



Dissolved gas ‘concentrations’ or ‘concentration estimates’ – A comment on “Origin, distribution and hydrogeochemical controls on methane occurrences in shallow aquifers, southwestern Ontario, Canada” by Jennifer C. McIntosh, Stephen E. Grasby, Stewart M. Hamilton, and Stephen G. Osborn



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1. Introduction

The need for research into the occurrence, origin, and fate of groundwater gases is reflected in an almost exponential increase in peer-reviewed publications involving dissolved groundwater gases. We enthusiastically endorse all efforts to develop baseline inventory of groundwater methane concentrations, and other markers, prior to exploitation of unconventional gas sources, as McIntosh et al. (2014) have done. In our view, however, the lack of verified, standard approaches for the combined sampling, storage, manipulation, and analysis of dissolved groundwater gases challenges our research community. While we by no means seek to implicate McIntosh et al. (2014) specifically, their paper is typical of some commonly-used approaches that we believe contribute to inaccurate estimations of groundwater gas concentrations, in addition to containing several unfortunate formulaic errors. Indeed, our concerns are strongly held enough that we suggest McIntosh et al. (2014) are presenting *methane concentration estimations*, not *concentrations* per se, particularly when they report *in situ saturation* (we assume the more serious of the formulaic errors shown are

not carried over into the data). These methane concentration estimations are clearly correlated to geologic formations in the study area, and are hence salient to McIntosh et al.’s objectives. We do not believe they should be considered accurately measured concentrations, however.

In this comment, we i) point out some calculation or formulaic errors as evident in the text, ii) identify some issues with sampling that may lead to greater uncertainty in dissolved methane concentration estimations, and finally, iii) briefly discuss the reliability of using domestic wells for dissolved gas sampling. We do not expect these issues will alter the main conclusions of the work. Rather it is hoped that this comment will provide insight into sources of error and inaccuracy in dissolved gas estimations.

While the groundwater community does not have a clear tolerance for error in dissolved gas calculations, a charge balance error less than 5% is ideal, and less than 10% is typically tolerable. Many of the calculation errors below are apparently minor, but with propagation of error calculations, it is difficult to know how serious they would be when considered as a whole.

2. Calculation or formulaic errors

- i) The authors estimate barometric pressure (p_{atm}) as that for average sea level, though it declines with increasing elevation

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and varies on a daily/seasonal basis. Elevation in the study area can reach ~500 m a.s.l., which equates to an average p_{atm} of 94 kPa. At the highest sampling elevations, this error contributes to a ~6% overestimation of the gas concentrations. Up to date barometric pressure data are readily available from weather station data and there are many pressure gages that can provide reliable values for field and laboratory air pressure.

- ii) The use of several different ratios for Henry's Law coefficients (two of which are the inverse of one another; Sander, 2014) commonly presents challenges. McIntosh et al. used the Henry's Law coefficient (K_s) for methane at standard pressure and temperature (Lide, 1995) of $0.0014 \text{ mol kg}^{-1} \text{ bar}^{-1}$, which coincides with the Henry's law form that is a ratio of the aqueous concentration, $CH_{4(aq)-meas}$ [mol kg^{-1}], divided by the gas concentration, $CH_{4(g)}$ [bar]:

$$CH_{4(aq)-meas} = K_s \cdot CH_{4(g)};$$

This is different than that presented in McIntosh et al.

- iii) In the third equation on p. 42,

$$CH_{4(aq)} = \frac{(CH_{4(aq)-meas} \times V_{(W)}) + (CH_{4(g)} \times \frac{V_{(g)}}{22.4})}{V_{(W)}},$$

the dissolved and the gas phase methane masses are summed to calculate the total mass of methane in the sample bottle, and then divided by the groundwater sample volume to calculate the aqueous methane concentration.

The first term of the numerator is the estimated molar methane mass in the aqueous phase, while the second numerator term is meant to calculate the mass of methane in the gas phase (or headspace) of the sample bottle.

The second numerator term estimates the number of moles in the headspace using the ideal gas law, where $n = \frac{p \cdot V}{R \cdot T}$, by multiplying the partial pressure by the volume of gas ($CH_{4(g)} \cdot V_{(g)}$) and dividing by the gas constant multiplied by the temperature ($R \cdot T$). McIntosh et al. do not present the units for their product of $R \cdot T$, and report a value of 22.4. Given the gas constant value of $8.314 \times 10^{-2} \text{ kg bar mol}^{-1} \text{ K}^{-1}$ for fresh water, where density is one kg L^{-1} , one arrives at a temperature of 269.4 K or -3.7°C .

The temperature used for this calculation should be that at which lab analyses were conducted. In this case, the samples were allowed to reach room temperature prior to analysis (not given exactly, but most laboratories are near 25°C or 298 K). The product of $R \cdot T$ using this temperature and the gas constant above would be $24.78 \text{ kg bar mol}^{-1}$.

- iv) The fourth equation on p. 42 is used to estimate the total downhole pressure at the sampling depth (p) in order to subsequently estimate the *in situ* percent saturation of methane, where $p = 1.013 + \frac{D-H}{10}$, in bars. The total downhole pressure is the sum of atmospheric pressure (reported as 1.013 bar) and gage water pressure (calculated in their equation as $(D-H)/10$).

Gage water pressure (P_{H_2O}) = ρgh , where ρ = water density (1 kg L^{-1} for fresh water, but as high as 1.009 kg L^{-1} in McIntosh et al.), g = acceleration due to gravity (9.81 m s^{-2}), and h = hydraulic head acting on the point of measurement; Freeze and Cherry, 1979). The equation estimates the hydraulic head as the height of the water column above the measuring point (h) as $D - H$ [m], where D = the depth to the measuring point (assumed to be the bottom of the well), and H = the depth of the water level in the

well (both with units of meters below ground surface). The authors used a factor of ten (the denominator in the second term) as the pressure (in bar) exerted by one meter of water. However, given that P_{H_2O} per meter of water = $1.00 \text{ kg L}^{-1} \times 9.81 \text{ m s}^{-2} \times 1 \text{ m}$ for fresh water, the conversion factor should be 10.19 m/bar, rather than 10 m/bar (ignoring the density difference noted above).

- v) In the fifth equation (second column, p. 42), the authors attempt to calculate the degree (or percent) of methane saturation, as the ratio of the measured methane concentration (here they used $CH_{4(g)}$, in bar) and the calculated saturated methane concentration (or 'bubbling pressure' in this context; Roy and Ryan, 2013) associated with the temperature and total pressure, p , of the well water sampling point. The equation presented for the *in situ* percent methane saturation is:

$$CH_{4(g)\%Sat} = \frac{CH_{4(g)}}{K_{gw} \cdot 1.013 \cdot p} \cdot 100,$$

where $CH_{4(g)}$ is the measured headspace concentration [bar], K_{gw} is the Henry's Law constant at the *in situ* groundwater temperature [$\text{mol kg}^{-1} \text{ bar}^{-1}$], 1.013 is assumed atmospheric pressure [bar], and p is total pressure [bar].

Clearly, considering a unit dimensional analysis, this equation is incorrect.

We suggest that the numerator of the first term should be the calculated aqueous groundwater methane concentration ($CH_{4(aq)}$) [mol kg^{-1}], rather than the measured methane partial pressure in the gas phase ($CH_{4(g)}$ [bar]). In addition, the authors should remove 1.013 (bar) from the denominator since it is already considered in the total pressure estimation (see above). This results in full cancellation of units on the right side of the equation, as required.

We note that part of the issue with this equation may be associated with the second point above.

Further, there is no mention of the contribution of capillary pressure, in addition to total water pressure (McIntosh et al.'s fourth equation), toward the maximum saturation of methane, or bubbling pressure, within the aquifer that is used to determine the degree of saturation in the fifth equation. Capillary pressure is usually negligible compared to water pressure at depth in most aquifer (coarse) materials, but this should be stated.

Finally, the degree of saturation calculation ignores any contribution from dissolved gases other than methane, which was not stated. Given McIntosh et al. did not measure all of the common groundwater gases (N_2 , O_2 , CH_4 , N_2O , CO_2 , H_2S ; Ryan et al., 2000) in any of their well water samples, we cannot determine how these other gases may affect their estimates of the percent methane saturation.

- vi) The authors report that the salinity values of their samples were too low (between 85 and 9279 mg/L) to need to consider 'salting out' of dissolved methane. They failed to substantiate this statement with any citations. A rough estimation of decreased methane solubility at 298°K would be 6% at 10,000 mg/L (Yamamoto et al., 1976).

3. Methane sampling and analysis issues

The groundwater community lacks standard practices for the sampling and analysis of dissolved gases, which contributes to the use of a wide range of practices (Hirsch and Mayer, 2007) that have not been rigorously tested or compared. The McIntosh et al. approach has not been published elsewhere to our knowledge, and we believe that the following concerns justify the use of methane

concentration 'estimates' rather than reported concentration.

- i) The water well samples were exposed to the atmosphere during the partial filling of the sample bottle (leaving about 600 mL of water, and about 575 mL of headspace). Gas ebullition is fast (Walsh and McLaughlan, 1999), and partial bottle filling would have allowed for methane losses to the atmosphere, via bubbling out in the sample bottle or transport across the water–air interface before the sample bottle was capped. The water sample could conversely have been contaminated with atmospheric gases present in the bottle before partial filling (more on this below). We note that McIntosh et al.'s supplementary data indicate bubbles were observed during sampling in a significant fraction of the water wells sampled.

If one has one liter of water saturated with methane at room temperature (298° K) and one atmosphere pressure (i.e. 1.4 mmol L⁻¹ or 22.7 mg L⁻¹ CH_{4(aq)}), from which one mL volume of bubbles are exsolved and 'lost' to the atmosphere during sampling (easy to visualize and imagine happening), the associated methane mass loss can be calculated. One liter of methane-saturated water (standard temperature and pressure) would have 1.4 mmol methane. One mL gas bubbles would have (ignoring capillary forces of the bubble):

$$n = \frac{PV}{RT} = \frac{1 \text{ atm} * 0.001 \text{ L}}{0.08205 \frac{\text{L atm}}{\text{mol K}} * 298 \text{ K}} = 0.04 \text{ mmol},$$

or about 3% of the dissolved methane. Perhaps even ten mL of bubbles might be lost per liter of pumped groundwater (we are not aware of actual data on the volume of gas bubbles produced during groundwater sampling); this would equal 0.4 mmol methane (or about 29%) loss of methane.

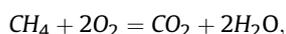
Since gas solubility (or saturation) is linearly related to water pressure (i.e. ~depth below water table), and water well pumping causes decreased water pressure to occur, in-well gas ex-solution occurs when gas-rich water wells are pumped (Roy and Ryan, 2010). One liter of methane-saturated groundwater sampled from 10.19 m depth would exsolve an estimated 1.4 mmol of methane when allowed to equilibrate to atmospheric pressure. At 20.38 m, 2.8 mmol of methane gas would exsolve. Thus, it is possible that higher bubble volumes than described in our example above might exsolve from gas-saturated waters from deep wells, resulting in even greater concentration errors.

- ii) There was no sample preservation (and ample opportunity for oxygen contamination of the sample water during sampling, and overnight equilibration of sample water with air purposely contained in the sample bottle), so bacterial methane oxidation may have occurred during transport and storage. This too could have led to lower estimated methane values.

We can estimate a maximum amount of methane that could be oxidized if bacteria consumed all of the atmospheric O₂ in the headspace. A 575 mL volume of headspace at initially 21% O₂ composition (i.e. atmospheric composition) would contain

$$n = \frac{PV}{RT} = \frac{0.21 \text{ atm} * 0.575 \text{ L}}{0.08205 \frac{\text{L atm}}{\text{mol K}} * 298 \text{ K}} = 4.94 \text{ mmol O}_2$$

Using a simplified equation for methane oxidation,



the 4.94 mmol O₂ could oxidize about 2.5 mmol CH₄. This is

considerable given methane solubility of 1.4 mmol L⁻¹ at 25 °C (298 K) and one atmosphere pressure. Further, this estimate doesn't consider any oxygen dissolved into the water.

- iii) The headspace gas analytical method (1st round of samples) used an Eagle® multigas meter, a handheld gas detector, to "sniff" the headspace and report methane concentrations. Presumably methane could escape when the lid of the sample bottle is opened to allow this measurement, causing a further bias toward underestimated concentrations.
- iv) For the GC analysis of gases (2nd round of samples), gas volume and water mass were measured in the sample bottle, along with atmospheric pressure, but the gas pressure of the headspace, which could may have been above atmospheric pressure due to exsolution of methane-charged groundwater (e.g., dissolved gas pressure over 200 kPa measured for groundwater with high methane content by Roy and Ryan, 2010) was not determined. This excess pressure, or the volume of the expanded gas phase once brought to atmospheric pressure, are needed for proper calculation of dissolved methane concentrations (Roy and Ryan, 2013).
- v) The authors state that it is "likely that most free gas rises past the pump without being captured by it" (p. 42). This means that gas bubbles forming within the well due to degassing as the well water is pumped (depressurized), as illustrated by Roy and Ryan (2010), will also be largely lost by ebullition. Thus, the water (and any gas bubbles that were also captured) collected at the surface may be degassed in comparison to the *in situ* groundwater.
- vi) The authors report that monitoring of "field parameters (temperature, pH, electrical conductivity and redox potential) was performed to [ensure] collection of fresh water samples". We suggest it would be beneficial to include field meters that monitor dissolved gases (e.g. total dissolved gas pressure sensor; Manning et al., 2003; Roy and Ryan, 2013) to assess the appropriate amount of water to pump before sampling for groundwater gases. Roy and Ryan (2013) also note that ebullition in methane groundwater increases with increased drawdown, and that minimizing drawdown in the well is needed to prevent in-well ebullition and methane mass loss.

4. Issues with sampling domestic wells

Sampling well waters for dissolved gases (and particularly reactive gases like methane) is challenging at the best of times. The authors did not discuss the substantial variations in methane concentrations in water wells, which are pumped frequently but intermittently, that have been observed (e.g. Harder et al., 1965; Gorody, 2012; GWPC, 2012).

The observed variability in groundwater methane concentrations reflect a number of issues that are exacerbated when sampling from domestic wells as opposed to monitoring wells. First, water and gas sampling must occur at the surface rather than within the well screen because few investigations risk removing the domestic down-hole pump. This increases the likelihood of degassing losses, which may occur in the well, the distribution pipes, pressure tank, or holding tank, and in association with the sampling approach.

Atmospheric contamination is more likely when surface sampling. There is also less control over the pumping rate applied, and thus, the amount of drawdown that occurs, which can affect in-well degassing caused by depressurization (Roy and Ryan, 2010).

Finally, domestic wells also prevent the use of down-hole total dissolved gas pressure sensors to guide sampling procedures and improve the accuracy of dissolved gas concentrations (Roy and Ryan, 2013). Unfortunately we are unaware of any studies that have quantified the losses of dissolved gases when sampling from domestic wells. Given the number of groundwater gas sampling programs being conducted that use domestic wells, it seems that this would be very useful.

5. Summary

Assuming that the major formulaic problems are just errors within the text and did not apply to the data calculations, the general trends and conclusions reported by McIntosh et al. are likely still valid. However, there is likely larger uncertainty in the 'concentration' values than is portrayed, with potential that some reported values are substantially lower than they should be due to the combination of calculation and sampling issues we have identified. We suggest that these values should be considered 'concentration estimates' and urge greater care in dissolved gas sampling of groundwater, and encourage those involved in water well sampling to recognize and quantify the bias in domestic wells sampling. Finally, one needs to report dissolved gas concentrations as 'estimates' unless either i) the total mass of gas molecules are fully captured and preserved (i.e. under *in situ* water pressure) and included in the analytical approach, or ii) *in situ* total dissolved gas pressure is measured and combined with robust gas composition analyses.

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