COMPARISON OF INLINE PRODUCED WATER MONITORS

by

Adam P. Goulden

Submitted in partial fulfilment of the requirements

for the degree of Master of Applied Science

at

Dalhousie University

Halifax, Nova Scotia

July 2015

Table of Contents

List of Figures

List of Tables

Abstract

Produced water represents the largest waste stream in the oil and gas production industry. Water drawn up from oil and gas formations contains many substances, the disposal of which is heavily regulated. Offshore oil platforms must ensure that these regulations are met with great accuracy, as the disposal of the water means its reintroduction into the environment. For this reason it is essential that hydrocarbon measuring equipment be effective and accurate when deployed on these platforms.

A pilot scale project was designed to test and compare four instruments currently employed on offshore oil platforms. The project compared the instruments for accuracy, responsiveness, maintenance requirements, and fouling by manipulating four variables. The variables tested were flow rate through the instruments, particulate and gas addition to the produced water, hydrocarbon and production chemical spiking, and heat addition. Each variable was manipulated one at a time, but their lingering effects (such as particles) were not removed due to the design of the system.

Instrument readouts were compared with lab tested produced water samples taken from the system stock using infrared technology. A ranking system was devised to compare the monitors in the categories of accuracy, precision, maintenance requirements, and reliability. This system was used to determine which monitor was the most effective in terms of those categories and this project.

List of Abbreviations Used

ASL	Advanced Sensors Limited
ASLSS	Advanced Sensors side stream
BTEX	Benzene, toluene, ethyl benzene, and xylenes
FTIR	Fourier-transform infrared
GC/MS	Gas chromatography/ mass spectroscopy
GPM	Gallons per minute
IR	Infrared
LIF	Laser induced fluorescence
PAH	Polycyclic aromatic compounds
PW	Produced water
UV	Ultraviolet

Acknowledgements

I would like to start by thanking the person who has helped support me, both financially and otherwise throughout my time as an undergraduate and a graduate student, my beautiful girlfriend, Kerry Matthews. She has been a pillar by which I have been able to stand for so long, and as such, my success is her success. Also, I wish to acknowledge the other member of my household, Duzell. Though he may be just a cat, his unconditional love and affection has kept me positive throughout all my hardships.

I would like to thank my supervisor, Dr. Graham Gagnon, for his limitless knowledge, patience, and confidence, as well as the other members of my supervisory committee, Dr. Margaret Walsh, and Dr. Amyl Ghanem, for their support and understanding.

Over the course of my research, I encountered many challenges and could not have met them without the support and counsel of my fellow graduate students and lab technicians. Particularly, I would like to thank Judy Lee and Jesse Keane for their direct support in my work. I could not have met my deadlines without their help. I would also like to thank lab technicians Heather Daurie and Elliot Wright and facilities technicians Brian Kennedy and Blair Nickerson for their aid in difficulties.

Finally, I would like to thank my family for their support and occasional coffee shop meetings. In particular, I thank my brother, Tristan, for his knowledge and advice about research and the graduate program.

CHAPTER 1 INTRODUCTION

Continuous, in-line oil-in-water analyzers are used by many operators in the oil and gas industry in order to analyze hydrocarbon concentrations in produced water. However, some operators have reported unsatisfactory performances with these analyzers, citing a variety of issues, such as accuracy, reliability, maintenance requirements, Regulator acceptance, and operating parameters.

To address these concerns, this project report describes tests that were conducted to compare the performance of commercially available oil-in-water analyzers over an extended period of time. Following a technical review, four analyzers were selected and were tested using actual produced water samples obtained from an offshore platform. The hydrocarbon concentrations in the produced water were varied in order to test the responsiveness of the equipment. Samples were periodically drawn for lab analysis, providing a basis for comparison between the monitors and the analytical methodology required by the Offshore Waste Treatment Guidelines (produced by the National Energy Board, the Canada-Nova Scotia Offshore Petroleum Board, and the Canada-Newfoundland and Labrador Offshore Petroleum Board 2010). The operating performances of the oil-in-water analyzers were evaluated based on criteria established by the upstream petroleum industry operating in the Atlantic Region; this includes considerations such as maintenance, reliability, accuracy, recalibration requirements, etc.

In the industry of oil and gas production, produced water represents the single greatest and most important waste stream of concern. In 2007, twenty one billion barrels of produced water were generated by the onshore and offshore petroleum industries combined, with 87 percent of that being amount being as a result of oil production (Clark and Veil, 2009). In fact, in many cases the ratio of produced water to oil in a drilling operation is about eight to one (Tellez et al., 2005). The production of produced water increases over the course of the lifetime of an oil production project. At the first stages of production, very little is produced, but as the demands to maintain production efficiency increase with ever depleting oil content, more and more is produced (Mccormack et al., 2001).

There are several options available to oil and gas companies regarding the disposal of produced water, including reinjection into the reservoir for pressure maintenance and to enhance oil recovery, surface discharge, and beneficial reuse. Typically, oil platforms will inject the produced water into the reservoir, but as the ratio of water to oil increases with the lifetime of the project, some of it must be discharged into the oceans, rivers, and other bodies of water (Lu et al., 2005). Since the water contains many highly impactful compounds and materials, of which, the environmental fate is not entirely known (Holdway, 2002), naturally, surface disposal of produced water is heavily controlled.

The regulations, as stated by the Offshore Waste Treatment Guidelines, indicate that discharged produced water should not contain any more than 30 mg/L of oil and grease as a rolling average over a thirty day period (NEC *et al*., 2010). In addition, discharged produced water should not contain more than 44 mg/L of oil and grease over a twenty four hour period, averaged over at least two samples from that timeframe. (NEC *et al.,* 2010)

As many oil platforms involved in the extraction of oil from hydrocarbon bearing formations are automated and unmanned, it is very important that the equipment onboard be able to accurately and reliably measure the concentrations of oil and grease in the produced water. As such, a primary supporting industry to oil and gas exploration is the development on inline and online monitors that can reliably perform this task.

Benefits of this research may include increased system control and performance, shortened response times to upset conditions, reduced analyzer maintenance, improved produced water monitoring, increased sampling frequency enhancement, reduction of the cost of regulatory compliance, and ultimately reduced discharge of hydrocarbons into the marine environment.

1.1 Objectives

The hypothesis of this research was that by testing a selection of inline produced water monitors at the pilot scale under varying conditions, a single monitor could be determined that would be considered the most effective. The objectives of the research project were to:

- Measure and analyze the response of monitors to variations in flow rate, gas and particle addition, chemical spiking, and heating.
- Compare monitors for maintenance requirements, precision, accuracy, and reliability.
- Determine which monitor is the most effective in terms of the above factors.

1.2 Thesis Organization

Following this introduction, Chapter 2 will present the literature review where detailed information about the origin and chemical makeup of produced water was provided, as well as information describing the technology and methods used to treat produced water, the environmental impacts of produced water discharge. The regulations of produced water discharge are reviewed as well. Chapter 3 provides details on the methodology used in the lab work pertaining to this thesis project, which was the guiding project of this thesis. It describes the procedures used in executing the pilot scale portion of the project, as well as those used in the analysis of laboratory samples. Chapter 4 discusses the results of the this project. The results section includes an in depth analysis of each instrument with regard to the changes made to the system over the testing period. The section presents the response data of each instrument along with statistical analyses, while the discussion describes the background information of each instrument and day, and explains the patterns and postulates reasons for those patterns. The other factors, including maintenance requirements, accuracy, and precision of the instruments will also be discussed. Chapter 5 summarizes the conclusions and offers recommendations based on the results of this project.

1.3 Originality of Research

There is a great deal of research available in which produced water is studied. Such research includes the treatment methods and technologies in practice, or those being researched. Ahmadun *et al.* (2009) reviewed many of these methods, including physical, chemical, and biological options available, and compared their effectiveness. Robinson (2013) discussed available treatment technologies and their optimization for produced water treatment in different areas of the world, given that regulations vary by location. Other research has examined the potential impact of produced water discharges into the ecosystem (Bakke, 2013). In addition, there is published research concerning the physical and chemical fate of produced water and its constituents in ocean and land environmental systems, as well as its potential impacts on marine life, both near and far from the discharge point (Holdway, 2002).

Much of the existing research examines produced water as is found in the geological formation, the treatment of the produced water and its effectiveness in meeting discharge guidelines, and the impact of produced water on the ecosystem. There is a shortage of information from a stage in the produced water train that is downstream from treatment, but still upstream from discharge, and that is the monitoring phase. This is the stage at which point it is determined if treated produced water is suitable to proceed downstream, or if it must be rerouted for additional treatment. As rerouting water for retreatment accrues additional cost, it is important for accurate and reliable measurements to take place at this stage.

Oilfield produced water is measured in two different ways. Samples can be taken and tested in a lab for oil and grease, aromatics, and other hydrocarbons, but this option is time consuming and can be costly. The next option is inline monitors. Monitors can be operated remotely and autonomously, and are capable of taking many more readings than is feasible with grab samples. There is a research gap where the capabilities of and quality of data collected from these monitors are concerned. It is important that this gap be filled, given the costs associated with the treatment and disposal of produced water, and the regulations governing produced water discharges.

CHAPTER 2 LITERATURE REVIEW

2.1 Produced Water

Produced water is a form of wastewater drawn up along with oil or gas from hydrocarbon bearing formations during oil and gas exploration. When drawn, the oil or gas is in complex with the water, and once it has been processed so as to separate the two, the water left over becomes produced water. Produced water can contain any number of chemicals, depending on the formation and the processing used to separate the water from the oil, as well as the stage in the lifetime of the oil well (GAO, 2014). Such chemicals include aromatic compounds, dispersed oil, heavy metals, naturally occurring radioactive materials, and PAH (polycyclic aromatic compounds, and BTEX (benzene, toluene, ethyl benzene, and xylenes) are of primary concern (Neff et al., 2011). Process chemicals involved in the separation of the oil or gas from the water can also be found in produced water that has been reinjected for pressure maintenance in a well. These chemicals can include coagulants, flocculants, and detergents (Neff, 2002).

Produced water is the largest waste stream associated with both on-shore and off-shore oil and gas exploration. Approximately seven parts produced water for every one part oil or gas is produced over the lifetime of well (Tellez et al., 2005). With so much water to manage, produced water management is also the greatest expense in the oil and gas industry. For this reason, it is in the interest of all oil and gas producers to deal with produced water in the most efficient way possible.

There are a number of ways to deal with produced water as a waste stream. The typical options include reinjection into the formation for pressure maintenance and discharge into the environment. Each option is appropriate at different points in the lifetime of the well (Lu et al., 2006). Reinjection is appropriate during the earlier stages of production because it maintains pressure in the well, enhancing pumping efficiency. As the life of the well advances, though, more and more water is drawn with less and less oil, and the larger volumes of water necessitate its discharge into the surrounding environment, be it seas, lakes, rivers, or soils. With this inevitable discharge, there is growing concern over the accuracy and reliability of the measurement tools and processes.

2.2 Environmental Impacts

Produced water is classified as a wastewater, and thus is known to have negative impacts to the environment if discharged in its raw or partially treated state. As all formations are different, all produced waters vary from one another in their characteristics, and therefore can affect the environment differently.

Produced waters that contain high salinity are found at all oil and gas production regions, and are a major contributor to toxicity (Neff, 2002). Produced water salts can cause the degradation of ground and surface water quality, and can cause the deaths of plants and the destruction of soil textures. In addition, salts can result in the erosion of soils and siltation of nearby waterways. If the produced water is radium bearing, the salts can cause the contamination of production equipment and soils via the water, scale, and sludge associated with the produced water. (Otton, 2006).

Dispersed oil droplets present in produced water rise to the surface of a body of water and can evaporate. These contaminants can be toxic, and increase the biochemical oxygen demand of the water (Stephenson, 1992). Nonpolar hydrocarbons from produced water almost invariably toxic (Elias-Samlalsingh, 2003). Hydrogen Sulfide and hydrocarbons found in produced water are examples of some compounds that are highly toxic to freshwater animals. These compounds exist in low salinity concentrations of produced water (Neff, 2002).

Chemicals used in the production of oil and gas can be included in discharge water. Production chemicals can have varying effects on the marine environment. Those that are oil soluble have a more significant impact than those that are water soluble at comparable concentrations (Henderson, 1999). Chemicals involved in the treatment of produced water tend to accumulate in marine sediments (Grigson et al., 2000).

Heavy metals that are found in produced water are typically of a higher concentration that those found in seawater, and, for that reason, dilute rapidly when discharged. As such, they are not known to have significant adverse effects on animals of marine life (Stephenson, 1992). Other materials that can be found in produced water, such as radionuclides, are not associated with any significant risk to marine life (Hamilton et al., 1992).

2.3 Produced Water Breakdown

Table 2.1 below details the chemical composition of produced water from main discharges in the Norwegian Sector of the North Sea.

Table 2.1: Chemical Composition of Produced Water from Main Sources in the Norwegian Sector of the North Sea (1999-2000) (Utvik *et al.*, 2002)

Compound Group	**Unit**	**Low**	**High**
Dispersed Oil	mg/L	10.0	40.0
BTEX	mg/L	1.0	40.0
NPD	mg/L	0.9	10.0
PAH	mg/L	0.01	0.13
Organic Acids	mg/L	55.0	760.0
Phenol	mg/L	0.1	6.0
C1 – C4 alkylated phenols	mg/L	0.17	11.3
C4 – C7 alkylated phenols	mg/L	0.1	0.8
Radioactive elements	Bq/L	0.1	10.0

BTEX: Benzene, Toluene, Ethyl benzene, Xylene
NPD: Naphthalene, Phenanthrene, Dibenzothiophene, including their C1-C3 alkyl homologues
PAH: Polycyclic aromatic hydrocarbons represented by 16 EPA PAH, except naphthalene and phenanthrene

Table 2.1 indicates the levels at which produced water discharge contained various chemical components. Of particular note were organic acids, BTEX, and dispersed oil.

Dispersed oil is a component of total oil and grease, along with dissolved liquid hydrocarbons and other organic compounds, including aromatic hydrocarbon compounds and process compounds used in produced water treatment (Arnold, 2008). Oil and grease concentration, due to its ease of measurement, is the primary parameter used in compliance monitoring and regulatory standards (Arnold, 2008). Dispersed oil itself refers to oil droplets present in the produced water. The amount of dispersed oil in produced water is dependent on the density of the oil, the mechanical processes and shear forces the oil has been subjected to, and the interfacial tension between the oil and water (Arnold, 2008).

Dissolved oil refers to hydrocarbons that are soluble, or partially soluble, in water. The amount of dissolved oil in produced water is dependent on the source of the oil. Gas or condensate produced water usually has a greater amount of dissolved oil than crude oil produced water (Arnold, 2008). The solubility of oil in produced water varies by temperature and salinity. Produced water subjected to treatment processes that heat it over 75 ºC typically has more dissolved oil, as that is the temperature at the solubility of oil begins to increase significantly. Below that temperature, solubility does not change a great deal (Arnold, 2008). High salinity has the effect of reducing the solubility of oil in water. As salinity increases, the dissolved oil are forced out of solution and into either a vapour phase or dispersed oil droplets (Arnold, 2008).

Produced water is saline, and the salinity is important to know for reasons related to oil solubility, as mentioned above, but also its environmental impacts. For example, salinity has been found to affect a plant root's ability to uptake water (Horpstad *et al.*, 2001). The salinity of water is measured by its conductivity, while a conductivity of 3 mS/cm is considered saline, typical drinking water is between 0.005 and 0.05 mS/cm, while seawater is 50 mS/cm. As conductivity is a measure of total dissolved solids, it increases as more ionic species are dissolved in the water (Lenntech). Produced water can have a conductivity of as high as 300 mS/cm (Arthur, 2005).

2.4 Treatment of Produced Water

Produced water is a wastewater, and thus is treated using techniques that treat wastewater.. Depending on the unique components of a produced water, returning to formation specificity, different levels and types of treatment may be appropriate. There are several types of treatment techniques available, including: physical, chemical, and biological. Each category has additional sub-categories that differentiate them further. As is appropriate with the wide variety of produced waters, the types of treatment can be combined to various degrees.

Physical treatment types involve techniques that do not change the chemistry of the produced water. Adsorption is a common option to remove organics from the water, and is often used as a method of pre-treatment before additional procedures are carried out. Activated carbon is able to remove materials of consequence like benzene, toluene, ethyl benzene, and xylenes(BTEX), while organoclay can remove insoluble free hydrocarbons, andcombined, they are able to lower hydrocarbon concentrations to within the necessary standards (Doyle, 2000). Copolymer beads can be used to lower the overall oil in water concentration (Carvalho et al., 2002). Zeolites, and other ion exchange resins can be used to treat different types of produced water to remove sodium, magnesium, calcium, and other materials, including BTEX, from water. (Ahmadun, 2009).

Other examples of physical treatment methods include sand filtration, which is effective in the removal of particulates from water, and cyclonic separation. Traditionally, sand filtration is an effective method in removing finer particles that tend not to settle (Adewumi et al., 1992). Cyclone separation, including centrifuges, hydrocyclones, and plate separators, are useful in separating the phases of produced water. They are capable of separating out oil, gas, and solids, as needed, but are not effective at removing hazardous or dissolved material (Van den Broek, 1998). Evaporation and distillation methods can be employed in treating produced water if it is saline and contains oil components (Bertness, 1989). Such methods are able to recover 95 % or more of the input energy, making them extremely cost effective.

Dissolved air flotation (DAF) is often used as a step in the treatment of many wastewaters, including produced water. Used on its own or in conjunction with other removal methods, it is effective in the removal of a many forms of dissolved hydrocarbon, including octane, ethylbenzene, and micro-dispersed decane (Thoma et al., 1999).

The primary form of chemical treatment of produced water is coagulation and flocculation. Many wastewater treatment trains involve coagulation or flocculation in some way. Coagulation and flocculation are effective in the removal of suspended and colloidal particles. When treating produced water, lime softening is the typical method of water softening, while a modified hot lime method can result in comparable particle removal, but reducing the amount of sludge produced (Garbutt, 1997). Removal of hydrocarbons, arsenic, and mercury can be achieved with the combination of ferric ion oxidants and flocculants (Frankiewicz, 2000).

Chemical oxidation is an effective method in the decomposition of refractory chemicals, should they be found in a produced water. Such chemicals are typically not found in produced water, but oil bearing formations vary widely. In addition to strong oxidants, chemical oxidation utilizes irradiation and catalyzation as part of the process (Renou et al., 2008). Electrochemical processes are capable of rapidly reducing the chemical and biological oxygen demand of produced water, and can facilitate the coagulation of organic pollutants (Ma, 2006). Though much less cost effective and with a high demand of energy, ozonolysis has been shown to effectively decompose many extractable organic compounds in produced water (Morrow et al., 1999).

Production chemicals that enter produced water during separation or earlier treatment phases can affect the efficiency of later phases. Surfactants in the produced water work to stabilize the oil droplets, keeping them from uniting. The use of a demulsifier disrupts the stability of the droplets and natural emulsions that occur in oil (Deng et al., 2005).

Biological treatment of produced water is based on aerobic and anaerobic microorganisms. Activated sludge is the typical biological method of wastewater treatment (Tellez et al., 2002). Depending on the bacteria used, the salinity of the produced water can be a factor in the efficiency of the chemical oxygen demand (COD) removal (Wei et al., 2003). With some types of bacteria, high salinity creates an environmental stress, causing microbial lysing and loss of biomass, which significantly reduces the rate of biodegradation of the oil in produced water (Dfaz et al., 2000).

Due the high cost of operation of chemical and biological waste water treatment options, membrane treatment options have been under steady development in recent years. Membrane filtration is available in a variety of incarnations, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Membrane treatment employs a pressure driven process that separates out the components of a waste water according to membrane pore size (Sonune, 2004).

At each level of membrane, a different type of component is designed to be separated from the water. Microfiltration membranes remove suspended particles, ultrafiltration membranes remove macromolecules, and reverse osmosis separates ions and dissolved components (Madaeni, 1999). Nanofiltration membranes, similarly, remove nano-sized components from waste water, which is useful in achieving guideline thresholds for irrigation and potable water (Xu et al., 2008).

Membranes are constructed using various materials. They can be constructed to tailor to the conditions required. The factors that affect whether membranes are cost effective are flux rate, flux degradation, and membrane life uncertainty. In addition, they can exhibit sensitivity to chemicals that can exist in produced water from the pretreatment and purification processes (Zaidi, 1992). Zeolite membranes can be considered due to their stable chemical, mechanical, and thermal properties. Reverse osmosis zeolite membranes are effective in high solvent environments, and are capable of removing various ions from produced water (Liu et al., 2007). Bentonite clay membranes can also be used to purify produced water, but are less effective at removing total dissolved solids (Liangxiong et al., 2003). Such clay membranes, along with all other forms of treatment are more effective when combined with other forms of treatment.

2.5 Regulations

Regulations for produced water discharges vary by location, country, and time. In Canada, discharged produced water must meet two overlapping standards. The oil in water concentration of produced water discharge must not exceed 30 mg/L over a 30 day period rolling average. In addition, the oil in water concentration, as calculated at least twice per day, must not exceed 44 mg/L within a 24 hour period. A sample must be drawn downstream of the last treatment process, but upstream of the discharge point, and must be taken every 12 hours (NEB et al., 2010). Produced water sampling must occur every 12 hours, at minimum, and the 30-day and 24-hour averages calculated. Samples should be collected at a point which is downstream of the last treatment process, but upstream of the discharge point. Oil in produced water should be analyzed according to *Standard Methods for the Examination of Water and Wastewater*, 20th Edition (or as updated), specifically Partition-Infrared Method 5520C for oil and grease, and Method 5520F for hydrocarbons (NEB *et al.* 2010).

In the United States, oil and grease concentrations in produced water discharge must not exceed 42 mg/L daily, and must not exceed 29 mg/L monthly (USEPA). In Australia, the limit of oil and grease concentration in produced water discharge is an average of 30 mg/L per day, and 50 mg/L instantaneously (Neff, 2002). China holds much more strict regulations for discharges; oil and grease concentration must be 10 mg/L on average on a monthly basis, and chemical oxygen demand must be below 100 mg/L on average per month (Tellez et al., 2002). The guidelines for the north-east Atlantic Ocean state that dispersed oil in produced water discharge must not exceed an annual average of 40 mg/L (OSPAR, 2005).

2.6 Measurement Techniques

The analysis of petroleum hydrocarbons (and thus, produced water), both qualitative and quantitative, can be performed using several methods. The preferred method is gas chromatography/ mass spectroscopy (GC/MS), as it is capable of providing detailed compositional information able to identify and characterize oil samples better than any other method. GC/MS is a highly efficient method of analysis in the monitoring of bioremediation of oil, and is a standard in monitoring the biodegradation of oil. That being said, there are disadvantages in the use of GC/MS, including longer times of analysis, higher costs, sample storage, and off-site shipping (Tellez et al., 2005).

Visual light spectrophotometry is another method of analysis; one that avoids many of the disadvantages of GC/MS. The equipment necessary for GC/MS can cost in excess of ten times that of a visual light spectrophotometer (Pharr et al., 1992). Additionally, visual light spectrophotometry can be performed easily on-site, eliminating the need for transport and storage. In order for visual light spectrophotometry to be useful, the compound being analyzed must have a property or that a definite color characteristic that is proportional to the concentration of the compound of interest (Tellez et al., 2005). Many biological substances exhibit either absorbance of light directly or can be converted into a compound that absorbs light. This property allows such substances to be quantified based on the degree of absorbance and related to an equivalent concentration via calibration (Yang et al., 2006).

Compounds that absorb light in amounts that correlate to their concentration in solution follow both Beer and Lambert's law (Miller, 1993). The absorbance is related to the ratio of the intensity of the light incident on the sample to the intensity of light leaving the sample. The greater the concentration of the sample, the greater the absorbance (Miller, 1993).

In addition to visible light spectrophotometry, ultraviolet and infrared spectrophotometry follow the same principle. Ultraviolet light is absorbed by aromatic hydrocarbons, while infrared is absorbed by aliphatic hydrocarbons at certain wavelengths. Thus, if these types of molecules are present in a sample, ultraviolet or infrared light can be used in the same fashion as visual light, by correlating absorbance to a series of known concentrations. By preparing this type of calibration, the hydrocarbon concentration of an oil sample can be determined. Tellez et al. (2005) determined that UV spectrophotometry can achieve results equivalent to GC/MS when measuring n-alkane concentrations in produced water.

2.7 Instrument Reliability Analysis

Reliability can be approached in several ways. An instrument is only useful if it can return consistent data under the same conditions when subjected to repeated tests. The reliability of an instrument can be affected by a number of factors, including degradation of sensors, continual exposure to adverse conditions, or detrimental operation (Betty, 2014). Studies that focus on instrument reliability involve the repeated running of the instrument under the same conditions and then applying a statistical comparison of the results. It is important to be able to discern if an instrument is producing incorrect data that may indicate a reduction in reliability. An experiment designed by Chen et al. (2009) developed a probability model that indicated the likelihood of a change in data output being due to an internal failure of instrument components. Statistical modelling is useful in a reliability study, as instrument output, particularly in the case of sensors or detectors, is very unlikely to be exactly the same twice. As such, data produced in the study can vary between tests, but is not necessarily indicative of a lack of reliability.

In addition, reliability can be described as the probability of success, or the number of failures, in terms of an electronic system (IEEE, 1990). It is essentially a measure of the capability of a system to function without failure. Reliability can also be described by the availability of a system or instrument (IEEE, 1990). This refers to the readiness of a system to begin operation at a random time. Availability is affected by factors such as maintenance downtime and system, or instrument, failure (Elsayed, 1996). Furthermore, availability can be broken down into several categories, including point availability, inherent availability, and operational availability. The former two of these categories are examples of *a priori* availability and the latter an example of *a posteriori* availability (Elsayed, 1996). *A priori* availability can be estimated using models, while *a posteriori* availability is based on observation (Elsayed, 1996).

2.8 Inline Produced Water Monitors

There are many monitors available that can be grouped together based on the type of sensor or technique each employs.

The first technique is focused ultrasonic acoustics, in which a focused acoustic transducer is inserted into a produced water stream (Anaenson et al., 2006). After determining the measurement volume, the transducer detects acoustic echoes made by particles, such as oil droplets, passing through the measurement volume, and then oil concentration is determined based on particle sizes and size distributions.

Image analysis technology utilizes a high resolution microscope to capture images of the sample stream. Particles can then be counted and analyzed, yielding their volumes, and ultimately the concentration of oil in the sample. Shape factors can be used to distinguish oil droplets from solid particles (Butler et al., 2001). This type of technology is popular in process optimization, and also produced water re-injection applications where size and size distribution of oil droplets and solid particles is important in addition to concentration (O'Donoghue et al., 2009).

Instruments that employ light scattering pass a beam of visible light through a sample of oily water. If droplets or particles are present, the light will be scattered, reducing the amount that is transmitted. By measuring the transmittance, and the amount of scattered light from different angles, the oil droplets can be distinguished from solid particles and gas bubbles and the concentration determined (Yang, 2011).

Ultraviolet (UV) fluorescence can be employed using either a UV lamp as a light source, or laser induced fluorescence (LIF) (Yang, 2011). When aromatic hydrocarbons absorb UV light, fluorescent light is emitted at a longer wavelength, the intensity of which can be used to determine the amount of aromatic hydrocarbons, which is related to the total hydrocarbons, assuming the ratio of aromatics to total hydrocarbons is constant (Yang, 2011).

CHAPTER 3 MATERIALS AND METHODS

3.1 Testing Loop and Project Description

Produced water samples were provided by the Sable Offshore Energy Project, an offshore natural gas and light hydrocarbon producing project located offshore Nova Scotia, Canada. Produced water was shipped in a tote tank, and received at Dalhousie University. Approximately 1500 to 2000 L were provided, and were stored in tank T100 which formed a part of the test apparatus loop. Initial produced water samples were taken for manual analysis, or preserved for later analysis as described in Section 3.8. Figure 3.1 below details the testing loop.

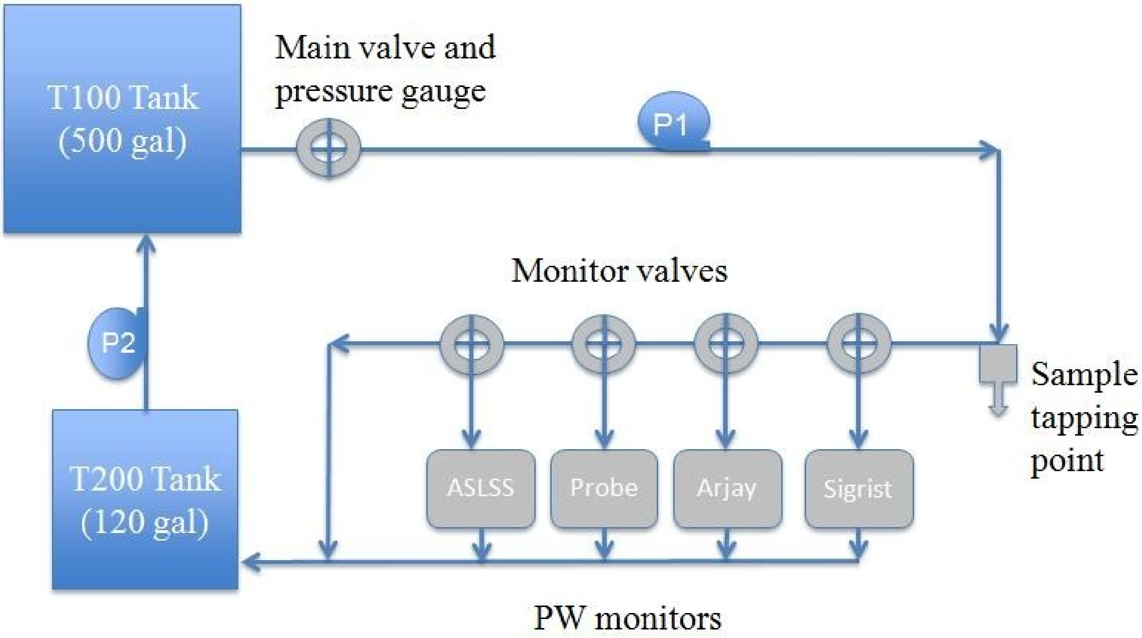

Figure 3.1: Simple schematic of testing loop detailing the positions of each tank, monitor, valve, and tapping point; P1 and P2 indicate the pumps responsible for moving the water through the system.

Water was pumped through the system using the main pump (P1). Tank T100, shown on the upper left-hand side is the tote containing the sample, and tank T200 is the smaller recirculation tank into which the water flowed, post-monitor. The pathways through each of the four monitors could be individually closed by valves. If all four valves were closed, the water was able to bypass the monitors and flow directly into the recirculation tank. Once the T200 tank was filled to a certain level, the return pump (P2) activated automatically to move the water into the T100 again. The main pathways through which water moved were constructed using 2 inch diameter steel piping, and any alternate pathways, including those through the monitors, were connected using 1 inch diameter transparent, flexible polyvinyl chloride (PVC)water hose.

Figure 3.2 below shows the setup of the testing loop before operation.

Figure 3.2: Testing loop setup showing the T200 tank (left), the Arjay monitor (center), and Sigrist monitor (right). Not shown: ASLSS and probe monitors, T100 tank.

Due to its size, the T100 tank was kept in an adjacent room for ease of movement. The ASLSS and probe monitors were not attached directly to the structure, but were connected by tubing to the system, and positioned nearby.

During testing, the analyzers were operated in parallel to allow for valid comparisons. Ideally, the system would be run continuously for about five weeks in order to evaluate cleaning and maintenance requirements, as well as any calibration drifts. Running the system continuously over this time frame, however, posed a safety problem to the Dalhousie facilities, as there would be no personnel available to monitor it overnight. Instead, it was determined that the system would run continually during daytime hours. Any required stops during this period (for example, for solution mixing or maintenance) were to be made as short as possible.

3.2 In-line Analyzers

The four in-line analyzers selected for this project all function on the principle of ultraviolet fluorescence. This makes the units insensitive to measurement errors due to the presence of solids. Fluorescence is the phenomenon that occurs when aromatic compounds emit visible light as a response to exposure to ultraviolet light. The intensity of the emitted light is proportional to the concentration of aromatic compounds in the sample, and, through correlation, the total oil in a sample can be determined. (Maxoil, 2008).

Fluorescence as a measurement technique requires relatively constant oil droplet sizes in a sample. Homogenisation is a method that can be used to compensate for oil droplet size, but assumes that the ration of aromatics to total oil remains relatively constant between calibrations. It is also possible for some chemical residuals to be read as oil. (Maxoil, 2008).

Each analyzer was commissioned and calibrated on site by technicians employed by their respective companies. Technical details of each monitor are shown below in Table 3.1. Following Table 3.1, the monitors are described in further detail.

Table 3.1: Technical details comparative of each monitor.

	ASLSS	Probe	Arjay	Sigrist
Power (V)	240	240	110	230
Max Pressure (psi)	2175	2175	100	145
Max Temperature (ºC)	100	100	100	95
Optimal Flow (L/min)	10-25	10-25	5	5-7
Light Source	LIF	LIF	UV Lamp	UV Lamp
Method of Water Sampling	Capture Chamber	Inline Pipe	Glass Flow Plate	Freefall Stream

** LIF: Laser induced fluorescence

3.2.1 Advanced Sensors OIW-EX1000

The first of two units provided by Advanced Sensors, the OIW-EX1000 unit utilizes a side stream method of sampling. Water is captured in a testing chamber using an air pressure controlled valve system. It is then bombarded with ultrasonic pulses which homogenize the oil droplet size. The measurement is recorded by way of laser induced ultraviolet fluorescence, and then the valves are opened, allowing flow to resume. The ultrasonics of this unit also serve as a maintenance tool to keep the sensor head clean. (Advanced Sensors Ltd., 2009).

The unit is designed to function from a nominal 240V AC power supply. The maximum working pressure within the measurement chamber is 150.0 bar. The optimal flow rate through the system is within the range of 10-25 L/min. The unit is able to run a sample temperature of 0 to 100 ˚C. (Advanced Sensors Ltd., 2009).

The side stream unit (ASLSS) was calibrated using gas condensate from the Sable Island Gas project (see Section 3.5). A series of known dilutions of the condensate in water were developed, and a multiple point calibration curve was input into the unit.

3.2.2 Advanced Sensors OIW-EX1000P

The Advanced Sensors OIW-EX1000P is the second unit provided by Advanced Sensors. It differs from the EX1000 unit in that it uses an inline probe method of sampling, and no capturing of water takes place in the sampling. It is also the only unit which does not use a side stream sampling method. Water passes through the section of pipe into which the probe head is inserted, and the probe takes readings using its UV fluorescence sensor. This unit uses ultrasonics, similar to the EX1000, in order to homogenize droplet sizes, as well as clean the sensor head. (Advanced Sensors Ltd., 2009).

The unit is designed to function from a nominal 240V AC power supply. The maximum working pressure within the measurement chamber is 150.0 bar. The optimal flow rate through the system is within the range of 10-25 L/min. The unit is able to run a sample temperature of 0 to 100 ˚C. (Advanced Sensors Ltd., 2009).

The probe was calibrated using the same procedure and standards as the ASLSS unit. It was calibrated at the same time, and by the same technician.

3.2.3 Arjay Hydrosense 2410

The Arjay Hydrosense 2410 unit is unique among the units, in that it employs a flow dispersion plate to its measurement process. Water passes over a glass plate, which spreads it into a thin layer, allowing the UV sensor to accurately measure the oil in the water. This technique minimizes the effect of particulate matter that may occasionally enter the flow system. (Arjay Engineering Ltd.).

The unit functions from an 110V AC power supply. The recommended optimal inlet flow rate is 5 L/min, with a maximum inlet pressure of 100 psi. The unit is able to run a sample temperature of 0 to 100 ˚C. (Arjay Engineering Ltd.).

The Arjay unit was calibrated using the same gas condensate as were the ASLSS and probe units. The calibration curve was a two point curve input into the unit, between municipal tap water, and a known concentration of gas condensate in water.

3.2.4 Sigrist Oilguard EX

The Sigrist Oilguard EX (Figure 4) uses a gravity fed stream method of measurement; the water pours through a sensor chamber (the free-fall flow cell) where a network of prisms and reflectors are used in conjunction with a UV sensor to take measurements. The configuration of the unit at Dalhousie includes a de-aeration vessel, attached inline with the stream, above the UV sensor chamber. The vessel facilitates the de-gassing of the water, but also serves as a flow control in that it can be configured such that it can maintain a certain head of water. (Sigrist Photometer AG, 2007).

The unit functions with a 230 V power supply. The unit is able to run a sample temperature of 0 to 95 ˚C without additional pressure or temperature control. The optimal flow rate through the free-fall flow cell is 5 to 7 L/min. (Sigrist Photometer AG, 2007).

The Sigrist unit was calibrated using gas condensate, like the other units. The calibration curve was input into the unit by running controlled concentrations of condensate in water through the unit in increasing doses and recording the unit output.

3.3 Week 1: Flow Rate

Flow rate was the easiest parameter to adjust, and thus was tested first. The purpose of testing flow was two-fold. First, it was simple to control, and thus it allowed the operator to become more familiar with system functions. Additionally, it was an applicable variable to real world systems, and its testing at the pilot scale would help determine how much flow control would be required in those systems. As each monitor had a specified ideal flow rate, this part of the testing period was used to test how much the flow rate could be adjusted up or down before the analyzers would begin to operate improperly.

The flow rate in the system was measured using a water flow gauge. The gauge was attachable to any point in the system where piping could be easily removed. There was only a single flow gauge available to be used among four monitors, and moving it between them was a slow process that could cause significant delays in operation, therefore the gauge was used only as part of a calibration procedure that correlated the flow rate through each monitor to the number of valve turns. This way, the flow rate could be controlled through all the valves without the need to move the gauge between them.

The valves were calibrated using the following stratagem. The flow meter scale was in percent flow. The conversion formula to GPM, found on the side of the flow meter, is indicated below:

$$scale * 0.028 = GPM$$

GPM can be further converted to L/min by:

$$GPM * 3.785 = L/min$$

This means that the maximum measurable flow rate, by this flow meter was 10.598 L/min (when the scale read 100).

The calibration of valve turns was based on a constant back pressure of 13 psi. This procedure could be completed, by one person, in one hour. As such it was repeated at the beginning of each testing section.

The calibration procedure is as follows:

The system was activated, ensuring that the valves to each monitor were closed, and the back pressure was 13 psi. The flow gauge was attached to the hose inline with one monitor. The flow to this monitor was opened slowly using the valve, ensuring that the back pressure, indicated by the main pressure gauge, remained constant at 13 psi. The number of turns, in terms of quarter and half turns, relative to the closed position of the valve and associated flow rate as indicated on the flow gauge were recorded. The valve was then closed, and the gauge removed. This process was repeated for the other monitors.

A main pressure gauge mentioned in the procedure above was located just before the valves directing the water toward each monitor. This gauge was monitored closely throughout the entire testing period, as the calibrations were based on the gauge reading 13 psi.

Table 3.2 below shows the flow changes made throughout the section. Up to three changes were made during a single day. The system was allowed to run for several hours between changes. The general strategy was to slowly increase the flow rate until the monitors began to act adversely. In the event that a change was made that adversely affected one of the monitors, that change was immediately repealed and the flow to the affected monitor was restored to a flow that was not known to cause a problem. The initial flow rates were based on the minimum recommended flow rates stated in the monitor user manuals, or technician recommendations.

Table 3.2: Flow rate settings by day, time, and monitor during week 1.

		Flow by Monitor (L/min)			
Date	Time	ASLSS	ASL Probe	Arjay	Sigrist
18/07/12	8:15	10.60	10.60	4.24	8.48
19/07/12	8:30	10.60	10.60	4.24	6.89
19/07/12	14:27	10.60	10.60	9.54	6.36
19/07/12	15:35	6.36	6.36	4.24	4.77
20/07/12	8:30	6.36	6.36	4.24	6.36
20/07/12	12:50	15.90	15.90	8.48	4.24
20/07/12	14:24	15.90	15.90	8.48	6.36
20/07/12	14:30	21.20	21.20	8.48	6.36
23/07/12	8:15	21.20	21.20	8.48	6.36
23/07/12	11:27	21.20	21.20	10.60	7.42
23/07/12	11:37	21.20	21.20	4.24	7.42
23/07/12	11:41	21.20	21.20	4.24	8.48
23/07/12	11:53	26.50	26.50	5.30	6.36
23/07/12	13:46	26.50	26.50	5.30	7.95
23/07/12	13:50	10.60	8.48	8.48	7.95
24/07/12	8:20	10.60	8.48	8.48	7.95
24/07/12	9:19	6.36	6.36	8.48	7.95
24/07/12	12:55	2.12	2.12	8.48	7.95
24/07/12	14:08	0.00	0.00	8.48	7.95
24/07/12	15:25	10.60	10.60	8.48	7.95

3.4 Week 2: Gas and Particulates

The purpose of this section of the testing period was to determine the effect of particulate matter on the fouling of the monitors. Gas was introduced into the system by connecting two aquarium pumps to submersible and floatable aquarium stones and placing them into the small recirculation tank. Solids were introduced by dropping sand into the small tank. Tests during this week started with gas only, then solids only, and finally both simultaneously. All other parameters were held constant. Gas was added to the system to test if dissolved gases or gas bubbles would affect the readings of the monitors. Similarly, sand was added to test for the same responses, but also to test the manufacturer claim that the monitors were insensitive to particles in a system. Furthermore, as gases and particles are often present in produced water, they were applicable variables to test to determine if their presence in the water stream could affect monitor readings.

Gas and sand were added to the system as outlined in Table 3.3. The table is organized by order in which changes were made. Each row indicates a change that was made to the system, whether it was an increase in the amount of gas aeration, or a sand dose, or both. After each change, the system was allowed to run for several hours to allow time for the changes to affect the system. During the course of a single day, two to three changes were made. The first change of each day took place after the first sample was drawn for that day. Table 3.3 describes the gas and sand doses made to the system during the second week.

Table 3.3: Gas and sand dose by time and date during week 2.

Date	Time	Gas (L/hr)	Sand (mL dose/mL total)
25/07/12	13:30	150	--
26/07/12	8:30	300	--
26/07/12	15:00	600	--
27/07/12	12:40	--	15/15
30/07/12	9:10	--	15/30
30/07/12	10:23	--	15/45
30/07/12	14:00	--	30/75
31/07/12	9:15	300	15/90
31/07/12	10:48	300	30/120
31/07/12	14:38	600	15/135
01/08/12	9:06	600	15/150
01/08/12	12:18	600	30/180

The aquarium pumps used were Tetra (©Tetra) "Whisper" air pumps, each capable of aerating a tank of 113 to 227 L of water. As such pumps are intended for use in large fish tanks, it was assumed that the only gases aerating the water were those found in the surrounding environment. Also, as a single unit of this type of pump was intended for a tank approximately half the size of the recirculation tank, a second was required for additional aeration. The pumps were run both singularly and in unison over the course of this section of testing.

The sand used in this section was a local, fine grained type used for covering foot paths and recreational sites by the city of Halifax.

3.5 Week 3: Spiking

The produced water was spiked with additional hydrocarbonsin order to simulate changes in oil concentration. Both hydrocarbons and production chemicals were tested, beginning with hydrocarbons.

The spiking was done in two ways. The first was the direct addition of condensate, in known volumes, to the produced water. This was done incrementally using larger and larger amounts of condensate. Samples were taken before, and just after, the condensate was added. The second was the addition of production chemicals, which were added in the same way as the condensate; in known volumes.

The condensate used was a gas condensate supplied from the same source as the produced water itself, Sable Island Gas. It was added in its raw form, which had a density of approximately 783 mg/mL. The chemical chosen for use in this project was the surfactant Triton-X. It was chosen because it was a readily available detergent, and such detergents are often used separation and treatment processes undergone by produced water. As with the condensate, it was added undiluted.

The spiking was scheduled and performed according to Table 3.4 below. Each time a dose was made, the volume of the dose was recorded. An ongoing tally of the total volume of chemical added to the system in this way was recorded as well.

Table 3.4: Chemical dose, time and date of spikes made during week 3.

Date	Time	Dose (mL/ total mL)	Chemical
03/08/12	9:13	5 mL	Condensate
06/08/12	10:45	10 mL/ 15 mL	Condensate
07/08/12	9:10	15 mL/ 30 mL	Condensate
08/08/12	9:06	5 mL/ 35 mL	Condensate
10/08/12	9:33	50 mL	Triton-X100
15/08/12	10:41	100 mL/135 mL	Condensate
15/08/12	13:54	200 mL/ 335 mL	Condensate
16/08/12	9:20	200 mL/ 535 mL	Condensate

As shown in Table 3.4, incremental condensate additions were made, and then the system was allowed to run for several hours, in order for any effects of the spike to be observed. This was necessary as the spikes were added to the smaller tank, and in order for the system to be affected, the added material needed to be mixed into the large sample tank so that it could be routed to the monitors. For this to happen, the material needed to be subject to the recirculation cycle at least once.

After the condensate, Triton-X was added in much the same fashion. Once the Triton-X was in the system, the condensate doses were increased significantly.

3.6 Week 4: Heating

Heating the produced water sample was done last in case it caused the compounds in solution to vaporize or decompose. Aquarium heaters were submersed into the smaller recirculation tank. The water was gradually heated. Temperature measurements were taken from samples drawn for analytical analysis. These samples were collected from a point that is immediately before the produced water is directed to the analyzers.

Two aquarium heaters, capable of multiple settings were used during this section of the testing period. The heaters were Marina submersible aquarium heaters (©Marina), 200 W each, designed to heat aquariums up to 200 L. Table 4 below shows the heating schedule for this section. The heat level was reported based on the heater settings, as temperature measurements were taken in the lab only.

Table 3.5: Heating settings and number of heaters by date and time during week 4.

Date	Time	Number of Heaters	Heater(s) Setting (W total)
20/08/12	12:23	Single heater	100
21/08/12	8:15	Single heater	200
22/08/12	8:38	Single heater	100
22/08/12	9:58	Dual heaters	200
23/08/12	8:12	Dual heaters	300
23/08/12	12:08	Dual heaters	400

Heating changes were reported in two levels: the number of heaters in employ, and the settings on those heaters. Each heater produced power based on a scale of 0 to 200 W and a setting on that scale.

3.7 Week 5: Buffer Period

A buffer period was included in the project description to allow for extra time in conducting the testing. This was useful, as delays could occur, throwing off the testing schedule, such as electrical or mechanical interruptions. If the required testing during a week or section was not completed, additional testing time was allotted from the buffer period until the section was finished.

3.8 Sampling Stratagem and Lab Procedure

While regulations require testing every 12 hours, the operation timeframe affected when samples could be drawn from the testing loop. Samples were drawn thirty minutes after operation began and then again at the end of the operation day, eight hours later. Samples were drawn from a port on the test loop that is in line with, but before the point at which produced water was directed towards the analyzers. Two samples were drawn each time, a one litre sample for oil and grease and hydrocarbon analysis, and a 100 mL sample for conductivity, pH, turbidity, and temperature measurement. Temperature readings were taken as quickly as possible after the sample was drawn. The time at which manual sampling occurred was documented along with the readings on each of the analyzers at that point.

Temperature readings were taken using an Ever-Safe glass thermometer. The thermometer was placed in the sample and allowed one to two minutes to stabilize. Sample pH was measured using an Accumet pH probe, and conductivity using an Accumet conductivity probe. Turbidity was measured using a HACH 2100AN Turbidimeter. A glass vial was filled with distilled water and placed in the turbidimeter and a reading obtained. The vial was emptied, then filled with a sample of produced water, and placed in the turbidimeter for another reading. The turbidity recorded was the difference between these two readings.

Special collection and preservation techniques were followed, in order to test for oil and grease and hydrocarbons. One litre of sample volume was collected in a glass container with a PTFE-lined cap. The container was prewashed with soap, rinsed with water, and then rinsed with solvent; on occasion, the container was capped with aluminum foil and baked at 200 to 250°C for one hour in lieu of solvent rinsing. Bottle cap liners were washed with soap, rinsed with water, and then baked at 110 to 200°C for 1 hour before use. Only grab samples were acceptable. If the sample concentration was expected to exceed 1 g/L of extractable material, then proportionally smaller volumes were collected. Unless analyzed within 2 hours after collection, samples were acidified to pH 2 or below with either 1:1 HCl or 1:1 H_2SO_4 and refrigerated. Preserved samples were analyzed within 28 days of collection (Standard Methods, 2001).

3.8.1 Calibration Curve Development

The concentration associated with the peak absorbance was determined via a calibration procedure. A series of dilutions of produced water condensate dissolved in solvent were prepared. Each dilution was scanned in the IR, as with the samples, and the magnitude of the peak near 2930 cm^{-1} was recorded. Through this procedure, the magnitude of the peak absorbance near 2930 cm^{-1} was correlated to concentration.

A Fourier Transform Infrared spectrophotometer (FTIR) was used to measure the absorbance of standards and establish a calibration curve in this process, and was used to measure the absorbance of subsequent samples as well. When taking a measurement, as is required by the FTIR, first, a cuvette of pure tetrachloroethylene extractant was scanned to establish a baseline. After that, the sample was scanned. The FTIR was set to a resolution of 4 cm^{-1}, 20 scans per sample, with a path length of 50 mm. The OPUS software accompanying the FTIR was used to determine the peak absorbance.

3.8.2 Oil and Grease Analysis Procedure

The procedure used to determine the oil and grease concentration of the samples was drawn from that of Standard Methods 5520C. Approximately 1 L of PW sample was collected in a clean, solvent rinsed bottle. The filled bottle was weighed using a Sartorius ED 224S analytical weighing balance. The sample was acidified to a pH below 2 using 1:1 HCl and refrigerated in order to preserve it. The refrigeration was necessary if the analysis was not to take place immediately after the sample was drawn.

The sample was poured into a 2 L separatory funnel, and the empty bottle weighed. The empty weight was subtracted from the filled weight in order to determine the mass and volume of the PW sample.

As some sample was likely to remain in the bottle, 30 mL of solvent (PCE) was transferred into the bottle, which was then shaken in order to rinse the remaining sample. The contents of the bottle were then transferred to the separatory funnel. The funnel was shaken vigorously for 2 minutes, and then allowed to sit for 10 minutes to allow the solvent and aqueous layers to separate. After settling, the lower layer was collected and poured through a funnel containing Whatman 40 filter paper and 10 g of Na_2SO_4. This process was then repeated two more times.

The 3 extracts were collected into a 100 mL volumetric flask. The filter paper and Na2SO4 were rinsed with approximately 10 mL of solvent, and the resulting rinsings were added to the flask. The volume of the extract was made up to 100 mL using additional solvent.

A portion of pure solvent was transferred to an IR cell. The IR was used to take a reading between 3200 and 2700 cm-1 in order to establish a baseline. The sample extract was then transferred to the cell and scanned. The peak absorbance near 2930 cm^{-1} was determined.

While this method calls for trichlorotrifluoroethane as a solvent, this substance is a banned CFC and was thus unobtainable. Instead, tetrachloroethylene was substituted. Tetrachloroethylene is non-volatile, infrared transparent, and was found to be a suitable replacement for trichlorotrifluoroethane in this method (Farmaki *et al.* 2007).

During the testing period, select samples were sent to Maxxam, an analytical laboratory, for comparison to tests performed at Dalhousie. While the tests performed at Dalhousie utilized the Standard Methods procedure, tests done by Maxxam utilized methods drawn from the United States Environmental Protection Agency (EPA). As Maxxam was not instructed to use a particular method, for measurements taken by Maxxam, the 5520 Standard Method was not used. Maxxam samples were typically taken at the same time as in-house samples, so they could be compared directly.

Concentrations of oil and grease and hydrocarbons were reported in parts per million (ppm). The equivalent SI units for ppm was mg/L, referring to the mass of compound, be it oil and grease, or hydrocarbons, per litre of liquid. Each monitor and both the Dalhousie and Maxxam labs reported concentrations in these units.

3.9 Analysis Terms and Definitions

The monitors being tested in this study were to be compared by four categories: accuracy, precision, reliability, and maintenance requirements. As the goal was to determine which monitor exhibited the highest ranking of these categories, a ranking system was first necessary to be developed.

For the purposes of this research, ranking the monitors for highest accuracy was defined using the general definition of accuracy. Over the course of testing, the monitors were to produce data describing the detected concentration of oil and grease, while the lab would test regular samples and determine actual concentrations. Each monitor was therefore to be ranked by the closeness of their readings to the actual concentration determined by the lab. This was determined by calculating the difference between the mean concentration read by the instrument and the actual concentration according to lab results. The absolute value of this difference was used.

Ranking the monitors according to precision require the collection of their output data and observing how close the majority of their readings approached a single value. This was to be done by determining the mean value of the data for a monitor during a single day, separating out the upper and lower quartiles of data, and observing how narrow the range between the quartiles was. This was to be visualized using box and whisker charts. In general, the monitor with the narrowest upper and lower quartile exclusion range was to be ranked the most precise for that day. In terms of calculation, the width of the box was the difference between the upper and lower quartile, so that value was used to quantify precision.

Reliability was defined, in terms of this research, as behaving the same way under the same conditions on an ongoing basis. For this factor, the unique response of a monitor to changes, and the periods before and after the changes, and comparing them for similarities was observed. If a monitor exhibited a predictable response to a change, even if that change was unique (such as a small increase in flow compared to a large increase), it was considered more reliable. The higher rank was given to the more reliable monitor.

Reliability was defined, in terms of this research, as the operational availability of a monitor. The operational availability was expressed as a fraction, and was based on the number of observed hours that a monitor was in service, the total hours of the project, and the required time spent on maintenance per each monitor. It was calculated using the following equation:

$$R = \frac{(T - T_m)}{(T_{tot})}$$

Where R was the reliability of the monitor, T was the observed time during which the monitor was in use, T_m was the time during which the monitor was undergoing maintenance, or was otherwise temporarily not in operation, and T_{tot} was the total time during which the system was in operation. All time factors were measured in hours, and the reliability factor was dimensionless. This equation was an interpretation of a similar equation, drawn from Elsayed (1996), and shown below.

$$Ao = \frac{Uptime}{Operating\ cycle}$$

Where Ao was the operational availability, in terms of an electronic system, the operating cycle was the time during which the system was needed to operate, and uptime was the actual observed time the system operated (Elsayed, 1996).

Maintenance requirements were ranked according to the number of times a monitor needed maintenance attention over the course of the testing period. The higher rank was given to the monitors that required less attention. In addition, if the maintenance required delicate attention, such as repositioning or exchanging a small part, or removing a part to be cleaned, effectively removing the monitor from service temporarily. Maintenance requirements were quantified simply by the number of times a monitor required maintenance. The lower the number, the higher the rank.

For each category, the monitors were ranked from 1 to 4, where 1 was the strongest representation of that category, and 4 the weakest. At the end of the study, the monitor with the highest rankings overall was determined. For posterity, the second to fourth highest ranked monitors were determined as well.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Small Jar Test Analysis

Figure 4.1 below shows the data collected over the testing period concerning the sample water temperature just after drawing the sample.

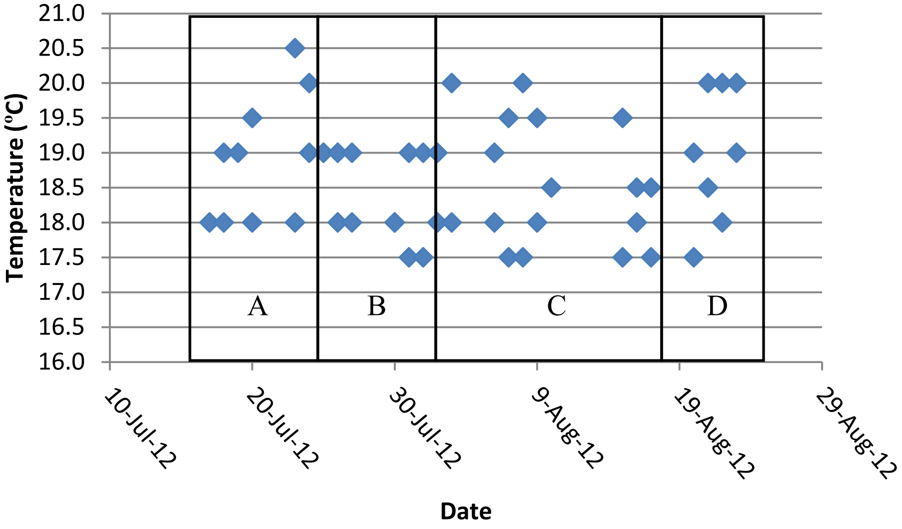

Figure 4.1: Temperature data recorded for small jar tests throughout the testing period. Blocked off sections indicate weekly variable testing periods; (A) flow, (B) gas and particles, (C) spiking, (D) heating.

The tendency of the temperature was to stay at ambient temperature, with small deviations. The average temperature was 18.65 degrees Celsius. As the testing period took place during the summer months, it was not unexpected that temperatures remained in the range shown.

During the final week of testing, heat was added to the system. Water heaters were placed in the small (T200) at varying heat intensities while the water was circulating. As shown by the data during the final week in Figure 4.1, adding heat to the system did not change the overall temperature of the system.

Figure 4.2 shows pH data taken from small jar water samples collected at each sample time.

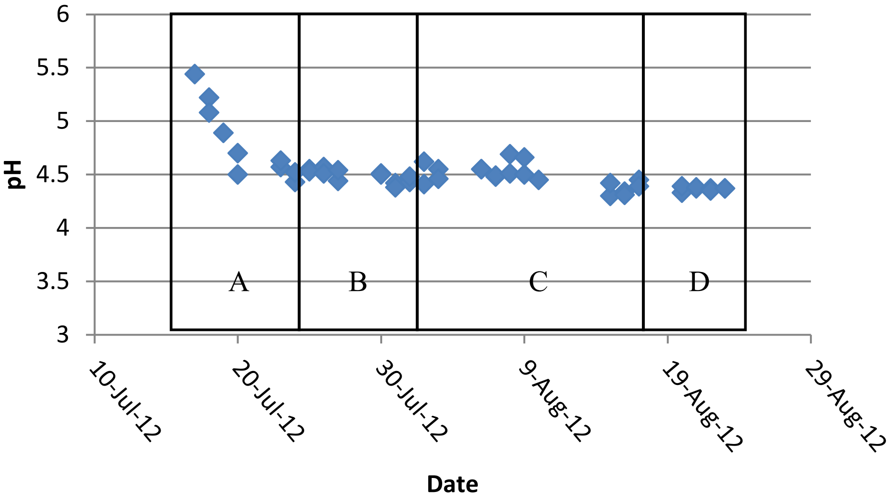

Figure 4.2: pH data recorded for the small jar tests during the testing period. Blocked off sections indicate weekly variable testing periods; (A) flow, (B) gas and particles, (C) spiking, (D) heating.

As shown in Figure 4.2 above, pH displayed two distinct patterns. During the first four days of testing, a rapid decrease in pH was observed, from 5.5 to 4.5. After this initial drop, however, the pH retained a much more gradual decreasing pattern, staying within 0.2 of 4.5.

Figure 4.3 shows the conductivity measured throughout the testing period.

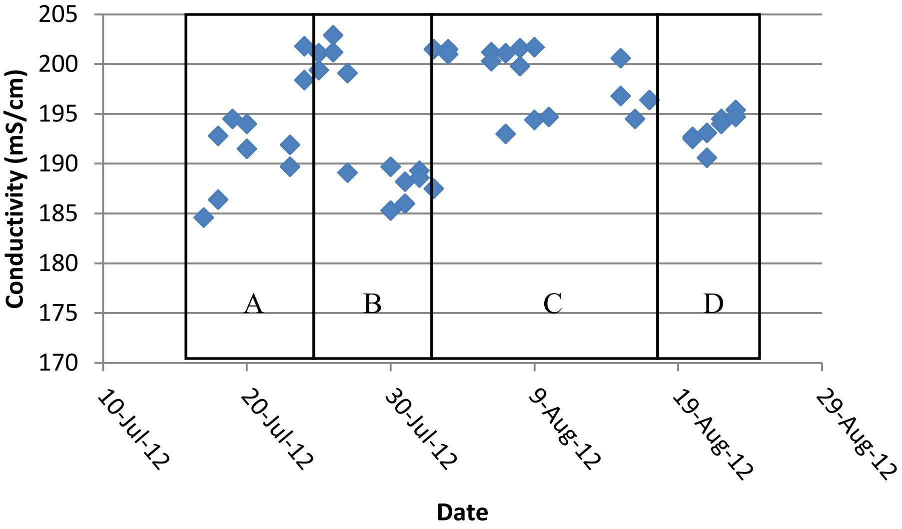

Figure 4.3: Conductivity readings taken in small jar tests throughout the testing period. Blocked off sections indicate weekly variable testing periods; (A) flow, (B) gas and particles, (C) spiking, (D) heating.

The range of values for conductivity was wide, extending from 184 mS/cm to 203, indicating that this was a typical produced water; produced water occasionally having conductivities as high as 300 mS/cm. There did not appear to be a significant pattern in conductivity data, although the range appeared to stabilize between 190 and 195 by the end of the testing period. Without further data focused on conductivity, concluding that heating the produced water correlated to this range was not possible.

Figure 4.4 below shows the results of the turbidity measurements over the course of the testing period.

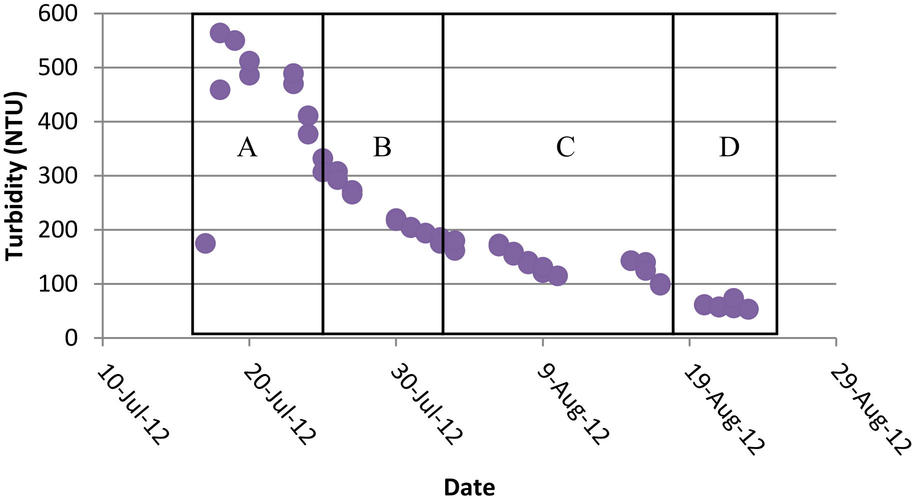

Figure 4.4: Small jar test turbidity data recorded over the testing period. Blocked off sections indicate weekly variable testing periods; (A) flow, (B) gas and particles, (C) spiking, (D) heating.

During the testing period, turbidity continually decreased. The rate of decrease was greater earlier in the testing period, but lessened after the first week.

Turbidity and pH both showed patterns of decrease over the course of the testing period. In general, their patterns were similar; decreasing rapidly at first, and then slowing for the remainder of the testing period. The similar patterns suggest there could be a link between the two factors, but where the turbidity declines more continuously over the course of the testing period and does not change abruptly (like the pH) further study would be necessary to draw a more defined conclusion.

Figure 4.5 above show the overall concentration results from the large jar samples taken throughout the project.

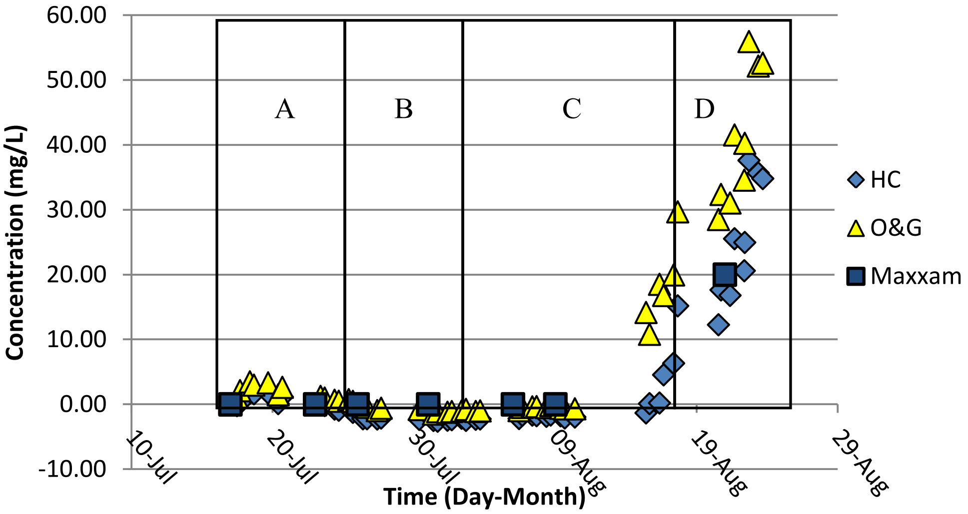

Figure 4.5: Oil and grease (O&G), hydrocarbon (HC), and Maxxam lab results for oil and grease. Blocked off sections indicate weekly variable testing periods; (A) flow, (B) gas and particles, (C) spiking, (D) heating.

The figure details both total hydrocarbon concentration (HC), as well as the oil and grease concentration measurements taken at the Dalhousie (O&G) and Maxxam labs (Maxxam). Both HC and O&G concentrations followed the same pattern throughout the testing period. This was as expected, since hydrocarbon concentration was determined using the oil and grease concentration lab result. According to the lab results, the initial oil and grease concentrations were low, and very soon after testing began, decreased to zero for much of the remainder of the testing period. Once the hydrocarbon spiking trials began, the concentrations began to climb rapidly. The results from Maxxam supported the Dalhousie lab results. They indicated that the water contained no, or undetectable oil and grease throughout the testing period until the spiking section began.

Table 4.1 below summarizes the lab results taken at Dalhousie with those taken by Maxxam.

Table 4.1: Collection of oil and grease, and hydrocarbon concentrations as determined by Dalhousie and Maxxam labs.

Date	Time	O&G (mg/L)	HC (mg/L)	Maxxam (O&G) (mg/L)
17/07/12	11:00	1.10	0.0	0.0
23/07/12	13:35	1.23	0.0	0.0
26/07/12	16:07	0.0	0.0	0.0
31/07/12	16:00	0.0	0.0	0.0
06/08/12	15:53	0.0	0.0	0.0
09/08/12	8:51	0.0	0.0	0.0
21/08/12	16:26	41.54	25.54	20.0

Table 4.1 describes and compares the lab results from both Dalhousie and Maxxam labs. As shown, the total oil and grease and hydrocarbon concentrations were minimal until the spike testing week began. At that time, the results did not agree with one another, but as a reminder, each lab used a different procedure to determine the concentration; Dalhousie used the Standard Methods 5520 procedure, where Maxxam used that of the EPA

4.2.1 Flow Testing Results of ASLSS

Figure 4.6 below, and many of the other figures to follow, show periods when the concentration reading from the ASLSS equipment jumped briefly from one level to another that was much higher. These spikes occurred at regular intervals, and at the same times across all the monitors. The spikes coincided with periods during which the second pump activated and was running, emptying the T200 tank of water back into the main (T100) storage tank. During this pump cycle, the pressure of the system changed from 13 psi to about 15 psi. The existence of these spikes coincided with the second pump running along with the increased pressure, and therefore, flow rate in the system, suggested that the monitors were sensitive to the rate of water flow.

The flow in the piping of the system varied between laminar, transitional, and turbulent, depending on the location in the system and the rate of flow. The type of flow was determined by calculating the Reynolds number using the following equation.

$$Re = (\rho \, v \, D_H)/\mu$$

In the equation, Re is the Reynolds number. The fluid density of the water is ρ. The fluid density was assumed to be that of seawater, 1025 kg/m^3. The velocity of the water, v, was determined using the flow rates in Table 3.2, and was calculated by dividing the volumetric flow rate by the cross sectional area of the pipe through which the water was moving. For this calculation, the cross section area was calculated using the equation for the area of the circle, using the pipe radii at various positions in the system. These radii measured 1 inch (0.0254 m) for the sections of steel piping, and 0.5 inches (0.0127 m) for PVC tubing. The hydraulic diameter, D_H, in the equation was 0.0508 m for the piping, and 0.0254 m for the tubing. Finally, μ is the dynamic viscosity, which was, again, assumed to be similar to that of seawater, 0.00111 kg/ms. Table 4.1 shows the Reynolds number as calculated within the piping and tubing, and at three general rates of flow.

Table 4.2: Calculated Reynolds numbers for three rates of flow within the two types of water transport pathways in the system.

Flow rate (L/min)	Steel Pipe	PVC Tube
2.0	770	1500
6.0	2300	4600
10.0	3800	7700

When the Reynolds number is calculated to be 2300 or less, the flow is laminar, and between 2300 and 4000, transitional, and above 4000, turbulent. As Table 4.1 indicates, the flow was laminar at lower flow rates, became transitional above 6.0 L/min in the pipe, and turbulent in the tubing, and became turbulent in the piping above 10 L/min.

Each of the upcoming graphs will also feature the lab results in terms of concentration and their time of withdrawal from the system. At times the lab results shown in the figures appear as a negative value. The reason for this is because the values are determined mathematically using values determined in the lab. For example, the hydrocarbon concentration was determined by subtracting a value from the oil and grease concentration. A negative value should be considered to be zero. Additionally, some figures will indicate samples drawn to sent to Maxxam for analysis. These points are shown in the same way as the lab samples taken in house.

Figure 4.6 below shows the data of the Advanced Sensors side stream (ASLSS) unit recorded on July 23, 2012.

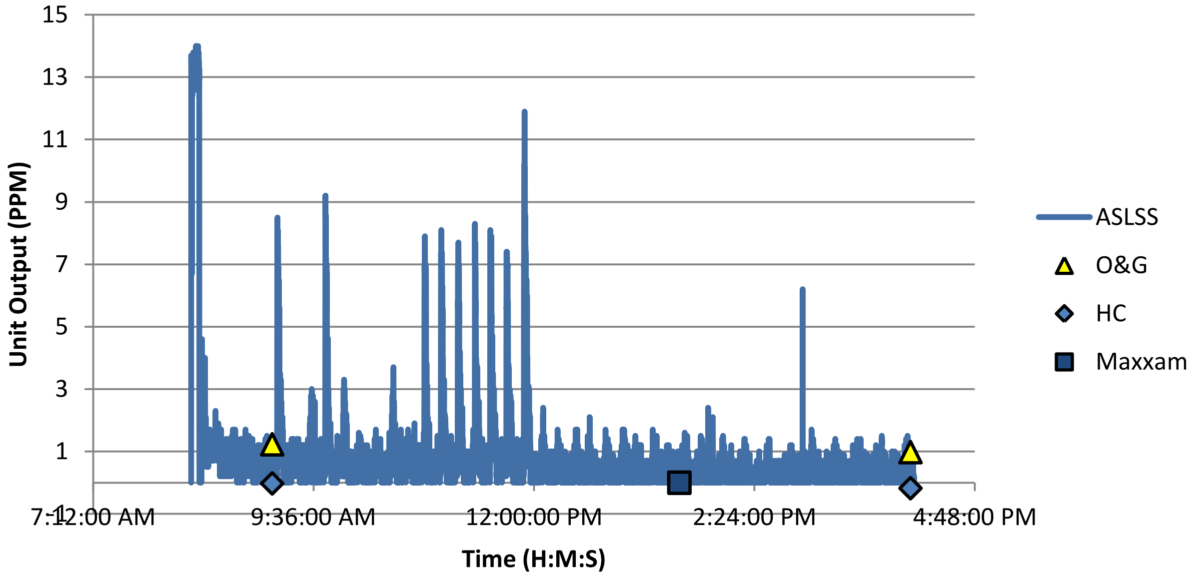

Figure 4.6: ASLSS flow test data for July, 23, 2012;flow increased from 21.20 L/min to 26.50 L/min at 11:53, and then was decreased to 10.60 L/min at 13:50.

Indicated on this graph, and each graph hereafter, is the output of the unit as well as the times at which samples were taken, which are shown as concentrations as determined by the lab. During this day, the flow to the side stream unit was increased from 21.20 L/min to 26.50 L/min at 11:53, and then was decreased to 10.60 L/min at 13:50 (refer to table 3.2). Throughout the day, the unit recorded data that retained a minimal value, which was consistent with the lab results, as well as Maxxam. From the beginning of operation until the increase in flow, the response of the unit to the pump cycle was to increase to a concentration value very high compared to the concentration otherwise. At the time of the increase, this pattern seemed to stop; the unit showed very little response to the pump cycle afterwards. At the same time, no change in the concentration was observed after the increase. 26.50 L/min was the highest flow rate sent to this unit. It was apparent that the unit was not sensitive to increases to the flow rate of such magnitude. Furthermore, increasing the flow to this level appeared to negate the effect of the pump cycle, stopping it from spiking.

Regarding the decrease in flow at 13:30, the purpose was to determine if there was a lower threshold of flow that would cause the unit to stop functioning normally. At the 13:30 timeframe shown in Figure 4.6, there was no apparent change in the response of the instrument to the decrease in flow. The evidence further suggested that the side stream unit was not sensitive to flow changes, whether increasing or decreasing. In order to make a further statement about the lower flow threshold, it was necessary to examine the data from a day in which the low threshold was tested.

Appendix A shows additional data recorded for the ASLSS monitor during the week of flow. Significantly, a change made to the flow to the monitor on July 24, 2012, reduced the flow to the monitor to zero. The response of the unit was insignificant, indicating further that it was insensitive to flow changes.

4.2.2 Flow Testing Results of ASL Probe

Figure 4.7 shows the data collected during July 23, 2012 by the Advanced Sensors probe unit.

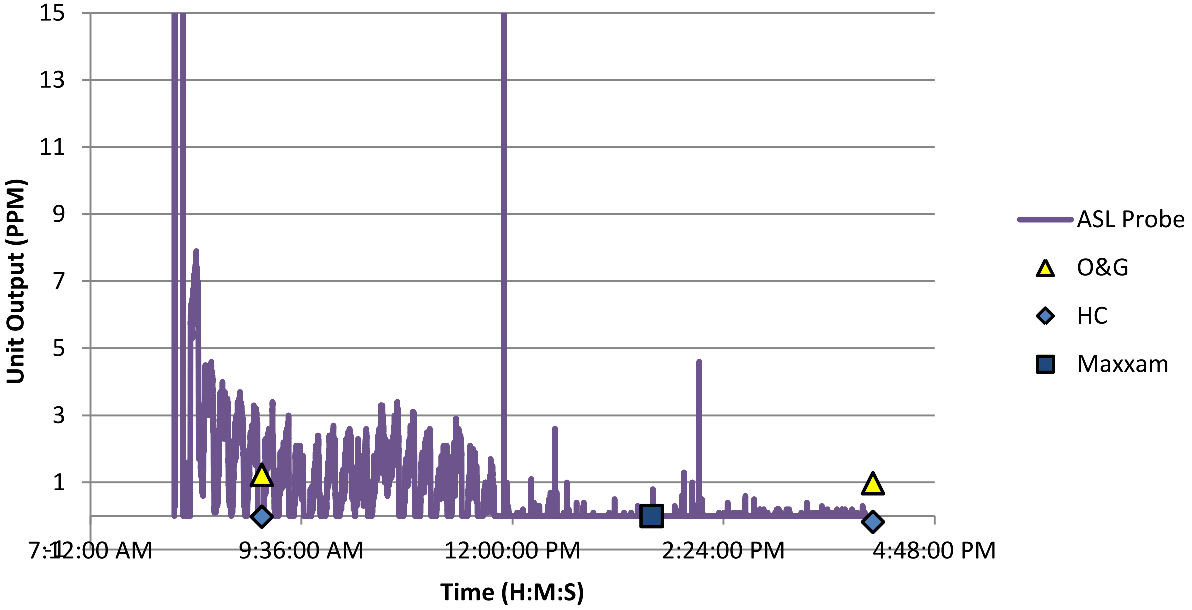

Figure 4.7: Flow testing data for ASL Probe on July 23, 2012; flow increased from 21.20 L/min to 26.50 L/min at 11:53, then decreased to 8.48 L/min at 13:50.

During this day, the flow to the probe unit was changed twice throughout the day. At 11:53, the flow was increased from 21.20 L/min to 26.50 L/min, then, the flow was decreased from that value to 8.48 L/min at 13:50. At 11:53, the unit responded by showing decreased readings of concentration. The readings reduced to a minimal value, centered on zero. For the remainder of this period, before the next change, the unit read values at zero, but showed the spikes associated with the pump cycle.

At 13:50, the flow was reduced a great deal, to 8.48 L/min. The probe showed no response to this change, which was unexpected. As increasing the flow resulted in a decrease in concentration, as detected by the unit, it was thought that decreasing the flow again would cause the unit to revert to a previous state and read higher concentration. This did not happen, although it should be noted that there was no reason to believe that the underlying factor (the gradually decreasing concentration reading) did not continue to occur while the unit was reading a concentration of zero at higher flow rates. Based on a projected pattern estimate, the gradual decrease of the concentration reading would have placed the line on the graph in Figure 4.7 at zero at approximately 13:00.

Appendix A shows additional data recorded for the probe unit during July 24, 2012. During the flow testing that followed, the probe unit demonstrated responses that were unexpected. When the flow to the unit was shut off, the response was to read values that were erratic and steadily increasing, relative to when the flow was on. Additionally, when the flow was raised to its highest rates tested, 21.20 and 26.50 L/min, the response of the probe was to drop readings to a minimal value. This evidence supports the belief that the probe was sensitive to flow rate changes.

Some factors of the response of the probe to the flow being shut off were not unexpected, given the positioning of the probe. The probe head was inserted into a pipe that was lying on the floor. Once the flow stopped, any water that was in that pipe would stop moving and settle at the lowest gravitational point, at which point, also, the probe head was located. Thus, the probe would continue taking measurements of this water. This does not, however, explain the continued pump cycle response. It was not expected that the pressure change brought about in the system by the second pump would, apparently, continue to affect water that was not moving.

It is important to recall that the pump cycle was not the only cycle progressing within the system. Both of the Advanced Sensors units employed an ultrasonic cleaning cycle periodically as part of their self-maintained maintenance functions. The function of the cleaning cycle was to ensure that the sensor heads were clean. The ultrasonics would vibrate such that any material sticking to the sensor head would be removed. This would also vibrate and affect the water surrounding the sensor head, applying a shearing force to the oil droplets, which could have been the cause of the increase in concentration. In addition, it is possible that the ultrasonic cleaning cycle could have caused the erratic patterns while the flow was shut off, coinciding with, and mimicking the pump cycle effect. This was conjecture, though, as the timing of the cleaning cycle was not recorded. In addition, the pump cycle, while the second pump was active, lasted several minutes, while the cleaning cycle lasted only a few seconds at a time. As such, it was unlikely that the cleaning cycle was effectively mimicking the pump cycle.

4.2.3 Flow Testing Results of Arjay

Figure 4.8 below shows the data recorded during July 20, isolating the Arjay unit.

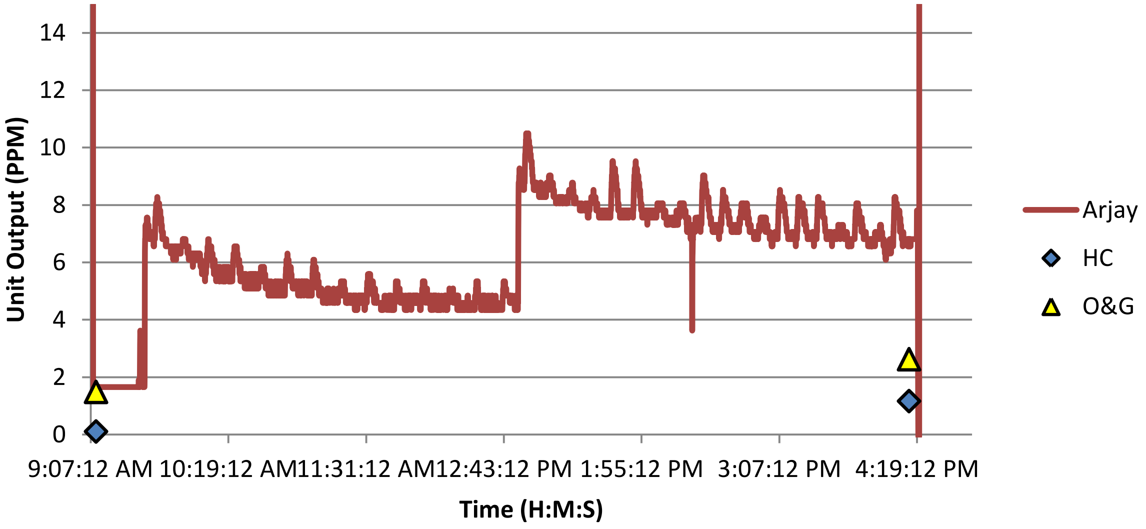

Figure 4.8: Flow test data recorded for Arjay, July 20, 2012; flow increased from 4.24 L/min to 8.48 L/min at 12:50.

At about 1:00 PM, the Arjay unit was discovered to have uneven flow over its flow plate. As the unit can only function properly under uniform flow over its flow plate, it was required that the flow to the unit be increased. When the flow was increased from 4.24 L/min to 8.48 L/min, the monitor output responded with the jump in apparent concentration shown in the graph. This direct response in monitor output to a change made to the flow rate, along with the spikes associated with the pressure change in the system, indicates that the Arjay monitor produces output that is strongly influenced by flow rate.

Additional figures detailing the Arjay during flow testing are shown in Appendix A. The Arjay was found to have an upper functional limit of flow of 10.60 L/min, as the unit was found to experience internal overflow of its flow plate at and above that flow rate.

It was known at this point that the amount of flow to the Arjay influenced the concentration that it detected. It was also known that there was a gradual decline in flow through the system throughout the testing period. Though the cause of the declining flow was unknown, it was clear that the phenomenon had an effect on all the instruments.

4.2.4 Flow Testing Results of Sigrist

Figure 4.9 below shows the data collected during July 19, 2012.

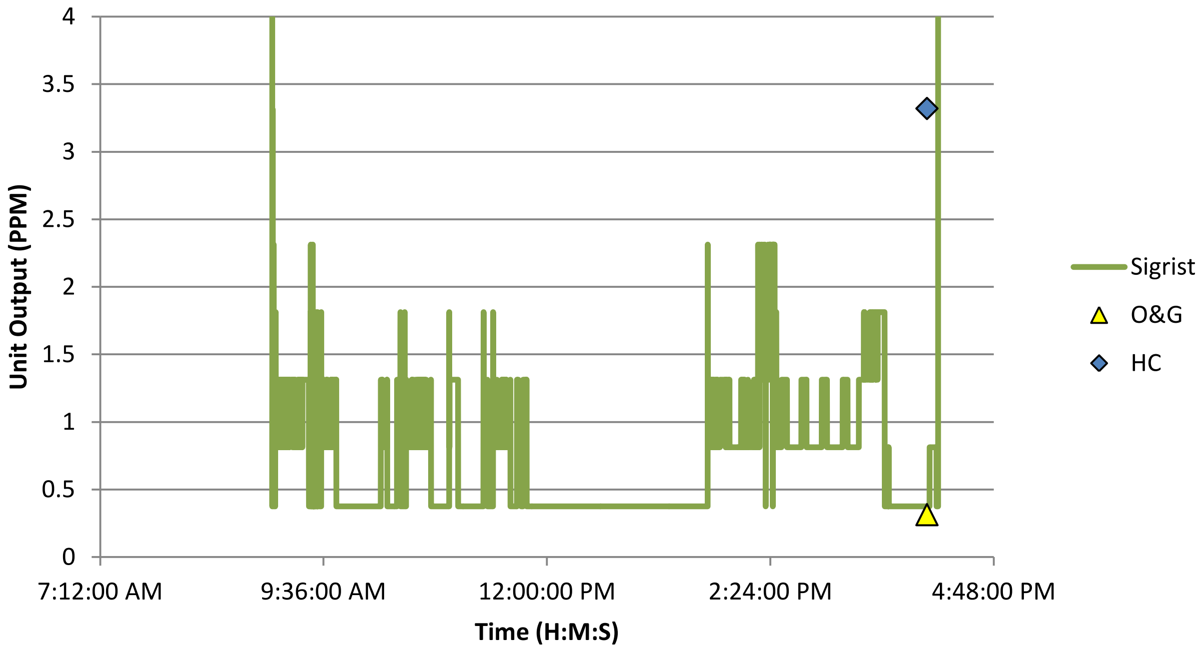

Figure 4.9: Flow data recorded for Sigrist unit on July 19, 2012; flow decreased from 6.89 L/min to 6.36 L/min, then to 4.77 L/min at 15:35.

During this day, the system was shut down for a period of time from approximately 11:45 until 13:45 to investigate a problem. The graph shows this period as a long, flat line. Otherwise, the unit displayed a steady value of about 1 ppm. It is notable that the readings did not drop to zero while the system was shut off, even though there was no flow. However, the value at which the concentration rested during this period was, in view of the activity of the rest of the day, the minimum value.

During this day, a single change was made to the flow through the Sigrist unit. At 14:27, the flow to the Sigrist unit was increased from 6.89 L/min to 8.48 L/min. The unit responded in two ways. First, there was a spike in concentration, heavier than those associated with the pump cycle, and larger in magnitude. Second, the water entering the unit overflowed and backed up into the de-gas tube above the unit. This signified that the unit could not function properly at this flow rate. The de-gas tube must be kept clear in order for the unit to function reliably. While it may not necessarily affect the readings of a given instrument, the flooding of the tube prevents excess gases from being removed from the unit. This did not affect the system at the pilot scale, but in industrial practice, it is a requirement for safety reasons, and thus was considered when determining the optimum functioning range.

The flooding of the tube was almost immediately visible, therefore the flow rate was reduced quickly back to 6.36 L/min. As such, the response to the increase, as shown in the figure, was very brief. That being said, it was indicated that the upper functional flow rate limit of the Sigrist unit was within the range of 6.36 and 8.48 L/min. In addition, an easily recognizable visual cue was discovered (the flooding of the de-gas tube) that identified the upper limit.

Additional figures showing the data recorded for the Sigrist unit are shown in Appendix A. It was observed that if the flow reached a lower limit of 4.24 L/min, the flow through the unit would become uneven, resulting in sporadic readings. When this reaction was observed, the flow to the unit was increased to 6.36 L/min to avoid the uneven flow. When the flow was increased to 8.48 L/min, the upper functional limit of the unit was observed, signified by the flooding of the de-gas tube equipped to the unit, when this reaction was observed, the flow was immediately decreased to 6.36 L/min.

Unlike the other units, the Sigrist did not show, graphically, a gradual decrease in concentration. It was subject to the same decrease in flow rate as a result of the back pressure loss, but, while the readings of the other units, correlating concentration with flow rate, decreased over time, those of the Sigrist did not. Because there was obviously a response to the pump cycle, it was suggested that the unit was sensitive to flow rate changes, so it was unexpected, when considering the other units, that the Sigrist did not reflect the decline in flow in its concentration readings. It could be guessed that the nature of the design of the unit, a free fall water flow design, which was unique among the other units, was related to the cause. The Sigrist was not unaffected by the gradual decrease in flow, however. Rather, it was observed in the unit through other ways.

4.2.5 Gas and Particulates Testing Results for ASLSS

Figure 4.10 below shows the output of the side stream unit for July 26, 2012.

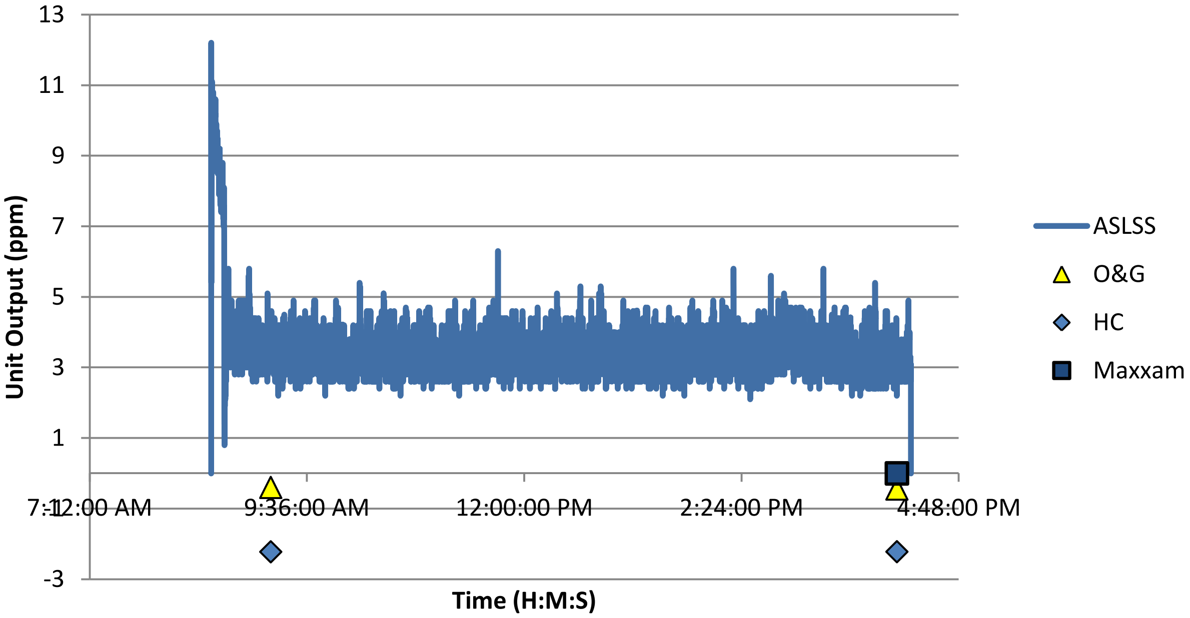

Figure 4.10: ASLSS data output for July 26, 2012, gas addition. Gas added increased from 300 L/hr to 600 L/hr at 15:00.

During this day, the gas added to the system was performed using two aquarium pumps. At the start of the day, two dispensers on one pump were used, adding 300 L/hr of gas (150 L/hr per dispenser). Then, at 15:00, the second pump was added, with both its dispensers contributing gas, for a total of 600 L/hr of gas addition.

The concentration reading retained a constant value throughout the day, above the concentration indicated by the lab. There was no significant response by the unit to the change in gas addition. This suggested that adding gas to the system did not affect the readings of the side stream unit.

Figure 4.11 below shows the data collected for the side stream unit on July 30, 2012.

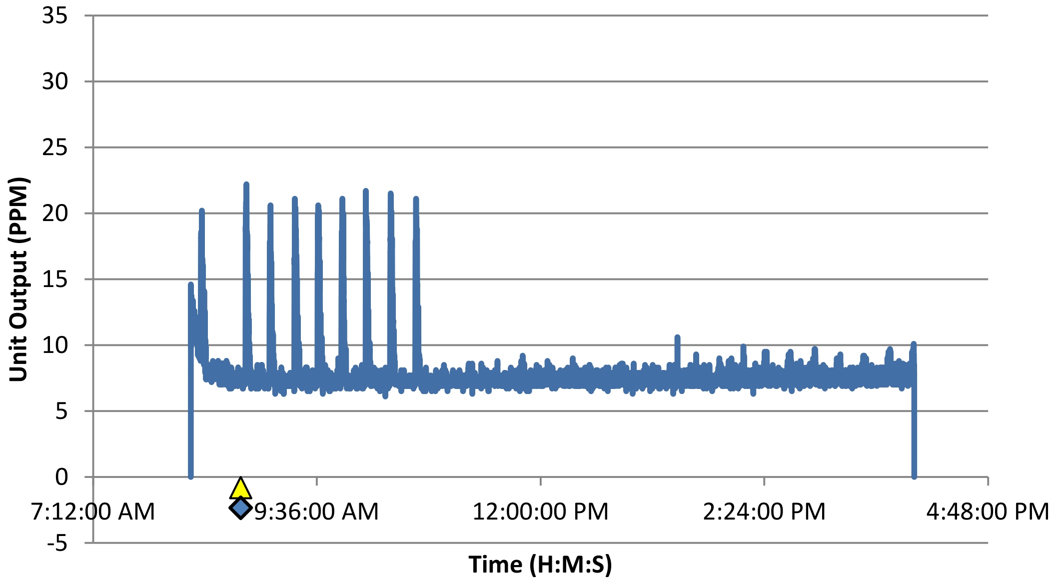

Figure 4.11: ASLSS response data to addition of sand, July 30, 2012. 15 mL added at 9:10, then 15 mL at 10:23, then 30 mL at 14:00.

Sand was added to the system three times during this day. At 9:10, 15 mL of sand was added to the system, then another 15 mL at 10:23, and finally 30 mL at 14:00.

Once again, the side stream showed an average concentration reading that was constant, but again greater than the actual concentration. The average reading was approximately 7 ppm. There was no visual response to the sand dosing that was consistent with all three times of sand addition. The sand did not appear to affect the readings of the unit.

After the sand was added, it was observed that, rather than circulating throughout the system, much of it was settling on the bottom of the T200 tank. If this was an indication that the sand was not moving through the system, and therefore the monitors, it suggests that the performance of the monitors was not influenced, as intended, by the addition of sand.

An additional figure showing the addition of sand and gas is shown in Appendix A. Both gas and sand were added to the system during this day. First, 15 mL of sand was added to the system while one aquarium pump, running both dispensers, was active at 9:15. A second, larger dose of sand (30 mL) was added under this condition at 10:48. At 14:27, the second pump was activated, using both its dispensers. Shortly after, at 14:38, a dose of sand of 15 mL was added to the system.

The average response of the side stream unit throughout the day was uniform.It is noteworthy that the unit showed an increase in concentration, on average throughout the day. The spikes associated with the pump cycle also were greater in magnitude than in previous days. Unlike on July 30, the pump cycle spikes occurred throughout the entire day, and typically reached values in excess of 20, with a few exceptions. It is also noteworthy that the gradual decline in concentration effect seen in previous days was not apparent on this day.

The side stream unit exhibited little to no direct response to any changes made during this day. No visible response was observable when the additional pump and dispensers were added, nor were there any changes at the times of the sand doses. Based on this data and that of the previous four days, the only changes apparent were that the decline in concentration associated with the gradually decreasing flow was not observed, and the average concentration as read by the instrument was incrementally greater on each day.

Though there were no immediate responses by the instrument to the changes being made, it is possible that the incrementally increasing concentration reading every day was, itself, an effect of the changes being made during this week of testing. This pattern was not apparent during the week of flow testing, and, while there were small variations in the average concentration readings, they were not as large in magnitude as those occurring during this second week.

During this week of testing, sand was added in doses and gas was added at various rates, but not always simultaneously; there were times when sand was added without gas being added, and vice versa. The incremental increase in concentration as read by the instrument was consistent throughout the week, though. It is not clear if this effect was as a result of the sand or gas additions, or as a result of some other variable that was not known or controlled.

4.2.6 Gas and Particulates Testing Results for ASL Probe

Figure 4.12 shown above shows the data collected for the probe unit during July 25, 2012.

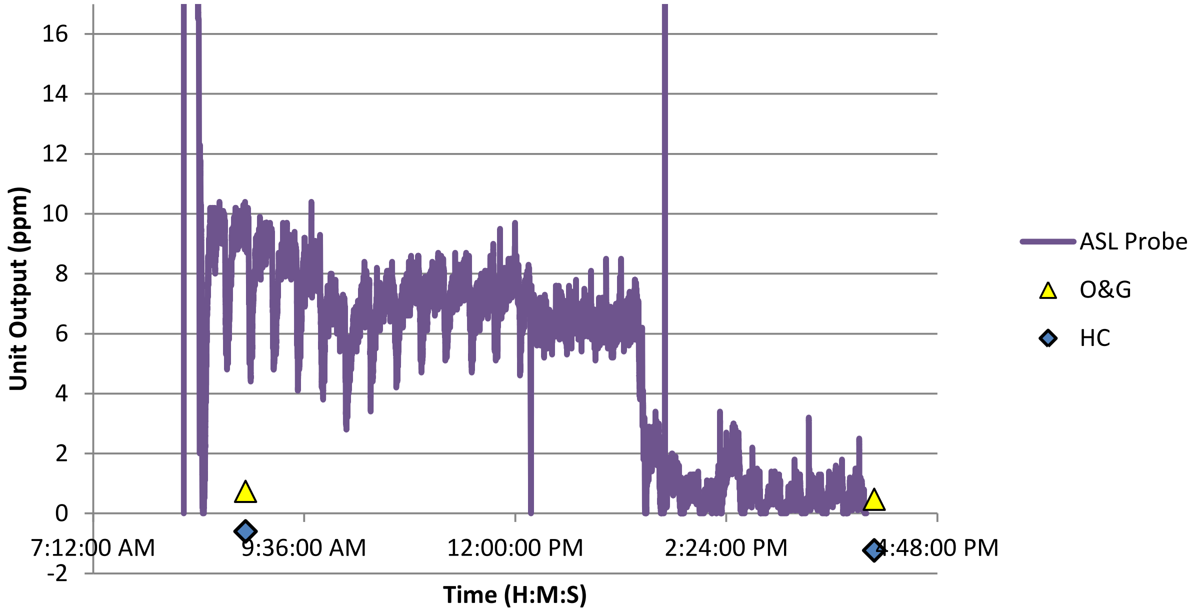

Figure 4.12: ASL Probe data recorded on July 25, 2012, gas addition. Gas added at 150 L/hr starting at 13:30.

The only change made to the system during this day was to activate one aquarium pump with a single dispenser active, adding 150 mL/hr of gas. This change was made at 13:30.

The Probe behaved similarly to its behavior during the week of flow testing: it reflected the pump cycle with downward spikes, and, throughout the day, the concentration readings slowly declined while a wave-like pattern emerged. The actual concentration reading varied between about 10 and 6 ppm, with the spikes reaching below 3 ppm.

The response of the probe at the time of the aquarium pump activation was to quickly drop in the reading to about 2 ppm and lower. The pattern of the unit then continued from that point, decreasing in concentration reading to 0. The response of the unit suggests a sensitivity of the probe unit to gas.

Additional figures showing the probe response to gas, sand, and both gas and sand additions are shown in Appendix A. In each case, the probe showed responses were not reflective of significant influence by the sand or gas. However, it did demonstrate responses that were inconsistent with what was observed in Figure 4.19. For example, on July 26, it did not respond in a comparable way to the gas addition than it did on July 25. In addition, the probe seemed less sensitive to the variables being tested, but more responsive to the pausing and resuming of the system when those variables were altered. This suggests an insensitivity to sand and gas, potentially and partially due to the observation with the ASLSS that the sand was settling and not moving through the system was much as was intended.

A notable observation about the readings of the probe on later days was that it was reading a much higher concentration than previous days. In addition, certain aspects of what had become typical of its behavior were not apparent, such as the gradual decline in concentration, and the consistent inverted spikes during the pump cycles. On July 30, the average concentration remained, approximately, at 23 ppm throughout the day, but this was a jump from approximately 9 ppm from the previous day.

At the end of the week of gas and particles testing, the probe was discovered to have a severe leak in its outer casing. The leak was such that produced water droplets would spray out through the opening when the unit performed its cleaning cycle. For this reason, the probe was deemed unsafe to continue testing, and was deactivated for the remainder of the testing period. As this leak was discovered after it had formed in the unit, and was present during the two weeks of testing conducted already, it was possible that the readings of the unit were affected. Though it is unknown, it is a possibility that the daily increase in concentration readings could have been as a result of the leak.

4.2.7 Gas and Particulates Testing Results for Arjay

The data recorded on July 25, 2012, is shown below in Figure 4.13.

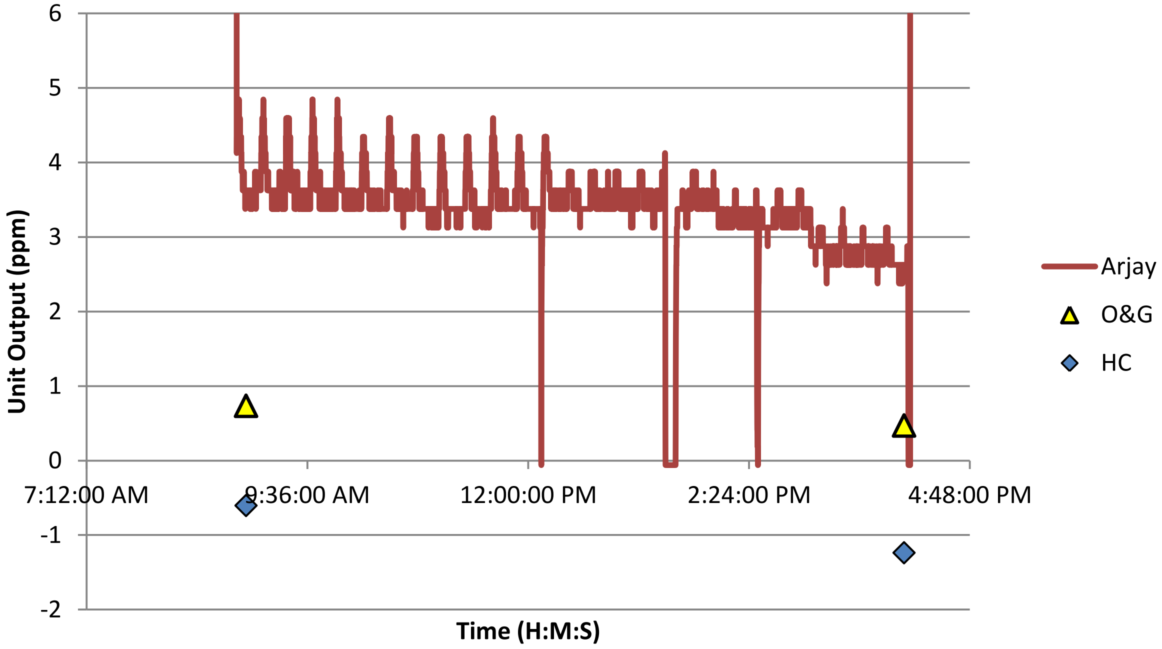

Figure 4.13: Arjay data recorded on July 25, 2012, gas addition. Gas added at 150 L/hr starting at 13:30.

An aquarium pump utilizing a single dispenser added gas, beginning at 13:30. The system was paused while the pump was installed.

The Arjay unit showed a slight decline in concentration reading throughout the day; the decline was more steep in the latter half of the day, after the aquarium pump was activated. The average concentration reading began at about 3.5 ppm, and decreased to 2.5 ppm by the end of the day. The pump cycle spikes were greater in magnitude until approximately 12:00, after which they became much smaller. There were two cases of inverted spikes, the first of which occurred at approximately the same time as when the pump cycle spikes decreased in magnitude. The cause of such a spike is unknown, although they may have been associated with a brief variance in flow rate.

Appendix A shows additional figures detailing the Arjay data in response to sand and gas added to the system. The Arjay unit showed little response to the pumps at the times of their activations. This suggests that, in the short term, the unit was not sensitive to gas being added. As it was known, at this point, that the Arjay was sensitive to flow rate changes, it was possible that the response of the unit upon resuming the system after installing the second pump was a result of the pause and not the gas addition.

There was no observable response to the sand doses while the single aquarium pump was active, suggesting insensitivity to both factors at that threshold. In cases were the second pump was included, the readings decreased steadily until they reached 1.5 ppm. This suggests either that the addition of gas at twice the previous rate or the system pause and resume resulted in the unit registering a decline in concentration.

4.2.8 Gas and Particulates Testing Results for Sigrist

Figure 4.14 below shows the July 25, 2012 data recorded by the Sigrist unit.

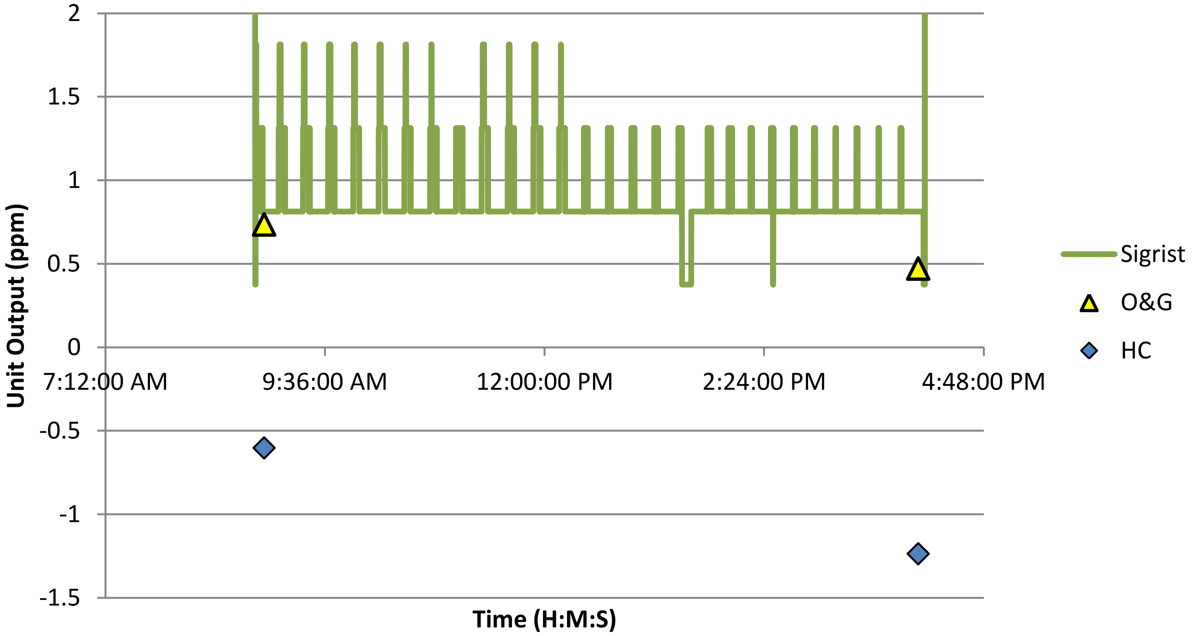

Figure 4.14: Sigrist data recorded on July 25, 2012, gas addition. Gas added at 150 L/hr starting at 13:30.

At 13:30, as the sole change to the system, one aquarium pump was activated with one dispenser active, adding 150 mL/hr of gas to the water.

Throughout the day, the Sigrist maintained an average concentration reading of about 0.8 ppm. The pump cycle manifested regularly with vertical spikes reaching 1.3 ppm, typically, but as high as 1.8 ppm during the first half of the day.

As the system was paused when the aquarium pump was installed, it is easy to see where the section during which there was gas addition began. After the gas addition began, the unit did not behave any differently than before, with the exception of a single inverted spike during one of the pump cycles. As it was isolated and inconsistent, it is unlikely that it was a result of the gas addition. This lack of a response indicated that the unit may have been insensitive to gas.

Appendix A contains several additional figures detailing the Sigrist responses to sand and gas. As no consistent response to gas or sand additions seemed to manifest, it was clear that the gas was having little to no effect on the performance of the monitor. Similarly, the sand was having no noticeable effect, or it was simply not moving through the system, as mentioned before, such that it was not impacting the instrument.

4.2.9 Spike Testing Results for ASLSS

The side stream data for August 7, 2012 is shown in Figure 4.15.

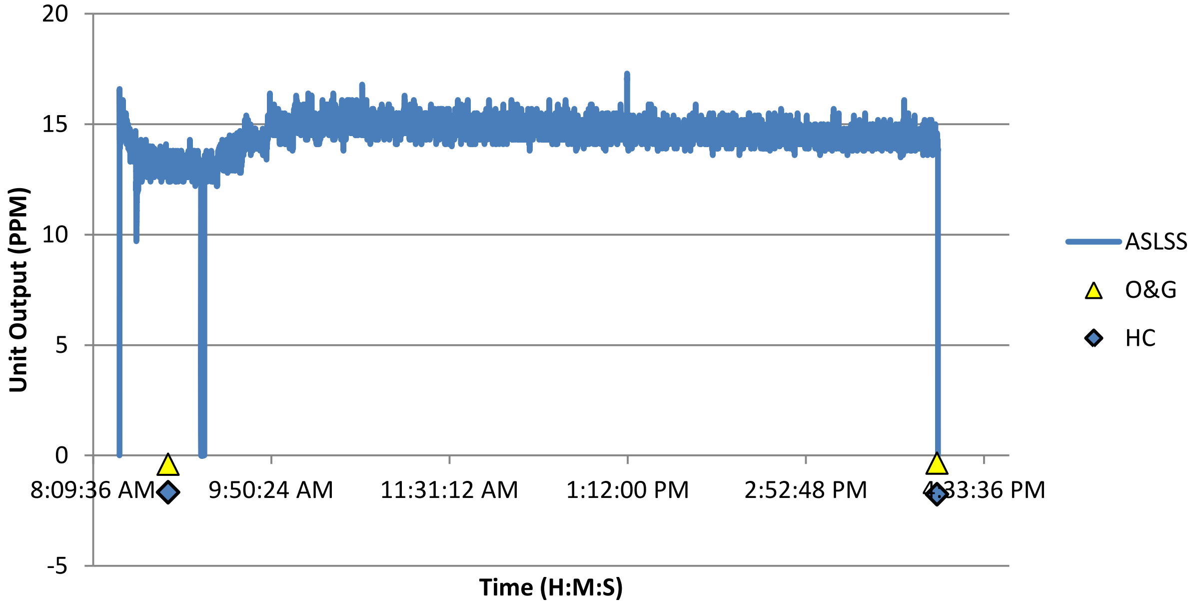

Figure 4.15: ASLSS data recorded for Aug. 7, 2012, condensate spike. 15 mL condensate dose at 9:10.

On August 7, 2012, a 15 mL dose of condensate was made to the system. The dose was made at 9:10, pausing the system to do so.

It was noted that, after the spike was made, the concentration as detected by the side stream unit jumped from about 12 to 15 ppm. The concentration remained at that level for the rest of the day, with only a slight decline. At this point, as the lab results were still saying that the concentration of oil and grease in the water was negligible, only the change in what the unit was reading was of interest.

Based on the calculated volume of the sample at this time (559.84 L), and the assumed density of the condensate (783.43 mg/mL), along with the dose volume, it was calculated that the approximate concentration increase to the system was 7 ppm. The side stream unit only detected an increase of 3 ppm. As the condensate was introduced to the water in a raw state, it may not have dissolved or mixed entirely with the water. As the calculation assumed one hundred percent dissolution, this could explain the low increase in concentration.

Shown below is Figure 4.16, which details the side stream response to spiking made on August 15, 2012.

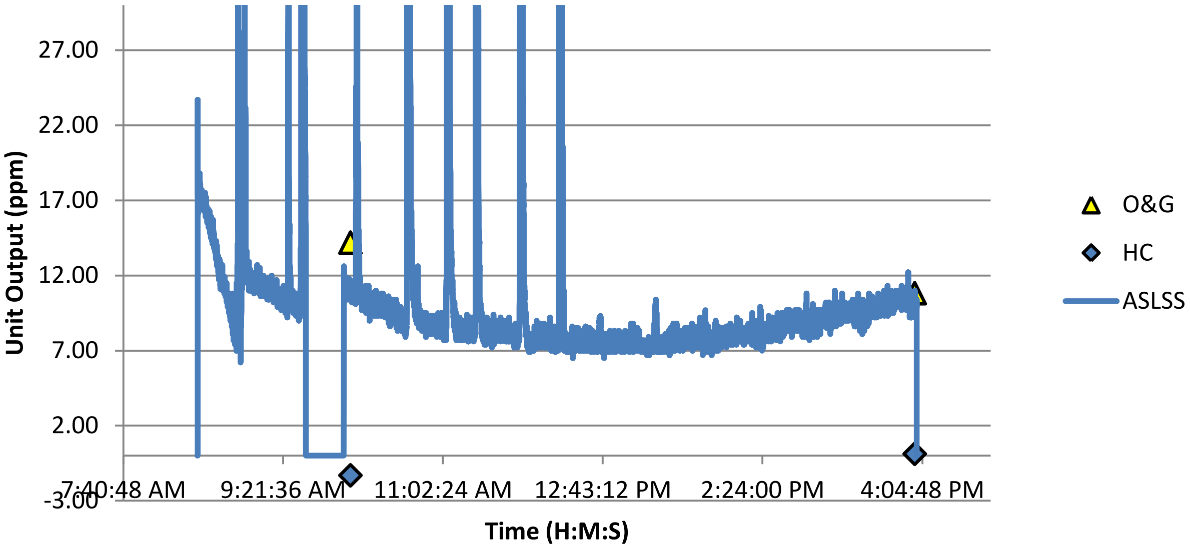

Figure 4.16: ASLSS data recorded on Aug. 15, 2012, condensate spikes. 100 mL condensate dose at 10:41, then 200 mL dose at 13:54.

On this day, the system began with 50 mL of the surfactant Triton-X, and a spike of 100 mL of condensate was added at 10:41, then another of 200 mL was made at 13:54. The system was paused when the first spike was added, but not for the second.

The purpose of the surfactant in the system was to determine if it, alone, would have an effect on the readings, and also if it would cause further dissolution of the condensate, which in turn would affect the readings. Given that the lab results for this day showed oil and grease concentrations of about 11 to 14 ppm, where, before, they showed negligible amounts, it was apparent that this was the case.

The side stream response for this day was a pattern not seen before by any of the units; starting at a high concentration, dipping down to a minimal of about 7 ppm, and then slowly increasing again. The pump cycle spikes were of great magnitude, but, as usual, were brief. The unusual response of the unit throughout the day could be explained by the fact that the condensate was added raw while the Triton-X was in the system. The condensate could have required enough time within the mechanical action of the system before dissolving enough that the units would detect the resulting increase in concentration. This would explain why, where the spikes were made during the first half of the day, the increase in concentration did not appear until the second half. This does not explain the decline in concentration apparent during the earlier hours of the day, though. During earlier weeks, a pattern of gradual decline was visible in the data, and the decline in Figure 4.15 could be that pattern again. The transition from decreasing to increasing concentration shown in the figure could be the decline pattern being overtaken in rate by the added concentration from the condensate.

4.2.10 Spike Testing Results for Arjay

Figure 4.17 below shows the Arjay data for August 3, 2012.

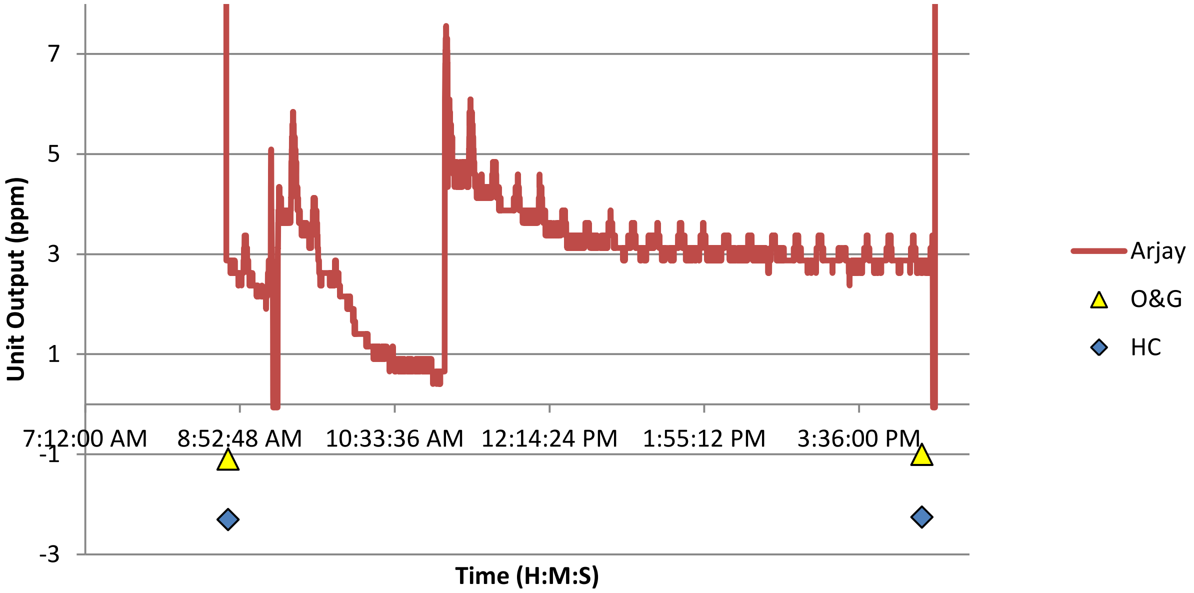

Figure 4.17: Arjay data for Aug. 3, 2012, condensate spiking. 5 mL condensate dose at 9:13.

A single spike of 5 mL of produced water condensate was made to the system. The spike was made at 9:13, and the system was paused to do so.

After the spike was made, the Arjay responded with a brief spike in readings, and then showed a steep decline until reaching a minimal value of about 0.5 ppm. At this time, it was observed that the unit was not receiving an appropriate flow rate, and the flow was boosted. This boost can be seen in the figure at the point just past 10:48. At that time, a spike in values similar to the spike after the earlier condensate spike was observed. After that, the readings declined slowly throughout the rest of the day.

The fact that the spike in readings associated with the increase in flow at 10:48 suggests ambiguity between the effect of the flow and the response to the condensate spike. As the system was paused to add the condensate, resuming the system also changed the flow to the unit from 0 to a positive rate. In order to observe a response to a condensate spike only, the spike would need to be made without pausing the system. It could also indicate that, in order to function optimally, the Arjay would need to receive an appropriate feed of water within its optimal range at all times.

Figure 4.18 shows the Arjay data for August 15, 2012.

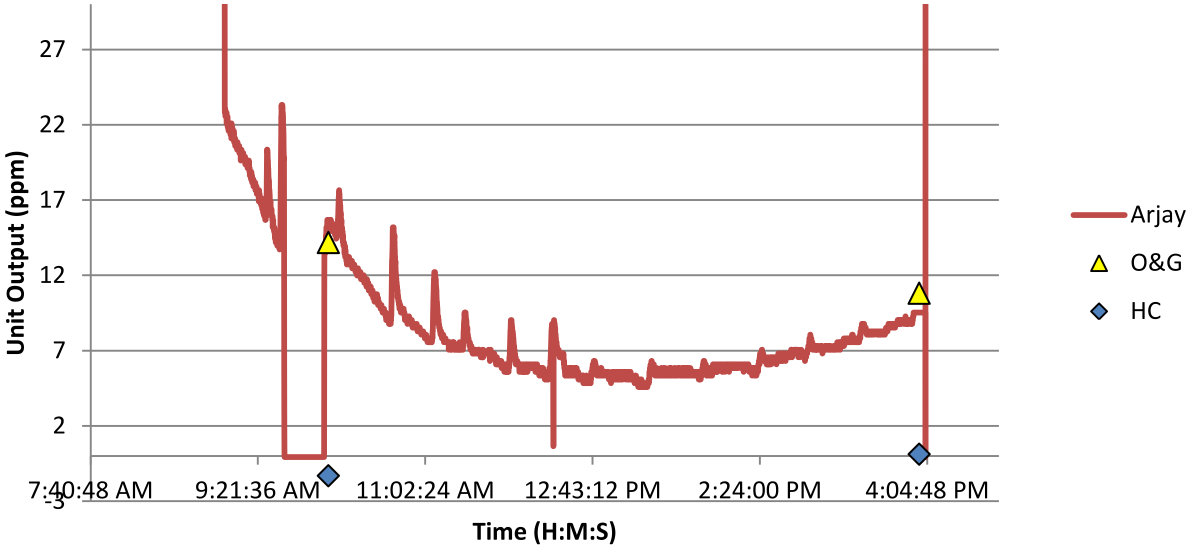

Figure 4.18: Arjay data recorded on Aug. 15, 2012, condensate spiking. 100 mL condensate dose at 10:41, then 200 mL at 13:54.

As mentioned earlier, there was Triton-X in the system during this day when the condensate spikes were made. There were two spikes were made. The first was made at 10:41 and was 100 mL. The system was paused for this spike. The second spike was made at 13:54, without pausing the system.

The response pattern of the Arjay was similar to that of the side stream unit, exhibiting a U-shape. It is noteworthy that the Arjay was highly accurate during this day with regard to the actual concentration, as determined by the lab. At the time of the second spike, there was no visible response by the Arjay. This suggests that the response on August 3 was related to the boost in flow and not the condensate being added. Also, as the pause in the morning did not result in a notable spike upon resuming the system, it suggests that the response on August 3 was isolated.

Given these results, it is indicated that the Arjay unit did not exhibit an acute response to condensate spikes made to the system. However, it does appear that it will detect an increase in concentration gradually. It is crucial that the optimum flow rate to the unit be maintained.

4.2.11 Spike Testing Results for Sigrist

Figure 4.19 below shows the data recorded by the Sigrist unit during August 3, 2012.

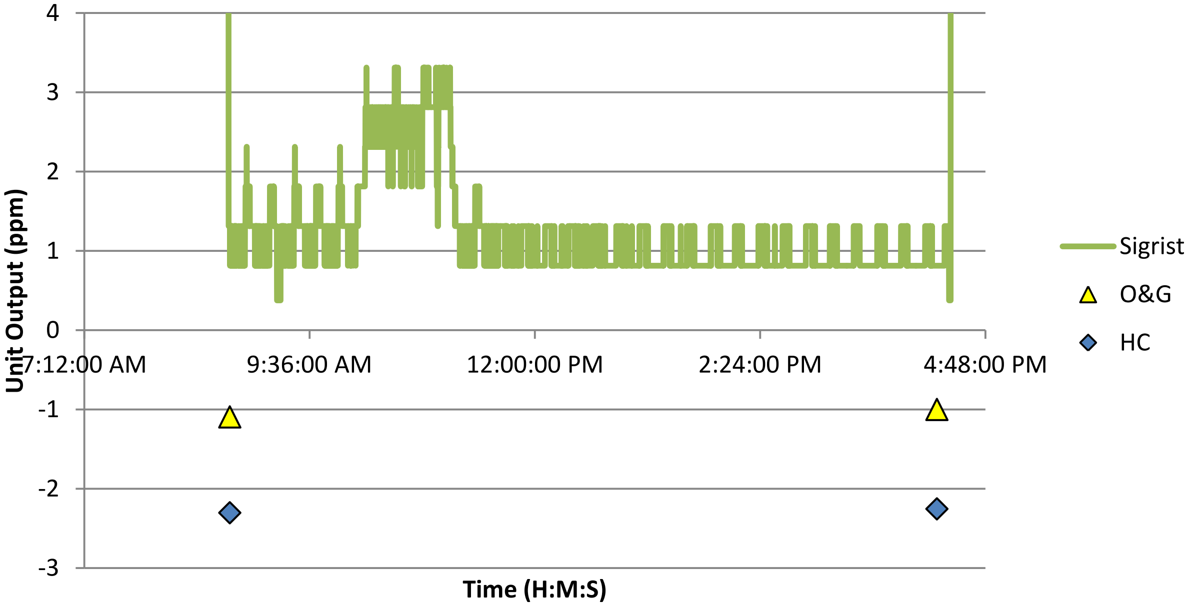

Figure 4.19: Sigrist data recorded on Aug. 3, 2012, condensate spiking. 5 mL condensate dose at 9:13.

During this day, a single dose of condensate was added. The condensate spike was of volume 5 mL, and was added at 9:13.

The Sigrist experienced a delayed response after the spike; at shortly after 10:00, the readings increased from an average of about 1 pp to 2.5 ppm. This elevated reading remained in effect until shortly after 11:00, when the value dropped back to where it was before. The unit did not show a permanent increase in concentration at this stage.

Figure 4.20 below shows the Sigrist data recorded on August 7, 2012.

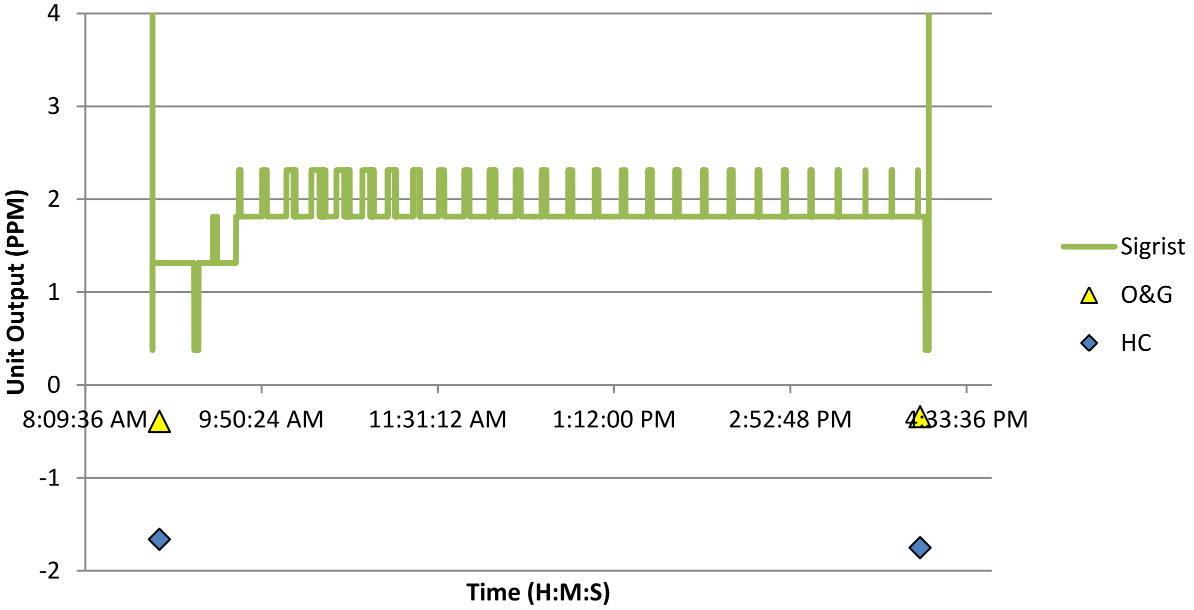

Figure 4.20: Sigrist data recorded on Aug. 7, 2012, condensate spiking. 15 mL condensate dose at 9:10.

At 9:10, a 15 mL dose of condensate was added to the system, pausing the system to do so.

As indicated by the graph, the Sigrist exhibited a response to the spike, though it was not immediate. The readings jumped, permanently, from 1.3 ppm to 1.8 ppm, on average. This jump occurred upon the second pump cycle after the dose was made, not unexpectedly, as the condensate needed to move to the larger sample tank via the pump cycle before it could be moved through the monitors. Though the jump was quite small, it was definitely noticeable. This change in concentration, unlike on August 3, was permanent, suggesting that the unit is able to both detect the acute effect of a spike, and is able to quickly respond to a change in concentration.

As with earlier, the expected increase in system oil and grease concentration was calculated to be 7 ppm, assuming a known volume of 559.84 L, a condensate dose of 15 mL, and a condensate density of 783.43 mg/mL. The actual increase detected was 0.5 ppm. Like the ASLSS side stream unit, this detected increase was much smaller than the calculated increase, but, again, as the condensate was added raw, it may not have had sufficient time to dissolve evenly throughout the system. As the calculation assumed full dissolution, it was possible that there was some error.

4.2.12 Heat Testing Results for ASLSS

Shown below in Figure 4.21 is the data recorded on August 20, 2012. During this day, the effect of heat on the produced water in the system was investigated. A single aquarium heater was used to add heat to the system by placing it in the smaller, T200 tank, through which all the water ultimately moved.

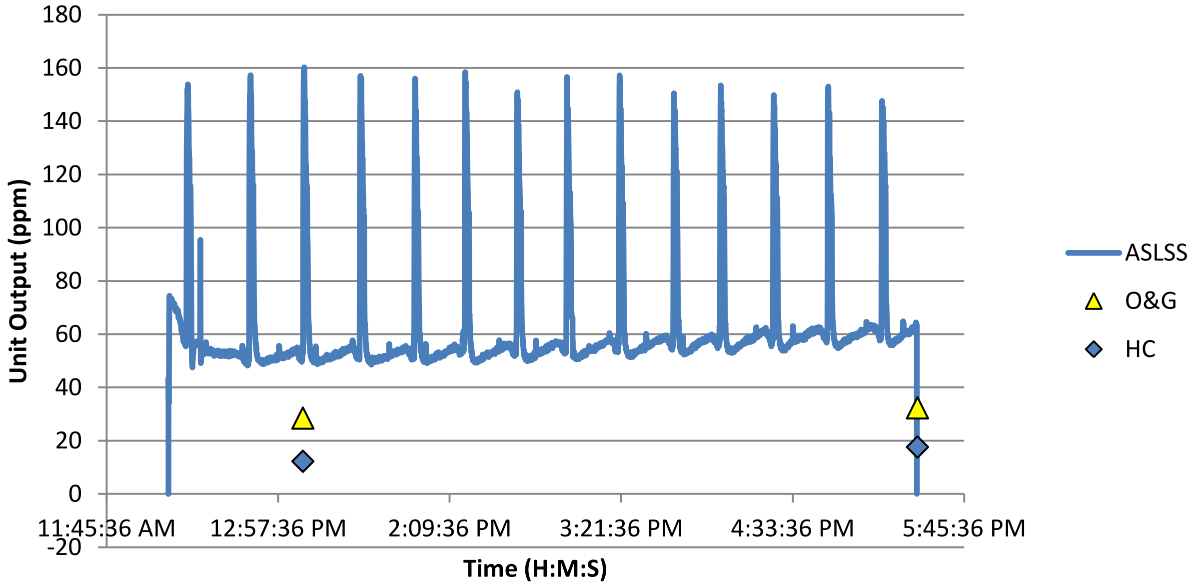

Figure 4.21: ASLSS data recorded on Aug. 20, 2012, heat addition. Heater at 50 % setting beginning at 12:23.

As shown in the figure, an effect from the previous week of spiking is shown, which is the very large increase in concentration of oil and grease in the water. The lab determined the oil and grease to be about 30 ppm, but the side stream unit read considerably higher than that. A noticeable effect during this day was the great magnitude reached by the pump cycle spikes, reaching well above 150 ppm. This effect was observed during the spiking week with this instrument, though, so it was surmised that these spikes were as a result of either the added condensate or the surfactant in the system, and not the heat. As the spikes were much greater than the previous week, though, the heat may potentially have had the effect of magnifying the spike response. Other than this, there was no observable acute effect of the heat on the system.

Additional figures showing the response of the ASLSS monitor to heating are shown in Appendix A. The pattern of the additional figures, August 21 and 23, was the same; very large pump cycle spikes, and a gradually increasing concentration reading.

The concentration of oil and grease in the system was increasing, as indicated by the lab results. As no further spikes of condensate were being added at this point, it was suggested that heating the system, even with a single heater, was causing the increase. It is possible that, even while the surfactant in the system was being retained, some of the condensate doses were not completely integrated into the water. In that case, it would seem apparent that the heating of the system may cause, or support, the further dissolution of materials into the water.

At this point, based on the volume of water, the room temperature, and the lab results, it was clear that the heaters were not affecting the overall temperature of the water. In addition, no further increase in oil and grease concentration was observed in the lab results. The side stream read a concentration of about 118 ppm, on average.

Assuming properties similar to seawater for the produced water: a specific heat of 4.006 KJ/kgK at 19^{o} C, and a density of 1025 kg/m^3 at the same temperature, and considering an approximate volume of produced water of 550 L, it was calculated that about 2258.4 KJ of heat was needed to raise the temperature of the water by 1^{o} K. This value was calculated using the following equation for heat.

$$Q = mc\Delta t$$

In the equation, Q is heat energy in KJ, m is the mass of the water in kg, c is the specific heat in KJ/kgK, and Δt is the change in temperature in degrees Kelvin (K).

Each heater was able to provide up to 200 W of power, indicating that a single heater at its maximum setting should have been able to raise the temperature of this amount of water by 1° in 11.3 seconds. This time decreases to 5.6 seconds when a second heater is included. Based on the temperature readings taken during the small jar tests, the temperature of the water sample did not raise an appreciable amount as a result of the heaters. As the system was open to the air and surroundings, it was apparent that it was losing heat at a rate equal to, or greater than, the rate at which it was being added, resulting in an ineffectual manipulation of the system temperature.

4.2.13 Heat Testing Results for Arjay

The data recorded by the Arjay unit on August 21, 2012 is shown in Figure 4.22. A single heater, at its maximum setting was used to heat the system on this day.

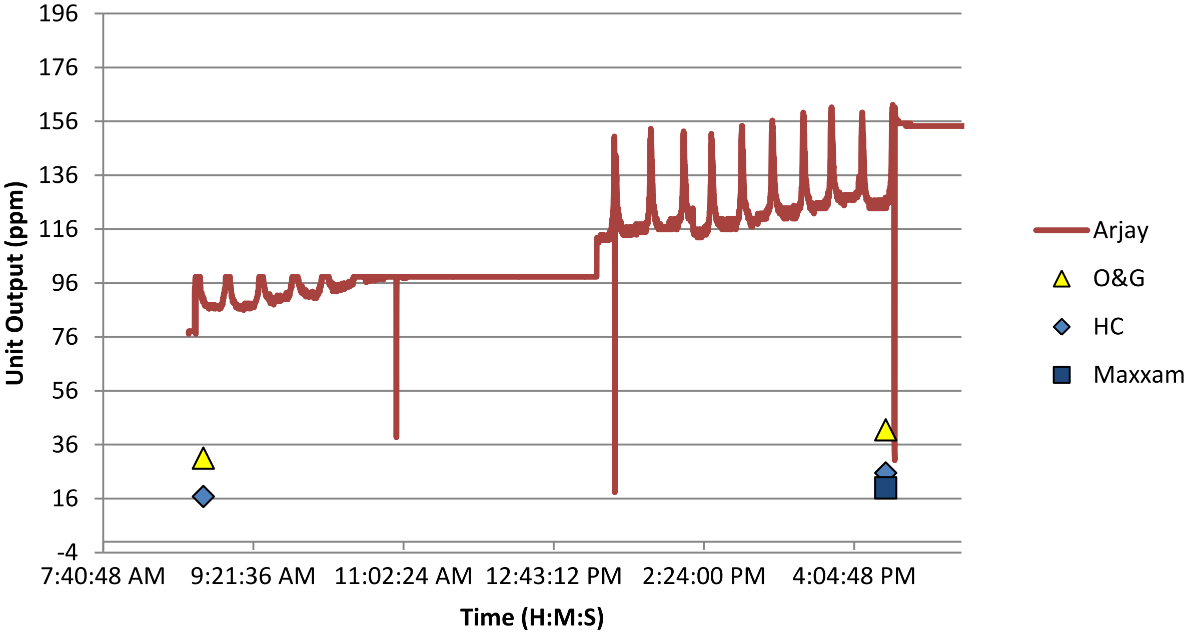

Figure 4.22: Arjay data recorded on Aug. 21, 2012, heat addition. Single heater at 100 % setting beginning at 8:15.

At 13:12, it was found that the maximum milliamp setting of the Arjay, 100 mA, was insufficient to measure the greatly increased concentration in the system. When the unit was first calibrated, it was set to correlate milliamps on a 0 to 100 scale to ppm on a 0 to 50 scale. As the concentration increased, it was required that the milliamp setting be modified such that the datalogger could report meaningful data. The unit reflected the same gradually increasing concentration reading as did the ASLSS unit. Similarly, no acute response to the heat was observed either.

4.2.14 Heat Testing Results for Sigrist

The below Figure 4.23 shows the data recorded for the Sigrist on August 21, 2012.

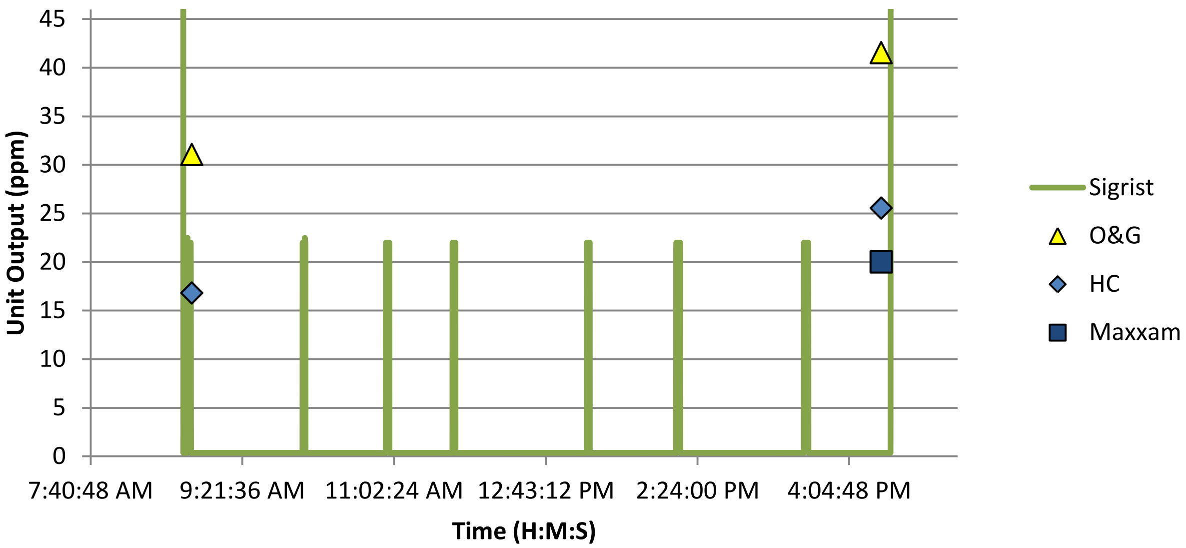

Figure 4.23: Sigrist data recorded on Aug. 21, 2012, heat addition. Single heater at 100 % setting beginning at 8:15.

The Sigrist had an adverse response to the addition of surfactant during the week of spiking. Consequently, it could not be operated continuously along with the other units, thereafter. The unit could only be operated for brief periods, after which a period of idleness was required to avoid having the prism chamber of the unit get flooded from underneath the exit tube. Shown in the figure are a series of periods during which the unit was in operation. Though the data is limited, a few factors can be determined.

Upon activation, at each period, the Sigrist read approximately the same concentration. As indicated by the lab results, the concentration was increasing throughout the day due to the surfactant and condensate combination in the water. The unit was not detecting this increase, likely because it was not able to run long enough. At this final stage, of the remaining units, the Sigrist was only one to read a concentration near that as determined by the lab and Maxxam. Though no increase in concentration was apparent, it is possible that the Sigrist, by virtue of its design, was insensitive to the effect of the heat that was affecting the readings of the other two units.

4.2.15 Instrument Precision Analysis

In order to make any statements about the accuracy and precision of the instruments, it was necessary to examine the quartile ranges of the data recorded. In this section, each active unit during each section of testing will be examined and compared.

Figure 4.24 shows the box and whisker diagrams reflecting the data recorded on July 20, 2012.

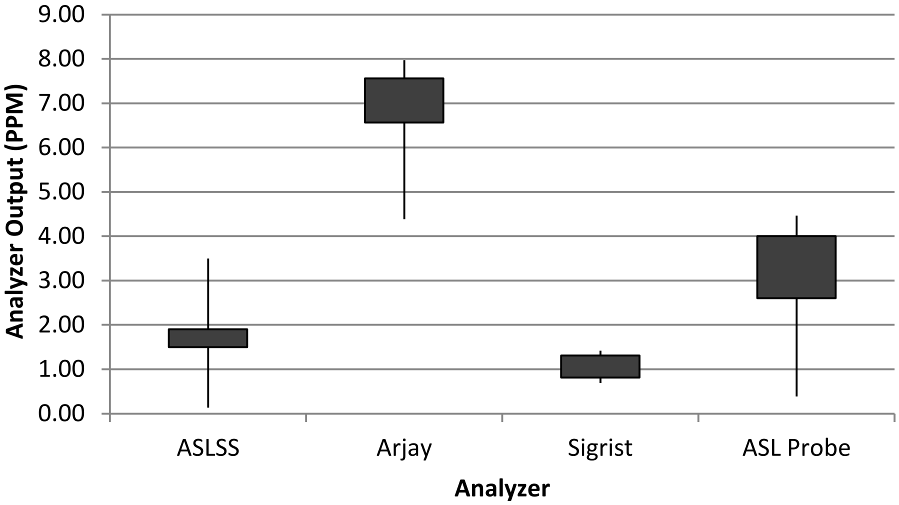

Figure 4.24: Box and whisker charts indicating precision and accuracy of each unit for data recorded on July 20, 2012, during flow testing. At 12:50, the flow to the ASLSS and probe was increased from 6.36 to 15.90 L/min, the Arjay 4.24 to 8.48 L/min, the Sigrist 6.36 to 4.24 L/min (then back to 6.36 L/min at 14:24). At 14:30, the ASLSS and probe were increased to 21.20 L/min.

These diagrams were generated using the overall standard deviation of the data of each instrument, as well as the upper and lower quartiles. Each box shows the bulk of the data, excluding the upper and lower quartiles. The whiskers show the mean plus and minus the standard deviation. The purpose of this type of diagram was to describe overall precision and accuracy of each instrument with regard to one another. Since the effect of the pumping cycle and other factors was to create noise in the data recorded, this type of chart was ideal for examining the data without such noise. Figure 4.24 represents a typical set of charts for the instruments during the week of flow testing. The usefulness of the whiskers on each chart was to visualize the effect of the pump cycle. Longer whiskers indicated larger pump cycle spikes. Table 4.2 below summarizes the quantified data regarding the accuracy and precision of the monitors.

Table 4.3: Quantified accuracy and precision data for each monitor during the flow testing period.

	ASLSS	Probe	Arjay	Sigrist
Accuracy	0.18	0.42	4.18	0.95
Precision	0.40	0.50	1.40	1.00

In terms of the accuracy of the instruments, it was determined by the lab that the concentration of oil and grease in the water sample on July 20 was approximately 2 ppm. While none of the instruments registered a concentration of that value, the ASLSS and Sigrist units showed readings that averaged 1 ppm (two samples averaged). As Table 4.2 shows, the Arjay unit detected a value much higher than the others; more than twice that of the third most accurate unit: the ASL probe.

The precision of the instrument can be described by the width of the boxes of their respective chart. If the box is slim, then the majority of the data points are clustered around a single value, indicating high precision. Referring to Figure 4.24 and Table 4.2, the instruments showing higher precision were the ASLSS and Sigrist units. Strictly speaking, the ASLSS chart had a slimmer box section, while the Sigrist had a slightly wider box. The widest box chart was held by the ASL probe unit, indicating that it was the least precise during the week of flow testing.

Figure 4.25 shown below shows the box and whisker charts for each instrument on July 31, 2012.

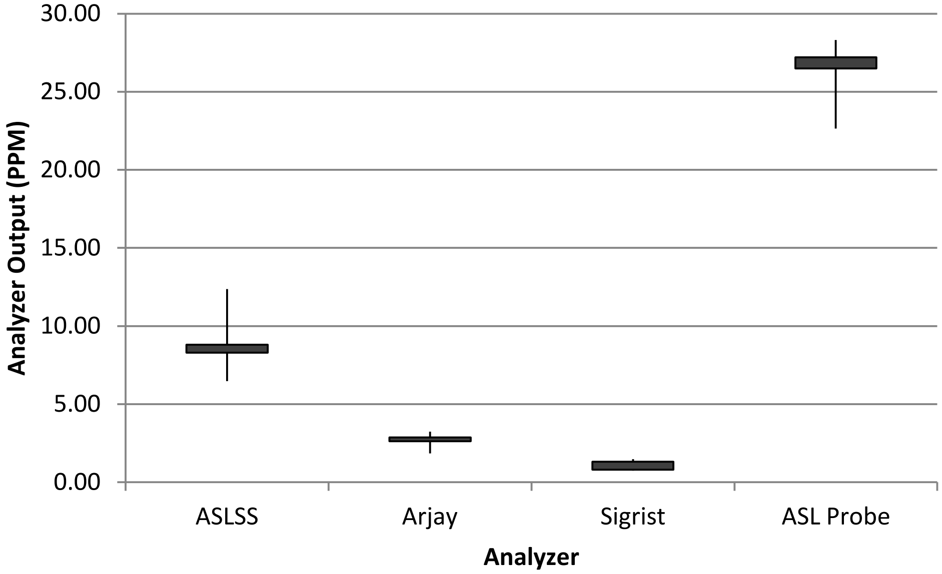

Figure 4.25: Box and whisker charts indicating precision and accuracy of units recorded on July 31, 2012, during heat and gas testing. Gas/ sand was added at a dose/ rate of 15 mL/ 300 L/hr at 9:15, 30 mL/ 300 L/hr at 10:48, and 15 mL/ 600 L/hr at 14:38.

Referring to Table 3.3, the testing done on this day was both sand and gas addition. The lab determined the concentration of the oil and grease and hydrocarbons to be negligible on this day. The probe unit stood out on the chart, having read a much higher mean concentration.

Table 4.3 below details the quantified accuracy and precision data for the monitors during gas and particle testing.

Table 4.4: Quantified accuracy and precision data for each monitor during gas and particles testing

	ASLSS	Probe	Arjay	Sigrist
Accuracy	9.41	25.48	2.55	1.11
Precision	0.50	0.70	0.25	0.50

The Sigrist unit achieved the highest accuracy, with a mean value of 1 ppm.Both of the ASL units showed lower accuracy, with the probe being the least accurate. The mean concentration registered by the probe was about 26.5 ppm; well above the other three units. It was near this point in the testing period that the probe was discovered to be damaged, and it was possible that this damage caused the unit to read much higher values.

Each instrument showed high precision, in terms of the earlier described definition, with the Arjay achieving the highest precision, .Relative to the other three units, the probe unit showed the least precision. The probe precision was not affected in the same way as its accuracy by the damage to the unit.

Figure 4.26 shows the box and whisker charts for the three remaining units on August 15, 2012, during the week of spiking.

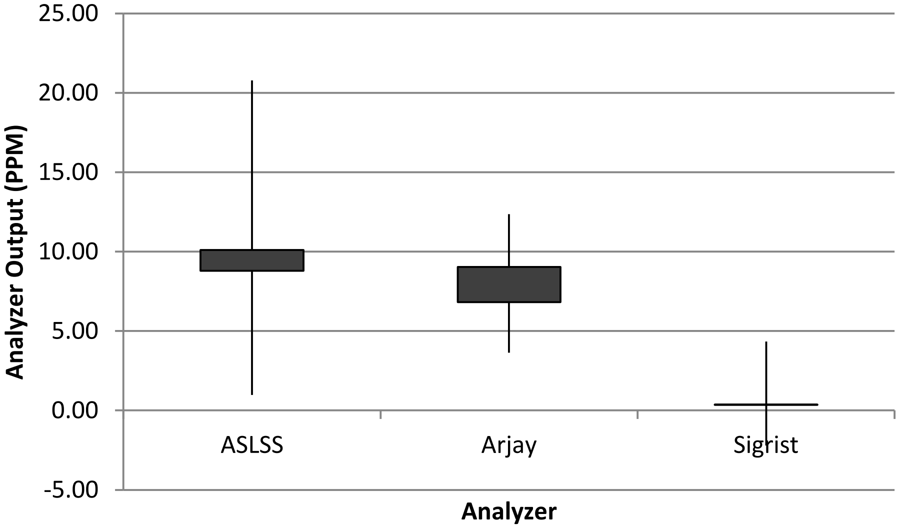

Figure 4.26: Box and whisker charts indicating precision and accuracy for the active units on Aug. 15, 2012, during spike testing. A 100 mL spike was made at 10:41, and a 200 mL spike was made at 13:54.

At this stage in the testing period, the Triton-X was present in the system, and the Sigrist unit was only able to operate for brief periods of time. Two large spikes of raw condensate were added to the system during this day (refer to Table 3.4).

Table 4.5 below summarizes the quantified accuracy and precision data for spike testing period.

Table 4.5: Quantified accuracy and precision data for each monitor during spike testing.

	ASLSS	Arjay	Sigrist
Accuracy	1.61	4.49	11.43
Precision	1.30	2.22	0.00*

*Minimal operation affected quartile ranges

As shown in Table 4.5, where the concentration of oil and grease in the sample was 12.49 ppm, on average, the ASLSS was the most accurate and the most precise monitor. Though it appears as though the Sigrist achieved the highest precision, it should be noted that the Sigrist was in a state of limited operation, thus its precision score was not reflective of a full day of operation.

Figure 4.27 below shows the box and whisker charts for each of the units still in operation during the week of heat testing. The Sigrist unit was only operational for brief periods of time due to the foam build-up in the system, and therefore was not included in this figure.

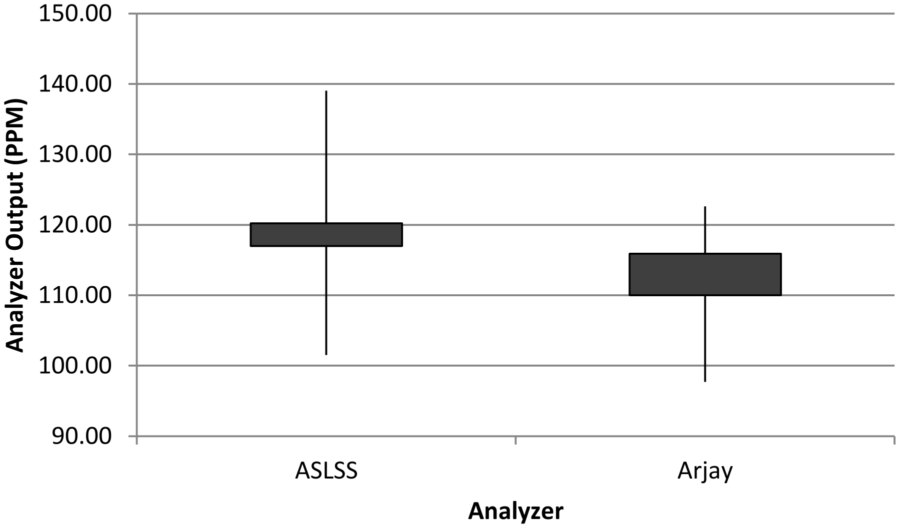

Figure 4.27: Box and whisker charts indicating precision and accuracy for active instruments on Aug. 23, 2012, during heat testing. Using dual heaters, the heat was raised from 300 to 400 W at 12:08 during this day.

According to the lab, the average concentration of oil and grease in the system at this time was 52.39 mg/L. The ASLSS and Arjay units read mean concentrations much higher than this value, thus neither exhibited remarkable accuracy at this time. Though the ASLSS demonstrated higher precision than the Arjay, both instruments were considerably less precise than in previous weeks.

Table 4.6 below summarizes the quantified accuracy and precision data for the monitors during heat testing.

Table 4.6: Quantified accuracy and precision data for each monitor during heat testing.

	ASLSS	Arjay
Accuracy	67.88	57.75
Precision	3.20	5.88

Table 4.6 indicates that the Arjay achieved the highest accuracy, where the ASLSS was the most precise. As they were calibrated using produced water that did not contain significant amounts of other chemicals, specifically surfactants, the addition of such chemicals that affect the monitor readings would cause them to read much higher, while the actual oil and grease concentration remained lower. If this were the case, the fact that the results of both monitors were similar, where each used a different type of measurement technology, suggests that both types of technology, LIF and UV lamp, are able to detect surfactant chemicals in the water stream.

4.2.16 Summary and Synthesis

Table 4.7 details some of the information determined by the testing during this research.

Table 4.7: Summary of monitor data.

Factor	ASLSS	Probe	Arjay	Sigrist
Max. Flow (L/min)	26.5	21.2	10.6	8.28
Min. Flow (L/min)	2.12	2.12	4.24	4.24
Flow Sensitivity	No	Yes	Yes	Yes
Gas Sensitivity	No	No	No	No
Sand Sensitivity	N/A*	N/A*	N/A*	N/A*
Min. Spike Detect (mL)	5.0	N/A	5.0	5.0
Heat Sensitive	N/A**	N/A**	N/A**	N/A**

*Sand was not moving through system

**Heat was insufficient to raise temperature

The ASLSS unit demonstrated the widest range of flow in which it could function without problems, while the Sigrist demonstrated the narrowest. The ASLSS unit showed negligible sensitivity to variations in the flow. In terms of flow rates, these results indicate that the ASLSS was the most reliable monitor to use in a system with high variation in flow rates. In the case of the other units, each had a narrower range of function, and exhibited sensitivity to changes in flow, such as the Arjay altering its reading proportionally to the rate of flow. It was found that each monitor was able to operate under flow conditions outside of their recommended flow ranges. The ASLSS and probe were recommended to operate between 10 and 25 L/min, but were found function between 2.12 and 26.50 L/min, in the case of the ASLSS, and 2.12 to 21.20 L/min in the case of the probe. The Arjay and Sigrist also were able to operate over a wider than recommended range, but those ranges were significantly smaller than the ASLSS and probe. The Arjay was recommended to work at 5 L/min, but was found to operate between 4.26 and 10.60 L/min. The range recommended for the Sigrist was 5 to 7 L/min, but it was able to operate between 4.24 and 8.28 L/min.

The differences in the technology of the monitors may have accounted for the differences in the results shown in Table 4.7. The Arjay and Sigrist both utilize a UV lamp as a light source, and both were found to have high sensitivity to flow changes. Also, observation of their function indicated that the type of flow through the units was important to their effectiveness. If the flow was too low, than it became uneven through both unit's detection cells, resulting in erratic readings. The ASLSS and probe monitors, utilizing LIF systems, were able to operate at wider ranges, but continued to read positive values, even if flow was stopped. This was likely due to the method of sampling, as the ASLSS captured samples in a chamber, and the probe was at a low position in the system where water tended to accumulate if not being driven by a pump.

None of the units exhibited significant and consistent sensitivity to particles or gases in the system. As the units all relied on fluorescence detection technology, the insensitivity to particles was not surprising. Also, it appeared that the sand added to the T200 tank tended to remain in that tank, rather than moving through the system. This could have been a result of the type of sand chosen, or simply because the doses were too small. Future research projects should consider these factors in their experimental design. Similarly, the gas may not have affected the instruments because it may not have been able to enter the system by the nature of the design. As it was an open air system, the added gas could have gassed off while still in the T200 or T100 tank. In addition, where the gas was added may have been a factor in the effect it had on the monitors. It was added to the water in the T200 tank, which had to be moved to the T100 first before being moving through the monitors. If the gas had been added directly to the T100 tank, then the effects, if any, may have been more observable. The T100 tank was open air if the tank was opened from the top, but was otherwise sealed. If the gas had been added within the T100, there would have been less opportunity for it to escape to the atmosphere.

With the exception of the ASL Probe unit, all instruments were able to detect added condensate spikes that were a minimum of 5 mL, relative to the total volume of liquid in the system. Assuming an even distribution, and a system volume of approximately 550 L, this means the units are able to detect a spike of 0.001% of the system volume. It was not determined if the probe could make a detection at this range, as it was not in operation during the spiking period due to safety issues.

The effect of the heating was not as clear as the other factors. The units that were fully operational (ASLSS and Arjay) experienced a similar effect, which was to detect a gradually increasing concentration, and to experience an intensified pump cycle response. The Sigrist, while still functioning, could only be operated for brief periods, and was unable to establish response patterns in such small timeframes. Given the lack of temperature change, however, it appeared as though the heat being added to the system was insufficient to affect the intended change. Before the spiking began, the lab continually found that the concentration of oil and grease was negligible. While the units occasionally read values that were near zero, they typically read positive values. Once condensate spikes were introduced, the lab showed increasing concentration, and, while the units did as well, they still were not able to accurately detect the actual concentrations. The precision of a unit was always related to the pump cycle response of that unit, but as the response was typically consistent over the course of a testing week, it was still possible to make judgements. During flow testing, the ASLSS was the most precise. This was due to its insensitivity to changes in the flow rate. The other instruments changed their readings when the flow rate changed, which affected their range of readings on the day of the change; the ranges widened, lowering the precision of the units. While in operation, the probe unit demonstrated the least precision. As the unit had suffered damage, it was possible that the low precision was due to that cause, and as such, it was difficult to judge if the unit had low precision or not.Table 4.9 below shows the reliability and maintenance requirements data. For the reliability calculation, the system was in operation for 24 days, eight hours per day, so T_{tot} was 192 hours. Each monitor had differing values of T, and for T_m, each time a monitor had to undergo maintenance, 1 hour was added to T_m.

Table 4.8: Quantified reliability and maintenance requirements data for each monitor.

	ASLSS	Probe	Arjay	Sigrist
Reliability	1.0	0.50	0.98	0.67
Maintenance Requirements	0	0	4	2

As Table 4.9 indicates, the ASLSS was the most reliable monitor, followed by the Arjay. These were the only two units to stay in full operation during the full testing period. The Arjay had a slightly lower score due to its maintenance downtime. Though the Sigrist was still operable, the surfactant foam necessitated its downtime, thus its lower score. In terms of maintenance, the ASLSS and probe required the least maintenance due to their self cleaning machanisms, while the Arjay required the most frequent maintenance, at once per week.

Table 4.9 below shows the collected rankings resulting from this study. In the cases of the accuracy and precision categories, the rankings were determined using weekly data, whereas the reliability and maintenance requirements rankings were determined using overall data.

Table 4.9: Overall monitor rankings by category.

	1	2	3	4
Accuracy	ASLSS	Arjay	Sigrist	Probe
Precision	ASLSS	Sigrist	Arjay	Probe
Maintenance Requirements	ASLSS	Probe	Sigrist	Arjay
Reliability	ASLSS	Sigrist	Arjay	Probe

The accuracy and precision rankings were developed using data from each testing period. In both categories, the monitors achieving the highest rank in each testing period were tallied, and then the monitor appearing most frequently at rank 1 over the four testing periods was placed in the overall rank 1 position for the category. Then, the monitor appearing in the rank 2 position most often was placed in the overall rank 2 position, and so on.

It was determined through the ranking system that the Advanced Sensors side stream monitor was the highest performing monitor in terms of the factors and categories studied in this research.

CHAPTER 5 CONCLUSIONS

5.1 Conclusions

This study set out to show that, through a series of tests and measurements, a single monitor could be determined to be the most effective of a group of monitors all performing the same task. In order to address this question, a set of primary objectives were made, and are reiterated as follows:

- Measure and analyze the responses of monitors to variations in flow rate, gas and particle addition, chemical spiking, and heating.
- Compare monitors for maintenance requirements, precision, accuracy, and reliability.
- Determine which monitor is the most effective in terms of the above factors.

To address the first objective, four monitors were connected in parallel to a water recirculation system driven by pumps. Controls were built into the system that allowed the flow of water through the monitors to be manipulated. Each variable was adjusted continually for a week or more before the next variable was tested.

The second objective was approached by comparing monitor readouts to one another, and to lab results. As such, the accuracy, precision, and reliability (in terms of measurements) of the monitors were determined. The maintenance requirements and physical reliability of the monitors was determined based on the ongoing attention and behavior of the monitors over the course of the entire testing period.

The third objective was determined by collecting all the data gathered during the testing period for each monitor and ranking their performance with regard to one another. Consideration was given to all the variables tested and all the factors observed with regard to the first two objectives. It was determined through this approach that the most effective monitor was the Advanced Sensors side stream monitor.

Due to the technical approach followed in this research, the Advanced Sensors side stream monitor was found to be the highest performing monitor in terms of all factors and variables studied. It achieved the highest rankings in accuracy, precision, reliability, and maintenance requirements as defined by the parameters of this research. Additionally, it was found to operate the most effectively under the conditions variables tested. It was found to operate without issue over the largest range of flow variance (2.12 to 26.5 L/min), was insensitive to gas, and was found to be capable of detecting a minimal change in concentration (5.0 mL/550 L).

5.2 Recommendations

In a system in which flow variation is expected to occur often, the most suitable unit to employ is the ASLSS. The Arjay, probe, and Sigrist units tested in this study are suitable if the flow rate is to be controlled.

There are some areas of interest found in this study that are suitable for future work. The gradual drop in turbidity and the gradually decreasing concentration of oil and grease observed in this study could indicate a treatment option that has yet to be studied. It was suspected that the open air system, combined with the continuous mechanical action of the pumps contributed to this phenomenon, but as it was not directly applicable to this study, it was not investigated further. Additionally, a bench scale study utilizing the principles of this research would be useful in determining the individual effect of each variable. The nature of the design of this study made it necessary for the variables to accumulate. For example, the surfactant could not be removed from the system, and potentially masked the effect of the heating during the following week. A study isolating each variable could provide more information regarding the unique effect of a variable.

As the effects of the sand on the system was not apparent, due to it settling in the T200 tank rather than moving through the system, additional study is required to determine the effect of sand on a system like the one used in this research. Finer particles could be used, and a mixing mechanism could be installed to ensure the particles do not simply settle. Similarly, the heat provided by the heaters was insufficient to raise the temperature of the water in the system. Further study is required to determine the effect of heat. As no increase in temperature was effected by the heaters used, more heat could be added in the form of additional, or more powerful heaters. Also, studying a smaller system with less exposure to ambient temperatures could mitigate the heat loss that affected this project. A bench scale study of the heat on a system would likely be sufficient.

REFERENCES

Adewumi, M.A., Erb, J.E., Watson, R.W. (1992). Design considerations for a cost effective treatment of stripper oil well produced water. In: J.P.Ray, F.R. Engelhardt (Eds.), *Produced Water: Technological/ Environmental Issues and Solutions* (pp. 511–523.), New York: Plenum Publishing Corp.

Advanced Sensors Ltd. (2009). OIW-EX Series of Oil in Water Monitors. *User Handbook.* OIW-HBO-0002 Version: EX-002

Ahmadun, F., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., Abidin, Z. Z. (2009), Review of technologies for oil and gas produced water treatment. *Journal of Hazardous Materials, 170*, 530–551.

Anaensen, G., Volker, A. (2006). Produced water characterization using ultrasonic oil-in-water monitoring – recent development and trial results. In *A paper presented at NEL's 8th oil-in-water monitoring workshop, 21 September 2006.* Aberdeen, UK.

Arjay Engineering Ltd. (n.d.). Hydrosense 2410 On-line Oil in Water Monitor. *User Manual.* Retrieved from: http://www.arjayeng.com/pdf_manuals/HS2410_REV4.2.pdf

Arnold, K., Stewart, M. (2008). *Surface Production Operations: Design of Oil Handling Systems and Facilities.* Gulf Professional Publishing.

Arthur, J.D., Langhus, B.G., Patel, C. (2005). *Technical Summary of oil and gas produced water treatment technologies*. Retrieved from http://www.all-llc.com/publicdownloads/ALLConsulting-WaterTreatmentOptionsReport.pdf

Bakke, T., Klungsøyr, J., Sanni, S. (2013), Environmental impacts of produced water and drilling waste discharges from the Norwegian offshore petroleum industry. *Marine Environmental Research, 92*, 154–169. DOI: 10.1016/j.marenvres.2013.09.012

Bertness, T.A., Lipoma, S.P. (1989). Method of treating saline water. *US Patent No. 4,877,536*. Washington, D.C.: U.S. Patent and Trademark Office.

Butler, E., Roth, N., Gaskin, R. (2001). A new approach to online oily water measurement-field experience in BP installations. In *A paper presented at TUV NEL's 3rd oil-in-water monitoring workshop, 23 May 2001*. Aberdeen, UK.

Carvalho, M.S., Clarisse, M.D., Lucas, E.F., Barbosa, C.C.R. (2002). Evaluation of the polymeric materials (DVB copolymers) for produced water treatment. In: *SPE International Petroleum Exhibition and Conference, Abu Dhabi, UAE, 13–16 October.*

Chen, I., Wang, Y., Wang, D. (2009). Reliability of wireless sensors with code attestation for intrusion detection. *Information Processing Letters, 110*, 778-786.

Clark, C.E., Veil, J.A.; Argonne National Laboratory. (2009). *Produced water volumes and management practices in the United States, ANL/EVS/R-09/1*. Prepared by the Environmental Science Division.

Deng, S., Yu, G., Jiang, Z., Zhang, R., Ting, Y.P., (2005). Destabilization of oil droplets in produced water from ASP flooding. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 252*, 113–119.

Dfaz, M.P., Grigson, S.J.W., Peppiat, C.J., Burgess, G., (2000). Isolation and characterization of novel hydrocarbon-degrading euryhaline consortia from crude oil and mangrove sediments. *Marine Biotechnology, 2*, 522–532.

Doyle, D.H., Brown, A.B. (2000). Produced water treatment and hydrocarbon removal with organoclay. In *SPE Annual Technical Conference and Exhibition*, *Dallas, Texas, USA, 1–4 October.*

Elias-Samlalsingh, N., Agard, J.B.R. (2003) Application of toxicity identification evaluation procedures for characterizing produced water using the tropical mysid, *Metamysidopsis insularis*. *Environmental Toxicology and Chemistry, 23* (5), 1194–1203.

Elsayed, E. A. (1996). *Reliability Engineering*. Addison Wesley, Reading, MA.

Esmaeilirad, N., Carlson, K., Omur Ozbek, P. (2015). Influence of softening sequencing on electrocoagulation treatment of produced water. *Journal of Hazardous Materials, 283*, 721–729.

Farmaki, E., Kaloudis, T., Dimitrou, K., Thanasoulias, N., Kousouris, L., Tzoumerkas, F. (2007). Validation ofa FT-IR for the Determination of Oils and Grease in Water using Tetrachloroethylene as the Extraction Solvent. *Desalination*, 210, 52–60.

Frankiewicz, T.C., Gerlach, J. (2000). Removal of hydrocarbons, mercury and arsenic from oil-field produced water. *US Patent No. 6,117,333.* Washington, D.C.: U.S. Patent and Trademark Office.

Garbutt, C.F. (1997). Innovative treating processes allow steam flooding with poor quality oilfield water. In: *SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA, 5–8 October.*

Grigson, S. J. W., Wilkinson, A., Johnson, P., Moffat, C. F., McIntosh, A. D. (2000). Measurement of oilfield chemical residues in produced water discharges and marine sediments. *Rapid Communications in Mass Spectrometry, 14* (23), 2210–2219.

Hamilton, L.D., Meinhold, A.F., Nagy, G. (1992). Health risk assessment for radium discharged in produced waters. In: J.P. Ray, F.R. Engelhardt (Eds.) *Produced Water: Technological/Environmental Issues and Solutions* (pp. 303–315). New York: Plenum Publishing Corp.

Henderson, S.B., Grigson, S.J.W., Johnson, P., Roddie, B.D. (1999). Potential Impact of production chemicals on the toxicity of produced water discharges from North Sea oil platforms. *Marine Pollution Bulletin, 38*, 1141–1151.

Holdway, D. A. (2002), The acute and chronic effects of wastes associated with offshore oil and gas production on temperate and tropical marine ecological processes. *Marine Pollution Bulletin, 44,* 185–203.

Horpestad, A., Skaar, D., Dawson H. (2001). Water Quality Impacts from CBM Development in the Powder River Basin, Wyoming and Montana. *Water Quality Technical Report.* December 18.

Institute of Electrical and Electronics Engineers (IEEE). (1990). *IEEE Standard Computer Dictionary: A Compilation of IEEE Standard Computer Glossaries.* New York, Lenntech. (n.d.). *Water Conductivity*. Retrieved from http://www.lenntech.com/applications/ultrapure/conductivity/water-conductivity.htm

Liangxiong, L., Whitworth, T.M., Lee, R. (2003). Separation of inorganic solutes from oil-field produced water using a compacted bentonite membrane. *Journal of Membrane Science, 217*, 215–225.

Liu, N., Lu, J., Li, L., Lee, R. (2007). Factors determining the reverse osmosis performance of zeolite membranes on produced water purification. In: *SPE International Symposium on Oilfield Chemistry, Houston, Texas, USA, 28 February to 2 March.*

Ma, H., Wang, B. (2006). Electrochemical pilot-scale plant for oil field produced wastewater by M/C/Fe electrodes for injection. *Journal of Hazardous Materials, B132*, 237–243.

Madaeni, S.S. (1999). The application of membrane technology for water disinfection. *Water Research, 33*, 301–308.

Maxoil Solutions, Inc. (2008). Assessment of On-Line Oil in Water Monitors. MAX-WSP-001-REP-001-REV02.

Mccormack, P., Jones, P., Hetheridge, M.J., (2001). Analysis of oilfield produced waters and production chemicals by electrospray ionisation multi-stage mass spectrometry. *Water Research, 35* (15), 3567–3578.

Miller, D. J., Böhm, R. (1993). Optical studies of coalescence in crude oil emulsions. *Journal of Petroleum Science and Engineering, 9* (1) 1-8.

Morrow, L.R., Martir, W.K., Aghazeynali, H., Wright, D.E., (1999). Process of treating produced water with ozone. *US Patent No. 5,868,945*. Washington, D.C.: U.S. Patent and Trademark Office.

National Energy Board, Canada-Nova Scotia Offshore Petroleum Board, & Canada-Newfoundland and Labrador Offshore Petroleum Board. (2010). *Offshore Waste Treatment Guidelines.* Retrieved September 22, 2011 from www.cnsopb.ns.ca/pdfs/owtg_redraft.pdf.

Neff, J.M. (2002). *Bioaccumulation in Marine Organisms: Effects of Contaminants from Oil Well Produced Water*. Amsterdam: Elsevier.

Neff, J. (Ed.), Lee, K. (Ed.), DeBlois, E.M. (2011). Produced water: overview of composition, fates, and effects. *Produced Water*. New York: Springer.

O'Donoghue, A., Relihan, E. (2009). Inline oil in water particle analysis and concentration monitoring for process control and optimization in produced water plants. In *A paper presented at TUV NEL's 7th produced water workshop, 29-30 April 2009.* Aberdeen, UK.

OSPAR Commission. (2005). *Report on Discharges Spills and Emissions from Offshore Oil and Gas Installations.* Retrieved from http://www.ospar.org/documents/dbase/publications/p00221 Offshore%20report%202003.pdf.

Otton, J. K. (2006). *Environmental Aspects of Produced-water Salt Releases in Onshore and Coastal Petroleum-producing Areas of the Conterminous*. Retrieved from http://www.worldcat.org/oclc/72671289.

Pharr, D. Y., McKenzie, J. K., Hickman, A. B. (1992). Fingerprinting petroleum contamination using synchronous scanning fluoescence spectroscopy. *Ground Water, 30* (4), 484-489.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., Moulin, P., (2008). Landfill leachate treatment: review and opportunity. *Journal of Hazardous Materials, 150*, 468–493.

Robinson, D. (2013). Oil and gas: Treatment and discharge of produced waters offshore. *Filtration + Separation*, *50* (2), 20–23.

Sigrist Photometer AG. (2007). Oilguard EX, Sigrist Fluorescence Measuring Instrument. *Instruction Manual.* Document No. 10175E, Version: 2.

Sonune, A., Ghate, R. (2004) Developments in wastewater treatment methods. *Desalination, 167*, 55–63.

Standard Methods. (2001). Standard Methods for the Examination of Water and Wastewater. *5520 Oil and Grease: 5520C Partition-Infrared Method and 5520F Hydrocarbons.*

Stephenson, M. T. (1992). A survey of produced water studies. In: J.P. Ray, F.R., Engelhardt (Eds.), *Produced Water: Technological/Environmental Issues and, Solutions* (pp. 1-12). New York: Plenum Publishing Corp.

Teal, J., Farrington, J., Burns, K., Stegeman, J., Tripp, B., Wodin, B., Phinney, C. (1992). The West Falmouth oil spill after 20 years: Fate of fuel compounds and effects on animals. *Marine Pollution Bulletin, 24* (12), 607-614.

Tellez, G.T., Nirmalakhandan, N., Gardea-Torresdey, J.L. (2002). Performance evaluation of an activated sludge system for removing petroleum hydrocarbons from oilfield produced water. *Advances in Environmental Research, 6* (4), 455–470.

Thoma, G.J., Bowen, M.L., Hollensworth, D., (1999). Dissolved air precipitation solvent sublation for oilfield producedwater treatment. *Separation and Purification Technology, 16*, 101–107.

United States Government Accountability Office (GAO). (2014). *Information on the Quantity, Quality, and Management of Water Produced During Oil and Gas Production.*

USEPA, http://www.epa.gov.

Utvik, T., Hasle, B., Hasle, J. (2002). Recent Knowledge about Produced Water Composition and the Contribution from Different Chemicals to Risk of Harmful Environmental Effects. *SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production* (pp. 1-5). Kuala Lumpur, Malaysia: Society of Petroleum Engineers Inc.

Van den Broek, W.M.G.T., Van der Zande, M.J., (1998). Comparison of plate separator, centrifuge and hydrocyclone. In: *SPE International Oil and Gas Conference and Exhibition, Beijing, China, 2–6 November.*

Veil, J.A., Puder, M.G., Elcock, D., Redweik Jr., R.J.; Argonne National Laboratory. (2004). *A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane*. Prepared for: U.S. Department of Energy, National Energy Technology Laboratory.

Wei, N., Wang, X.H., Li, F.K., Zhang, Y.J., Guo, Y. (2003). Treatment of high-salt oil field produced water by composite microbial culture. *Urban Environment and Urban Ecology, 16*, 10–12.

Woodall, D.W., Gambrell, R.P., Rabalais, N.N. (2001). Developing a method to track oil and gas produced water discharges in estuarine systems using salinity as a conservative tracer. *Marine Pollution Bulletin, 42* (11), 1118–1127.

Xu, P., Drewes, J.E., Heil, D., (2008). Beneficial use of co-produced water through membrane treatment: technical-economic assessment. *Desalination, 225*, 139–155.

Yang, M., Lee, K., Neff, J. (2011). *Measurement of Oil in Produced Water.* Glasgow, UK: Spring Science + Business Media, LLC.

Zaidi, A., Simms, K., Kok, S., (1992). Use of micro/ultrafiltration for the removal of oil and suspended solids from oilfield brines. *Water Science and Technology, 25*, 163–176.

APPENDICES

Appendix A: Additional Figures

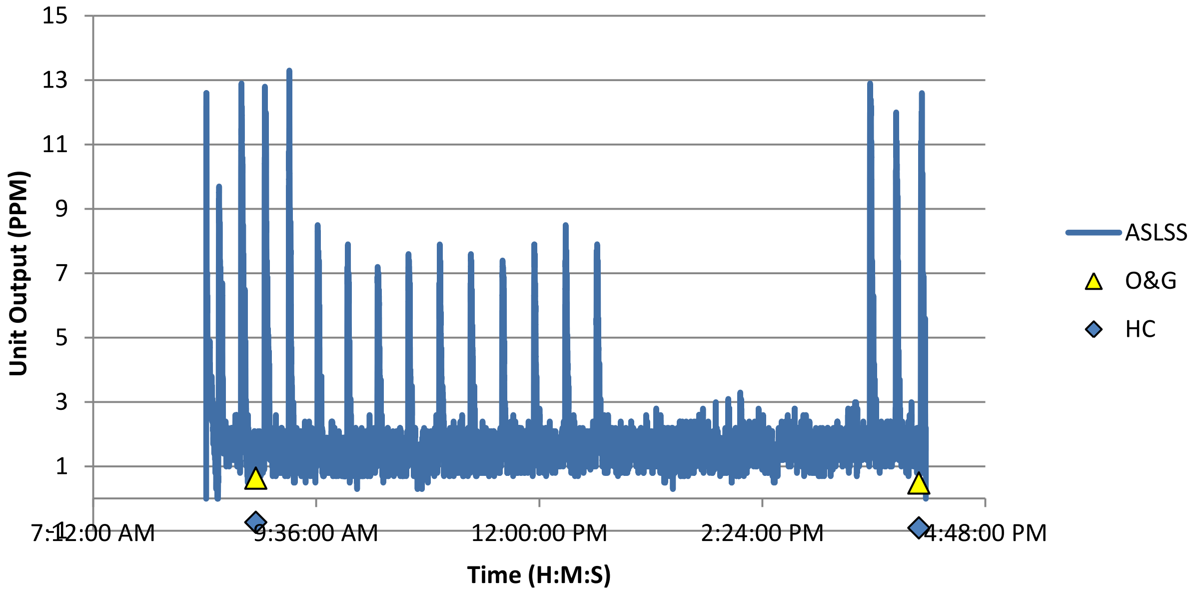

Figure A-1: ASLSS flow test data recorded on July 24, 2012;flow decreased from 10.60 to 6.36 L/min at 9:19, then to 2.12 L/min at 12:55, then to 0.0 L/min at 14:08, then up to 10.60 at 15:25.

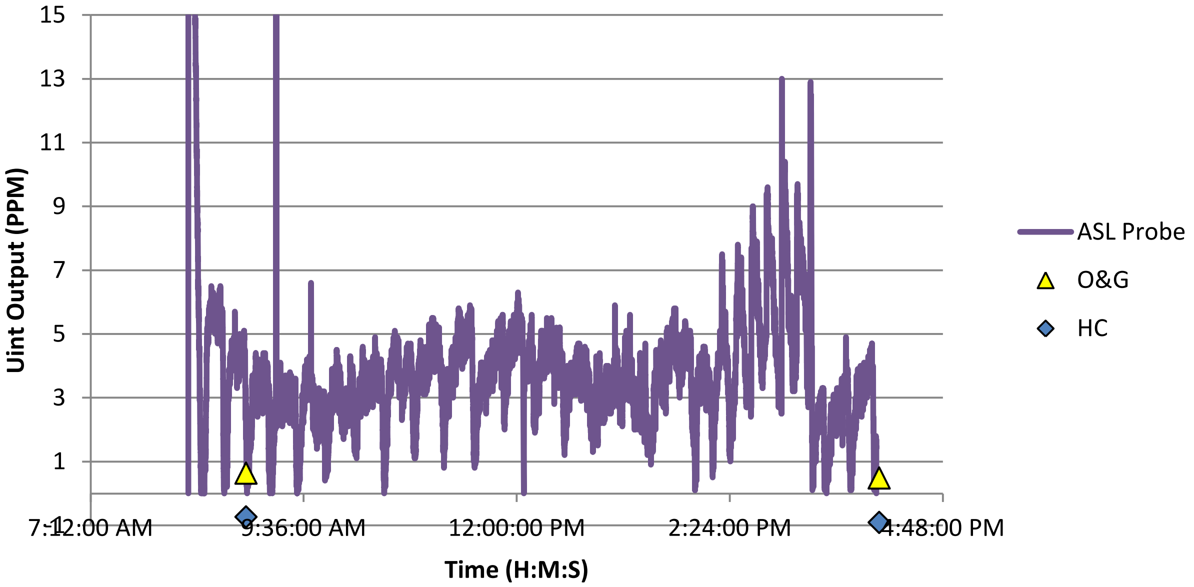

Figure A-2: July 24, 2012 flow test datafor the ASL Probe; flow decreased from 8.48 L/min to 6.36 L/min at 9:19, then to 2.12 L/min at 12:55, then to 0.0 L/min at 14:08, then back up to 10.60 L/min at 15.25.

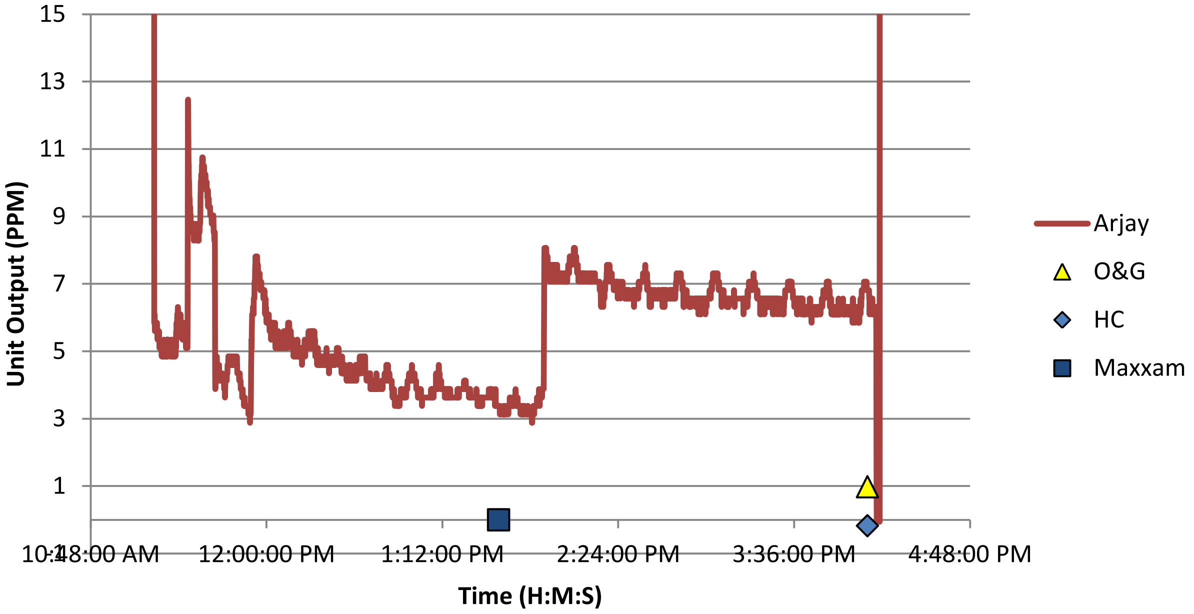

Figure A-3: July 23, 2012 flow data recorded for Arjay; flow increased from 8.48 L/min to 10.60 L/min at 11:27, then decreased to 4.24 L/min at 11:37, then increased to 5.30 L/min at 11:53, then to 8.48 L/min at 13:50.

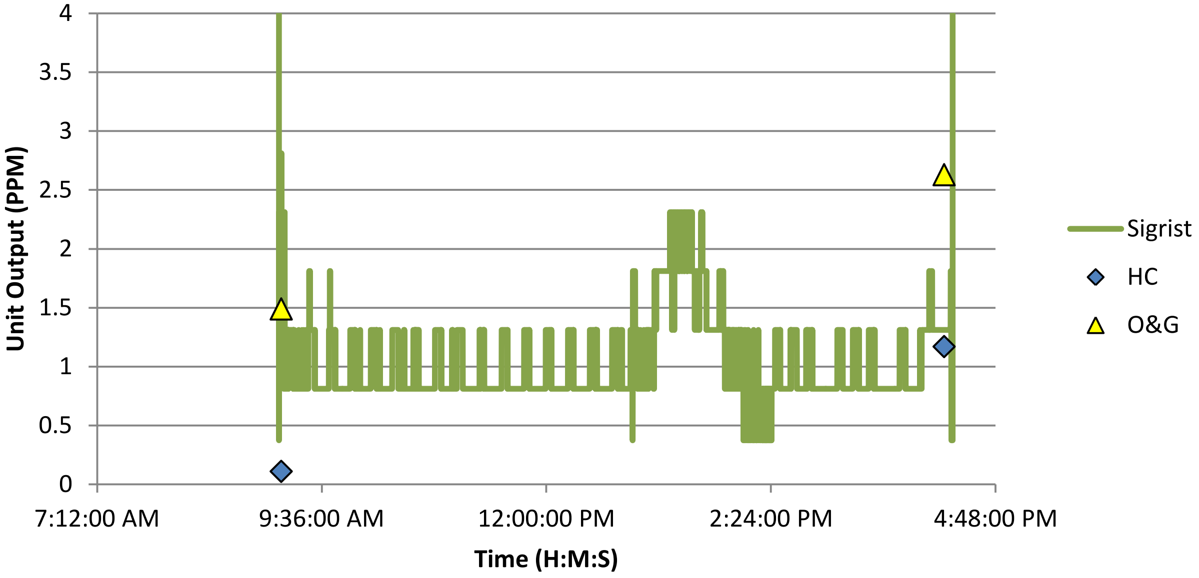

Figure A-4: Flow testing data recorded for Sigrist on July 20, 2012; flow was decreased from 6.36 L/min to 4.24 L/min at 12:50, then increased to 6.36 L/min at 14:24.

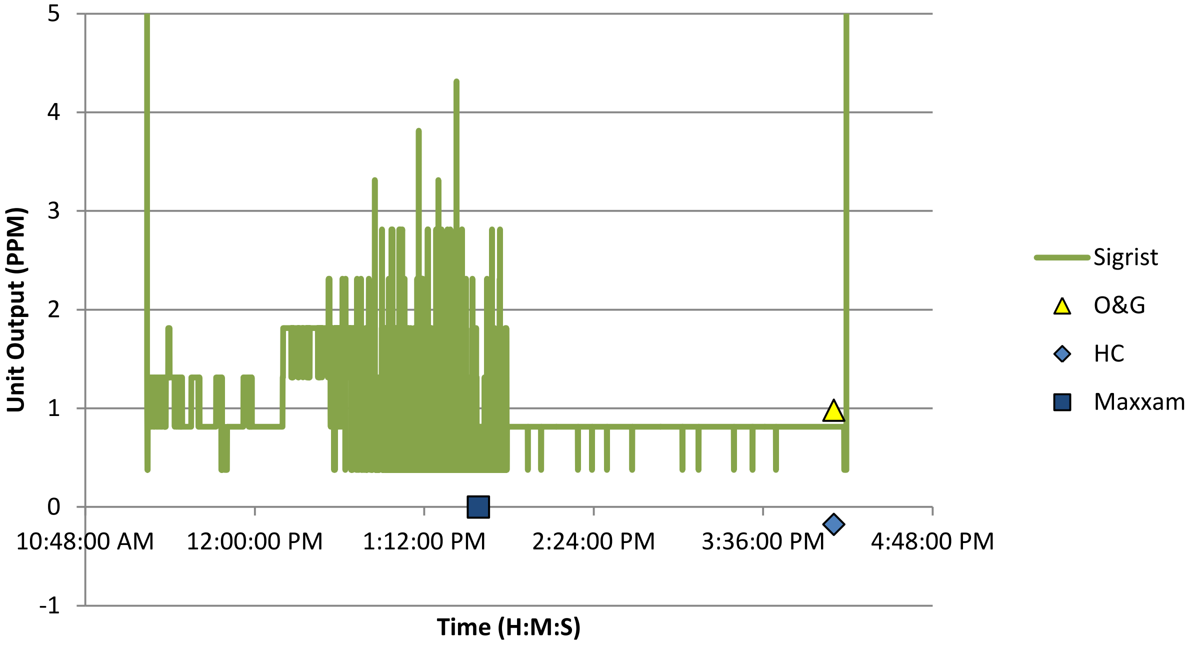

Figure A-5: Flow data recorded for Sigrist on July 23, 2012; flow increased from 6.36 to 7.42 L/min at 11:27, then increased to 8.48 L/min at 11.41, then decreased 6.36 L/min at 11:53, then increased to 7.95 L/min at 13:46.

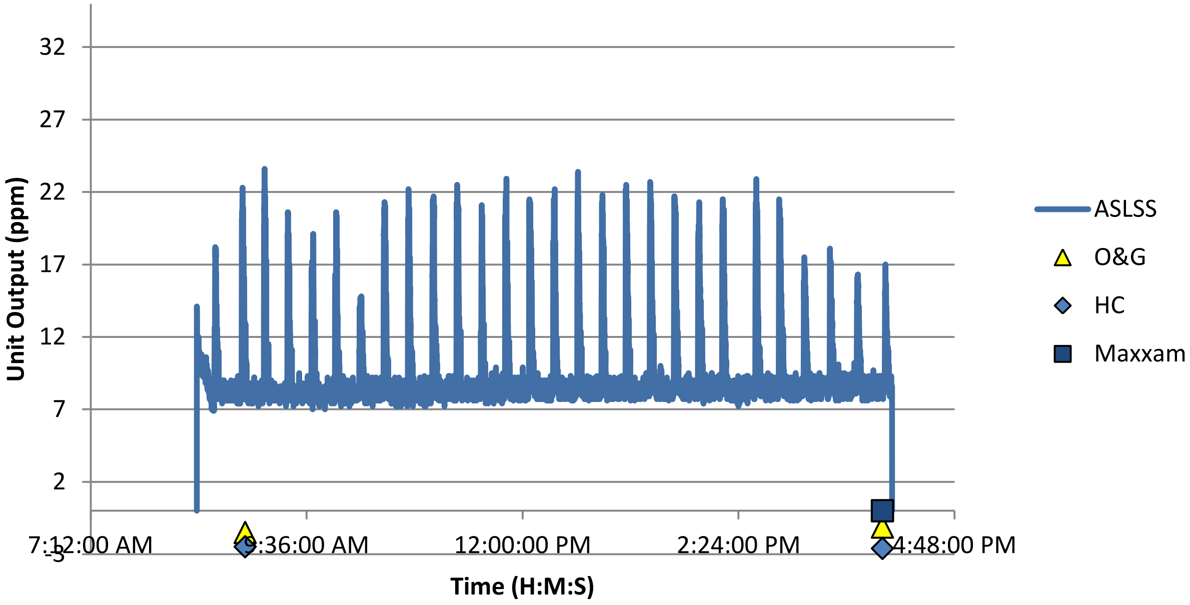

Figure A-6: ASLSS data recorded on July 31, 2012, sand and gas addition. 15 mL sand and gas added at 300 L/hr rate at 9:15, then 30 mL/ 300 L/hr at 10:48, the 15 mL/ 600 L/hr at 14:38.

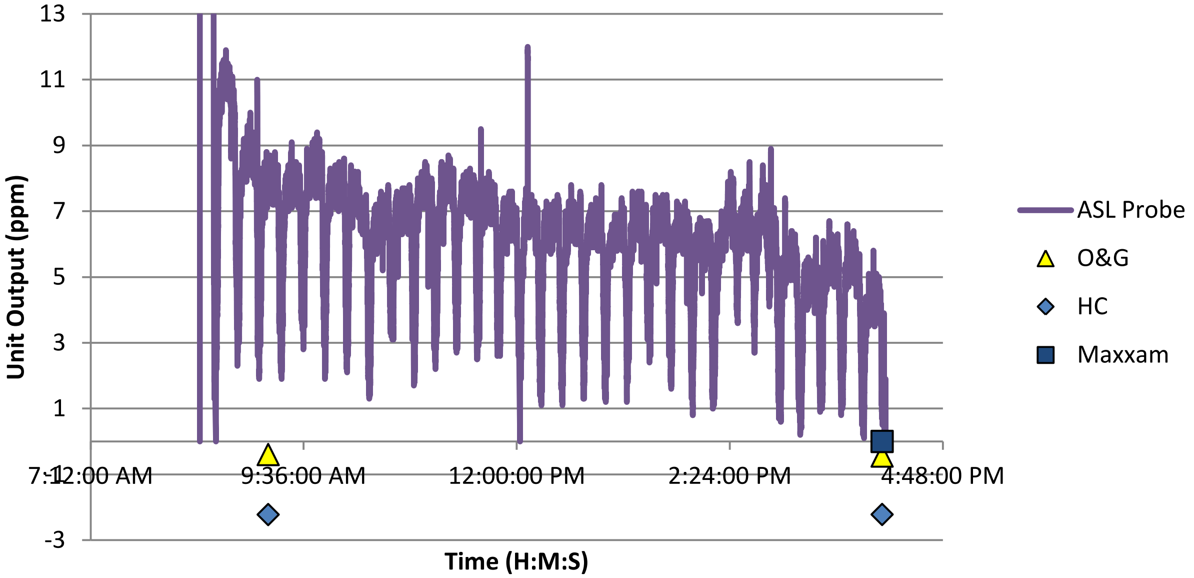

Figure A-7: July 26, 2012 data for ASL Probe, gas addition. Gas added at 300 L/hr at 8:30, and increased to 600 L/hr at 15:00.

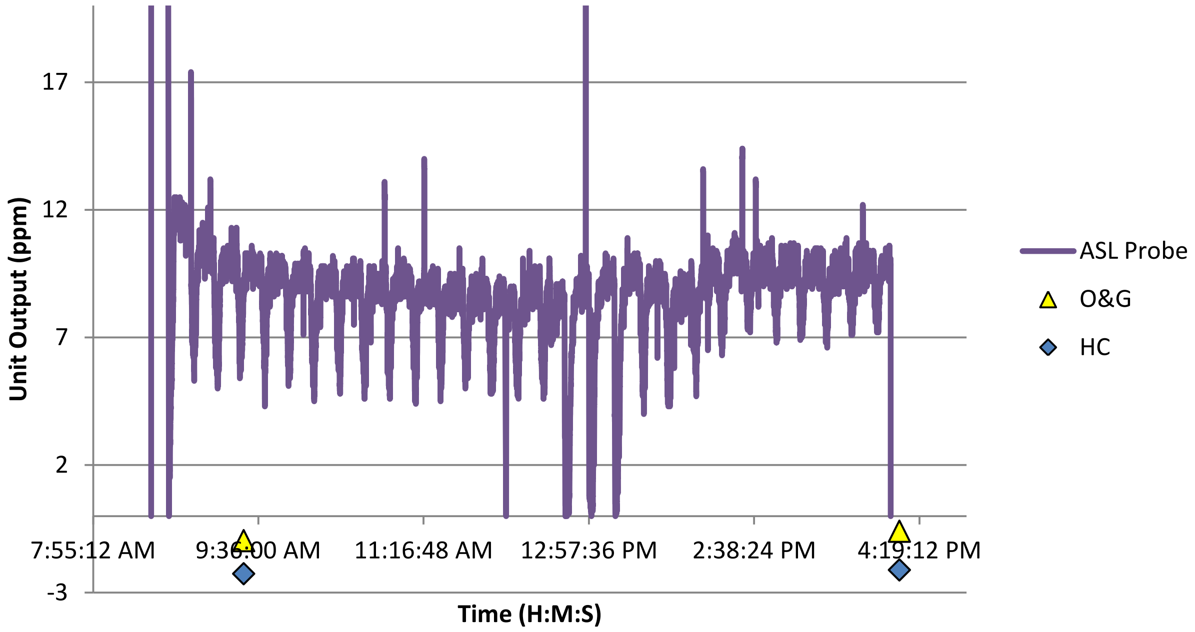

Figure A-8: ASL Probe data recorded on July 27, 2012, sand addition. 15 mL of sand added at 12:40.

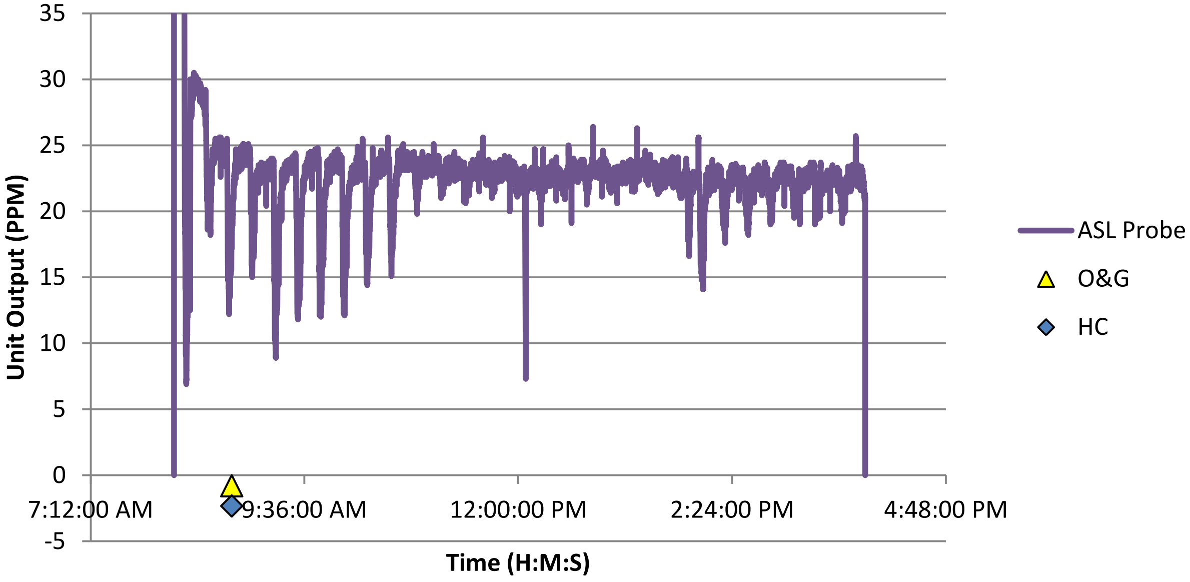

Figure A-9: ASL Probe data recorded on July 30, 2012, sand addition. Sand doses were 15 mL at 9:10, 15 mL at 10:23, and 30 mL at 14:00.

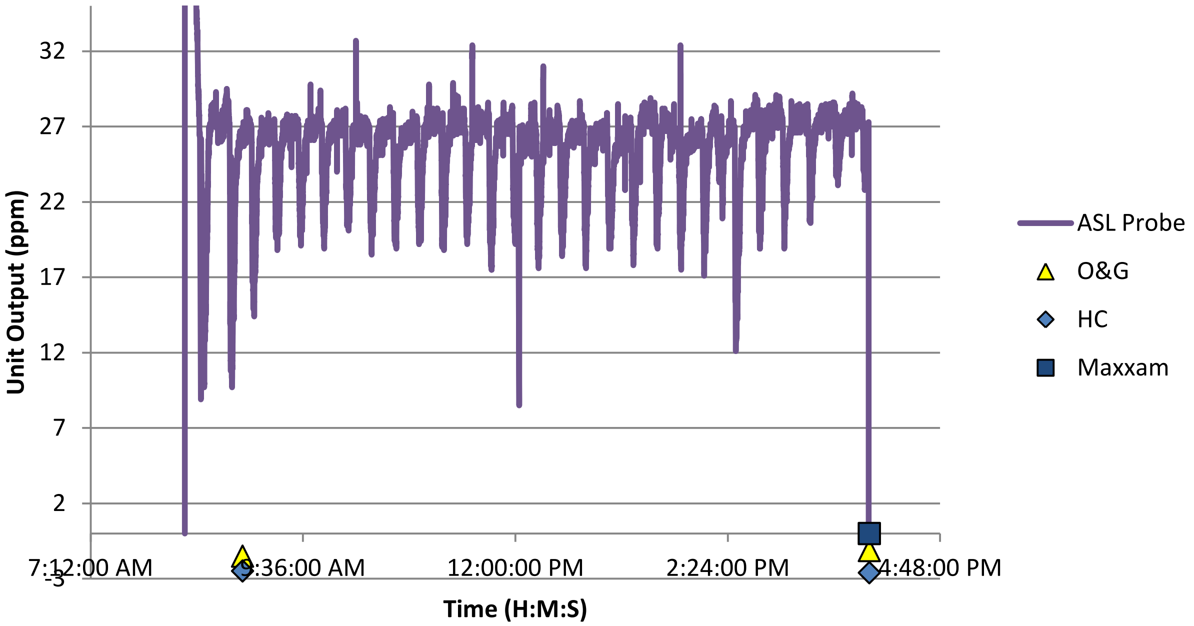

Figure A-10: ASL Probe data recorded on July 31, 2012, sand and gas addition. At 9:15, 15 mL sand added while gas added at 300 L/hr; then at 10:48, 30 mL sand while 300 L/hr gas; then at 14:38, 15 mL sand while 600 L/hr gas.

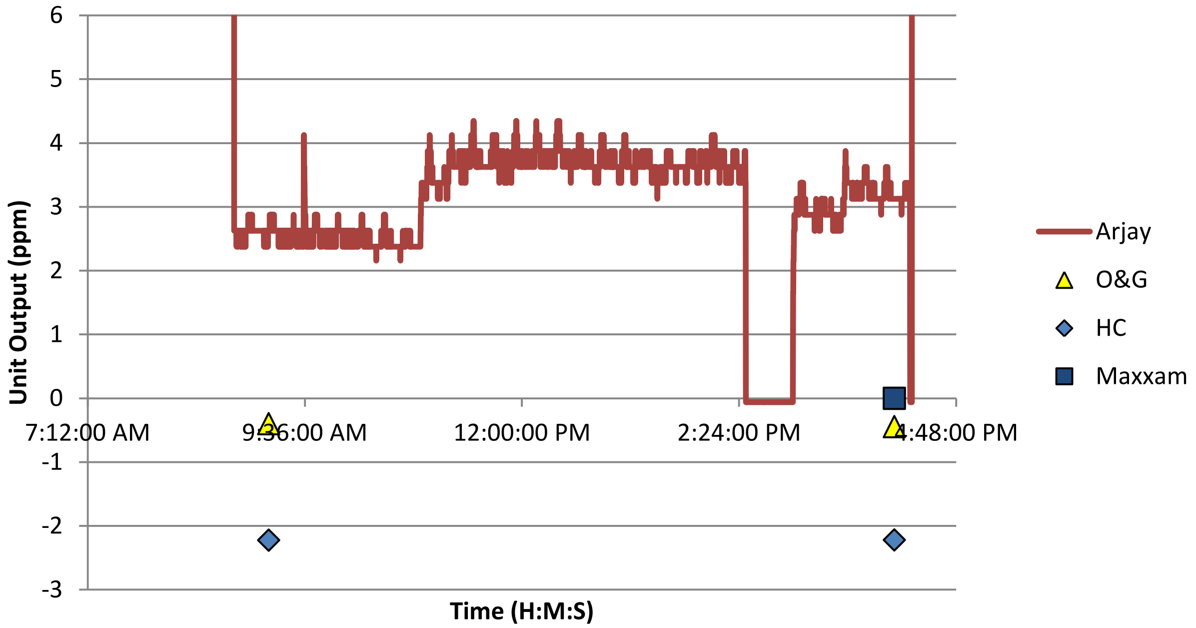

Figure A-11: Arjay data recorded on July 26, 2012, gas addition. Gas added at 300 L/hr starting at 8:30, then 600 L/hr at 15:00.

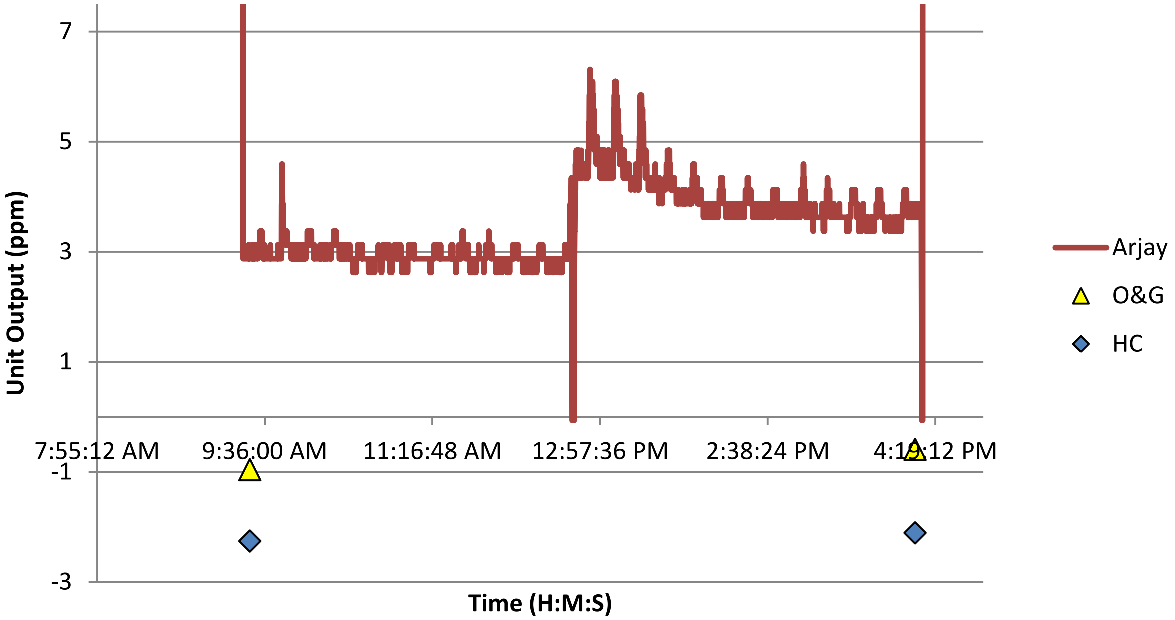

Figure A-12: Arjay data recorded on July 27, 2012, sand addition. 15 mL of sand added at 12:40.

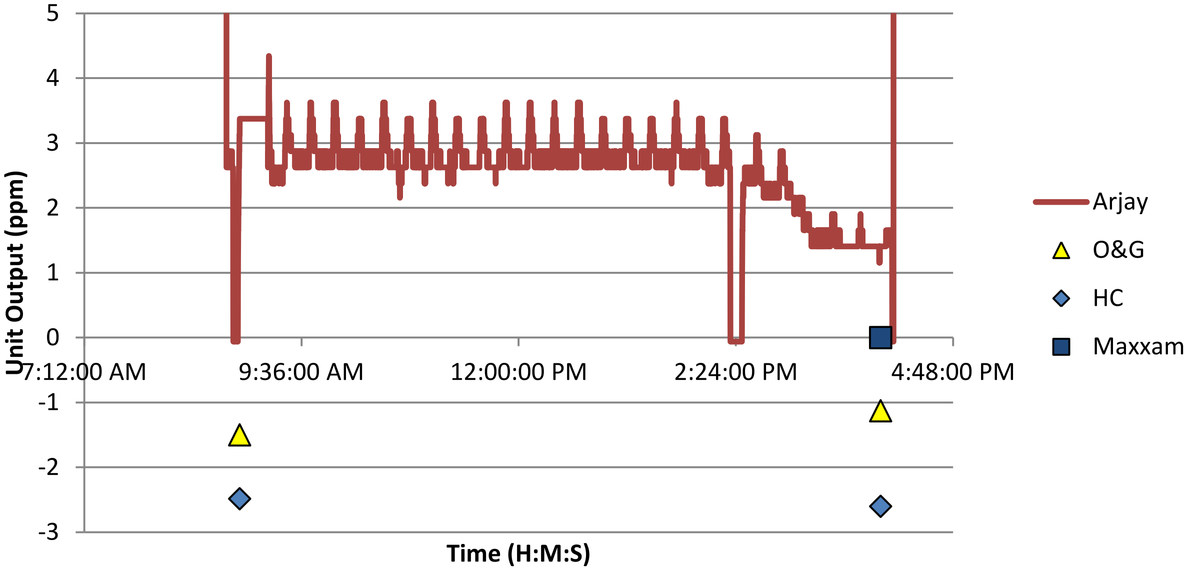

Figure A-13: Arjay data recorded for July 31, 2012, sand and gas addition. 15 mL sand added while gas added at 300 L/hr at 9:15, then 30 mL sand and 300 L/hr at 10:48, then 15 mL and 600 L/hr at 14:38.

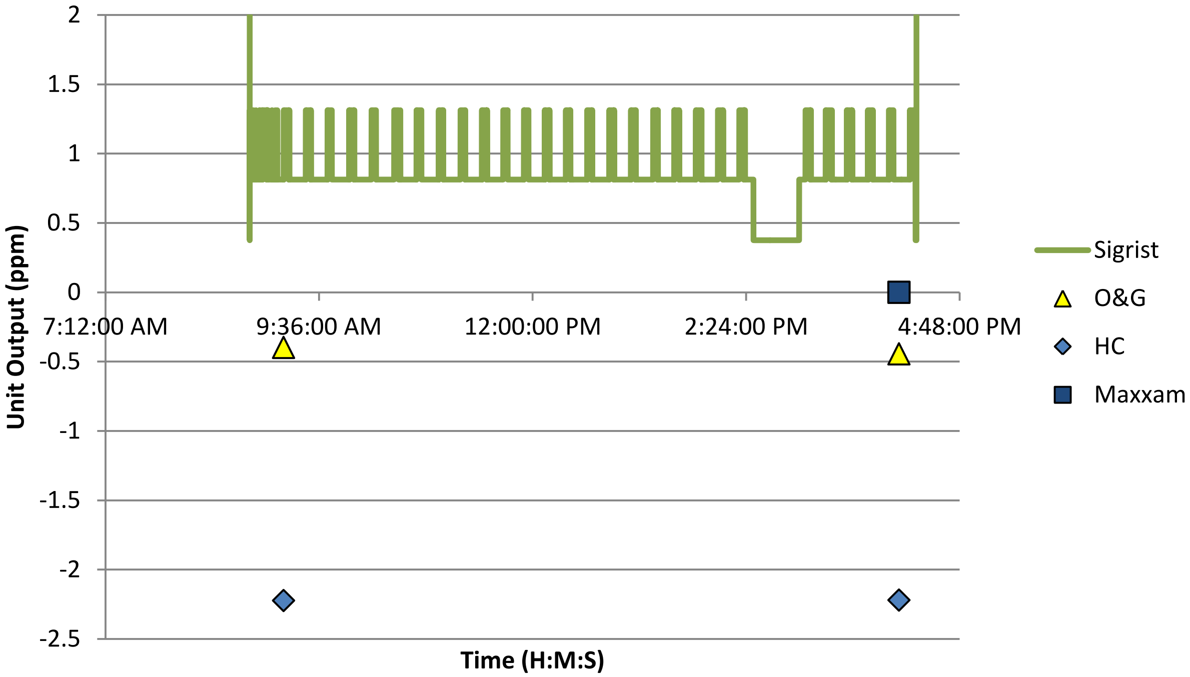

Figure A-14: Sigrist data recorded on July 26, 2012, gas addition. Gas added at 300 L/hr from 8:30, then increased to 600 L/hr at 15:00.

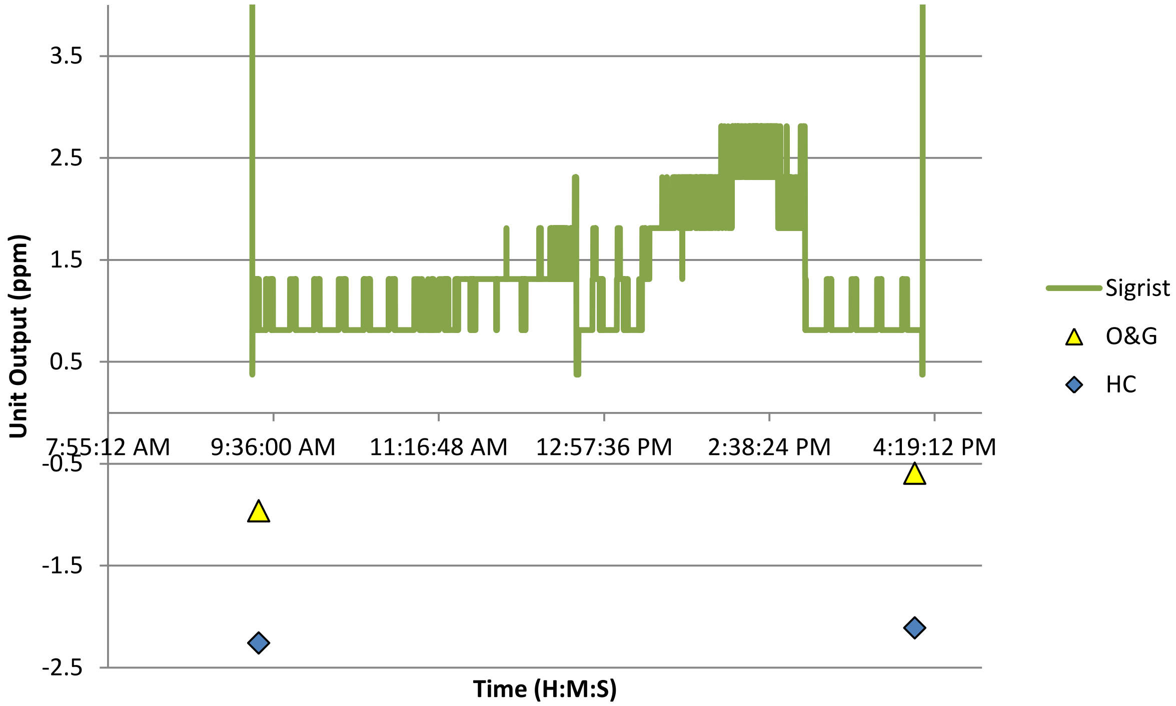

Figure A-15: Sigrist data for July 27, 2012, sand addition. 15 mL sand added at 12:40.

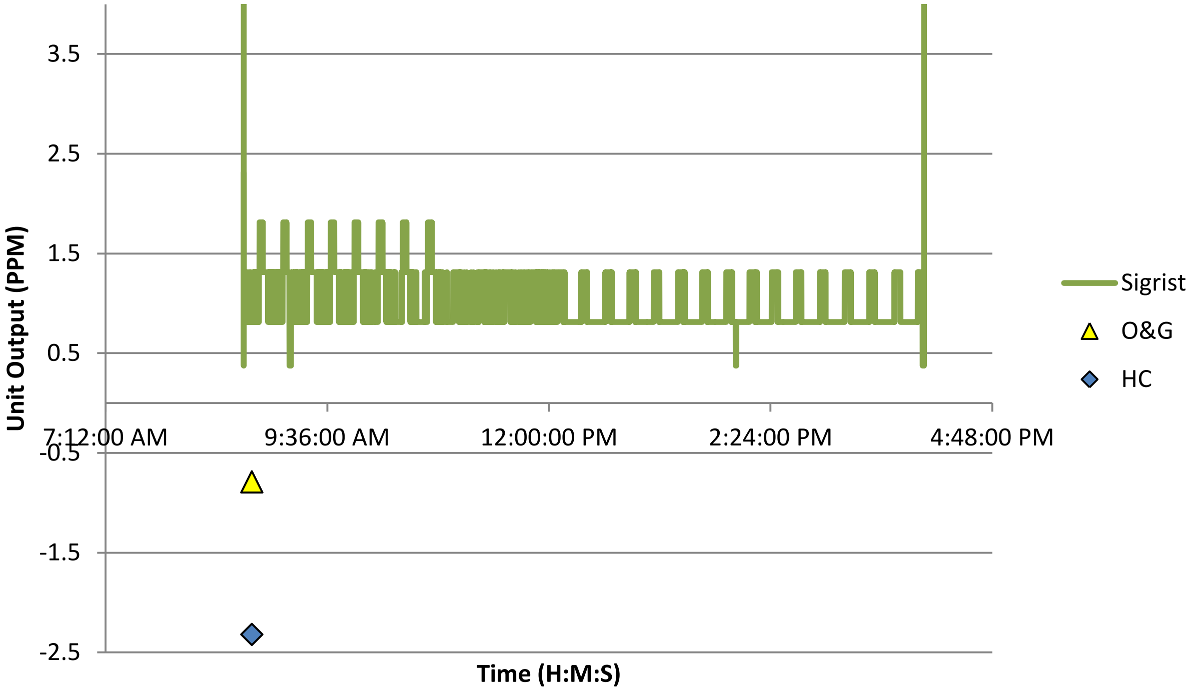

Figure A-16: Sigrist data for July 30, 2012, sand addition. 15 mL sand added at 9:10, then 15 mL added at 10:23, then 30 mL at 14:00.

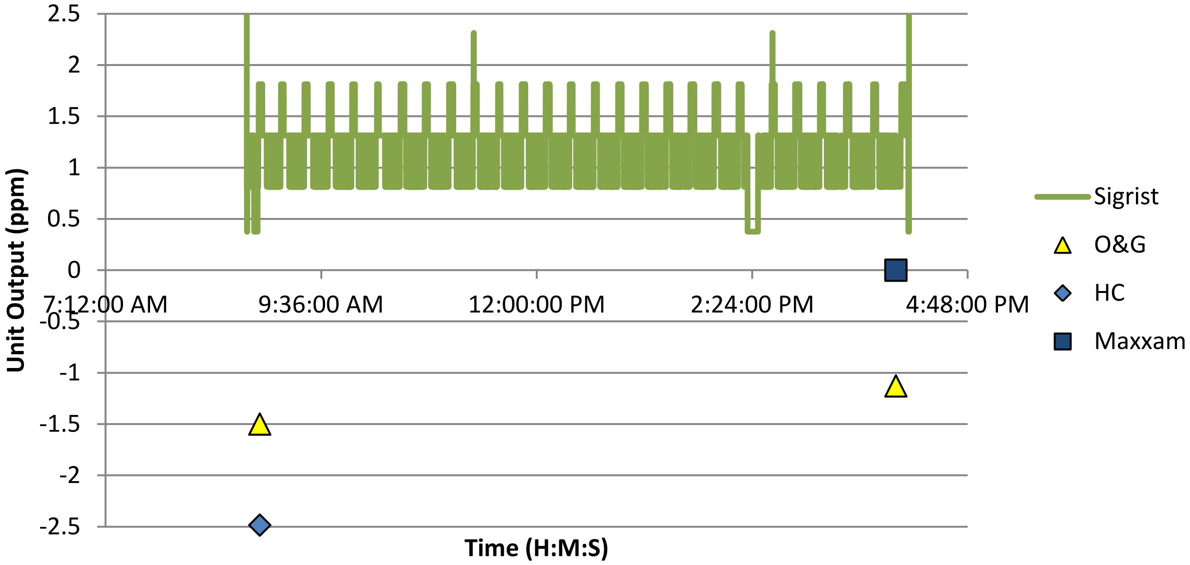

Figure A-17: Sigrist data for July 31, 2012, sand and gas addition. 15 mL added while gas added at 300 L/hr at 9:15, then 30 mL sand and 300 L/hr gas at 10:48, then 15 mL sand and 600 L/hr gas at 14:38.

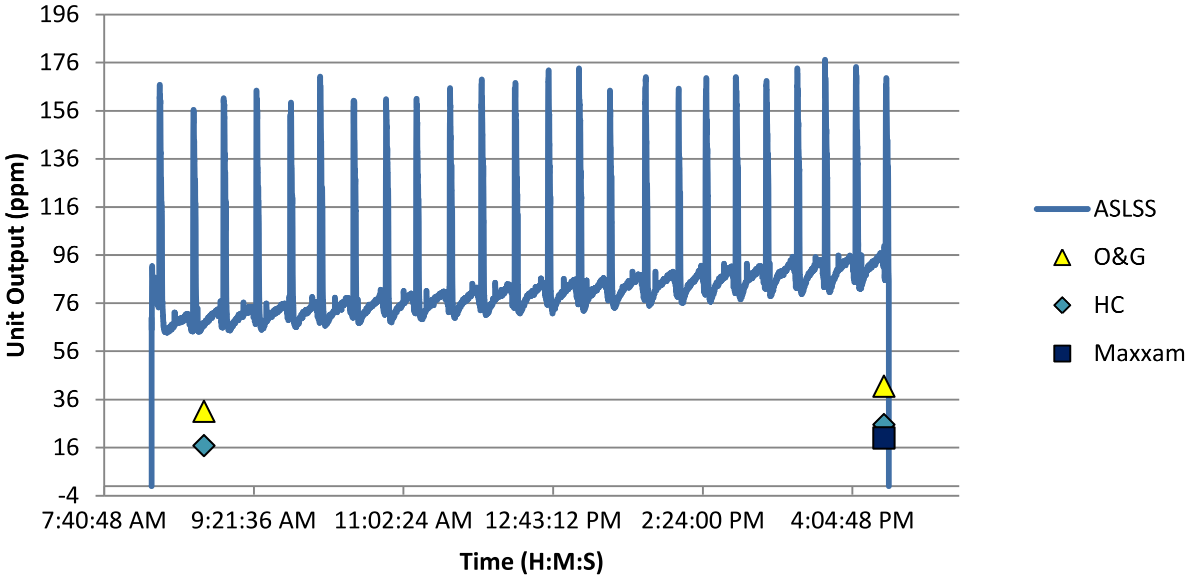

Figure A-18: ASLSS data recorded on Aug. 21, 2012, heat addition. Single heater at 100 % setting added at 8:15.

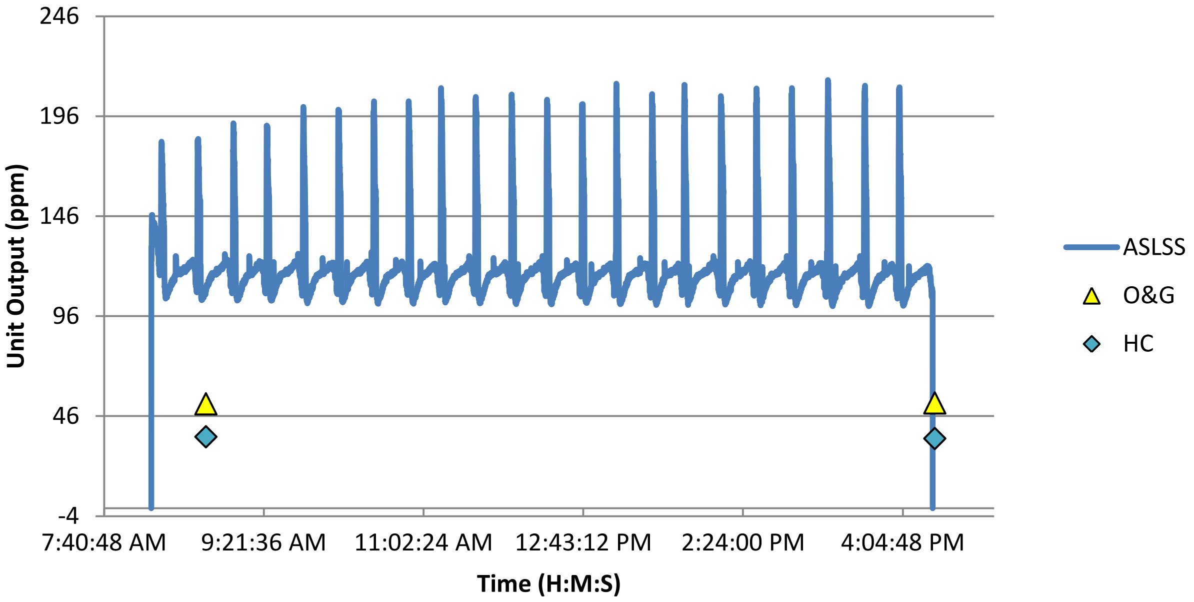

Figure A-19: ASLSS data recorded on Aug. 23, 2012, heat addition. Dual heaters at 75 % setting at 8:12, the both heater settings increased to 100 % at 12:08.