# Hydrogeochemical Prospecting for Natural Gas: The Geochemical Chimney, Shallow Groundwater Hydrogeology, and Interpretation of Near-Surface Data

Matthew V. Kohlbecker, RG GSI Water Solutions, Portland, Oregon, USA mkohlbecker@gsiwatersolutions.com

#### and

Dimitri Vlassopoulos, PhD S.S. Papadopulos and Associates, Portland, Oregon, USA

## **Summary**

Near-surface geochemical prospecting methods are playing an increasingly important role in the search for new natural gas accumulations, especially in onshore frontier areas. The approach involves analysis of soil gas samples from shallow borings and gas/water samples from shallow water wells for hydrocarbon gas concentrations and composition, stable isotopes (carbon, hydrogen), and ancillary hydrochemical parameters. These data are then used to identify the location, origin, source, extent, and thermal maturity of gas accumulations at depth. Nearsurface exploration techniques commonly assume that fugitive hydrocarbon gas leaks from a deep gas reservoir and migrates vertically upward by buoyancy to the surface, so that the surface expression is located essentially vertically above the hydrocarbon accumulation. This vertical upward migration of hydrocarbon gas has been referred to as a "geochemical chimney," and is traditionally used as a working model for interpreting near-surface geochemical prospecting data. However, the geochemical chimney model for gas migration implicitly assumes certain hydrogeologic conditions are met (i.e., very little or no lateral groundwater flow, negligible vertical gradients, and/or separate phase transport of hydrocarbon gases). If these conditions are not met, then the plume of upward-migrating fugitive gases can be deflected laterally within the shallow (< 1000 meters bgs) groundwater system, or even downwards, depending on the local hydrogeologic regime. In addition, groundwater transport would mix hydrocarbon gases, thereby affecting gas concentration and isotope signature. Hydrogeochemical and hydrocarbon gas data from the Columbia River Basin of Washington and Oregon are used to illustrate the effects of lateral transport and downwelling of fugitive hydrocarbon gases. A properly planned and executed groundwater investigation can result in a more accurate characterization of the underlying hydrocarbon gas accumulation.

### Introduction

Seepage of hydrocarbon gas from a deep hydrocarbon accumulation into shallow groundwater or soil has been documented in several studies, and is well known from reports of visible seeps encountered during early hydrocarbon exploration (Price, 1985). As discussed by Toth (1996), the simplified conceptual model commonly used for hydrocarbon gas seepage investigations assumes that gas escapes from a hydrocarbon accumulation and migrates vertically upwards through overlying sediments by buoyancy or diffusion. The gas signature at the surface is located vertically above the hydrocarbon accumulation. Pirson (1971), used the term "geochemical chimney" to describe the rock above hydrocarbon accumulations that has been modified by vertical migration of hydrocarbons, and the concept of a chimney has become a common spatial reference point used in several near-surface geochemical prospecting studies (e.g., Yang et al., 2000). However, the geochemical chimney model for vertical migration of hydrocarbons is only appropriate under certain hydrogeologic conditions (i.e., little to no lateral groundwater flow, negligible vertical gradients, pure gas-phase transport) (Toth, 1996) that are not met in shallow groundwater systems. Therefore,, migration pathways, composition, and

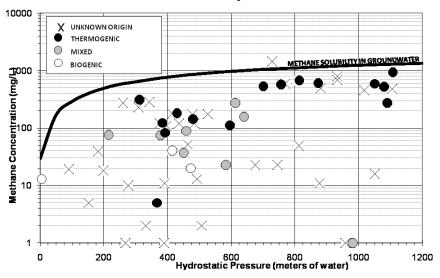
isotope signatures of hydrocarbon gases can be significantly altered by the hydrodynamic conditions within the shallow groundwater system.

# Theory

Fugitive gas can be transported by diffusion, buoyancy, and advection:

- **Diffusion.** Diffusion is gas migration due to random particle motion on the molecular level as described by Fick's First Law. Diffusion of hydrocarbon gas is negligible on the aquifer scale (Fetter, 1994; Hunt 1979). Therefore, diffusion is not a significant migration mechanism for hydrocarbon gas from the perspective of near-surface prospecting.
- **Buoyancy.** Buoyancy is upward gas migration caused by density differences between gas and groundwater (Price, 1985; Toth, 1996; Webb, 2006).
- **Advection.** Advection is lateral and vertical solute transport by average groundwater velocity, and would affect hydrocarbon gas dissolved in groundwater (Webb, 2006).

Therefore, hydrocarbon gas movement in groundwater is primarily due to two mechanisms: buoyancy and advection. Most near-surface geochemical prospecting implicitly assumes purely-buoyant transport (e.g., Yang et al., 2000), and consideration of advective transport is much more rare (e.g., Toth, 1996; Holysh et al., 1994). However, because fugitive hydrocarbon gases in shallow groundwater occur primarily in the dissolved state, advection is also an important mechanism for hydrocarbon gas transport for near-surface geochemical prospecting studies. This is shown in Figure 1, which displays in situ concentrations of methane in groundwater from shallow wells at the Hanford Site in Washington. The methane concentrations generally plot below the solubility curve (after Duan and Mao, 2006), indicating that groundwater is generally undersaturated with methane, and that methane occurs dissolved in groundwater.



CH4 Concentration vs. Hydrostatic Pressure

Figure 1: Methane Concentrations in Groundwater, Hanford, Washington.

Because hydrocarbon gas is dissolved in groundwater at Hanford, advection can be expected to transport methane in groundwater both laterally and vertically, and the implicit assumptions of the geochemical chimney model are not met.

# **Examples of Advective Transport of Hydrocarbon Gases**

The remainder of this paper discusses examples of advective transport of hydrocarbon gas in groundwater based on data from the Hanford Site in Washington State, USA. The data is publically available in Early and et al., (1986) and Reidel et al. (2002).

The Hanford Site is a former nuclear production facility operated by the United States government, and is located in the Columbia River Basin geologic province of Oregon and Washington. The Miocene Columbia River Basalt Group (CRBG) underlies the site, and reaches a maximum thickness of about 13,000 feet in the central portion of the Columbia Basin (Reidel at al., 2002). Deep (i.e., up to approximately 1,300 meter) basalt borings at the Hanford Site encounter methane in groundwater. Hydrocarbon gas isotopes suggest that the methane is a mixture of bacterial gas generated in situ and fugitive thermogenic gas originated from coals within the Eocene and Oligocene fluvial sediments beneath the basalt (Johnson et al., 1993).

Hydrocarbon gas data collected from the Hanford site provides an excellent case study of the shallow groundwater system deflecting hydrocarbon gas vertically and laterally. Vertical transport of dissolved hydrocarbon gases by advection occurs in response to vertical gradients in hydraulic head. For example, if hydraulic head decreases with depth in the aquifer, then a downward vertical gradient is present, and downward groundwater flow is favored. An example of the effect of vertical gradients on hydrocarbon migration at the Hanford site is shown in Figure 2(A). Methane concentrations in groundwater and groundwater elevations are plotted versus depth in corehole DC-16. A downward vertical gradient is present from ground surface to approximately 1,700 feet below ground surface (bgs). Thermogenic methane is only present at depths greater than 1,700 feet bgs, which is likely due to vertical gradients preventing upward migration of hydrocarbon gas.

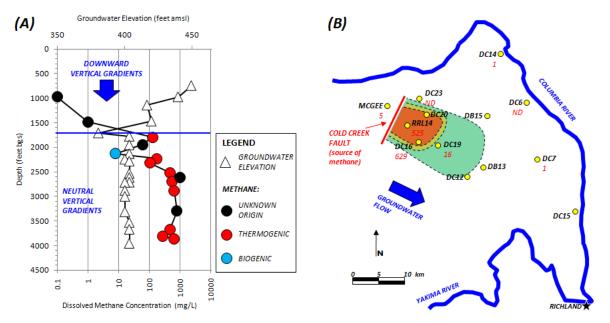


Figure 2: Advective Controls on Methane in Groundwater both vertically (A) and laterally (B). In (B), all methane concentrations (mg/L, in red) are from wells completed in the same member, with the exception of DC-16, which is completed in a deeper member.

Groundwater flows laterally from recharge areas (i.e., where groundwater enters the hydrogeologic system) to discharge areas (i.e., where groundwater exits the groundwater system). Hydrocarbon gas entering the groundwater system can be transported laterally with groundwater flow, potentially several miles from the location where the gases enter the hydrogeologic system. As shown in Figure 2(B), methane enters the shallow groundwater

system along the Cold Creek Fault (Johnson et al., 1993) and is then transported several kilometers southeasterly towards the Columbia River, along the groundwater flowpath.

#### Implications

Advective transport of hydrocarbon gas in the shallow hydrogeologic system complicates the simplified conceptual model depicted by the geochemical chimney. Specifically, the surface expression of a hydrocarbon accumulation may not necessarily be positioned directly above the accumulation. In addition, during transport by groundwater, significant mixing can occur [differential advection of Mercado (1967)] that can decrease hydrocarbon gas concentrations and alter hydrocarbon isotope ratios (e.g., mixing of a thermogenic gas that originated from depth with a bacterial methane produced in-situ within the aquifer). Groundwater transport could also mix hydrocarbon gas entering the shallow groundwater system by macroseepage with hydrocarbon gas entering the shallow groundwater system by microseepage. A properly planned and executed groundwater investigation can help resolve these complicating factors.

#### Conclusions

Shallow groundwater flow can potentially deflect dissolved hydrocarbon gas plumes laterally or vertically. The geochemical chimney model for vertical hydrocarbon gas migration does not allow for lateral or vertical deflection of hydrocarbon gases, and therefore is only appropriate when vertical gradients are negligible, there is no lateral groundwater flow, and pure gas-phase transport occurs. Although groundwater complicates the geochemical chimney model for vertical gas migration, many of these complications can be resolved by a groundwater study.

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