rapidly declines in a series of pulses.

Two-phase flow through the subsurface groundwater environment also explains rapidly declining rates of both headspace gas concentrations measured in im-

acted water wells and gas bubbling observed at seeps. As soon as the source of gas pressure is sealed, shunted, or depleted, hydrostatic and capillary pressures drive water to invade the free gas path to the surface. Water imbibition generally operates in the opposite direction of nonwetting-phase drainage; the smallest pore throats in the free gas path are closed off first. Hydrostatic pressure also drives higher imbibition rates in deeper aquifers than in shallow aquifers. Shut off from its source, a residual free gas plume loses energy quickly as water imbibes into the gas-saturated pore space. Once gas pressure declines below the minimum capillary entry pressure at any point along an interconnected free gas path, gas flow ceases instantly.

Preferential free gas migration through large connected pore space networks helps explain another empirical observation regarding some water well complaints. Some well owners have reported a perceived decline in water well yield shortly before the onset of documented free gas phase invasion. If a local aquifer's hydraulic conductivity is dominated by connected networks of small-scale preferential flow paths, such as through large pore spaces and/or fractures (Zheng et al., 2011), then free gas invasion into those spaces can significantly reduce the relative permeability of water through the aquifer. In other words, the effective hydraulic conductivity of the aquifer can become significantly reduced under the right circumstances (Yager and Fountain, 2001). Reduced hydraulic conductivity can affect the recharge rates of fluids entering a water well from an impacted aquifer.

If free-phase stray gas migrating through the subsurface encounters other free gas sources along the path toward the surface, mixing of multiple gas sources is possible (Jenden et al., 1993). For this reason, one of the objectives of baseline surveys should be to compile a catalog of gases encountered during baseline sampling and operation activities. Useful baseline data are derived from sampling and analysis of gas shows detected while drilling, of gas in casing heads exhibiting increasing gas pressures, and of headspace hydrocarbon gases encountered in water wells.

Technological improvements using rack-mounted gas tube collection systems in mud logging units now allow gas show samples to be collected and stored for several months without degrading gas sample quality. Chromatographic and stable isotope analysis of stored gas samples can then be deferred until needed to address stray gas issues should they arise. Alternatively, gas composition data reported by mud loggers can be

Table 1. Completion Data from Five Dog-Legged Wells Drilled at a Single Pad, Mamm Creek Field, Piceance Basin*

Well	Completion Date	Top Perf (ft)	Base Perf (ft)	Perf Interval (ft)	Number of Holes	Stages	Formation	Number of BHD Samples	Number of Prod Samples
A315C	November 24, 2004	4142	5658	1516	316	6	Williams Fork	15	4
A316C	May 17, 2003	4174	5546	1372	188	N/A	Williams Fork	15	4
M101	N/A	4074	5616	1542	280	5	Williams Fork	8	4
M101A	September 30, 2004	4094	5494	1400	86	4	Williams Fork	0	4
M102	December 28, 2004	4162	5610	1448	276	5	Williams Fork	8	4

*Multiple produced (Prod) and casing head (BHD) samples were collected from these wells during the last quarter of 2010 as indicated. Perf. = perforated.

used to select a subset of samples to be more completely analyzed with stable isotope measurements. At a minimum, samples of gas shows should be collected while logging the first gas well at every new well pad.

Dissolved Gas Phase

After free gas flow to the surface is shut off, residual gas contaminants in groundwater aquifers consist of free gas immobilized in capillary traps and dissolved gas. The soluble gas fraction migrates along groundwater flow lines from once gas-invaded pore spaces and from capillary traps containing residual free gas contaminants. Such contaminated groundwater plumes travel fastest through the rock matrix at the maximum groundwater velocities governed by a water-saturated rock matrix; the relative permeability of water in the matrix is much lower in partially gas-saturated pores. For these reasons, it may take more time for dissolved hydrocarbons in an impacted water well or spring to dissipate and return to baseline conditions than the time it takes for headspace gas concentrations to decline below detection limits or for bubbling to subside. Remediation rates are then dependent on rates of plume dilution, dispersion, and intrinsic bioremediation.

The solubility of methane in groundwater is low and is approximately equal to 32 mg/L at 1 atm of pressure and ambient average groundwater temperatures of 10°C (Yamamoto et al., 1976). At ambient shallow groundwater temperatures, the saturation concentration of methane is most sensitive to water depth; dissolved methane concentrations increase by approximately 32 mg/L for every increment in water depth of 33 ft (10 m). Because groundwater samples that are saturated with dissolved methane will effervesce as water is brought from the pump intake to the surface, it becomes difficult to accurately determine the saturation concentration at depth (Roy and Ryan, 2010). Accordingly, if a deep aquifer is saturated with methane,

a small amount of water level decline of water can lead to exsolution and effervescence. Such effects can allow headspace gas concentrations to increase from near detection limits to above the lower explosive limit (LEL). For this reason, baseline headspace measurements at a water well should be conducted and recorded both before and after well purging protocols are completed.

In rare instances, high-volume and high-rate pumping of certain aquifers used as water sources can provide another source for stray gas if aquifers contain naturally occurring high concentrations of dissolved hydrocarbons. Pressure drawdown associated with pumping can cause the aquifer to become supersaturated, thereby releasing stray gas into an aquifer system (Yager and Fountain, 2001). Baseline sampling projects should therefore plan on sampling and analyzing fluids and gases from such aquifers whenever a large volume of groundwater is extracted for use in drilling and completion operations.

A water well close enough to be in pressure communication with a pumped aquifer can become directly affected by stray gas if local water levels decline sufficiently to allow dissolved gas to exsolve into a well's headspace. Aquifers associated with relatively thick coal or lignite seams can be particularly susceptible to such effects. Gas desorption induced by rapidly declining ambient hydrostatic pressure equilibrium conditions can release additional stray gas into the groundwater aquifer.

VARIABILITY OF STRAY GAS COMPOSITION FROM COMMERCIAL GAS WELL POINT SOURCES

A general assumption made in most stray gas forensic investigations is that analysis of a single produced or casing head gas sample is adequately representative of drilling-related stray gas point sources. However, forensic investigations designed to address point sources

Table 2. Range of Selected Gas Composition Parameters in Produced Gas Samples from Vertical Wells at a Single Pad, Mamm Creek Field, Piceance Basin

Parameter	Units	A315C	A316C	M101	M101A	M102	Mean Range	Minimum (all)	Maximum (all)	Range (all)
(C ₁ /C ₂ + C ₃)	Decimal	0.61	1.20	0.41	0.53	1.23	0.80	5.85	7.96	2.11
C ₂ /C ₁	Decimal	0.0053	0.0127	0.0051	0.0045	0.0157	0.0087	0.0943	0.1184	0.0241
C ₂ /C ₃	Decimal	0.12	0.4	0.14	0.39	0.41	0.29	2.26	3.03	0.77
iC ₄ /nC ₄	Decimal	0.05	0.05	0.04	0.02	0.15	0.06	0.93	1.1	0.17
δ ¹³ C C ₁	‰ VPDB	0.22	0.99	0.01	1.46	0.33	0.60	-41.98	-40.3	1.68
δD C ₁	‰ VSMOW	1.9	9.9	5	13.4	7.9	7.62	-208.1	-193.6	14.5
δ ¹³ C C ₂	‰ VPDB	0.09	0.54	0.16	0.54	0.37	0.34	-29.09	-28.36	0.73
δ ¹³ C C ₃	‰ VPDB	0.07	0.53	0.23	0.43	0.26	0.30	-26.39	-25.79	0.6
δ ¹³ C iC ₄	‰ VPDB	0.08	0.45	0.27	0.27	0.49	0.31	-27.31	-26.62	0.69
δ ¹³ C nC ₄	‰ VPDB	0.01	0.37	0.36	0.23	0.21	0.24	-25.83	-25.2	0.63

of stray gas in groundwater and surface water resources need to consider variability. There may be, and there often are, large differences between point source gas compositions if source gases invading the shallow groundwater environment are derived from mixtures.

For example, recent results of a study conducted in the Garfield County, Colorado, part of the southern Piceance Basin demonstrate that produced gas samples can have variable compositions when the completion interval is long. Table 1 provides completion and sample collection data from five dog-legged wells drilled at one pad location in the Mamm Creek Field. Multiple samples of both produced and casing head gases were collected to address the source of hydrocarbons in casing head gases between October 14, 2010, and December 20, 2010. All gas samples were collected

in Isotubes™ and sent to Isotech Laboratories, Champaign, Illinois, for compositional and stable isotopic analyses. Tables 2 (results of produced gas samples) and 3 (results of bradenhead gas samples) summarize in detail the range of gas composition parameters commonly used for characterizing stray gas sources (Schoell, 1983; James, 1990; Whiticar, 1994; Prinzhofer and Pernaton, 1997; Prinzhofer et al., 2000). Results shown in Table 2 illustrate that the composition of produced Williams Fork gases from multiple wells drilled from a single pad is variable.

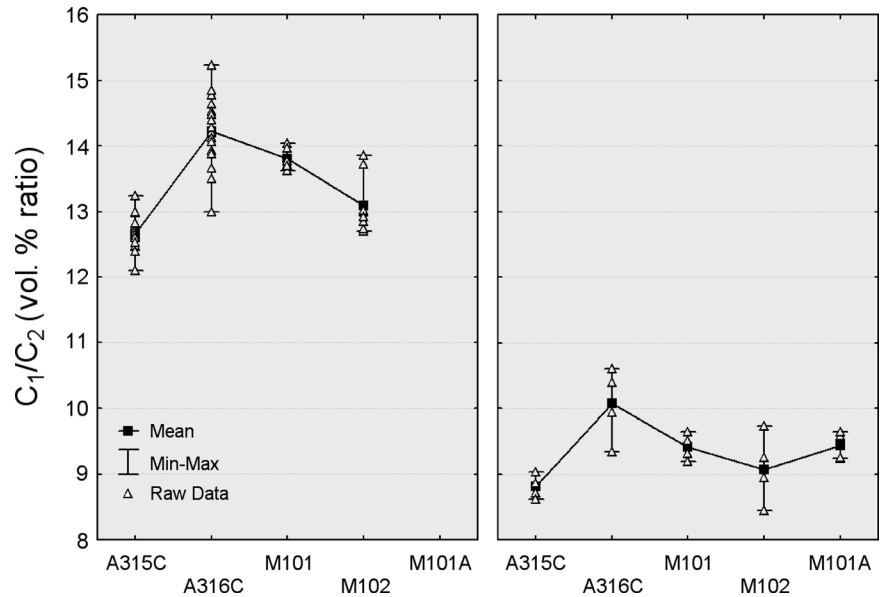
Results summarized in Tables 2 and 3 further demonstrate that the casing head (bradenhead) hydrocarbon gases are not derived from the underlying production interval of the Williams Fork Formation. For example, Figure 1 illustrates that although there is significant

Table 3. Range of Selected Gas Composition Parameters in Casing Head Samples from Five Wells on a Single Pad, Mamm Creek, Piceance Basin

Parameter	Units	A315C	A316C	M101	M101A	M102	Mean Range	Minimum (all)	Maximum (all)	Range (all)
(C ₁ /C ₂ + C ₃)	Decimal	1.01	2.00	0.36	No BHD	0.34	0.93	8.52	11.69	3.17
C ₂ /C ₁	Decimal	0.0071	0.0113	0.0021	No BHD	0.0066	0.0068	0.0657	0.0827	0.017
C ₂ /C ₃	Decimal	0.38	0.74	0.1	No BHD	0.87	0.52	2.21	3.69	1.48
iC ₄ /nC ₄	Decimal	0.11	0.75	0.06	No BHD	0.34	0.32	0.85	1.6	0.75
δ ¹³ C C ₁	‰ VPDB	1.14	0.1	0.06	No BHD	2.98	1.07	-42.42	-38.46	3.96
δD C ₁	‰ VSMOW	3.8	4.7	9.3	No BHD	26.2	11.00	-210.2	-183.7	26.5
δ ¹³ C C ₂	‰ VPDB	0.39	0.14	0.03	No BHD	0.12	0.17	-28.35	-27.96	0.39
δ ¹³ C C ₃	‰ VPDB	0.23	0.17	0.03	No BHD	0.56	0.25	-26.03	-25.35	0.68
δ ¹³ C iC ₄	‰ VPDB	0.33	0.31	0.04	No BHD	0.05	0.18	-26.71	-26.02	0.69
δ ¹³ C nC ₄	‰ VPDB	0.28	0.33	0.04	No BHD	1.11	0.44	-25.38	-24.08	1.3

BDH = bradenhead or casing head; C₁ = methane; C₂ = ethane; C₃ = propane; iC₄ = isobutane; nC₄ = normal butane; δ¹³C = carbon isotope ratio; δD = hydrogen isotope ratio.

Figure 1. Example of range and differences in methane-to-ethane ratios in casing head and produced gases from five wells at a single well pad and all wells completed in the Williams Fork Formation.



variability in methane to ethane ratios among wells within sample sets, the differences between produced and casing head sample sets are consistently different. A comparison of other gas parameters presented in Tables 2 and 3 also shows that there is no overlap in the range of values between sample sets for parameters $C_1/C_2 + C_3$, C_2/C_1 , and $\delta^{13}C_{C2}$. Furthermore, the range of values (difference between maximum and minimum values recorded) among casing head samples is consistently larger than those among produced gas samples for all the other parameters except for $\delta^{13}C_{iC4}$.

Among the fixed gas data in sample sets (not shown here), all Williams Fork gases contain more than 0.2% by volume with maximum concentrations of 2.7%. Casing head samples, on the other hand, all contain less than 0.008% CO_2 . The stable isotope ratio of carbon in CO_2 also varies on average by 10‰. Williams Fork gases have more negative values.

The overall similarity in hydrocarbon gas parameter values between sample sets shown in Tables 2 and 3 indicates that stray gases in casing head samples are genetically related to the source rock maturation and gas migration history of the area (Johnson and Rice, 1990; Ellis et al., 2009). This conclusion is supported by shallow gas shows collected from other wells located at different pads while drilling through the overlying Wasatch Formation. Wasatch samples are drier and the stable isotope ratios indicate a higher degree of thermal maturity than the underlying gas from the Williams Fork Formation.

Variability in produced gas parameters observed among the Piceance Basin data documented here can

be explained as resulting from mixtures. The Williams Fork Formation is composed of multiple sand lenses that are laterally discontinuous and difficult to correlate (Cole and Cumella, 2003; Pranter et al., 2008). Because sandstone lens reservoir compartments are each likely to have their own gas filling history (Smalley et al., 1994; Cubitt and England, 1995), the long completion intervals in each well allow gases from different compartments to mix in the wellbore environment. Similarly, variable casing head gas compositions indicate multiple sources of shallow gas.

Another kind of data set indicates that one should also expect to observe variable mixing relationships to occur in produced gas sampled from Marcellus Shale Formation gas wells. No published multiple sample data sets of produced gases from individual Marcellus Shale gas wells exist. However, mud gas data can provide a clue to the likely lateral heterogeneity in gas composition present within long horizontal well completions. For example, Figure 2 illustrates the variability in methane-to-ethane ratios and stable carbon isotope ratios of methane in mud gas samples from 3 Marcellus Shale wells drilled in the Pennsylvania part of the Appalachian Basin. The range in C_1/C_2 and $\delta^{13}C_{C1}$ values among samples from a single well is even larger than those documented in the produced gas sample data sets from the Piceance Basin.

Because casing head and produced gases from wells suspected to be sources of stray gases contaminating groundwater can have variable gas compositions, it is best to sample those source gases multiple times. Too often, a single analysis from a potential gas well point

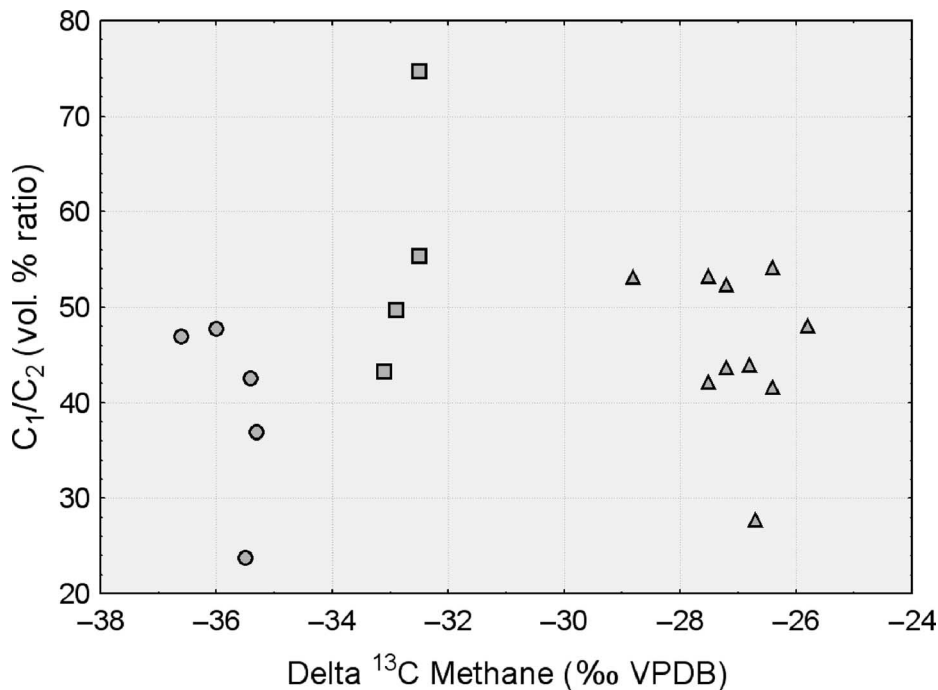


Figure 2. Variability of selected parameters in mud gas samples from three different wells drilled within the Marcellus Shale interval, Pennsylvania.

source is deemed similar to, but not identical to, the composition of gases in contaminated well. Collecting and analyzing multiple gas samples from such sources might instead show considerable overlap and help identify gas well point sources with greater confidence. The suggested best practice is to sample potential point sources multiple times to coincide with times when gas and water quality samples are collected from a contaminated water well or surface water resource.

VARIABILITY OF STRAY GAS CONCENTRATION IN WATER WELLS

Variability Caused by the Sampling Environment

The main body of groundwater sampling and analysis literature applies mostly to minimizing sampling error and variability inherent in activities related to the drilling, completion, and sampling of monitor wells (Barcelona et al., 1985, 2005). The ability to interpret analytical data collected in the field and via laboratory analysis is challenged by the complexity and heterogeneity of groundwater environments. This is true even when fluid sources are restricted to well-defined and small screened depth intervals in monitor wells. In contrast, variables needed to address the source of fluids in domestic water supply wells are poorly documented.

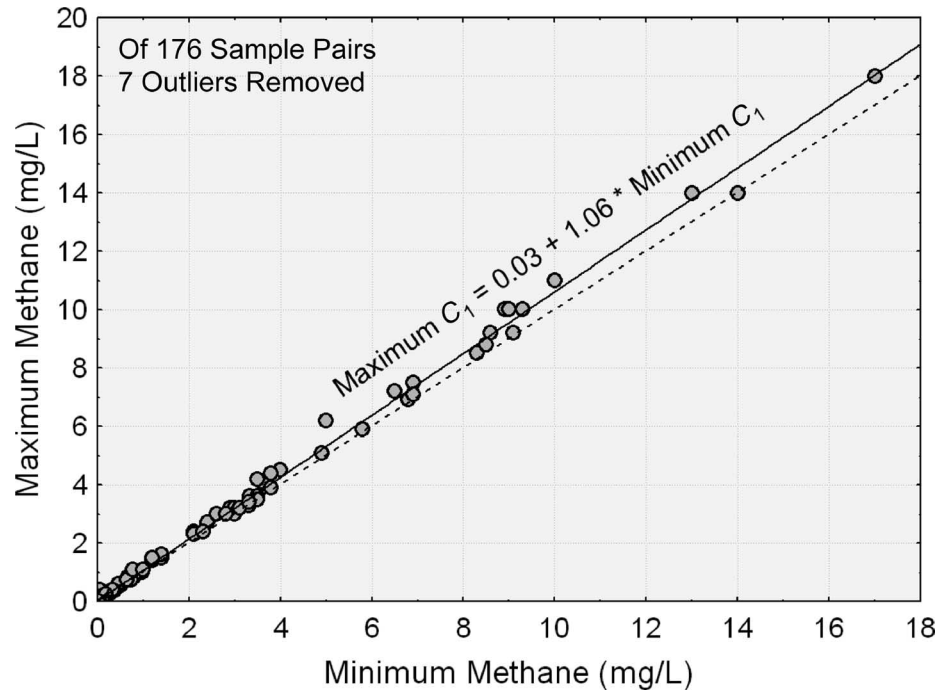
For example, domestic water well completion data are often unavailable and even when available tend to

be unreliable. Verifying such data is further vexed by the general reluctance of both operators and regulators to accept the potential liability for removing sanitary seals, pumps, and tubular equipment from water wells. Even when well completion data are known, most of the water wells have relatively long open-hole completions and/or extensive gravel packs. Such environmental conditions allow fluids from multiple layered aquifers to recharge a well (Church and Granato, 1996; Pohlman and Aldino, 1996; Hutchins and Acree, 2000). Thus, variable mixing of multiple fluid sources from a well tends to influence analytical results.

Low-yield water wells set with deep casing intervals used to store water can sometimes make it difficult to obtain representative fresh aquifer samples. For this reason, the uncensored use of well depth data as surrogates for aquifer depth in low-transmissivity aquifers tend can lead to erroneous conclusions regarding the source depth of wellbore fluids.

Other factors that can significantly affect the concentration of dissolved organic compounds include the types of pumps and sampling devices used (Parker, 1994), length of time that a well is pumped (Harder and Whitman, 1963), water sampling flow rates (Harder and Whitman, 1963; Barcelona et al., 2005), and the location of available sampling ports such as those on either side of water treatment or pressure tanks. Because such varied environmental conditions can significantly affect groundwater data, few domestic water wells met the restrictive criteria needed to satisfactorily address and

Figure 3. Results of duplicate analyses, Piceance Basin water samples.



characterize water quality in well-defined aquifers sampled for the U.S. Geological Survey National Water Quality Assessment program (Lapham et al., 1995).

Hydrocarbon gas concentration data obtained from water well samples can be expected to be variable because of the large number of unquantifiable environmental variables governing the source of fluids in water well samples. However, the extent of such variability is seldom documented. Dissolved hydrocarbon gases are not toxic, and their concentrations in groundwater are not regulated. Consequently, their presence is rarely included or reported in most publications dedicated to addressing groundwater quality (Darling and Goody, 2006). The following subsections address some of the other key factors affecting the variability of dissolved methane in groundwater.

Variability Caused by Sampling and Analytical Error

Figure 3 illustrates the variability in dissolved methane concentrations among duplicate samples collected from water wells, monitor wells, and surface waters in the Piceance Basin along the I70 corridor between Silt and Battlement Mesa, Colorado. Samples from both water wells and monitor wells were collected in volatile organic analysis (VOA) vials under a head of well water in 5-gal buckets and sent to commercial laboratories for analyses of dissolved methane using method RSK-175 (Kampbell and Vandegrif, 1998). Paired samples collected in this way are not duplicates sensu

stricto but are samples collected consecutively while water was flowing at low sampling rates from each well. Because no preservatives or biocides could be added using this sampling method, analyses of refrigerated samples were routinely performed within 48 h of the laboratory receiving the samples. Results show that the difference between the reported minimum and maximum dissolved methane concentrations increases linearly with increasing concentration. On average, the maximum concentration of a sample pair can be estimated by multiplying the minimum concentration by 1.06 and adding 0.03 mg/L. In other words, there is an average 6% difference between minimum and maximum values, ± 0.03 mg/L.

In contrast, Figure 4 illustrates the variability in dissolved methane concentrations among split samples sent to two different laboratories and collected from water wells, monitor wells, and surface waters in the same area of the Piceance Basin. As with duplicate samples, sample pairs represent consecutive samples collected. Results show that the average difference between the reported minimum and maximum dissolved methane concentrations in paired samples varied by 40%, ± 0.3 mg/L. Such large differences are most likely related to calibration errors because duplicate samples from the same set of commercial laboratories, as demonstrated, are not nearly as variable.

The results presented here are relevant to any forensic investigation directed to addressing the significance of temporal changes in dissolved methane concentrations at a well. When multiple samples are collected

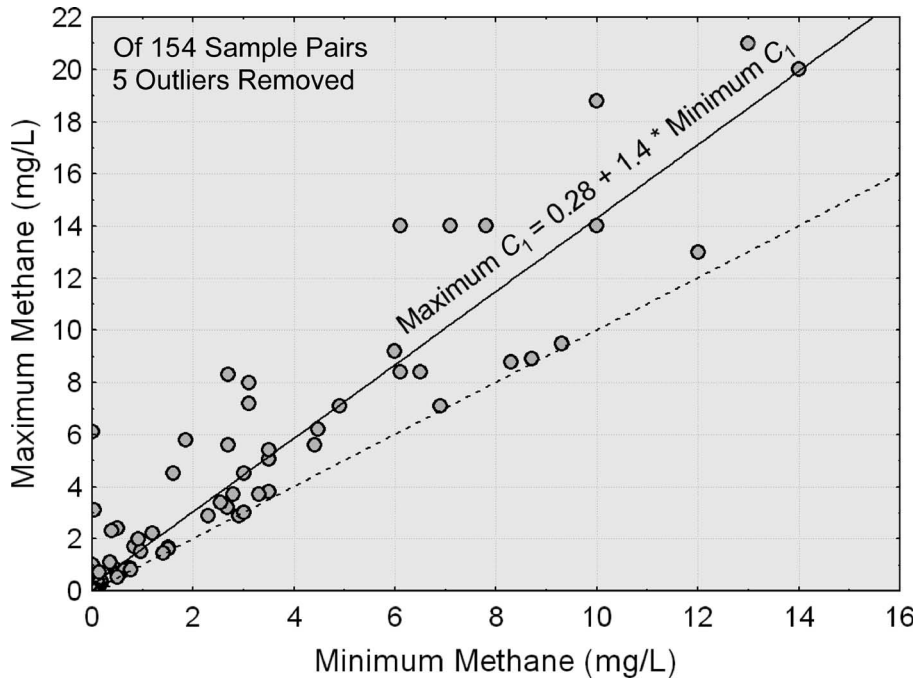


Figure 4. Results of split sample analyses sent to different commercial laboratories, Piceance Basin water samples.

from a well, it is important to demonstrate that any measured decreasing or increasing concentration trends are significantly greater than the variability arising from the additive effects of both sampling and analytical errors. In this context, it is necessary to routinely collect blind duplicate samples. It is ideal to collect one duplicate sample for every 10 samples collected in small sample sets or, at a minimum, one duplicate sample for every 20 samples collected in large sample sets such as those typical of regional baseline sampling programs.

Variability Caused by Mixed Fluid Sources

Fluid mixing dynamics in water wells can have a significant impact on dissolved methane concentrations. A good example of this is illustrated in Figure 5. As indicated by the annotated dates on the sample points, multiple samples were collected from a single domestic water well in the Piceance Basin for a period of 6 months during the same year. All samples were collected as previously described and sent to the same commercial

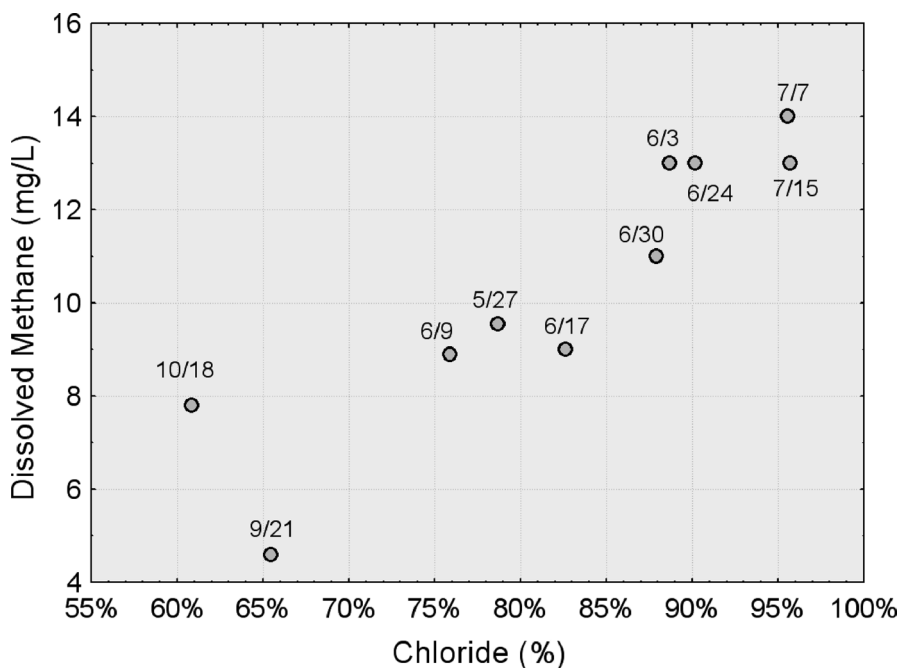
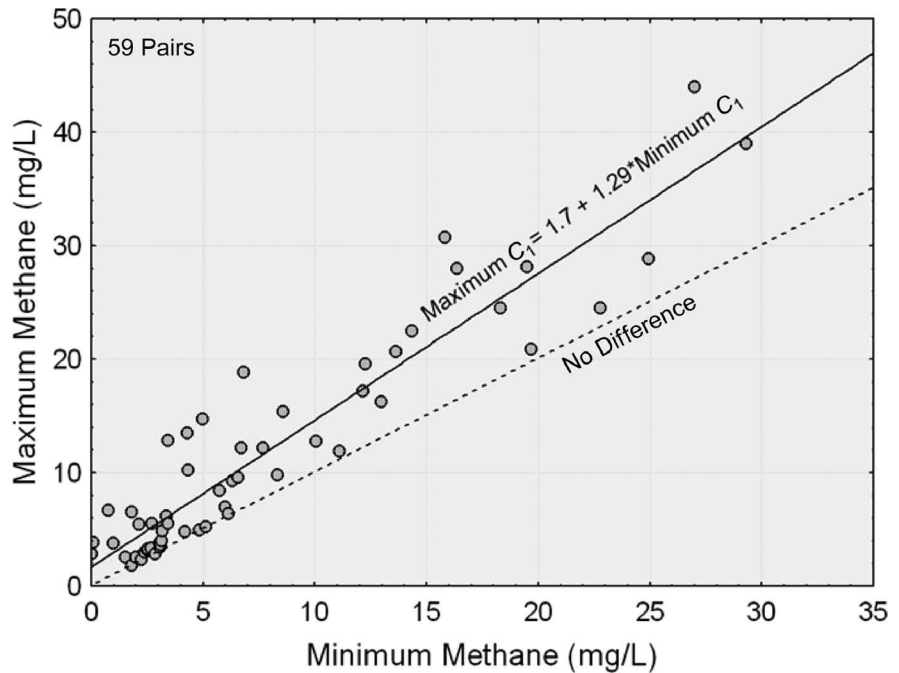


Figure 5. Dissolved microbial methane concentrations from a water well in the Piceance Basin vary proportionately as a function of the relative concentration of dissolved chloride (Cl^- [meq/L]/total anions [meq/L]). Cation-anion balances of all samples less than 10%.

Figure 6. Minimum and maximum dissolved methane concentrations corresponding to the pair of samples with the largest difference in calculated TDS concentrations in water wells sampled multiple times, San Juan Basin.



laboratory for RSK-175 analysis. Major ion analyses were also performed at the same laboratory, and only those sample results within a cation-anion charge balance of $\pm 10\%$ are included in the illustration. Stable isotopic data were used to demonstrate that the methane is of microbial origin and not related to any impacts from oil and gas operations.

The abscissa in Figure 5 indicates the relative concentration of chloride that, in this example, is equal to the ratio of chloride equivalents to the sum of all anion equivalents. Results show a linear and positively correlated relationship between the relative concentration of chloride in sampled fluids and their dissolved methane concentration. This can only occur as a result of mixing between fluids containing different dissolved ion and methane concentrations. One of those fluid sources is an end member of the fluid mix and is approximately composed of 100% chloride with an estimated dissolved methane concentration of 15 mg/L.

This author has observed similar fluid mixing relationships in more than one third of all water wells drilled to depths greater than 30 ft (>10 m) below ground surface and sampled multiple times in the Piceance, San Juan, Raton, and Powder River basins. The effects of aquifer fluid mixing can only be observed when baseline water samples are collected and routinely analyzed for both dissolved methane concentrations and major ion analyses. In this context, it is important to regularly monitor and ensure that analytical results of major ion

analyses have cation-anion charge balances of at least $\pm 10\%$ (Fritz, 1994).

Variability Caused by Bacterially Mediated Hydrocarbon Oxidation

Colorado Oil and Gas Conservation Commission (COGCC) orders 112-156 and 112-157 require San Juan Basin operators to sample dissolved methane in water wells before and 1, 3, and 6 yr after drilling new coalbed methane wells. Results of these analyses provide a unique opportunity to analyze water quality and dissolved methane data from water wells sampled multiple times over a large geographic region: the Colorado part of the San Juan Basin.

Figure 6 illustrates the distribution of the lowest and highest dissolved methane concentrations among sample sets from 84 wells sampled two or more times within a 14-yr period. Data shown are all derived from water wells with submersible pumps. All samples for dissolved methane were collected in VOA vials under a head of water in a 5-gal bucket at sample line flow rates of less than 1 gallon per minute. Each of the samples was analyzed by the same analytical service company within less than 24 h of the time they were collected. At least one of the samples in each pair has a dissolved methane concentration of 2 mg/L. This is the threshold concentration in COGCC regulations requiring stable isotopic analysis of dissolved methane.

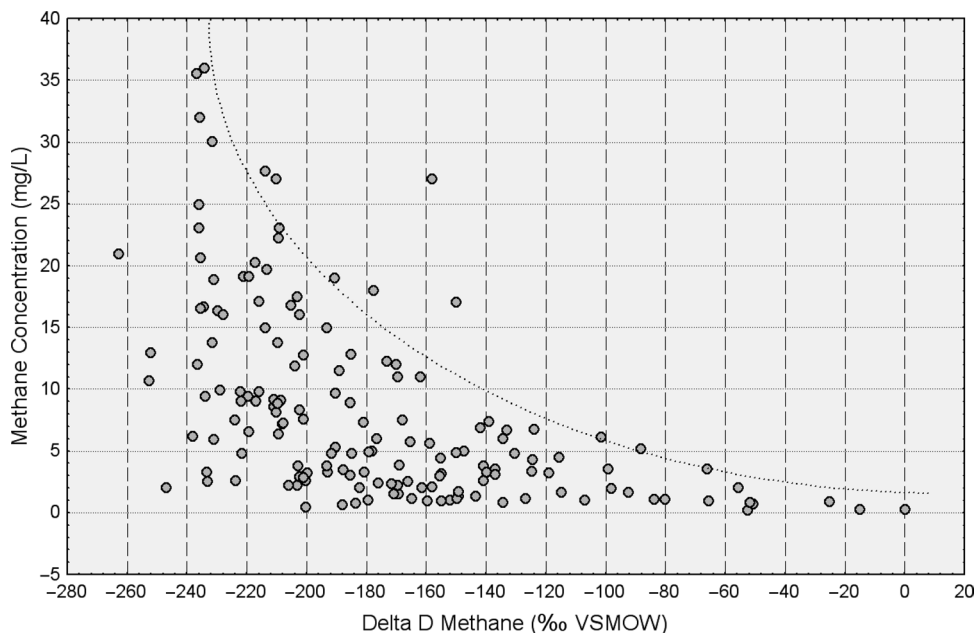


Figure 7. Maximum dissolved methane concentrations at any given δD_{C1} ratio decline with increasing enrichment toward positive values as indicated by the dotted line.

None of the samples come from wells that have been impacted by oil and gas operations as determined on the basis of stable isotopic analytical data.

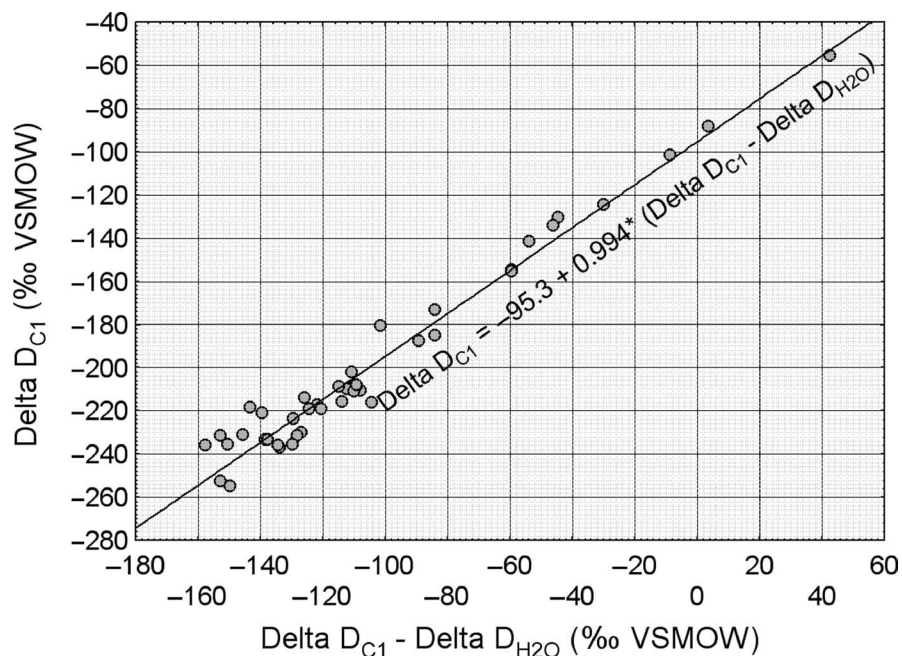
Results show that the average long-term variability of dissolved methane in water wells from the Colorado part of the San Juan Basin is approximately 25%, ± 2.5 mg/L. Such variability is nearly double that of the reported 14%, ± 0.5 mg/L, difference in minimum and maximum dissolved methane concentrations among multiple sample sets collected within a period of less than 95 days (Gorody et al., 2005). Aquifer fluid mixing between sodium bicarbonate, sodium sulfate, and sodium chloride water types accounts for only part of the observed variability in dissolved methane concentrations. Bacterially mediated methane oxidation also plays a significant role in controlling dissolved methane concentrations.

Figure 7 shows the relationship between the dissolved methane concentration and the stable isotope ratio of hydrogen in dissolved microbial methane. To qualify for inclusion in the illustration, dissolved hydrocarbons had to have stable carbon isotope ratios in methane of less than delta -50 ‰ and dissolved methane-to-ethane ratios more than 1000 (Whiticar, 1999). Results show that maximum dissolved methane concentrations decrease systematically as the stable isotope ratio of hydrogen increases. This is readily explained as resulting from kinetic fractionation associated with bacterially mediated methane oxidation. When the rate of methane oxidation (bacterial consumption) in a water well exceeds the rate at which unfractionated methane is re-

plenished from the surrounding aquifer, then the stable hydrogen isotope ratio of residual dissolved methane in the well increases. Figure 8 further demonstrates that decreasing stable hydrogen isotope ratios are related to oxidation of biogenic methane derived from the reduction of dissolved carbon dioxide.

Empirical observations have established that the fractionation of hydrogen isotopes between groundwater and biogenic methane produced in groundwater as a result of the carbon dioxide reduction is approximately delta 160 ‰, ± 10 ‰ (Schoell, 1980; Whiticar et al., 1986; Whiticar, 1999). The range of stable hydrogen isotope ratios in groundwater from San Juan Basin samples is between delta -82 ‰ and -105 ‰ (VSMOW), with an average value of delta -95 ‰, as shown by the intercept of the regression equation. Therefore, with a fractionation factor of delta 160 ‰, ± 10 ‰, the expected hydrogen isotope ratio of fresh methane in groundwater with an average hydrogen isotope ratio of delta -95 ‰ would be between delta -245 ‰ and delta -265 ‰. This is exactly the relationship observed in Figure 8. The linear 1:1 relationship between the decreasing stable hydrogen isotope ratio of methane and the decreasing difference between hydrogen isotope ratios in both dissolved methane and its solvent is entirely caused by kinetic fractionation effects of bacterially mediated oxidation. Although such oxidation also enriches the deuterium concentration in reacted water, the volume of fractionated water is too small relative to that present in aquifer to have a measurable effect on the bulk stable isotope composition (Hackley et al., 1996).

Figure 8. The effect of dissolved methane oxidation is confirmed by the linear relationship between the stable hydrogen isotope ratio in methane and the difference between this ratio and that of the groundwater in which methane is dissolved.



Based on bacterial activity reaction test (BART™) cultures routinely collected from San Juan Basin water well baseline samples, nearly all domestic water wells are infected with aggressive bacterial colonies of sulfate-reducing bacteria (SRB), iron-related bacteria, and slime formers (Cullimore, 2008). The term “aggressive” is defined by the rapid growth rates detected on the basis of the BART technique (time lag to a colorimetric response). The SRB bacterial groups alone occur in most water wells as high-density colonies totaling more than 1 million CFU/mL (BP America, proprietary data). Elevated dissolved sulfide concentrations commonly measured in a range of 1 to 5 mg/L using colorimetric HACH™ test kits further confirm the presence of aggressive SRB colonies. Their ubiquitous presence and occurrence in high population densities provide empirical evidence linking bacterially mediated sulfate reduction, isotopically fractionated dissolved methane, and declining dissolved methane concentrations in water well samples.

ADDRESSING THE SIGNIFICANCE OF DISSOLVED METHANE IN GROUNDWATER

Detectable concentrations of dissolved hydrocarbons occur in most anoxic groundwater aquifers (Harder and Whitman, 1963; Barker and Fritz, 1981; Coleman et al., 1988; Grossman et al., 1989; Zhang et al., 1998; Martini et al., 2003; Gorody et al., 2005; Darling and Gooddy, 2006; White and Mathes, 2006; Breen et al.,

2007; Osborn et al., 2011). Dissolved methane in groundwater is derived from at least three major source populations, two of them biogenic (derived either from fermentation or carbon dioxide reduction metabolic pathways) and one thermogenic. The statistical distributions of each of these naturally occurring stray gas sources are controlled by environmental variables that must be first assumed to be largely independent of one another. For example, the presence of thermogenic gases in shallow groundwater is governed by complex geologic variables that direct vertical migration from depth over geologic time. Biogenic gas, on the other hand, is ubiquitous and generated in situ within anoxic groundwater environments. Therefore, any statistical analysis addressing differences in the local or regional distribution of dissolved methane concentrations must both statistically test and account for the presence these major population groups. For these reasons, the spatial distribution of dissolved methane concentrations in baseline groundwater samples alone cannot be used to say anything statistically meaningful about any potential impacts of gas-drilling operations.

Another common assumption that must be questioned on a case-by-case basis is that the potential impact of drilling operations can only be confirmed if stray gases are identified as being thermogenic. If stray gases are released as a result of poor cement bonding from shallow gas reservoirs containing free gas-phase biogenic methane, then such assumptions are inappropriate.

Both methane and ethane are the most abundant hydrocarbon gases in nature. Accordingly, free and dissolved methane to ethane ratios provide the most useful

baseline sampling and analysis screening tool needed to differentiate between thermogenic and biogenic stray gas sources. As a rule and as documented here, thermogenic gases have methane-to-ethane ratios of less than 100, whereas biogenic gas sources have ratios more than 1000 (Aravenaa et al., 1995; Zhang et al., 1998; Breen et al., 2007; Hirsche and Mayer, 2007). For these reasons, all groundwater samples should be routinely analyzed for both dissolved methane and ethane using method RSK-175. All samples with low (<100) methane-to-ethane ratios should be routinely sent for, at a minimum, stable isotope analysis of carbon in methane and ethane and stable isotope analysis of hydrogen in methane. Although propane and butane are also excellent indicators for the presence of thermogenic gas in groundwater, their low concentrations relative to methane and ethane in thermogenic gas sources often render them undetectable in groundwater samples.

CONCLUSIONS

This article has primarily documented factors that affect stray gas concentration and composition in water wells under baseline conditions unaffected by drilling operations. Presumably, water wells that have been impacted by stray gases derived from drilling activities should be influenced by similar variables such as those described that affect both gas concentration and composition. Understanding and interpreting such interactions depend on collecting multiple samples and using a variety of analytical methods.

- Analyzing and collecting gas show samples while drilling are the most effective means for cataloging the vertical distribution of hydrocarbon gases that can be potential sources of stray gases in casing heads, water wells, and springs. Associated stable isotopic analyses of such samples can be deferred as needed to address forensic investigations of stray gas sources. If gas shows indicate the presence of biogenic gas in shallow gas reservoirs, then the recommended best practice is to analyze baseline groundwater samples containing free or dissolved gases for stable carbon isotopes of carbon in methane, ethane, and dissolved inorganic carbon, stable isotopes of hydrogen in methane and water, and stable isotopes of oxygen in water.
- Sampling and analysis of multiple samples from a single casing head at a commercial gas are useful

for addressing whether stray gas sources are derived from one or more shallow gas reservoirs, from production intervals, or from one or more mixed sources.

- Multiple samples and analyses of free and dissolved hydrocarbons from affected water wells can help unravel the effects of mixing, dilution, and intrinsic bioremediation on gas composition and gas concentration data. Interpreting such dynamics can be greatly facilitated by including water quality data, such as major ion analyses, with every sample collected for dissolved hydrocarbon analysis. Results from such a multidisciplinary approach are particularly useful, if not necessary, for demonstrating the effectiveness of remediation activities and a return to baseline conditions.

To minimize the inherently large variability in analytical data derived from springs and water wells, sampling and analytical protocols need to be fully documented and consistently applied. Laboratory data should also be routinely evaluated for quality control using splits and blind duplicate analyses.

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