

## **Application of Diffusion Samplers in Assessing Monitored Natural Attenuation (MNA) of Hydrocarbons at Upstream Oil and Gas Sites**

Monitored natural attenuation (MNA) is becoming a more commonly accepted remediation option for hydrocarbon contamination of groundwater encountered at upstream oil and gas sites. MNA is the process of collecting data to demonstrate that the natural attenuation processes are effectively degrading the hydrocarbon contamination without impacting nearby receptors. The key component of MNA is obtaining accurate groundwater samples. An investigation of the effects of alternative sampling technologies on groundwater samples is one focus of the Consortium for Research on Natural Attenuation (CORONA) research program. One study component is the implementation of a diffusion sampling using regenerated cellulose dialysis membranes.

Diffusion sampling works on the fundamental principle that all systems will come into a state of chemical equilibrium. Application of diffusion sampling for assessing MNA in hydrocarbon-contaminated groundwater is in its infancy. Most previous diffusion sampling research involved VOCs in groundwater using polyethylene diffusion bags, which do not allow dissolved inorganic and other organic constituents to be sampled. Research has been done using regenerated cellulose membranes to measure dissolved inorganic constituents, such as nitrates (Ronen et al., 1986) and irons and manganese (Vrobley et al., 2002). Ehlike et al. (2004) found inorganic equilibration within seven days and VOC equilibration in 3 days.

Field research conducted by Vrobley et al. (2002) was reviewed for guidance on using diffusion samplers to measure inorganic constituents. This USGS research demonstrated that diffusion samplers can effectively measure inorganics, but most of the results were for diffusion samplers using nylon-screens, not dialysis membranes. The limited dialysis membrane results meant that further tests would need to be conducted to more accurately understand the equilibration time for inorganic compounds. Research was also needed on the relative equilibration rates for inorganic compounds with varying ionic charges, and the potential for water loss due to osmotic gradients (in saline groundwater environments) and hydraulic gradients (seasonal water table fluctuations).

Field dialysis samplers in this study are fabricated by cutting tubular dialysis membrane into 75 cm lengths. The membrane is sealed by tying a knot on one end and using o-rings to connect a capped brass sampling nozzle on the other end. The membrane is slid into a 65 centimeter length of 37 mm inner diameter PVC pipe with holes throughout the pipe to allow equilibration, and is then filled with deoxygenated, deionized water through the nozzle. The dialysis samplers are transported to site in airtight PVC canisters that are completely filled with deionized, deoxygenated water. The dialysis samplers are pushed to the desired sampling depth in a conventional 50 mm diameter, three meter screen wells using a rigid system of PVC pipe.

A study using monovalent and divalent dissolved salts was initiated to investigate ionic charge effects on equilibration time and the impact of salinity on dialysis water loss. Two membranes were suspended in five sodium chloride solutions ranging from 10 to 5000 mg/L and five calcium sulfate solutions ranging from 10 to 2000 mg/L. One membrane was weighed periodically to examine mass loss and the other was used to measure electrical conductivity (EC), where similar EC values in the vessel and the membrane indicated equilibration. The dialysis membranes were found to equilibrate within the first 24 hours. After 70 days, mass loss ranged from 5 to 10% for the various solutions. The study found that ionic charge did not have an apparent effect on equilibration and that salt concentration had a minor effect on water loss.

Very limited research was found in the literature on equilibration times for dissolved organic compounds. Also, the issue of the membrane being a possible carbon source to microbes, which could lead to degradation of the membrane during sampling, needed to be examined. A laboratory study involved suspending dialysis membranes in vessels containing groundwater taken from a hydrocarbon-impacted well. The water in the vessel and the membrane were analyzed at 2, 4 and 6 weeks for benzene, toluene, ethylbenzene, xylene (BTEX) and petroleum hydrocarbon F1 fraction minus BTEX. The findings demonstrated equilibration of all components occurred between 2 and 4 weeks, with the likely time being approximately 3 weeks. Visual inspection of membrane integrity showed no degradation over the 6 weeks.

A study was initiated to examine potential water loss due to hydraulic gradient and evaporation effects if the sampler became partially exposed above the water table due to seasonal fluctuations. Three diffusion samplers were suspended in a 50 liter barrel. Two were situated in normal atmospheric conditions, with one sampler installed just below the water surface and the other half-submerged. To examine the amount of evaporation, another membrane was half-submerged in a 100% humidity cold room where no evaporation could occur. It was observed that hydraulic head and evaporation effects resulted in complete water loss in the half-submerged sampler under normal conditions after 28 days. The half-submerged sampler in the 100% humidity room lost water until the water level in the membrane was the same as the barrel. This took over 70 days and was the result of hydraulic head effects. The fully submerged sampler only lost 2% of its weight over 40 days. The findings demonstrated that hydraulic head and evaporation affect water loss, however evaporation has the largest impact. The study illustrates the importance of ensuring that the diffusion samplers remain completely below the water table during sampling.

As part of a larger study to evaluate sampling effects on MNA groundwater parameters, diffusion samplers were installed within a cluster of well types placed in close proximity to a preexisting traditional three-meter well screen to minimize spatial heterogeneity. One site has a well nest adjacent to a former flare pit in northwestern Alberta. The second site has two well nests within a condensate-contaminated groundwater plume at a gas processing facility in Southeastern Alberta.

The diffusion sampler results were compared to those from the adjacent conventional three meter screened wells, multilevel wells and drive point wells. The data obtained from three sampling events to both sites demonstrates close correlation for anions (chlorides and bicarbonate), cations (sodium, calcium, magnesium and manganese) and hydrocarbon constituents (BTEX and F1-BTEX). The only variability for the diffusion samplers was a general trend of elevated iron concentrations and lower sulfate concentrations encountered at both sites. The preliminary data indicate dialysis membrane diffusion sampling may be useful for developing an effective MNA groundwater monitoring program.

## References

- Ehlke, T.A., Imbrigiotta, T.E. and Dale, J.M. 2004. Laboratory Comparison of Polyethylene and Dialysis Membrane Diffusion Samplers. *Ground Water Monitoring & Remediation*. **24**(1): 53-59.
- Ronen, D., Magaritz, M. and Levy, I. 1986. A Multi-Layer Sampler for the Study of Detailed Hydrochemical Profiles in Groundwater. *Water Resources*. **20**(3): 311-315.
- Vroblesky, D.A., Petkewich, M.D. and Campbell, T.R. 2002. Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water Discharge Zone. U.S. Geological Survey, Water Resources Investigations Report 02-4031. 24 pgs.