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The Assessment of Instruments for Detecting Surface Water Spills Associated with Oil and Gas Operations

2 December 2016

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Office of Fossil Energy

NETL-TRS-14-2016

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Cover Illustration: Recovery of a water quality instrument sonde after a field test in West Run, adjacent to the NETL site in Morgantown, WV (U.S. DOE photo).

Suggested Citation: Harris, A.; Hopkinson, L.; Soeder, D. *The Assessment of Instruments for Detecting Surface Water Spills Associated with Oil and Gas Operations*; NETL-TRS-14-2016; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV*,* 2016; p 58.

The Assessment of Instruments for Detecting Surface Water Spills Related to Oil and Gas Operations

Aubrey E. Harris[1,2,3], Leslie Hopkinson[1], Daniel J. Soeder[2]

[1]West Virginia University, Department of Civil and Environmental Engineering,
395 Evansdale Drive, Morgantown, WV 26506

[2]U.S. Department of Energy, National Energy Technology Laboratory, 3610 Collins Ferry Road, Morgantown, WV 26507

[3]U.S. Bureau of Reclamation, 555 Broadway NE, Albuquerque, NM 87102-2352

NETL-TRS-14-2016

2 December 2016

NETL Contacts:
Daniel J. Soeder, Principal Investigator
J. Alexandra Hakala, Technical Portfolio Lead
Cynthia Powell, Executive Director, Research & Innovation Center

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Acronyms, Abbreviations, and Symbols

Term	Description
API	American Petroleum Institute
AT	AquaTROLL 200
C_{up}	Peak concentration
CS	Campbell Scientific CR-1000 Data-logging System
d	Distance traveled
D'_a	Empirical value representing average drainage area
D_a	Drainage area
$D_{a,g}$	Gaged stream drainage area
$D_{a,u}$	Ungaged stream drainage area
$D_{a,u\text{-}g}$	Ungaged stream drainage area as predicted by Emerson et al.’s method (2005)
DO	Dissolved oxygen
EPA	U.S. Environmental Protection Agency
k	Skew of the gamma distribution
NWIS	National Water Information System
Θ	Scale of the gamma distribution
ORP	Oxidation reduction potential
PA DEP	Pennsylvania Department of Environmental Protection
Q	Instantaneous river flowrate
Q'_a	Empirical value representing average annual flowrate
Q_a	Mean annual river discharge
$Q_{a,u}$	Average annual discharge
Q_g	Gaged stream average annual flowrate
Q_u	Ungaged stream average annual flowrate
RWQMN	Remote Water Quality Monitoring Network
SRBC	Susquehanna River Basin Commission
TDS	Total dissolved solids
T_p	Travel time of peak concentration
USGS	United States Geological Survey
V_p	Velocity of peak concentration

Acknowledgments

This work was completed as part of National Energy Technology Laboratory (NETL) research for the U.S. Department of Energy's (DOE) Complementary Research Program under Section 999 of the Energy Policy Act of 2005. The authors wish to acknowledge Ray Boswell (NETL Strategic Center for Natural Gas and Oil) and Elena Melchert (DOE Office of Fossil Energy) for programmatic guidance, direction, and support.

The authors would like to thank Roger Lapeer and Karl Jarvis for their assistance with the instrumentation set-ups and testing, and Tim Ford for the photography.

Stream gage versus gauge: This report uses the spelling "gage," preferred by the U.S. Geological Survey.

ABSTRACT

Surface water and groundwater risks associated with unconventional oil and gas development result from potential spills of the large volumes of chemicals stored on-site during drilling and hydraulic fracturing operations, and the return to the surface of significant quantities of saline water produced during oil or gas well production. To better identify and mitigate risks, watershed models and tools are needed to evaluate the dispersion of pollutants in possible spill scenarios. This information may be used to determine the placement of in-stream water-quality monitoring instruments and to develop early-warning systems and emergency plans.

A chemical dispersion model has been used to estimate the contaminant signal for in-stream measurements. Spills associated with oil and gas operations were identified within the Susquehanna River Basin Commission's Remote Water Quality Monitoring Network. The volume of some contaminants was found to be sufficient to affect the water quality of certain drainage areas. The most commonly spilled compounds and expected peak concentrations at monitoring stations were used in laboratory experiments to determine if a signal could be detected and positively identified using standard water-quality monitoring equipment. The results were compared to historical data and baseline observations of water quality parameters, and showed that the chemicals tested do commonly affect water quality parameters.

This work is an effort to demonstrate that hydrologic and water quality models may be applied to improve the placement of in-stream water quality monitoring devices. This information may increase the capability of early-warning systems to alert community health and environmental agencies of surface water spills associated with unconventional oil and gas operations.

1. INTRODUCTION

1.1 BACKGROUND

The use of chemicals in the industrial production of materials creates a risk that these compounds may contaminate surface water and groundwater in the event of a leak or spill. As such, regulations such as the U.S. Environmental Protection Agency's (EPA) Clean Water Act and Toxic Substances Control Act include requirements for best management practices, reporting, and controlling these substances (EPA, 2015). When water-soluble compounds or chemicals enter a stream, advective transport processes move the bulk of the chemical downstream. Eventually, dispersion processes dilute the chemical to the point of non-detection (Jobson, 1996). Large spills with concentrated contaminants near the spill point can significantly degrade stream water quality, affecting both aquatic ecosystems and human populations.

This study investigated water quality impacts to surface streams from the oil and gas industry, primarily unconventional shale gas operations. The development of natural gas resources from shales such as the Marcellus in the Appalachian Basin has become economically viable in recent years because of the application of directional drilling and staged hydraulic fracturing (Soeder, 2012). However, such development has not been without environmental impacts. Field operations typically encompass multiple acres of cleared land needed for drill pads, large drill rigs and associated support equipment, and significant quantities of chemicals stored on-site for hydraulic fracturing operations (Soeder et al., 2014). Chemicals are transported and stored in trucks or above ground storage vessels, and remain in concentrated form until being blended with the hydraulic fracturing fluid during the injection process (King, 2012). Unconventional oil and gas development also produces thousands of gallons of highly-saline formation water from each well (NETL, 2009). Regulations restrict the release of such water containing a high total dissolved solids (TDS) content to the environment, and many regulatory agencies now require that the produced water be stored in tanks on site, and disposed of by injection into Class II disposal wells (Rodriguez and Soeder, 2015). Nevertheless, the storage and transport of these large volumes of concentrated fluids and chemicals may result in spills to the environment surrounding a shale gas well pad.

Non-profit river advocacy organizations, State agencies, and the U.S. EPA have been concerned that the production of shale gas may contribute to the degradation of stream water quality in watersheds where such development occurs. As such, regulatory organizations like the Susquehanna River Basin Commission (SRBC) in Pennsylvania have deployed electronic monitoring technology in the mainstem and tributaries of the Susquehanna River. This Remote Water Quality Monitoring Network (RWQMN) is designed to observe if shale gas resource development activities from the Marcellus Shale within the watershed have resulted in adverse impacts on water quality (SRBC, 2013). Electronic water quality monitoring equipment was placed at the mouths of a number of small watersheds, primarily to continuously monitor specific conductivity and temperature of the streams. Changes in these two field parameters were thought to be the most indicative of a release of drilling fluids, hydraulic fracturing chemicals, or produced water from a drilling site. A few locations also received instrumentation to monitor dissolved oxygen (DO), pH, and oxidation-reduction potential (ORP). The SRBC also collects periodic streamflow measurements, macro-invertebrate assessments, and a suite of more detailed chemical analyses from annual water sampling (SRBC, 2014). The goal of such monitoring is to develop methods for the early detection of spills to mitigate the amount of material entering the stream, and allow for rapid remediation that may prevent a bigger disaster.

The electronic monitoring technology is widely in use by various watershed stakeholder groups, but a method has not been established to integrate and interpret the data in a manner to detect surface water spills in an early warning system. The objective of this study was to characterize the performance of commercially-available water monitoring sensors to determine the effectiveness of such instrumentation for detecting surface water spill incidents related to oil and gas operations. Data analysis and interpretation under this study was intended to help industry, regulators, and watershed advocacy organizations develop monitoring programs and protocols for spill detection and mitigation.

1.2 WATER QUALITY MONITORING NETWORKS

A water-quality monitoring network consists of a series of sampling locations and reporting procedures to track changes in water quality. Such networks may consist of random spot checks in an industrial process, known as "ambient monitoring" (Stednick and Roig, 1989) or a series of fixed sites where periodic sampling takes place indefinitely, known as "fixed station quality monitoring" (Ward et al., 1990). Fixed station monitoring can be used to describe water quality over a large region and over long time periods. An example of a nationwide fixed station monitoring program is the National Water Information System (NWIS) of the U.S. Geological Survey (USGS), which has been collecting data for more than 100 years, and presently has over 1.5 million sites across the United States.

Water quality monitoring networks combine in-stream sensors at fixed locations, synoptic sampling, and on-going observations of the surrounding watershed (Hirsch et al., 1988). Statistical evaluation and quality assurance procedures on the samples, including duplicates and blanks, are required to properly characterize water quality and prevent any bias in interpretation (EPA, 2006). Potential problems with a water monitoring network can arise from biased sampling locations selected for ease of access, analytical techniques defined by available laboratory capabilities rather than specific data requirements, and restrictions on sampling frequency imposed by limited agency budgets or other management priorities (Ward et al., 1990).

The major factors limiting the size and scope of a water quality monitoring network are the cost of the equipment, the analytical laboratory techniques available, and the required labor, all of which are typically dictated by the types of data and samples being collected (EPA, 2006). For example, a water monitoring network focused on organometallic pesticides will have more elaborate sample collecting/preservation procedures and much higher analytical costs than a similar network focused on major ions. Poorly-planned water monitoring networks with a lack of documentation and haphazard organization are often said to be "data rich, but information poor" (Ward et al., 1990). A monitoring network is more likely to be successful when the analytical parameters and the frequency of sampling are clearly linked to the program objectives (Sanders and Ward, 1979; Dixon and Chiswell, 1996).

In recent years, water quality monitoring networks have been used to observe phenomena of regulatory concern. Some examples include eutrophication of water bodies near wastewater treatment facilities in need of better nutrient management (Kelly, 1998), total maximum daily loads in streams based on environmental stressors (Davies and Tsomides, 2002), and erosion from development (Ward et al., 1990; Strobl and Robillard, 2008). It is especially important in a regulatory environment that water monitoring programs use properly calibrated equipment and adhere to approved measurement procedures, ensuring that all quality assurance and data custody protocols are followed. This could become crucial if the data are to be used for legal proceedings or entered as evidence in a court of law.

1.3 WATER QUALITY MONITORING TECHNOLOGY

Access to water-quality monitoring systems has expanded with the creation of near real-time remote data transmission. Remote monitoring is a synthesis of in-stream measurements of electronic water-quality data transmitted from the field to a central processing location using wireless telecommunications (Telliet et al., 2002). The USGS began using satellite telemetry in the 1970s to obtain hydrologic data from remote monitoring sites (stream stage and precipitation) without having to send personnel into the field, which reduced demands on human resources (Turner and Woodham, 1980). The 3-G and 4-G mobile data networks were engaged as a cheaper alternative to overburdened satellites for water data telemetry in the 1990s and 2000s at locations where a signal was available.

Clean Water Act legislation initiated in 1972 focused on spot sampling as an established method to acquire water quality data (Ward et al., 1990). In spot sampling, water is collected at a prescribed location and time, and the sample is sent to a laboratory for analysis (Sanders and Ward, 1979). The use of laboratory analysis with proper quality assurance provides consistent results and high-resolution information about the concentration of various chemical constituents in the water (Hirsch et al., 1988; Ward et al., 1990; Smith and McBride, 1990).

Spot sampling is appropriate for monitoring general trends, but it does not have the high time resolution needed to identify random, discrete events. For measurements of hydrologic events, the frequency of sampling is based on the residence time of water in a particular water body such as a stream, large river, or lake. Synoptic sampling of a spill event is likely to focus on an area for 1–2 weeks (Dixon and Chiswell, 1996), after which a contaminant will generally disperse and pass out of a moving body of water (Jobson, 1996). Spot-sampling requires either a substantial field lab or sample transport to an established off-site laboratory, resulting in relatively slow turnaround data analysis of hours to days (Pellerin and Begamaschi, 2014). Time-sensitive, emergency situations, such as catastrophic spills that may threaten human health, need electronic data collection and telemetry for real-time monitoring (Grayman and Males, 2002; Rodriguez-Mozaz et al., 2004; Allan et al., 2006; Telci et al., 2009).

Spills into surface water bodies are likely to be accidental and unpredictable, and therefore continuous monitoring of water quality is necessary. In-stream electronic sensors are capable of nearly continuous data collection with a sampling frequency of seconds to minutes, and rapid interpretation (Allan et al., 2006; Strobl and Robillard, 2008). Continuous monitoring techniques may help to avoid the bias common in discrete monthly water sample collection, such as diurnal chemistry changes that may be missed if samples are only collected during daylight hours, or the impact of runoff on water quality that would not be picked up by baseflow sampling. The sheer number of data points collected by electronic sensors results in observations that are more representative of the actual water quality of the stream (Pellerin and Begamaschi, 2014). The variety of available in-stream water quality sensors include biological early warning systems, passive membrane samplers, electronic field parameter detectors for pH, turbidity, conductivity, ORP, temperature, DO, biosensors, and optical sensors (Allan et al., 2006).

For electronic water-quality monitoring equipment to be useful for detecting spill events the contaminant must be concentrated enough to cause measurable changes in water quality on the sensors (Pellerin and Begamaschi, 2014). If the detector is not sensitive enough, the chemical change in water will not be observed. Likewise, if the sampling rate is too infrequent, the detector could miss the more concentrated part of the chemical plume passing the sensor location. Natural variations of water quality may also mask the chemical signal (Pellerin and Begamaschi, 2014).

This study attempted to quantify changes in water quality variables that can be detected from a natural gas development-related spill in a drainage catchment, especially spills that occur close to streams. The hypothesis being investigated was that spills of oil and gas-related liquids (broadly defined as drilling fluids, hydraulic fracture chemicals, and produced liquids) would have a significant chemical signature with respect to baseline surface water chemistry, and should be detectable electronically by the effects on common water quality parameters. The goal of the study was to show how electronic water quality monitoring could be used as a valid tool for spill detection in shale gas development areas.

1.4 SURFACE WATER MIXING MECHANISMS

Spills into surface water bodies may occur from pipe ruptures, storage tank failure, loss of integrity of the surface storage liner, or any number of accidents (Ziemkiewicz et al., 2014b). If spills are not contained, aqueous chemicals will infiltrate the soil and may eventually reach a nearby stream (Winter et al., 1998).

It is unlikely that a continuously monitoring sensor would happen to be placed immediately downstream of a random, accidental chemical spill. A sensor in any location measures the accumulating discharge of the entire upstream watershed. Contaminants become more diluted with greater transport distance due to dispersion and from the increasing volume of discharge in the larger downstream watershed drainage area (Jobson, 1996). Because discharge rate varies throughout the year, discharge (Q) is a random variable with a distribution proportional to annual flow in a watershed. The flow rate contributes greatly to the diluting capacity of a body of water; lower flows allow greater concentrations of contaminants to persist.

Contaminants are diluted along the flow path by mechanisms of advective transport and mixing due to turbulence and dispersion (Jobson, 1996). As the chemical travels downstream, lateral dispersion becomes less influential as the water becomes completely mixed vertically and from bank to bank. Longitudinal dispersion continues to have an effect, creating a stretched-out plume along the flow direction with low-concentrations at the leading and trailing edges. The highest concentration, called the peak concentration, remains in the middle maximum part of the plume. The peak concentration of the spill can be estimated by calculating the average velocity and travel times from the average annual discharge, a technique available from empirical observations (Jobson, 1996).

There has been significant field research for hydrologic phenomena to estimate dispersion (Jobson, 1996; Emerson et al., 2005). Tracer studies are used to measure the dispersion due to mixing in streams and rivers. Drainage area, flow-rate, and velocity are particular variables that determine the magnitude of dispersion. Pollutant travel time and longitudinal dispersion can be derived from average annual flows and physical characteristics of the basin involved (Jobson, 1996). Some measurements, like stream stage and discharge, are available from USGS gaging stations (USGS, 2015). Data about the physical characteristics of a specific drainage basin may be unavailable or difficult to acquire. In this case, models can be used to determine the physical and environmental relationships of stream paths, accumulated flow, and average stream velocity from readily available spatial data such as digital elevation models (Strager, 2012).

1.5 RISKS ASSOCIATED WITH OIL AND GAS OPERATIONS

Unconventional shale gas wells generate large-volume solid and liquid waste streams, including flowback water, produced (formation) water, precipitates, drilling fluids, mud, and drill cuttings (Ziemkiewicz et al., 2014a). Typical Marcellus Shale gas wells use 2–4 million gallons of water for the hydraulic fracturing process, of which only about 10% to 30% returns to the surface as flowback fluid (Soeder, 2012). The hydraulic fracturing fluid itself consists of approximately 99.51% water and proppant sand with about 0.49% chemical additives (DOE, 2009). Formation water produced with the gas contains inorganic dissolved solids composed of Na, Cl, Ca, Mg, Br, Ba, and Sr (Vidic et al., 2013). Benzene and radium have also been detected in produced waters. TDS concentrations up to 200 g/L have been documented in produced waters from the Marcellus Shale (Ziemkiewicz et al., 2014a); these are even higher in some other shale plays like the Bakken. TDS concentrations are variable, but tend to increase in produced water over time (Haluszczak et al., 2013; Ziemkiewicz et al., 2014a).

Drilling fluids are a necessary component of the drilling process. These fluids serve to cool and lubricate the downhole bit, flush cuttings out of the hole, support the borehole walls to prevent collapse, and in the case of directional drilling, supply hydraulic power to the downhole drilling motor integrated into the bottomhole assembly (Soeder, 2012). The hydraulic fracturing process introduces elevated fluid pressures into the borehole that exceed the rock tensile strength, causing the target formation to fracture in the direction of least principal stress (Soeder, 2012). Additional fluid is pumped into the well during the course of the hydraulic fracturing operation to propagate the cracks farther into the formation, and to transport sand downhole to prop the fractures open after pressure is released.

To ensure that sufficient volumes of fluid are available for the drilling and hydraulic fracturing activities, drillers commonly excavate containment ponds or pits to hold water. Because of issues with leaking pond liners, the use of steel storage tanks is becoming more common (DOE, 2009). Flowback fluid from Marcellus Shale wells in the Appalachian Basin is commonly recycled into additional hydraulic fracturing operations, while the remaining residual waste is disposed of by injection into Class II disposal wells. In West Virginia, 43% of the residual waste is disposed of out of state, and an even greater percentage leaves Pennsylvania. The lag time between the recovery of fluids from a hydraulic fracture operation and their ultimate disposal imposes additional risks of fluid loss in transport and storage (Downstream Strategies, 2013).

The volume and type of chemicals used in hydraulic fracturing fluid varies among operations, dictated by the geology and geochemistry of the formation, the quality of the water, and the operator’s preferences (Soeder et al., 2014). The chemicals are added on-site during the hydraulic fracturing process. Before injection, concentrated forms of the chemicals (typically biocides, thickeners, corrosion inhibitors, friction reducers, and others) are stored on-site either in trucks or in above-ground storage tanks, sometimes in significant volumes (King, 2012; Soeder et al., 2014). Examples of additives are listed in Table 1 (GWPC, 2014).

Table 1: Approximate liquid volumes in any one hydraulic fracturing fluid composition (DOE, 2009; GWPC, 2014)

Hydraulic Fracturing Additive (Example Chemical)	Average % of Total Fluid Volume*	Approximate Volume Needed per Fracture job* (gallons)
Gellant (Guar gum or ethylene glycol)	0.5	10,000
Friction Reducer (Polyacrylamide or ethylene glycol)	0.05	1,000
Biocide (Glutaraldehyde)	0.001	20
Water	99	2 to 5 million

*Calculated based on 2 million gallons of hydraulic fracturing fluid

In a review of Pennsylvania Department of Environmental Protection (PA DEP) Notice of Violation reports, 31 significant spills (>9.5 barrels) were recorded over the course of 7,000 well spuds (0.4%) and 4,000 completed wells (0.775%) from 2005 to November 2013 (Brantley et al. 2014). This incident rate falls within the typical range of reportable environmental violations on approximately 0.5% of all U.S. oil and gas wells, including shale gas wells (Kell, 2011; Vidic et al., 2013; Glosser, 2013). The reported incidents included fuels (1), frac chemicals (7), produced fluids (9), sediments (5), and drill cuttings (9). The violations were due to a variety of causes, including vehicular accidents, pipe failure, well blowouts, and leaky storage containers.

1.6 OBJECTIVES

The objective for this study was to determine how standard water quality sensors would respond to spill events associated with unconventional gas and oil development, primarily on the Marcellus Shale play. The approach consisted of estimating the peak concentrations of contaminants from typical surface water spill volumes in monitored watersheds, followed by laboratory tests for standard in-stream instrumentation to detect a change in water quality at the estimated peak concentrations. The goal was to obtain information that could be applied to the design of water quality networks for continuously monitoring surface water near shale gas development operations. The purpose of such monitoring is to provide early warning for industry to contain spills in tributary watersheds before contaminants move downstream, reduce the risks to aquatic ecosystems and human health, and help regulatory agencies better enforce contaminant control.

2. METHODS

2.1 SELECTING SPILL EVENTS

Twenty-two spill events were selected from the PA DEP's Oil and Gas Compliance Report database as case studies to determine a range of contaminant concentrations for laboratory testing. Information captured in this database includes the date of the violation, the American Petroleum Institute (API) well number as a unique site identifier, and a brief description of the incident. The spill events of interest occurred within the Susquehanna River Basin Commission Remote Water Quality Monitoring Network (SRBC-RWQMN) from January 2011 to early 2014 (details in Appendix A). Incidents for the case study were selected from violation notices that contained information about the actual chemicals or compounds spilled, along with an approximate volume. These parameters were necessary for determining peak concentrations and investigating water quality field parameters that might have been affected.

The case study incidents summarized in Table 2 were consistent with previously published findings (Brantley et al., 2014) in terms of the volumes and type of chemicals spilled. Produced water and drilling mud were sometimes spilled in large quantities, with an average volume exceeding 30 barrels, and maximum amounts of more than 100 barrels of fluid (Brantley et al., 2014). Figure 1 shows the location of each notice of violation identified by the geographic coordinates from the API well designation.

Table 2: List of contaminants reported as spills in PA DEP Notice of Violation reports; all within the SRBC RWQMN since January 2011.

Hydraulic Fracturing Additive	Purpose	Average Volume, [Maximum volume] (barrels)	Number of Incidents in Study Area
Drilling mud	Used to keep the bit wet during drilling	34 [104]	4
Produced water	Effluent from the well after drilling	34 [150]	12
Diesel fuel	Powers equipment and vehicles on the well pad	4 [6.5]	3
Corrosion inhibitor (i.e. ethylene glycol)	Used as a winterizing agent or to prevent pipe deterioration	0.5 [0.5]	1
Mixture of mud, water and/or fuel	Effluent from the well or from an accidental spill	0.8 [0.9]	2

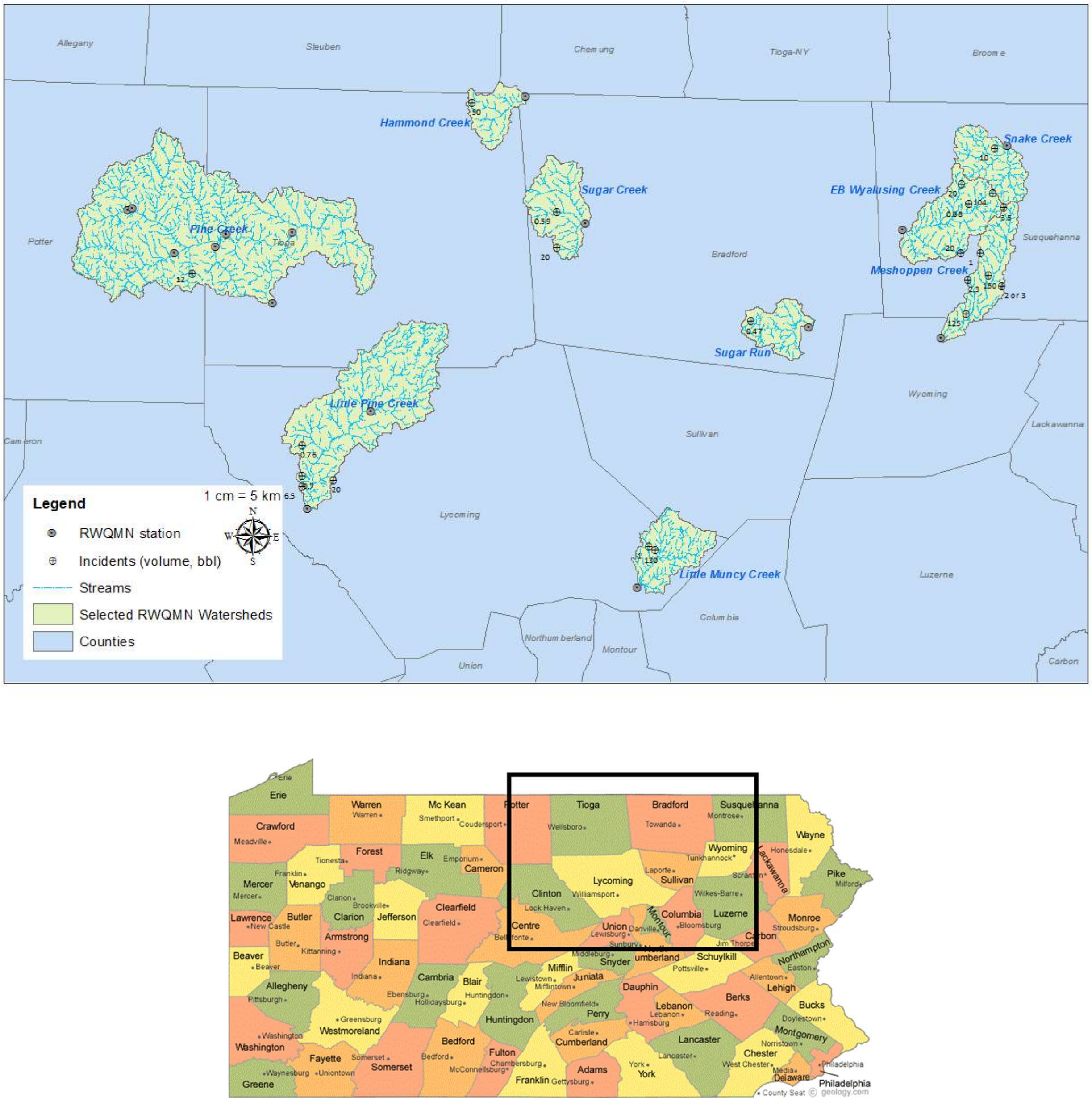

Figure 1: Upper map shows location of the case study spills in the RWQMN watersheds. Lower county map shows approximate location of watershed map within the Commonwealth of Pennsylvania.

2.2 ESTIMATING A RANGE OF FLOW-RATES FOR THE UNGAGED WATERSHEDS OF THE RWQMN

The spatial variables of drainage area ($D_{a,u}$) and average annual discharge ($Q_{a,u}$) for watersheds were obtained by RWQMN (see Appendix B). Discharge data from USGS monitoring stations of the surrounding Susquehanna River Basin were used to approximate a range of discharges from the average annual value. One set of USGS monitoring stations were selected based on their watersheds as encompassing drainage areas of RWQMN stations. The second set was composed of USGS stations in close proximity that had similar drainage area and the same stream order. USGS reports average daily values and an average annual discharge; the drainage-area ratio method for determining stream flow in ungaged watersheds (Emerson et al., 2005) was applied to determine if the USGS station was comparable to the RWQMN station. The best fit was based on the accuracy of the method reported by Emerson et al. (2005) for estimating the unmonitored watershed's drainage area and average annual discharge from the analysis of gaged drainage areas (Table 3). Percent error was calculated by the following equation:

$$\% \text{ Error} = D_{a,u} - D_{a,u\text{-}g}/D_{a,u} \qquad (1)$$

where $D_{a,u}$ is the drainage area of the ungaged watershed, provided by SRBC; $D_{a,u\text{-}g}$ is the drainage area estimated by the Emerson et al. (2005) method.

Table 3: Rate of error for the Emerson et al. (2005) method to estimate the drainage area and discharge of an ungaged watershed ($D_{a,u}$ and Q_u, respectively), from data of a gaged drainage area (D_{ag}) and average annual discharge (Q_g)

RWQMN Watershed Name	$D_{a,u}$ (km^2)	Q_u (cms)	USGS Monitoring Station	D_{ag} (km^2)	Q_g (cms)	% Error
EB Wyalusing	179	2.85	1533400	22,600	365	-9.00%
Mesohoppen	134	2.15	1533400	22,600	365	-8.6%
Snake Creek	117	2.12	1452500	117	1.75	-7.2%
Hammond Creek	75	0.99	1603500	78	0.91	-15.0%
Sugar Run	85	1.39	1569000	85	1.70	-26.0%
Sugar Creek	145	1.98	1531325	243	3.11	-2.8%
Pine Creek	997	15.6	1548500	1,550	24.0	-15.0%
Little Muncy Creek	132	2.32	1473120	139	2.27	15.0%
Little Pine Creek	466	7.08	1549700	2,430	40	-15.0%

USGS monitoring stations within the same stream network as the RWQMN station are the most accurate for drainage areas on the scale of hundreds of square miles. For drainage areas less than 130 km^2 (50 mi^2), the use of smaller drainage areas nearby was consistently more accurate. Full results can be found in Appendix C. This method of comparison was rather versatile; all but one of the RWQMN watersheds (Little Muncy Creek) had a USGS monitoring station within its same stream network.

Average daily discharge rates were generalized with a histogram and data were fit to a gamma distribution. A gamma distribution is appropriate for modeling the annual variation of river discharge (Bedient and Huber, 2001). The shape (*k*) and the scale (Θ) of the gamma distribution for USGS daily average annual discharge (Table 4) were placed in Excel's inverse gamma distribution function, which estimated a random flow-rate for the USGS gaged watershed. This was then used to estimate a range of flows from the SRBC ungaged watersheds using Equation 2.

$$Q_u = (D_{a,u}/D_{a,g})Q_g \tag{2}$$

where Q_u= average annual flow for ungaged watershed; $D_{a,u}$= drainage area of ungaged watershed; $D_{a,g}$= drainage area of gaged watershed; Q_g= average annual flow for gaged watershed.

Table 4: Results of the gamma distribution calculation from USGS gaged watersheds

USGS Station	Range of Daily Average Discharge Data	Skew	Shape, k	Scale, Θ
01603500	1933 to 1982	0.90	2.0	16
01569000	1938 to 1974	4.1	2.4	25
01452500	2007 to 2015	5.1	6.5	8.8
01473120	1966 to 1994	1.3	2.5	32
01531325	2010 to 2015	5.8	0.12	870
01533400	2007 to 2015	1.1	3.4	3,800
01549700	1957 to 2014	1.1	3.5	400
01548500	1918 to 2013	1.1	2.1	400

Graphical results of the gamma distribution calculations can be found in Appendix C. The gamma distribution was found to be a better fit for data that had accumulated for more than 5 years.

2.3 CALCULATING A RANGE OF PEAK CONCENTRATIONS FOR THE CASE STUDIES

One hundred random flows were generated for the SRBC watersheds according to the gamma distribution of USGS gaged watersheds. The peak concentration is related to the time for the contaminant to travel from the source to the monitoring location. The velocity of the contaminant is determined by Equation 3 (Jobson, 1996).

$$V_p = 0.020 + 0.051(D'_a)^{0.821}(Q'_a)^{-0.465}\,(Q/D_a) \qquad (3)$$

where V_p= velocity of peak concentration; D'_a= adjusted drainage area; Q'_a= adjusted annual flow; Q= discharge at the cross-section of the monitored watershed; D_a= drainage area of the monitored watershed.

The distance for the spill to travel was determined by a straight-line measurement from the API well location to the monitoring station, irrespective of the actual path of streams. This length is an underestimation of the actual travel distance, because streams seldom flow in a straight line. This caused the predicted peak concentrations to be slightly overestimated, because the effects of longitudinal dispersion increase with greater distances travelled (Fischer et al., 1979).

The travel-time was determined by the distance the contaminant would have traveled and the velocity of the peak concentration, ($T_p=d/V_p$). The travel time is a necessary variable for calculating peak concentration (C_{up}) in Equation 4.

$$C_{up} = 857T_p^{\,-0.760(Q/Q_a)^{-0.079}} \qquad (4)$$

where T_p= travel time of peak concentration; Q_a= mean annual river discharge; Q= river flow at the section at the time of measurement (Jobson, 1996).

The peak concentration gives a realistic magnitude to test with water quality monitoring devices. It incorporates dilution due to surface water dispersion during transport and the typical discharge rates of streams. This information for each case study spill generated a range of peak contaminant concentrations (Table 5). The peak concentration results demonstrate the desired detectable limit for the SRBC RWQMN continuous monitoring systems. These concentrations were used in the laboratory experiments for instrument testing.

Table 5: Ranges of peak concentration that would be measured at the RWQMN monitoring stations for the case study spills

RWQMN Watershed	Material Spilled	Volume (bbl.)	Distance Traveled (km)	Range of Concentration (ppm)
Mesohoppen	Production fluid (flowback)	150	14	1.1–2.1
Little Muncy Creek	Production fluid (flowback)	130	7.4	0.99–3.07
Hammond Creek	Production fluid	50	9.9	0.85–1.87
EB Wyalusing	Drilling mud (bentonite), cement	104	18	0.53–1.1
Snake Creek	Drilling mud	10	2.4	0.20–0.39
EB Wyalusing	Drilling mud (freshwater)	20	11	0.12–0.30
EB Wyalusing	Production fluid	20	13	0.11–0.26
Sugar Creek	Production fluid	20	7.0	0.07–0.60
Little Pine Creek	Production fluid (brine)	20	7.0	0.07–0.15
Little Pine Creek	Diesel fuel	6.5	4.3	0.03–0.07
EB Wyalusing	Diesel fuel	3.5	19	0.02–0.04
Mesohoppen	Diesel fuel	2.3	12	0.02–0.04
Mesohoppen	Production fluid	3	14	0.018–0.049
Pine Creek	Production fluid	12	14	0.014–0.033
Sugar Run	Production fluid (water)	0.59	3.5	0.013–0.036
Little Muncy Creek	Production fluid (flowback)	1	7.9	0.007–0.022
Mesohoppen	Production fluid (flowback)	1	17	0.006–0.013
Sugar Run	Corrosion Inhibitor	0.47	11	0.006–0.013
EB Wyalusing	Mixture of drilling mud and water	0.88	13	0.005–0.011
Sugar Creek	Drilling mud	0.59	5.9	0.002–0.020
Little Pine Creek	Production fluid	0.7	6.1	0.002–0.005
Little Pine Creek	Mixture of (drilling) mud, oil, diesel fuel	0.76	12	0.002–0.004

The concentration of a contaminant decreases over a distance. The volume of a spill significantly affects its persistence as a high peak concentration. Figure 2 demonstrates the median peak concentration from the case studies.

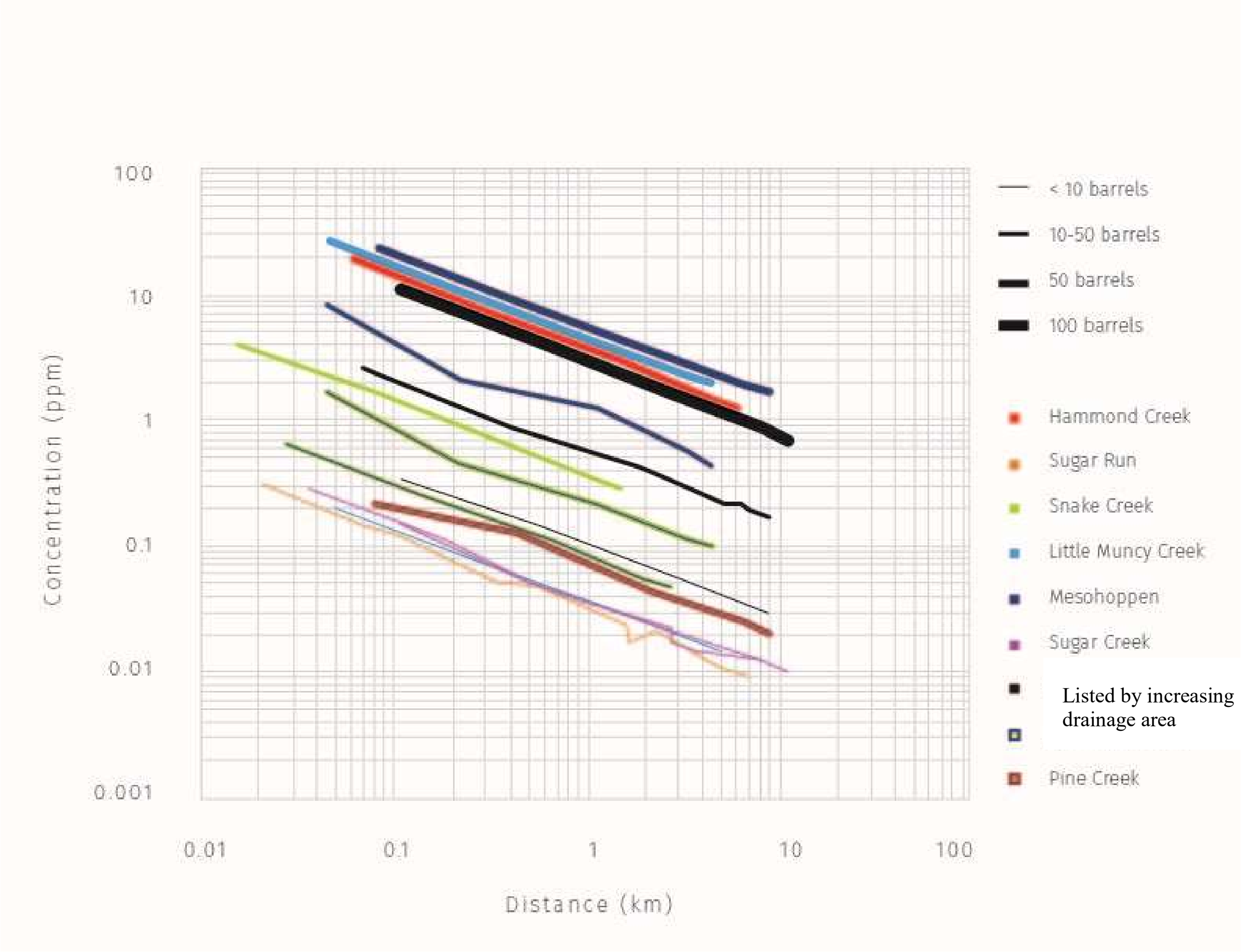

Figure 2: Median peak concentration for chemical spills as a function of distance travelled in the watershed.

2.4 LABORATORY EXPERIMENTS

The results from the peak concentration calculations were used as a guide for the concentrations to be measured for chemicals in the laboratory experiments. The chemicals tested were ethylene glycol, saline produced water from a Marcellus Shale gas well, and a representative drilling mud created in the laboratory.

The ethylene glycol was purchased from a laboratory supply house. The produced water was collected in the summer of 2014 from a Marcellus Shale well that had been drilled in March 2012 in Greene County, Pennsylvania. Details about this well and NETL field studies related to it were published in a DOE report by Hammack et al. (2014).

The drilling mud was created in the laboratory from published values for the composition of common, water-based muds typical of those used on shale (Caenn et al., 2011). The formula consisted of 4 L of water into which had been added 20 g of xanthan gum, 56 g of bentonite clay, 40 g of carboxymethyl cellulose, and 1.8 g of barite. For the mud mix used in the NETL lab experiments, guar gum was substituted for xanthan gum as an equivalent thickening agent. The stock chemicals were prepared at full concentration and then diluted to lower concentrations using deionized water. The laboratory set-up is shown in Figure 3.

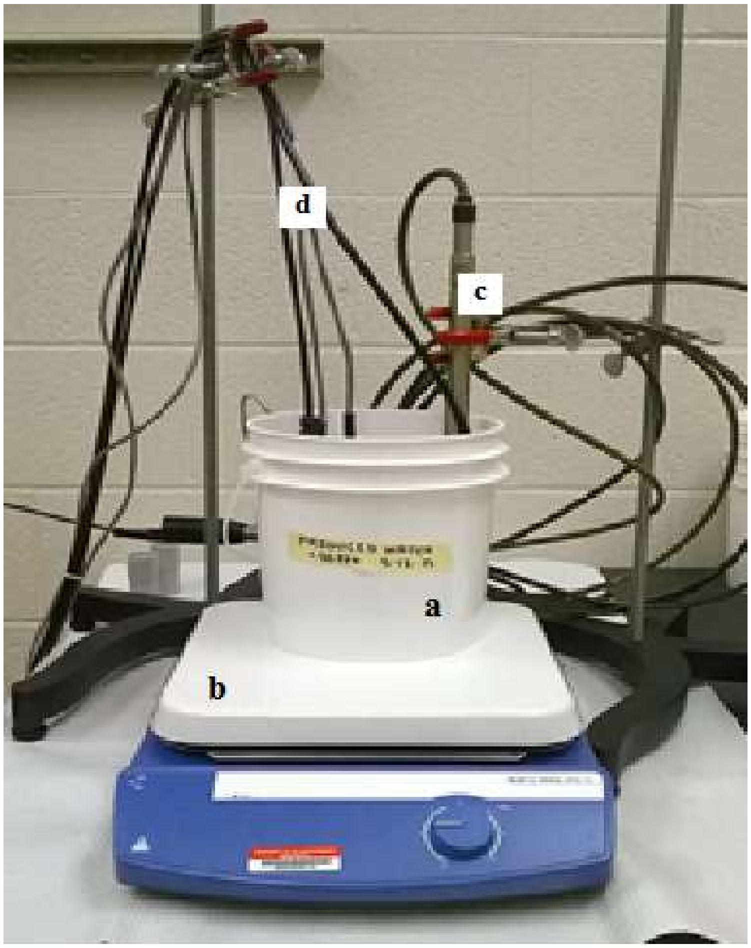

Figure 3: Laboratory apparatus: a) pail containing deionized water; b) magnetic stirrer; c) AquaTROLL 200; and d) Campbell CR-1000 probes for pH, dissolved oxygen, ORP and temperature/conductivity.

Peak concentrations were calculated from less than 0.16 km (0.1 mile) to the maximum distance traveled in the case studies about 16 km (10 miles). The target concentration for the laboratory studies was 50 ppm to ensure both consistency and detectability. The study recognized that it is possible for a peak contaminant concentration of 50 ppm at a distance of 0.16 km from the source to be diluted to the parts per trillion level after traveling 16 km downstream. However, the study also recognized that larger volumes of spilled contaminants, such as drilling mud and produced water could still have detectable peak concentrations of approximately 1 ppm after traveling 16 km downstream.

In the laboratory experiments, the contaminant was prepared in a dilute solution, and incrementally added to a container holding deionized water. Sensors measuring common water quality parameters were submerged in the container to continuously record water quality as the contaminant concentration increased, with the intention of capturing both the detection threshold and the response of the instruments to the contaminant.

Two water quality monitoring instruments, the Campbell Scientific (CS) CR-1000 data-logging system (sensors are designated by the letter “d” in Figure 3) and the AquaTROLL 200 (designated by the letter “c” in Figure 3) were submerged in a vessel consisting of a 3.78 L (1 gallon) plastic container, 19 cm in diameter and 18-cm deep. The plastic pail was initially filled to a water depth of 3.5 cm with 1.2 L of deionized water, which was the minimum water depth needed to submerge both instruments. The instruments were suspended from a mounting rod.

Diluted chemicals were added to the initial set up at standard intervals of 5 min, while the solution was constantly stirred. Temperature was not controlled but was recorded with both submerged sensors throughout the study. All sensors were calibrated according to manufacturer standards.

The CS CR1000 data-logger had four attachments: the CS-511 dissolved oxygen (DO) sensor, the CSIM-11 pH sensor, the CS A547 temperature and conductivity sensor, and the CSIMM-11 oxidation reduction potential (ORP) sensor. The DO and conductivity sensors were calibrated for operating temperature twice during the 2-week duration of experiments using 1,280 µS/cm standard calibration fluid. The pH and ORP sensors were calibrated by standard pH 4 and pH 7 buffers and Zobell solution once a week. The data-logger scanned the sensors every 15 sec and output the data to a nearby desktop computer.

The AquaTROLL (AT) 200 instrument measured temperature and conductivity. It was also calibrated using the 1,280 µS/cm standard. The AT recorded measurements every minute, which was the minimum frequency available. Specifications for the instruments are in Table 6.

Table 6: Laboratory tested instrument ranges of operation and accuracy

	AquaTROLL 200 CTD Data Logger		Campbell Scientific CR-1000 Data-Logger		
Conductivity (µS/cm)	5-100,000	±0.5% + 1	CS547A	5-7000	± 5%
Dissolved oxygen (ppm)	N/A		CS511-L	0.5- 50	± 2%
pH	N/A		CSIM11-pH-L	0-14	±0.1%
Temperature (°C)	-5 -50	±0.1	CS547A	0-50	< 0.1
Oxidation reduction potential (mV)	N/A		CSIM11-ORP-L	-700- >1100	± 0.1%
Minimum recording frequency (seconds)	60		1		

2.5 DATA ANALYSIS

A paired t–test, which correlates two sets of measurements with each other and looks at the differences (McDonald, 2014) was conducted between experimental trials to determine if the measurements were consistent. A paired t-test was also conducted between the two instruments to determine if their measurements across the range of values were the same. A value of 0.05 was assumed for α in all tests. From these results, further correlation analysis was conducted to determine if certain water quality parameters correlate with increasing chemical concentration. For purposes of this report, a strong correlation was defined as 0.85 to 1.0, a moderate correlation was defined as 0.25 to 0.84, and weak correlation was defined as less than 0.24.

3. RESULTS/OBSERVATIONS

3.1 DRILLING MUD

Drilling mud was added gradually to the deionized water containing the probes as the system was continually stirred. The concentration of the drilling mud increased from zero to 50 ppm over the course of approximately 2 hours while measurements were taken. The rate of increase was more rapid near the end of the trials.

3.1.1 Drilling Mud Impact on Water Quality Parameters

The drilling mud affected specific conductivity, DO, and pH. The specific conductivity increased at a rate of 0.1 to 0.2 µS/cm per ppm in concentration. Dissolved oxygen decreased by 0.2 ppm/50 ppm drilling mud. The pH had a tendency to converge at 6.3, even from Trial 1 which had a starting pH of 8. ORP had a tendency to converge at -200 mV, except from Trial 1 which had an initial reading of 1,300 mV that decreased exponentially to 600 mV. Temperature increased throughout the trials, probably due to the apparatus. The temperature throughout trials 2, 3, and 4 increased at a rate of 0.018 °C/min, Trial 1 increased at a rate of 0.003°C/min. The measurements from the CS probes are shown in Figure 4.

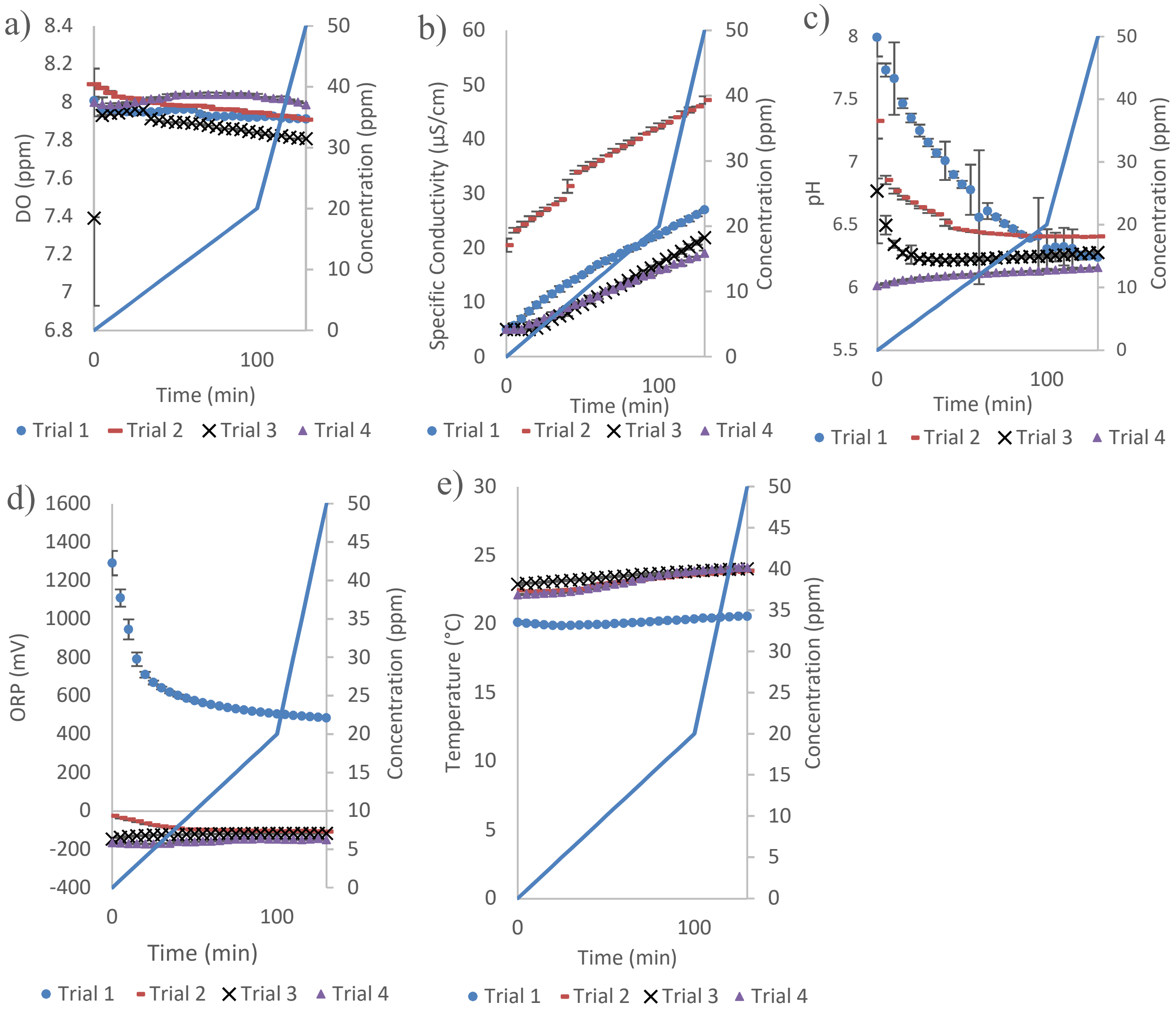

Figure 4: Campbell Scientific measurements from the drilling mud experiments. a) dissolved oxygen, b) specific conductivity, c) pH, d) oxidation reduction potential, and e) temperature over time. Increased concentration of drilling mud added to the solutions is plotted against time with a solid line.

The AquaTROLL results are shown in Figure 5. This instrument was able to detect the change in conductivity below 5 µS/cm, which is below the range for the Campbell; this is observable in lower concentrations of drilling mud (see Trial 3 of Figure 5b). The phase shift of specific conductivity in drilling mud, Trial 2, was detected with both instruments.

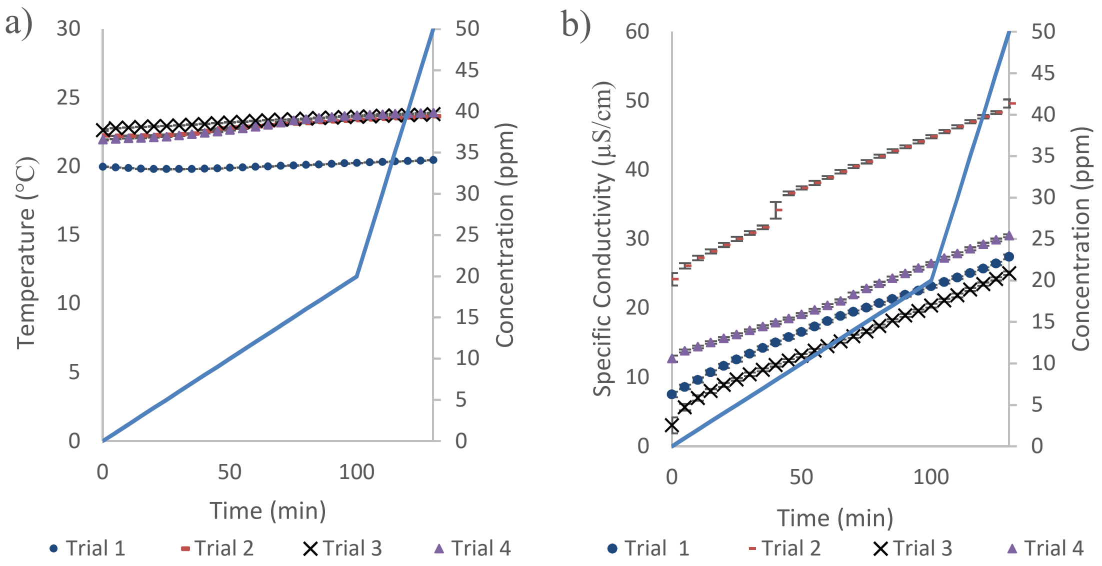

Figure 5: AquaTROLL measurements from the drilling mud experiments: a) temperature, and b) specific conductivity over time. Increased concentration of drilling mud added to the solutions is plotted against time with a solid line.

The results for specific conductivity were combined for both instruments (Figure 6). A phase shift was included such that the specific conductivity was 0 when at the beginning concentration of 0 ppm. These results show the general response of the probes. For concentrations less than 2 ppm, the measured specific conductivity increases at a rate of approximately 0.8 µS/cm per ppm. For large concentrations, the response reduces to a rate of approximately 0.14 µS/cm per ppm.

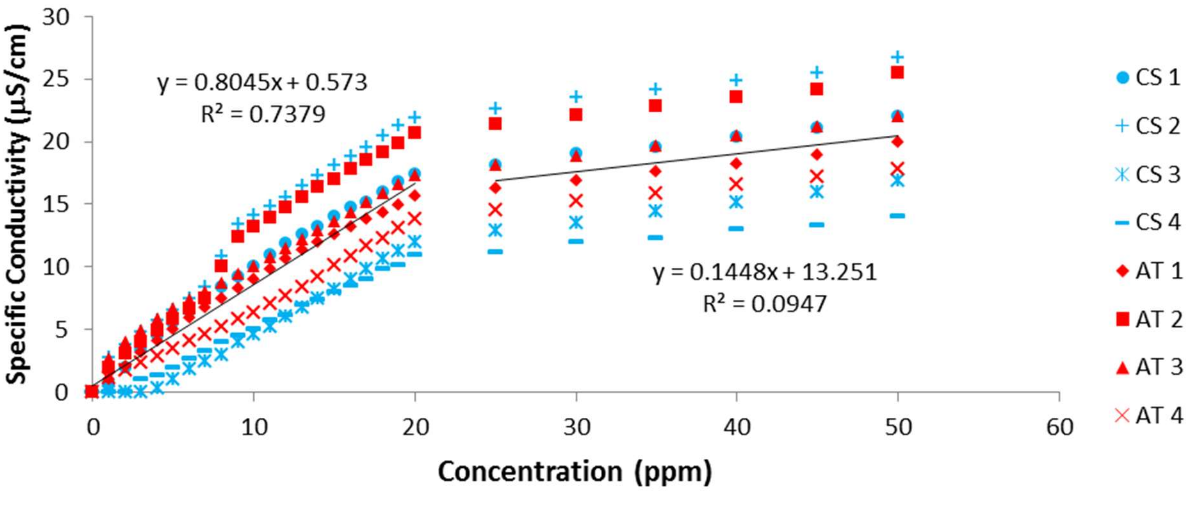

Figure 6: Specific conductivity vs. concentration for both instruments, including phase shift.

3.1.2 Paired T-Test and Correlation Results

The laboratory measurements were repeated four times. Statistical results suggest that the instrument response was significantly different among the trials for the CS probes when testing temperature, specific conductivity, pH, ORP, and DO (*p*-values≤0.0013). Similarly, the instrument response was significantly different when using the AT to measure temperature and specific conductivity (*p*-values<0.0001*)*. There was only one exception. The temperature for Trials 2 and 4 for both the CS and AT instruments response were similar (*p*-value=0.079-0.35, Table 7).

Table 7: p-value results of the paired t-test comparing the trials of the drilling mud tests

Campbell Scientific				AquaTROLL			
Temperature				**Temperature**			
	1	*2*	*3*		*1*	*2*	*3*
2	<0.0001			*2*	<0.0001		
3	<0.0001	<0.0001		*3*	<0.0001	<0.0001	
4	<0.0001	0.25	<0.0001	*4*	<0.0001	0.079	<0.0001
Specific Conductivity				**Specific Conductivity**			
	1	*2*	*3*		1	*2*	*3*
2	<0.0001			*2*	<0.0001		
3	<0.0001	<0.0001		*3*	<0.0001	<0.0001	
4	<0.0001	<0.0001	<0.0001	*4*	<0.0001	<0.0001	<0.0001
pH							
	1	*2*	*3*				
2	0.00026						
3	<0.0001	<0.0001					
4	<0.0001	<0.0001	<0.0001				
ORP							
	1	*2*	*3*				
2	<0.0001						
3	<0.0001	<0.0001					
4	<0.0001	<0.0001	<0.0001				
DO							
	1	*2*	*3*				
2	<0.0001						
3	0.0013	<0.0001					
4	<0.0001	<0.0001	<0.0001				

While the responses were different among trials, the type of response was similar among trials for specific conductivity and temperature. The correlation tests (Table 8) showed that both the CS and AT instruments responded with strong positive correlations for temperature and specific conductivity.

There was less consistency for the additional parameters monitored with the CS probes. pH results showed moderate to strong negative and positive correlations. Trial 4 had negative correlation with the other three trials. Trial 4 had the lowest starting pH, and pH increased over the course of the test. ORP showed both negative and positive correlations among trials well. Trials 3 and 4 had a moderately positive correlation, and Trials 1 and 2 had a strong positive correlation. The remaining comparisons moderate to strong negative correlations. The ORP had the greatest change at concentrations lower than 10 ppm, but above this concentration all trials converged with exception of Trial 1. DO showed weak negative correlations in three comparisons, and moderate to strong positive correlations in three comparisons. Again, the first part of the trial at about 5 ppm did not have consistent response, but above 5 ppm the dissolved oxygen generally decreased.

Table 8: Correlation coefficients comparing the trials of the drilling mud trials

Campbell Scientific				AquaTROLL			
Temperature				**Temperature**			
	1	*2*	*3*		*1*	*2*	*3*
2	0.90			*2*	0.92		
3	0.88	0.99		*3*	0.89	0.99	
4	0.92	0.99	0.99	*4*	0.92	0.99	0.99
Specific Conductivity				**Specific Conductivity**			
	1	*2*	*3*		1	*2*	*3*
2	0.99			*2*	1.0		
3	0.98	0.97		*3*	1.0	0.99	
4	0.99	0.98	1.0	*4*	0.99	0.98	0.99
pH							
	1	*2*	*3*				
2	0.90						
3	0.61	0.87					
4	-0.99	-0.89	-0.60				
ORP							
	1	*2*	*3*				
2	0.97						
3	-0.99	-0.98					
4	-0.66	-0.77	0.73				
DO							
	1	*2*	*3*				
2	0.87						
3	-0.27	-0.077					
4	0.44	-0.077	0.50				

3.2 PRODUCED WATER

Produced water was added gradually to the deionized water containing the probes as the system was continually stirred. The experiment was designed to increase the concentration of the produced water from zero to 50 ppm over the course of approximately 2 hours while measurements were taken. The rate of concentration increase was different for two of the four trials (Trials 2 and 3), which led to some data interpretation challenges.

3.2.1 Produced Water Impact on Water Quality Parameters

The water quality parameter results for the Campbell Scientific probes are shown in Figure 7. The different rate of concentration increases among the trials are evident in the specific conductivity measurements in Figure 7b. For all four trials, the specific conductivity increased at a rate of 1.7 to 2.4 µS/cm per ppm of produced water added to the test vessel. Produced water is released from the geological formation during oil and gas production activities, and typically contains significant concentrations of TDS. Water produced from the Marcellus Shale has TDS contents measured as high as 200 g/L. Nearly half of TDS consists of chloride, and the remaining TDS consists of various metals at concentrations of hundreds of milligrams per liter (Hayes, 2009). Specific conductivity is a positive indicator for the presence of these dissolved ions.

The ORP increased by about 20 mV during the first 35 min of all trials, followed by diverging results in either an increasing or decreasing direction. Divergence in the increasing direction had a magnitude of 10 mV after the first 35 min; divergence in the decreasing direction had a magnitude of about 5 mV. The phase shift in Trial 4 may have to do with an offset from either the instrument calibration or the instruments' sensitivity to temperature. However, the shape of the ORP signal, due to increasing concentration of produced water, is similar for all trials, irrespective of the starting condition.

The DO parameter did not react consistently among trials. Two trials showed a decrease by about 0.15 to 0.20 ppm dissolved oxygen per 50 ppm of produced water, while the two other trials (Trial 1 and 4) had a parabolic trend. In the fourth trial, DO increased 0.17 ppm followed by a decrease to a net change of 0.9 ppm at 50 ppm produced water. The first trial showed an increase by 0.01 ppm halfway through the trial, and decreased for net loss of 0.07 ppm over the course of the entire trial.

Generally, the pH decreased at a rate from the range of 0.004 to 0.01 units/min and the measurements converged at about 6.5 at the end of the four 130 min trials. Both specific conductivity and pH are affected by produced water, suggesting a possible detection strategy.

The results for the AquaTROLL measurements are shown in Figure 8. The response in specific conductivity and temperature parameters are similar to those of the Campbell Scientific conductivity and temperature probes.

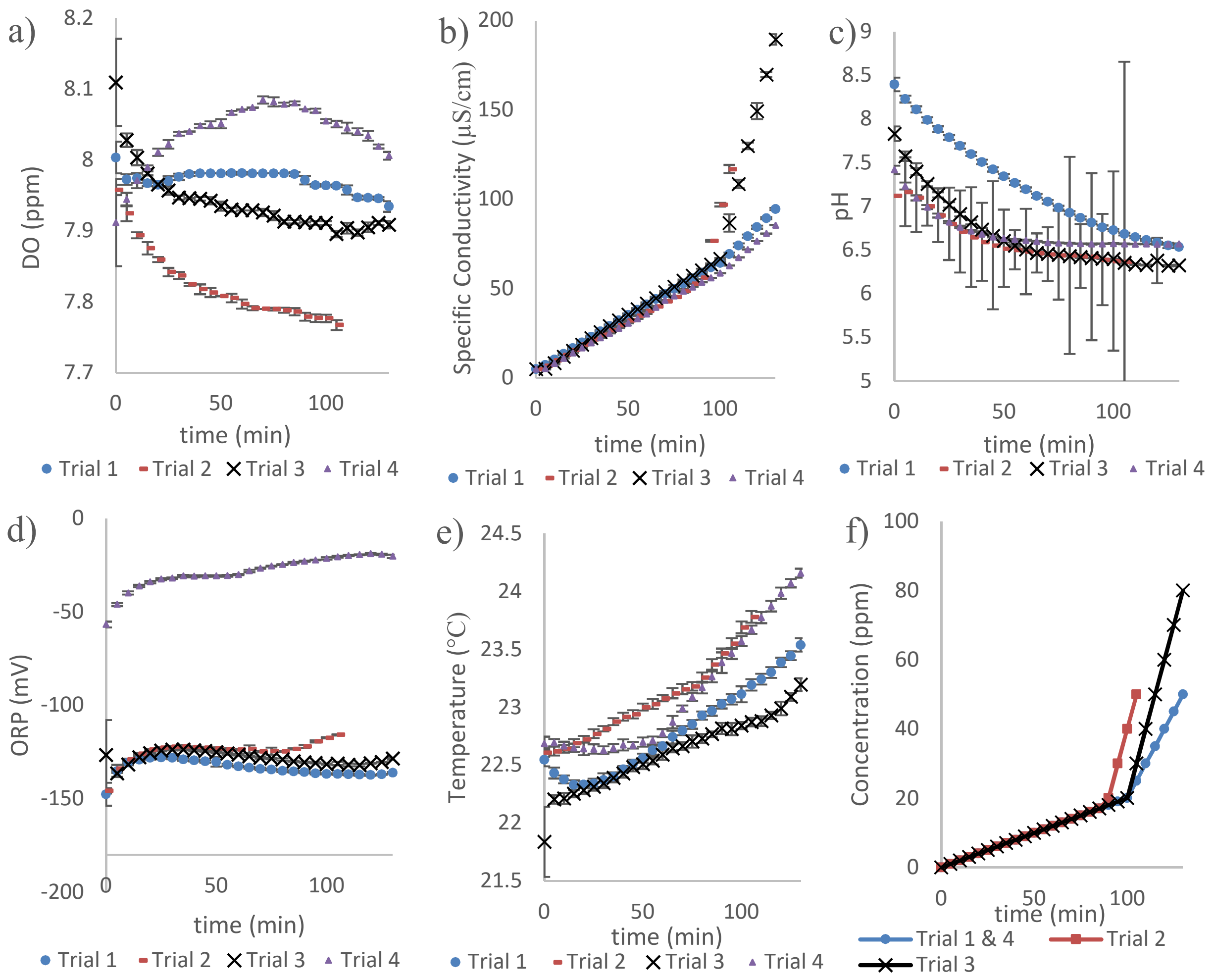

Figure 7: Campbell Scientific measurements from produced water experiments over time: a) dissolved oxygen, b) specific conductivity, c) pH, d) oxidation reduction potential, e) temperature, and f) increased concentration of produced water added to the solutions over time.

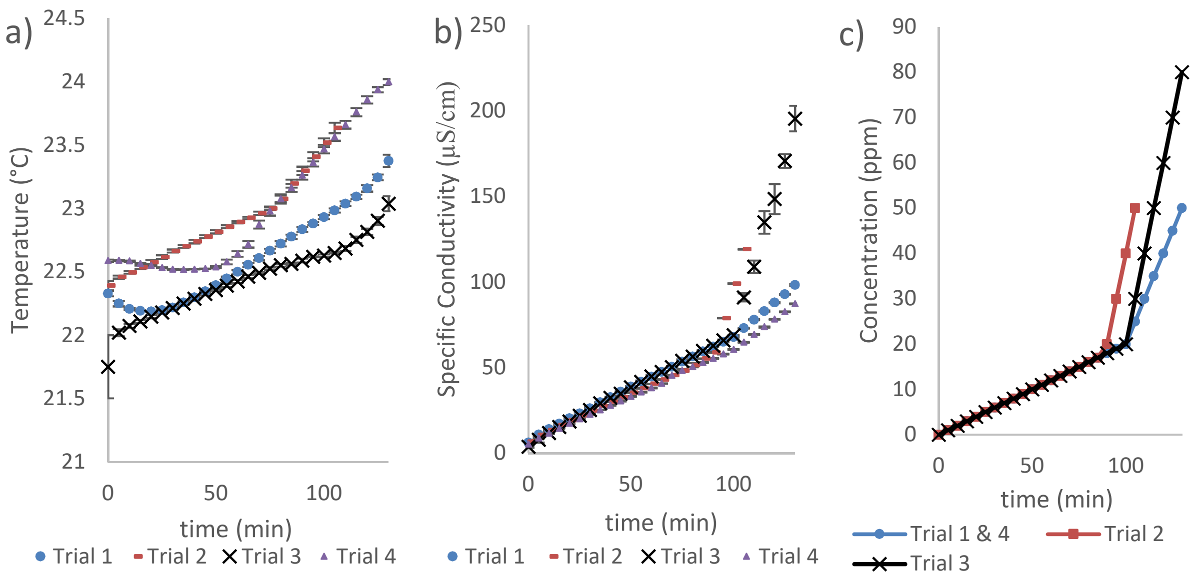

Figure 8: AquaTROLL results from the produced water trials: a) temperature, b) specific conductivity, and c) increased concentration of produced water added to the solutions over time.

3.2.2 <u>Paired t-test and the Correlation Results</u>

Generally, statistical results suggest that the instrument response was significantly different among the trials for the CS probes when testing temperature, specific conductivity, pH, ORP, and DO (*p*-values≤0.020), but there were some exceptions. For temperature, Trials 1 and 3 were statistically similar (*p*-value=0.10). For specific conductivity, Trial 1 was similar to both Trial 2 and 3 (*p*-values=0.067-0.19). For pH, Trial 3 was similar to Trial 4 (*p*-value=0.48). The responses among all trials were significantly different for dissolved oxygen (*p*-values≤00.0021) (Table 9).

Similarly, the instrument response was generally significantly different when using the AT to measure temperature and specific conductivity (*p*-value<0.0020*).* There were also exceptions. The temperature for Trials 2 and 4 for were similar (*p*-value=0.30). Like the CS results, Trial 1 was similar to both Trial 2 and 3 for specific conductivity (*p*-values=0.11-0.21) (Table 9).

Table 9: p-values for the paired t-test comparing the trials of the produced water

Campbell Scientific				AquaTROLL			
Temperature				**Temperature**			
	1	*2*	*3*		*1*	*2*	*3*
2	<0.0001			*2*	<0.0001		
3	0.10	<0.0001		*3*	0.00014	<0.0001	
4	<0.0001	0.048	<0.0001	*4*	<0.0001	0.30	<0.0001
Specific Conductivity				**Specific Conductivity**			
	1	*2*	*3*		1	*2*	*3*
2	0.19			*2*	0.21		
3	0.067	0.0002		*3*	0.11	0.0010	
4	<0.0001	0.017	0.00090	*4*	<0.0001	0.0084	0.0020
pH							
	1	*2*	*3*				
2	<0.0001						
3	<0.0001	0.0054					
4	<0.0001	<0.0001	0.48				
ORP							
	1	*2*	*3*				
2	<0.0001						
3	<0.0001	0.020					
4	<0.0001	<0.0001	<0.0001				
DO							
	1	*2*	*3*				
2	<0.0001						
3	0.0021	<0.0001					
4	<0.0001	<0.0001	<0.0001				

While the responses were different among trials, the type of response was similar among trials for specific conductivity, temperature, and pH. The correlation tests (Table 10) showed that both the CS and AT instruments responded with strong positive correlations for temperature and specific conductivity. One negative correlation resulted between Trials 1 and 3 of the CS temperature measurements. This trend was attributed to the apparatus. There were also strong, positive correlations among trials for pH with the CS probe.

There was less consistency among the trials for ORP and DO, which is monitored with CS probes, when compared to the consistent response found in the drilling mud experiments. In produced water, ORP showed moderate positive correlation in three of the comparisons. The exceptions were associated with the fourth trial, where it was weakly correlated in both negative and positive directions, and one strong correlation to Trial 2. That correlation is attributed to a similar water quality response in all trials within the first 20 ppm of the trial. As shown in Figure 7d, the shape of the response curve is unique to this contaminant. Above 20 ppm the shape of the response curves diverge. DO showed mixed positive and negative strong correlations in the comparisons between Trials 2, 3, and 4; Trial 1 demonstrated weak positive correlations to the other three trials. It does not appear that DO had a consistent response due to the increasing concentration of produced water in the test vessel.

Table 10: Correlation coefficients for the water quality parameters across the four produced water trials

Campbell Scientific				AquaTROLL			
Temperature				**Temperature**			
	1	2	3		1	2	3
2	0.97			2	0.96		
3	-0.26	0.94		3	0.85	0.94	
4	0.98	0.93	0.81	4	0.97	0.92	0.77
Specific Conductivity				**Specific Conductivity**			
	1	2	3		1	2	3
2	0.98			2	0.98		
3	0.98	1.0		3	0.98	1.0	
4	1.0	0.98	0.98	4	1.0	0.98	0.98
pH							
	1	2	3				
2	0.92						
3	0.96	0.93					
4	0.89	0.96	0.98				
ORP							
	1	2	3				
2	0.60						
3	0.44	0.053					
4	<0.0001	0.90	-0.16				
DO							
	1	2	3				
2	0.31						
3	0.39	0.98					
4	0.013	-0.87	-0.85				

3.3 ETHYLENE GLYCOL

As with the other two experiments, ethylene glycol was added gradually to the deionized water containing the probes as the system was continually stirred. The experiment was designed to increase the concentration of the ethylene glycol from zero to 50 ppm over the course of approximately 2 hours while measurements were taken. The rate of concentration increase was greater in the last part of each trial, similar to the drilling mud and more consistently than the produced water.

3.3.1 Ethylene Glycol Impact on Water Quality Parameters

The average dissolved oxygen did not change substantially throughout the trials, but the standard deviation was about 0.5 ppm per 5 min time interval (Figure 9a). This is an indication of unstable readings, a phenomenon not observed in the produced water or drilling mud laboratory tests.

The specific conductivity had a positive trend with the addition of ethylene glycol, at a rate of about 0.1 to 0.2 µS/cm per minute, except in Trial 2 where the rate of increase was 0.4 2 µS/cm per minute. The pH did not converge in the glycol trials, but each trial had a decreasing linear trend of about -0.0003 to -0.01 units/min (Figure 9). The oxidation reduction potential had two trials around 400 mV, and two trials around -50 mV. All trials showed a trend towards zero, but at neither large nor consistent rates. Neither the ORP nor the pH responded consistently among the trials.

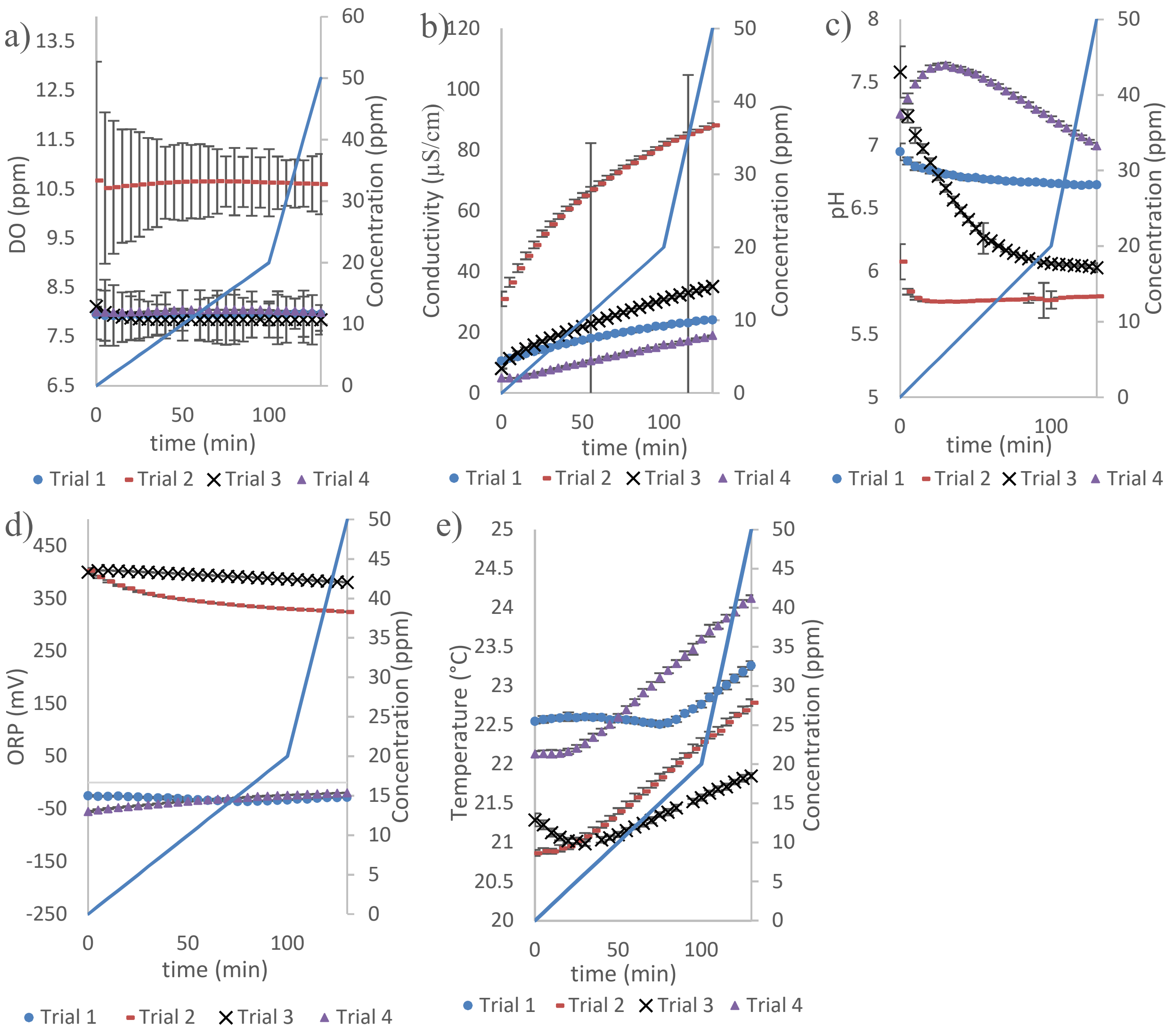

Figure 9: Campbell Scientific measurements from ethylene glycol experiments: a) dissolved oxygen, b) specific conductivity, c) pH, d) oxidation reduction potential, and e) temperature over time. Increased concentration of ethylene glycol added to the solutions over time is shown with a solid line.

The results from the AquaTROLL measurements of ethylene glycol are in Figure 10. There appeared to have been some type of environmental disturbance that occurred in the fourth time step of the second trial. Both the Campbell and AquaTROLL show elevated temperature, and in the case of the AquaTROLL the specific conductivity reading was zero. This may have been interference from the magnetic stirrer, but the reason for these high readings is unknown.

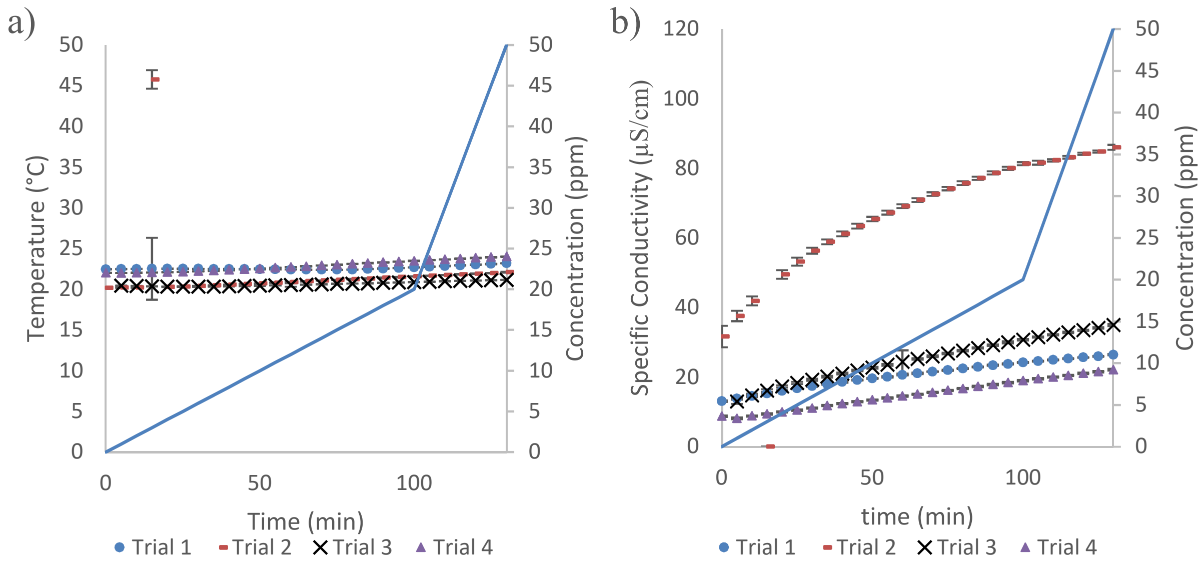

Figure 10: Results from the AquaTROLL for the ethylene glycol trials: a) temperature, and b) specific conductivity over time. Increased concentration of ethylene glycol added to the solutions over time is shown with a solid line.

3.3.2 Paired T-Test and Correlation Results

Statistical results suggest that the instrument response was significantly different among the trials for the CS probes when testing specific conductivity, pH, ORP, and DO (p-values≤0.0001). Similarly, the instrument response was significantly different when using the AT to measure specific conductivity (p-values<0.0001) (Table 11). This indicates at particular concentrations, the water quality parameter measurements are not unique. This was not entirely unexpected for ethylene glycol. It is an organic material, and water instrumentation probes are largely designed for measuring inorganic constituents and physical properties of water. Nevertheless, significant amounts of organic chemicals are used in oil and gas development, and a lab test was performed on one of the more common (and benign) organic compounds to assess the performance of the probes.

Temperature measurements resulted in exceptions. Trial 3 for the CS probe showed significant similarity with the other trials. For the AT, Trial 2 showed similarity with the other trials (Table 11). Changes in temperature were attributed to the apparatus rather than to the addition of the chemical.

Table 11: Results from the paired t-test comparing the trials of the ethylene glycol tests

Campbell Scientific				AquaTROLL			
Temperature				**Temperature**			
	1	2	3		1	2	3
2	<0.0001			2	0.25		
3	0.10	0.087		3	<0.0001	0.081	
4	0.0070	<0.0001	0.11	4	0.0057	0.17	<0.0001
Specific Conductivity				**Specific Conductivity**			
	1	2	3		1	2	3
2	<0.0001			2	<0.0001		
3	<0.0001	<0.0001		3	<0.0001	<0.0001	
4	<0.0001	<0.0001	<0.0001	4	<0.0001	<0.0001	<0.0001
pH							
	1	2	3				
2	<0.0001						
3	<0.0001	<0.0001					
4	<0.0001	<0.0001	<0.0001				
ORP							
	1	2	3				
2	<0.0001						
3	<0.0001	<0.0001					
4	0.15	<0.0001	<0.0001				
DO							
	1	2	3				
2	<0.0001						
3	<0.0001	<0.0001					
4	<0.0001	<0.0001	<0.0001				

For specific conductivity, correlations of instrument response among trials were strong and positive for all comparisons except one, including both CS and AT comparisons (Table 12). Specific conductivity may be a valid indicator of ethylene glycol, but it is not a very strong one.

Weak to strong positive correlations for pH were observed in the trials, with one negative weak correlation between Trials 2 and 4. The pH did not appear to converge as it had with the other tested contaminants (Table 12).

Oxidation reduction potential had a negative moderate to strong correlation in all comparisons to Trial 4. The other three comparisons ranged from weak to strong positive correlation. The oxidation reduction potential trials appear to have dissimilar rate of change across trials (Table 12).

Dissolved oxygen had four trials with both weak positive and negative correlations. Trial 4 showed moderate strong correlation to Trials 1 and 2. The magnitude of change for these trials was not very large (i.e. range of 0.01 ppm oxygen throughout each trial) (Table 12).

There was little consistency among the comparisons using temperature. Three moderate to strong positive correlations and three weak negative correlations were noted for the CS instrument. For the AT, three comparisons showed moderate to strong positive correlations, but these trials were different than the ones that correlated in the Campbell Scientific comparisons. Three AT trials showed weak negative and positive correlations (Table 12). These results suggest that the apparatus, not the ethylene glycol, was affecting the temperature.

Table 12: Correlation coefficients for the water quality parameters across ethylene glycol trials

Campbell Scientific				AquaTROLL			
Temperature				**Temperature**			
	1	*2*	*3*		*1*	*2*	*3*
2	0.77			*2*	0.030		
3	-0.088	-0.030		*3*	0.82	-0.086	
4	0.78	1.0	-0.039	*4*	0.75	-0.12	0.98
Specific Conductivity				**Specific Conductivity**			
	1	*2*	*3*		1	*2*	*3*
2	0.99			*2*	0.88		
3	1.0	-0.27		*3*	1.0	0.87	
4	0.99	0.97	0.99	*4*	0.99	0.85	1.0
pH							
	1	*2*	*3*				
2	0.61						
3	0.99	0.45					
4	0.99	-0.33	0.45				
ORP							
	1	*2*	*3*				
2	0.67						
3	0.44	0.22					
4	-0.61	-0.98	-0.96				
DO							
	1	*2*	*3*				
2	0.27						
3	-0.11	-0.14					
4	0.090	0.80	-0.49				

3.4 COMPARING THE CROSS-INSTRUMENT SIMILARITIES

The Campbell Scientific instrument measures more parameters at a higher frequency than the AquaTROLL. The two similar parameters, specific conductivity and temperature, were compared using a paired t-test (Table 13). For all but two comparisons (i.e. ethylene glycol, Trials 2 and 3 for temperature), the measured response was statistically different between the two instruments (*p*-values≤0.0001). While the type responses were similar, the magnitudes were different between the instruments. This result may be due to the placement in the lab setup, difference in frequency of measurement, and sensor accuracy. This result shows the necessity of frequent calibration in field applications.

Table 13: p-values and correlation coefficients between the Campbell Scientific and AquaTROLL sensors for the laboratory experiments.

Drilling Mud		**Trial 1**	**Trial 2**	**Trial 3**	**Trial 4**
p-value	Specific Conductivity	<0.0001	<0.0001	<0.0001	<0.0001
	Temperature	<0.0001	<0.0001	<0.0001	<0.0001
correlation coefficient	Specific Conductivity	1.0	1.0	0.99	1.0
	Temperature	1.0	1.0	1.0	1.0
Produced Water		**Trial 1**	**Trial 2**	**Trial 3**	**Trial 4**
p-value	Specific Conductivity	<0.0001	<0.0001	<0.0001	<0.0001
	Temperature	<0.0001	<0.0001	<0.0001	<0.0001
correlation coefficient	Specific Conductivity	1.0	1.0	1.0	1.0
	Temperature	1.0	1.0	1.0	1.0
Ethylene Glycol		**Trial 1**	**Trial 2**	**Trial 3**	**Trial 4**
p-value	Specific Conductivity	<0.0001	<0.0001	<0.0001	<0.0001
	Temperature	<0.0001	0.39	0.071	<0.0001
correlation coefficient	Specific Conductivity	0.99	0.97	1.0	1.0
	Temperature	1.0	-0.12	-0.089	1.0

4. DISCUSSION

4.1 INSTRUMENT RESPONSE TO CHEMICALS

In the study watersheds, peak concentration after 16 km (10 mi) of travel is on the order of less than 1 ppm to approximately 3 ppm. Across smaller distances of less than 1.6 km (1 mi) of travel, 50 ppm is possible. Even at low concentrations, the contaminants ethylene glycol, produced water, and drilling mud have measureable effects on water quality parameters (Table 14).

Table 14: Summary of the water quality parameters that were affected by low concentrations of contaminants. (nt. =no observed trend)

	Drilling Mud	Produced Water	Ethylene Glycol
Specific Conductivity	Increased by an average of 21 µS/cm per 50 ppm.	Increased by an average of 101 µS/cm per 50 ppm	Increased by an average of 27 µS/cm per 50 ppm
pH	Decreased to an average value of 6.27	pH decreased to an average value of 6.57	nt.
DO	Decreased at a rate of 0.08 ppm per 1ppm contaminant	nt.	Variance in dissolved oxygen values was 1 ppm, though average value did not change.
ORP	nt.	Oxidation reduction potential had a unique shape in the measurement curve	nt.

Specific conductivity was a major indicator for the contaminants, with 5 ppm concentration of the produced water being significant enough to diverge from a signal that would be expected from a rain event. Likewise, pH appeared to be a useful proxy for produced water and drilling mud at low concentrations. Dissolved oxygen was affected by both drilling mud and ethylene glycol. With additional assessments to understand sensitivity thresholds and response patterns to other contaminants, electronically-measured water quality parameters show promise as useful indicators for oil and gas-related spill events.

The water quality parameters tested in the lab experiments are commonly measured in field water quality monitoring systems. In addition to specific conductivity, pH, DO, ORP, and temperature, other readily-available field parameters that can be measured with these instruments include turbidity or water clarity, chlorophyll to assess biological activity, and pressure for determining water depth.. Quick response to a spill minimizes the amount of watershed damaged, reduces remediation costs and mitigates against additional liabilities.

4.1.1 The Placement and Measurement Strategy of Monitoring Systems

The likelihood that a contaminant would be detected depends on the peak concentration as it reaches a monitoring station. A strong correlation was observed between the decrease in peak concentration of a contaminant and the distance traveled. Dispersion across the stream and along the flowpath affects concentration and plume distribution. In the case studies, as shown in Figure 11, it was found that 50 barrel spills showed a persistent concentration of more than 1 ppm in medium and small watersheds (approximately 65–120 km^2). The size of the drainage area affects the peak concentration of the contaminant, even when the travel distance and spill volume are the same. This is because the discharge volume is a factor in the dilution of a contaminant. It was shown that even small spills may persist at a higher concentration during short travel distances. For the average spill volume of 34 barrels, a detectable peak concentration may persist for only 800 m. Over greater distances, the contaminant plume becomes dispersed, so the length of the contaminant signal will be more prevalent than its magnitude. The density of a contaminant may also affect transport properties, and this remains to be investigated.

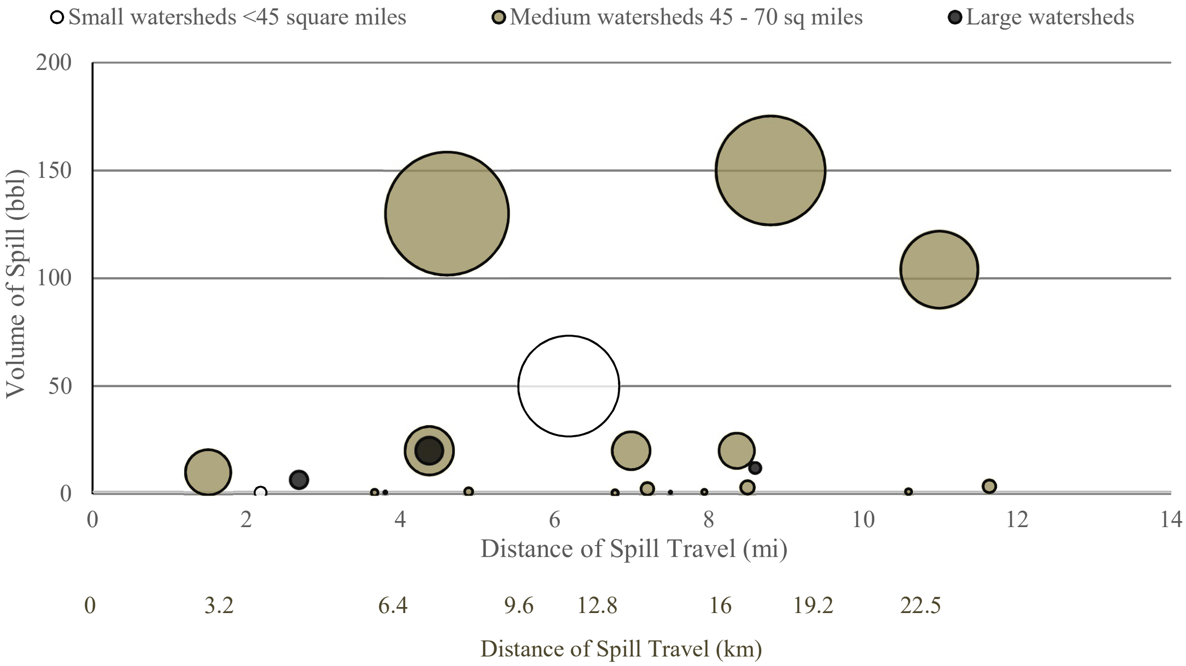

Figure11: Peak concentration (marker size) based on distance traveled and volume; the largest marker represents a concentration of 1.5 ppm.

In the laboratory, the experiments demonstrated that it was difficult to repeat the trials and achieve the same water quality parameter values. The water quality at the beginning of the experiments varied, and temperature variations can affect the baseline measurements for the instruments. In the field, it would be expected that the sensors would be under similar external influences. Monitoring for change may be more effective than determining a threshold parameter value, because there were correlations of water quality parameters with increasing concentration.

In order to measure rate of change of water quality parameters, the measurement frequency may be best determined by evaluating the river geometry. River discharge and drainage area affect the peak velocity, the amount of dilution, and the travel distance for a surface water contaminant as it travels through a surface water system (Jobson, 1996). Other parameters, such as the range of channel velocities and discharges, channel slope, and stream order (general channel size) may be used in decision making to set sensor locations.

If data storage is a limiting factor in the cost-effectiveness of water quality instruments, then a standard deviation from the average of several scans should be used. Of the case studies, most examples were found in medium sized watersheds (about 130 km^2). A medium sized drainage area may be sufficient to encompass several spill risks without diluting the contaminants beyond spill detections. Fifty barrel spills can be detected over distances greater than 10 km (about 6 mi) in even the large watersheds (about 260 km^2).

Monitoring frequency depends on the objective of the monitoring program. When it comes to spill detection, the monitoring frequency should be high enough to confirm that changing water quality is associated with a spill plume. It is recommended that the frequency should allow for five measurements over an empirical estimation of the duration of a possible spill's residence time. In the SRBC RWQMN watersheds, the measuring frequency is every 4 hrs. In the case of the Little Muncy spill event, one of the case studies evaluated, 4 hours may not have been a sufficient frequency to detect a spill with a residence time of only 12 hrs. Though a change in water quality was evident, more measurement events could confirm a characteristic contaminant concentration lead time, peak, and lag.

4.1.2 Environmental Effects on Water Quality Parameters

In addition to the presence of contaminants, there are natural phenomena that occur in the environment that have an effect on water quality parameters. Conductivity may decrease with increased river discharge because the contribution of TDS from groundwater baseflow is diluted (Caissie et al., 1996). Conversely, run-off from a rain event may also be a source of dissolved solids, contributing ions that affect conductivity and pH. Literature shows that this change can be up to 25 µS/cm and 0.8 pH units; these changes correspond to the increasing discharge immediately after a storm event (Caissie et al., 1996).

Dissolved oxygen experiences diurnal variations due to biological activity. Variations could also be seasonal, because temperature affects the maximum oxygen saturation. Studies have found that the magnitude of change due to diurnal variations may be on the order of 0.32 ppm in the winter months and 1.5 ppm in the summer the shift occurring during the daylight hours (Guasch et al., 1998, Mulholland et al., 2005). Additionally, diurnal variations in biological activity and temperature fluctuations may also affect the saturation of dissolved carbon dioxide in the water, shifting the pH.

4.1.3 Identifying a Spill Signal from the Case Studies and More Recommendations

Of the twenty-two case studies, five spills occurred when the monitoring network was offline, not recording data. Because spills will probably be unexpected, it is imperative to decrease the downtime of sensors. Of the remaining nineteen case studies, three of the spills were diesel fuel spills, which were not measured in the laboratory study. Of the remaining sixteen case study spills, it was found that the detectable response in the watershed occurred where the calculated peak concentration was greater than 1 ppm. The contaminant events were from produced water spills with magnitudes of one hundred barrels. One recommendation is to perform an analysis of the contaminants most likely to be spilled in a watershed to ensure detection is possible.

The signal shown in Figure 12 was identified from a 130-barrel spill of produced water that occurred in July 2014 in Little Muncy Creek. The monitoring station is located approximately 8 km downstream of the spill location. The empirical value for the time of travel for the peak concentration was about four days, and the length of time for the spill to be present was roughly 12 hours (Jobson, 1996). The actual travel time may have been over-estimated because of the slower rate of transport in headwater streams.

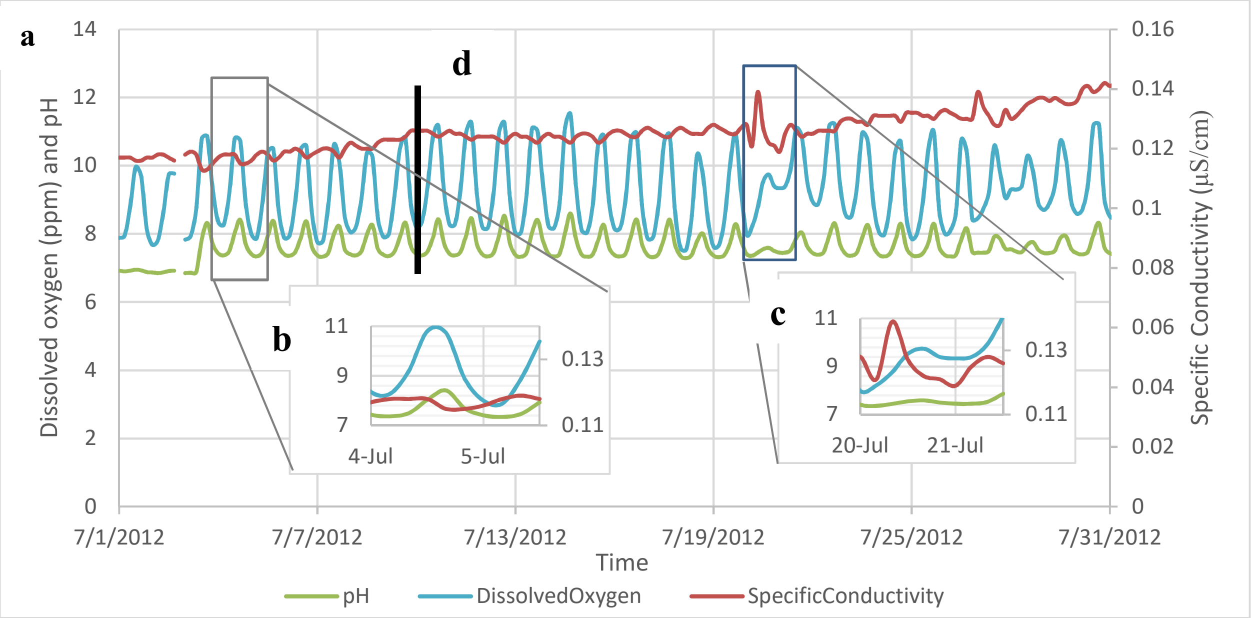

Figure 152: Little Muncy Creek pH, DO and specific conductivity. Data collected from SRBC RWQMN. a) July 1 to July 31, 2014; b) July 3 at 12:00PM to July 5 at 4:00 PM; c) July 19 at 12:00 PM to July 21 at 4:00 PM; and d) earliest arrival time predicted by empirical methods.

As previously discussed, produced water may affect water quality parameters by increasing specific conductivity and lowering the pH from the baseline water quality. A signal was identified to occur 2 weeks after the spill event, as shown in Figure 12. The water quality signal shown is identified as a produced water spill event rather than a rain event because of the increase in pH. Rain events also cause an increase in specific conductivity, but because of acidic precipitation, the pH usually decreases.

There was not enough information to validate this observation. It is recommended that the precipitation information be collected on a watershed basis, so that signals from rain events may not be confused with a contaminant spill. It would also be helpful for a secondary system, such as passive sampler or another sensor that can provide more information about the water quality as it passes to confirm whether it is indeed a spill-related contaminant affecting water quality.

In determining the placement of spill detection systems, the water systems manager would have to decide the appropriate volume of a spill that warrants attention. A prior study suggested that a 9.5 barrel spill is significant (Brantley et al., 2014). The placement of the monitoring system should be within a drainage area and a travelling distance that would allow for the peak concentration of a spilled chemical to be at least 1 to 5 ppm.

5. CONCLUSIONS

Water quality parameters monitored with commercially available field sensors show promise as useful indicators for oil- and gas-related spill events. When using the instruments tested in this work, or similar instruments, the following should be considered if spill detection related to gas extraction is desired:

- Placement of sensors: The chemical volume spilled and the distance traveled were important parameters affecting the peak concentration of a contaminant, and are important considerations for designing a spill detection program. For the drilling mud, produced water, and ethylene glycol assessed in this study, results showed that a 50 barrel spill showed a persistent concentration of more than 1 ppm in watersheds up to 120 km^2. Sensor placement should be optimized for the size of the watershed and location of potential spill locations. Water quality managers may consider the volume of chemical storage, the watershed characteristics such as channel slope and travel distances, along with personal priorities of risk, such as chemical toxicity or regulatory requirements. The size of the drainage area affects the peak concentration of the contaminant, even when the travel distance and spill volume are the same. Therefore, sensor placement may change with varying stream order.
- Sensor maintenance: The differences that were detected among trials indicate the necessity of proper sensor maintenance and calibration in the field.
- Parameter monitored: Specific conductivity showed promise as a proxy for indicting spill events. pH may be important for produced water and drilling mud at low concentrations, and dissolved oxygen may be important for drilling mud and ethylene glycol. Monitoring of precipitation and streamflow should be included with water quality measurements so that storm and environmental effects can be determined.
- Support for high frequency data and quick analysis: Relative change of proxy parameters is likely more important than a threshold value for detecting spill events. For early detection, quick analysis would be required, as the spill events can move through a stream reach quickly, especially during storm events. Filtering out the baseline water quality from diurnal fluctuations would be necessary for identifying a divergence from baseline conditions.

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APPENDIX A: SUSQUEHANNA RIVER BASIN SPILLS

Table A1: Spills related to oil and gas operations within the Remote Water Quality Monitoring Network (RWQMN) in the Susquehanna River Basin

Well ID (API #)	DATE	LEASE NAME	COUNTY	SPILL TYPE	VOL (BBL)	SRBC Watershed
115-20263	1/26/2011	R WARRINER 2	Susquehanna	Freshwater Mud	20	EB Wyalusing
115-20404	1/6/2012	COSNER 5	Susquehanna	Production Fluid	2 or 3	Mesohoppen
115-20447	2/13/2012	FRASER 1	Susquehanna	Production Fluid	20	EB Wyalusing
115-21242	8/2/2013	CASTROGIOVANNI A 4	Susquehanna	Diesel Fuel	3.5	EB Wyalusing
115-20240	8/27/2013	DEPAOLA 2	Susquehanna	Flow back Fluid	1	Mesohoppen
115-21406	10/22/2013	STARZEC E 6	Susquehanna	Bentonite drilling mud, cement	104	EB Wyalusing
115-20487	7/28/2011	BONNICE 1H	Susquehanna	Mud and water	0.88	EB Wyalusing
115-20228	1/10/2011	TEEL UNIT 2H	Susquehanna	Flow back Fluid	150	Mesohoppen
115-21214	8/7/2013	OLIVER UNIT 3H	Susquehanna	Diesel Fuel	2.3	Mesohoppen
115-20461	3/4/2011	DEPUE 8H	Susquehanna	Drilling Mud	10	Snake Creek
117-20197	1/26/2011	ROOT 1	Tioga	Production Fluid	50	Hammond Creek
015-20352	3/6/2012	BONNIE 2H	Bradford	Corrosion inhibitor	0.47	Sugar Run
015-20334	11/8/2013	WELLES 3 2H	Bradford	Water	0.59	Sugar Run
015-20489	6/24/2011	CASTLE 01 047 01 J 1H	Bradford	Production Fluid	20	Sugar Creek
015-22058	4/10/2012	FEUSNER 03 044 05 J 5H	Bradford	Drilling Mud	0.59	Sugar Creek
081-21214	1/30//2014	COP Tract 357 B 1008H	Lycoming	Brine	20	Little Pine Creek
081-20353	7/3/2012	Arthur Unit 1H	Lycoming	Flow back Fluid	130	Little Muncy Creek
081-20255	7/6/2012	Kensinger Unit 3 H	Lycoming	Flow back Fluid	1	Little Muncy Creek
081-20182	8/29/2011	COP Tract 293 Pad A 2401	Lycoming	Diesel Fuel	6.5	Little Pine Creek
081-20948	5/7/2013	COP Tract 293 Pad H 2609	Lycoming	Production Fluid	0.7	Little Pine Creek
081-21133	5/12/2014	COP Tract 322 Pad B 2663	Lycoming	Mixture of mud, oil, diesel fuel	0.76	Little Pine Creek
105-21665	5/11/2011	Coon Hollow 904 5h	Potter	Production Fluid	12	Pine Creek

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APPENDIX B: CASE STUDY SPILLS

Table B1: RWQMN watershed profiles (SRBC 2012)

RWQMN Watershed	Drainage Area [km^2] (D_a)	Average Annual Flow [cms] (Q_a)
Sugar Run	85	1.4
Sugar Creek	145	2.0
Little Pine Creek	466	7.1
East Branch Wyalusing	178	2.8
Little Muncy Creek	132	2.3
Meshoppen	135	2.1
Snake Creek	116	2.1
Pine Creek	997	15
Hammond Creek	75	0.98

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APPENDIX C: DRAINAGE AREA RATIO

Table C1: Results of Emerson et al.'s (2005) Drainage Area Ratio Technique comparing ungaged monitoring stations to gaged monitoring stations

RWQMN watershed name [$D_{a,u}$ (km^2), Q_u (cms)]	1) USGS monitoring station name	% Error	2) USGS monitoring station name	% Error
Hammond Creek [75, 1.0]	1533400 Susquehanna River at Mesohoppen PA [22,584; 365]	-37%	1603500 Evitts Creek near Centerville, PA [77, 0.9]	-15 %
Sugar Run [85, 1.4]	1530332 Chemung River at Elmira, NY [5,594; 0.68]	29%	1569000 Stony Creek near Dauphin PA [85, 1.8]	-26%
Snake Creek [116, 2.1]	01503000 Susquehanna River at Conklin, NY [5,775; 125]	-16%	1452500 Monocacy Creek at Bethlehem PA [116, 1.8]	-7.2%
Little Muncy Creek [132, 2.3]	None available	N/A	1473120 Skippack Creek near Collegeville, PA [139, 2.3]	15%
Mesohoppen [134, 2.2]	1533400 Susquehanna River at Mesohoppen, PA [22,584; 365]	-8.6%	1473120 Skippack Creek near Collegeville, PA [139, 2.3]	4.5%
Sugar Creek [145, 2.0]	1531325 Sugar Creek at West Burlington PA [243, 3.1]	-2.8%	1451800 Jordan Creek near Schnecksville, PA [137, 3.4]	-43 %
EB Wyalusing [178, 2.9]	1533400 Susquehanna River at Mesohoppen, PA [22,584; 365]	-9.0%	1574500 Codorus Creek at Spring Grove, PA [197, 2.8]	5.0%
Little Pine Creek [466, 7.1]	1549700 Pine Creek bl L Pine Creek near Waterville, PA [2,434; 39]	-15%	01550000 Lycoming Creek near Trout Run [440, 9.6]	-29%
Pine Creek [997, 15]	1548500 Pine Creek at Cedar Run, PA [1,554; 24]	-15%	03079000 Casselman River at Markleton, PA [984; 20]	-23%

Note: 1) Of the same stream network; 2) of similar sized watersheds. D_{au} is ungaged watershed drainage area; D_{ag} is gaged watershed drainage area.

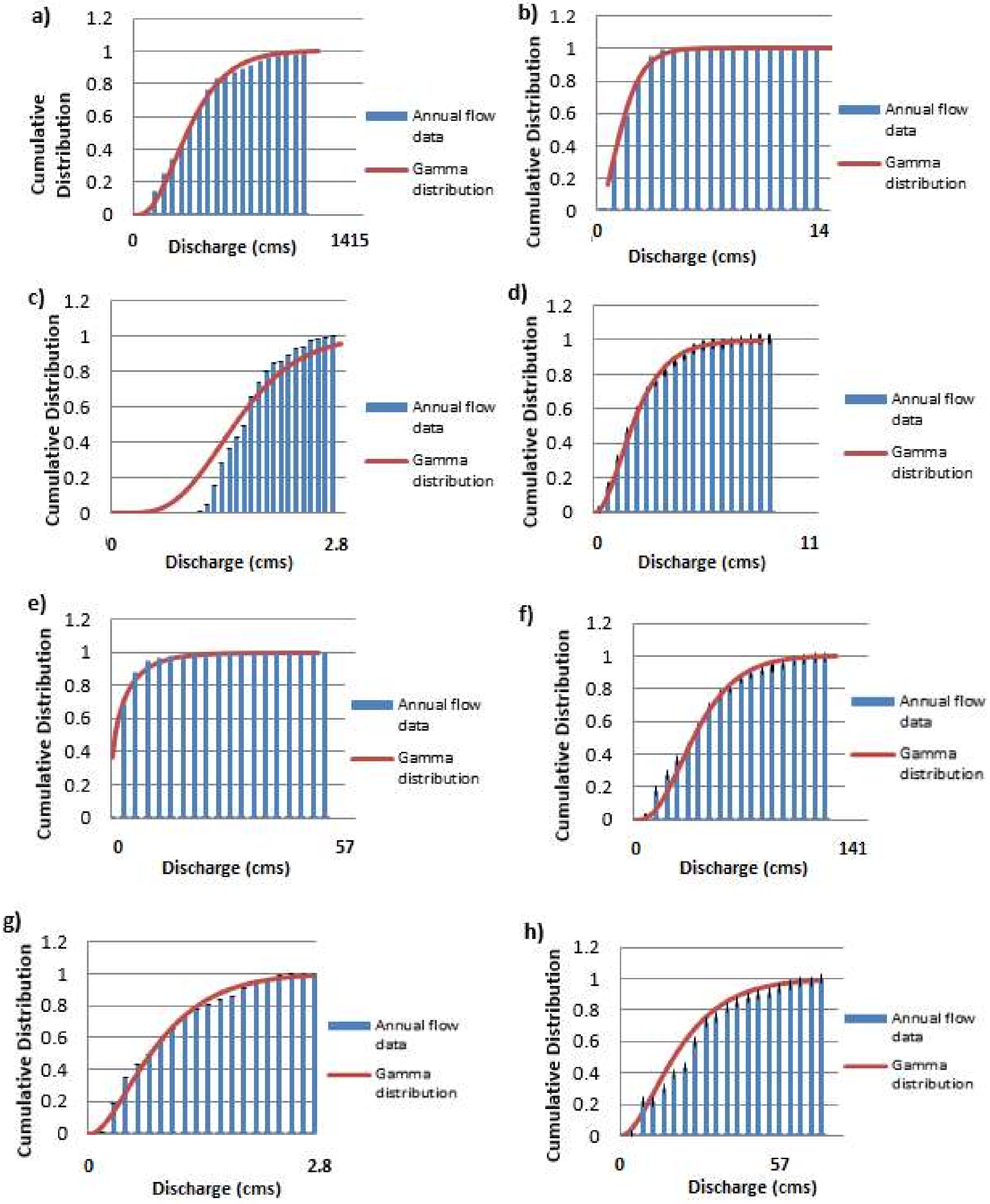

Figure C1: Gamma distribution for the USGS monitored watersheds: a) USGS station 01533400 at the Susquehanna River; b) USGS station 01569000 at Stony Creek; c) USGS station 01452500 at Monocacy Creek; d) USGS station 01473120 at Skippack Creek; e) USGS station 01531325 at Sugar Creek; f) USGS station 01549700 at Pine Creek below Little Pine Creek; g) USGS station 01603500 at Evitts Creek; and h) USGS station 01548500 at Pine Creek.

Sean Plasynski
Executive Director
Technology Development & Integration Center
National Energy Technology Laboratory
U.S. Department of Energy

Jared Ciferno
Associate Director
Oil and Gas
Technology Development & Integration Center
National Energy Technology Laboratory
U.S. Department of Energy

Elena Melchert
Director
Division of Upstream Oil and Gas Research
U.S. Department of Energy

Cynthia Powell
Executive Director
Research & Innovation Center
National Energy Technology Laboratory
U.S. Department of Energy