

Real-Time Surrogate Monitoring of Groundwater Pollutants at Oil and Gas Production Sites

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Using surrogates to monitor groundwater quality in real time

The development of oil and gas resources, especially by hydraulic fracturing, has increased concerns about potential groundwater contamination (Figure 1). Typically, grab sample collection and expensive analytical tests are required to determine whether or not groundwater quality has been compromised. Time-consuming analytical methods may be expensive and difficult to perform. Site operators, stakeholders, regulatory agencies, and the public often need information instantly in order to meet regulatory requirements and to prevent contamination and exposure.

Real-time data can keep interested parties informed and able to quickly address potential contamination of groundwater supplies. But real-time monitoring of criteria pollutants such as methane and hydraulic fracturing fluid is not practical with currently available technologies. However, by identifying reliable pollutant indicators or surrogates, operators and regulatory agencies can monitor sites efficiently and respond to groundwater quality changes that may indicate potential breakthrough of contaminants.

Real-time water quality monitoring networks can be established by using telemetry systems, robust water quality sensing technologies, web-based data centers, and mobile devices that can receive alarm notifications (text, email, phone call). Before such a monitoring network can be established, pollutant-surrogate relationships must be established.

A surrogate is something that replaces or acts as a substitute for another, and surrogate measurements



Figure 1. Drilling rig at a hydraulic fracturing site

can be monitored continuously and used to estimate concentrations of a certain water-quality parameters for which continual data are not available or not practical. Using surrogates reduces grab sampling and analytical testing costs, decreases manual data analysis, and provides real-time information on a system's physical properties (Christensen et al 1999). For example, significant research has been conducted on using conductivity as a surrogate for chloride (Granato et al. 1999; Hem 1992). Conductivity sensors offer stable operation and are not sensitive to drift.

ORP Correlation to Methane

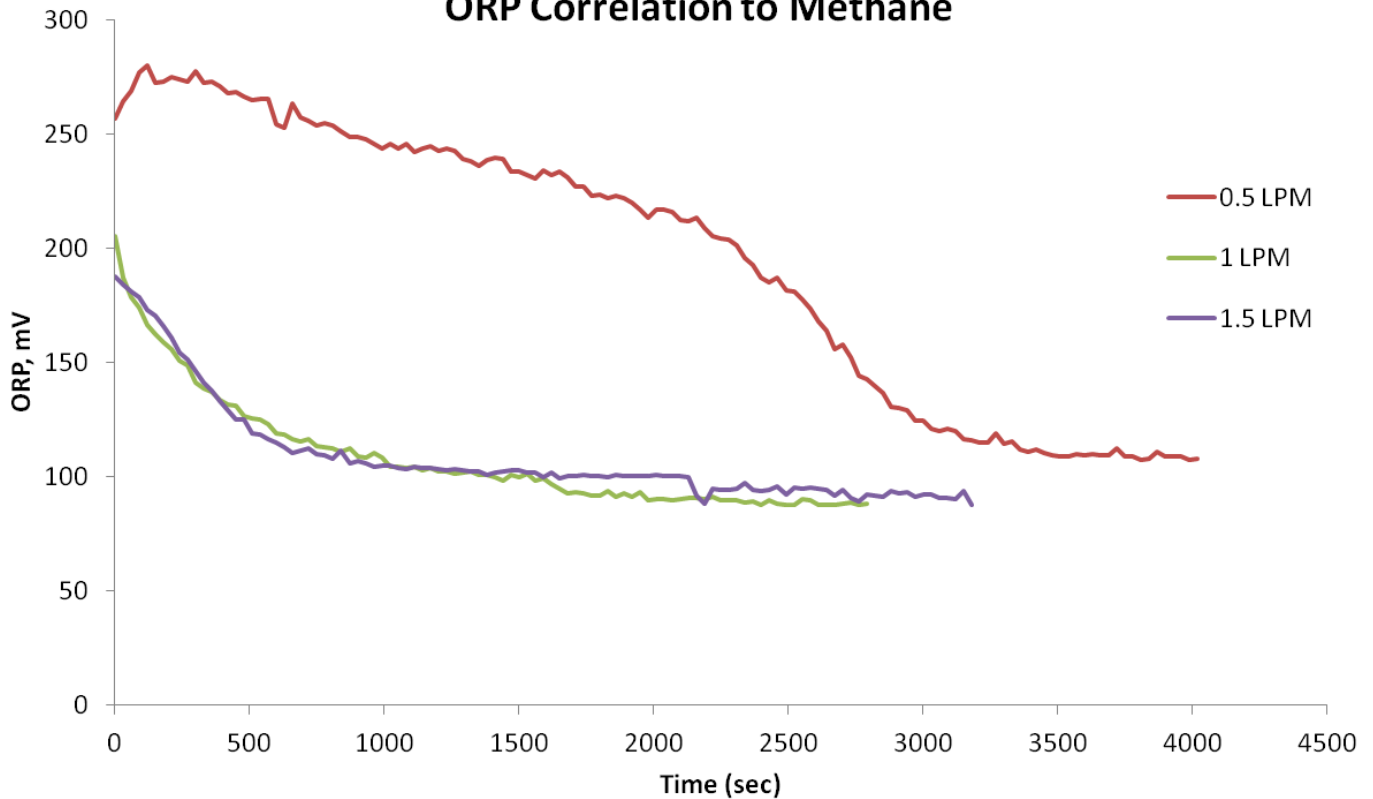


Figure 2. Preliminary research was conducted to demonstrate that changing methane levels are detected by an ORP sensor (Son et al 2013). Different rates of methane (0.5, 1, and 1.5 LPM) were injected into a sample to determine the response rate of the ORP sensor. As the sample became saturated with methane, ORP values decreased until the sample was saturated with methane.

For oil and gas operations, the potential exists to use oxidation-reduction potential (ORP) or dissolved oxygen (DO) as a surrogate for methane and to use conductivity/total dissolved solids (TDS) as a surrogate for hydraulic fracturing (fracking) fluid (Table 1). Like conductivity sensors, ORP sensors offer a stable, low-cost solution for monitoring groundwater quality in real time.

Table 1. Pollutants and surrogates	
Pollutant of Concern	Real-Time Surrogate Measurement
Aquifer contamination by fracturing fluid and produced fluids from hydraulic fracturing	Conductivity/TDS
Methan leakage to aquifer	ORP or DO

Establishing a pollutant-surrogate relationship

Every site has unique geochemical properties, which means that the use of real-time monitoring of a surrogate may not be possible in all locations.

To establish a pollutant-surrogate relationship, groundwater quality profiles of several monitoring wells throughout an oil/gas development site must be established. Representative samples are collected from monitoring wells throughout the site, and a certified lab conducts a bench-scale study to establish a correlation between the pollutant and the potential surrogate. A standard curve can be developed and used to estimate the in-field pollutant concentration through real-time measurement of the surrogate.

An established regression equation may be used for all monitoring stations in an area (Cain 1987). Regression models can have disadvantages in that the predictive ability of the regression model is a function of the number and distribution of available measurements from the population being studied (Granato et al. 1999). Once a good correlation has been established between a pollutant and surrogate, a real-time water quality monitoring network can be set up.

Dissolved Oxygen Correlation to Methane

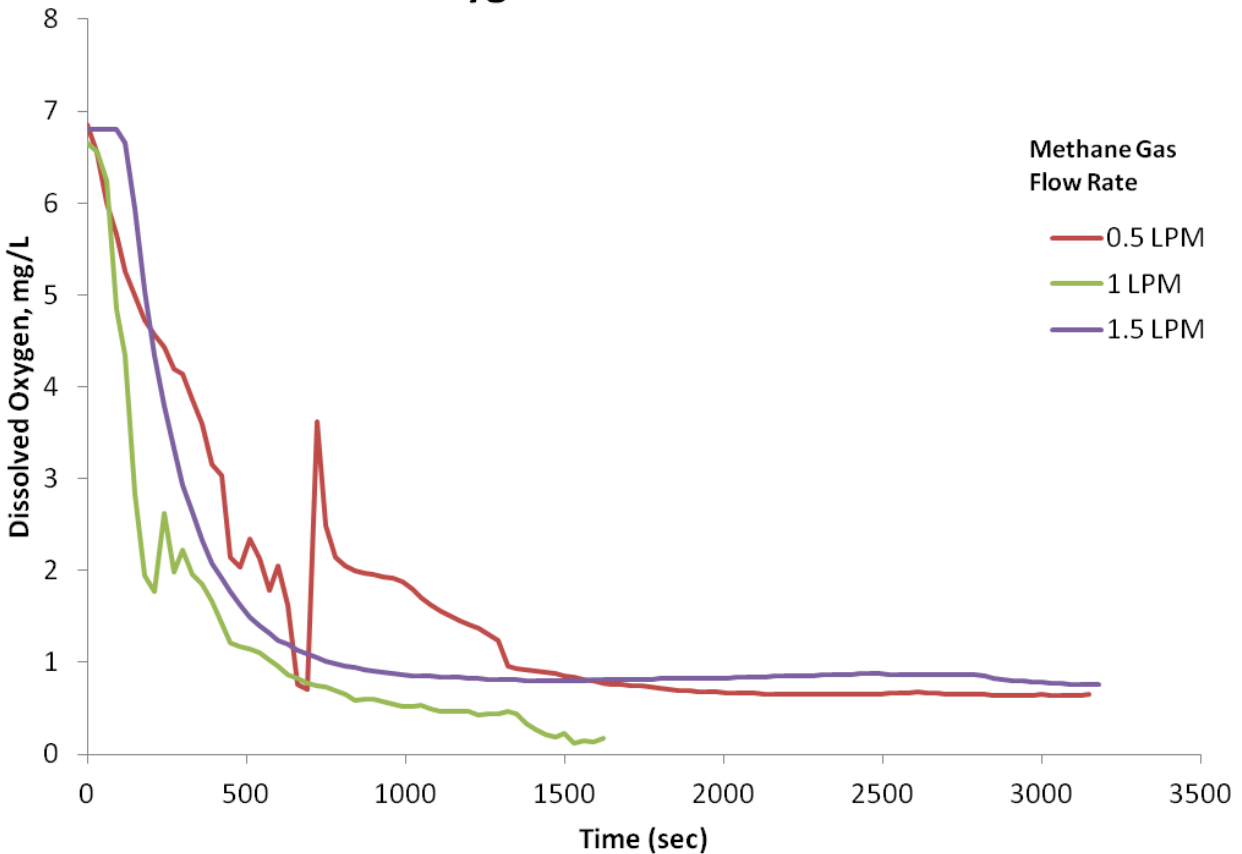


Figure 3. Preliminary research was conducted to demonstrate that changing methane levels are detected by a dissolved oxygen (DO) sensor (Son et al 2013). Different rates of methane (0.5, 1, and 1.5 LPM) were injected into a sample to determine the response rate of the DO sensor. As the sample became saturated with methane, DO values decreased until the sample was saturated with methane.

Correlating ORP and DO to methane

Based on research by Rulik et al. (2000) and Darling and Goody (2006), correlations of methane with ORP (redox potential) and dissolved oxygen (DO) in groundwater were established. The Department of Civil and Environmental Engineering at Colorado State University has been investigating the use possibility of using ORP or DO as surrogates for methane. Current studies are quantifying the response of ORP and DO sensors to various dissolved methane conditions, and that data has the potential to establish the use of ORP or DO as a surrogate for the presence of methane (see Figures 2 and 3 for preliminary results). By developing a technique to monitor methane surrogates, easy-to-use, cost-effective monitoring systems can be established to detect the presence of methane in groundwater.

Correlating conductivity/TDS to fracturing fluid

In addition to CSU's work on using ORP or DO as a surrogate for methane, researchers are also investigating the use of conductivity/TDS as a surrogate for fracturing fluid (Son et al 2013). If methane contamination did occur, the TDS value would change in a fresh-water aquifer. Current studies are quantifying the response of conductivity sensors (which can be used to derive TDS values) to hydraulic fracturing fluid, and that data has the potential to establish the use of conductivity/TDS as a surrogate for the presence of fracturing fluid (see Figure 4 for preliminary results).

Conductivity/TDS Correlation to Fracking Fluid

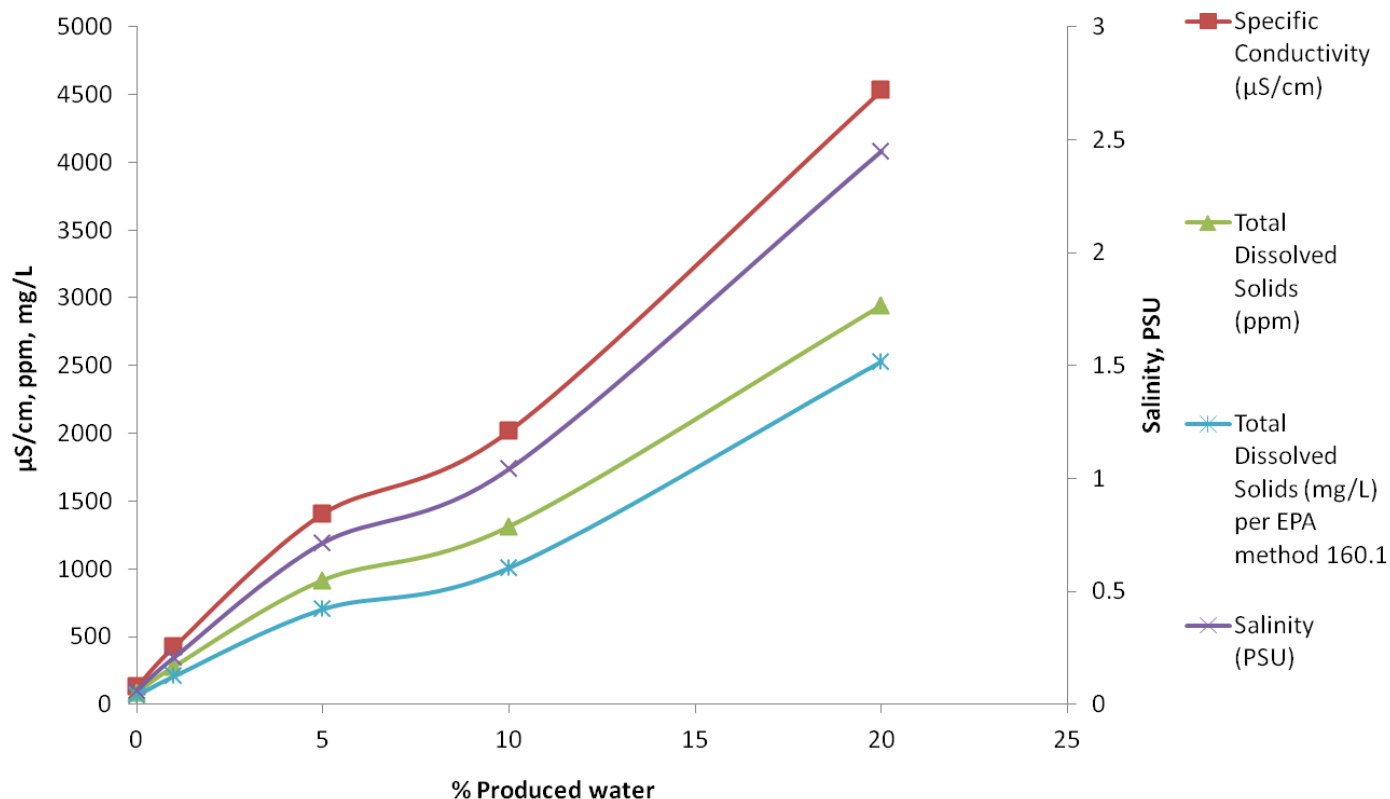


Figure 4. Relation of specific conductivity/TDS to fracking fluid concentrations of up to 20 percent produced water (Son et al 2013). The relationship shows a correlation coefficient of 0.999 under stable conditions for both specific conductivity and TDS.

Establishing a real-time groundwater quality monitoring network

Once you've characterized your site and established pollutant-surrogate relationships, you can establish a real-time water quality monitoring network. Real-time measurement of surrogate values can offer a quick, safe, and low-cost method for tracking potential contaminants. By deploying water quality instruments into monitoring wells (see Figure 5) and by connecting instruments to a telemetry system, all interested parties can stay informed around the clock.

The telemetry system sends data to a web-based data center and can be programmed to send alerts to operators if water quality conditions change. Data can be accessed without removing water quality instruments from the wells, which reduces grab sampling events, labor hours, trips to the site, and analytical lab fees. Time-intensive grab sampling only needs to occur when necessary. And real-time data retrieval methods can help technicians closely monitor fracturing operations and ensure that contaminants are not moving into fresh-water aquifers.

Resources

Darling, W.G., Goody, D.C., 2006. The hydrogeochemistry of methane: Evidence from English groundwaters. *Chemical Geology*. 229:293-312.

Granato, G.E. and K.P. Smith. 1999. Estimating concentrations of road-salt in highway-runoff from measurements of specific conductance: USGS Water-Resources Investigations Report 99-4077.

Hem, J.D. 1992. Study and interpretation of the chemical characteristics of natural water (3rd edition): USGS Water-Supply Paper 2254

Rulík, M., Čáp, L., Halaváčová, E., 2000. Methane in the hyporheic zone of a small lowland stream (Sitka, Czech Republic). *Limnologia*. 30:359-366.

Son, J. and K.H. Carlson. January 2013. ORP efficacy as aqueous methane surrogate. Experimental plan. Department of Civil and Environmental Engineering at Colorado State University.



In-Situ Inc. resources that discuss the use of surrogates

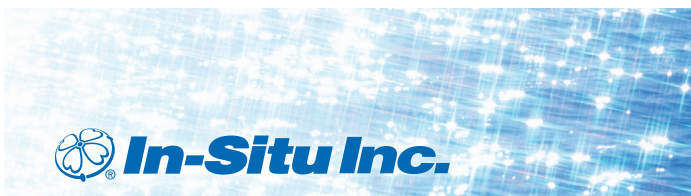
In-Situ Inc. Application Note: Real-time conductivity monitoring provides estimates of chloride levels in Minnesota watershed (http://www.in-situ.com/force_download.php?file_id=249)

In-Situ Inc. Application Note: Aqua TROLL Instrument tracks saltwater intrusion and provides real-time data and event notification: Conductivity measurements can be used as a surrogate for chloride concentration (http://www.in-situ.com/force_download.php?file_id=248)

Fernandes, L. 2011. In-Situ Inc. Application Note: Successful remediation pilot study uses TROLL 9500 Instrument for real-time monitoring (discusses use of conductivity as a surrogate for sodium permanganate; http://www.in-situ.com/force_download.php?file_id=1151)

Windsor, C., et al. In-Situ Inc. White Paper. Verifying the use of specific conductance as a surrogate for chloride in seawater matrices (http://www.in-situ.com/force_download.php?file_id=440)

Figure 5. An operator deploys an Aqua TROLL® 400 Multiparameter Instrument into a monitoring well. The Aqua TROLL 400 Instrument, with open communication protocols (RS485, SDI-12, and 4-20 mA), can be used in real-time water quality monitoring networks. The instrument integrates with radios, controllers, data loggers, and telemetry systems. The probe monitors 12 parameters including actual conductivity, specific conductivity, salinity, TDS, resistivity, density, DO, ORP, pH, temperature, water level, and water pressure.



For more information, contact In-Situ Inc.

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