

Dissolved methane monitoring for ground gas risk assessment

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Ground gas monitoring data for risk assessment should ideally be obtained from monitoring wells installed in the unsaturated zone. Where groundwater is present in gas monitoring wells it may contain dissolved methane that can influence the measured gas concentrations in the well headspace. The source of the dissolved methane can be from a diverse range of sources including residual gas from historic landfill, groundwater in Alluvial soils or methane released as a result of shale gas production. This paper provides information on the influence of dissolved methane on headspace gas concentration and shows how monitoring of dissolved methane can be used to help interpret ground gas monitoring results.

Introduction

Ground gas monitoring wells should ideally be installed in the unsaturated zone, above the groundwater table (BSI 2013). However, in practice it can be difficult to identify the long term groundwater levels at the time of drilling and gas monitoring wells may end up with groundwater in them.

Groundwater can contain dissolved methane and when it is present in monitoring wells it will cause elevated gas concentrations in the well headspace that are not representative of the surrounding soil gas concentrations.

Where elevated methane concentrations are recorded in the well headspace and groundwater is present in the well, understanding the dissolved methane concentration can help interpret the gas monitoring data and give a better understanding of the risks any gas poses to development.

The Infrastructure Act (2015) places a legal duty on licensees to monitor methane in groundwater for a minimum of 12 months prior to hydraulic fracturing. It will also be required through the operational life of a well to post abandonment as part of the requirements of an Environmental Permit.

Methane in groundwater

Methane is widely present in groundwater (Darling and Goody 2006). It is present in non-polluted aquifers at relatively low concentrations (up to 1500µg/l) that are not likely to significantly influence gas monitoring results. However, it can be present at greater concentrations that will affect gas monitoring results in the following situations:

- Where landfill gas generation is or has occurred as a result of anaerobic degradation of organic material;
- Where hydrocarbon contamination is degrading in the ground;
- Within groundwater in Coal Measures or shale gas bearing rocks;
- Within anaerobic groundwater environments such as alluvium, peat bogs, lignite deposits, and glacial, lacustrine and aeolian sediment (Goody and Darling 2005);
- As a result of carbon dioxide reduction (Whiticar et al 1986).

The solubility of methane in groundwater depends on pressure, temperature and the concentration of other gases or minerals in the water. Pressure has the most dominant effect on methane concentration in water (Hooker and Bannon 1991). This is most significant when water is pumped from depth into a space at atmospheric pressure. This is similar to opening a fizzy drink and large volumes of gas can be released.

Methane generally has a low solubility in water and the saturation concentration at 1 atmosphere and 10°C is 29.9mg/l. If water is in equilibrium with fresh air at 10°C and there are no other sources of methane in the water, then the concentration of dissolved methane will be 4.78×10^{-5} mg/l (Hooker and Bannon 1991).

It is common to measure dissolved methane in groundwater at concentrations well more than 1.600mg/l which can cause elevated gas concentrations in the well headspace because of continuous partitioning in and out of the gaseous phase.

Elevated concentrations of dissolved methane are only likely to pose a risk if the water discharges into a confined space. The presence of high dissolved concentrations in groundwater below a building will not normally pose a risk because there is no significant change in pressure and migration to the surface is driven by diffusion. Unless the groundwater is at the underside of the building it cannot migrate quickly enough to pose a risk. There are no published cases where dissolved methane has partitioned to soil gas and migrated through soil into buildings.

Careful assessment is needed where groundwater is pumped, and water flows into confined spaces (pumping chambers, shafts, tunnels, etc). Dissolved methane is an important consideration when designing basement waterproofing systems on sites where gas is present in the ground. In particular careful assessment of the use of cavity drainage systems is required, and the impact of dissolved methane entering such systems in groundwater.

When compacting landfill or general Made Ground to reduce settlement (e.g. using surcharging or dynamic compaction) excess pore pressures may develop within the fill. If the pore water contains dissolved methane it could cause elevated gas concentrations in gas monitoring wells as it flows into them.

Headspace vs unsaturated zone gas concentration

If groundwater contains dissolved methane and it enters a monitoring well gas will partition from the water to the air in the well headspace until equilibrium is achieved. The gas is trapped in an air space and will give high concentrations when the headspace is sampled during gas monitoring. Trapping of gas in the headspace is 100% effective when the response zone of the well is flooded.

Outside a well methane will also partition from groundwater into the soil air space in the capillary fringe and unsaturated zone above the groundwater. However, in the soil the methane will be oxidised and/or diluted, and a high concentration of methane will only exist in the

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soil air spaces immediately above the groundwater. Thus, the overall gas concentration in the unsaturated zone will be a lot less than that measured in the well headspace.

Henry's constants

Henry's Law states that the equilibrium ratio between chemicals in the gas phase and the aqueous phase is constant for a dilute solution. The amount of dissolved gas is proportional to its partial pressure in the gas phase. It is dependent on temperature and pressure (as well as the concentration of other gases and minerals in the water).

There are many variants of Henry's Constants which can be classified into two fundamental types: the aqueous phase as numerator and gas phase as denominator (A/G), and vice versa (G/A).

A and G are quantities describing the equilibrium composition of the aqueous and gas phases respectively. Unfortunately, the name Henry's Constant is used for both types, which for the dimensionless constant can cause problems. For clarity this Information Sheet uses H^{cc} for solubility and H^{ccv} for volatility.

For both H^{cc} and H^{ccv} there are several variants with different units, and also a number of different symbols. Some symbols are used for different variants, and some variants use more than one symbol, so it really is a tangled web. However, for the purposes of comparing gas monitoring results to theoretical concentrations caused by gas dissolved in groundwater the dimensionless version of the Henry's Constant is easiest to use.

This Information Sheet uses the symbols as detailed in 'Compilation of Henry's law constants (Version 4.0) for water as a solvent', (Sander 2015) and will be looking at dimensionless constants only. Conversion factors from other variants are available in the same document.

The dimensionless Henry's Constant for solubility – H^{cc} – water-air partitioning coefficient

H^{cc} can be expressed as the dimensionless ratio between the aqueous phase concentration c_a and the gas phase concentration c_g .

$$H^{cc} = c_a/c_g$$

For an ideal gas, the conversion is:

$$H^{cc} = H^{cp} \times RT \text{ where:}$$

$$H^{cp} = c_a/p \text{ where:}$$

p = partial pressure.

The dimensionless Henry's Constant for volatility – H^{ccv} – the air-water partitioning coefficient

H^{ccv} can be expressed as the dimensionless ratio between the gas-phase concentration c_g and its aqueous phase concentration c_a .

$$H^{ccv} = c_g/c_a = 1/H^{cc}$$

How to work it all out:

A handbook of Henry coefficients (Henry constants), for just about any gas you can think of at STP is available from the link below:

<http://www.atmos-chem-phys.net/15/4399/2015/acp-15-4399-2015.pdf>

It also explains the temperature dependency, and gives conversions between the different units that the constants come in.

The aqueous concentration of gas in water can be estimated from a known concentration of gas in the air using the rearranged equation from above:

$$c_g \times H^{cc} = c_a$$

Using H^{ccv} will give an estimation of the gas concentration in air from a known aqueous concentration by rearranging the equation as follows:

$$c_a \times H^{ccv} = c_g$$

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To allow for temperature variation of the groundwater the Van't Hoff equation can be used (Smith and Harvey 2007).

$$H_1 = H_2 \times \exp \left[C \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$

Where:

H₁ = Henry's constant at Temperature T₁

H₂ = Henry's constant at Temperature T₂

T₁ and T₂ = Temperature (K)

C = Δ_{sol}H/R (in K). Δ_{sol}H = solute enthalpy of solution and R = molar gas constant. For CH₄, C = 1900.

Henry's Constant is sensitive to temperature differences, although for groundwater in temperate climates such as the UK the variation of temperature in groundwater should not be significant. It is however important to use an appropriate value for the groundwater temperature and not a reference value at 25°C.

Example

Gas monitoring was carried out in monitoring wells installed in fill material that had been placed at a site. The material was excavated landfill that had been processed to produce an engineering fill. The landfill had been completed over 20 years previously and the soils that were excavated would be expected to have a high concentration of dissolved methane in the pore water.

The material had been placed and compacted to meet an engineering specification, so it would provide a suitable development platform. It comprised a sandy clay with gravel and was compacted to 95% maximum dry density and 5% to 10% air voids. Monitoring wells installed in the material recorded elevated gas concentrations. The monitoring wells contained groundwater and it was suspected that methane in the pore water of the compacted fill was entering the wells as they acted as a drainage pathway for excess pore water pressure.

Water samples were taken and tested for dissolved methane and carbon dioxide. The results showed that the headspace gas concentrations were in general agreement with the theoretical partitioning concentration using the dissolved methane results (Figure 1).

There was a strong correlation between the presence of water and gas and also between the dissolved methane and head space concentration. The results, along with the absence of flow rates, show that most of the gas being recorded in the wells was the result of partitioning from groundwater rather than gas flow through the unsaturated zone. The gas had then accumulated in the well headspace because of high groundwater levels and the solid top part of the well.

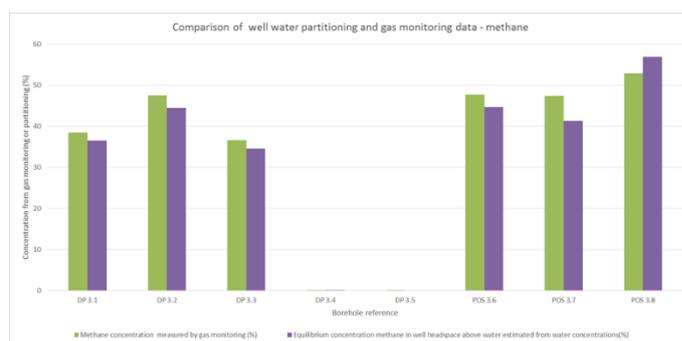


Figure 1 Measured vs predicted methane

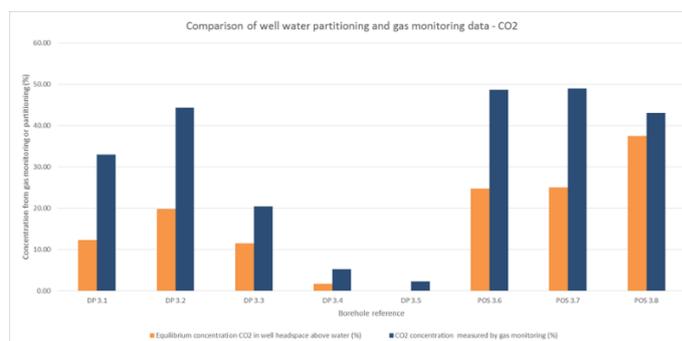


Figure 2 Measured vs predicted carbon dioxide

The correlation was less accurate when comparing the theoretical partitioning concentration of carbon dioxide (Figure 2). Carbon dioxide in water reacts to produce

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hydrated carbon dioxide and then carbonic acid, so the chemical interactions are more complex.

Conclusions

It is key, as with all gas risk assessments, to have a good understanding of the ground model to enable realistic interpretation of any data.

Elevated concentrations of methane measured in well head spaces are not always representative of the concentrations within adjacent soil pore spaces. When concentrations of methane dissolved in groundwater are higher than normal 'background' concentrations, it can cause unrepresentative elevated gas concentrations in the headspace.

Elevated concentrations of dissolved methane are only likely to pose a risk if the water discharges into a confined space (shafts, tunnels, etc). The presence of high dissolved concentrations in groundwater below a building will not normally pose a significant risk. Dissolved methane is an important consideration when designing basement waterproofing systems on sites where gas is present in the ground.

It is also possible that when compacting landfill or general Made Ground to reduce settlement (e.g. using surcharging or dynamic compaction) that dissipation of

excess pore water pressure occurs into gas monitoring wells. If the pore water contains dissolved methane it could cause elevated gas concentrations in the wells.

References

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