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# Investigating the Origin of Elevated $H_2S$ in Groundwater Discharge from Abandoned Gas Wells, Norfolk County, Ontario

*Richard E. Jackson, Maurice B. Dusseault, Shaun Frape, Walter Illman, Thai Phan and Colby Steelman, Department of Earth & Environmental Sciences, University of Waterloo*

## Summary

The emission of methane ($CH_4$) and hydrogen sulphide ($H_2S$) gas from legacy gas wells in southwestern Ontario is an emerging public-health issue. In Norfolk County, to the north of Lake Erie, there are over 2,600 gas wells. These often date to before the 1960s (55%) and were abandoned to standards of the time, i.e., filled with rubble, pounded lead "*seals*" and trees, with the steel casings often removed. While this is a *chronic* condition across this area, particularly in Norfolk County, the condition is *acute* in the incised valleys created by meltwater erosion and subsequent bedrock valley flexure. In these valleys, artesian discharge containing elevated levels of $H_2S$ has led to public-health concerns from exposure of property owners to $H_2S$ gas emissions. The origin of this problem is currently being investigated by the University of Waterloo with financial support from the Ontario Ministry of Natural Resources & Forestry and Norfolk County.

## Introduction

Natural gas in varying quantities is found throughout the sequence of Paleozoic sedimentary rocks in southwestern Ontario. Even with the historical exploitation of commercial sites, vast volumes of gas remain in place because well abandonment occurs with partial and local pressure depletion in the reservoir formation and gas-flow inhibition due to relative permeability effects.

Groundwater containing $H_2S$ gas is known as "*sulphur water*"; the $H_2S$ gas is very soluble and most of the dissolved $H_2S$ exsolves from groundwater upon discharge at the surface, creating a distinct and unpleasant odour. This gas comes out of solution at the surface because of the drop of pressure, a process similar to the exsolution of carbon dioxide after a can of soda water is opened. However, above 100 ppm, $H_2S$ gas is toxic, denser than air, and exposure to it in lower concentrations is regulated under occupational health and safety guidelines. This is in contrast to exposure to methane, as methane itself is not toxic and because it is buoyant in the atmosphere (much lighter than air), chances of asphyxiation are very low. Thus, $H_2S$ emissions are a public health concern.

## The Legacy Gas-Well Problem

The legacy wells in southwestern Ontario were abandoned to standards of the time, being filled with rubble, pounded lead "*seals*", and trees, with the steel casings sometimes removed. Such poorly abandoned wells provide a pathway for fluids to migrate from the artesian Devonian bedrock, in which the groundwater of the Dundee Formation (Fm.) contains abundant dissolved sulphate ($SO_4^{2-}$) ions. Furthermore, these wellbores penetrate down about 350-400 m to the

Silurian formations (Clinton-Cataract Group strata) that were exploited for their gas, and their pathways potentially provide a long-term source of methane to the shallow bedrock aquifer in the Dundee-Lucas Fms. In the incised valleys and lowlands of Norfolk County to the north of Lake Erie as shown in Figure 1, this groundwater discharges to the surface. We conceptualize this discharge in Figure 2, in which artesian conditions within the Dundee-Lucas aquifer are sustained by regional recharge of the groundwater from higher elevations. The focus of groundwater discharge in the incised valleys is enhanced by uplift, stress relief, and coupled bedrock fracture enhancement in the valley floor following meltwater incision of the valleys during glacial retreat.

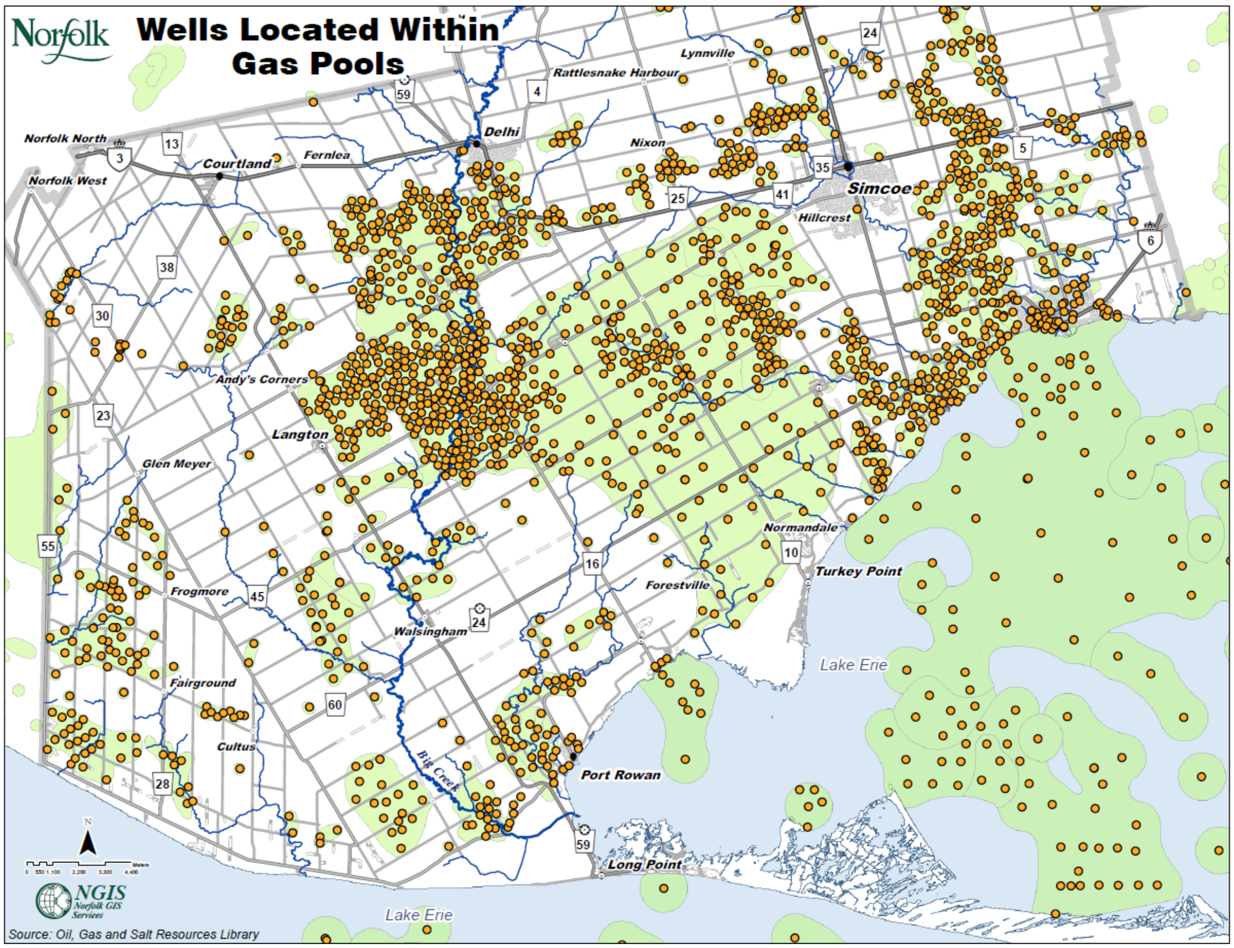


Figure 1: Gas well locations in Norfolk County showing the outlines of the gas pools and Big Creek, which is deeply incised south of Delhi where there are many abandoned and some active gas wells

This hypothesis for the generation of "*sulphur water*" was outlined in Armstrong and Carter's (2010) monograph on the Paleozoic bedrock of southern Ontario. It was discussed in greater detail by Carter et al. (2014) at an earlier CSPG meeting in Calgary. However, the Carter hypothesis did not identify the agent causing the reduction of the dissolved sulphate nor how the reducing agent came into contact with the sulphate.

From a perspective of chemical thermodynamics (Stumm and Morgan, 1981), it is most likely that methane (or hydrogen) gas causes the sulphate reduction. Methane ($CH_4$) may occur naturally in relatively small concentrations in the Dundee-Lucas aquifer; however, a more important source would be residual methane that buoyantly seeps upwards (Dusseault and Jackson, 2014) from the deep Silurian gas reservoir in the Clinton-Cataract Group, which Armstrong and Carter (2010, p. 75) indicate as being the major natural gas reservoir beneath Norfolk County. If this is the case, for all practical purposes, there is no limit to the continued development of small but significant concentrations of $H_2S$ in the gypsum-rich shallow Dundee-Lucas aquifer.

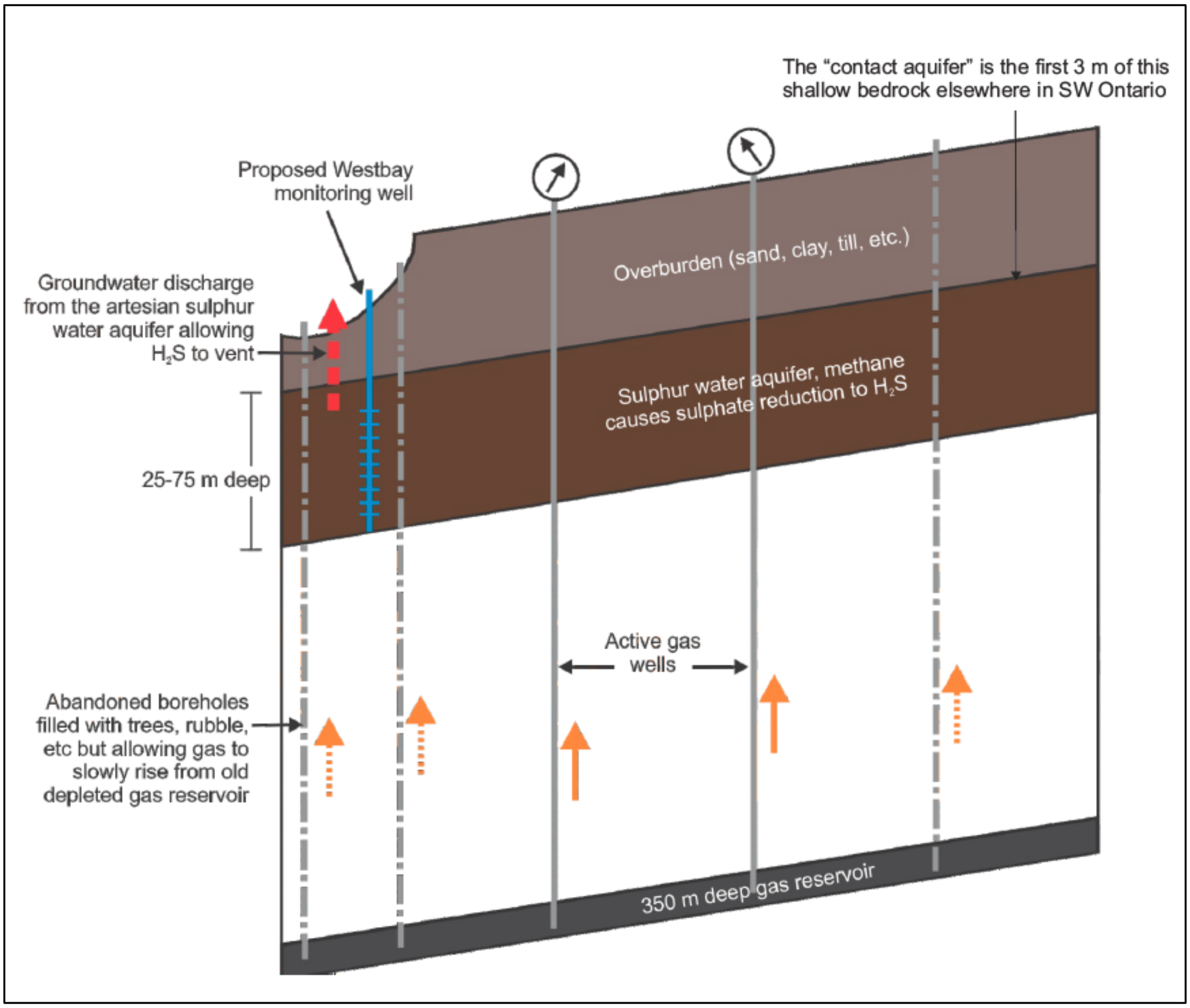


Figure 2: Conceptual model of artesian discharge from the "*sulphur water aquifer*" (Dundee-Lucas Fm.) and buoyant methane migration up abandoned boreholes. A Westbay monitoring well, shown above, is to be installed in early 2020. It will be used (i) to investigate the hydraulic properties, fracture distribution and isotope geochemistry of the Dundee-Lucas aquifer and (ii) to estimate the anticipated discharge from this aquifer once a "*relief*" well is installed to allow $H_2S$ (gas) to be stripped from the groundwater before release to Big Creek. The "*contact aquifer*" is also shown.

The oxidation of methane by the reduction of dissolved sulphate can be a bacteriologically mediated reaction (Van Stempvoort et al., 2005) when dissolved methane is in the presence of dissolved sulphate derived from gypsum ($CaSO_4 \cdot 2H_2O$). A conceptual model involving deep $CH_4$ migration to shallow groundwaters accompanied by $SO_4^{2-}$ reduction is reported by Smal (2016) in her study of the Niagara Peninsula. Smal concluded that a sample collected from a 60-m wide spring in the Norfolk Quarry near Port Dover was indicative of sulphate reduction by $CH_4$ that she suggested might originate with abandoned gas wells. In this case, the Dundee-Lucas aquifer would be the obvious source of dissolved sulphate for methane-facilitated reduction, which she suspected was thermogenic $CH_4$ in origin.

Although now it is largely depleted as a commercial source, the Clinton-Cataract reservoir still contains significant amounts of $CH_4$ and over 500 active gas wells operate in Norfolk County (20% of total gas wells). In most cases in Norfolk County, this depletion has resulted in abandonment of the gas wells because the gas can only be recovered inefficiently – and thus uneconomically – by producing wells. However, by migrating upwards through poorly abandoned boreholes (see Figure 2) because of the buoyancy of methane gas slugs and the properties of the methane-brine interface (Dusseault and Jackson, 2014), $CH_4$ would continue indefinitely to contact the sulphate-rich groundwaters within the Dundee-Lucas aquifer and generate $H_2S$. This same buoyancy is displayed when a transparent plastic water bottle with a small air bubble is overturned causing the air bubble to buoyantly rise to the top of the overturned bottle.

Our limited groundwater sampling to date has shown clear evidence of sulphate reduction through sulphur isotope enrichment in samples from a flowing abandoned gas well in the incised valley. The discharge has a strong $H_2S$ odour (at times in excess of 100 ppm), is saturated with sulphate salts and contains no tritium; therefore, groundwater recharge was pre-1960s in origin.

The piezometric surface of the artesian Dundee-Lucas aquifer – the "*sulphur water aquifer*" shown in Figure 2 – is approximately 5 m above ground surface in the incised valley of Big Creek. This has caused the contamination of (at least) the upper 3 m of the aquifer, which elsewhere in SW Ontario is relatively fresh water and known as the "*contact aquifer*" or "*freshwater aquifer*" (Fig.2).

In an abandoned water well drilled into this contact aquifer and located just 700 m from the flowing abandoned gas well, artesian flow indicates ferrous sulphide supersaturation, sulphate ~ 300 mg/L, negative Eh and pH ~ 7.0. The sample was much enriched in $\delta^{34}S_{SO4}$ relative to the reservoir groundwater reported by Skuce et al. (2015). An analysis of a 2018 groundwater sample from the same water well by the Ontario Geological Survey indicated over 400 mg/L of dissolved $H_2S$.

When drilled in 2007, the water level in this water well was ~17 m below ground surface, whereas today it is at ground surface. The cause of this increase appears to be the 2015 plugging of a "relief well" sited 4 km down-valley draining the Dundee-Lucas aquifer, after which several abandoned gas wells located in the incised valley began to flow. It appears that stress-relief uplift had enhanced the natural fracture network in the Dundee-Lucas aquifer along the incised valley with hydraulic communication between water wells tapping the "*contact aquifer*" and those abandoned gas wells with corroded casings that were drilled it through to access the deeper Silurian gas reservoir. Ironically, the plugging of such flowing gas wells further north in Big Creek Valley near Delhi had been recommended by provincial hydrogeologists (Yakutchik and Lammers, 1970) as a means to protect Big Creek from saline groundwater discharge without regard of the consequences of plugging the discharge from a regional artesian aquifer.

## Conclusions

Four issues indicate that gas and groundwater emission problems – both acute and chronic cases – will continue to develop in the future, perhaps with an increasing frequency:

1) Buoyant migration of gas slugs from depth in the gas-rich bedrock;
2) Sulphate-induced failure of cements (deterioration) used in the past to seal wells and their casings and of steel casings (corrosion) isolating the 'sulphur water' aquifer that allows the hydrogen sulphide gas to migrate toward the ground surface;
3) Suburban sprawl into old gas fields with many abandoned gas wells, which may experience any or all of these problems; and
4) Slow re-pressurization of the depleted gas reservoir by gas migration into the formation will sustain buoyant methane migration up the abandoned and poorly-plugged gas wells.

### Acknowledgements

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