

**ASSESSMENT OF POTENTIAL ODOR PROBLEMS ON MCCOOK
RESERVOIR, CHICAGO, IL**

By

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Abstract

The City of Chicago and neighboring communities are served by combined sewer systems, which carry both stormwater and raw sewage. The combined sewer overflows (CSOs) could exceed the capacity of the wastewater treatment plant (WWTP) to process water. To avoid hazardous flooding and retain CSO systems without exceeding the treatment capacity of the plant, the U.S. Army Corps of Engineering has designed a series of retention ponds, including the McCook Reservoir. Because of the proximity of large populations near the reservoir, it is necessary to determine if sediments accumulated in the McCook Reservoir may generate odor problems around its surroundings. The objective of this research is to determine if odor problems may occur after emptying the McCook Reservoir. To achieve these objectives, experiments involving sediment characterization, olfactometry tests (OT), and H₂S flux determinations were conducted. Experiments were conducted using sediments with similar characteristics to those found at the McCook Reservoir. All tests were performed under different water contents and sediment-aging times. OT involved measuring the dilution ratios and H₂S concentration at the point when odor was detected. The flux of odor-causing compounds from the sediments was determined using a flux chamber, which was designed to control and provide accurate measurements of pressure, air flow, temperature, and H₂S concentrations. Potential odor problems were quantified statistically through the measurement of the threshold odor numbers (TON) and the H₂S concentration of exposed sediments at different environmental conditions. Results show that the TON and H₂S flux tend to decrease with increasing of sediment aging times. This tendency, together with (i) the high results obtained of TON and H₂S concentrations during earlier aging times, (ii) the observations obtained in odor intensity tests, (iii) the relation found between the H₂S average flux and sediment aging times; and (iv) the decreasing tendency in average flux with a water layer above the sediment, propose the possibility that there will be potential odor problems in the McCook vicinity during a earlier sediment aging times. This suggests the possibility of exploring new odor control techniques as the addition of water

content to the sediment to increase water content and thus reduce odor problems in the vicinity of the Reservoir.

Resumen

La ciudad de Chicago y comunidades vecinas son servidas por sistemas de alcantarillados combinados, que arrastran aguas turbulentas y aguas residuales crudas. Los desbordamientos de los alcantarillados combinados (CSOs) pueden exceder la capacidad de la planta de tratamiento de aguas residuales (WWTP) para procesar el agua. Para evitar inundaciones peligrosas y para retener el sistema de CSO sin exceder la capacidad de la planta de tratamiento el “U.S. Army Corps of Engineering” ha diseñado una serie de charcas de retención, incluyendo la reserva de McCook. Debido a la proximidad de grandes poblaciones cerca de esta reserva, es necesario determinar si los sedimentos acumulados en ésta pueden generar problemas de olores a sus alrededor. El objetivo de esta investigación fue determinar si pueden ocurrir problemas de olores después de vaciar la reserva. Para lograr estos objetivos, se hicieron experimentos que implicaban la caracterización del sedimento, pruebas de olfactometría (OT) y determinaciones de flujo másico de H_2S (moles de H_2S /min). Se utilizaron sedimentos con características similares a aquellos encontrados en la reserva de McCook bajo diferentes contenidos de agua y tiempos de envejecimiento en los sedimentos. Las pruebas de OT se hicieron midiendo las razones de diluciones y la concentración del H_2S a la cual el olor fue detectado; y el flujo de los componentes causantes de olor de los sedimentos fue determinado usando una cámara de flujo, el cual fue diseñado para controlar y proporcionar medidas exactas de presión, flujo de aire, temperatura, y concentraciones del H_2S . El potencial a problema de olores fue cuantificado estadísticamente a través de la medida del número de diluciones para detectar olor (TON) y de la concentración del H_2S de los sedimentos expuestos a diferentes condiciones ambientales. Resultados demuestran que los tiempos de envejecimiento afectó la medida de TON causando una reducción con el aumento en los tiempos de envejecimiento del sedimento. Esta tendencia, junto a (i) los altos resultados de TON obtenidos y las altas concentraciones de H_2S durante los primeros tiempos de envejecimiento; (ii) las observaciones obtenidas en las prueba de intensidad del olor; (iii) la relación encontrada entre el flujo promedio de H_2S y los tiempos del envejecimiento del sedimento; y (iv) la disminución en el flujo promedio con la capa de agua, proponen la posibilidad de que

potenciales problemas de olores pueden ser generados en la vecindad de McCook durante un corto período de tiempo de envejecimiento del sedimento. Esto sugiere la posibilidad de explorar técnicas donde la adición de alto contenido de agua puede causar reducción en problemas de olores.

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... “to God for give my health and courage to achieve this goal in my life”.

... “to my family for their help and always believe in me”.

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List of Symbols and Abbreviations

A&WMA - Air & Waste Management Association
ANOVA - Analysis of variance
ASTM - American Society for Testing and Materials
NH₃ – Ammonia
CO₂ - Carbon Dioxide
CAA - Clean Air Act
CA - Clean Air Line
R²- Coefficient of determination
CSOs - Combined Sewer Overflows
CSS - Combined Sewer Systems
Dil₅₀ – Dilution₅₀
DO - Dissolved Oxygen
prEN 13725 - Draft European Odour Standard
ED₅₀ - Effective Dosage at the 50% level
EMWTP - El Maní Wastewater Treatment Plant
EE-6 - Environmental Effect Committee
EEL - Environmental Engineering Laboratory
OD - External Diameter
GLM - General Linear Model
H₂S - Hydrogen Sulfide
ID - Internal Diameter
JCI - Jerome Communications Interface Software
CH₄ - Methane
NAAQS - National Ambient Air Quality Standards
NEPA - National Environmental Protection Act
NIOSH - National Institute for Occupational Safety and Health
OSHA - Occupational Safety and Health Administration
OU/m³ - Odour Units per cubic meter

OT - Olfactometry Tests
OM-PLPT - Omega Portable Low Cost Pressure and Temperature Data Logger
ppm – Part per million
PA - Phosphorous Available
PRASA – Puerto Rico Aqueduct and Sewer Authority
RMA - Research Management Act
STW - Sewage Treatment Works
SSF - Soil surface flux
SWRP - Stickney Water Reclamation Plant
TONs - Threshold Odor Numbers
TKN - Total Kjeldahl Nitrogen
TP - Total Phosphorous
TS – Total Solid
TVS – Total Volatile Solid
TOM - Triangle Olfactometer Method TARS - Tropical Agricultural Research Station
UA - Unclean Air Line
U.S. EPA - United State Environmental Protection Agency
VFA - Volatile Fatty Acids
WWTP - Wastewater Treatment Plant

Chapter 1: Introduction

1.1 Justification

The City of Chicago and 51 neighboring communities are served by combined sewer systems (CSSs), which carry both stormwater and raw sewage. Due to the highly developed urban nature of the area, stormwater runoff frequently exceeds the sewer capacity, backing up into basements and sending overflow into waterways. The combined sewer overflows (CSOs) also exceed the capacity of the wastewater treatment plant to process water. To avoid hazardous flooding of 530,000 houses in 37 communities near Chicago and also retain the CSO system without exceeding the treatment capacity of the plant, the U.S. Army Corps of Engineering has designed a system of retention ponds (Whelan, 2003). One of the system's components, the McCook Reservoir, is a vertical-walled limestone quarry. The McCook Reservoir was designed to collect CSOs before they enter the treatment plant during flood events in the city of Chicago, IL. McCook Reservoir has been designed with a maximum depth of 77.4 m and a storage capacity of $2.7 \times 10^7 \text{ m}^3$ (22,111 acre-ft). When the McCook Reservoir is completed it will be the largest reservoir of its type in the world (Whelan, 2003) and therefore, of vital environmental, economical, and public safety importance.

Odor pollution is a growing environmental issue. Odors remain at the top of air pollution complaints to regulators and government bodies around the U.S. and other countries and may cause sickness (Gostelow and Parsons, 2000). Odor problems may be generated after emptying the McCook Reservoir to the sewage treatment plant, because this residence time (10 to 20 days for small hydrologic events and from 60 to 90 days for large events) may be long enough to leave a significant organic residual on the walls. Previous studies (Padilla et al., 2002) indicate that a potential odor problem may exist after emptying the McCook Reservoir and that this problem may be quantified statistically through the measure of the Threshold Odor Number (TON). Another potential odor problem after emptying the McCook Reservoir may arise from

accumulated sediments. The degree to which accumulated sediments may cause odor problems must be, however, determined and quantified.

This investigation focused in conducting a series of odor detection and flux determination experimental studies using sludge sediments with similar characteristics to those found at the McCook Reservoir. The studies were designed to quantify if accumulated sediments may cause odor problem and under what conditions they may cause odor problem in the vicinity of McCook Reservoir. The odor detection and flux data can be applied to assess and predict the odor impact in the vicinity of the McCook Reservoir, provide information on the strength and intensity of odor, identify the causes of odor problems, and quantify the scale of odor emission from a particular source. Odor impact assessment can provide an effective tool to develop appropriate regional and local plans for odor control. This data may also be used to plan remediation of contaminated sites and monitor the effectiveness of remediation efforts. In addition, thought dispersion modeling, emission measurement may provide a mean for assessing air impacts, health human risk and effects.

1.2 Objectives

The main objective of this research was to determine if potential odor problems may exist after emptying the McCook Reservoir. Specific objectives involved:

- Quantifying odor threshold of exposed sediments under different environmental conditions
- Quantifying the hydrogen sulfide (H₂S) concentrations at odor threshold of exposed sediments
- Determining the flux of H₂S from sediments under different environmental conditions
- Evaluating potential relationships between flux of H₂S and potential odor problems near McCook Reservoir under different environmental conditions

The environmental conditions that were used included three different water contents for odor tests and two water contents for flux tests. All evaluations were conducted at standard room temperature (293.15-298.15° K) and at five aging times. The fluxes of odor-causing compounds from the sediments were determined under the same temperature and aging conditions as for the TON experiments. In addition, flux tests were conducted with a layer of water over the sediments, higher temperature, and some degree of sediment mixing. Measured concentrations and flow rates were used to quantify the emission rates of odorous compounds through the sediments.

Chapter 2: Literature Review

2.1 Situation in Cook County

McCook Reservoir is located in Cook County in the state of Illinois. Cook County has a total area of 1,635 square miles, of which 946 square miles is covered by land and 689 square miles by water. It has a population of 5,376,741. About 23% of the County is served by a combined sewer system. These sewer systems carry raw sewage from homes and industries slurry during dry periods, but they also carry storm runoff after rainfall events. Consequently, storm runoff mixes with sewage flows, producing large amounts of contaminated water (MWRDGC, 1999). This additional amount of untreated water may spill over to streams causing severe stream pollution and violation of the Clean Water Act (MWRDGC and USARCE, 2003).

To avoid hazardous flooding, the U.S. Army Corps of Engineers Corps in conjunction with other agencies developed a Tunnel and Reservoir Plan (Whelan, 2003). The Reservoir Plan contains the O'Hare, Thornton and McCook Reservoirs. The O'Hare Reservoir has a capacity of 350 million gallons and the Thornton will be constructed with a potential total capacity of 6-8 billion gallons. The U.S. Army Corps of Engineers is responsible for constructing the McCook Reservoir. This will be a flood-control reservoir to store combined stormwater and raw sewage until it can be safely released into the sewer system (U.S. Army Corps of Engineers, 2000). McCook Reservoir is expected to be constructed by 2014. This will be the largest reservoir of this type in the world with a potential capacity of 7.5 billion gallons (Whelan, 2003).

2.2 Combined Sewer Systems

Combined sewer systems are generally the older sewer systems designed to convey both sewage and stormwater (combined in one pipe) to a Waste Water Treatment Plant (WWTP) (Engler and Harding, 2001), where it is treated and then discharged to a water body. These systems are designed to carry wastewater during dry periods to a treatment facility (Cornwell and Mackenzie, 1998). During rain storms, the excess water is discharged directly into a river, stream, or lake without treatment. Unfortunately, the stormwater is mixed with untreated sewage (Cornwell and Mackenzie, 1998). When the untreated wastewater and stormwater do overflow into a stream, this is called a Combined Sewer Overflow. Sewage from CSOs may enter to the environment through overflow during rain storm, direct release of a broken pipes, and/or intentional releases from a sewer system to prevent basements within the system from flooding (Engler and Harding, 2001).

In recent years, pollution caused by CSO has become a serious environmental concern. Historically, CSOs are among the major sources for beach closings and other water quality impairments (Engler and Harding, 2001). Common contaminants in the CSOs include untreated human and industrial waste, suspended solids, oils and grease, chemicals, toxic materials, nutrients, floatable, pathogenic microorganisms and other pollutants (EPA, 1999). Sewage solids deposited in CSS during dry weather are major contributors to the CSO pollution load (Pisano et al., 1998). The main impact of CSO is generally a depletion of oxygen in the receiving waters due to an input of organic matter and bacteria. The degree of impact, however, depends on the sewer type, the rainfall intensity, sewage characteristics, and the properties of the receiving waters (Seidl et al., 1998). The emission of pollutants from CSSs into the receiving water represents only a fraction of the total pollutant amounts that are processed by the wastewater treatment plant (Bauwens et al., 1996). Nevertheless, the impact of CSO on the receiving water cannot be neglected, mainly with respect to peak concentrations and to the accumulation of toxic substances. Moreover, CSOs may decrease the treatment efficiency.

Overall, a CSOs overflow event causes danger to the environment, public health, aquatic species, aquatic habitat and aesthetic property values. Under the U.S. Environmental Protection Agency (U.S. EPA)'s CSO Control Policy, discharge permits issued to communities with CSSs are expected to include minimum controls that can reduce the magnitude, frequency and impacts of CSOs without significant construction or expense (EPA, 1999). Maximization of storage in the collection system is one of the minimum CSO Control Policies.

In order to reduce the impact of the CSO, when the stormwater and wastewater system cannot be separated, the best measure for attenuating peak combined sewer flows is additional storage and real-time control in the sewer system. This control may be implemented through the construction of retention and/or treatment basins, which are designed to capture the combined sewage and storm runoff waters. Storage facilities have been used extensively for CSO mitigation (EPA, 1999). Typically, the CSO retention methods include underground storage (e.g., tunnels), in-receiving water storage, and retention basins. The retention basins can be designed to control both flow rate and water quality. CSO storage provides time for initial treatment and disinfections, minimizes water quality impacts and attenuates peak flows, eliminates or reduces sewer backups, improves the efficiency of existing treatment capacity, and improves effluent quality at the treatment facility (EPA, 1999).

2.3 Sediment Characteristics

Combined sewer systems contain organic and inorganic matter that settle into sludge sediments in the retention reservoir. The composition and characteristic of sediment/sludge vary widely (Nathanson, 2000). One of the most important factors that possibly influence the sediment characteristics is the source of wastewater and the type of the treatment where they have been generated (Kiely, 1997). A treatment plant may have several different types of sludge depending on the treatment processes involved. The most common unit process in wastewater treatment is primary sedimentation to remove settleable solid that can be thickened by gravity settling. The sludge consists of organic

solids, grit and inorganic fines (Kiely, 1997). Secondary sludge is essentially biological, the result of conversion products from soluble (non-settleable) wastes from the primary effluent (Kiely, 1997). Chemical sludge results when lime, aluminum or ferric salts, etc., are added to improve the suspended solids removal or to chemically precipitate phosphorous. The septic sludge has normally high content of readily biodegradable organic matter due to the long retention time in the septic tank. This sludge does almost always smell bad and contain hydrogen sulfide (Einarsen et al., 2000).

The chemical constituents of wastewater are typically classified as inorganic and organic. Inorganic chemical constituents of concern include nutrients, metals, gases and nonmetallic constituents, such as; pH, nitrogen, phosphorous, alkalinity, chlorine, sulfur, gases, and odor (Tchobanoglous et al., 2003). Sediments normally contain high concentrations of readily biodegradable organic matter and inorganic compounds, degradable and non-degradable matter, solids, water content, and high content of microorganisms. Secondary/biological sludge has less readily biodegradable organic matter, but more active biomass. The organic compounds contained within the sediment include carbohydrates, fats, oils, and protein that are high in carbon and sulfur. Microbes, such as bacteria, viruses, and protozoa, nutrients such as phosphorous and nitrates, and a variety of household and industrial chemicals may also be found in sediment sludge.

Sludges contain nitrogen and phosphorus in significant amounts. Phosphorus may appear in many forms in wastewater (Sawyer et al., 1994). One of them is from the human excrement. Most of the phosphorous found in wastewater is contributed by human waste as a result of the metabolic breakdown of proteins and elimination of the liberated phosphates in the urine (Sawyer et al., 1994). Nitrogen in wastewater is present in many organic and inorganic forms, but it is originally present in the form of organic (protein) nitrogen and ammonia (Sawyer et al., 1994). Total Kjeldahl nitrogen (TKN) is a measure of the total organic and ammonia nitrogen in the wastewater. TKN gives a measure of the availability of nitrogen for building cells, as well as the potential nitrogenous oxygen demand that have to be satisfied.

Sewage sludge or sediments may be characterized based on physical, chemical and biological characteristics (Kiely, 1997). Physical characteristics include percent of total solid (TS) and volatile solid (TVS), specific gravity, shear strength, and particle size. Chemical characteristics include inorganic and organic content, metal content, pH, alkalinity, nutrient content (e.g., N, P, K), and amount of PCBs and Dioxins. Biological characteristics are based on the number of indicator and pathogenic organisms present. Commons characteristics found in general sludge are summarized in Table 1.

Table 1: Physical characteristics of sludge (Kiely, 1997)

Parameter	Primary sludge	Secondary sludge	Dewatered sludge
Dry solids	2–6%	0.5–2%	15–35%
Volatile solids	60–80%	50–70%	30–60%
Sludge specific gravity	~ 1.02	~ 1.05	~ 1.1
Sludge solids specific gravity	~ 1.4	~ 1.25	~ 1.2– 1.4
Shear strength, (kN/m ²)	< 5	< 2	< 20
Energy content (MJ/kg VS)	10–22	12–20	25–30
Particle size (90%)	< 200 μm	< 100 μm	< 100 μm

2.4 Odor

Odor is one of the five senses. The sense of smell is the most complex and unique in structure and organization (McGinley et al., 2000). Odor is defined as a sensation resulting from the reception of a stimulus by the olfactory sensory system. Olfactory system plays a major role as defense mechanism by creating an aversion response to malodors and irritants. This is accomplished by two main nerves: the olfactory nerve, which processes the perception of chemicals; and the trigeminal nerve, which processes the irritation or pungency of chemicals (McGinley et al., 2000).

It is important to distinguish between odorants and odors, because frequently and incorrectly the two terms are used interchangeable. Odorants are the compounds responsible for imparting odor (chemical), whereas an odor is the perceived effect of the odorants as detected and interpreted by the olfactory system (Gostelow et al., 2003). Odor perceptions occur when one or many odorants are present (McGinley et al., 2000).

Odor pollution problems are complex because of the somewhat nebulous (undefined) nature of odors. Consequently, they are classified as non-criteria pollutants by the EPA (Wark and Warner, 1981). Environmental odors are commonly recognized to have four sensory parameters: threshold concentration, intensity, character and hedonic tone (McGinley and McGinley, 2000). The lowest concentration at which an odor can be detected by a certain percentage of population is known as the threshold concentration. Intensity is associated with the perceived strength by the human. The term character is related to what the odor is like. Odor character is sometimes called the “quality” of the odor or the "offensiveness" of the odor. More offensive odors are more annoying (McGinley et al., 2000). Hedonic tone is defined as the degree of pleasantness or unpleasantness associated with the odor (McGinley et al., 2000; EPA, 2002). Human response to odors is highly subjective; perceptions vary usually from person to person, and are strongly influenced by previous experience and emotions at the time of odor perception (EPA, 2002).

The determination of odor source strength is the first step in solving an odor problem, but unfortunately, odors are difficult to measure. Basically two classes of odor measurement are frequently used: analytical and sensory measurements. Analytical measurements evaluate odorant type and concentrations whereas sensory measurements employ human subjects to analyze odor (Gostelow et al., 2003). Sampling and measurement are complicated by the fact that most odor emission consists of many individual odorants and the overall odor of complex mixture cannot easily be predicted. A range of measurements may, consequently, be required.

It is important to measure and assess odor problems, because they may cause effects in humans and affect the quality of life. Odor may cause health effects such as headaches, nausea, gastrointestinal distress, fatigue, eye irritation, sleep disturbance, inability to concentrate, classical stress response, (McGinley et al., 2000) loss of appetite, and irrational behavior (Gostelow and Parsons, 2000). Measurement and characterization of odors is not only important in assessing the magnitude of the problem, it is also crucial for the proper design of odor control systems. For systems which remove odorous

compounds from air, accurate data on atmospheric concentrations of odorants are essential.

2.5 Odor Causing Agents

Odor problems most commonly result from biological degradation of sulfur-bearing organic matter in the absence of oxygen or nitrate (Einarsen et al., 2000; Winter and Duckham, 2000). Degradation under these conditions, also known as septic conditions, promotes the formation of sulfides and other gases including hydrogen sulfide (H_2S), ammonia (NH_3), carbon dioxide (CO_2), and methane (CH_4) (Tchobanoglous et al., 2003). Although H_2S is the gas most often associated with odor problems, there are other compounds, such as mercaptans, ammonia, amines, indole, skatole, and volatile organic acids may also contribute to objectionable odor (EPA, 1985). Table A.1 (see Appendix A) shows the odorants associated with waste treatment. Mercaptans are reduced organic-sulfur compounds commonly found in wastewater. They have been found to have extremely low threshold odor number (EPA, 1985), indicating high potential for odor problems. Amines are common by-products of proteins decomposition, some of which contain sulfur.

The source of sulfate in the environment is organic sulfur-containing compounds. The sulfur ion occurs naturally in most water supplies and is present in wastewater as well (Tchobanoglous et al., 2003). Most of the planet's sulfur is found underground in sedimentary rocks and minerals, which over the time erode to release sulfur-containing compounds into the ocean (Raven and Berg, 2004). Sulfur gases enter into the atmosphere from natural sources in both the ocean and land. Some sources of sulfur gases into the air are: the seaspray which delivers sulfates (SO_4^{2-}), volcanoes which release hydrogen sulfide and sulfur oxides (SO_x) (Raven and Berg, 2004), and human activities. Sulfur gases comprise a minor part of the atmosphere and are not long-lived because atmospheric sulfur compounds are reactive.

The sulfur cycle (Figure 1) is complicated by the large number of oxidation states the element can assume. Inorganic processes are responsible for many of these

transformations, but living organisms (essential component of proteins), especially bacteria, also sequester sulfur in biogenic deposits or release it into the environment (Cunningham and Woodworth, 2001). The reduction of sulfur compounds occurs in anaerobic environments and oxidation of sulfur compounds occurs in aerobic environments (Reinhart and Townsend, 2003). The occurrence of sulfide in municipal wastewater results principally from the biochemical reduction of inorganic sulfur compounds (EPA, 1985).

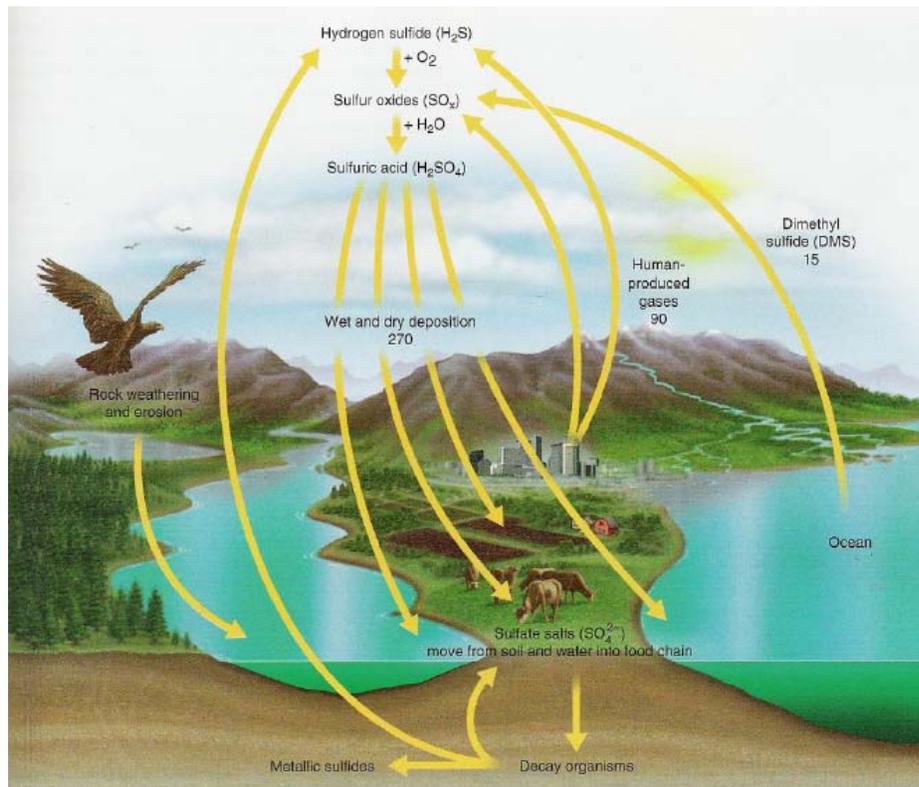


Figure 1: Simplified model of sulfur cycle (Raven and Berg, 2004)

In addition to severe odor problem, H_2S may cause serious health risks, corrosion, and reduced treatment efficiency (Einarsen et al., 2000). The toxic effects of hydrogen sulfide, especially at high concentrations, are well documented (Einarsen et al., 2000); however, health problems have also been reported after exposure to low concentrations over a long period. Other malodorous compounds, like mercaptans, are also defined as health hazardous. Corrosion can be a result of chemical reaction or bacteriological activity where H_2S is oxidized to sulfur acid. Hydrogen sulfide and volatile fatty acids

(VFA) attack concrete and metal construction, as well as mechanical and electrical equipment.

2.6 Odor measurements

Odor is one of the environmental nuisances that may affect quality of life and create health problems (Gostelow and Parsons, 2000). To control odors, they must be measured first. Because these measurements are made with the objective of preventing and controlling odors by humans, it is necessary to make measurements which relate directly to human smell (Yang and Hobson, 2000). This is a difficult task, which is further complicated by subjective response to odors and incomplete understanding of the sense of smell (Gostelow and Parsons, 2000). Response to odors is highly variable, i.e. diverse people find different odorous offensive, and at a different concentrations. In addition many odorous emissions, including those from sewage treatment works (STW), consist of many individual odorous components and the overall odor complex mixtures cannot be easily predicted. For these reasons, there is no universally accepted method for the quantification of odors, and odor measurement has often been regarded as an art as opposed to a science (Gostelow and Parsons, 2000).

2.6.1 Olfactometry

Olfactometry is a psychophysical process based upon olfactory responses of individuals sniffing diluted odors presented by an olfactometer to determine or measure odor strength or odor concentration. Olfactometry employs a panel of human noses as sensors (Environodour Australia Pty Ltd, 2005). As already mentioned, the sensitivity of odors is variable between different persons, for this reason is recommended to use 4 to 10 panelists. Generally, panelists are presented with ascending odor concentrations to minimize olfactometry fatigue, adsorption, and exposure to potential toxics substances in the sample (Gostelow et al., 2003; Environodour Australia Pty Ltd, 2005).

Several factors as adaptation, memory, age and gender, affect individual odor perception (Environodour Australia Pty Ltd, 2005). Adaptation is the fatigue from continued exposure to an odor. This depends on odor concentration experienced. Memory development is also a common experience during odor detection. It helps identifies that it is familiar odors and assigns them to general categories. Increasing age is correlated with decreasing acuity in odor perception (Environodour Australia Pty Ltd, 2005). Female panelists normally have greater sensitivity than male panelists from same age group. It has been reported that smokers have less sensitivity than non smoker (Environodour Australia Pty Ltd, 2005). Factors such as health (allergy, cold), personality, education background, and training may also affect the ability to assess odors (Environodour Australia Pty Ltd, 2005; St. Croix Sensory, Inc., 2003).

Odor measurements are commonly performed using an olfactometry system. This system generally consists of an odor-delivery module connected to “sniffing” ports, where a panel of individuals detects the odor. Some standard methods exist for olfactometry, but their development is still ongoing. Examples of these standard methods include: American Society for Testing and Materials (ASTM E 679-91, 1991), the draft European odour standard (prEN 13725) and a method developed by the Environmental Effect Committee (EE-6). The ASTM E 679-91, “Determination of Odor and Taste Thresholds by a Forced-Choice Ascending Concentration Series of Limits” is based on the use of dynamic olfactometry to automatically perform dilutions of odorous air, which are subsequently assessed by human panelists for odor detection. The EE-6 standard is generated by the Air & Waste Management Association (A&WMA). It is a Draft Odor Testing Guidance Document. This document is entitled “Guidelines form Odor Sampling and Measurement by Dynamic Dilution Olfactometry”. The draft European Odour Standards identified as prEn 13725 is entitled “Air Quality-Determination of Odour Concentration by Dynamic Olfactometry”. This document discusses the equipment, panel selection, test, and calculation procedures for odor measurement. It has greatly improved repeatability (McGinley and McGinley, 2001). Even with standardization, however, it should be remembered that olfactometry is not a precise measurement (Gostelow and Parsons, 2000).

Two methods are commonly used for panelists to indicate whether and odor can be detected at a particular dilution: yes/no and forced-choice. The mechanism employed in the yes/no method is the use of a single sniffing port where the panelist is asked if the odor can be detected or not. In the forced-choice method, also known as triangle olfactometer, the diluted odorous air sample is presented at one sniffing port, and two or more sniffing ports have odor free air (blanks samples). The panelist is asked at which port contains the odors sample. The typical method employed in measurement and assessment of odor is the triangle olfactometer method (Gostelow et al., 2003). The strength of an odor is determined by the number of dilutions with odor-free air needed to reduce an odor to a barely detectable level (EPA, 1985). Dilution may be static or dynamic (Gostelow et al., 2003). Static dilution involves the mixing of fixed volumes of odorous-free air; whereas dynamic dilution involves the mixing of known flows. It is considered that dynamic dilution is superior to static because the sample can be delivered to the sniffing port at a constant flow rate (Gostelow et al., 2003). This factor contributes to improved repeatability of results. A supplementary parameter can be added to both olfactometry methods. Additional to the procedure established by in yes/no method and forced choice method, the panelists may be asked to indicate the degree of accuracy of their response. This alternative may add assurance measure when interpreting panelist perception.

2.6.2 TON

Conventional olfactometric techniques have been used to evaluate odors from sewage treatment and sludge storage facilities in terms of concentration (or “strength”) at their limits of detection (Tchobanoglous et al., 2003). The threshold odor of a water or wastewater samples is determined by diluting the sample with odor-free water. The threshold odor numbers corresponds to the greatest dilution of the sample with odor-free water at which an odor is just perceptible (Tchobanoglous et al., 2003) or until the least definitely perceptible odor is achieved (Heber et al., 2000). If odor from a source is

strong it has a high TON values and detection occurs even at lower amounts of odorous-air (high dilution). Higher TON value thus represents high detection and greater odor problems.

The odor detection threshold approach has been adopted as an objective olfactometric indicator of odor nuisance. Odor concentration derived by threshold olfactometry is dimensionless, mathematically expressed as:

$$TON = \frac{Q_o + Q_f}{Q_o} \quad (1)$$

where Q_o is the flow rate of odourous sample, and Q_f is the flow rate of odor-free air required for odor detection. Although TON is a dimensionless parameter, it has become common to envisage them as physical mass concentrations, in which case they tend to be termed odor units per cubic meter (OU/m^3) (Gostelow et al., 2003). TON it is expressed as OU/m^3 in order to calculate odor emission rates. Consequently, the TON is an abstract measure of odor concentration (Heber et al., 2000). Measurements of odor concentration alone are insufficient to assess human perception of odor (Lambert et al., 2000). It is recommended to evaluate odor samples by determining TON, intensity, and/or hedonic tone.

2.6.3 Effective Dosage at the 50% Level (ED_{50})

Other terminology commonly used to measure odor strength is the effective dosage at the 50% level (ED_{50}) (Tchobanoglous et al., 2003). This is used for a wide range of study of toxicity and health effects, biological and environmental responses, such as toxicity of chemicals, stunted development in the offspring of a pregnant animal, reduced enzyme activity, onset of hair loss, and/or odor problems. The ED_{50} is the dose that causes 50% of the population to exhibit whatever response is under study (Raven and Berg, 2004). The ED_{50} may be obtained following the triangle olfactometer method using

human panelist to detect odors. For a gas sample, the ED₅₀ value represents the number of times an odorous air samples must be diluted before the average population (50 percentile) can barely detect an odor in the diluted sample (Tchobanoglous et al., 2003). A dose-response curve (Figure 2) shows the effect of different doses on a population of test organisms. This concept reflects the concentration/dilution factor at which 50 % of the panel would detect odor in the sample.

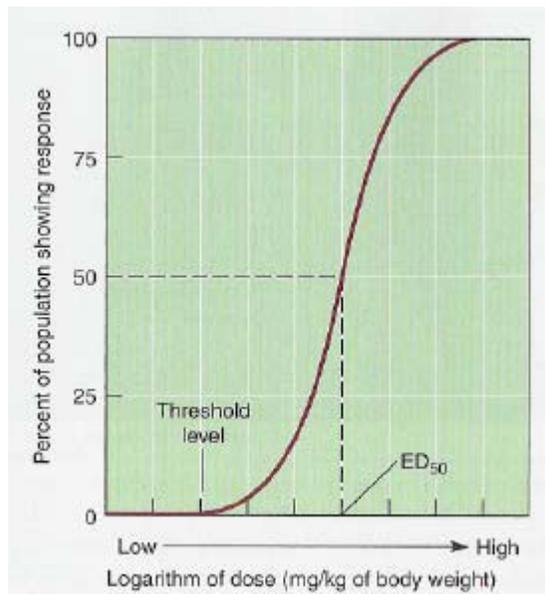


Figure 2: Dose-response curves

2.6.4 Intensity

Odor intensity is the relative perceived psychological strength of an odor that is above its detection threshold and is independent of the knowledge of the odor concentration (McGinley et al., 2000). However, while concentration may be the most important property of dilute odor at their limit of annoyance (Lambert et al., 2000), other characteristics are also of significance in the normal perception of odors, including variability in the sense of smell between different people exposed to odor. Using dynamic olfactometry to determine odor threshold (and therefore odor concentration) and then

odor intensity, a suitable relationship between concentration and intensity can be determined, allowing different odor types to be compared (EPA, 2002).

Odor intensity may be measured using several methods, including magnitude estimation and intensity scales methods. Magnitude estimation is a procedure where the intensity of one odor is compared to another odor. This method is very difficult to compare across many odors. Intensity is normally measured subjectively usually using ordinary categorical scales, also known as scales descriptive word category (Gostelow et al., 2003) (St. Croix Sensory, Inc., 2003). Odor intensity scale is a useful dimension to quantify, because some odors are perceived as being stronger than others. This method provides a qualitative description of odor intensity with a numerical scale (EPA, 2002). Intensity method may be employed using three to ten categories, but six category scales is the alternative most commonly used. The six category scales are shown below:

- | | |
|------------------------|------------------------|
| 0: No odor perceivable | 3: Clearly perceivable |
| 1: Barely perceivable | 4: Strong odor |
| 2: Faint perceivable | 5: Very strong odor |

The shortcomings of this approach are that the five points on the scale do not represent a linear increase in perception and that each assessor may interpret the scale differently, regardless of the assessor's training (St. Croix Sensory, Inc., 2003).

The subjective measurements, as intensity method, have the advantage that require no special equipment and can be obtained quickly at low cost. The disadvantages include difficult interpretation of measurements due to the variation of odor perception (Gostelow et al., 2003; Heber et al., 2000). Because of these variations, the use of the subjective measurement as regulatory purposes is limited.

A generally acceptable relationship between odor intensity and odorous contaminant concentration, as illustrated in Figure 3, is given by the Weber Fechner equation:

$$P = K \log S \quad (2)$$

where P is the magnitude of sensory response, or odor intensity, K is a constant, S is the magnitude of stimulus, or odor concentration. Values of K have been found to vary from 0.3 to 0.6.

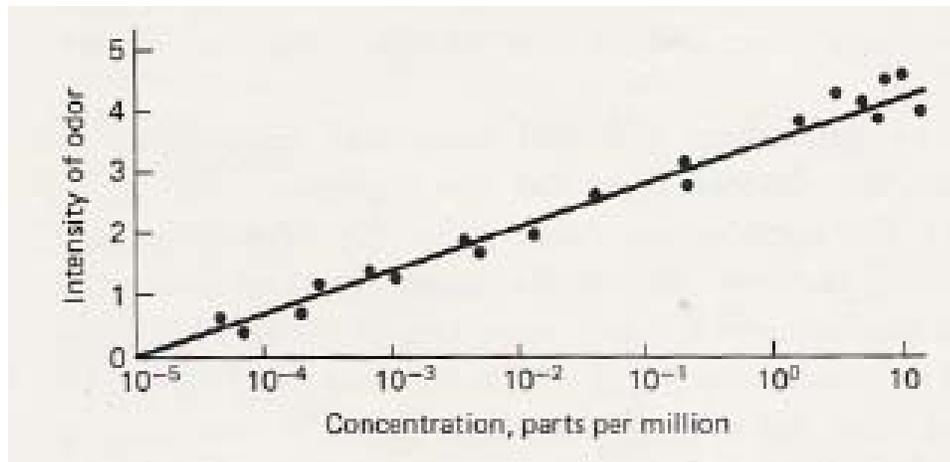


Figure 3: Relationship between odor intensity and concentration (Wark and Warner, 1981)

The Weber-Fechner relationship has been developed for H₂S and butanol using data from the German VDI 3882 standard (EPA, 2002). The relationship between odor intensity and concentration for these particular odorants is consistent, but the coefficients used within this relationship differ for the two odorants. As can be seen from Figure 4, if an odor concentration of 10 odor units was chosen as the appropriate criterion, butanol would be perceived as a weak odor, whereas hydrogen sulphide would be perceived as a distinct odor. To have equivalent protection against odors would require choosing an intensity level for the criterion and then working across the graph to determine the appropriate concentration for that odorant. For example, if the criterion were set at a “distinct” perceived odor (in the laboratory) then the appropriate concentrations would be 11 and 33 odor units for hydrogen sulphide and butanol respectively (EPA, 2002).

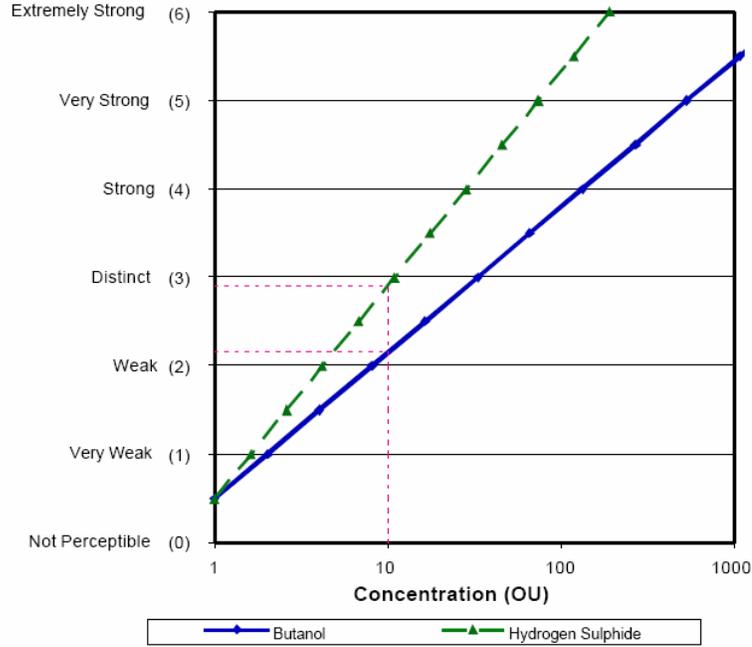


Figure 4: Relationship between Perceived Odor Intensity and Odor Concentration for butanol and hydrogen sulfide using the Weber-Fechner Law (EPA, 2002)

Current methods used to measure odor intensities rely either on the use of H₂S as a surrogate for determining odor strengths or the use of panels of odor assessors to determine human detection threshold, generally using dynamic dilution olfactometry (Stuetz et al., 1999). H₂S is used as a surrogate because it is a common component of malodors from wastewater treatment works and it is reported to be more sensitive than TON. In addition, H₂S can be related to liquid-phase measurements and theoretical models of sulfide formation, and it is easily and rapidly measured down at low ppb levels (Gostelow and Parsons, 2000).

Data relating odor intensity and H₂S concentration (Table 2) indicate that as H₂S concentration increases odor detection also increases (Thrasher, 2001).

Table 2: Concentration and Odor of hydrogen sulfide (Thrasher, 2001)

0.02 ppm	No odor
0.13 ppm	Minimal perceptible odor
0.77 ppm	Faint, but readily detectable odor
4.6 ppm	Easily detectable odor, moderate odor
27.0 ppm	Strong, unpleasant odor, but not intolerable

Because of the noxious effect of H₂S several institutions have set concentrations standards. The Illinois Institute for Environmental Quality recommends a standard for gaseous hydrogen sulfide of 0.015 mg/m³ (0.01 ppm) to minimize adverse health effects from chronic exposure in urban air (Thrasher, 2001). The Occupational Safety and Health Administration (OSHA) has set an acceptable ceiling limit for H₂S of 20 parts hydrogen sulfide per 1 million parts of air (20 ppm) in the workplace and the National Institute for Occupational Safety and Health (NIOSH) recommended a 10 minute ceiling limit of 10 ppm (Agency for Toxic Substances and Disease Registry, 2004). Table A.2 (see Appendix A) shows some of the Hazardous characteristics of hydrogen sulfide gas.

2.7 Flux of odor-causing agents from sediments

The flux of odor gaseous components from sediments is defined as the rate of mass exchange of gaseous components across a given length per unit area. At the sediment surface this exchange occurs between the sediments and the atmosphere. The need to measure gas flux at the soil/sediments surfaces arises from the interest in quantifying the emission of gases from soils and sediments and sinks of gases within the soil and sediments (Rolston, 2002). Because of similarities between soils and sediments, flux theory in soils can be applied to flux in sediments.

2.7.1 Flux

Soil (or sediments) surface flux (SSF) is the rate of exchange per unit area of one or more gases between soils and the atmosphere. Diffusion is the principal mechanism in the flux of gases between the sediments/soil and the atmosphere (Rolston, 2002) but it is difficult to measure in the field because the gas diffusion coefficient is normally not known (Jury et al., 1991). The most common methods for estimating gas flux involve flux chambers at soil surface (Reichman and Rolston, 2002). These chambers either allow gas to accumulate in a box placed over the surface or trap the gas at the surface while maintaining at low concentration. In either method, only the gas escaping at the surface is measured. These might be different from the rate of gas production (Jury et al., 1991) in soil and sediments.

Gas flux from soil and sediments depend on environmental conditions and the gas and soil/sediments characteristics. Environmental conditions affecting this flux may include temperature, moisture content, and exposure period. These environmental parameters directly influence the diffusion of gases and may also influence the production or production of odor-causing compounds.

2.7.2 Diffusion

Diffusion is the principal mechanism in the exchange of gases between the soil/sediments and atmosphere (Rolston, 2002). The exchange results from concentration gradients established by the respiration of microorganisms and other living organisms and, by production of gases associated with biological reactions such as fermentation, nitrification, and denitrification. The diffusion of water and other vapors within the soil and sediments also occurs due to differences in vapor pressure gradients induced by temperature differences or by evaporative conditions at the soil surface. Several gases are of particular interest in relation to gaseous diffusion in soils. The steady state diffusion of gases in soil and sediments can be described by Fick's first law:

$$\frac{F}{(At)} = f = -D_p \left(\frac{\partial c}{\partial x} \right) \quad (3)$$

where F is the amount of gas diffusing (g gas), A is the cross-sectional area of the soil/sediment (m^2 soil), t is time (s), f is the gas flux density (g gas m^{-2} soil s^{-1}), c is concentration in the gaseous phase (g gas m^{-3} soil air), x is distance (m), and D_p is the soil-gas diffusivity constant (m^3 soil air m^{-1} soil s^{-1}) (Rolston, 2002). Fick's second law is used in non-steady state diffusion, ie., when the concentration within the diffusion volume changes with respect to time.

$$\frac{\partial c}{\partial t} = D_p \frac{\partial^2 c}{\partial x^2} \quad (4)$$

where c is the concentration in the gaseous phase (g gas m^{-3} soil air), D_p is the soil-gas diffusivity constant (m^3 soil air m^{-1} soil s^{-1}), x is distance (m) and t is time (s).

2.7.3 Flux Chamber

Flux chambers are commonly used to measure the emission of many gases and chemicals from soil (Reichman and Rolston, 2002) and sediments. Accurate measurement of soil/sediments gases emission in the atmosphere is essential for estimating amounts of hazardous materials emitted into the atmosphere, and consequently for assessing the effects of such emissions upon the environment. The emission isolation flux chamber is a device used to make direct emission flux measurements from land or liquid surfaces such as landfills, spill sites, and surface impoundments. The isolation flux chamber system was developed by the United State Environmental Protection Agency in 1983 (Environodour Australia Pty Ltd, 2005). It has been used by researchers to measure emission fluxes of a variety of gaseous species including sulfur-containing species and

volatile organic species (Reichman and Rolston, 2002). The mixing characteristics of the chemicals and the carrier gas are the critical design parameters.

Flux chamber measurements involve placing an open-bottom chamber over a small area of soil surface and measuring the gas emitted into an enclosed chamber. (Reichman and Rolston, 2002). Clean dry sweep air is passed to the chamber at a fixed controlled rate. The volumetric flow rate of sweep air through the chamber is recorded and the concentration of the species of interest is measured at the exit of the chamber (Schmidt, 1993). An example of flux chamber is show in Figure 5.

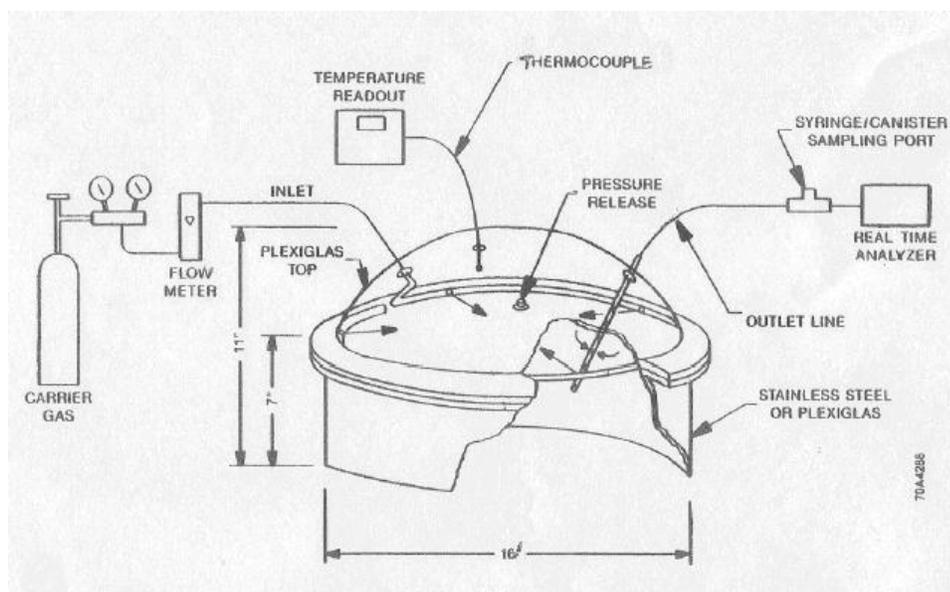


Figure 5: Diagram of Emission Flux Chamber and Supporting Equipment (EPA, 1985)

Unfortunately, there are no regulatory guidance documents governing flux chamber protocols, but there are basically three different types of flux-chamber methods: (i) the Static-(Closed) Chamber Method; (ii) the Dynamic-Chamber Method (Blayne, 2003); and (iii) Wind Tunnels (Gostelow et al., 2003). Table A.3 (see Appendix A) illustrates the advantage, disadvantage and potential applications of emission flux chamber hood (flux chamber) area source emission rate measurement methods. Static Chamber consists predominantly of a collection device with sampling port, where there is no sweep gas. Contaminants diffuse into the device and the gas concentration is allowed

to reach equilibrium within the chamber. During the period of time to reach equilibrium, mass transfer by molecular diffusion takes place above the confined space. Measured emission rates largely depend on the configuration of the enclosure and operating procedure (Leyris et al., 2000). Emitted odor and odors compounds concentration are measured in the enclosed chamber, either at the end of the incubation period or at regular intervals during the incubation period (Leyris et al., 2000). The absence of flowing inlet and outlet gases minimizes potential disturbances of the natural flux conditions. The emission rate in static chamber is determined by the change in emission concentration over time using the following equation (Gostelow et al., 2003):

$$N = \frac{V_c}{A_s \Delta t} \left[C_{t_2} - C_{t_1} \right] \quad (5)$$

where N is the emission rate, V_c is the chamber volume, A_s is enclosed surface area, and Δt is the time interval (t_2-t_1) over which concentration C_{t_2} and C_{t_1} are measured.

Dynamic chambers require more complicated and expensive equipment than static chamber. They include gas tanks, flow regulators and pressure gauges. These chambers have the advantage of having minimum effects caused by concentration build-up in the chamber. Dynamic chamber systems have a continuously sweep gas, which must be operated carefully to avoid potential disturbance of the natural flux. A small a small airflow, typically in the range of $1.67 \cdot 10^{-5} \text{ m}^3/\text{seg} - 6.67 \cdot 10^{-4} \text{ m}^3/\text{seg}$ (1-40 L/min) is recommended (Gostelow et al., 2003). The emission rate is determined by the product of the airflow through the chamber and the odor concentration (Gostelow et al., 2003).

The isolation flux chamber is not designed to take into account convective mass transfer caused by the air movement. The integration of airflow improves the emission rate measurement from these devices, but they are still susceptible to emission rate reduction due to high concentration within the chamber if the airflow is low, and they may be susceptible to poor mixing and dead zones (Gostelow et al., 2003). Special

arrangements as a circulation fans may also be included within the chamber to promote good mixing (Gostelow et al., 2003). It is important to allow for steady-state condition to be achieved. Initial concentrations in the chamber may be high if it is placed on the emission surface prior to allowing the sweep air to flow through; this could produce an artificially high emission rate measurement if not allowed to stabilize (Gostelow et al., 2003).

A wind tunnel is other alternative of flux chamber method. There are numerous examples of portable wind tunnel which have been used for emission rate measurement (Gostelow et al., 2003). An odor hood was introduced by Lindervall to compare the strength of odor from different areal emission sources (Wang et al., 2001). Later, Lockyer designed a wind tunnel system was developed at the University of New South Wales to measure odor emission rates from sewage and industrial wastewater treatment plants, cattle feedlots, mushroom, composting, piggeries, etc. (Kaiyun and Kaye, 1996). Essentially this consist of a rectangular measurement section, open to the emission surface, with contraction and expansion sections allowing for air to be blown through the measurement section (Gostelow et al., 2003). The system operated with carbon activated filtered air supplied at a controlled rate by a blower, and the aerodynamics is controlled by a set of diffusers, and a perforated baffle (Kaiyun and Kaye, 1996). The portable wind tunnel is designed to create an environment where the boundary layer is well developed and convective mass transfer occurs. The aerodynamic performance of the wind tunnel system can be repeated in the sampling process.

In general, a flow-through chamber can be analyzed with the principle of mass balance. The mass change of the target gas within the chamber headspace (dM) depends on the mass input and output, which can be expressed as:

$$dM = VdC^a(t) = AJ_g(t)dt + QC_{in}(t)dt - QC_{out}(t)dt \quad (6)$$

where V is the volume of the chamber headspace, dC^a is the change of the target gas concentration within the chamber headspace, A is the enclosed soil/sediment surface area,

J_g is the flux of the target gas at the enclosed soil surface, Q is the airflow rate, and $C_{in}(t)$ and $C_{out}(t)$ are the target gas concentrations in the chamber for the incoming air and outgoing air, respectively. A hidden assumption in equation [6] is that the air stream through the chamber sweeps over the entire covered soil surface with a uniform velocity, and its direction is parallel to the enclosed soil surface. If the chamber is operating under steady state, that is, the rate of airflow through the chamber is constant and not a function of time, we have:

$$J_{steady} = \frac{Q(C_{out} - C_{in})}{A} \quad (7)$$

which is a commonly used equation to calculate steady state fluxes for dynamic chambers (Reichman and Rolston, 2002).

2.8 Odor Control

2.8.1 Methods of Odor Control

Treatments of odor include technical process as chemical treatment, adsorption of odors by activated carbon, chemical scrubbing of odor emissions, and complete destruction of malodorant emissions by bacterial metabolism in biofilters (Table 3 and Table A.4 -see Appendix A) (EPA, 1994). There are some important factors to be considered when choosing a method for odor control. Some of these are: process control, effect, costs, practical solution in technical installation, chemical handling, functionality, and operation.

The addition of chemicals such as hydrogen peroxide, potassium permanganate, sodium nitrate or chlorine may be effective for odor control in follow-on unit processes such as trickling filters. Potassium permanganate and hydrogen peroxide are efficient as odor control in sludge processing operations such as dewatering. Sodium nitrate is used

successfully for odor control in anaerobic lagoons, carbon columns, trickling filters and sludge-storage lagoons (McIlvanine, 1990). The solution of chemical treatment may be efficient for odor control, but generally are too expensive due to high chemical demand. Nitrate has an advantage over oxygen as it is more soluble in water. Nitrate and iron salts have good effects on hydrogen sulphide, but nitrate have advantage over iron because it removes other malodorous compounds. Products that remove the odor compounds by chemical reactions have short reaction time, while biological reactions may vary depending on the biological activity of the sludge (Einarsen et al., 2000).

Table 3: Summary of Odor Treatment Alternatives (EPA, 1994)

Technique	Application	Cost Factor	Advantages	Disadvantage
Packed tower wet scrubbers	Moderate to high strength odors; medium to large facilities	Moderate capital and O&M cost	Effective and reliable; long track record	Spend chemical must be disposed of; high chemical consumption
Fine mist wet scrubber	Moderate to high strength odors; medium to large facilities	Higher capital cost than packet towers	Lower chemical consumption	Water softening required for scrubber water; larger scrubber vessel
Activated Carbon Adsorbers	Low to moderate strength odors; small to large facilities	Cost effectiveness depends of frequency of carbon replacement of regeneration.	Simple- few movie parts	Only applicable for relatively dilute air streams; longevity of carbon difficult to predict
Biofilters	Low to moderate strength odors; small to large facilities	Low capital and O&M cost	Simple; Minimal O&M	Design criteria not well established; may not be appropriate for very strong odors

Table 3. Continued

Technique	Application	Cost Factor	Advantages	Disadvantage
Thermal oxidizer	High strength odors; large facilities	Very high capital and O&M (energy) costs	Effective for odor and volatile organic compounds	Only economical for high-strength, difficult-to-treat air streams at large facilities
Diffusion in to activated sludge basins	Low to moderate strength odors; small to large facilities	Economical if existing blowers and diffuser can be used	Simple; low O&M; effective	Blower corrosion possible; may be not appropriate for strong odors
Odor counteractants	Low to moderate strength odors; small to large facilities	Cost depend on chemical usage	Low capital cost	Limited odor reduction efficiency (<50%)

Wet scrubbing of odorous gases with a scrubbing solution allows the transfer of the odorants solution allows the gas stream to the scrubber liquid (McIlvanine, 1990). The basic design objective of a chemical scrubber is to provide contact between air, water, and chemicals to provide oxidation or entrainment of the odorous compounds (Tchobanoglous et al., 2003). It is the most effective and economical method of odor control to date (McIlvanine, 1990). The principal wet scrubber types include single-stage countercurrent packed towers, countercurrent spray chamber absorbers, and cross-flow scrubbers (Tchobanoglous et al., 2003). Wet scrubbing is appropriate for large air flows contaminated with low odor threshold compounds such as mercaptans and hydrogen sulfide (McIlvanine, 1990).

The two principal process used for the treatment of odorous gases present in the vapor phase are (i) biofilters and (ii) biotrickling filters (Tchobanoglous et al., 2003). The odor is removed by biological processes, where the microorganisms are used to remove and oxidize compounds from contaminated air. The bacteria grow on inert supports, allowing intimate contact between the odorous gases and the bacteria. The process is self-sustaining (EPA, 1994). Biofiltration has emerged in recent decades as a preferred treatment technology for odor control at wastewater treatment plants worldwide

(Guilbault, 2000-2005), but the biotrickling filter is considered to be advantageous over other biological methods due to its relative short gas retention time, easy control of operation conditions, and high removal efficiencies for low soluble gas (Koe and Kang, 2000).

Chapter 3: Material and Methods

The main objective of this study was to determine if odor problems will occur after emptying the McCook Reservoir. Three essential tasks were completed for this purpose: (i) sediments characterization from the primary clarifier at the EMWTP; (ii) quantification of the odor threshold of exposed sediments; and (iii) determination of the flux of odor causing compounds from sediments. The sediment samples collected were allowed to age under different times and at different water content conditions before testing. This was done to assess the effect of sediment exposure time and sediment moisture on odor.

3.1 Sample Collection and Preparation

To achieve the tasks mentioned above, sediment samples were collected from the primary clarifier at the EMWTP in Mayagüez, Puerto Rico. A diagram of the EMWTP is showed in Figure B.1 (See Appendix B). Sediments from the EMWTP were used to simulate sediments at the McCook Reservoir. Because most of the water quality parameters observed for the EMWTP wastewater (Table C.1 - see Appendix C) fall within the range of those reported for the CSO in the Chicago area (Table C.2 - see Appendix C) it was presumed that sediments from the EMWTP have similar characteristics to the sediments in the McCook Reservoir.

Prior to the sample collection, 5-gallon (Table D.1- Figure A in Appendix D) containers were weighted, identified and prepared with an outlet filter. The containers were painted black to minimize further degradation in the sediments samples.

Sample collections of the primary clarifier and effluent water at the EMWTP were made using safety equipment, with the collaboration and supervision of the Supervisor of the EMWTP and his personal. Figure B.1 (see Appendix B) shows the samples collection

points in reference to the wastewater treatment process in EMWTP. The samples were collected in five gallons black plastic containers using a bucket. The sample containers were placed in ice boxes and transported to the Environmental Engineering Laboratory (EEL). In the EEL the water content condition of sediments samples was adjusted, by adding effluent water from the EMWTP. EMWTP effluent water was added to different containers to yield 1:3 (25% water content) and 2:2 (50% water content) water:sediment ratio (by volume). Some samples were left at 100% sediment (no water was added). Measurements were made to determine the water contents obtained for the different water:sediment ratios. These measurements yielded 95.84%, 97.09%, and 98.08% for the 0:4, 1:3, and 2:2 water: sediment ratios, respectively, in the samples used for odor threshold experiments, and 97.82% and 98.15% in the 0:4 and 2:2 water:sediment ratios for samples used in the flux experiments. The samples that were not used immediately were refrigerated at 277.15°K. Other samples were allowed to age in a closed room at ambient temperature.

The environmental conditions studied were three different water contents (95.84%, 97.09%, and 98.08% of water content) for samples used in Odor Threshold Quantification Tests, and two water contents (97.82% and 98.15% of water content) for Flux Determination Tests. All tests were executed at five different aging times; 1 day, 15 days, 30 days, 45 days, and 60 days.

3.2 Sediment Characterization

Sediment characteristics from the McCook Reservoir are expected to be similar to those from the Stickney Water Reclamation Plant (SWRP) (verbal communication U.S Army Corp of Engineers, 2003). Comparison of sediment characteristics from the SWRP and those from the EMWTP (Table C.3 - see Appendix C and Table 5- see Section 4.1) show that they are within the expected range. Comparison of the sediments was based on Total Solids (TS), Total Volatile Solids (TVS), Total Kjeldahl Nitrogen (TKN), Available Phosphorous (AP), Total Phosphorous (TP), pH, and Dissolved Oxygen (DO).

The characterization was done on all sediments tested under different environmental conditions used in experiments. The characterization was conducted following Standard Method Procedures (Clescer et al., 1998).

Total Solid tests were conducted following Method 2540 B of Standard Method Procedures (Clescer et al., 1998). In general, a sample volume of $1 \times 10^{-5} \text{ m}^3$ was dried in an evaporating dish for 7200 second at 377.15 °K in a Pro-Tronix II, Stabil-Therm Electric Oven of General Signal (Lindberg/Blue, Model number OV-510A-3; see Table D.1 Figure B in Appendix D). After this, the sample was moderately cooled down, collocated in desiccators for 3600 seconds to achieve final cooling, and weighted until a constant weigh was achieved. The residue was ignited at 823.15 °K in a Box Furnace (Lindberg/Blue, Model number BF51828C-1; see Table D.1 Figure C in Appendix D) to determine amount of total volatile solid (TVS) in the sample. The TVS tests were realized using Method 2540 E of Standard Method Procedures (Clescer et al., 1998), but maintaining an ignition period of 3600 seconds. The evaporating dish was cooled at room temperature, collocated in desiccators for 3600 seconds to achieve final cooling, and weighted until a constant weigh was achieved.

DO and pH were measured directly in the samples. DO measurements were conducted using a Heavy Duty Dissolved Oxygen Meter (Model 407510, Extech Instruments Corporation; see Table D.1 Figure D in Appendix D) and following Method 4500-O G. of Standard Method Procedures (Clescer et al., 1998) and the manufacturer specification (Extech Instruments Corporation, 2003). The pH measurements were realized using a pH Meter (Model 720 A; see Table D.1 Figure E in Appendix D) and following Method 4500-H⁺ B. of Standard Method Procedures (Clescer et al., 1998) and ORION 720Aplus Benchtop specifications.

TKN and AP analyses were performed in the Tropical Agricultural Research Station (TARS), with the collaboration of the TARS chemist. TKN analyses was completed following specifications of Method 4500-N_{org} B of Standard Method Procedures (Clescer et al., 1998) and the procedure described in the application notes for the Kjeltec System I (Tecator, 1979), but making some modifications. A sediment sample of 0.001kg was weighted in the digestion tube for each condition studied. A volume of

$1 \times 10^{-5} \text{ m}^3$ of H_2SO_4 , three Glass Beads Hollow # 400 (0.004 m) from Fisher Scientific, and triturated Kjeltab MT Catalyst ($0.0035 \text{ kg K}_2\text{SO}_4 + 4 \times 10^{-4} \text{ m}^3 \text{ Cu SO}_4$) were added to each sample tube. The chemicals added were mixed using a Touch Mixer (MT-31 of Yamato Company; see Table D.1 Figure F in Appendix D) for approximately 180 seconds to 300 seconds until a homogenized mix was achieved. The sample tubes were placed in a preheated digester (Digestion System 4, 1016 Digester of Tecator Company; see Table D.1 Figure G in Appendix D) for a period of 14,400 seconds at $653.15 \text{ }^\circ\text{K}$. After this, the samples were removed from the digester, placed on a stand inside the hood, and cooled at room temperature until the next day.

The following day, approximately $1 \times 10^{-6} \text{ m}^3$ of distilled water was added to each sample tube and mixed. A volume of $2.5 \times 10^{-5} \text{ m}^3$ of boric acid (H_3BO_3) 4% (2000 mL $\text{H}_3\text{BO}_3 + 32 \text{ mL Bromocresol/ green methyl red mixed indicator solution in methyl}$) and a magnetic stirrer were added in $1.25 \times 10^{-4} \text{ m}^3$ Erlenmeyer flasks, corresponding to the number of digestion tubes utilized. The Erlenmeyer flasks and the digesters tube were placed on the Kjeltac System-1002 Distilling System, as showed in Figure 6. The Alkali Tank was set up to disperse $5 \times 10^{-5} \text{ m}^3$ of 4% NaOH into the digestion tube. The Kjeltac System was programmed for 300 seconds to conduct the distillation process. Finally, the Erlenmeyer flask samples of $1.25 \times 10^{-4} \text{ m}^3$ were titrated with 0.15-0.20 N Hydrochloric Acid (HCl).



Figure 6: Kjeltec System-1002 Distilling System with Sediment Sample

TP was analyzed by Pace Analytical, Inc. (San Germán, Puerto Rico) for samples representatives of each aging times studied at 95.84 % of water content. Pace Analytical followed the EPA Method 365.2 for the analysis. In addition to these, the amount of available phosphorous was determined for all samples. Available phosphorous is a soil tests designed to predict the soil's available nutrient status. Analysis for available phosphorous was conducted in TARS following the Bray II method (Jones J., 2001) with some variation recommended by the TARS chemist. The Bray II method was selected because sediment samples had an average pH of approximately 7. This method requires weighting 0.005 kg of each sediment sample in $1.25 \cdot 10^{-4} \text{ m}^3$ Erlenmeyer flask and adding $3.5 \cdot 10^{-5} \text{ m}^3$ of Bray II Extracting Solution. The Bray II Extracting Solution

consists of 0.03 N NH_4F + 0.1 N HCl (20g NH_4F + 149 cc [HCl] to 18 L of distilled water). The sediment/Bray II Solution mixture is shaken for 300 seconds on a Thermolyne BigGer Bill Shaker (see Table D.1 Figure H in Appendix D) at 180 RPM. Extraction procedure is completed by gravimetric filtration of the mixture through a 0.15 m external diameter (OD), Whatman # 541 filter. After a day, $1 \times 10^{-5} \text{ m}^3$ of the sample is placed in a $5 \times 10^{-5} \text{ m}^3$ volumetric flask and approximately $1 \times 10^{-5} \text{ m}^3$ of distilled water is added to the flask.

The sample solution is prepared for analysis by mixing it with $1 \times 10^{-5} \text{ m}^3$ of L-Ascorbic Acid and Color-Developing Solution and adding distilled water to bring the total volume to $5 \times 10^{-5} \text{ m}^3$. The L-Ascorbic Acid and Color-Developing Solution is prepared by adding 0.00159 kg of L-Ascorbic Acid to a $4 \times 10^{-4} \text{ m}^3$ Erlenmeyer flask and mixing it with $3 \times 10^{-4} \text{ m}^3$ of Color-Developing Solution. The Color-Developing Solution is prepared by dissolving 0.012 kg of ammonium molybdate [$(\text{NH}_4)_6 \text{Mo}_7 \text{O}_{24} \cdot 4\text{H}_2\text{O}$] into 250 mL of distilled water and mixing it with $5 \times 10^{-4} \text{ m}^3$ of antimony potassium tartrate [$\text{K} (\text{SbO}) \text{C}_4\text{H}_4)_6 \frac{1}{2} \text{H}_2\text{O}$] acid solution and 250 mL of distilled water. The antimony potassium tartrate acid solution is prepared by mixing $2.908 \times 10^{-4} \text{ kg}$ of antimony potassium tartrate [$\text{K} (\text{SbO}) \text{C}_4\text{H}_4)_6 \frac{1}{2} \text{H}_2\text{O}$] with $5 \times 10^{-5} \text{ m}^3$ of 5 N sulfuric acid (H_2SO_4) (148 mL conc. $\text{H}_2\text{SO}_4 \text{ L}^{-1}$). The ready-for analysis sample solution is analyzed at 882 nm using a Perkin Elmer Lambda 3B-UV/VIS Spectrophotometer equipped with a Supper Sipper (Figure 7).



Figure 7: Perkin Elmer Lambda 3B-UV/VIS Spectrophotometer with a Supper Sipper

3.3 Odor Threshold Quantification

The potential odor threshold of accumulated sediments in a retention chamber was quantified by measuring the dilution rates and H₂S concentration, calculating the TON using equation 1, and determining the ED₅₀ of the sample at odor detection. The TON of sample is defined as the dilution ratio at which odor is detected during olfactometry testing. In practice, TON is calculated from a series of panel responses to samples presented by olfactometer over a range of dilution ratios. The dilution ratios at which 50% of panelists in the olfactometry analysis respond to the odor represent the ED₅₀ for the odor threshold.

3.3.1 Experimental Olfactometry System

The olfactometry system (Figure 8) used for the TON measurements was based on the “Triangle Olfactometer Method” (TOM) (Figure 9). The TOM consists of having panelists inhale the “sniffing” port at different dilution until odor was detected. The

system consisted of an air delivery unit, a sample unit, a mixing/dilution unit, and a detection unit (Figure 10).



Figure 8: Set up of the Olfactometry System



Figure 9: Triangle Olfactometer Method

The delivery unit consisted of an air source, a purifying system, and diverting fittings. The air source was generated with an air compressor (HUSKY Oil-less Air Compressor WL 6500 Series, Model No.WL650702AJ; see Table D.1-Figure I in Appendix D). The compressor was connected to the system using a compressor line (0.95 cm ID) with a maximum capacity of 300 psi. Prior to each experiment test, the compressor was switched ON for approximately fifteen minutes. After this period of time, the compressor tank was full and it shut down automatically. The flow valve in the compressor was subsequently opened and the necessary flow to conduct each odor test was established. The flow was regulated using two (BEL-ART RITERFLOW, Size 5, P/N 40407-0305) flow meters (see Table D.1-Figure J in Appendix D). The purifying system consisted of moisture and a water trap, and an activated carbon column (see Table D.1-Figure K, L, LL in Appendix D). The moisture and the water trap were used to control the moisture in the air. The activated carbon column was used to purify the air before delivery to the sample and dilution units. Air flow from the delivery unit was splitted into three flow lines. One of the lines delivered odor-free air (OFA) to two “sniffing” ports in the detection unit. A second line delivered flow to a valve flow meter, which was used to regulate the amount of OFA used to dilute the odorous-air (OA) in the mixing/dilution unit; the third line was connected to the sample unit, which was used to pick up the odor-causing vapors. The sample unit consisted of a 0.0022 m³ (2.2L) Teflon coated Nalgene Bottle (see Table D.1-Figure M in Appendix D), which housed the sediment sample. There are passing through the sample unit, was connected to a valve in the mixing/dilution unit, which was used to control the OA flow rate.

The mixing/dilution unit consisted of two valve flow meter and a mixing-flow fitting. One of the valves (the OFA valve) received odor-free air, and was used to control the diluting flow rates. The other valve, the OA valve, received odorous vapors, which were picked up from the sample unit. It was used to control the flow rate of the odorous air. Flow rates from the OA and the OFA valves were mixed in the mixing-flow fitting. The total flow of diluted odorous air (DOA) exiting the fitting was delivered to a flow splitter in the detection unit that delivered the flow to a “sniffing” port and to H₂S analyzer.

The detection unit consisted of flow splitters, three “sniffing” ports, a H₂S analyzer (see Table D.1-Figure N in Appendix D), and a data acquisition system (Figure 10). The “sniffing ports were placed behind a colored panel to prevent the panelist from seeing the samples (see Table D.1-Figure O in Appendix D). The H₂S analyzer was used to measure the H₂S concentration and consisted of a Jerome 631-X (Figure 11) analyzer having a capacity to measure concentration in the range between of 0.003 and 50 ppm (Arizona Instrument LLC, 2003). This instrument has been used big for Ambient Air Analysis, Quality Control, Odor Nuisance Monitoring and Regulatory Compliance (Arizona Instrument LLC, 2003). Although this instrument has the ability to connect directly to a power supply, it was charged the day before each experiment to ensure that enough power was available to perform all measurements. Configuration of the Jerome Data Logger (see Table D.1-Figure P in Appendix D) was programmed using Jerome Communications Interface Software (JCI) to record measurements every minute in the data acquisition system (see Table D.1-Figure Q in Appendix D). As recommended, the 0.25mm fritware filter was changed using the trimmer tool to avoid touching the new fritware disc with the finger. The Jerome instrument is factory calibrated, but calibration verification was routinely made using the Functional Test Module (see Table D.1-Figure R in Appendix D), as recommended in the Operational Manual of H₂S Functional Test Module (Arizona Instrument LLC, 2000).

The Functional Test Module (Figure 12) is an instrument that generates a known gas sample concentration that is introduced in the Jerome Analyzer to verify the operation. The gas standard is generated by passing a known flow of clean air at a fixed temperature over an H₂S permeation tube. The flow rate and temperature are factory set to provide a measured concentration of approximately 250 ppb (0.25 ppm) ± 20% (Arizona Instrument Corporation, 2000).

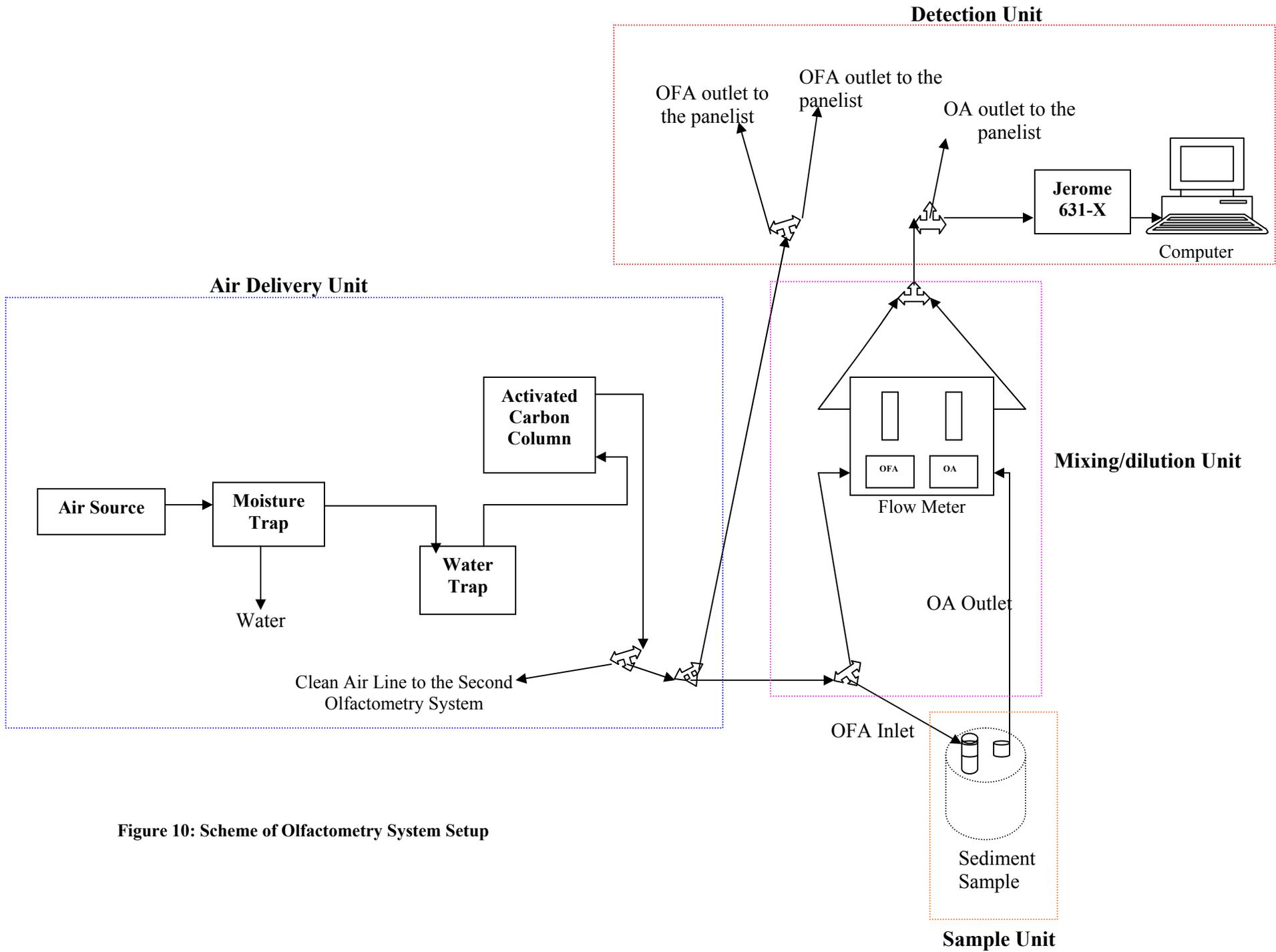


Figure 10: Scheme of Olfactometry System Setup



Figure 11: Jerome 631-X

During the experimental phase, the sensor in the Jerome analyzer required periodical regeneration for proper functioning (Arizona Instrument LLC, 2003). It also required verification of concentration levels (High level H, Low level L, and Zero level O) in the sensor and Zero readjustment. The Jerome analyzer is equipped with a data logger, which was configured and connected to the data acquisition system.

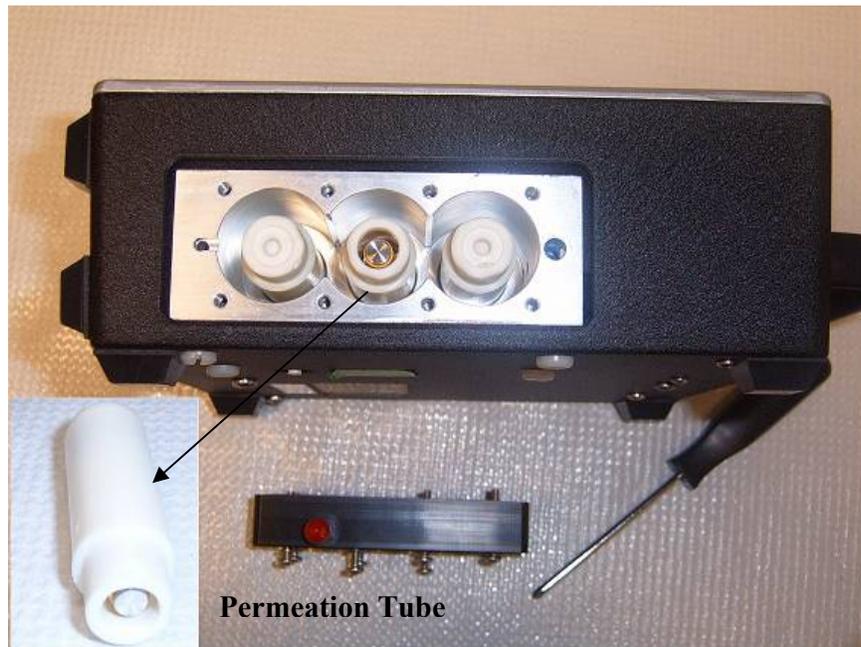


Figure 12: Functional Test Module

3.3.2 Olfactometry Test Procedure

The TON and the ED₅₀ were determined for sediment samples collected from the EMWTP for different aging times, and water contents. Sediments at three water contents, 95.84%, 97.09%, and 98.08%, were aged at 293.15 °K-298.15 °K for 1, 15, 30, 45, and 60 days. Samples were taken at the end of each aging period for testing.

The olfactometry tests were conducted by placing approximate 8×10^{-4} m³ of sediments sample on the sample unit and passing air through it to pick up the odor-causing agents. The odor-concentrated vapors were diluted with odor-free air in the mixing unit. The diluted air was delivered to the “sniffing” ports in the detection unit, where “sniffing” panelist could provide a response to odor detection.

Panelists were always exposed to low odor-concentration air (high dilution) initially by starting with high OFA and low OA flow rates. If odor was detected, the test for that sample was ended and a new test with different sample or panelist was commenced. If odor was not detected, the odorous-air flow rate was increased and OFA decreased to increase odorous-vapor concentration while maintaining constant total flow.

For the first test conducted (aging time of 1 day) a flow rate of 57235 mL min⁻¹ was initially established for the OFA and 3285 mL min⁻¹ for the OA. A stability problem with the air source caused a reduction in the flow rates used to the panelist 4 through 6 in this initial test. Consequently, starting flow rates of 31089 mL min⁻¹ in the OFA line and 3285 mL min⁻¹ in OA line had to be established for the rest of the panelists (7-10) in the first aging time of the olfactometry test. These starting flow rates were continued to be used in all other olfactometry test (aging times of 15 through 60 days). Table 4 shows the step changes in flow rates as the olfactometry test progressed for (a) 1-day aging time, panelist 1 through 6 and (b) panelist 7-10, 1-day aging time and all panelists for the other aging times.

Table 4: Step changes in flow rates in olfactometry tests per panelist

a)

Step	OFA (mL/min)	OA (mL/min)
1	57235	3285
2	52788	6977
3	48527	10812
4	43998	14659
5	39659	18617
6	35485	22698
7	31089	26905
8	26905	31089
9	22698	35485
10	18617	39659
11	14659	43998
12	10812	48527
13	6977	52788
14	3285	57235

b)

Step	OFA (mL/min)	OA (mL/min)
1	31089	3285
2	26905	6977
3	22698	10812
4	18617	14659
5	14659	18617
6	10812	22698
7	6977	26905
8	3285	31089

Initial flow rates blank (empty) for each sediment sample was set at first using a 0.0022 m³ (2.2L) Teflon coated Nalgene Bottle to prevent sediment back spills. When flow rates were settled, the blank bottle was replaced by a sediment-containing bottle.

Preliminary evaluations of the olfactometry system performed were conducted before the odor threshold quantification experiments to determine if the system was delivering constant odor concentrations. The evaluation involved similar methodology to the olfactometry tests except that panelists were not exposed to odors and flow rates were modified during the runs. The evaluations consisted of passing air through the sediments

samples at different odorous-air flow rates while measuring the H₂S concentrations in the detection unit. The procedure was repeated for sediments of different aging times (the sediments used were from an earlier batch than those used for the olfactometry tests). Flow modifications included different OA and dilution flow rates and interruptions and reinstatement of flow through the sediments. Sediment samples were exposed to specific OA flow rates (57235 mL/min, 26905 mL/min, 18617 mL/min and 3285mL/min). Dilution rates (OA: OFA) of 3285:57235 mL/min; 26905:31089 mL/min, 39659:18617 mL/min, 57235:3285 mL/min were used in these evaluations. The sediments were also exposed to different period of flow and no flow (flow interruptions).

The preliminary tests performed indicated that approximately five to ten minutes were necessary to achieve constant concentration of H₂S in sediment samples. It was, therefore, necessary to wait this period of time at the beginning of each odor test. After this period of time, the panelist was exposed to the sample in the “sniffing” port (Figure 13) and asked if odor was detected at each of the three “sniffing” ports. The response of the panelists and the concentration of H₂S were recorded. If odor was not detected, the flow rate in the OFA was decreased and that in the OA was increased while maintaining a constant total flow. This procedure was repeated until the panelists indicated odor detection. During the tests occasional verification of the level of moisture in the Moisture Trap and manual drainage was performed to avoid moisture in the lines. After finalizing olfactometry test with a panelist, the lines were swept with OFA for approximately 300 to 600 seconds before connecting the next sediment sample to the system. This procedure was completed and duplicated for sediment samples with 95.84%, 97.09%, and 98.08% water content and at the five different aging times.



Figure 13: Olfactometry Test

All panelist were exposed to three “sniffing” ports; two carrying OFA and one carrying the detection OA. Panels consisted of ten women for each odor-testing, because female panelists normally have a greater sensitivity than male panelists for the same age group (McIlvanine et al., 1990).

Sediment samples for each environmental condition were presented to all panelists at a temperature of approximately 293.15 °K-298.15 °K. This temperature was verified using a digital thermocouple, Type K (Model CL 23A, Omega Engineering, Inc; see Table D.1-Figure S in Appendix D). All tests for each aging time were conducted at the same aging day except for the first aging time (1 day). For the first aging day it was difficult to find all ten women panelists and it was necessary to conduct some test the following day. For this reason, sediment samples were refrigerated at 277.15 °K in the EEL. The samples were allowed to reach ambient temperature before conducting olfactometry test the following day. Sediments samples for the other aging times studied (15, 30, 45, and 60 days) were taken from the sample containers that were stored in a

closed room at ambient temperature, and analyzed in olfactometry test during the day of aging.

The ED₅₀ of each sediments sample was determined from the TON data. It was estimated from the TON value for each panel.

3.4 Flux Determination

Another fundamental part of this study was the flux determination of odor-causing compounds from sediments. Specifically, this research evaluated the flux of H₂S from the EMWTP sediments. To perform this task, it was necessary to use a laboratory-scale isolation flux chamber. The construction of the chamber was based on a modified version of the basic US. EPA chamber designed to measure gaseous emissions from land surface (Kienbush, 1985) (Figure 14). In general, the isolation flux chambers consist of semi-enclosed cylindrical domes that are inserted in contaminated soil to measure contaminant fluxes from the soil. Air inlet and outlet lines are used to sweep and sample the contaminants that emanate constantly from the soil. In these experiments, however, the chamber was designed to allow placement of sediments samples inside an enclosed chamber.

3.4.1 Experimental Flux System

The flux chamber system consisted (Figures 14 and 15) of an air delivery unit, the flux chamber unit, the detection unit, and the data acquisition unit. The air delivery unit was similar to that described in the olfactometry system (see Section 3.3.1).

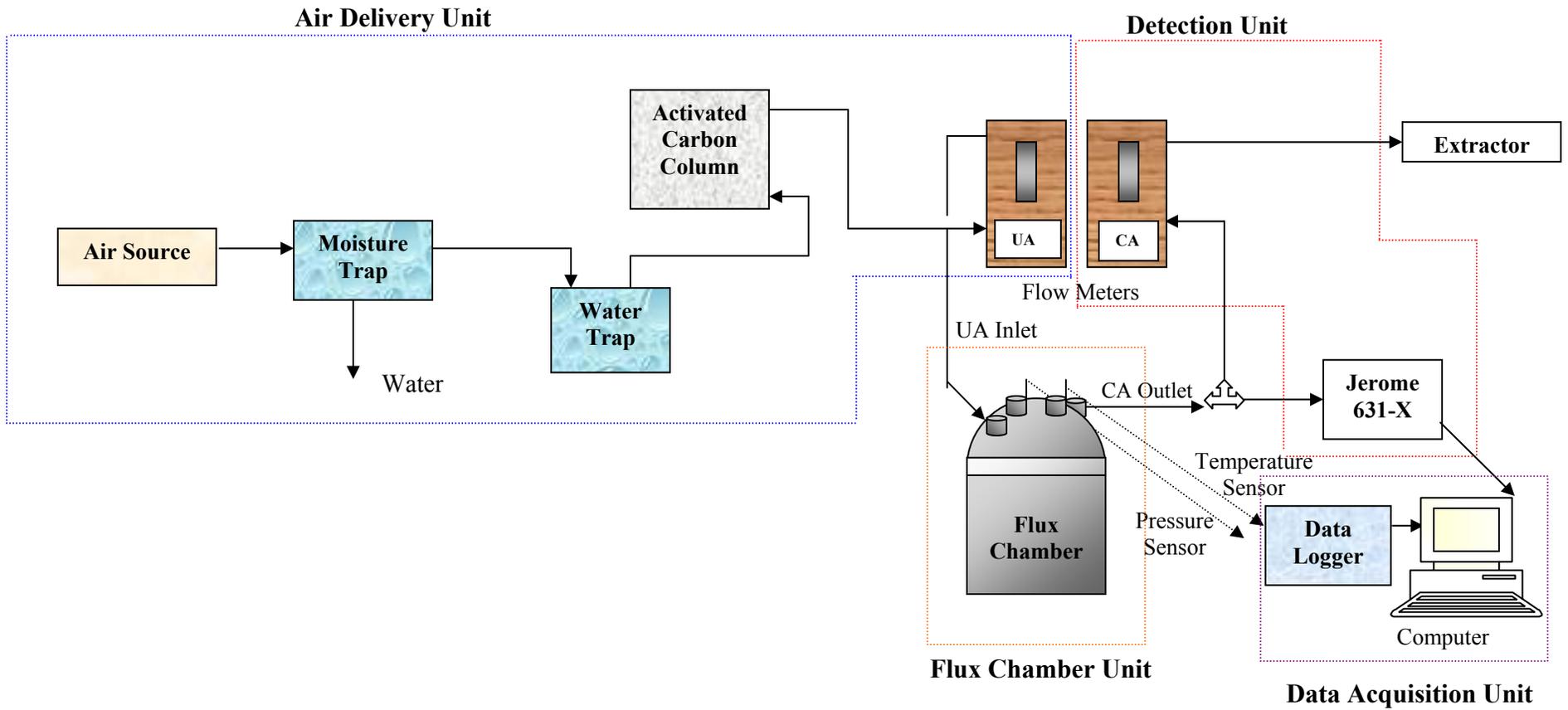


Figure 14: Scheme of Flux Test Setup



Figure 15: Flux Chamber Test

The flux chamber (Figure 16) consisted of a 316 Stainless Steel cylindrical container (38.1 cm internal diameter (ID), 43.82 cm of external diameter (OD) within rim, and 25.4 cm depth; see Table D.2-Figure A in Appendix D) and a cylindrical polypropylene dome-shape lid (Figure 17) (38.1 cm ID, 43.82 cm OD within rim; see Table D.2-Figure B in Appendix D). The chamber and the lid contained a 5.715cm rim with 21 holes (0.635 cm OD) that served to seal the chamber using (0.635 cm) stainless steel screws and nuts (see Table D.2-Figure C in Appendix D). A Neoprime Durometer 40A gasket (38.1 cm ID, 43.82 cm of OD and 0.32 cm thickness, see Table D.2-Figure D in Appendix D) was used to provide a tight seal between the dome-shape lid and the stainless steel container. The dome, the gasket and the flux chamber base was manufactured by Añasco Precision Mfg., Inc. (Añasco, Puerto Rico).



Figure 16: Flux Chamber System

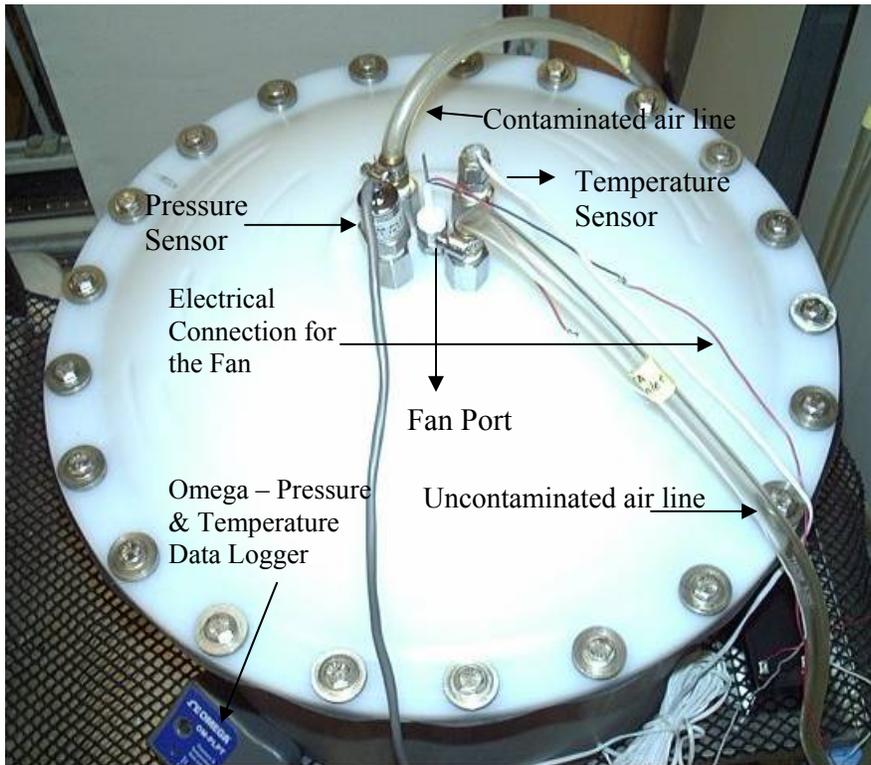


Figure 17: Flux Chamber Dome

The dome-shape lid contained five equidistant ports (Figure 17) fitted with 1.27 cm ($\frac{1}{2}$ " OD stainless steel Swagelock[®] fittings. A pressure transducer and a temperature sensor were inserted into the flux chamber dome through two of the ports using Swagelock[®] fittings to monitor the internal pressure and temperature inside the chamber. The transducer and the sensor were connected to a portable pressure and temperature data logger (Omega Portable Low Cost Pressure and Temperature Data Logger, OM-PLPT; see Table D.2-Figure E in Appendix D), which was programmed to record data every minute. The Data Logger was connected to a computer (see Table D.2-Figure F in Appendix D) using a 6 foot USB Cable to Serial Cable (Radio Shack; see Table D.2-Figure G in Appendix D). A 17.6 cfm DC axial fan (Model No. 4WT34; see Table D.2-Figure H in Appendix D) was screwed in the center port of the dome using septa within a 1.27 cm Swagelock[®] quick connection. The fan was electrically connected to a 12 Volt gel Battery Tender (Deltran Corporation; see Table D.2-Figure I in Appendix D). The remaining two ports were connected through Swagelock[®] hose fittings to R-3603 Tygon tubing (0.95 cm OD and 0.79 cm ID), which were used as inlet and outlet sweeping lines. The inlet line was connected to the uncontaminated-air (UA) valve-flow meter in the air delivery unit and was used to control the flow in the flux chamber unit. The outlet line was connected to the detection unit, which consisted of a flow splitter, a H₂S Jerome analyzer, and a valve-flow meter. The flow splitter diverted flow to (i) the Jerome 631-X analyzer (described in the odor threshold section) and (ii) the contaminated air (CA) valve-flow meter. The CA flow meter was used to control the amount of flow reaching the Jerome detector, so that it would not become saturated. The outlet of the CA flow meter was directed to an extractor to control odor in the EEL. The data acquisition system unit required pressure, temperature, and H₂S concentration data from the pressure transducer and temperature sensor data (OM-PLPT) and the Jerome 631-X analyzer. The connection between the data logger and the computer was established through USB to Serial Cable. An RS232 connected the Jerome 631-X analyzer to the computer. The Jerome 631-X analyzer was configured at the beginning of all flux experiments using the JCI according to the "User's Manual of the Jerome Communications Interface Software" (Arizona Instrument LLC, 1996). The pressure

transducer and temperature data logger was configured using the OM-PL Series Data Logger Interface Software following the manufacturer specifications (Omega Engineering, INC. 2003).

3.4.2 Experimental Flux Procedure

Flux determination test were performed by placing approximately 7.62 cm of sediment samples in the chamber. The chamber was rapidly sealed and shaken about 20 times to homogenize the sample before beginning the experiment and data collection. Data collection was started after configuring the Jerome 631-X analyzer and the pressure transducer and temperature data logger.

Air flow for the flux experiments was generated using an air compressor (HUSKY Oil-less Air Compressor WL 6500 Series, Model No.WL650702AJ). The compressor was always switched on 15 minutes prior to any flux experiment. Each experiment began by switching on the electrical fan in the chamber and passing uncontaminated air flow allowing the flux chamber at determined flow rates. The flow rate through the chamber was regulated with the valve-flow meter connected to the chamber's inlet line. Flow rates varied from $8 \times 10^{-6} \text{ m}^3/\text{s}$ (480 mL/min) to $3.8 \times 10^{-4} \text{ m}^3/\text{s}$ (22698 mL/min) (see Table E.1 in Appendix E).

The concentration of H₂S exiting the flux chamber was monitored inline at 1-minute intervals using the Jerome 631-X analyzer until a constant concentration (near 0.000ppm) concentration was reached. Once a constant concentration was reach, the inlet and outlet sweeping lines were closed and the system was allowed to rest for al least 1800 seconds.

All experiments were performed under constant temperature and pressure. Experimental temperatures and pressures were maintained at 293.15 °K to 298.15 °K and 1 atmosphere, respectively. The fluxes of odor-causing compounds from sediments were determined under two different water content (97.82 % and 98.15 % of water content) and the same aging times as for the TON experiments (1, 15, 30, 45, and 60 days). Samples and duplicates were analyzed for all water contents and aging times.

Flux tests were also conducted with a 5.08 cm layer of EMWTP effluent water over the sediments to quantify the effect of ponding water on the emission of odor-causing agents. The water layer on these experiments was added after the experimental aging period, but before the flux test commenced. The flow rates used for these experiments varied from $8 \times 10^{-6} \text{ m}^3/\text{s}$ to $8.55 \times 10^{-5} \text{ m}^3/\text{s}$ (see Table E.1 in Appendix E). These experiments were done for all aging times except day 1.

Other flux tests (see Table E.1 in Appendix E) were conducted using sediments with 97.82 % water content, aged for 67 and 85 days. All of these tests were conducted with a flow rate of $8 \times 10^{-6} \text{ m}^3/\text{s}$ (480 mL/min). The flux tests conducted with the 67-days aged sediments contained an added layer (5.08 cm) of EMWTP effluent water over the sediments. After completing the flux test, the flux chamber was closed and allowed to equilibrate for an additional day, when it was retested again at the same flow rate as before ($8 \times 10^{-6} \text{ m}^3/\text{s}$).

Flux test conducted with the 85-days aged sediments involved several experimental conditions (see Table E.1 in Appendix E). No water layer was added to these sediments. Some tests involved conducting the flux test, closing and equilibrating the sediments in the chamber for a day, and retesting again. Other tests involved placing the chamber on a shaker table and shaking the sediment during the flux experiments. One set of experiments was conducted at low shaking velocities and another at high shaking velocities. Other three tests were conducted using higher temperature, ranging from 296.15°K to 308.15°K. The increase temperature was achieved by placing the flux chamber on two hot plates. A final flux test was conducted on this sediment sample after equilibrium for about 2 days in the (closed) flux chamber at room temperature.

3.4.3 Determination of H₂S Flux

Flux of H₂S across the EMWTP sediment surface was determined using the method of moments for temporal concentration distributions. The absolute nth moment (M_n) is defined as:

$$M_n = \int_0^{\infty} t^n C(t) dt \quad (8)$$

where t is the time and C is concentration. The Zero Moment (M_0),

$$M_0 = \int_0^{\infty} C(t) dt = \sum_{i=0}^{i=t_{final}} \left(\frac{C_i + C_{i+1}}{2} \right) (t_{i+1} - t_i) \quad (9)$$

was used to calculate the total mass of H_2S passing through the system using

$$Mass = QM_0$$

where Q is the flow rate passing through in the flux chamber. Because H_2S concentrations were measured in ppm \forall , the ideal gas law equation was applied to determine the total number of moles emitted through the system. The ideal gas law establishes that:

$$\frac{n}{V} = \frac{P}{RT} \quad (10)$$

where n equals the number of moles of gas in the particular sample, V is the volume, P is pressure, R is a universal gas constant. The value of R depends on the units chosen for the measurement of P , V , and T . For this work situation a value of 0.082 L atm/mol $^{\circ}K$, a constant pressure of 1 atm, and a temperature of 298 $^{\circ}K$ were used.

The average flux in the flux test, in moles of H_2S /min, was computed dividing the moles of H_2S by the total time period (Δt).

$$F = \frac{Moles H_2S}{\Delta t} \quad (11)$$

The average time of H_2S emission was calculated as:

$$\bar{t} = \frac{M_1}{M_0} \quad (12)$$

where M_1 is the first moment, defined as:

$$M_1 = \int_0^{\infty} tC(t) dt = \sum_{i=0}^{i=t_{final}} \left(\frac{C_{i+1}t_{i+1} + C_it_i}{2} \right) (t_{i+1} - t_i) \quad (13)$$

3.5 Statistical Methods Analysis

The data collected in the olfactometry and flux experiments was analyzed to determine statistical properties of the data, including:

- the average TON and flux values from each condition and aging time
- the sludge sediment characteristics
- the ED₅₀ of the samples
- the variance of the TON, ED₅₀, flux data, and sediment characteristics

Statistical analysis was also performed to compare statistical properties and determine if:

- TON, flux, and sediment characteristics, were affected by sediment water content, aging time, or other environmental conditions
- TON and flux were influenced by sediment characteristics
- TON was related to H₂S concentrations

Statistical analysis of the data was performed using MINITAB 14 Statistical Software, which provides a wide range of basic and advanced data analysis and graphics capabilities. Basic statistic analyses were performed for TON, Flux Determination and Sediment Characterization data, and include:

Mean (μ): A commonly used measure of where the center of your distribution lies, which is also called the average. It is the sum of all observations (X) or samples divided by the number of (non-missing) observations (N) or samples.

$$\mu = \sum \frac{X}{N} \quad (14)$$

Variance (S^2): A measure of dispersion, or spread about the mean. It is regarded as the squared deviation from the mean.

$$S^2 = \frac{\sum (X - \mu)^2}{N - 1} \quad (15)$$

Standard deviation (StDev): The most common measure of spread or variability present in the sample. It represents the deviation from the mean and is given in the units of the measurement of the data.

$$S = \sqrt{\frac{\sum (X - \mu)^2}{N - 1}} \quad (16)$$

Standard error of the mean (SE MEAN): An estimate of the dispersion in the distribution of samples means that you would obtain if you took repeated samples from the same population.

$$SEMean = \frac{S}{\sqrt{N}} \quad (17)$$

Coefficient of variation (Coef Var): A measure of relative variability, usually calculated only when all values are positive. The coefficient of variation expresses the standard deviation of the data as a percentage of the mean.

Coefficient of variation = standard deviation / mean

$$CoefVar = \frac{S}{\mu} \quad (18)$$

Median: The middle observation of the data when the data is observed in ascending (or descending) order. Half the observations are above the median and half are below the median. If there are an odd number of observations, the median is the value in the middle, but if there are even numbers of observations, the median is extrapolated as the value midway between that of observation numbers.

Maximum: The largest data value in your data set.

Minimum: The smallest data value in your data set.

Range: The range is calculated as the difference between the largest and smallest data value.

The effect of system characteristics (independent variables such as water content, aging times, and sediment characteristics) on response variables (TON, H₂S flux, and sediment characteristics) was evaluated using analysis of variance (ANOVA) and regression analysis. ANOVA is similar to regression in that it is used to investigate and model the relationship between a response variable and one or more independent variables. It differs from regression in two ways: the independent variables are qualitative (categorical), and no assumption is made about the nature of the relationship.

ANOVA was applied by a General Linear Model. This model requires a response (TON, Flux or other parameters) or measurement taken from the units sampled as a function of one or more factors (e.g. aging time, water content, sediment characteristics). Using the general linear model procedure to conduct an ANOVA assumes that the variances of several samples are equal.

ANOVA and other comparative statistical analysis uses the following statistical parameters.

Degrees of freedom (DF): The degrees of freedom were used to calculate the mean square (MS). In general, the degrees of freedom measure how much "independent" information is available to calculate each sum of squares (SS).

DF for total = DF for all factors + DF for all interactions + DF for error.

DF total = $n - 1$ where n is the total number of observations.

DF for factor = $k - 1$ where k is the number of the factor levels.

DF for Interaction = $(k_1 - 1) * (k_2 - 1)$ where k_1 is the number of levels of factor one, and k_2 is the number of levels of factor two.

The degree of freedom for the error sum of squares (SSE) is the degrees of freedom of the total variation in the data (SST) minus the degrees of freedom for all the factors and covariates summed.

Sequential sums of squares (Seq SS): The sequential sum of squares for each term in the model measures the amount of variation in the response that is explained by adding each term to the model sequentially in the order listed under source.

Adjusted sums of squares (Adj SS): The adjusted sum of squares for a term in the model measures the amount of additional variation in the response that is explained by the term, given that all the other terms are already in the model.

Adjusted mean squares (Adj MS): The adjusted mean square for a term is simply the adjusted sum of squares (Adj SS) divided by the degrees of freedom.

F: The statistic that is used to test whether the effect of a term in the model (factor or interaction) is significant. F is used to determine the p-value. Generally, larger F values indicate greater impact of the independent variable on the response variable.

Level of significance (α): is the maximum probability of accepting statistical difference between samples, when they are not. A level of significance of 0.05 (one in twenty) was used for this analysis.

P-value (P): P is the probability that you would have obtained as extreme (or more extreme) if the indicated term (factor or interaction) has no effect on the response variable. It is indicative of the probability that a given characteristic has (does not have) an effect on the measured values and represents the smallest level of significance that allows the acceptance of significant difference between samples. If P is less than or equal to the α -level you have selected, then the term has a significant effect on the response. If P is larger than the α -level you have selected, the effect is not significant.

S: An estimate of σ , the estimated standard deviation of the error in the model.

R² (R-sq): Coefficient of determination; indicates how much variation in the response is explained by the model. The higher the R², the better the model fits your data.

Adjusted R² (R-sq Adj): Accounts for the number of predictors in your model and is useful for comparing models with different numbers of predictors.

Fitted value (Fit): The fitted response value for a given observation is the best estimate of the population mean for the given factor level or combination of factor levels.

Standard error of the fitted value (SE Fit): The standard error of the fitted value.

Residual: The residual for a given observation is equal to the value of the observation, minus the fitted value for the observation.

Standardized residuals (St Resid): The standardized value for a residual is equal to the residual divided by the standard deviation of the residuals. MINITAB includes any residuals with a standardized value greater than 2 or less than -2 in the table of unusual observations.

Statistical analysis was performed for 95% confidence intervals. Analysis of TON and flux data for similar conditions and aging times was performed to determine if odor threshold (TON) was statistically related to H₂S flux. To make this comparison, it was necessary to presume that the data for samples with 97.09% water content in olfactometry test was similar to the data for samples with 97.82% water content in flux determination test. Also, it was presumed that the data with 98.08% water content in the olfactometry test was similar to the data for samples with 98.15% water content in flux determination test. The probability of a system characteristic (e.g. water content, aging times, sediment characteristic) affecting the TON, and H₂S flux values was determined by comparing P-values with alpha.

Chapter 4: Discussion of Results

4.1 Sediment Characterization

Sediments from the primary clarifier at the EMWTP were characterized based on TS, TVS, TKN, AP, TP, pH, and DO measurements at different sediment aging times and water contents.

Results show that average characteristics for all tested sediments (Table 5) were within expected values for these sediments. The effects of aging time and water content on sediment characteristic were evaluated using ANOVA and regression models and described in Main Effects Plots. These plots project sediment characteristics values against independent variable (i.e., aging times, water contents). Statistical results for ANOVA and sediment characteristic are summarized in Table 6 and discussed below.

Sediment pH varied between 5.92 and 7.69, and averaged 7.08 for all tested sediments. The Main Effects Plot for pH (Figure 18) shows that average pH tends to increase with aging times, but is not affected by the water contents. In fact, ANOVA indicates that the water contents have less effect on pH than sediment aging times (Table 6). The p-value obtained for water contents is 0.236. As this value is greater than the level of significance selected ($\alpha=0.05$), it is concluded that water content is not a significant factor in the response of pH. On the other hand, a p-value of 0.000 for the factor of sediment aging times indicates that this factor is a significant factor in the response of pH. The much greater F value for sediment aging times (130.45) than for water content (1.45) also reflects the importance of sediment aging times on pH. The coefficient of determination (R^2) obtained in this analysis demonstrated that 92.79% of the variation in the response of pH was explained by the General Linear Model (GLM). This higher value of the R^2 confirmed a good model fit with the data obtained. Figure 19 shows a strong quadratic relationship between pH and the sediment aging times ($R^2=90.6\%$). An increase in pH has been previously related to lower H_2S concentrations

(Childs and A.J. Duna, 2001), and may also affect the volatility of H₂S in wastewater (Stuetz et al., 1999).

Table 5: Statistical Results of Sediment Characteristics for all tested sediments

Variable	Mean	StDev	Min	Median	Max	Range	Expected Value
Available Phosphorous (ppm)	117.6	76.2	5.17	113.9	313.6	308.4	0-19: low, 20-40: moderate, > 40 ppm high
pH	7.0753	0.4878	5.9200	7.3610	7.6850	1.7650	5-8 ⁽¹⁾
Dissolved Oxygen (mg/L)	0.534	0.958	0.100	0.300	5.400	5.300	NA
Total Solid (mg total solid/L)	31400	15120	10000	30000	60000	50000	NA
Total Volatile Solid (mg volatile solid/L)	17200	10110	0.000	20000	40000	40000	NA
Total Kjeldahl Nitrogen (%)	0.0781	0.0379	0.01247	0.06386	0.17575	0.16328	1.5-4 ⁽¹⁾
Total Phosphorous (ppm)	400	464	0.0420	164	1076	1076	Weak 5 Medium 10 Strong 20 mg/L (2)

Min: Minimum

Max: Maximum

(1) Kiely, 1997

(2) Cornwell and Mackenzie, 1998

NA: not available

Table 6: Statistical Results for ANOVA on Sediment Characteristics

Variable	P-value		F-value		GLM R ² (%)
	Water Content (%)	Sediment Aging Times (days)	Water Content (%)	Sediment Aging Times (days)	
Available Phosphorous (ppm)	0.000	0.000	10.64	8.35	64.95
pH	0.236	0.000	1.45	130.45	92.79
Dissolved Oxygen (mg/L)	0.048	0.109	2.63	2.03	31.24

Table 6. Continued

Variable	P-value		F-value		GLM R ² (%)
	Water Content (%)	Sediment Aging Times (days)	Water Content (%)	Sediment Aging Times (days)	
Total Solid (mg total solid/L)	0.077	0.054	2.28	2.55	31.99
Total Volatile Solid (mg volatile solid/L)	0.352	0.271	1.14	1.34	19.49
Total Kjeldahl Nitrogen (%)	0.000	0.008	14.04	3.95	63.71

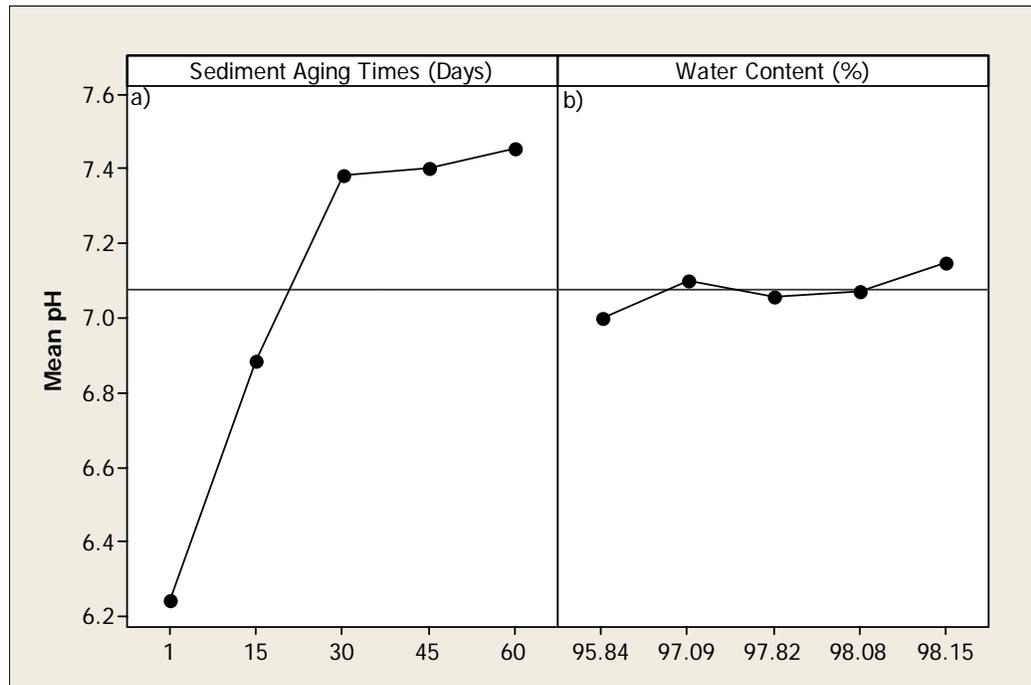


Figure 18: Main Effect Plot for pH as function of sediment a) aging times and b) water contents

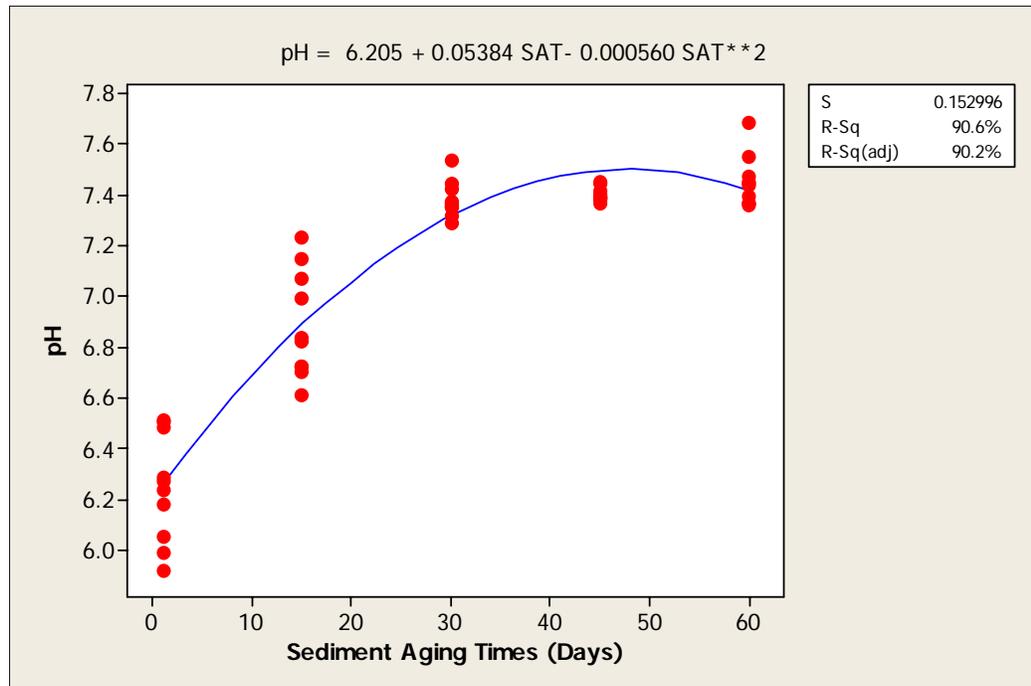


Figure 19: Relation of pH as a function of Sediment Aging Times

Total phosphorous content in sediments having a water content of 95.84% averaged 400 ppm and ranged from 0.042 to 1076 ppm. TP values show high variability among samples, but did not show any relation with aging times (Table 7). Total phosphorous was only measured in a selected number of sediment samples because of equipments constraints. Measurement of available phosphorous, however, was made on all samples.

Table 7: Results of Total Phosphorous Analysis of Sample with 95.84% of Water Content

Total Phosphorous Analysis-Pace Analytical Results		
Sediment Aging Times (Days)	Water Content (%)	Results (ppm)
1	95.84	686
15	95.84	73
30	95.84	1076
45	95.84	0.042
60	95.84	164

Sediment available phosphorous ranged between 5.17 and 313.6 ppm and averaged 117.6 ppm for all sediment tested. The Main Effect Plot for Available Phosphorous (Figure 20) shows that in average AP values tend to increase with aging

times and decrease with water contents. A Plot of AP versus water contents for all times (Figure 21) show that AP is inversely, but weakly, related ($R^2=32.3\%$) to water content. Sediment aging time seen to influence AP values at low water contents (Figure 22) but not at high water contents.

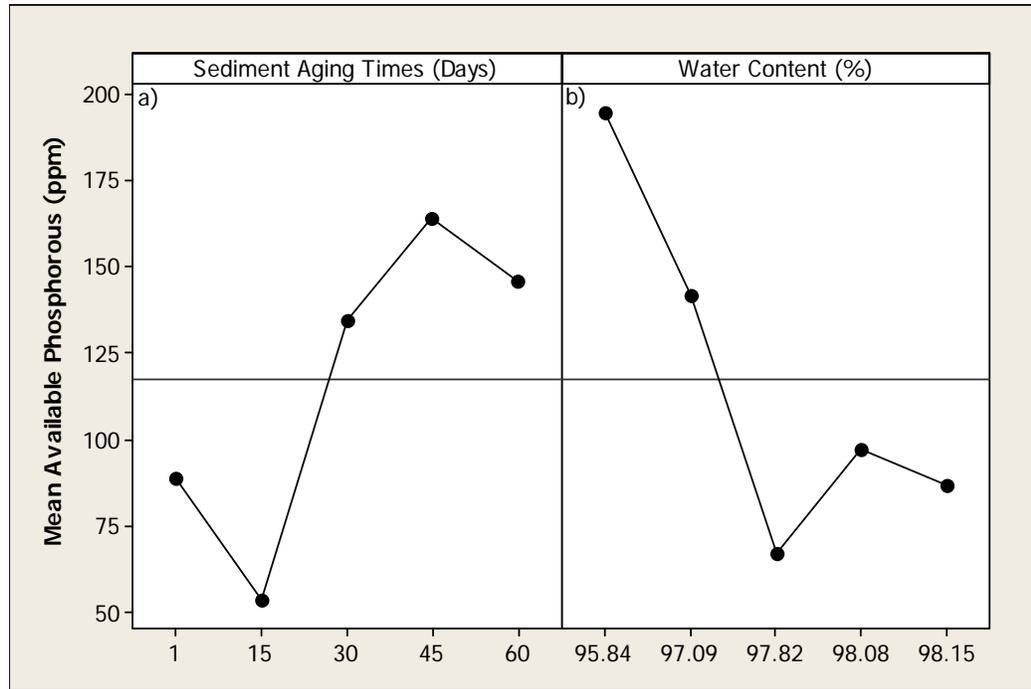


Figure 20: Main Effect Plot for Available Phosphorous as function of sediment a) aging times and b) water contents

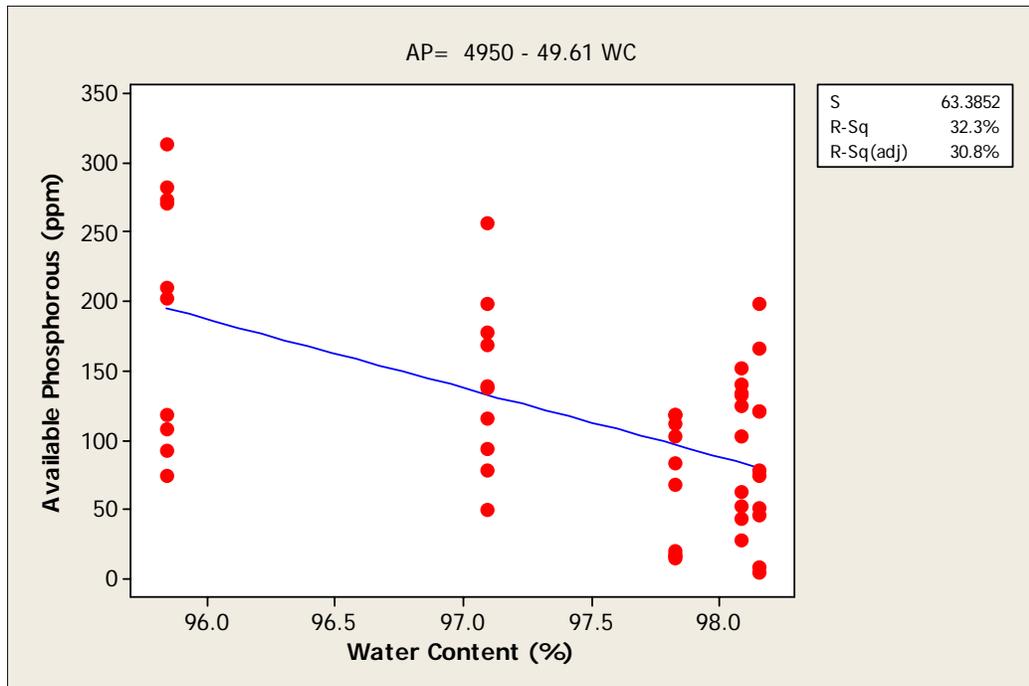


Figure 21: Relation of AP as a function of Water Contents

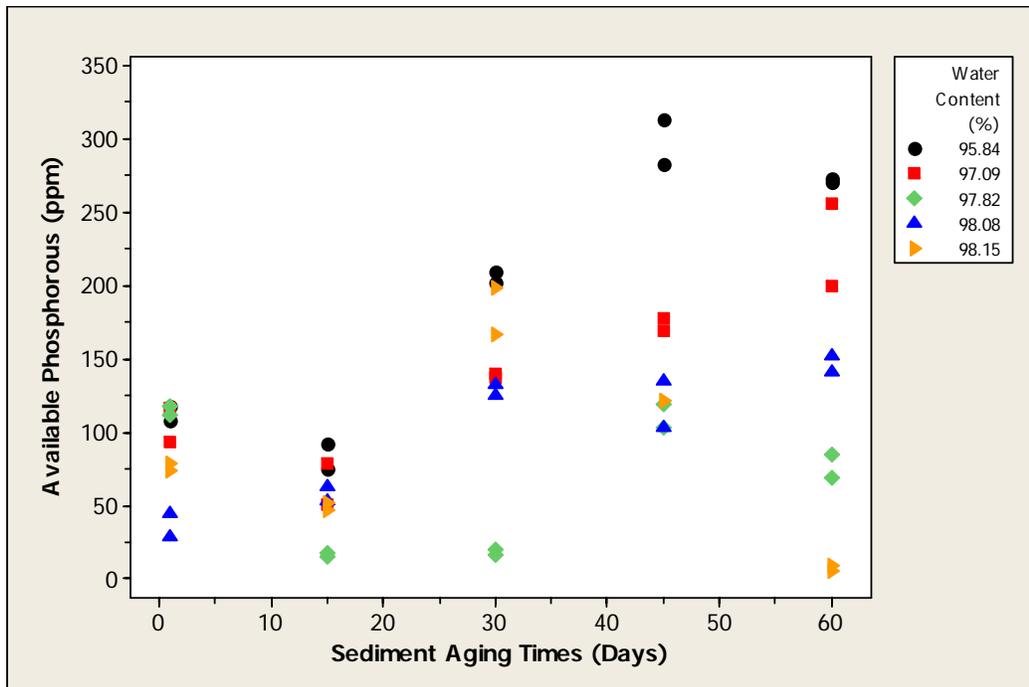


Figure 22: Behavior of Available Phosphorous as a function of Sediment Aging Times

The ANOVA results (Table 6) suggest that sediment aging times and water contents are significant factors in the response of PA, because both p-values are lower than the selected α value of 0.05. A slightly higher F value for the water content factor, however, suggests that water content is slightly more important in the response of AP, than sediment aging times. The ANOVA General Linear Model (GLM) describes the response of AP to sediment aging times and water contents (Table 5) and suggests that approximately 65% can be described by this model, but that 35% of the variations are described by others factors not evaluated in this study.

Attempts were made to correlate TP and AP, but no correlation was found (Figure 23).

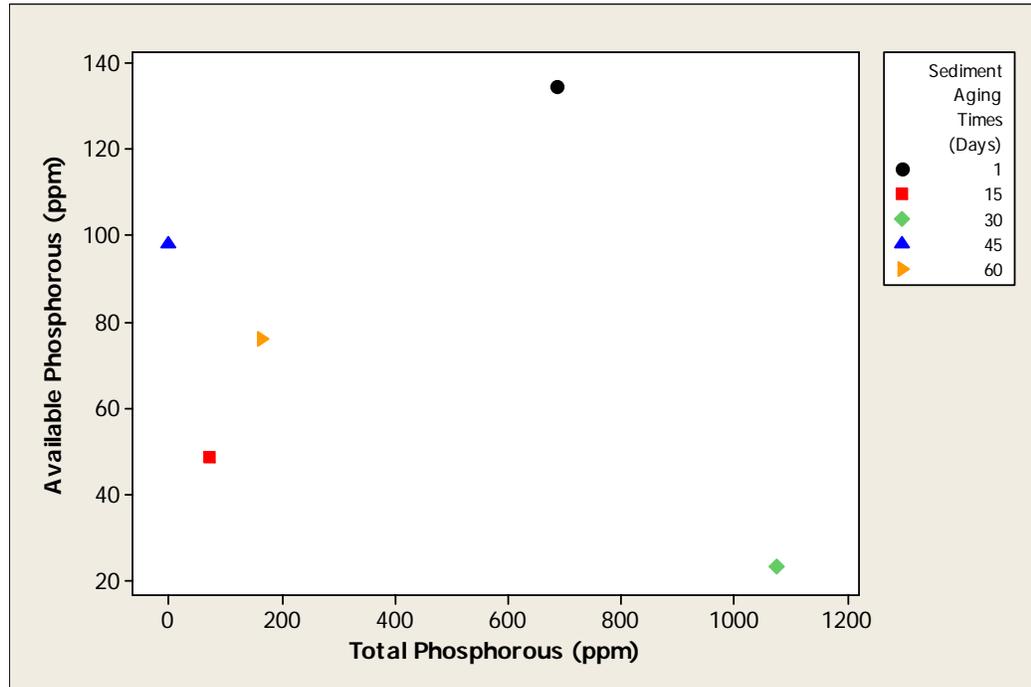


Figure 23: Available Phosphorous vs Total Phosphorous

As expected, DO values in the sediment samples were low, varying between 0.100 and 5.4mg/L and averaging 0.534 mg/L. Figure 24 illustrates the behavior obtained for DO with respect to the sediment aging times at the different water contents studied. It shows that DO is relatively constant at these environmental conditions. The maximum DO values were obtained at 30 days of aging and at 97.82% water content, are considered experimental error, because, on average, DO values are relatively constant (Figure 25).

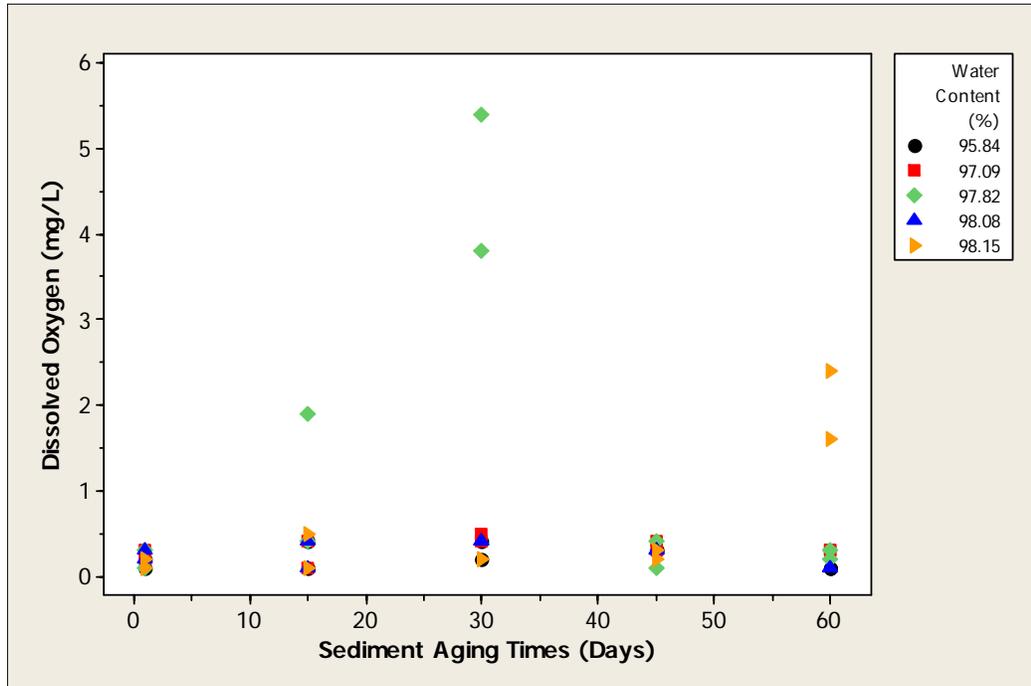


Figure 24: Behavior of DO as a function Sediment Aging Times at different Water Contents

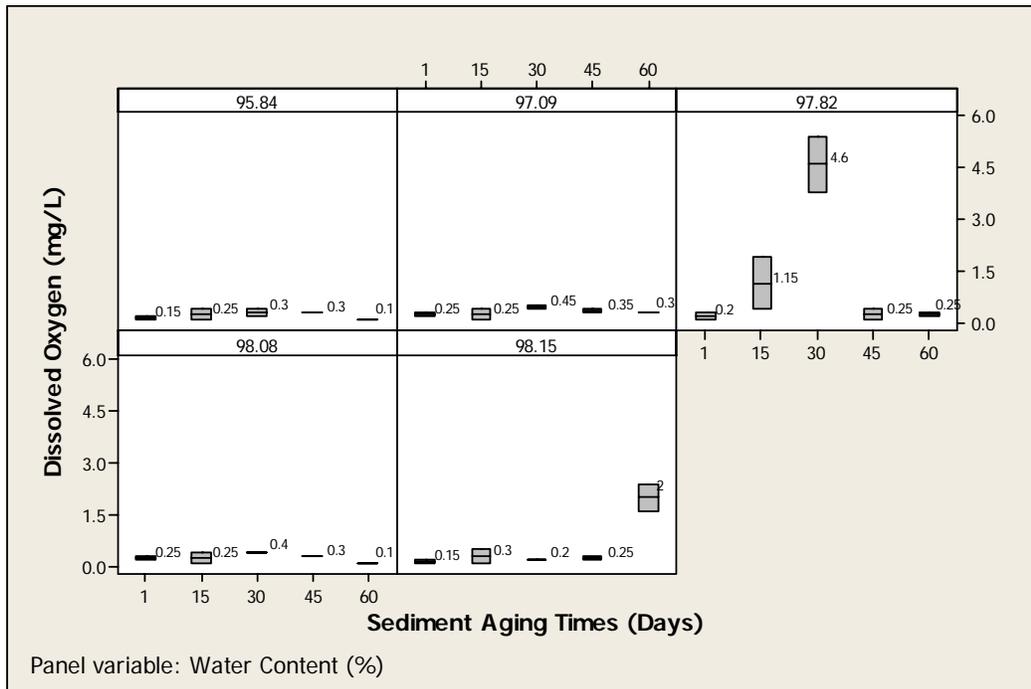


Figure 25: Tendency of Mean DO as a function of Sediment Aging Times at different Water Contents

The p-values and small F-values obtained from ANOVA on DO values also indicate that water contents and the sediment aging times are not important factors in the response of DO. The slightly smaller than alpha values for the DO response as a function of water content suggest that water content may be slightly affect the DO in sediments. Further statistical testing using One-Way ANOVA on the DO vs. water content data (see Section G.1.3- Appendix G), however, indicates that water content is not a significant factor influencing the DO response.

Values for TS and TVS (Table 5) average 31400 mg/L and 17200 mg/L, respectively, for all tested sediments. Graphical (Figure 26) and statistical analysis (Table 5) on the behavior of TS and TVS shows that these parameters do not vary with aging time or water content. Statistical analysis also indicates that the average obtained for these parameters are not significantly different. This is further supported by the ANOVA Results (Table 6), which indicate that the p-values are greater that the level of significance used and that F-values are considerably low.

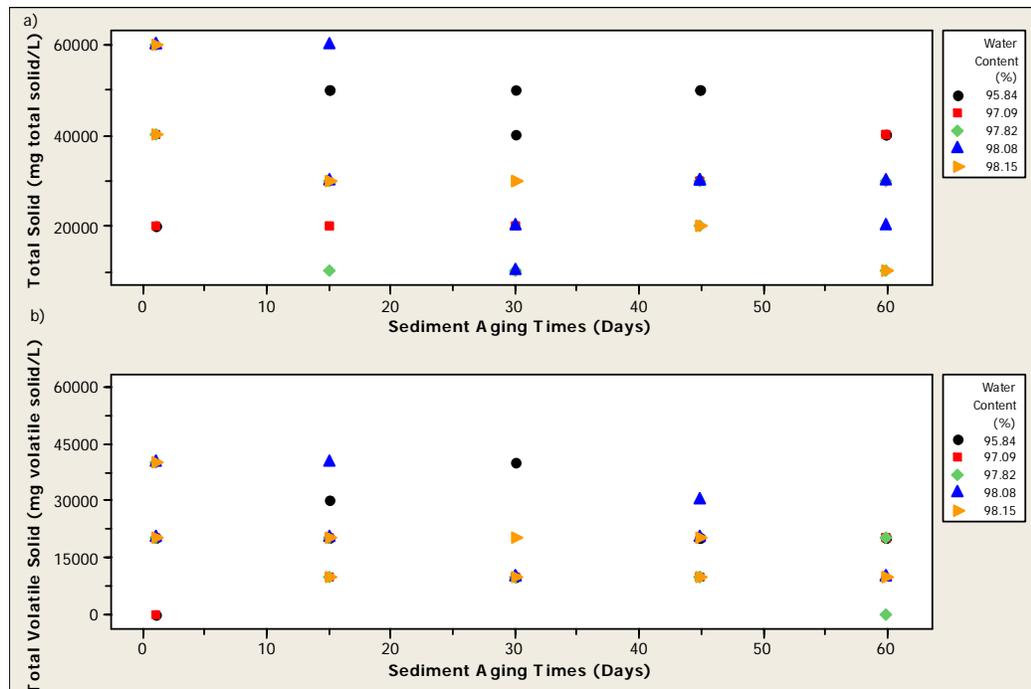


Figure 26: Behavior of a) TS and b) TVS as a function of Sediment Aging times at different Water Contents

Values of TKN ranged between 0.01247 and 0.17575% and average 0.0781% for all tested sediments. The tendency obtained in the results of TKN in relation to different sediment aging times and water contents is presented Figures 27 and 28. These figures show that both factors may influence the amount of TKN in the sediment samples. Generally, it is observed that TKN decrease with water content, but increase with aging times after 15 days (Figure 29). Higher TKN values with aging time reflect the slower decomposition of nitrogenous organic matter relative to carbonaceous organic matter.

Results from the ANOVA (Table 6) indicate that, although both the water content and the sediment aging times are significant factors ($P < 0.05$) on the behavior of TKN, water content affects the behavior of TKN to greater extent. This is observed in the higher F-values and lower p-values obtained for water contents than sediment aging times. The ANOVA using the GLM suggests that approximately 64% of the variation in the response of TKN is principally described by this model, but that around of 35% of the variation is described by others factor not evaluated in this study.

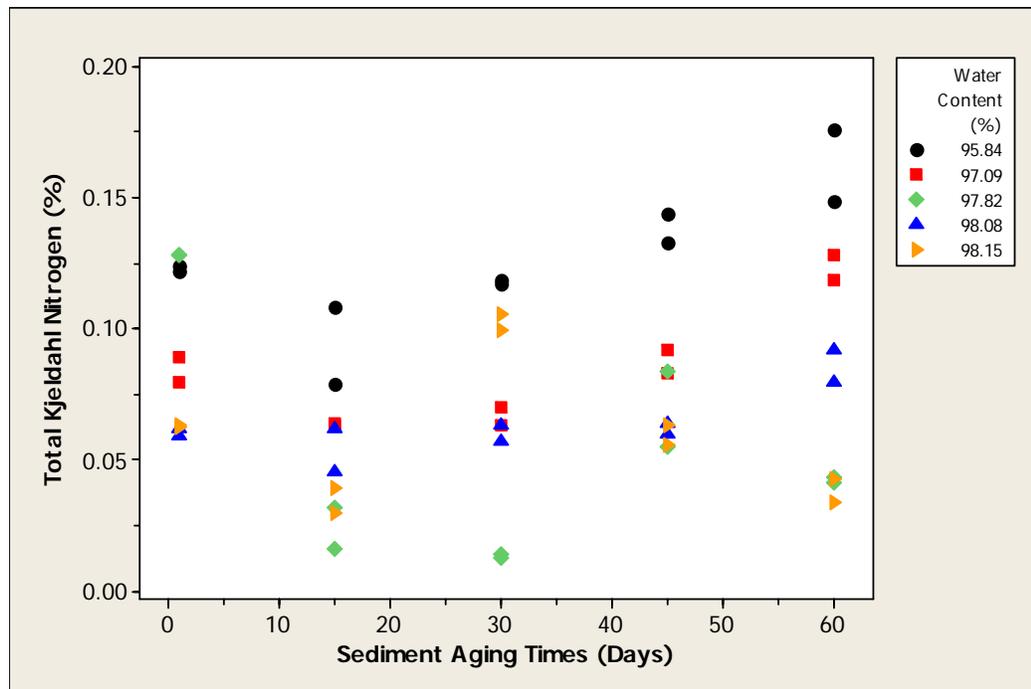


Figure 27: Behavior of TKN as a function of Sediment Aging Times at different Water Contents

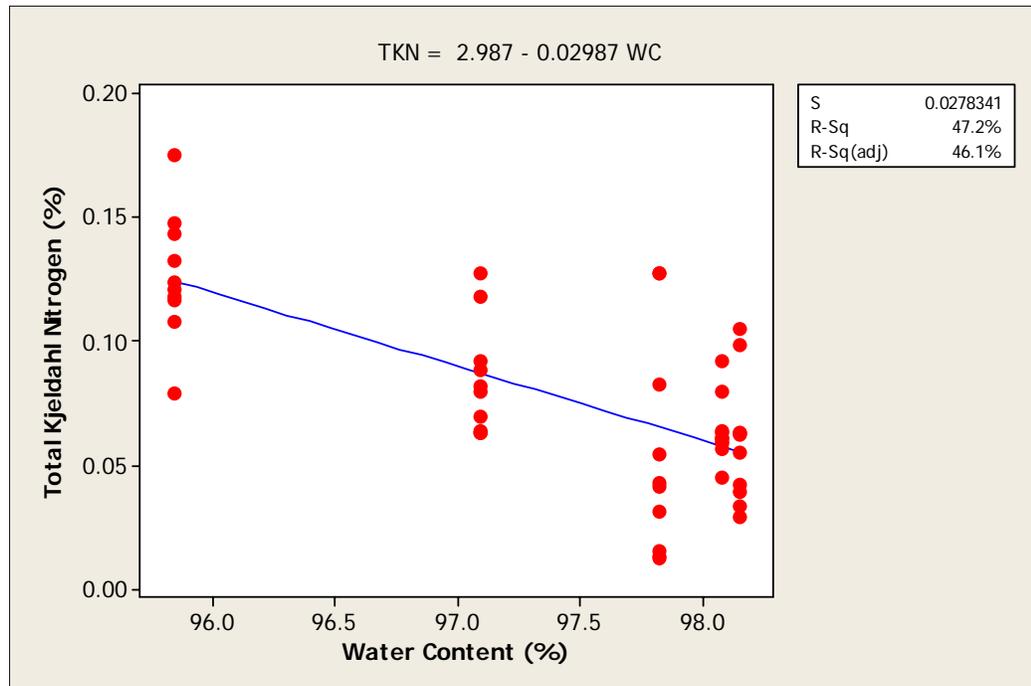


Figure 28: Relation of TKN as function of Water Contents

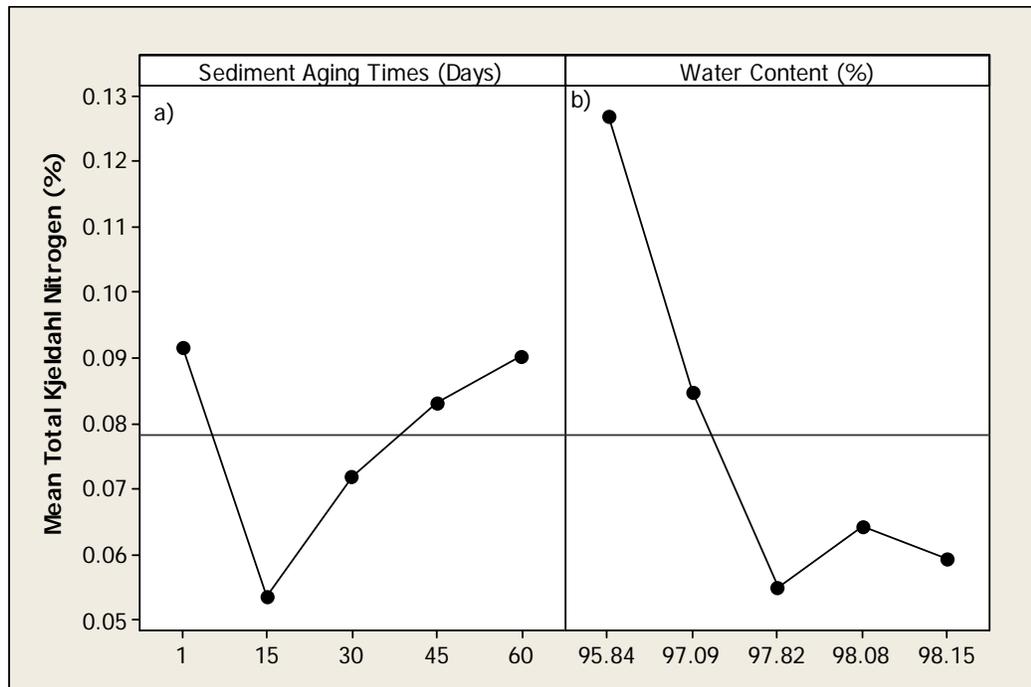


Figure 29: Main Effect Plot for the TKN as function of the sediment a) aging times and b) water contents

4.2 Odor Threshold Test

4.2.1 Preliminary Evaluation

The potential odor threshold of sediments from EMWTP was quantified using TON and H₂S concentrations obtained during the olfactometry tests. The experimental design of the test involved a series of preliminary evaluations, which also provided valuable information regarding the behavior of odorous compounds near sediment/atmosphere interfaces. Olfactometry studies generally presume that the concentration of the odor-causing vapor does not change with the time during the period of test. Results from preliminary tests show, however, that the concentrations of odorous vapor change as function of time (Figure 30). The tendency in the temporal behavior of H₂S concentration is to increase initially during the first or the second minutes and then decreases with time. Similar trends are observed for different OA flow rates.

A preliminary evaluation of H₂S concentration in the olfactometry systems using different OA and dilution rates through time indicate that H₂S concentration increases as OA flow rate increases and dilution rates decreases up to a point, after which decreasing dilution caused no change on lower concentrations (Figures 31 and 32). This may be caused by limited mass transfer from sediments to air and potential dilution of total mass caused by higher UA flow rate and constant transfer to air.

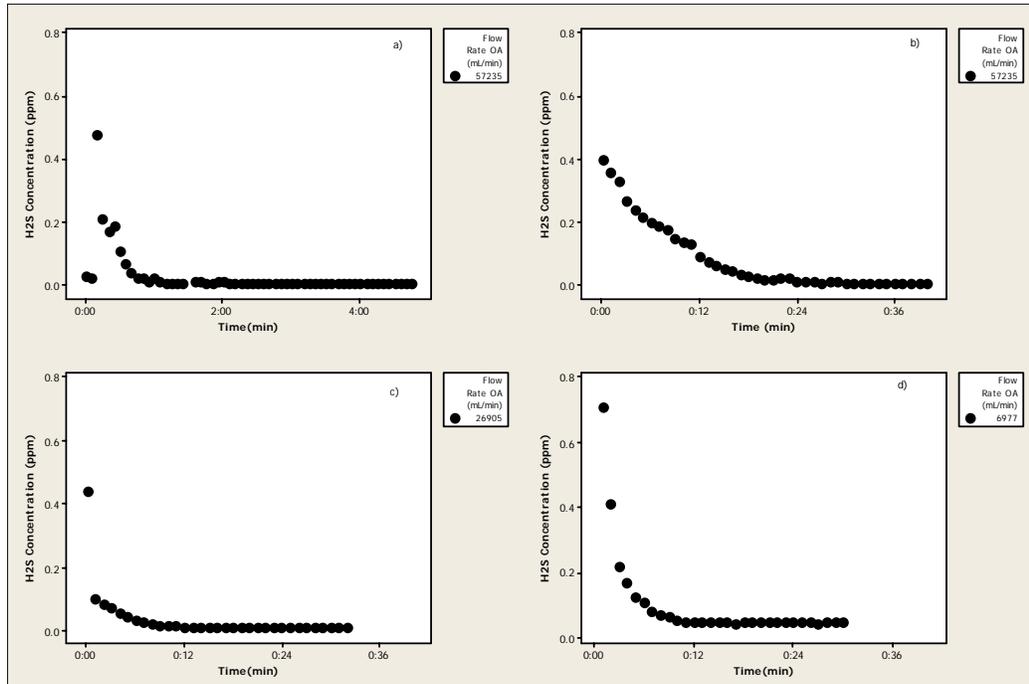


Figure 30: H₂S Response to OA flow rate of a) 57235 mL/min (Run 1), b) 57235 mL/min (Run 2), c) 26905 mL/min, and d) 6977 mL/min

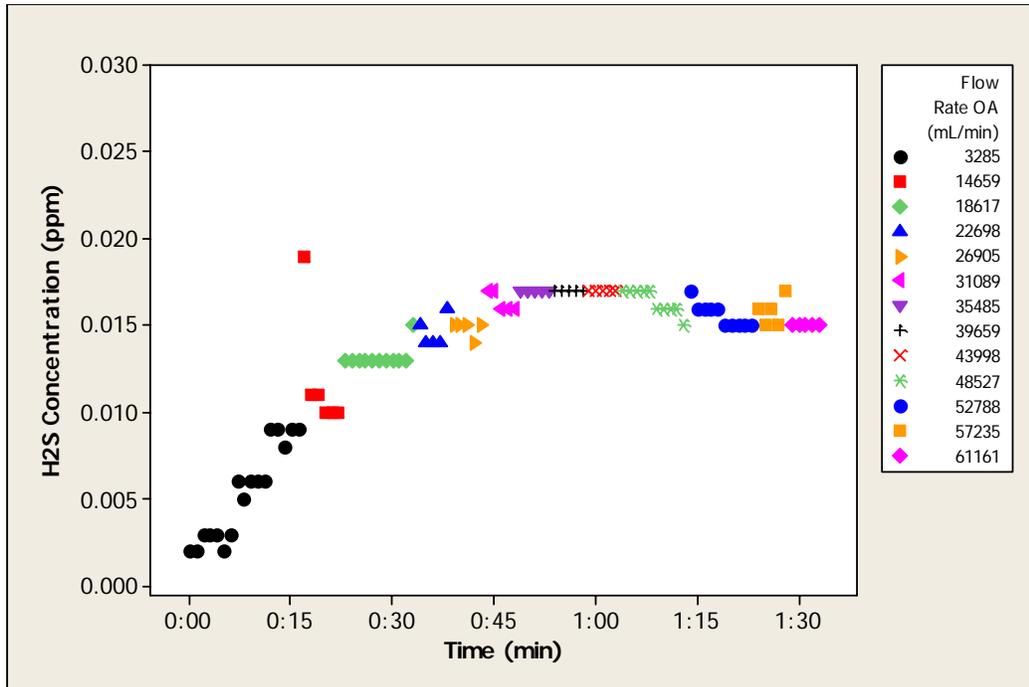


Figure 31: Behavior of H₂S in sediment samples at different rate of dilution during the first day of aging

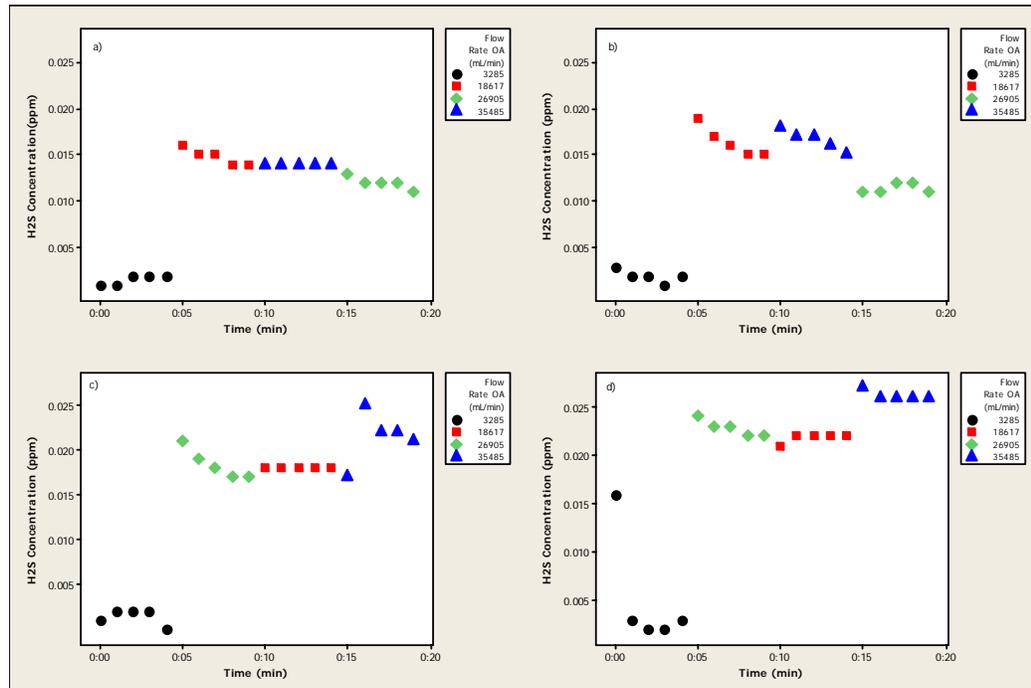


Figure 32: Behavior of H₂S Concentration at different Flow Rates during the a) second hour of exposition, b) third hour of exposition, c) 2 days of aging and d) 5 days of aging

Figure 33 illustrates the behavior observed in diverse analyses where the sample was exposed to different rates of dilution every five minutes during a total period of twenty minutes. All tests were started with higher dilution rates (low OA flow rates) and decreased stepwise through time. The tendency observed reflect that a sudden decrease in dilution rates (increase in OA flow rates) results in rapid increase, followed by a gradual decrease in concentrations. This behavior suggest that concentrations of odorous vapors change rapidly as dilution rates are changed and then change more gradually toward a constant value. As expected, the constant values are higher for lower dilution rates (higher OA flow rates).

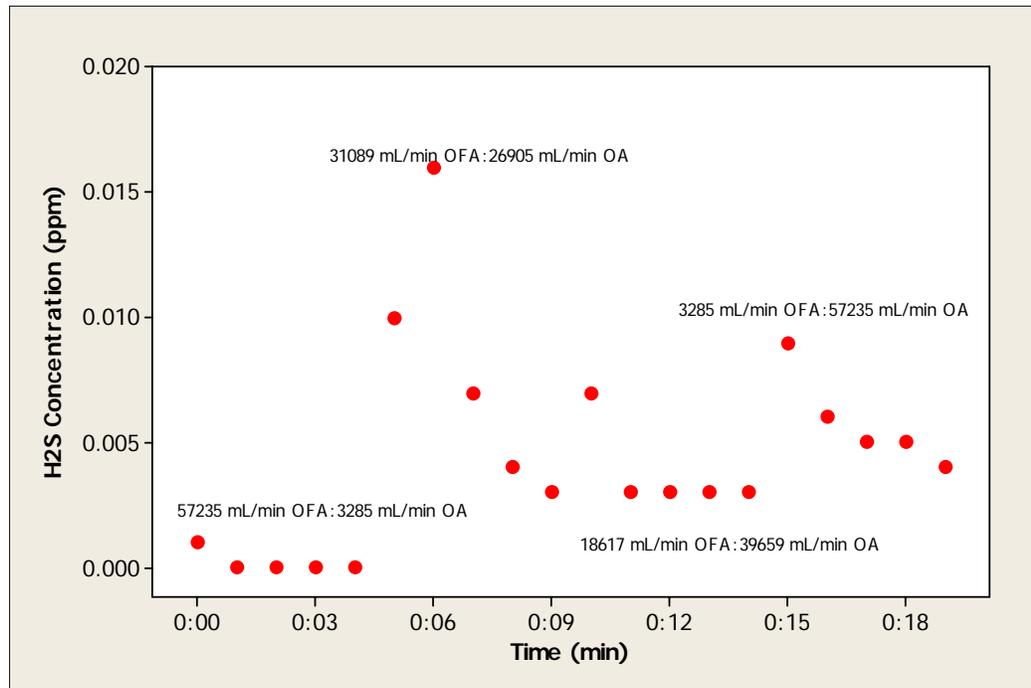


Figure 33: Temporal Behavior of H₂S Concentration at Different Rates of Dilution

In order to investigate the approximate time that it takes the system to reach a constant concentration after a sudden change and the effect of flow interruption on the behavior of H₂S concentration, sediment samples were exposed to specific OA flow rates for fifteen minutes, followed by a no-flow period of fifteen minutes. Figure 34 shows that H₂S concentrations increased rapidly after a decreased in dilution and then decreased with time. Relatively constant concentrations were reached at approximately five minutes. This tendency was also shown in Figure 35, at a flow lag interrupted at five minutes.

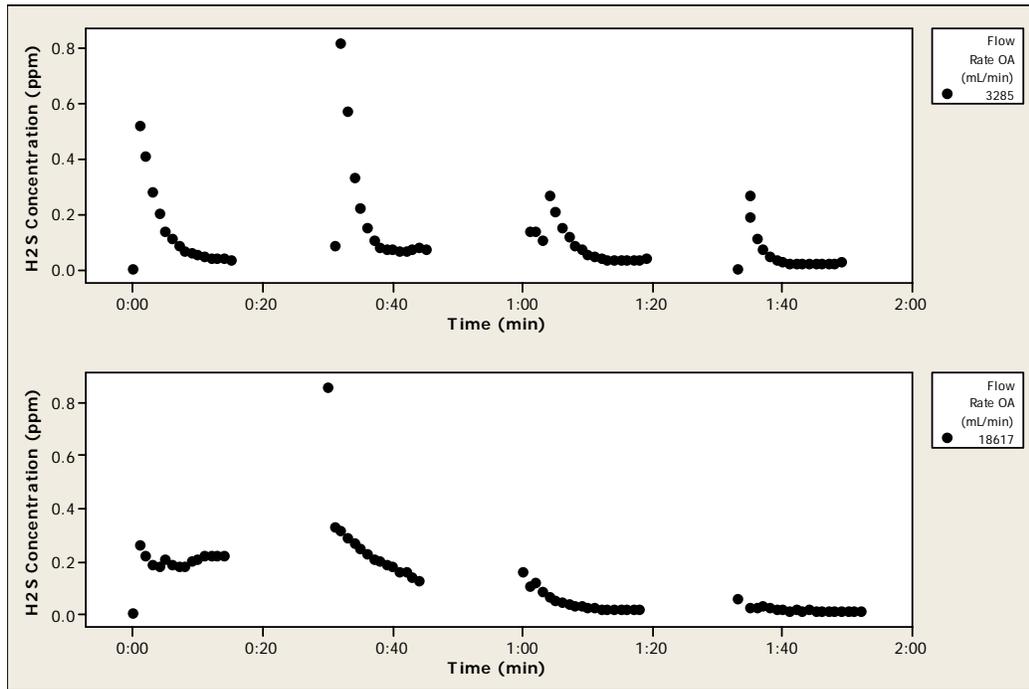


Figure 34: H₂S Response to 15-minute flow interruptions at a) 3285 mL/min and b) 18617 mL/min

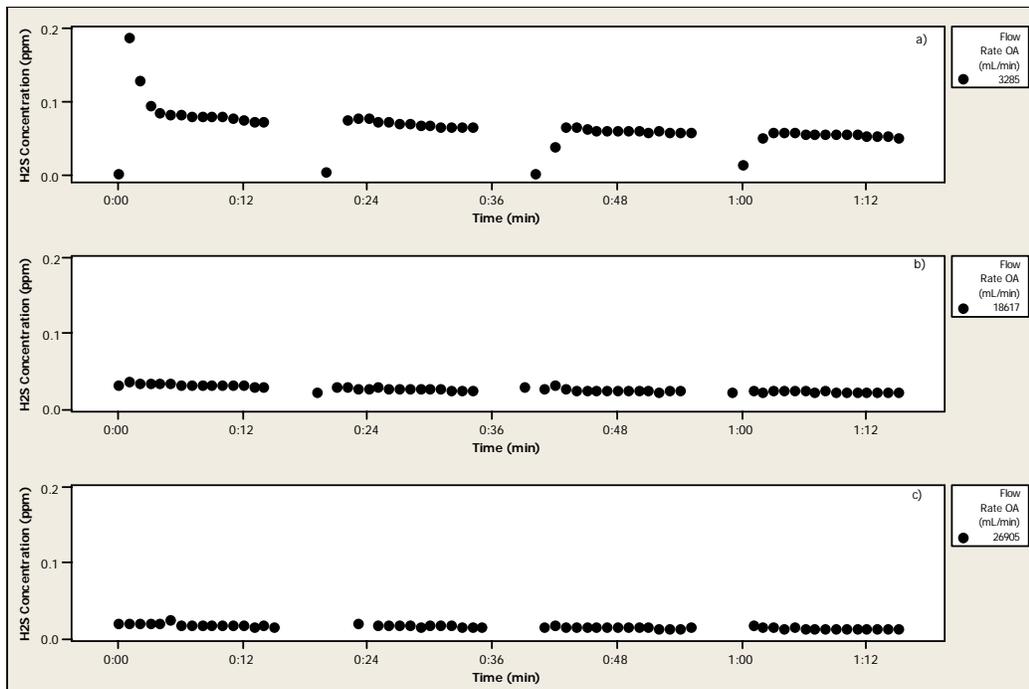


Figure 35: H₂S Response to 5-minute flow interruptions at a) 3285 mL/min b) 18617 mL/min and c) 26905 mL/min

Tests where the rate of dilution was changed (Figure 36) every ten minutes after a five minutes flow interruption period also reveal that the concentration was decreasing with time. A constant concentration was achieved approximately after five minutes after the sediment samples were exposed to the sweeping air. Tests completed at different rates of dilution in samples with 5 and 6 days of aging reflect that H₂S concentrations decrease with sweeping and aging time. This tendency is illustrated in Figure 37.

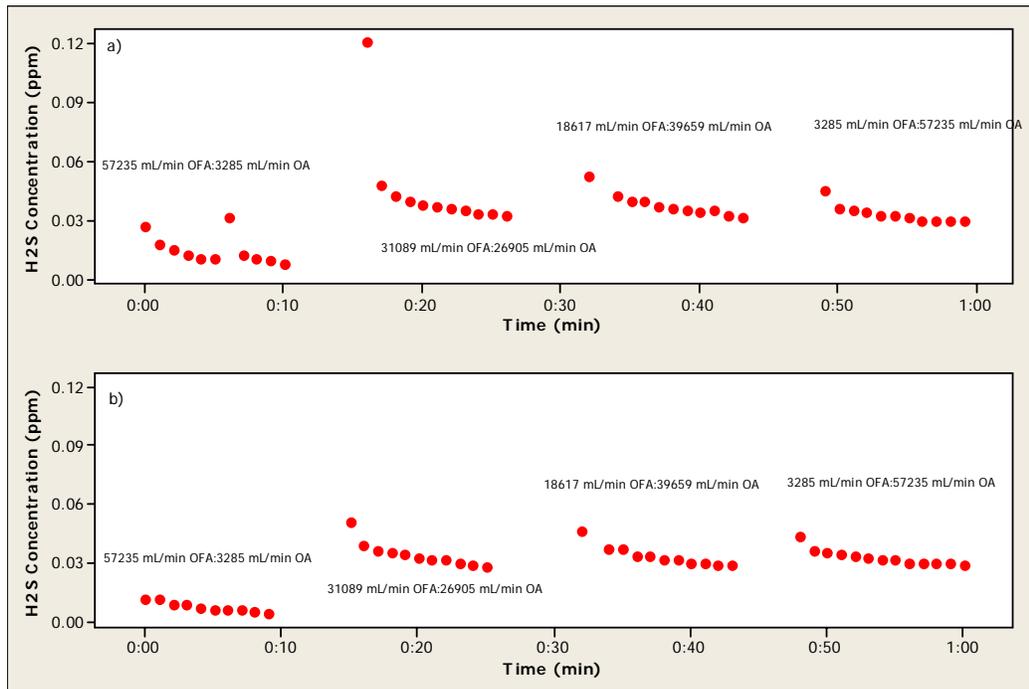


Figure 36: Temporal Behavior of H₂S Concentration at Different Dilution Rates followed by a 5-minutes flow interruption for a) sample and b) a later replicate

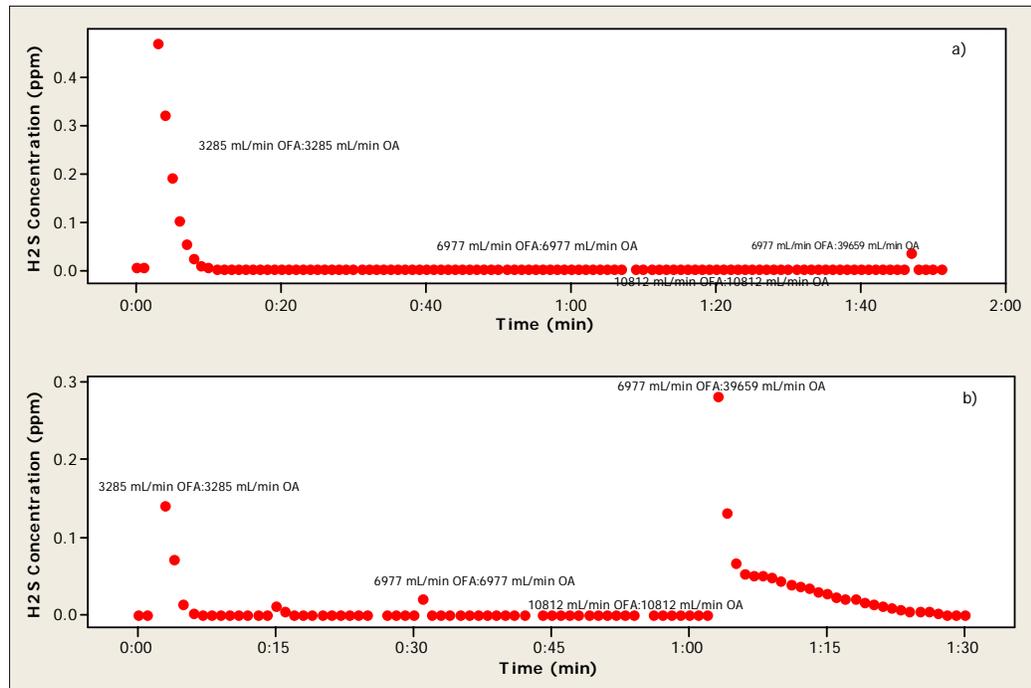


Figure 37: Behavior of H₂S Concentration in Sediments Samples for different dilution rates at a) 5 days and b) 6 days of aging

4.2.2 TON Results

Odor threshold of exposed sediments was quantified by determining the TON, which represents the dilution of odorous-air at which odor is detected. If odor from a source is strong it has a high TON values and detection occurs even at low amounts of odorous-air (high dilution). Higher TON value thus represents high detection and greater odor problems. Higher amounts of odorous-free air would, therefore, be required for detection not to occur.

In olfactometry tests, the amount of odorous-air delivered to a given panelist is increased in a stepwise fashion until odor is detected. Consequently, the number of panelist detecting odor is expected to increase as the test progresses. A plot of relative detection frequency (number of panelist detection over total number of panelist) as a function of the ratio of odorous to total air flow rate (Q_{OA}/Q_T) indicate that this, in fact is the case in our experiments (Figure 38).

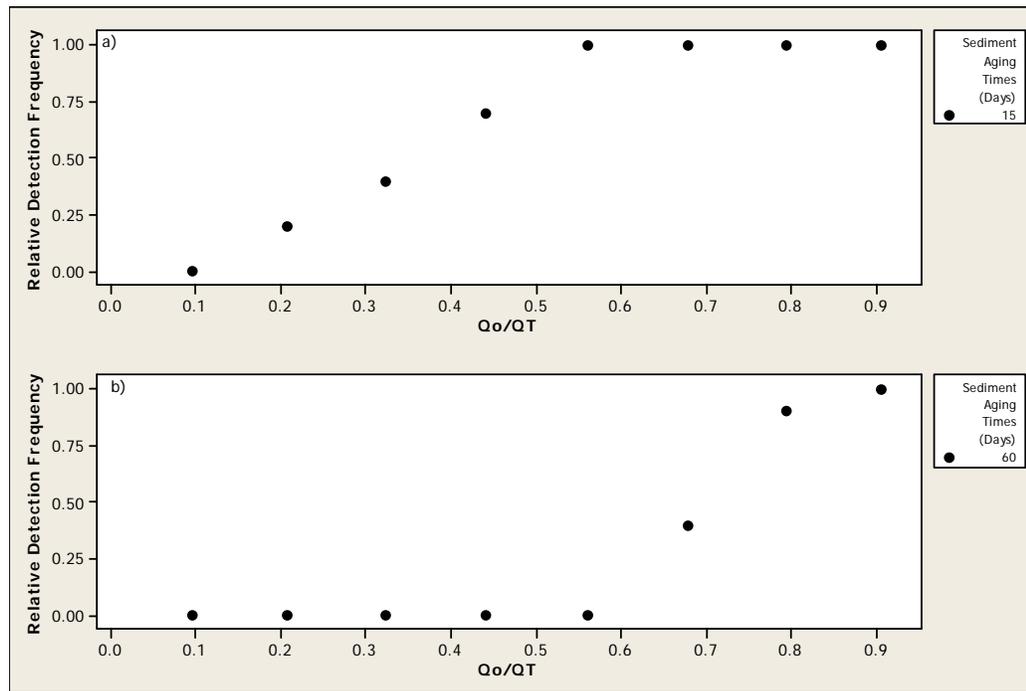


Figure 38: Relative Frequency of Odor Detection on function of Relative amount of Odorous Air at a) 15 and b) 60 days of aging

4.2.2.1 TON

TON was quantified for three different sediment water contents (95.84%, 97.09%, and 98.08%) and five sediment aging times (1, 15, 30, 45, and 60 days). Average TON values for different sediment aging times and water contents are summarized in Table 8.

Table 8: Analysis of Average

Sediment Aging Times (Days)	Water Contents (%)	ED ₅₀	Dil ₅₀	Average TON	Average Concentration (ppm)
1	95.84	3.099334	0.32265	3.6975	0.0288
1	97.09	3.977788	0.251396	4.9040	0.0903
1	98.08	3.502837	0.285483	4.3063	0.0371
15	95.84	3.099334	0.32265	2.9810	0.0112
15	97.09	2.270005	0.440528	2.6895	0.0072
15	98.08	2.270005	0.440528	2.6486	0.0212
30	95.84	3.099334	0.32265	2.7466	0.0000

Table 8. Continued

Sediment Aging Times (Days)	Water Contents (%)	ED₅₀	Dil₅₀	Average TON	Average Concentration (ppm)
30	97.09	3.099334	0.32265	2.7433	0.0009
30	98.08	2.270005	0.440528	2.2328	0.0002
45	95.84	2.028702	0.492926	2.2612	0.0008
45	97.09	1.476342	0.67735	1.6765	0.0003
45	98.08	1.367831	0.731085	1.6757	0.0006
60	95.84	1.367831	0.731085	1.4492	0.0005
60	97.09	1.367831	0.731085	1.6177	0.0015
60	98.08	1.476342	0.67735	1.8213	0.0030

Figures 39 and 40 shows a tendency for lower TON values with sediment aging times, but show no effect of water content on these values. Greater TON values during the first day of aging reflect more detection than at later times. TON values appear to decrease with increasing aging times at early times and approach a steady value thereafter. A box plot of TON median values (Figure 41) show that in fact TON values decrease with sediment aging times for all water contents studied. This behavior may be caused by the volatilization or degradation losses of odor-causing compounds in the sediments samples.

Higher variability and dispersion of TON values (Figures 39 and 41, respectively) during the first day of aging may have been caused by stability problems with the air source in the system. A plot showing the TON standard deviation and associated 95% (BonFerroni) confidence interval for different aging times and water content (Figure 42) reflect the results of Equal Variances Tests conducted on TON (see Section G.3.2-Appendix G). It shows that TON variance for the first sediment aging time was greater than those obtained at others aging times. Less dispersion (variability) of the TON data is observed when plotted as a function of water content (Figure 42.b)

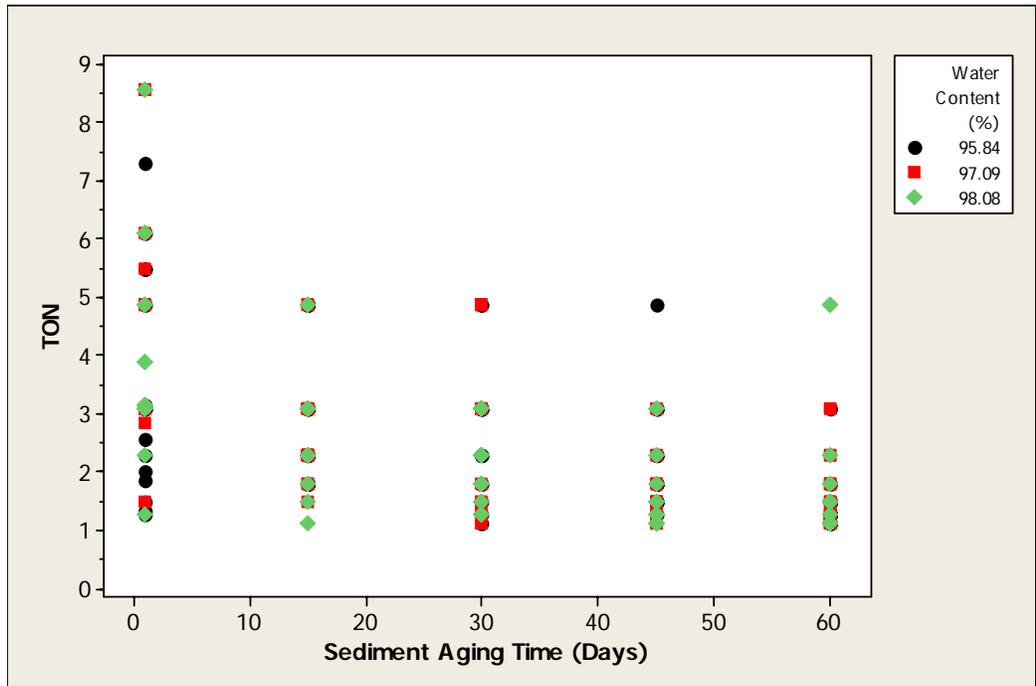


Figure 39: TON values for all panelist vs Sediment Aging Times at Different Water Contents

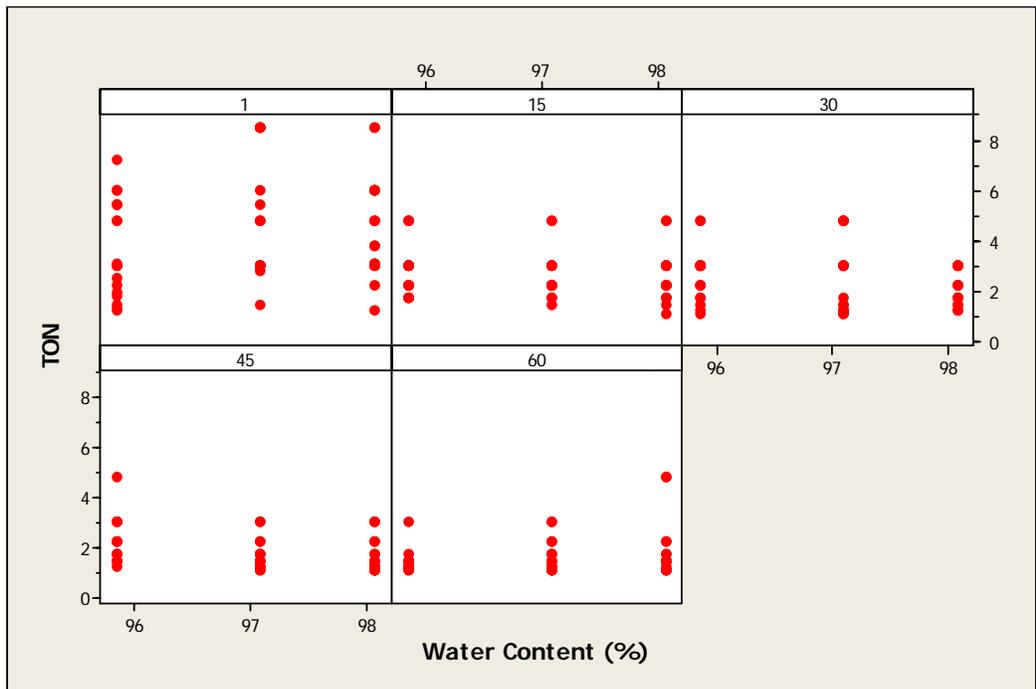


Figure 40: TON vs Water Contents at different Sediment Aging Times

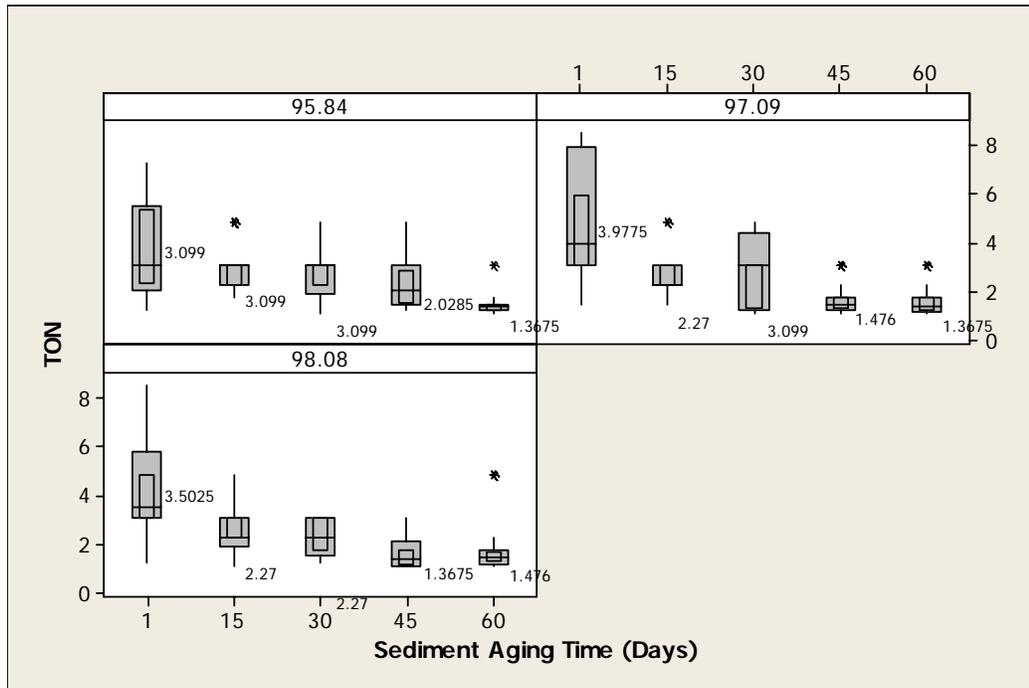


Figure 41: Box plot of TON Median vs Sediment Aging Times at Different Water Contents

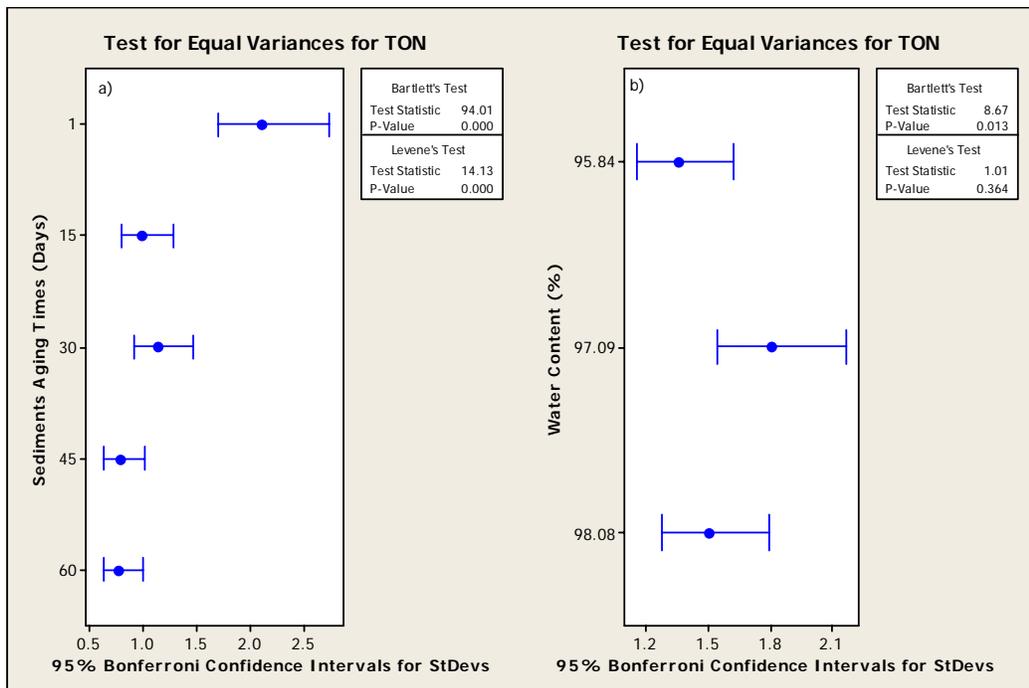


Figure 42: Test for Equal Variance for TON values a function of sediments a) aging times and b) water contents

The Main Effect Plot for TON (Figure 43) shows that, on average, the sediment aging time affects more the TON values than water contents, and that the average obtained for the factor of sediment aging times are significantly different from each other. Results from ANOVA tests (Table 9) (see Section G.3.3- Appendix G) also sustain that water contents have less impact on TON values than sediment aging times. Because ANOVA presumes a constant variance and the Test of Equal Variance reflects more dispersion during the first sediment aging time, ANOVA test was conducted using all the TON data except the data from the first sediment aging time. A similar trend was obtained in both ANOVA tests (Table 9). Higher F-value (41.87) and low p-value ($p=0.000 < 0.05$) for sediment aging times show that this is an important and significant factor affecting TON values. Much lower values F-value (0.57) and higher p-value (0.567) for water contents suggest that water content is not an important and significant factor affecting TON values. The analysis of variance using the General Linear Model shows that approximately 37% of the variation in the response of TON is explained by this model, but around 63% is described by others factor that not considered in this study. Although poor relation between TON values and sediments aging times were observed for all data, a strong linear relationship ($R^2=80.2$) is observed between average TON and sediment aging times (Figure 44).

Table 9: Summary of ANOVA Tests for TON data

Variable	ANOVA Test using all TON values		ANOVA Test excluding the data from the 1 st day	
	P-value	F-value	P-value	F-value
Water Contents (%)	0.567	0.57	0.182	1.72
Sediment Aging Times (Days)	0.000	41.87	0.000	21.24

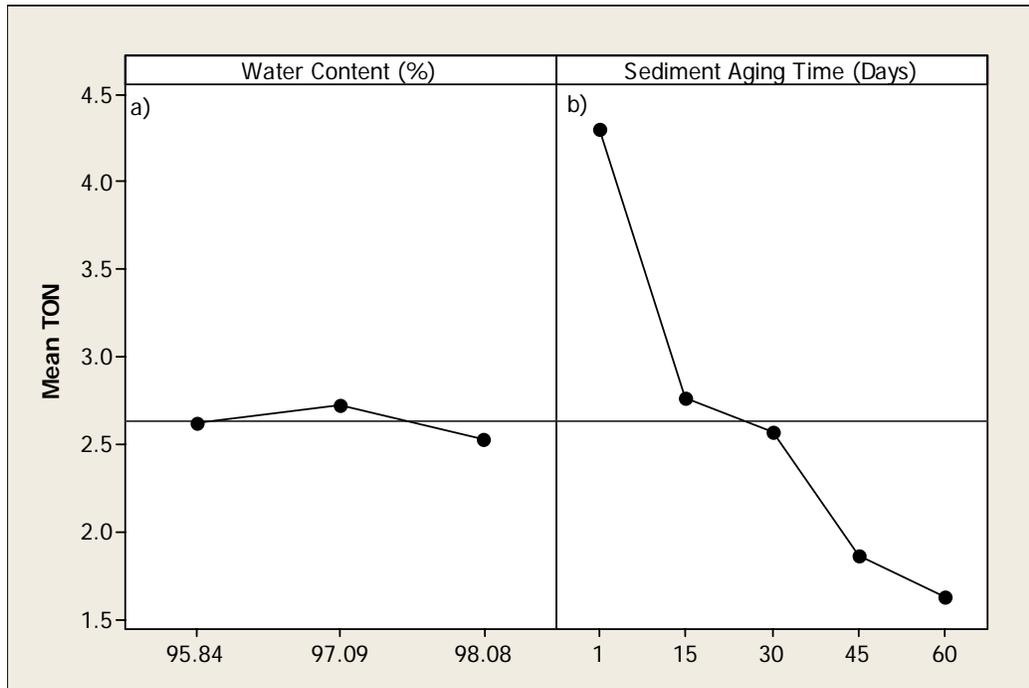


Figure 43: Main Effect Plot for TON as function of a) water contents and b) sediment aging times

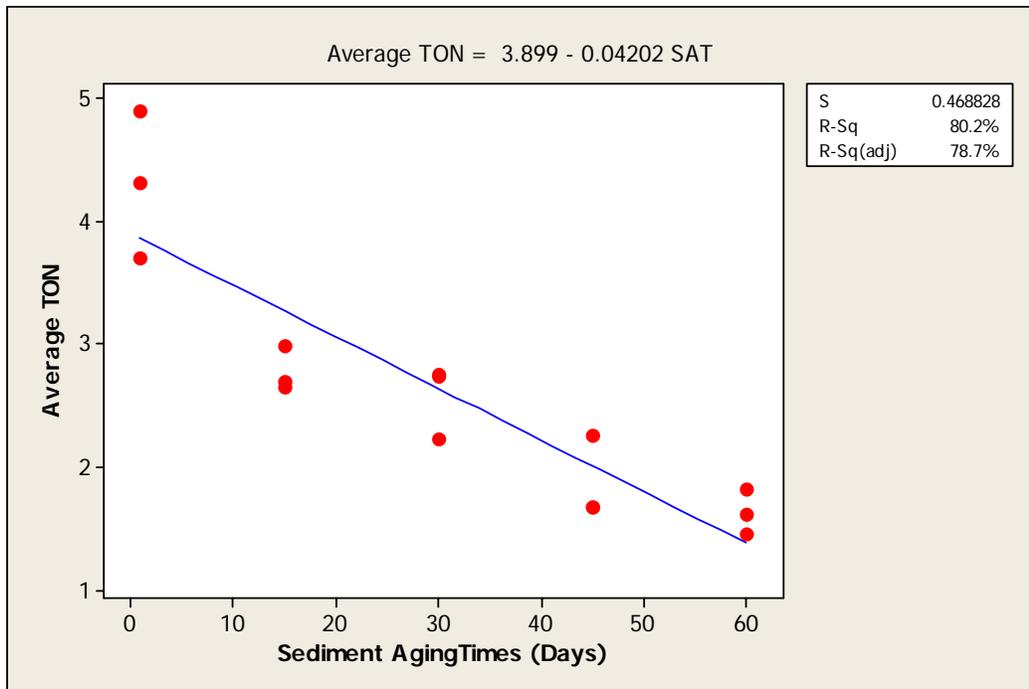


Figure 44: Relation Average TON vs Sediment Aging Times

A plot of the H₂S concentrations measured at the odor threshold of exposed sediments for the different environmental conditions (Figure 45) shows that H₂S concentrations tends to decrease with sediment aging times, invariably of the water contents conditions. The Individual Value Plot of H₂S concentration vs sediment aging times (Figure 46) shows clearly that approximately after 30 days of aging a constant concentration of H₂S is approached for the different environmental conditions studied. It is important to mention that zero H₂S concentration values (0.000 ppm) were obtained inclusive in the first aging time.

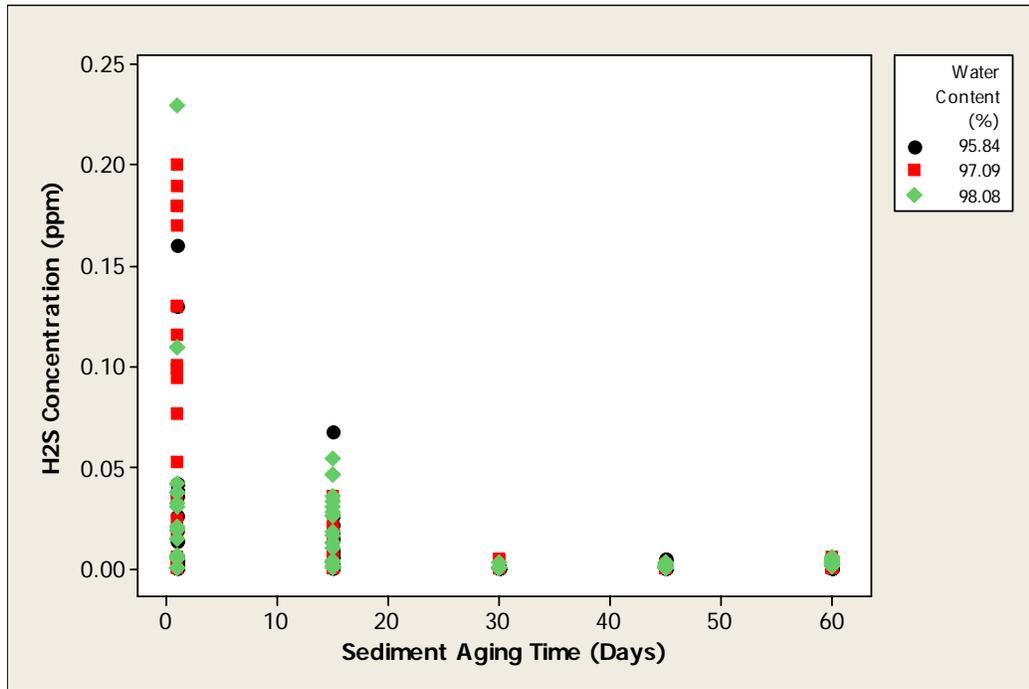


Figure 45: H₂S Concentration vs Sediment Aging Times at different Water Contents

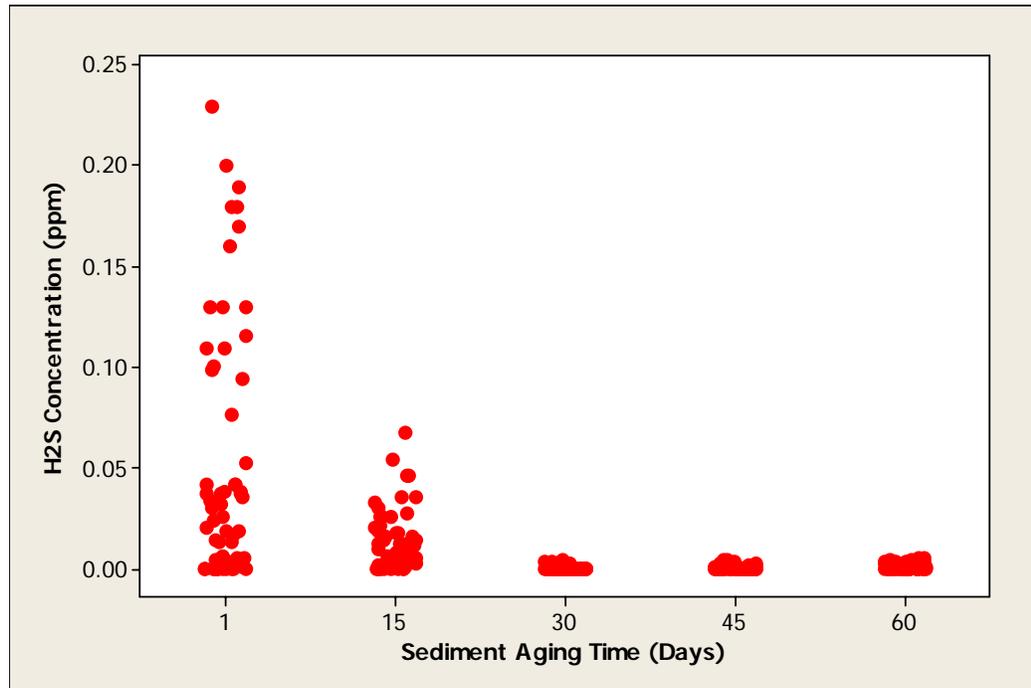


Figure 46: Individual Value Plot of H₂S Concentration vs Sediment Aging Times

The Main Effect Plot for the average H₂S concentration (Figure 47) shows that, on average the sediment aging times affect more the H₂S concentration than water contents. Average H₂S concentrations decrease from 0.052 ppm for the first day of aging to 0.0016 ppm at 60 days of aging (Figure 47). The variability of H₂S concentration measurements also decreased with sediment aging times (see Section G.4.1- Appendix G). A plot of Average H₂S concentration and sediment aging times (Figure 48) shows an inverse, weakly-linear relation between these parameters. The plot indicates that, on average, H₂S concentrations decrease with sediment aging times.

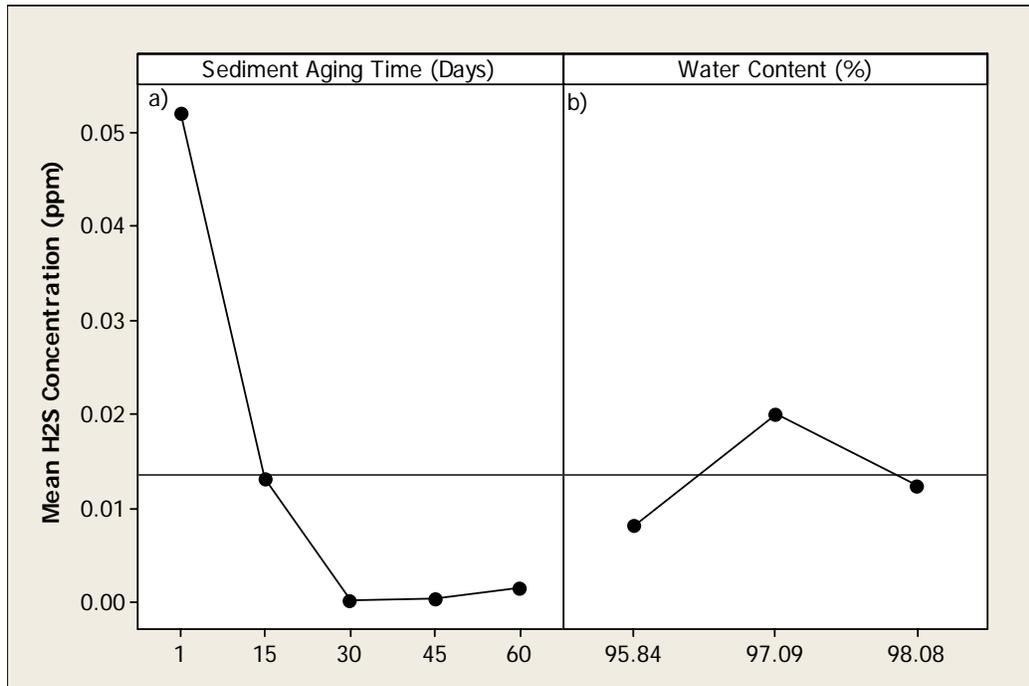


Figure 47: Main Effect Plot for H₂S Concentration as function of sediment a) aging times and b) water contents

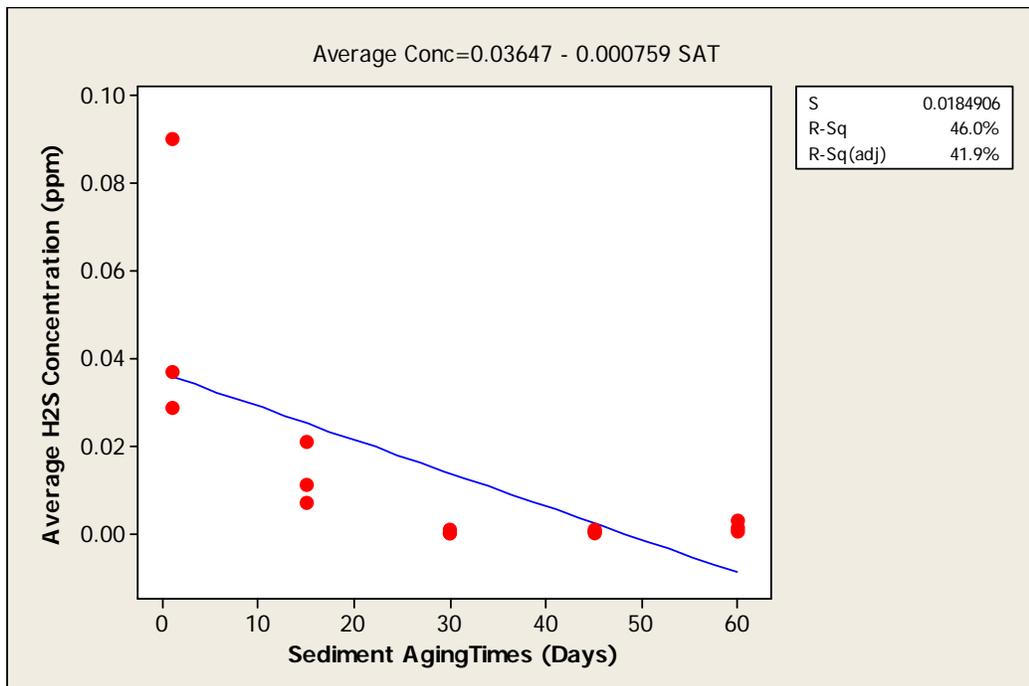


Figure 48: Relation Average H₂S Concentration vs Sediment Aging Times

Concentrations of H₂S were measured in the sniffing ports at the odor threshold (detection) for the different water contents and sediment aging times to establish a relationship between TON and H₂S concentration at the conditions studied. Figure 49 shows, however, that a strong relation does not exist between TON and H₂S concentration at the conditions analyzed in this investigation.

Higher measured (absolute) H₂S concentrations (0.23 ppm) and TON values (8.566) during the first day of aging than at 60 days of aging (0.005 ppm and 4.856, respectively) indicate that the perception of odor was more elevated during the first day of aging, when the H₂S concentrations was also relatively higher. These results show that both, TON and H₂S concentrations have a tendency to decrease with sediments aging times even if a strong relation is not established between TON and H₂S concentration. Qualitatively speaking, higher H₂S concentrations may include higher odor detection.

Lack of relationship between TON and H₂S concentrations have also been observed in other studies (Stuetz et al., 1999) and reflect that odor is also caused by other vapors emanating from the sediments. Although poor relations between H₂S concentration and TON were observed for all the data (Figure 50), a strong non-linear relation were observed between average TON and H₂S concentration (Figure 51).

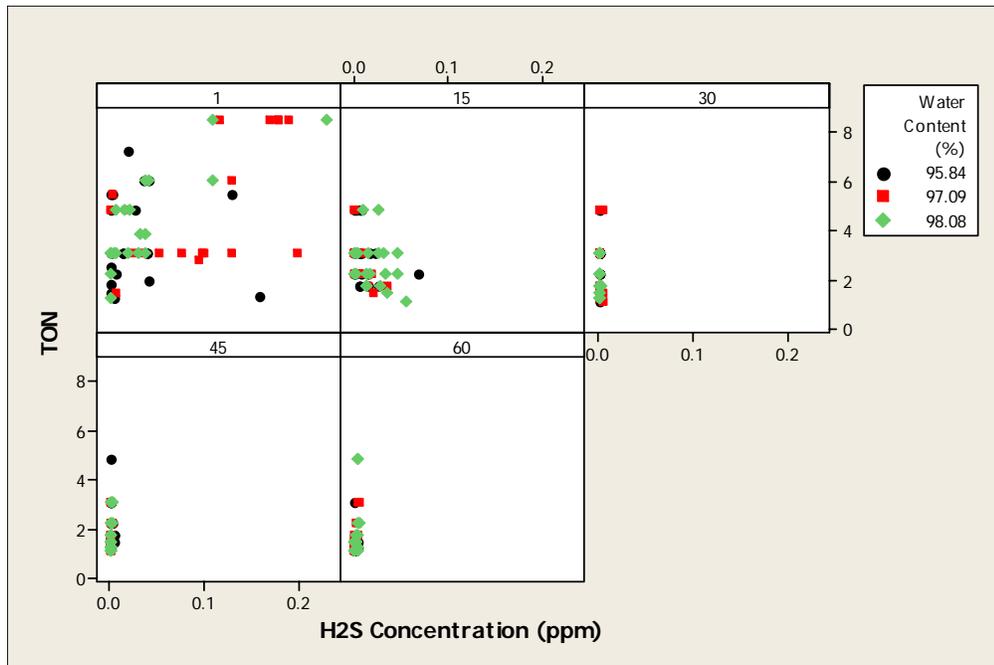


Figure 49: Ton vs H₂S Concentration at different sediment aging times and water contents

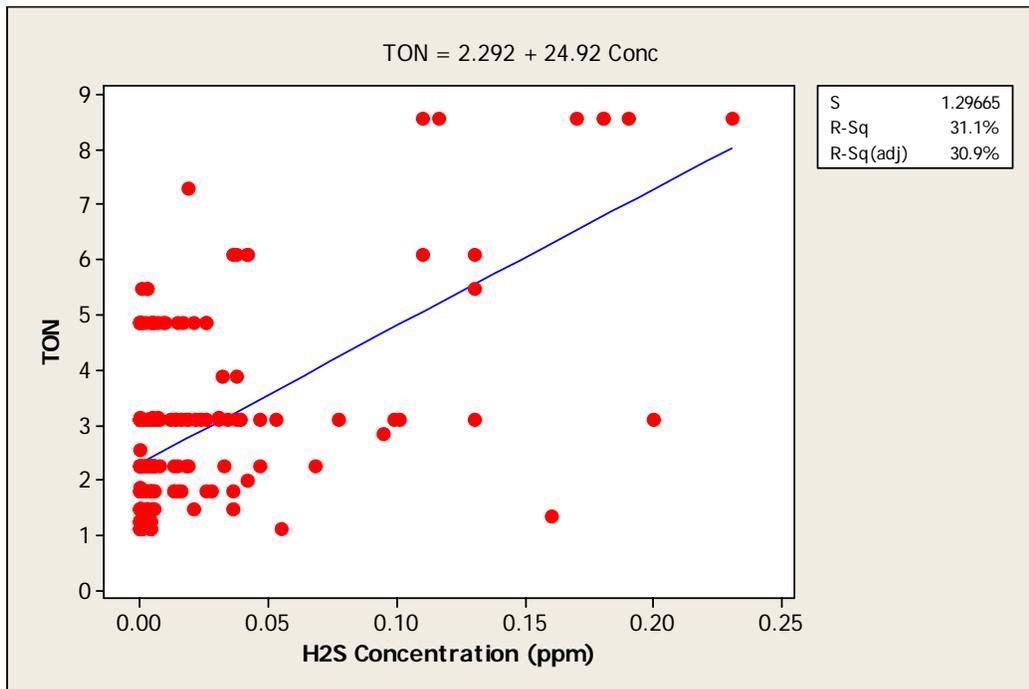


Figure 50: Relation TON vs H₂S Concentration

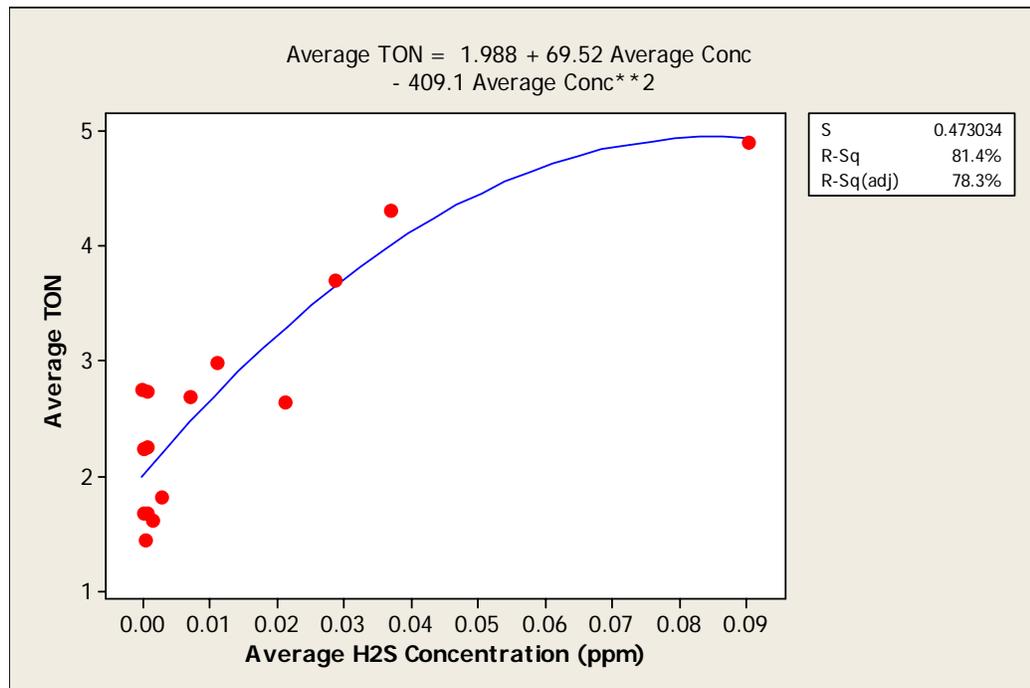


Figure 51: Relation Average TON vs Average H₂S Concentration

4.2.2.2 Analysis of Average

The effective dosage at which 50% of the population detects odor (ED₅₀) is given by the median TON value. Figure 52 and Table 8 show that ED₅₀ values follow similar trends to TON values. ED₅₀ tends to decrease with increasing sediment aging times and water contents. These results further suggest that odor is detected to a higher degree, and may, therefore, be a problem in the vicinity of the McCook Reservoir at early times after sediment deposition. The average dilution rate (Q_{OA}/Q_T) at which 50% of the population detects odor (Dil₅₀) increase with sediment aging times and water contents, reflecting the inverse relationship that exist between TON and dilution rates. This behavior indicates that odor is detected more at higher dilution rates (i.e., more dilution conditions) for early times and at lower dilution rates for later times. A greater flow (amount) of odor-free air it is therefore, necessary to lower odor detection during early times than at later times.

Comparison of Main Effect Plots for ED₅₀, the Dil₅₀, the Average TON and the Average H₂S Concentration (Figure 52) indicate that, sediment aging times affect more the results of Average TON, H₂S Concentration, and ED₅₀, than the water contents. This

figure also indicates that higher water contents may yield lower odor detection, thus lower odor problems.

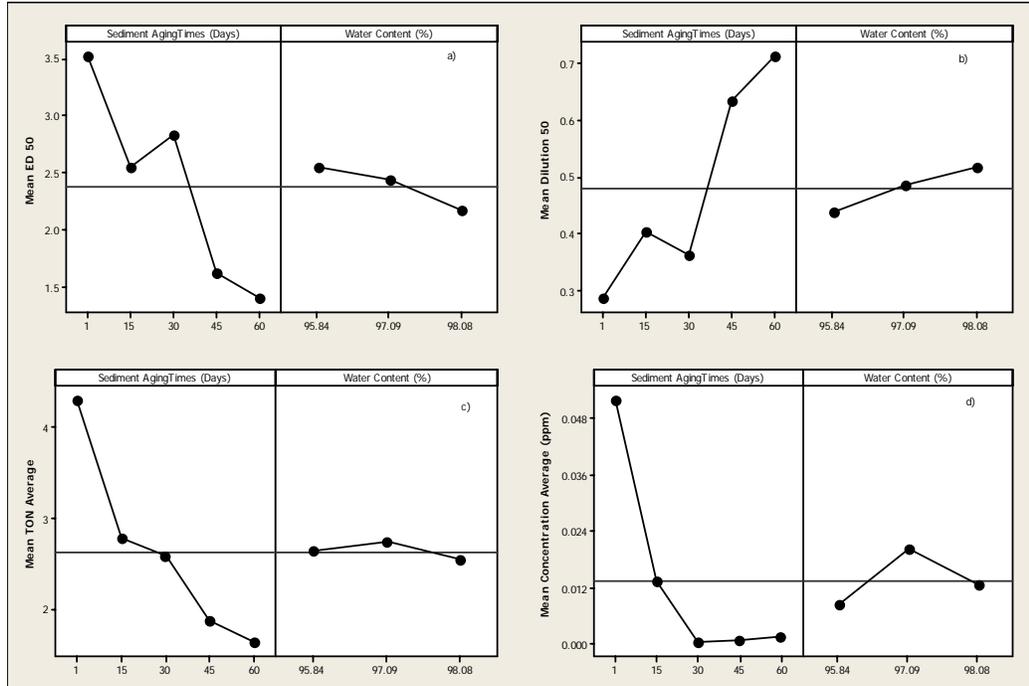


Figure 52: Main Effect Plot for the a) ED₅₀, b) Dil₅₀, c) Average TON and d) Average H₂S Concentration as function of sediment aging times and water contents

Similar to the TON data, linear analysis of the ED₅₀ vs sediment aging times suggest strong relation between these parameters, and indicate that the ED₅₀ decrease with sediment aging times (Figure 53). A linear plot of average TON vs ED₅₀ indicates that as the average TON increase, the ED₅₀ also increase (Figure 54). Poor relation (Figures 55 and 56) is, however, observed between average H₂S concentration at detection and ED₅₀ and Dil₅₀.

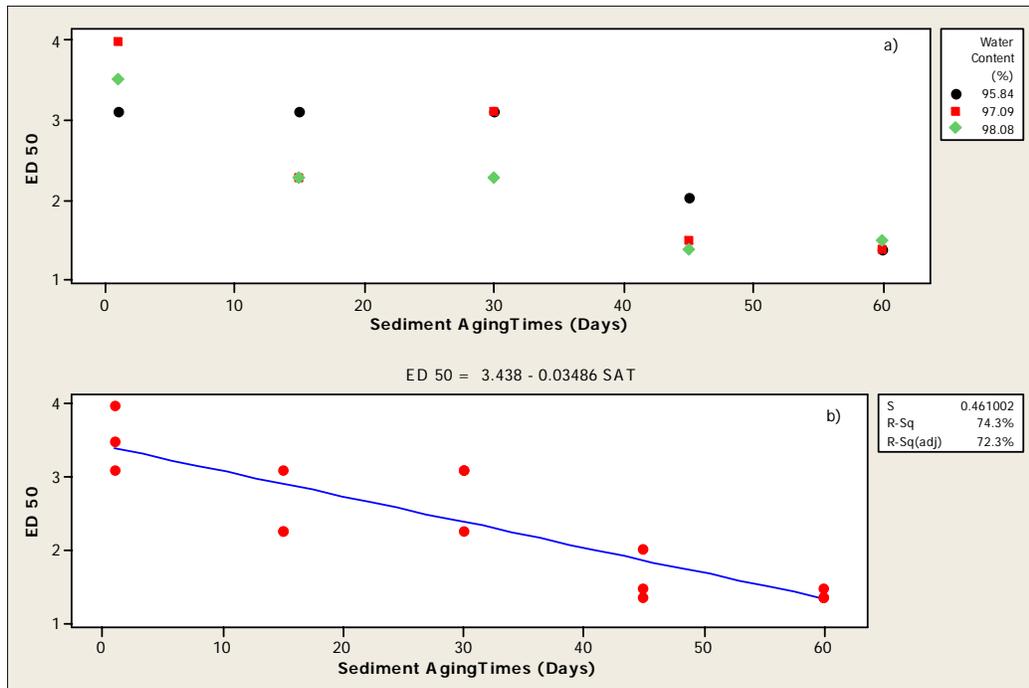


Figure 53: a) Relation ED₅₀ and Sediment Aging Times and b) Regression Analysis for ED₅₀ vs Sediment Aging Times

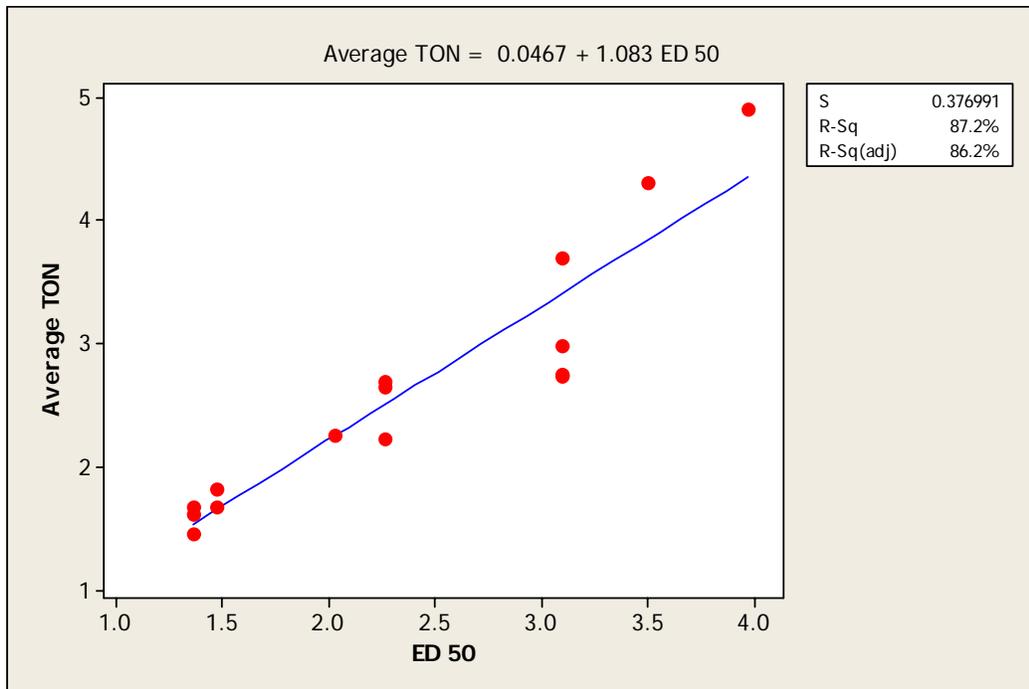


Figure 54: Relation Average TON vs ED₅₀

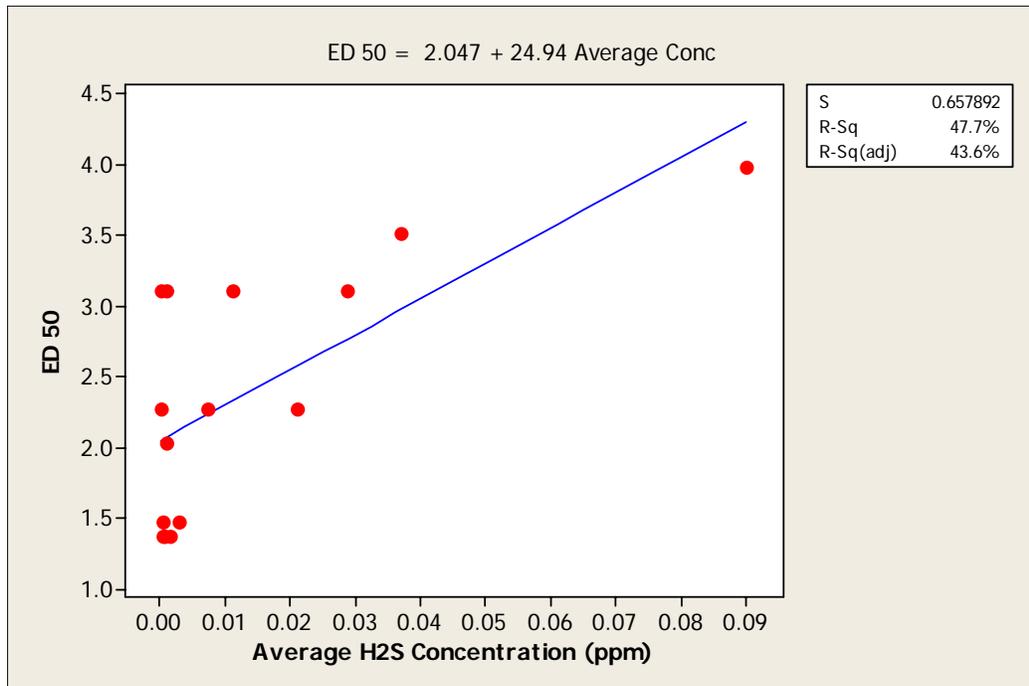


Figure 55: Relation ED₅₀ vs Average H₂S Concentration

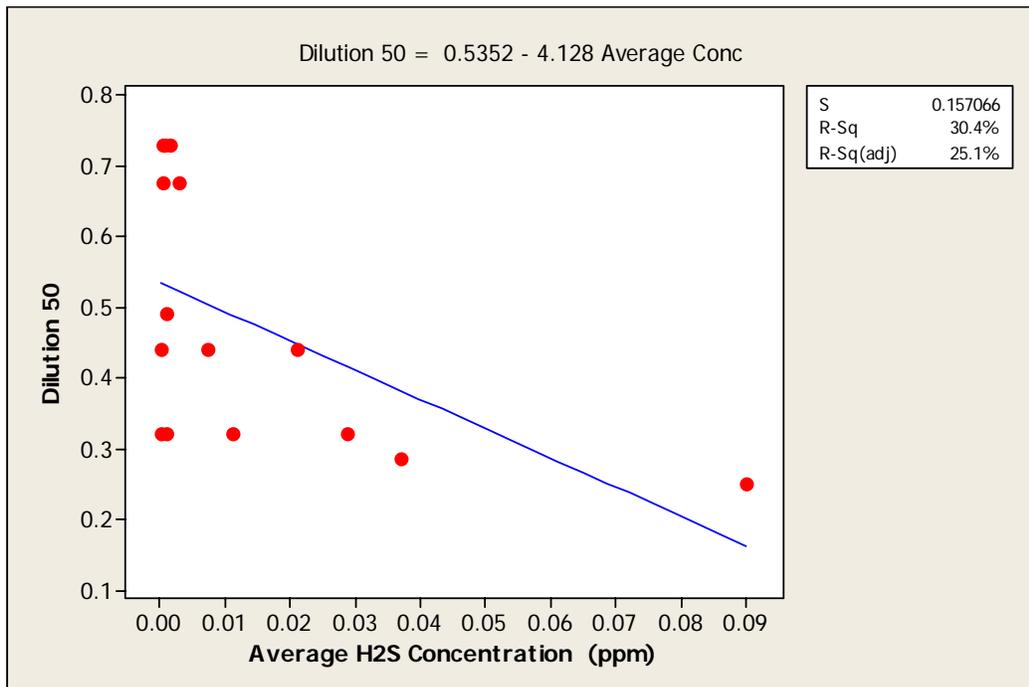


Figure 56: Relation Dilution₅₀ vs Average H₂S Concentration

The sediment aging times is an important and significant factor in the response of ED₅₀, Dil₅₀, Average TON, and Average H₂S Concentration. Also, it suggests that the water contents are not a significant factor in the response of these parameters. The greater percent obtained in the coefficient of determination reflect than principally the response of the parameters was explained for the GLM.

Table 10: Summary of Results of ANOVA for Average TON, ED₅₀, Dil₅₀, and Average Concentration

Parameter	Average TON		Dil ₅₀		ED ₅₀		Average Concentration	
	P-value	F-value	P-value	F-value	P-value	F-value	P-value	F-value
Sediment Aging Times	0.000	22.43	0.000	20.69	0.001	15.13	0.016	5.97
Water Contents	0.746	0.3	0.277	1.51	0.365	1.15	0.516	0.72
R ² (%)	91.86		91.47		88.70		75.99	

4.2.2.3 Relation TON and Sediment Characterization

The potential effect of sediment characteristic on TON was evaluated by performing a linear analysis between different predictors and average TON. Table 6 summarizes the coefficient of determination obtained in the ANOVA analyses. Greater values of R² suggest strong relation between the response (TON) and their predictor (sediment characteristics). A significant strong relation was obtained for average TON, ED₅₀ and Dil₅₀, with respect to the pH, suggesting that increasing pH, decreases average TON and ED₅₀, and increases Dil₅₀ (Figure 57). A modest relation was founded between these parameters and the AP, which suggest decreasing average TON and ED₅₀ with increase in AP. Poor or no relationship was observed between olfactometry parameters (average TON, ED₅₀, Dil₅₀) and DO, TS, TVS and TKN.

Table 11: Summary of Results in Analysis of relation for average TON, ED₅₀ and Dil₅₀ with Sediment Characterization

Parameter	R ² (%)		
	Average TON	ED ₅₀	Dil ₅₀
pH	76.2	54.7	49.9
AP	31.1	23.3	24.5
TKN	7.8	5.7	7.9
TS	2.1	1.8	1.0
TVS	0.0	0.0	0.1
DO	0.1	2.0	4.3

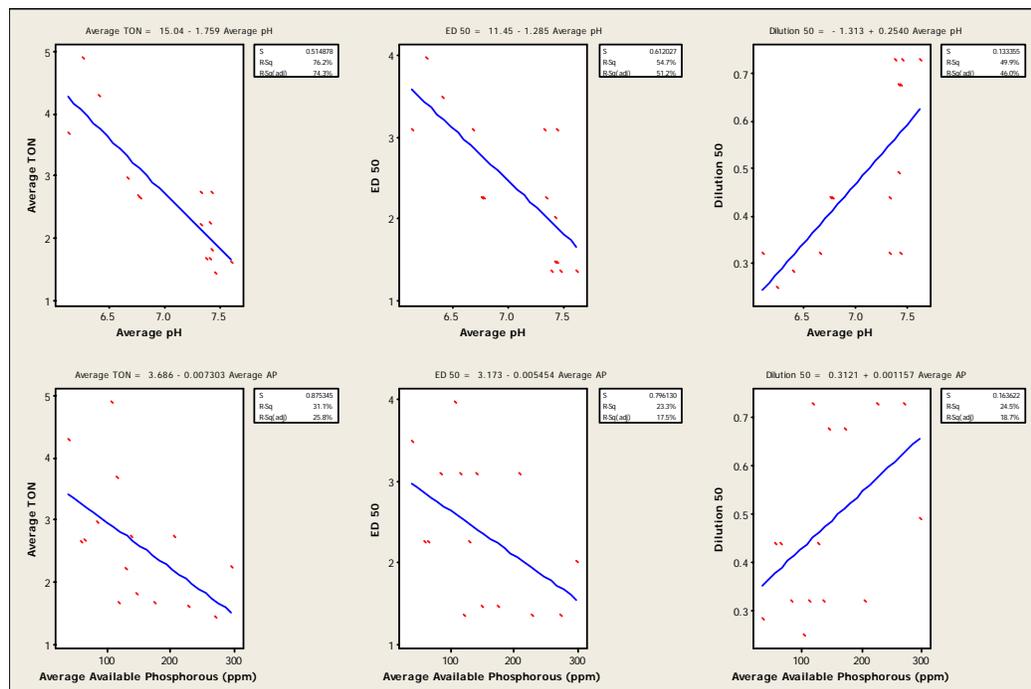


Figure 57: Relation for average TON, ED₅₀ and Dil₅₀ as function of pH and AP

4.2.2.4 Odor Intensity

Odor intensity was determined by categorizing the response of panelists into intensity categories (0: no perceivable - 5: very strong odor) and relating this average values to H₂S concentrations measured at detection. Results show (Figure 58) no relation between these parameters, indicating that H₂S concentration was not the only component influencing the detection of odor perceived by the panelists in this study. Other odorants not measured experimentally also influence the intensity of odor detection.

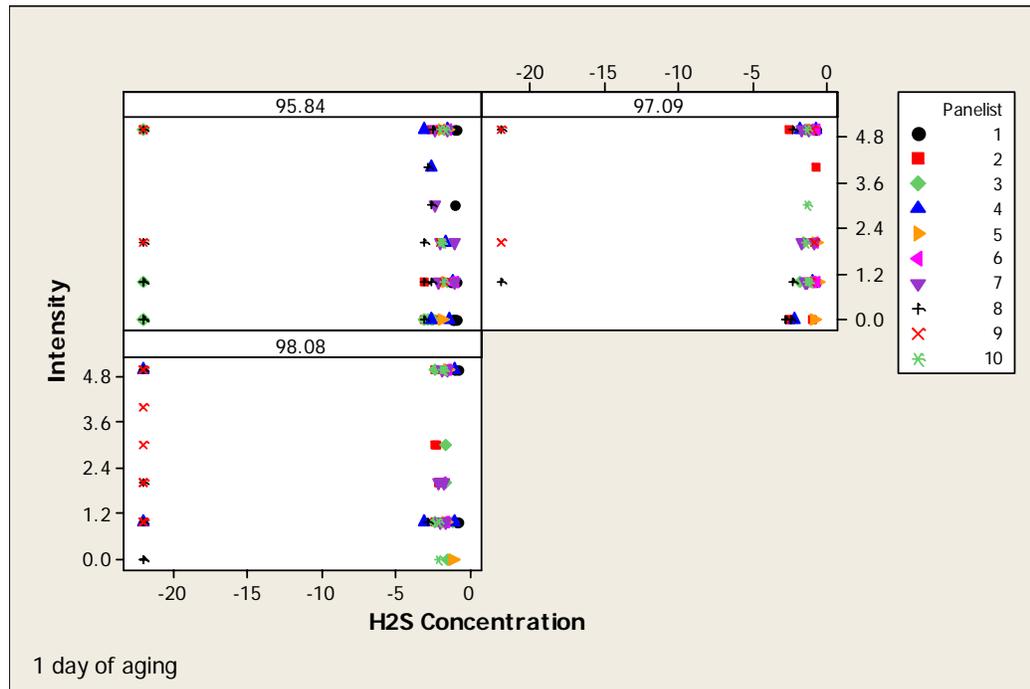


Figure 58: Odor Intensity Test at 1 Day of Aging

4.3 H₂S Flux from Sediments

The flux of H₂S from sediment samples collected at EMWTP was determined by measuring the H₂S concentrations eluted from the experimental chamber as a function of time. Flux measurement were performed on sediments samples of different water contents and aging times, under various experimental conditions, including flow rates, temperatures, ponding water and sediment mixing rates. Experimental results show that the emission of H₂S from the sediments increased rapidly when the experiments were started and then decreased gradually with the time (Figure 59). Although this tendency was observed for all conditions tested, the magnitude of the eluted concentrations and elution times varies with the environmental conditions imposed on the system (Figure 59). Generally, higher eluted concentrations and longer elution times were observed for early aging times. This behavior suggests that the flux of H₂S from sediments is rate-limited and that there is a finite amount of H₂S concentration in the sediments.

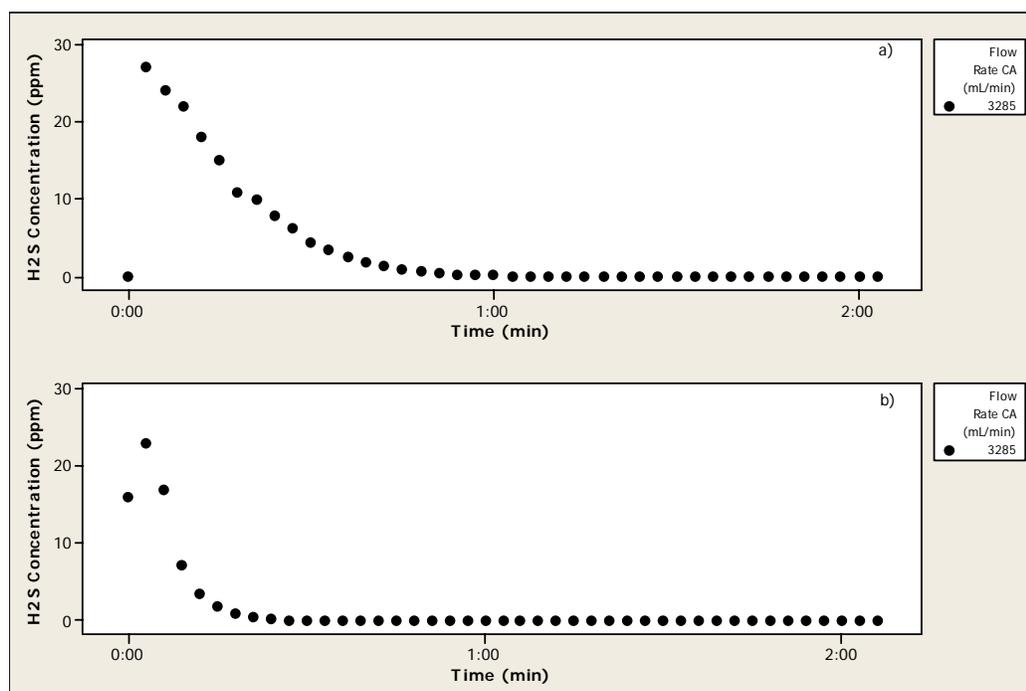


Figure 59: Temporal Behavior of H₂S Concentration in the Flux Test for sediment aged for 1 day with a) 97.87% water content and b) 98.15% water content

Average flux of H₂S from sediments samples collected from EMWTP was estimated using the analysis of moments for temporal concentration distribution. The zero moment provide an estimate of the total mass eluted from the system, where as the first moment yields the average time for the center of mass to be eluted. Average H₂S flux was calculated as the total mass eluted over the total period of elution (i.e., when H₂S concentration reached a constant concentration).

4.3.1 Total H₂S Mass Eluted

Results from the moment analysis indicate that the total mass eluted from the system decreases with sediment aging times (Figure 60), but does not change with water contents or air flow rates (Figure 61). The average time for the H₂S elution also decreases with sediment aging times (Figure 62), but not with water contents or air flow rates. The decrease on eluted mass with the sediment aging times reflects the lower amount of H₂S remaining in the system as a result of volatilization and reaction losses through time.

Smaller average elution times with sediment aging times reflect that it takes less time to elute the mass over an average flux.

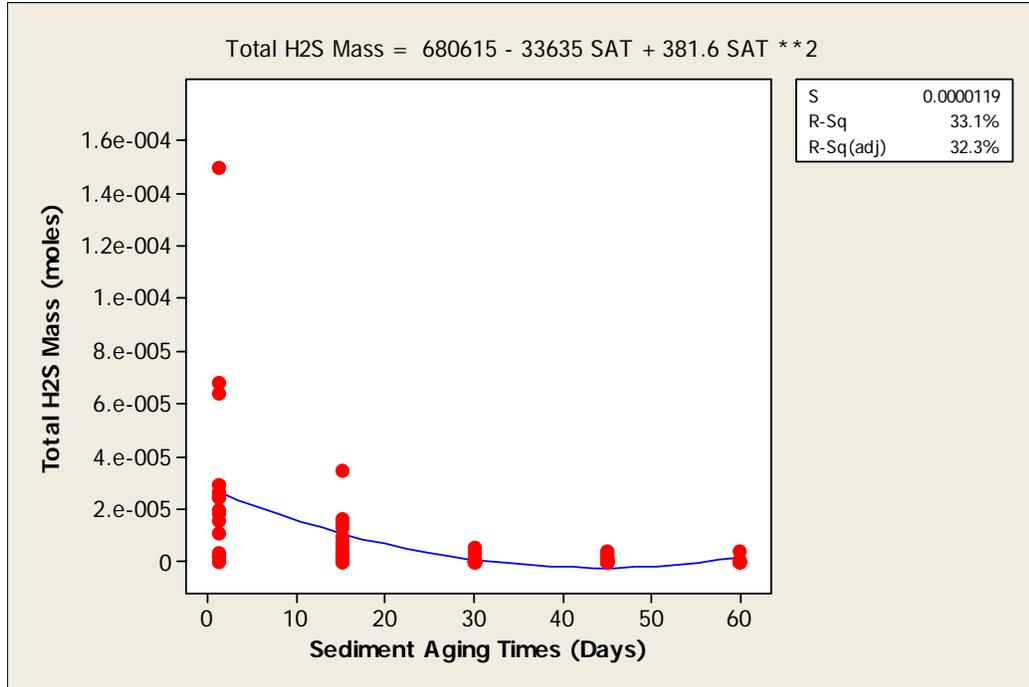


Figure 60: Relation between Total H₂S Mass eluted and Sediment Aging Times

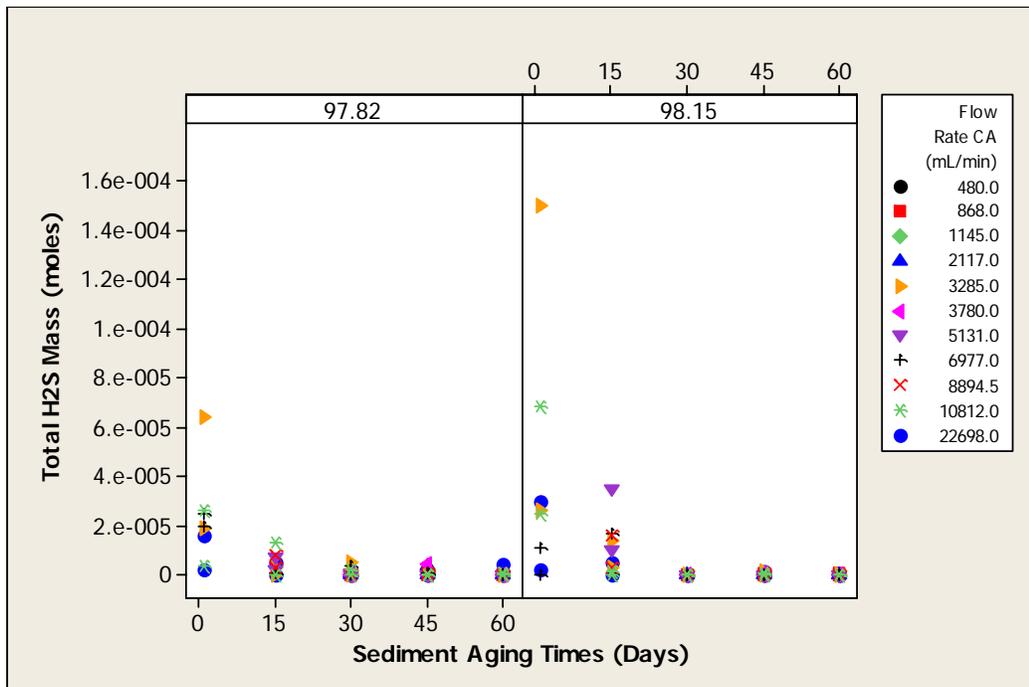


Figure 61: Behavior of Total H₂S Mass as function of Sediment Aging Times

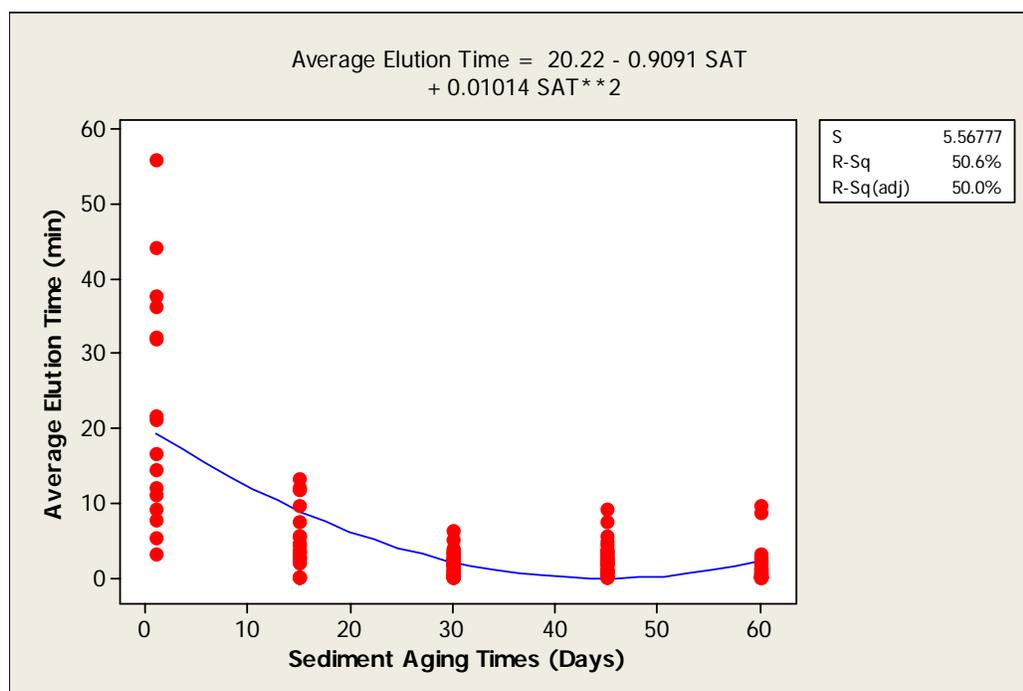


Figure 62: Average Time of H₂S elution for the Center of Mass Eluted as a function of Sediment Aging Times

Statistical analysis performed in the moment-calculated data show that the sediment aging times is the most significant and important factor influencing the total mass eluted from the system and its average time of elution, but can not be used as a predictor parameter. The relatively higher F-values obtained for sediment aging times in the ANOVA test (Table 12) suggest that sediment aging times is more important on influencing the response than water contents and flow rates. The percent of R² obtained reflects that approximately 42% of the variation in total H₂S mass and average time of elution is described by the GLM. Low p-value for sediment aging times (p<0.05) indicates that, it is a significant factor affecting the total H₂S mass and average elution mass behavior. A quadratic regression of the data (Figure 60), however, shows that sediment aging times is a poor predictor of these parameters and suggest that other factor are also affecting their response. High p-value (p>0.05) for water contents and flow rates (Table 12) indicate that these factors are not significant in affecting the behavior of the total H₂S eluted and the average elution time, and , therefore, should not be used as predictors.

Table 12: Summary of Results for ANOVA on Total eluted H₂S Mass and Average Time of Elution

Parameter	Mass of H ₂ S (moles)		Average Time of Elution (min)	
	P-value	F-value	P-value	F-value
Sediment Aging Times (Days)	0.000	21.37	0.000	56.65
Water Contents (%)	0.255	1.31	1.51	2.08
Flow (mL/min)	0.291	1.21	0.118	1.58
R ² (%)	41.56		41.56	

4.3.2 Average H₂S Flux

The average flux of H₂S from sediment samples collected from EMWTP ranged from 0.000 to 9.072* 10⁻¹⁰ moles/cm² min and showed a tendency to decrease with sediment aging times (Figure 63). The coefficient of determination obtained shows that approximately 32.2% of variation in the response of average flux is explained by the sediment aging times, and that others factors not considered in this investigation influence the response of average flux. No obvious tendency is observed for water contents and air flow rates (Figure 64).

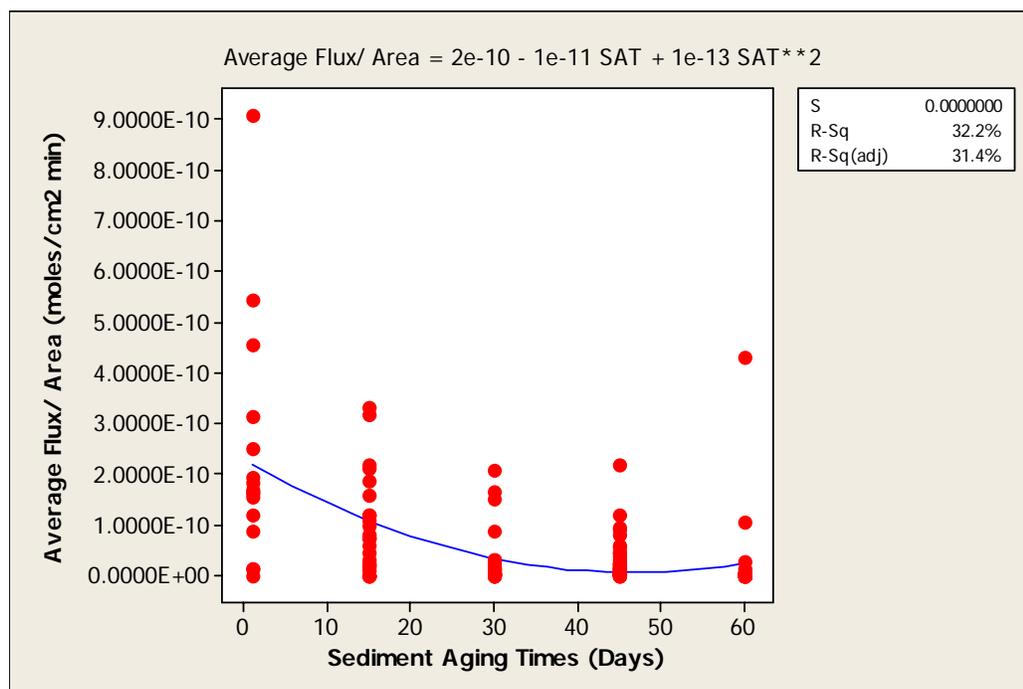


Figure 63: Relation of Average Flux and Sediment Aging Times

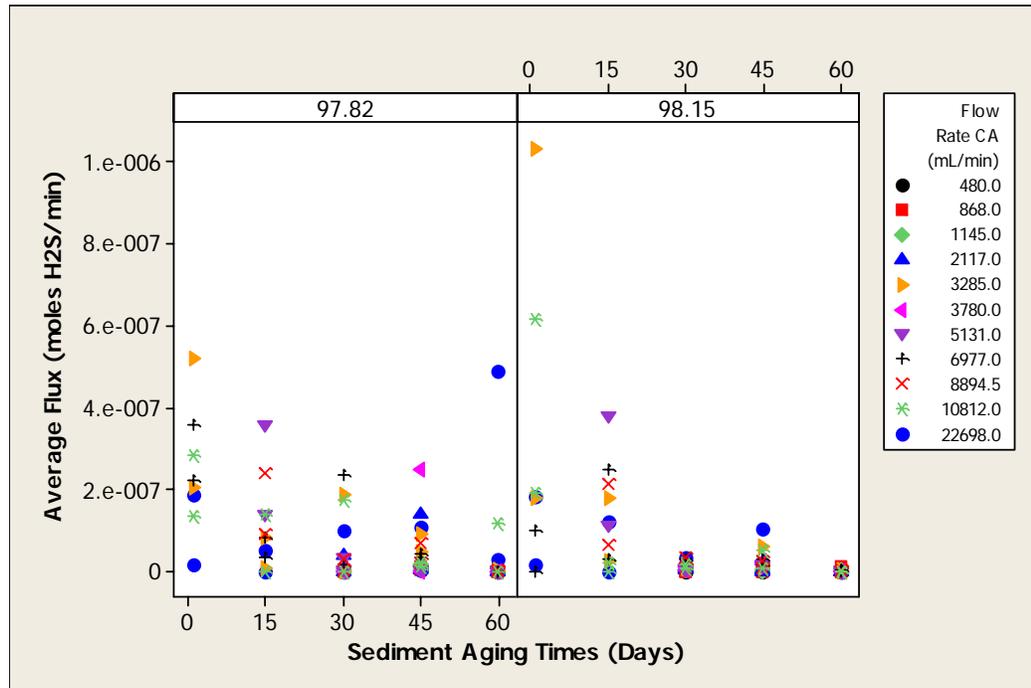


Figure 64: Average Flux as function of Sediment Aging Times at different Water Contents and Flow Rates

The Main Effect Plots (Figure 65) show that, on average, H₂S flux tends to decrease with sediment aging times and water contents, and increase with flow rates. These plots show that, on average, sediment aging times influence average flux more than water contents and flow rates. Results from One-Way ANOVA test (Table 13) indicate that averages are significantly different for different sediment aging times, but not for different water contents. The effect of air flow rates shows some degree of significance. Results also show that average flux varies more with sediment aging times for higher water contents, lower flow rates, and earlier aging times. Further analysis indicate that the averages for average flux are statistically different for aging times up to 15 days, but not for later times. These results suggest that average flux decrease rapidly at earlier times (15 days), but reaches a relatively constant value thereafter.

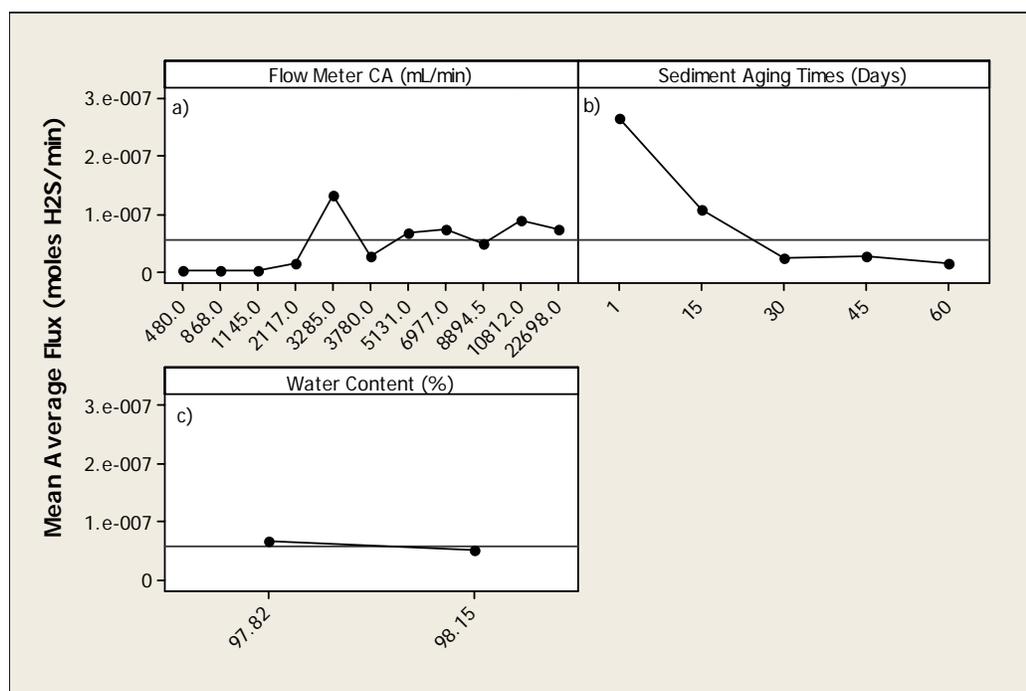


Figure 65: Main Effect Plot for the Average Flux as function of a) flow rate CA, b) sediments aging times and c) water contents

Table 13: Summary of Results for One-Way ANOVA on H₂S flux from sediment in relation to sediment aging times, water contents, and flow rates

Parameter	P-value	F-value	R ² (%)
Sediment Aging Times (Days)	0.000	21.53	33.89
Water Contents (%)	0.461	0.55	0.32
Flow (mL/min)	0.042	1.95	10.76

4.3.3 Relation of H₂S Flux and Sediment Characteristics

Evaluations of average H₂S flux versus sediment characteristics suggest that average pH (Figure 66), average TS (Figure 67.a) and average TVS (Figure 67.b) affect the flux from the system. No relation was found between the average flux and average TKN, average AP, and average DO (Figure 68). Higher H₂S flux rates at lower pH values may reflect higher losses through volatilization. Higher flux rates for TS and TVS may reflect greater amounts of H₂S present in the sediments for higher amount of solids.

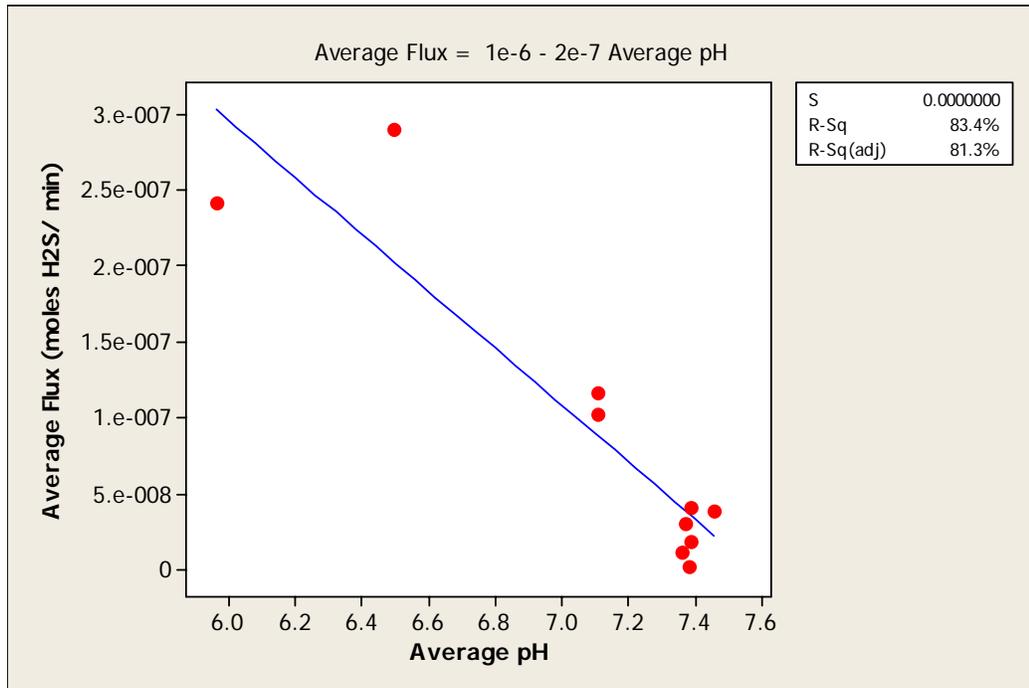


Figure 66: Relation between Average Flux and Average pH

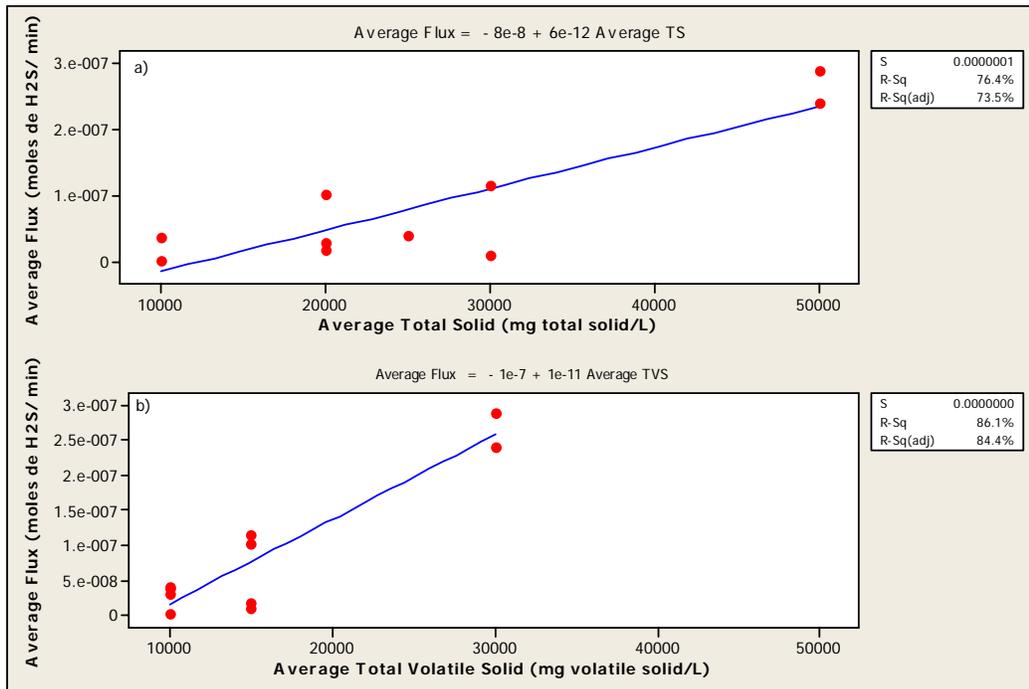


Figure 67: Relation between Average Flux and a) Average Total Solid and b) Average Total Volatile Solids

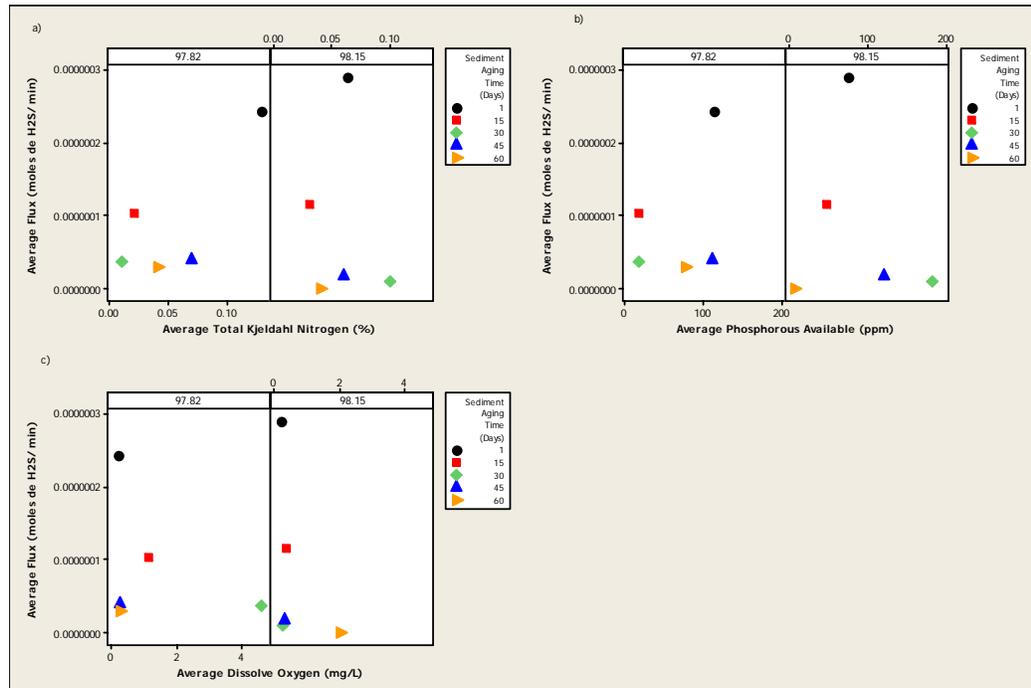


Figure 68: Behavior of Average Flux as function of a) TKN, b) AP, and c) DO

4.3.4 Relation of Average TON and Average H₂S Flux

The analysis on relation between average flux and average TON suggest a poor relationship between TON and H₂S flux (Figure 69). A considerably poor quadratic relationship was obtained for average TON and average H₂S flux. The emission of other odor-causing vapors from the sediments and the limited mass transfer between the sediments may affect the behavior obtained between average TON and average H₂S flux.

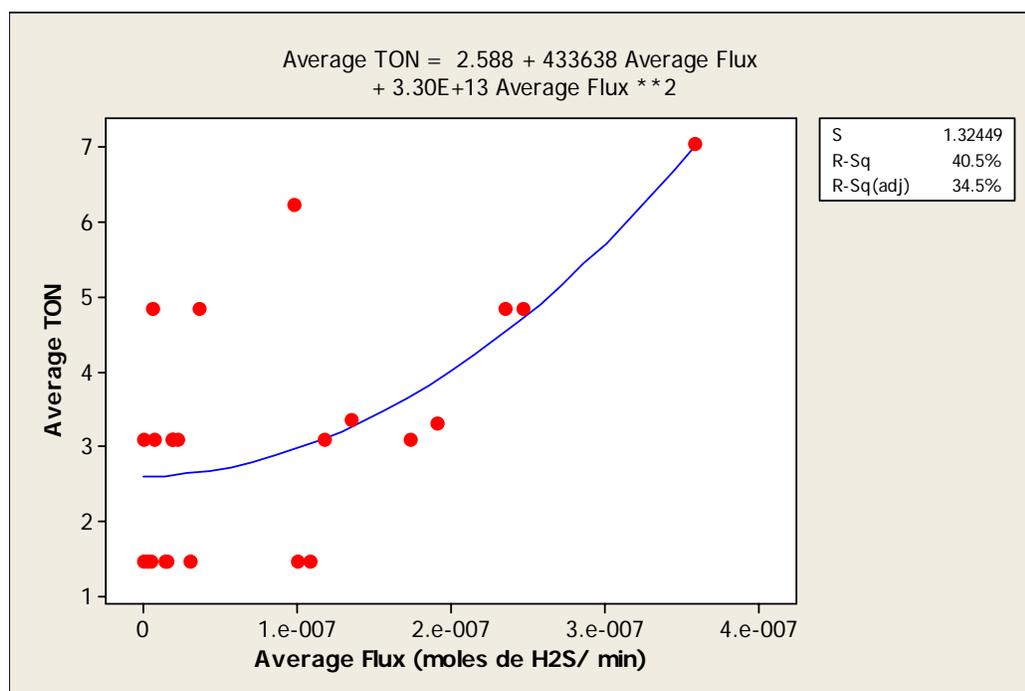


Figure 69: Average TON vs Average Flux

4.3.5 Average H₂S Flux Test with a Water Layer

Results from average H₂S flux test conducted with a layer of water over the sediments samples suggests lower average H₂S flux in the presence of a water layer (Table 14). Comparison of Main Effect Plots for the average flux of H₂S from sediments with a layer of water over the sediments (Figure 70) and those without a layer (Figure 65) shows that the magnitude of H₂S flux is much lower for sediments containing a water layer. On average the flux of H₂S from the sediments with an overlaying of water follow similar tendencies with respect to sediment aging times and water contents; it decreases with increasing sediment aging times and water contents. An air flow rate does not appear to affect the average flux under these conditions. The One-Way ANOVA (see Section G.8- Appendix G) performed for the average flux as function of sediment aging times in samples with a water layer indicates that one or more averages of the average flux is significantly different. On average the sediment aging times affects more the average flux response obtained for than water contents and flows. Further analysis indicates that the averages are statically different for earlier times. No statistical

difference exists between the average average flux with respect to water contents and air flow rates.

Table 14: Statistical Results of average H₂S flux with and without H₂O Layer

Variable	Mean	StDev	Min	Median	Max	Range
Sediment Sample without H ₂ O layer	1.92E-08	3.50E-08	0.000	4.47E-09	1.38E-7	1.38E-7
Sediment Sample with H ₂ O layer	9.99E-10	4.64E-09	0.000	0.000	2.18E-08	2.18E-08

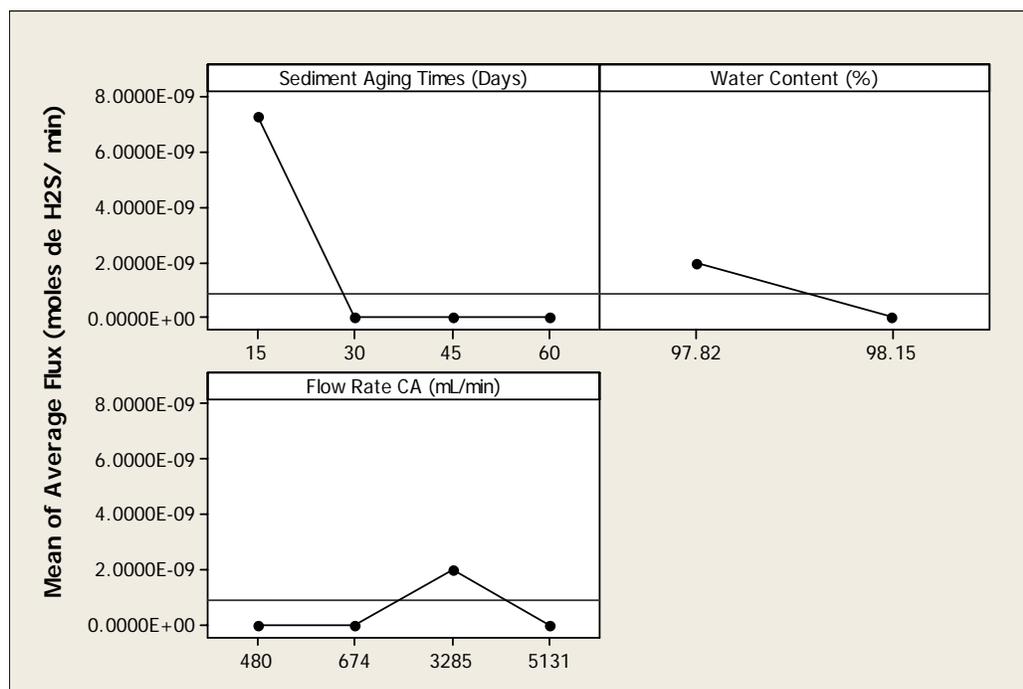


Figure 70: Main Effect Plot for Average Flux in Samples with a Water Layer as function of a) sediment aging times, b) water contents, and c) flow rates

Comparison of the average H₂S flux obtained in the presence and absence of a water layer over the sediment surface (Figures 71 and 72) show lower average flux for the sediments with a water layer. The difference between averages is, however, not statistically significant.

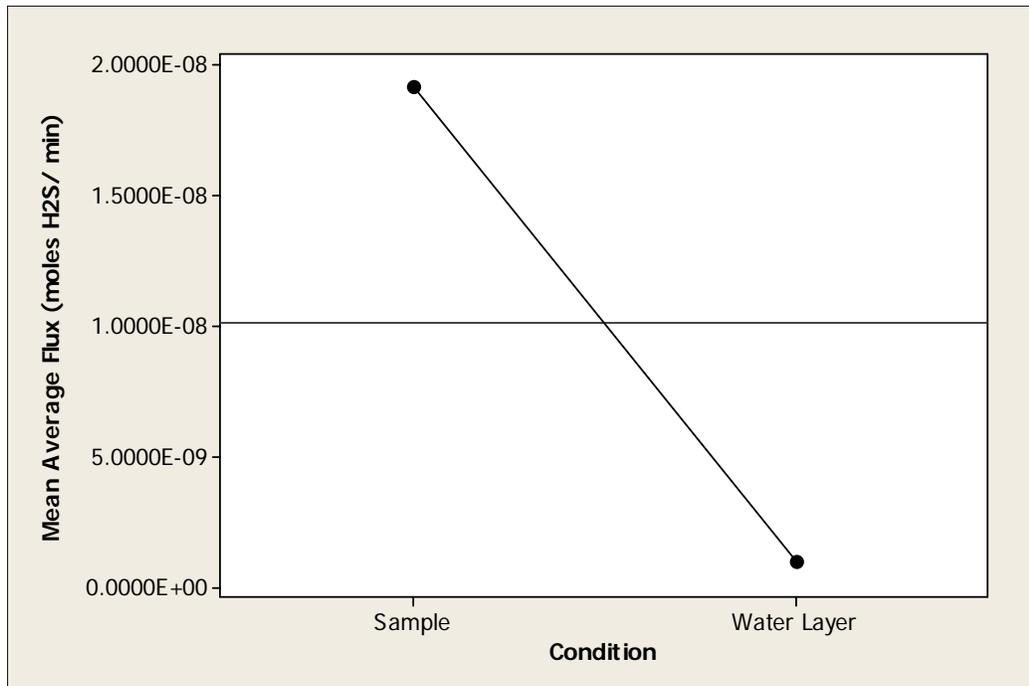


Figure 71: Comparison of Average Flux in Flux Test and Flux Test with a Water Layer

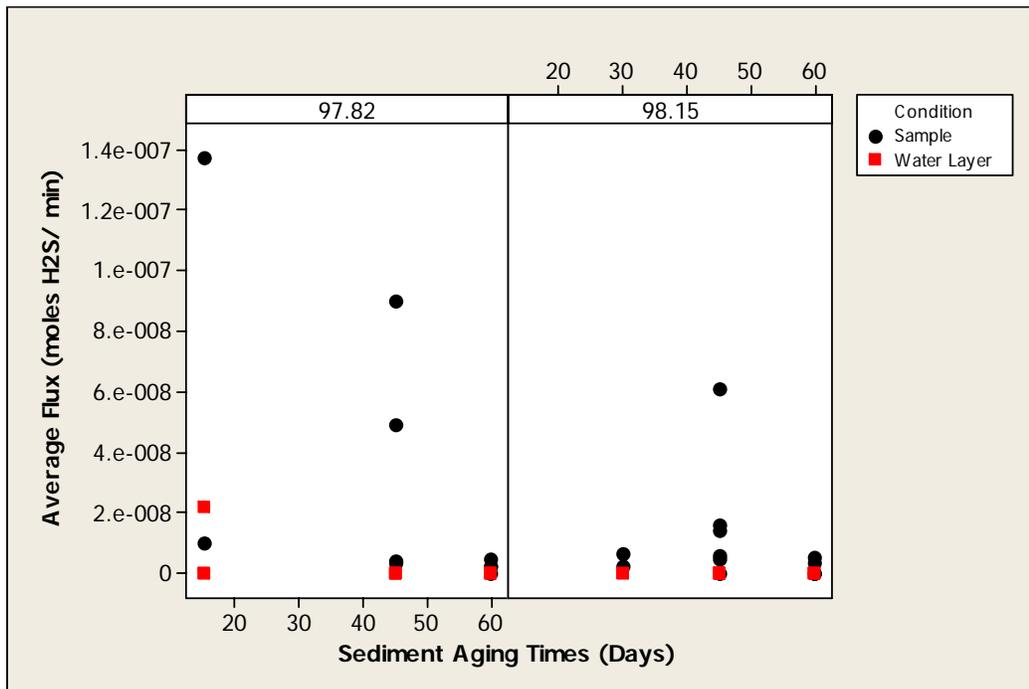


Figure 72: Behavior of Average Flux in Flux Test and Flux Test with a Water Layer

4.3.6 Additional Average H₂S Flux Test

Flux measurements after shaking a 67-days aged sediments samples covered with a water layer, show no significant difference in average H₂S flux between the shaken and not shaken samples (Table E.1-Appendix E). In fact, only two of the tests yielded average H₂S flux values higher than zero. Flux measurements for samples aged 85 days also show very low (near zero) average H₂S flux values. Shaking the sample during the flux test, increasing the sample temperature, and allowing time for mass transfer into the air above the sediments (Table E.1-Appendix E), result in no change on average H₂S flux rates at this aging time.

Chapter 5. Summary and Conclusions

Odor pollution has become a growing environmental issue that may affect quality of life and create health problems. A series of odor measurement and flux determination studies were completed in this investigation to determine if possible odor problems may occur after emptying the McCook Reservoir. Odor threshold of exposed sediments was quantified statistically through TON measurements at different sediment aging times and water contents. Flux of odor-causing vapor from the sediments samples was quantified using a flux-chamber. Measured TON and flux values were compared with each other and related to water contents, sediments aging times, sediment characteristics, and other environmental conditions. The analysis performed yield the following observations and conclusions:

- Concentration of odor-causing vapors in olfactometry test generally increases with decreasing dilution (increasing amount of odorous air) up to a point, after which it remained fairly constant.
- Results from olfactometry tests may be influenced by temporal effects on concentrations of odor-causing vapors. Measurements of H₂S concentration through time during olfactometry tests indicated that these values increase rapidly after dilution changes, but decrease gradually thereafter. Relative constant concentrations are achieved after five minutes, suggesting that odor threshold measurement should be fine after this period of time.
- Characteristics of sediments obtained from EMWTP in Mayagüez, Puerto Rico are within reported values of other primary effluent characteristics, and consequently, are representative of the sediment conditions that may be found at the McCook Reservoir. Measurement of sediment characteristics reflects that: pH and TKN tends to increase with sediment aging times, but are not affected by water contents. Available phosphorous increased with sediment aging times and decreased with water contents; and dissolved oxygen, total solid, and total volatile solid do not vary with sediment aging times nor water contents.

- TON, H₂S concentration at detection, and ED₅₀, values decreased with sediment aging times, suggesting higher potential for odor problems at early times after sediments deposition.
- Water content is not a significant factor affecting TON, ED₅₀, and H₂S concentration at detection for the conditions studied. Slightly lower ED₅₀ values obtained at higher average water contents, however, suggest that water contents may affect odor detection.
- Except for sediment pH and available phosphorous, average TON and ED₅₀ are higher not influenced by sediment characteristics. Average TON values measured at lower pH suggest that odor problem may exist for conditions of low sediment pH. Low sediment pH has also been related to higher average H₂S flux, indicating that the higher flux of odorous-vapors at low pH may result in higher odor detection. A general decrease on average TON values with increasing AP may reflect the effect of aging times on sediment composition and may not necessarily suggest a direct relation between odor detection and phosphorous content.
- Poor relationship between TON and H₂S concentrations emitted from the sample at detection suggest that other factors also influence odor detection. Although both TON and H₂S concentration at detection decrease with time and reach relatively constant values after 30 days, no specific relationship was observed between these parameters.
- Detection of odor from sediments yielding a zero (0.000 ppm) H₂S concentration indicates that other odor-causing vapors are producing odor. Consequently, H₂S concentration may not by itself be a good predictor of potential odor problems.
- Experimental results from flux test show that H₂S emission from the sediments is initially high at the onset of the experiments, but that it decreases gradually with elution times. These results suggest that H₂S flux from sediments is rate-limited. Average H₂S flux from sediment surfaces ranged between 0.000 to 9.072* 10⁻¹⁰ moles/cm² min and shows a tendency to decrease with sediment aging times. These results indicate that there is a high amount of H₂S in the samples at early times and that this amount decreases with time. Lower amount of these vapors as

time progress, therefore, result is lower flux and, subsequently, lower potential for odor.

- Average H₂S flux from sediments does not appear to be significantly affected by water contents and air flow rates for the conditions studied.
- Higher average H₂S flux is related to low pH and high TS and TVS conditions. Higher H₂S flux rates at lower pH may reflect higher losses through volatilization. Higher flux rates for higher TS and TVS may reflect greater amount of H₂S-bearing matter present in the sediments with higher amount of solids.
- The presence of the water layers over the sediments samples tends to decrease H₂S flux from sediments and it a possible alternative to reduce potential odor problems in the McCook vicinity.
- Average H₂S flux from aged sediments (> 30 days) is low and is not influenced by the sediment mixing and temperature.
- Some relationship was obtained between average TON and average H₂S flux, suggesting that a greater amount of H₂S emissions results in greater odor detection. The lack of a strong relationship, however, indicates that other odor-causing vapors emitting from the sediments also affect odor detection.

Chapter 6. Recommendations

After completing the scope of this research, some recommendations or suggestions can be made based in the experimental experience and the results from this study. This section will provide some additional information that could help in a better development and analysis in assessment of potential odor problems.

- Minimize variability among panels with respect to gender, level of education, age, and health condition.
- Increase the number of samples and reduce the number of variables.
- In addition to sediment samples use standard concentrations in olfactometry tests.
- Utilize other equipments in addition with the Jerome-631X for monitoring others odor-causing compounds.
- Increase the range of water contents and water layer in sediment samples.
- Minimize flow variations.
- Evaluate effect of an ample range on sediments samples temperatures and with condition of continues mixing in the samples of flux chamber.
- Utilize dispersion modeling.
- Based on the results from this study, odor problems may be reduced by leaving a water layer on the sediments and/or controlling the sediment pH.

Chapter 7. Bibliography

- Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Frequently Asked Questions for Hydrogen Sulfide, CAS# 7783-06-4, ATSDR Division of Toxicology, September 2004. <http://www.atsdr.cdc.gov/tfacts114.html>
- Allaire, S.E., S.R. Yates, F.F. Ernst, and J. Gan, "A Dynamic Two- Dimensional System for Measuring Volatile Organic Compound Volatilization and Movement in Soils", *Journal of Environmental Quality*, 31:1079-1087, 2002.
- Arizona Instrument LLC. "Jerome 631-X Hydrogen Sulfide Analyzer Operational Manual". Document #6J21-0002, Rev B. 2003. <http://www.azic.com>
- Arizona Instrument LLC. "Operational Manual of H₂S Functional Test Module", AZI P/N SS-112, Rev B, May, 2000, <http://www.azic.com>
- Arizona Instrument LLC. "User's Manual of the Jerome Communications Interface Software", Part Number SS-103, Rev. E, Doc.# 6J21-0004, July, 1996, 11-15, 23-27. <http://www.azic.com>
- Bauwens, W., P. Vanrolleghem, and M. Smeets, "An Evaluation of the Efficiency of the Combined Sewer-Wastewater Treatment System under Transient Conditions", *Water Science and Technology*, 33(2): 199-208, 1996.
- Blayne, H., "How to Collect Reliable Soil-Gas Data for Upward Risk Assessments Part 2: Surface Flux-Chamber Method", *LUSTLine Bulletin* 44, August 2003.
- Clescer, Lenore S, Arnold E. Greenberg, and Andrew D. Eaton, "Standard Method for the Examination of Water and Waste Water", 20th Edition, American Public Health Association, 2-54-2-60, 4-103-4-105, 4-123-4-127, 4-139-4-151, 1998.
- Cunningham, W. and Barbara Woodworth, "The Sulfur Cycle", *Environmental Science*, Sixth Edition, McGraw-Hill Companies, Inc. 67-75 2001.
- Cornwell, D. and L. Davis, Mackenzie. "Environmental System Overflow". *Environmental Engineering*, Third Edition, McGraw-Hill Companies, Inc., 12-13, 353. 1998.
- Einarsen, A. M, A. Aesoy, A-I.Rasmussen, S. Bungum and M. Sveberg, "Biological Prevention and Removal of Hydrogen Sulfide in Sludge at Lillehammer Wastewater Treatment Plant", *Water Science and Technology*, 41(6): 175-187, 2000.

- Encyclopedia Encarta, "Environment", Microsoft Corporation, Online Encyclopedia 2005, <http://encarta.msn.com>
- Engler, John and Russell J. Harding, "Combined Sewer Overflow (CSO) & Sanitary Sewer Overflow (SSO)", Annual Report, Michigan Department of Environmental Quality, 2001, <http://www.deq.state.mi.us/documents/deq-swq-csossoreport01.pdf>
- Environmental Protection Agency (EPA), "Odour Methodology Guideline", Department of Environmental Protection, March 2002.
- Environmental Protection Agency (EPA), "Combined Sewer Overflow Technology Fact Sheet Maximization of In-line Storage", U.S. Environmental Protection Agency Office of Water, Report EPA-832-F-99-036, 1999.
- Environmental Protection Agency (EPA), Odour Control Technologies, Environmental Emissions & Odour Laboratory, Centre for Water & Waste Technology, Report EPA-625-r-94-002, 1994. <http://www.odour.unsw.edu.au/odour-control.html>
- Environmental Protection Agency (EPA), Design Manual - "Odor and Corrosion Control in Sanitary Sewerage Systems and Treatment Plants", U.S. Environmental Protection Agency Office of Research and Development, Report EPA-625-1-85-018, 1985.
- Environodour Australia Pty Ltd, Frequently Asked Questions, 2005, <http://www.environodour.com.au>
- Extech Instrument Corporation, "User's Manual", Ver. 2.1, May, 2003
- Gomez, Maria, "Total Kjeldahl Nitrogen in Water and Biosolids by Automated Colorimetry with Preliminary Distillation/Digestion", U.S. Environmental Protection Agency Office of Water, Report EPA-821-R-01-004, 2001.
- Gostelow, P., P. Longhurst, S.A. Parsons, and R.M. Stuetz, "Sampling for the Measurement of Odours", Scientific and Technical Report No.17. 2003.
- Gostelow, P., and S.A. Parsons, "Sewage Treatment Works Odour Measurements", Water Science and Technology, 41(6): 33-40, 2000.
- Guilbault, Michael R., "Odor Control at Wastewater Treatment Plants", Biocube, LLC , 2000 – 2005, <http://www.biocube.com/odorcontrol.htm>.
- Jones, J., "Soil Analysis". Laboratory Guide for Conducting Soil Tests and Plant Analysis, CRC Press LLC, 2001. 68-79.
- Jury, William, Gardner, Wilford and Gardner, Walter. Soil Physics. Fifth Edition. John Wiley & Sons, Inc. 205. 1991.

- Heber, Albert J., Teng Teeh Lim, Jiqin Ni, and Alan L. Sutton, "Odor and Gas Emission from Anaerobic Treatment of Swine Manure", Final Report to the Indiana, 2000.
- Kiely, G., "Anaerobic Digestion and Sludge Treatment", Environmental Engineering, McGraw-Hill, Inc. 575-581. 1997.
- Kaiyun, Jiang and Ralph Kaye, " Comparison Study on Portabke Wind Tunnel System and Isolation Chamber for Determination of VOC's from Areal Sources, Water Science and Technology, 34 (3-4), 583-589,1996.
- Kienbush, M.R., "Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber": User's Guide, EPA User's Guide, # PB 86-223161, December, 1985.
- Koe, L.C.C. and F.Yang, "A bioscrubber for hydrogen sulphide removal", Water Science and Technology, 41(6): 141-145, 2000.
- Lambert, S.D., A.L. Beaman, and P. Winter, "Olfactometric characterization of sludge odours", Water Science and Technology, 41(6): 49-55, 2000.
- Leyris, C., F. Maupetit, J.-M. Guillot, L. Pourtier, J.-L. Fanlo, "Laboratory study of odour emissions from areal sources: evaluation of sampling system", ANALUSIS, 28(3), 199-206, 2000.
- Martins, Stan, "Soil Surface Flux Monitoring of Gaseous Emission", Lawrence Livermore National Laboratory (LLNL), Environmental Restoration Division, ERD SOP 1.11, 1999, <http://www-erd.llnl.gov/library/JC-137682>.
- McGinley, Charles M., Thomas D. Mahin, Richard J. Pope, "Elements of Successful Odor/Odour Laws", WEF Odor/VOC 2000 Specialty Conference, St. Croix Sensory Inc. McGinley Associates, 2000.
- McGinley, Michael A., and Charles M. McGinley, "The New European Olfactometry Standard: Implementation, Experience, and Perspectives", Annual Conference, St. Croix Sensory Inc. McGinley Associates, 2001.
- McGinley, Michael A., and Charles M. McGinley, "Odor Intensity Scales for Enforcement, Monitoring, and Testing", Air and Waste Management Association, 2000 Annual Conference, St. Croix Sensory Inc. McGinley Associates, 2000.
- McIlvanine, "New Treatment Schemes Control Odors", Water Engineering & Management; ABI/INFORM Global, 137(1): 28, Jan 1990.

- Metropolitan Water Reclamation District of Greater Chicago (MWRDGC) and US Army Corps of Engineers, Chicago Under Flow Plan McCook Reservoir, 2003.
- Metropolitan Water Reclamation District of Greater Chicago (MWRDGC). Tunnel and Reservoir Plan Article, 1999. <http://www.mwrldgc.dst.il.us/water/flood.htm>.
- Nathanson, J. “Sludge Characteristic”, Basic Environmental Technology. Third Edition. Prentice Hall. 2000.
- Omega Engineering, INC., OM-PL Series Datalogger Interface Software, User’s Guide, Version 2.0, July, 2003, 5-9.
- Padilla I, I. Santiago, and M. Castañeda, “Assessment of Potential Odor Problems on McCook Reservoir Limestone Wall”, Final Report submitted to U.S. Corps of Engineering Research and Development Center, Vicksburg, MS, 2002.
- Parsons, S.A., N.Smith, P.Gostelow, and J.Wishart, “Hydrogen Sulphide Dispersion Modeling-Urban and Rural Case Studies”, *Water Science and Technology*, 41(6): 117-126, 2000.
- Pisano, William C., James Barsanti, James Joyce and Harvey Sorensen, Jr., “Sewer and Tank Sediment Flushing: Case Studies”, Environmental Protection Agency, Report EPA/600/R-98/157, 1998.
- Raven, P. and Linda Berg, “The Sulfur Cycle”, Environment, John Wiley & Sons, Inc., 28, 105-112.2004.
- Rolston, D.E., “Gas Diffusivity”, Methods of Soil Analysis Part 1-Physical and Mineralogical Methods, SSSA Book Series: 5. Second Edition. Madison, Wisconsin US., 46: 1089-1102, 47: 1103-1118. 2002.
- Rolston, D.E., “Gas Flux”. Methods of Soil Analysis Part 1-Physical and Mineralogical Methods, SSSA Book Series: 5. Second Edition. Madison, Wisconsin US. 47: 1103-1118. 2002.
- Reichman, Rivka and Dennis E. Rolston, Technical Reports “Atmospheric Pollutants and Trace Gases, Design and Performance of a Dynamic Gas Flux Chamber”, *Journal of Environmental Quality*, 31:1774–1781. 2002.
- Reinhart, Debra R. and Timothy Townsend, “Control of Odors from Construction and Demolition Debris Landfills”, Project Summary of State University System Florida, Florida Center for Solid and Hazardous Waste Management, August 31, 2003.

- Sadek, E. Shafik, Terry C. Lee, J. Donald Smith, and Rolf Gebel, "Flux Chamber Measurements of Mass Transfer Rates", *Journal of Environmental Engineering*, 111-121, February 1998.
- Sawyer, Clair N., Perry L. McCarty and Gene F. Parkin, "Phosphorous and Phosphate" Chemistry for Environmental Engineering. Fourth Edition. McGraw-Hill, Inc. 597. 1994.
- Schmidt, C.E, Theory and Application of the U.S. EPA Recommended Surface Emission Isolation Flux Chamber for Measuring Emission Rates of Volatile and Semivolatile Species, *Sampling and Analysis of Airborne Pollutants*, Lewis Publishers, 39-55, 1993.
- Seidl, M., P.Servais, M.Martaud, C.Gandouin, and J.M. Mouchel, "Organic Carbon Biodegradability and Heterotrophic Bacteria along a Combined Sewer Catchment During Rain Events", *Water Science and Technology*, 37(1): 25-33, 1998.
- Stuetz, R.M., R.A. Fenner, and G. Engin, "Assessment of Odours from Sewage Treatment Works by an Electronic Nose, H₂S Analysis and Olfactometry", *Water Research*, 33(2): 453-461, 1999.
- Stuetz, R.M. and J. Nicolas, "Sensor arrays: an inspired idea or an objective measurement of environmental odours?", *Water Science and Technology*, 44 (9), 53-58, 2001.
- Sucker, K., R. Both and G. Winneke, "Adverse effects of environmental odours: reviewing studies on annoyance responses and symptom reporting", *Water Science and Technology*, 44 (9), 43-51, 2001.
- St. Croix Sensory, Inc., "A Detailed Assessment of the Science and Technology of Odor Measurement", 30 June 2003.
- Tchobanoglous, G., Franklin L. Burton, H. David Stensel, "Constituents in Wastewater", Wastewater Engineering Treatment and Reuse, Fourth Edition, Metcalf & Eddy, Inc., Mc McGraw-Hill, Inc. 27-137, 2003.
- Tecator - Application Note, Determination of Kjeldahl Nitrogen content by using the Kjeltec System I. 19 September 1979/AN 16 September, 1979.
- Thrasher D. Jack. *Toxicology of Hydrogen Sulfide*, 2001.
http://www.drthrasher.org/Toxicology_of_Hydrogen_Sulfide.html.
- U.S. Army Corps of Engineers, "One-Dimensional Simulation of Stratification and Dissolved Oxygen in McCook Reservoir, Illinois", U.S. Geological Survey, Water-Resources Investigations, Report 00-4258, Dale M. Robertson, 2000.

- Wang, X., J. Jiang and R. Kaye, "Improvement of a wind tunnel sampling system for odour and VOCs", *Water Science and Technology*, 44(9): 71-77, 2001.
- Wark, Kenneth and Cecil F. Warner, "Odor Measurement Techniques", *Air Pollution Its Origin and Control*. Second Edition. Harper Collins Publishers. 5, 473-485, 1981.
- Whelan, CELRC_PA. "About the Chicago District". Chicago IL. October 3, 2003. <http://www.lrc.usace.army.mil/about.htm>.
- Winter, P., and S.C. Duckham, "Analysis of Volatile Odour Compounds in Digested Sewage Sludge and Aged Sewage Sludge Cake", *Water Science and Technology*, 41(6): 73-80, 2000.
- Wolbach, P C. , "History of Clean Air Act, Mendocino County Air Quality Management District, Air Pollution Control Officer Publications, 02/15/2005, <http://www.co.mendocino.ca.us/aqmd/pages/CAA%20history.html>
- Yang, G. and J. Hobson, "Odour nuisance – advantages and disadvantages of a quantitative approach", *Water Science and Technology*, 41(6): 97–106, 2000.
- Zappa, Leo P., "Options in Odor Control", Article copied from the February Issue of *Water and Wastewater Products Magazine*, <http://www.biomagic.com/wwodorarticle1.pdf>

Appendixes

Appendix A. Complementary Literature

Table A. 1: Odorants Associated with Waste Treatment

Class	Compound	Formula	Character	Threshold (ppb)
Sulphours	Hydrogen sulphide	H ₂ S	Rotten eggs	0.5-1.11
	Methyl mercaptan	CH ₃ SH	Decayed cabbage, garlic	0.0014-18
	Ethyl mercaptan	CH ₃ CH ₂ SH	Decayed cabbage	0.019-0.32
	Allyl mercaptan	CH ₂ CHCH ₂ SH	Garlic	0.05
	Phenyl mercaptan	C ₆ H ₅ SH	Putrid, decay	0.062
	Benzyl mercaptan	C ₆ H ₅ CH ₂ SH	Unpleasant	0.19
	Crotyl mercaptan	CH ₃ CHCH ₂ SH	Skunk, rancid	0.029
	Butyl mercaptan	N/P	Unpleasant	1
	tButyl mercaptan	(CH ₃) ₃ CSH	Unpleasant	0.08
	Propyl mercaptan	N/P	Unpleasant	0.5
	Dimethyl sulphide	(CH ₃) ₂ S	Decayed vegetables, garlic	0.12-10
	Diethyl sulphide	(C ₂ H ₅) ₂ S	Nauseating, ether	0.3
	Diphenyl sulphide	(C ₆ H ₅) ₂ S	Unpleasant, burnt rubber	0.048
	Diallyl sulphide	N/P	Garlic	0.14
	Dimethyl disulphide	(CH ₃) ₂ S ₂	Putrification	0.3-11
	Carbon disulphide	CS ₂	Decayed vegetables	210
	Thiocresol	CH ₃ C ₆ H ₄ SH	Skunk, rancid	0.1
	Sulphur dioxide	SO ₂	Sharp, pungent, irritating	9

Table A.1: Continued

Class	Compound	Formula	Character	Threshold (ppb)
Nitrogenous	Ammonia	NH ₃	Sharp, pungent	37-15300
	Methylamine	CH ₃ NH ₂	Fishy	0.9-53
	Dimethylamine	(CH ₃) ₂ NH	Fishy	23-80
	Trimethylamine	(C ₂ H ₃) ₃ N	Fishy, ammoniacal	0.1-0.65
	Diamines, i.e.	NH ₂ (CH ₂) ₅ NH ₂	Decomposing	N/P
	Cadaverine	N/P	meat	N/P
	Pyridine	C ₆ H ₅ N	Disagreeable, irritating	3.7
	Indole	C ₈ H ₆ NH	Faecal, nauseating	1.4
	Scatole or Skatole	C ₉ H ₈ NH	Faecal, nauseating	0.002-1.2
Acids	Acetic (ethanoic)	CH ₃ COOH	Vinegar	16
	Butyric (butanoic)	C ₃ H ₇ COOH	Rancid, sweaty	0.09-20
	Valerie	C ₄ H ₉ COOH	Sweaty	0.6-2630
	Ethyl acrylate	CH ₂ CHCOOC ₂ H ₅	Earthy	N/P
Aldehydes and ketones	Formaldehyde	HCHO	Acrid, suffocating	370
	Acetaldehyde	CH ₃ CHO	Fruit, apple	0.005-66
	Butyraldehyde	C ₃ H ₇ CHO	Rancid, sweaty	4.6
	Isobutyraldehyde	(CH ₃) ₂ CHCHO	Fruit	4.7-7
	Isovaleraldehyde	(CH ₃) ₂ CHCH ₂ CHO	Fruit, apple	0.7-9
	Acetone	CH ₃ COCH ₃	Fruit, sweet	4580
	Butanone	C ₂ H ₅ COCH ₃	Green apple	270

Table A. 2: Hazardous Characteristics of Hydrogen Sulfide (EPA, 1985)

Chemical Formula:	H ₂ S
General Properties:	
	Irritant and poisonous volatile compound
	Exposure for 1 ½ to 2 minutes at 0.01 % impairs sense of smell
	Rotten egg odor in small concentrations
	Odor not evident at high concentrations.
	Colorless
	Flammable
Specific Gravity (compared to air = 1.0):	1.19
Physiological Effects:	Impairs sense of smell rapidly as concentration increases
	Death in few minutes at 0.2%
	Exposure to 0.07% to 0.1 % rapidly causes acute poisoning
	Paralyzes respiratory center
Maximum Safe 15-Minute Exposure:	20 ppm (OSHA)
Explosive Range, percent by volume in air:	Lower Explosive Limit: 4.3
	Upper Explosive Limit: 45.0
Likely Location of Highest Concentration:	Near bottom of confined space, but may be higher if air is heated and highly humid
	Areas of turbulence in collection system
	Low-lying flat sewers
Most Common Source:	Sewer gas or sludge gas resulting from wastewater or wastewater constituents that have undergone anaerobic decomposition

Table A. 3: Advantages, Disadvantages and Potential Applications of Hood Area Source Emission Rate Measurement Methods (Gostelow et al., 2003)

Technique	Advantages	Disadvantages	Applications
All	Isolates portion of emission surface, so can be used on complex sites with upwind interference. Higher concentrations measured – potentially more sensitive.	Many measurements required for heterogeneous sources. Potential to interfere with emission mechanisms; Can be difficult to relate conditions in the hood to field conditions. Suited to static surfaces only. Can be difficult to form effective seal on some surfaces.	Complex sites with upwind interferences. Detailed surveys of different emission sources on a site.
Static flux chambers	Little dilution of emissions - good for low emission rates; Low equipment requirements. Rapid measurements.	Diffusive emissions can be suppressed through high chamber concentrations. Poor representation of boundary layer. Poor mixing in the chamber. Not suited to emissions from liquid surfaces.	Useful for rapid measurements at many locations. Emissions from heterogeneous sites where spatial variability is being studied. Emissions from sheltered solid surfaces where wind effects
Dynamic flux chambers	Potentially greater control over measured concentrations by varying sweep airflows.	Convective emissions can be misrepresented due to pressure effects. Diffusive emissions can be suppressed through poor representation of boundary layer; Can be slow to stabilize. Greater equipment requirements. Not suited to emissions from liquid surfaces.	Emissions from relatively homogeneous sheltered solid surfaces where wind effects are negligible.
Wind tunnels	Greater control over variables influencing emissions. More accurate representation of wind effects. Potential to develop wind/ emission rate relationships for dispersion model input.	Large equipment requirements; Difficulties in selecting/measuring representative wind speeds. Care required in design, particularly in terms of velocity and concentration profiles and pressure effects.	Emissions from relatively homogeneous solid or liquid surfaces where wind effects are significant.

Table A. 4: Methods for Odour Control in Sludge Treatment (Einarsen et al., 2000)

Methods	Reaction	Comments
<u>Sludge treatment</u>		
Oxygen	$2\text{H}_2\text{S} + 3\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{S}_0 + 2\text{H}_2\text{O}$	Aerobic biological oxidation of H_2S and organic matter; formation of H_2S is prevented as the conditions for sulphate reducing bacteria are unfavourable. Other smell components may also be removed.
Nitrate	$2\text{H}_2\text{S} + 2\text{NO}_3^- \rightarrow \text{SO}_4^{2-} + \text{S}_0 + \text{N}_2 + 2\text{H}_2\text{O}$	Anoxic biological oxidation of H_2S and organic matter; formation of H_2S is prevented as the conditions for sulphate reducing bacteria are unfavourable. Other smell components may also be removed.
Iron salts	$4\text{Fe}^{3+} + 4\text{HS}^- + 2\text{S}^{2-} \rightarrow \text{Fe}_3\text{S}_4 + 3\text{H}^+ + \text{S}_0 + \text{FeS}$ $\text{Fe}^{2+} + \text{HS}^- \rightarrow \text{FeS} + \text{H}^+$	Iron precipitates sulphide and removes only smell caused by H_2S .
Lime/Caustic	$\text{H}_2\text{S} + \text{Ca}(\text{OH})_2 \rightarrow \text{S}^{2-} + 2\text{H}_2\text{O} + \text{Ca}^{2+}$	H_2S is dissolved as S^{2-} by increasing the pH to above 10.
Peroxide	$\text{H}_2\text{O}_2 + \text{H}_2\text{S} \rightarrow \text{S}_0 + 2\text{H}_2\text{O}$	H_2S is chemically oxidised. Any excess oxygen released prevents formation of H_2S . Other smell components may also be removed by oxidation.
Ozone	$\text{O}_3 + \text{H}_2\text{S} \rightarrow \text{S}_0 + \text{H}_2\text{O} + \text{O}_2$	H_2S is chemically oxidised. Any excess oxygen released prevents formation of H_2S . Other smell components may also be removed by oxidation.
<u>Off-gas treatment</u>		
Chemical scrubbers	$5\text{HOCl} + 2\text{H}_2\text{S} \rightarrow \text{SO}_4^{2-} + \text{S}_0 + 7\text{H}^+ + 5\text{Cl}^- + \text{H}_2\text{O}$	H_2S is chemically oxidised. HOCl is the most common chemical, but H_2O_2 and O_3 are also used. Other smell components will also be removed.
Biological filter/ bark filter	$2\text{H}_2\text{S} + \text{O}_2/\text{NO}_3^- \rightarrow \text{SO}_4^{2-} + \text{S}_0 + 2\text{H}_2\text{O}$	Biological oxidation of H_2S or other malodorous compounds, by the use of oxygen or nitrate.
Active carbon	$\text{H}_2\text{S} + \text{C}_n \rightarrow \text{C}_n\text{-H}_2\text{S}$	H_2S is adsorbed on activated carbon. Other malodorous compounds may be removed.

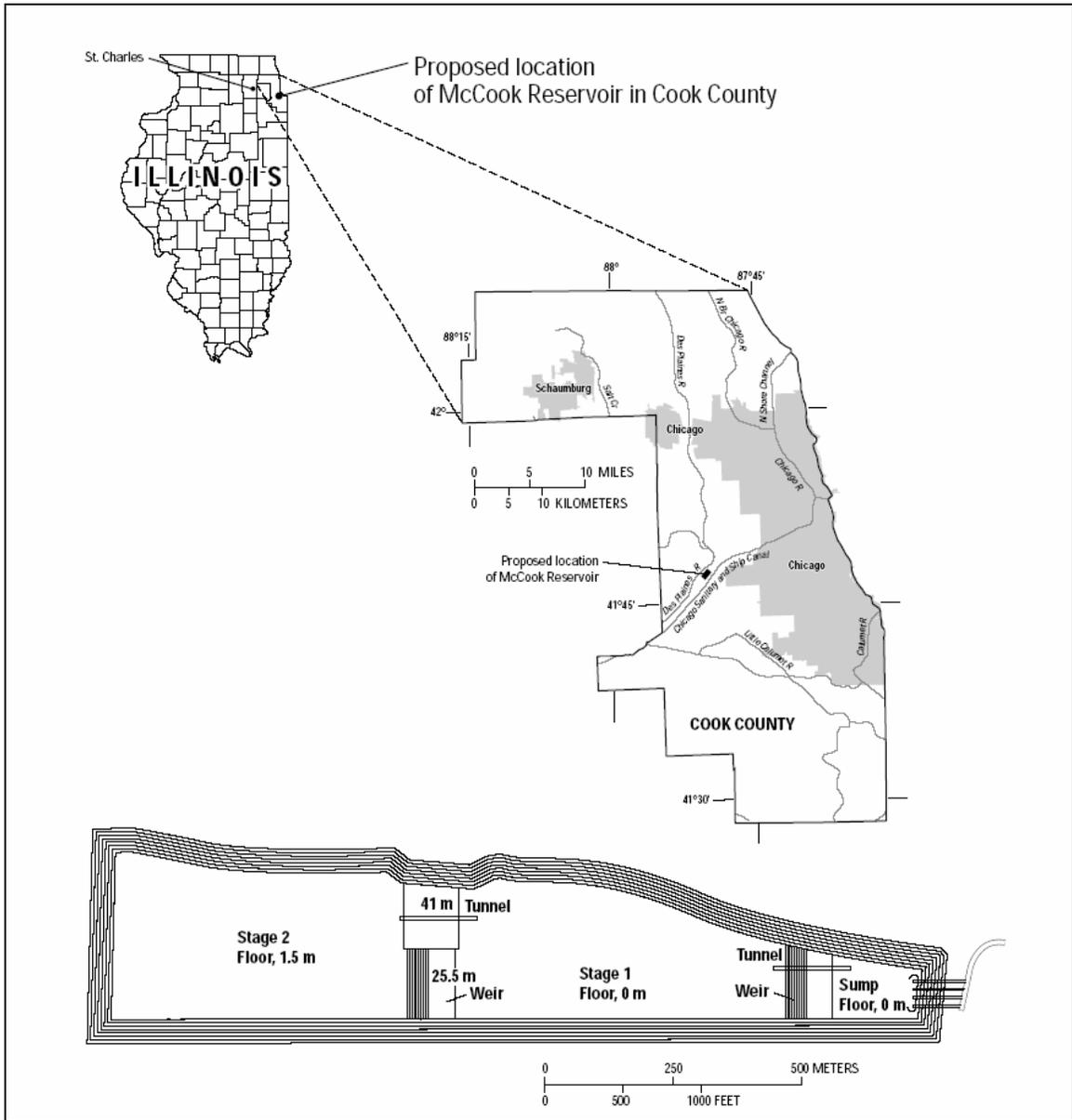


Figure A. 1: Proposed Location of McCook Reservoir in Cook County (U.S. Army Corps of Engineers, 2000)

Appendix B. Sampling Requirements

Table B. 1: Summary of Special Sampling and Handling Requirements (Standard Method, 1998)

Determination	Container†	Minimum Sample Size mL	Sample Type‡	Preservation§	Maximum Storage Recommended	Regulatory
Odor	G	500	g	Analyze as soon as possible; refrigerate	6 hr	N.S.
Organic Kjeldahl*	P, G	500	g, c	Refrigerate, add H ₂ SO ₄ to pH < 2	7 d	28 d
Total Phosphorus	P, G	100	g, c	Add H ₂ SO ₄ to pH < 2 and refrigerate	28d	N/P
Solids	P, G	200	g, c	Refrigerate	7 d	2-7 d
pH	P, G	50	g	Analyze immediately	0.25 h	0.25 h
Dissolved Oxygen (DO)	G, BOD bottle	300	g	Analyze immediately	0.25 h	0.25 h
Total Organic Carbon (TOC)	G(B)	100	g, c	Analyze immediately; or refrigerate and add HCl, H ₃ PO ₄ , or H ₂ SO ₄ to pH < 2	7 d	28 d

* For determination not listed, use glass or plastic container; preferably refrigerate during storage and analyze as soon as possible.

† P = plastic (polyethylene or equivalent); G = glass, G (B) = glass borosilicate.

‡ g = grab; c = composite.

§ Refrigerate = storage at 4°C ± 2°C; in dark; analyze immediately = analyze within 15 min sample collection.

|| See citation 10 for possible differences regarding container and preservation requirements, N.S. = not stated cited reference.

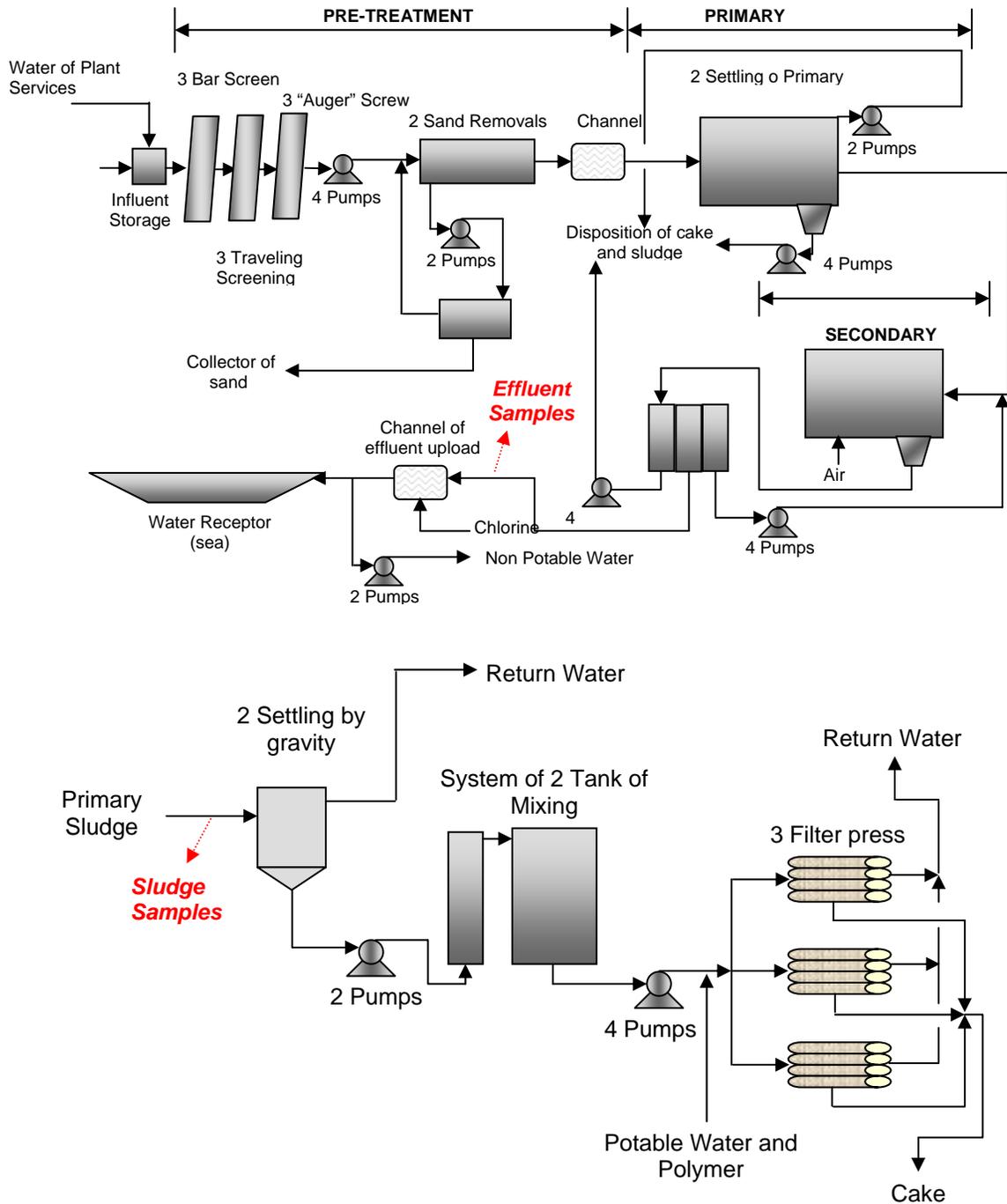


Figure B. 1: Scheme of EMWTP

Appendix C: Previous Data

Table C. 1: Data of Water Samples from in Experiments of 2001 (Mayagüez area)

Parameter	Method	Results	Units	Limits		Date	Time
				LOD	MCL		
Alterable Residue(TDS)	EPA 160.1	358	mg/L	5	N/A	4/30/2001	16:30
Non-Filterable Residue(TSS)	EPA 160.2	127	mg/L	5	N/A	4/30/2001	15:30
Oil and Grease (hexane)	EPA 1664	30	mg/L	1.4	N/A	4/30/2001	11:00
Barium-total	EPA 200.7	0.081	mg/L	0.005	N/A	5/4/2001	15:10
Copper-total	EPA 200.7	0.035	mg/L	0.005	N/A	5/4/2001	15:10
Zinc-total	EPA 200.7	0.128	mg/L	0.005	N/A	5/4/2001	15:10
Ion-total	EPA 200.7	1.88	mg/L	0.02	N/A	5/4/2001	15:10
Chromium-total	EPA 200.7	0.004	mg/L	0.002	N/A	5/4/2001	15:10
Cadmium-total	EPA 200.7	BDL	mg/L	0.002	N/A	5/4/2001	15:10
Aluminum-total	EPA 200.7	1.3	mg/L	0.01	N/A	5/4/2001	15:10
Arsenic-total	EPA 200.9	BDL	mg/L	0.003	N/A	5/2/2001	16:00
Selenium-total	EPA 200.9	BDL	mg/L	0.001	N/A	5/2/2001	8:30
Lead-total	EPA 200.9	BDL	mg/L	0.003	N/A	5/1/2001	11:00
Mercury-total	EPA 245.1	BDL	mg/L	0.0002	N/A	5/4/2001	14:03
Nickel-total	EPA 249.1	0.13	mg/L	0.02	N/A	5/3/2001	15:00
Alkalinity-bicarbonate	EPA 310.2	226	mg/L as CaCO ₃	10	N/A	5/3/2001	11:53
Alkalinity-total	EPA 310.2	227.1	mg/L as CaCO ₃	10	N/A	5/3/2001	11:54
Alkalinity-carbonate	EPA 310.2	BDL	mg/L as CaCO ₃	10	N/A	5/3/2001	11:54
Chloride-soluble	EPA 325.2	64.6	mg/L	3	N/A	5/3/2001	13:30

Table C.1: Continued

Parameter	Method	Results	Units	Limits		Date	Time
				LOD	MCL		
Ammonia	EPA 351.2	10.13	mg/L	0.1	N/A	5/4/2001	14:00
Total Kjeldahl Nitrogen (as N)	EPA 351.2	20.31	mg/L	0.2	N/A	5/7/2001	16:15
Total Organic Nitrogen	EPA 351.2	10.18	mg/L	0.2	N/A	5/8/2001	8:40
Nitrate as N	EPA 353.2	BDL	mg/L	0.01	N/A	4/27/2001	16:59
Nitrite as N	EPA 353.2	BDL	mg/L	0.01	N/A	4/27/2001	16:59
Dissolved Oxygen	EPA 360.1	2	mg/L	1	N/A	4/27/2001	16:50
Total Phosphorus	EPA 365.3	0.196	mg/L	0.01	N/A	5/1/2001	16:52
Phosphate	EPA 365.3	1.76	mg/L	0.01	N/A	4/27/2003	17:23
Sulfate-soluble	EPA 375.4	17.3	mg/L	1	N/A	5/2/2001	11:40
Biochemical Oxygen Demand	EPA 405.1	105	mg/L	1	N/A	4/28/2001	14:33
Chemical Oxygen Demand	EPA 410.4	347	mg/L	5	N/A	5/1/2001	13:32

BDL: below detection limit
MCL: maximum contaminant level
LOD: limit of detection

Table C. 2: Summary of CSO water quality in the Chicago area, based on readily available information

Parameter	Typical Range	Experimental target range or value
Ammonia	2.8-5.3 mg/L as N 0-21mg/L as N (MWRDGC CSO summary) 0.2-32.3 mg/L as N (TARP pumpback data)	7.5 mg/L as N
Biochemical Oxygen Demand(BODs)	6-910 mg/L as O ₂ 10-1200 mg/L as O ₂ (TARP pumpback data)	30 (large storm) or 75 (small storm) mg/L as O ₂
Chemical Oxygen Demand(COD)	14-319 mg/L as O ₂ 30-1188 mg/L as O ₂ (TARP pumpback data)	90 (large storm) or 225 (small storm) mg/L as O ₂
Total Suspended Solids	18-358 mg/L 22-380 mg/L (MWRDGC CSO summary) 5-6470 mg/L (Polls and Lanyon study) 12-6500 (TARP pumpback data)	100 (large storm) or 200 (small storm) mg/L as O ₂
Total Solids	144-6736 mg/L 254-7400 mg/L (TARP pumpback data)	250 (large storm) or 600 (small storm) mg/L as O ₂
Dissolved Oxygen	4.5 mg/L (at O'Hare inlet) 3.1-8.8mg/L (at TARP drop shafts) 0-8.8 mg/L (MWRDGC CSO summary)	4 mg/L initial condition (could range from 0 to saturation)
pH	6.5-9.7	7.5
Nitrate + Nitrite	0.5-3.1 mg/L as N 0.1-23.5 mg/L as N (Polls and Lanyon study) 0.1-13 mg/L as N (TARP pumpback data)	0.5 mg/L as N
Chloride	24-597 mg/L (TARP pumpback data)	105 mg/L
Sulfate	28-329 mg/L (TARP pumpback data)	85 mg/L
Phosphorus	0.01-2.2 mg/L as P 0.6-23.4 mg/L Total P (TARP pumpback data)	2.7 (Total P) mg/L as P
Total Kjeldahl Nitrogen (TKN)	0.1-12.9 mg/L as N 3.5-84.9 mg/L as N (TARP pumpback data)	12 mg/L as N
Iron	0.7-3.9 mg/L 0.6-15.9 mg/L (TARP pumpback data)	2.5 mg/L
Zinc	0-2.1 mg/L 0-1.6 mg/L (TARP pumpback data)	0.3 mg/L
Oil and Grease(FOG)	0-165 mg/L (TARP pumpback data)	30 mg/L

Table C. 3: Data from primary sludge of Stickney Water Reclamation Plant

Parameter	pH	TS	VTS	NH₃-N	TKN	TP
		%	%	% Dry	% Dry	% Dry
Minimum	5.54	0.10	45.30	0.17	1.91	0.54
Mean	6.40	0.81	62.49	0.50	4.65	1.19
Maximum	7.39	2.21	76.80	1.36	8.87	1.87

Appendix D. Materials and Equipments

Table D. 1: Description of Equipment used in Olfactometry Test

Description	Equipment	Figure
Five gallons black plastic sample container, Fisher Scientific		A
Oven, Pro-Tronix II, Stabil-Therm Electric Oven of General Signal, Lindberg/Blue, Model number OV-510A-3, Serial No. OV-8332, Motor only 115V-3.0A, Temperature Range: 38 °C-260 °C		B
Box Furnace, Lindberg/Blue, Model number BF51828C-1, Volts: 240; Amps: 24; Phase: 1; Watts 5.6KW; HZ: 50/60, Temp. Range Maximum: 1100 °C, Serial No. P28L-523517-RL		C

Table D. 1: Continued

Description	Equipment	Figure
Heavy Duty Dissolved Oxygen Meter, Model 407510 of Extech Instruments Corporation	 A photograph of an Extech Dissolved Oxygen Meter, Model 407510. The device is a handheld digital meter with a blue display showing '88.88'. It has a black probe connected to the top. Next to the meter are a white plastic bottle with a black cap, a red cap, and a small white container with a label that reads 'Heavy Duty Dissolved Oxygen Meter Model 407510'.	D
pH Meter ORION, Model 720 A	 A photograph of an Orion pH Meter, Model 720 A. The meter is a benchtop unit with a digital display showing '7.20'. It has a black probe connected to the top. To the left of the meter are three small bottles containing colored liquids (yellow, green, and blue).	E
Touch Mixer, MT-31 of Yamato Company	 A photograph of a Yamato Touch Mixer, Model MT-31. The mixer is a white, rectangular unit with a green control panel. The panel has the 'Yamato' logo, 'TOUCH MIXER', and 'MT-31' printed on it. There are three vertical switches labeled 'ON 1', 'ON 2', and 'OFF', and a 'POWER' button. A black lid is on top of the mixer, and a small amount of white powder is visible on the lid.	F

Table D. 1: Continued

Description	Equipment	Figure
<p>Digestion System 4, 1016 Digester of Tecator Company</p>		<p>G</p>
<p>BigGer Bill Shaker, Thermolyne</p>		<p>H</p>
<p>HUSKY Oilless Air Compressor WL 6500 Series, Model: WL650702AJ, Serial No. L6/25/03/01180, of Campbell Hausfeld, and distributed by Home-Depot, 5.5 HP, 150 psi Max, 26 gal, 5.1 SCFM @ 90 psi and 6.5 SCFM @ 40psi</p>		<p>I</p>

Table D.1: Continued

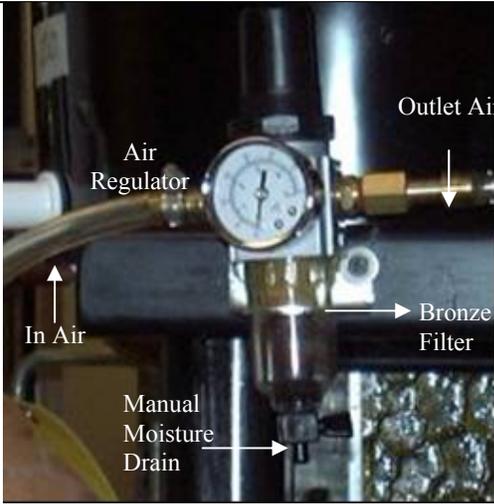
Description	Equipment	Figure
<p>BEL-ART RITERFLOW flow meters, Mounted Flow Meter for Air & Water of 150 mm, Size No. 5, P/N 40407-0305, Bel-Art Product and distributed by Fisher Scientific</p>		<p>J</p>
<p>Moisture Trap, R-75AR Regulator and Filter, Paasche Airbrush Company, Maximum primary air pressure 150 psi., Temperature Range: 277.6 °K- 324.8 °K, Accurate Regulation between 2-60 psi.</p>		<p>K</p>
<p>Water Trap, 2.2L Teflon coated Nalgene bottle of Nalgene Comany with Barbed BulKhead Fitting</p>		<p>L</p>

Table D.1: Continued

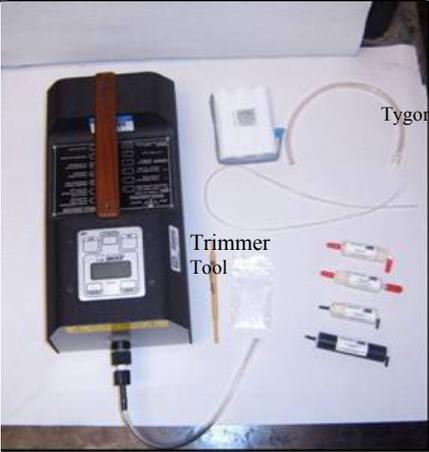
Description	Equipment	Figure
<p>Activated Carbon Column Column is molded polycarbonate and with maximum working pressure of 90 psi., Stock No. 26800, Cole-Parmer</p>		<p>LL</p>
<p>(2.2L) Teflon coated Nalgene bottle of Nalgene Comany with Barbed Bulkhead Fitting, PP, size 1/4", Cat. No. 6149-0002</p>		<p>M</p>
<p>Jerome 631-X Hydrogen Sulfide Analyzer, Include: Batery Pack Assembly, LFS Srcubber Filter, LFD scrubber Filter, Scrubber Filter, Zero Air Filter, 0.25 inch fritware and trimmer tool, tygon line and tubing adaptor, Arizona Instrument LLC.</p>		<p>N</p>

Table D.1: Continued

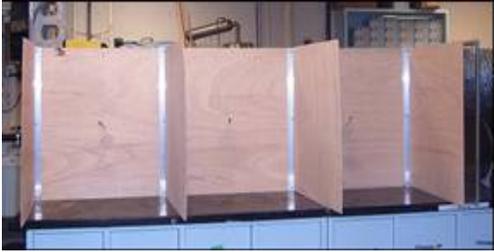
Description	Equipment	Figure
Colored Panel and “sniffing” port		O
Jerome Data Logger, Data Acquisition System, Y6100 0057, Arizona Instrument LLC.		P
Data Acquisition System for the Jerome 631-X		Q

Table D.1: Continued

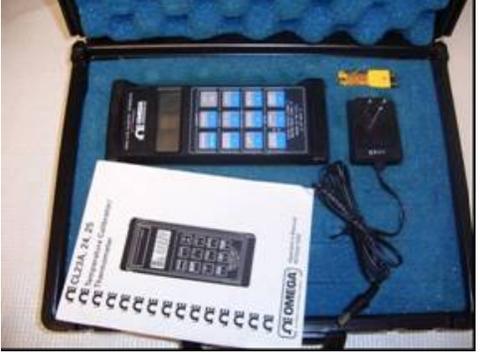
Description	Equipment	Figure
<p>Functional Test Module, Include a Permeation Tube, Part No. Z2600 0918, Arizona Instrument LLC.</p>		<p>R</p>
<p>Digital Thermocouple, Type K, Model CL 23A, Omega Engineering, Inc.</p>		<p>S</p>

Table D. 2: Description of Equipment used in Flux Chamber Test

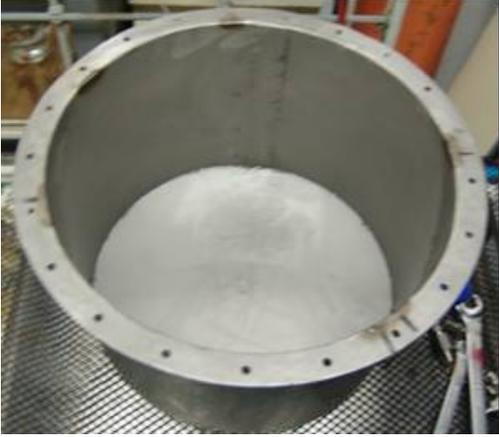
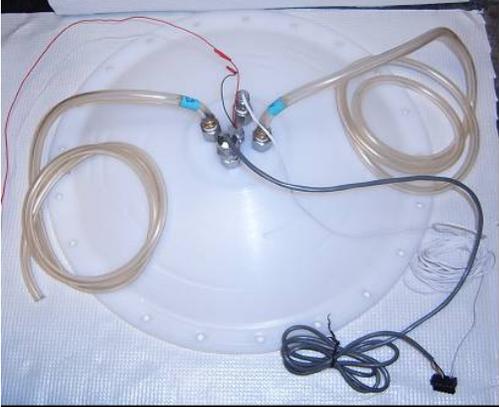
Description	Equipment used in Flux Chamber Test	Figure
<p>Stainless Steel 316 flux chamber dome pot shape container, Base: 38.1 cm (15") ID and 43.34 cm of OD, depth: 25.4 cm (10") and, thick: 0.952 cm (0.375"), Manufactured by Añasco Precision Mfg., Inc.</p>		<p>A</p>
<p>Cylindrical polypropylene lid dome shape, dimension: 38.1 cm (15") ID and 43.34 cm (17") OD, twenty one holes of 0.635 cm (1/4") OD, equipped with five Swagelok fittings of stainless steel of 1.27 cm (1/2") OD, Manufactured by Añasco Precision Mfg., Inc.</p>		<p>B</p>
<p>Bulkhead stainless steel screws, 0.635 cm (1/4") OD, Manufactured by Añasco Precision Mfg., Inc.</p>		<p>C</p>

Table D.2: Continued

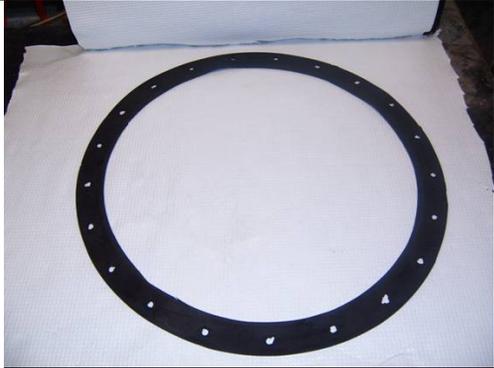
Description	Equipment used in Flux Chamber Test	Figure
<p>Neoprime Durometer 40A gasket, twenty one holes of 0.635 cm ($\frac{1}{4}$" OD, Manufactured by Añasco Precision Mfg., Inc.</p>		<p>D</p>
<p>Omega Portable Low Cost Pressure and Temperature Data Logger (OM-PLPT), one external temperature sensor 4.6 m (15') cable, epoxy coated tip, and one pressure transducer 1.8 m (6') cable, stainless steel pressure transducer with $\frac{1}{2}$" NPT male pressure port, Model No. OM-PLPT, Omega Engineering, INC.</p>		<p>E</p>
<p>Data Acquisition System for the OM-PLPT</p>		<p>F</p>

Table D.2: Continued

Description	Equipment used in Flux Chamber Test	Figure
<p>6 foot USB Cable to Serial Cable, Reference Num. 26-183, Radio Shack</p>		<p>G</p>
<p>Dayton DC Axial Fan, 17.6 cfm, connected using a 1.27 cm (1/2") Swagelock quick connection of with septa, Model No. 4WT34, Manufactured by Dayton Electronic and distribute by Grainger.</p>		<p>H</p>
<p>Gel Battery Tender, 12 Volt, Deltran Corporation</p>		<p>I</p>

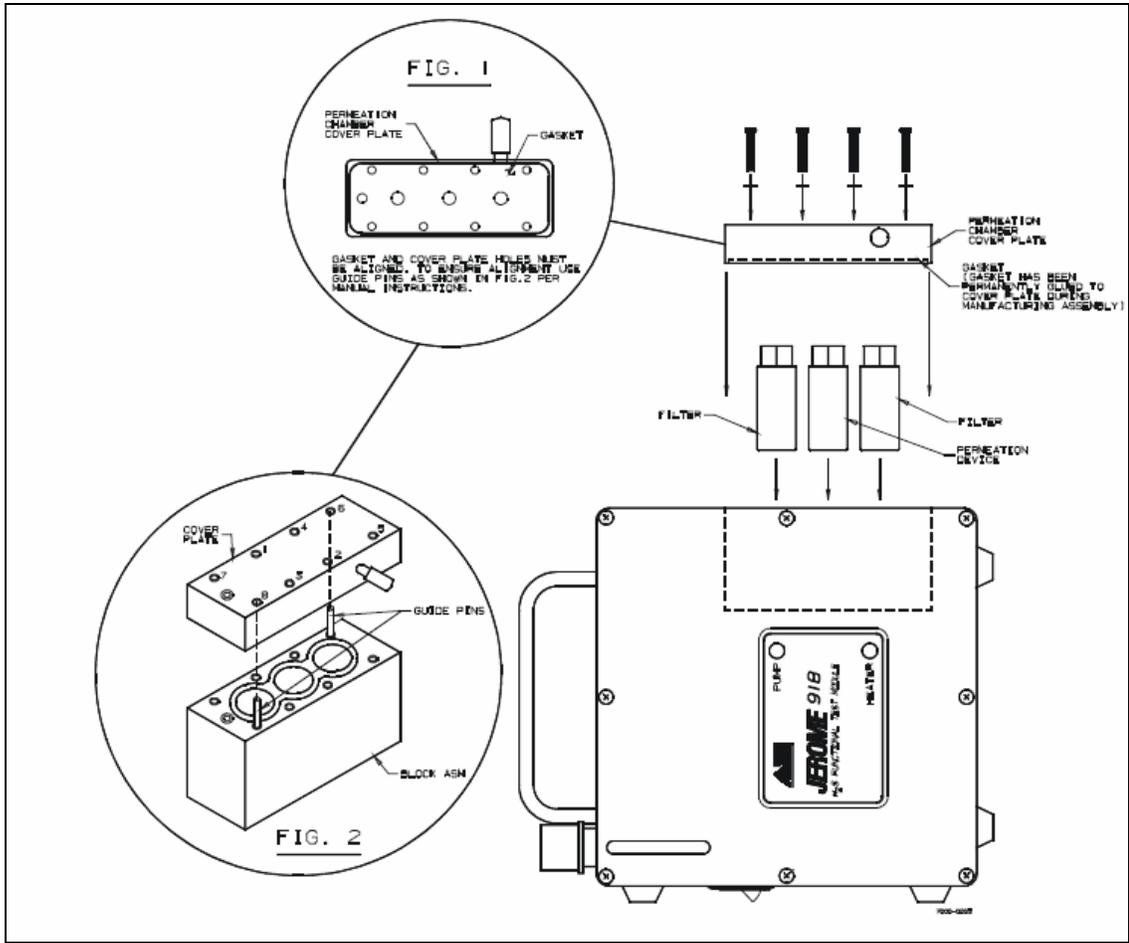


Figure D. 1: Scheme Functional Test Module (Arizona Instrument LLC, 2003)

Appendix E: Flux Experiments Conditions

Table E. 1 Flux Experiments Conditions

Run (¹)	Conditions						
	Sediment Aging Times (days)	Water Contents (%)	Flow Rates (mL/min)	Water Layer (²) (cm)	Temperature Range (°K)	Continuous Mixing (³)	Other
1	1	98.15	3285	0	293.15-298.15	N	N/A
2	1	98.15	6977	0	293.15-298.15	N	N/A
3	1	98.15	10812	0	293.15-298.15	N	N/A
4	1	98.15	22698	0	293.15-298.15	N	N/A
5	1	97.82	3285	0	293.15-298.15	N	N/A
6	1	97.82	6977	0	293.15-298.15	N	N/A
7	1	97.82	10812	0	293.15-298.15	N	N/A
8	1	97.82	22698	0	293.15-298.15	N	N/A
9	15	98.15	3285	0	293.15-298.15	N	N/A
10	15	98.15	5131	0	293.15-298.15	N	N/A
11	15	98.15	6977	0	293.15-298.15	N	N/A
12	15	98.15	8894.5	0	293.15-298.15	N	N/A
13	15	98.15	10812	0	293.15-298.15	N	N/A
14	15	98.15	22698	0	293.15-298.15	N	N/A
15	15	97.82	3285	0	293.15-298.15	N	N/A
16	15	97.82	5131	0	293.15-298.15	N	N/A
17	15	97.82	6977	0	293.15-298.15	N	N/A
18	15	97.82	8894.5	0	293.15-298.15	N	N/A
19	15	97.82	10812	0	293.15-298.15	N	N/A
20	15	97.82	22698	0	293.15-298.15	N	N/A
21	15	97.82	3285	5.08	293.15-298.15	N	N/A
22	15	97.82	3285	5.08	293.15-298.15	N	N/A
23	15	97.82	5131	5.08	293.15-298.15	N	N/A
24	30	98.15	480	0	293.15-298.15	N	N/A
25	30	98.15	868	0	293.15-298.15	N	N/A
26	30	98.15	1145	0	293.15-298.15	N	N/A
27	30	98.15	2117	0	293.15-298.15	N	N/A
28	30	98.15	3285	0	293.15-298.15	N	N/A
29	30	98.15	3780	0	293.15-298.15	N	N/A
30	30	98.15	5131	0	293.15-298.15	N	N/A
31	30	98.15	6977	0	293.15-298.15	N	N/A
32	30	98.15	8894.5	0	293.15-298.15	N	N/A
33	30	98.15	10812	0	293.15-298.15	N	N/A
34	30	98.15	22698	0	293.15-298.15	N	N/A

Table E.1: Continued

Run (¹)	Conditions						
	Sediment Aging Times (days)	Water Contents (%)	Flow Rates (mL/ min)	Water Layer (²) (cm)	Temperature Range (°K)	Continuous Mixing (³)	Other
35	30	97.82	480	0	293.15-298.15	N	N/A
36	30	97.82	868	0	293.15-298.15	N	N/A
37	30	97.82	1145	0	293.15-298.15	N	N/A
38	30	97.82	2117	0	293.15-298.15	N	N/A
39	30	97.82	3285	0	293.15-298.15	N	N/A
40	30	97.82	3780	0	293.15-298.15	N	N/A
41	30	97.82	5131	0	293.15-298.15	N	N/A
42	30	97.82	6977	0	293.15-298.15	N	N/A
43	30	97.82	8894.5	0	293.15-298.15	N	N/A
44	30	97.82	10812	0	293.15-298.15	N	N/A
45	30	97.82	22698	0	293.15-298.15	N	N/A
46	30	98.15	3285	5.08	293.15-298.15	N	N/A
47	30	98.15	5131	5.08	293.15-298.15	N	N/A
48	45	98.15	480	0	293.15-298.15	N	N/A
49	45	98.15	868	0	293.15-298.15	N	N/A
50	45	98.15	1145	0	293.15-298.15	N	N/A
51	45	98.15	2117	0	293.15-298.15	N	N/A
52	45	98.15	3285	0	293.15-298.15	N	N/A
53	45	98.15	3780	0	293.15-298.15	N	N/A
54	45	98.15	5131	0	293.15-298.15	N	N/A
55	45	98.15	6977	0	293.15-298.15	N	N/A
56	45	98.15	8894.5	0	293.15-298.15	N	N/A
57	45	98.15	10812	0	293.15-298.15	N	N/A
58	45	98.15	22698	0	293.15-298.15	N	N/A
59	45	97.82	480	0	293.15-298.15	N	N/A
60	45	97.82	868	0	293.15-298.15	N	N/A
61	45	97.82	1145	0	293.15-298.15	N	N/A
62	45	97.82	2117	0	293.15-298.15	N	N/A
63	45	97.82	3285	0	293.15-298.15	N	N/A
64	45	97.82	3780	0	293.15-298.15	N	N/A
65	45	97.82	5131	0	293.15-298.15	N	N/A
66	45	97.82	6977	0	293.15-298.15	N	N/A
67	45	97.82	8894.5	0	293.15-298.15	N	N/A
68	45	97.82	10812	0	293.15-298.15	N	N/A
69	45	97.82	22698	0	293.15-298.15	N	N/A
70	45	98.15	480	5.08	293.15-298.15	N	N/A

Table E.1: Continued

Run (¹)	Conditions						
	Sediment Aging Times (days)	Water Contents (%)	Flow Rates (mL/ min)	Water Layer (²) (cm)	Temperature Range (°K)	Continuous Mixing (³)	Other
71	45	98.15	480	5.08	293.15-298.15	N	N/A
72	45	98.15	3285	5.08	293.15-298.15	N	N/A
73	45	98.15	3285	5.08	293.15-298.15	N	N/A
74	45	98.15	5131	5.08	293.15-298.15	N	N/A
75	45	98.15	5131	5.08	293.15-298.15	N	N/A
76	45	97.82	3285	5.08	293.15-298.15	N	N/A
77	45	97.82	3285	5.08	293.15-298.15	N	N/A
78	45	97.82	5131	5.08	293.15-298.15	N	N/A
79	45	97.82	5131	5.08	293.15-298.15	N	N/A
80	60	98.15	480	0	293.15-298.15	N	N/A
81	60	98.15	868	0	293.15-298.15	N	N/A
82	60	98.15	1145	0	293.15-298.15	N	N/A
83	60	98.15	2117	0	293.15-298.15	N	N/A
84	60	98.15	3285	0	293.15-298.15	N	N/A
85	60	98.15	3780	0	293.15-298.15	N	N/A
86	60	98.15	5131	0	293.15-298.15	N	N/A
87	60	98.15	6977	0	293.15-298.15	N	N/A
88	60	98.15	8894.5	0	293.15-298.15	N	N/A
89	60	98.15	10812	0	293.15-298.15	N	N/A
90	60	98.15	22698	0	293.15-298.15	N	N/A
91	60	97.82	480	0	293.15-298.15	N	N/A
92	60	97.82	868	0	293.15-298.15	N	N/A
93	60	97.82	1145	0	293.15-298.15	N	N/A
94	60	97.82	2117	0	293.15-298.15	N	N/A
95	60	97.82	3285	0	293.15-298.15	N	N/A
96	60	97.82	3780	0	293.15-298.15	N	N/A
97	60	97.82	5131	0	293.15-298.15	N	N/A
98	60	97.82	6977	0	293.15-298.15	N	N/A
99	60	97.82	8894.5	0	293.15-298.15	N	N/A
100	60	97.82	10812	0	293.15-298.15	N	N/A
101	60	97.82	22698	0	293.15-298.15	N	N/A
102	60	98.15	3285	5.08	293.15-298.15	N	N/A
103	60	98.15	3285	5.08	293.15-298.15	N	N/A
104	60	98.15	5131	5.08	293.15-298.15	N	N/A
105	60	98.15	5131	5.08	293.15-298.15	N	N/A
106	60	97.82	3285	5.08	293.15-298.15	N	N/A
107	60	97.82	3285	5.08	293.15-298.15	N	N/A

Table E.1: Continued

Run (¹)	Conditions						
	Sediment Aging Times (days)	Water Contents (%)	Flow Rates (mL/min)	Water Layer (²) (cm)	Temperature Range (°K)	Continuous Mixing (³)	Other
108	60	97.82	5131	5.08	293.15-298.15	N	N/A
109	60	97.82	5131	5.08	293.15-298.15	N	N/A
110	67	97.82	480	5.08	293.15-298.15	N	Without moving the sample before the flux test
111	67	97.82	480	5.08	293.15-298.15	N	N/A
112	67	97.82	480	5.08	293.15-298.15	N	N/A
113	67	97.82	480	5.08	293.15-298.15	N	N/A
114	67	97.82	480	5.08	293.15-298.15	N	N/A
115	67	97.82	480	5.08	293.15-298.15	N	Sample enclosed 1-day on flux chamber
116	85	97.82	480	0	293.15-298.15	N	N/A
117	85	97.82	480	0	293.15-298.15	N	N/A
118	85	97.82	480	0	293.15-298.15	N	Sample enclosed 1-day on flux chamber
119	85	97.82	480	0	293.15-298.15	Y	Low velocity
120	85	97.82	480	0	293.15-298.15	Y	High velocity
121	85	97.82	480	0	298.15-299.15	N	N/A
122	85	97.82	480	0	302.15-306.15	N	N/A
123	85	97.82	480	0	306.15-308.15	N	N/A
124	85	97.82	480	0	293.15-298.15	N	Sample enclosed about 2-day on flux chamber

(1) Duplicate runs were done for all experiments. Run include sample and duplicate

(2) Water layer above sediment surface

(3) Continuous shaking of sediment during flux experiments

Appendix F: Calibration Plot

F.1 Air Flow Calibration Plot

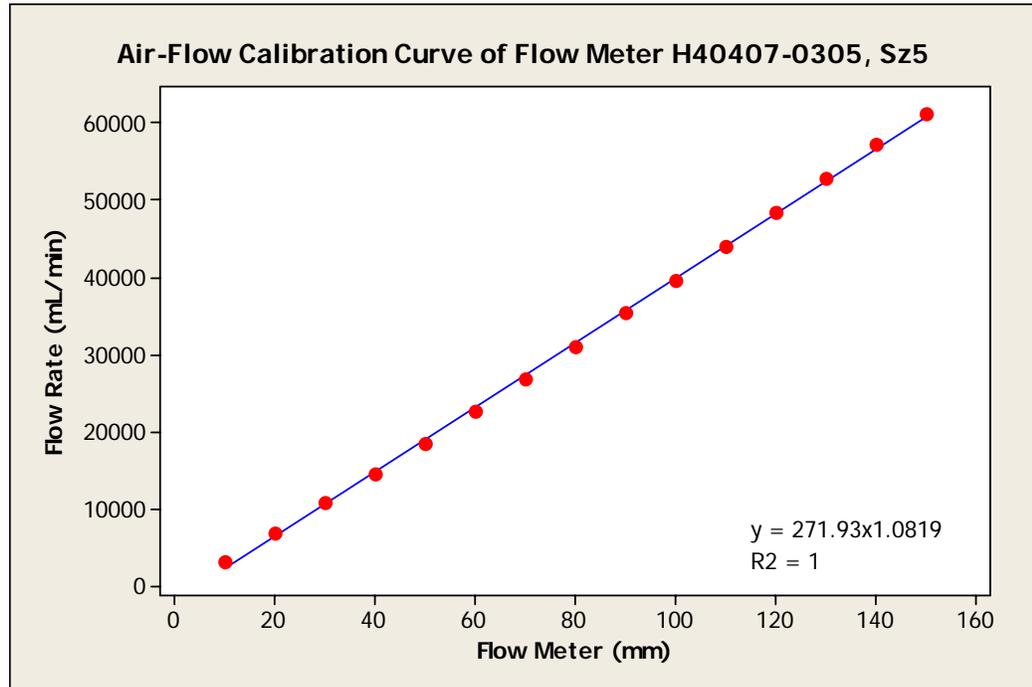


Figure F. 1.1: Calibration Curve of Flow Meter H40407-0305, Sz5

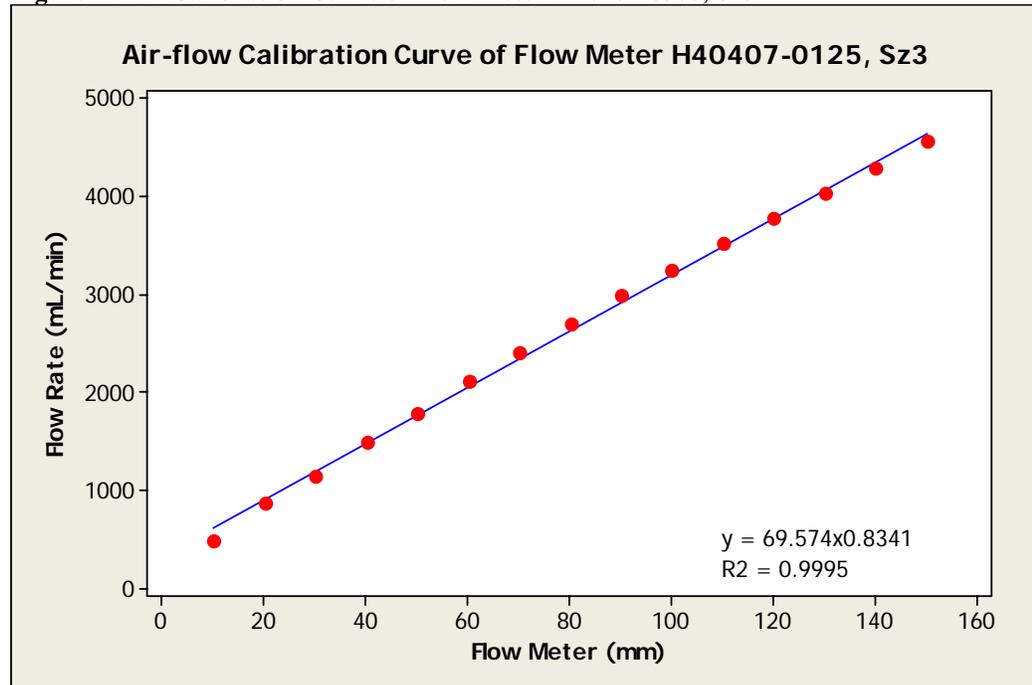


Figure F.1.2: Calibration Curve of Flow Meter H40407-0125, Sz3

F.2 Functional Test Verification

For verify the calibration and Quality Control in the Jerome 631-X it is used the Functional Test Module. The Functional Test Module is used to determine if the Jerome is within calibration tolerance between recommended annual factory calibrations. This test verifies proper instrument operation through the introduction of a know concentration of hydrogen sulfide (H₂S) into the Jerome analyzer. To conduct this test it is necessary to record ten analyzer samples, disregard the first five samples and average the last five samples. The acceptable average value ranges for the Jerome 631-X is 0.20-0.30 ppm H₂S. Various run was realized before conduct experimentation using the Jerome 631-X. The average value obtained in these tests was 0.22, .222 and 0.218, so that show us that the Jerome is working between the calibration tolerances ranges.

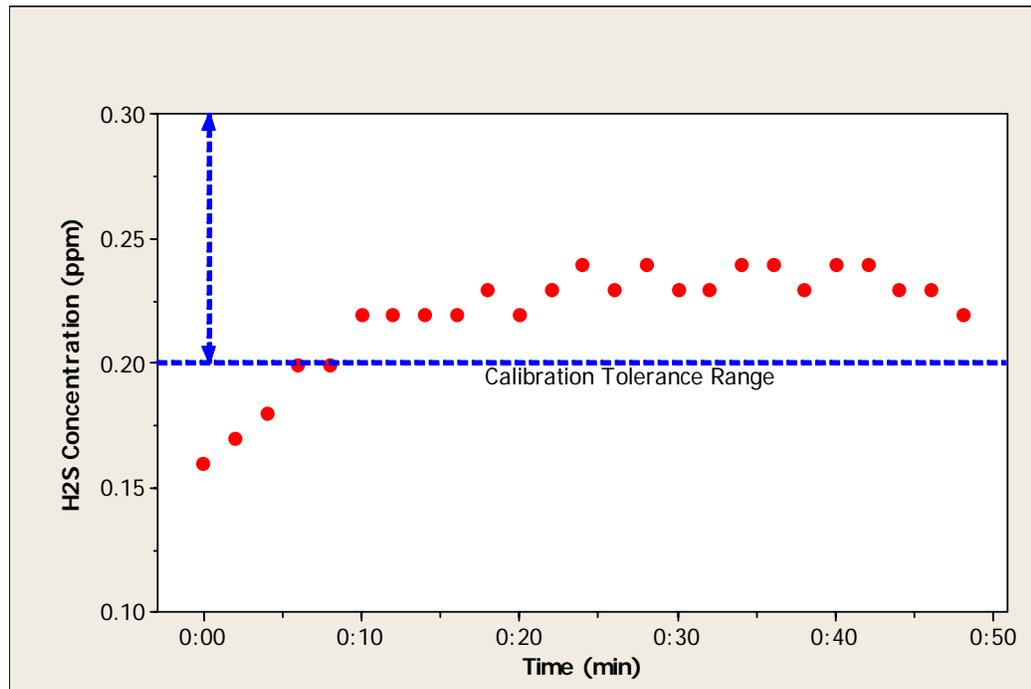


Figure F.2. 1: Verification of Jerome 631-X using the Functional Test Module

Appendix G: Statistics Results

G.1 Statistics Analysis for Sediment Characterization

G.1.1 Statistics Analysis for pH

Descriptive Statistics: pH

Variable	Water Content				Mean	SE Mean	StDev	Variance	CoefVar	Minimum
	(%)	N	N*							
pH	95.84	10	0		7.001	0.176	0.558	0.312	7.97	6.057
	97.09	10	0		7.100	0.171	0.542	0.293	7.63	6.240
	97.82	10	0		7.056	0.189	0.597	0.356	8.46	5.920
	98.08	10	0		7.071	0.138	0.437	0.191	6.18	6.289
	98.15	10	0		7.149	0.114	0.361	0.130	5.05	6.485

Variable	Water Content			
	(%)	Median	Maximum	Range
pH	95.84	7.333	7.472	1.415
	97.09	7.409	7.685	1.445
	97.82	7.366	7.538	1.618
	98.08	7.335	7.445	1.156
	98.15	7.359	7.394	0.909

Descriptive Statistics: pH

Variable	Sediment Aging Times				Mean	SE Mean	StDev	Variance	CoefVar	Minimum
	(Days)	N	N*							
pH	1	10	0		6.2459	0.0676	0.2138	0.0457	3.42	5.9200
	15	10	0		6.8880	0.0672	0.2125	0.0452	3.09	6.6130
	30	10	0		7.3842	0.0223	0.0704	0.00496	0.95	7.2930
	45	10	0		7.4040	0.00870	0.0275	0.000756	0.37	7.3670
	60	10	0		7.4544	0.0317	0.1001	0.0100	1.34	7.3600

Variable	Sediment Aging Times			
	(Days)	Median	Maximum	Range
pH	1	6.2575	6.5150	0.5950
	15	6.8320	7.2340	0.6210
	30	7.3670	7.5380	0.2450
	45	7.3935	7.4530	0.0860
	60	7.4435	7.6850	0.3250

General Linear Model: pH versus Sediment-Aging Times and Water Content (%)

Factor	Type	Levels	Values
Sediment-Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	5	95.84, 97.09, 97.82, 98.08, 98.15

Analysis of Variance for pH, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment-Ageing Times (Days)	4	10.7017	10.7017	2.6754	130.45	0.000
Water Content (%)	4	0.1186	0.1186	0.0297	1.45	0.236
Error	41	0.8409	0.8409	0.0205		
Total	49	11.6612				

S = 0.143209 R-Sq = 92.79% R-Sq (adj) = 91.38%

G.1.2 Statistics Analysis for Available Phosphorous

Descriptive Statistics: Available Phosphorous (ppm)

Variable	Sediment Aging Times (Days)						
	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Available Phosphorous	10	0	89.1	10.2	32.3	1041.1	36.22
	15	0	54.03	7.80	24.66	607.93	45.63
	30	0	134.8	21.8	68.8	4734.9	51.06
	45	0	164.3	23.7	75.1	5633.8	45.68
	60	0	145.9	32.5	102.9	10581.3	70.52

Variable	Sediment Aging Times (Days)				
	Minimum	Median	Maximum	Range	
Available Phosphorous	28.2	100.9	118.1	89.9	
	15.26	51.95	92.32	77.06	
	16.6	138.5	209.8	193.2	
	102.5	127.9	313.6	211.1	
	5.17	146.5	273.5	268.3	

Descriptive Statistics: Available Phosphorous (ppm)

Variable	Water Content (%)						
	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Available Phosphorous	10	0	194.5	28.3	89.6	8029.6	46.06
	97.09	0	141.6	19.4	61.4	3766.6	43.34
	97.82	0	67.2	14.4	45.6	2081.1	67.85
	98.08	0	97.4	14.6	46.1	2125.7	47.32
	98.15	0	87.2	20.3	64.2	4116.1	73.55

Variable	Water Content (%)				
	Minimum	Median	Maximum	Range	
Available Phosphorous	74.6	206.1	313.6	239.0	
	50.0	138.5	256.1	206.1	
	15.3	76.1	118.3	103.0	
	28.2	113.4	152.1	123.9	
	5.17	76.5	198.7	193.5	

General Linear Model: Available Phosphorous (ppm) versus Sediment Aging (Days) and Water Content (%)

Factor	Type	Levels	Values
Sediment-Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	5	95.84, 97.09, 97.82, 98.08, 98.15

Analysis of Variance for Phosphorous Available (ppm), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment Aging Times (Days)	4	81298	81298	20324	8.35	0.000
Water Content (%)	4	103617	103617	25904	10.64	0.000
Error	41	99774	99774	2434		
Total	49	284689				

S = 49.3307 R-Sq = 64.95% R-Sq(adj) = 58.11%

G.1.3 Statistics Analysis for Dissolved Oxygen

Descriptive Statistics: Dissolved Oxygen (mg/L)

Variable	Water Content (%)		Mean	SE Mean	StDev	Variance	CoefVar	
	N	N*						
Dissolved Oxygen	95.84	10	0	0.2200	0.0389	0.1229	0.0151	55.88
	97.09	10	0	0.3200	0.0359	0.1135	0.0129	35.48
	97.82	10	0	1.290	0.588	1.860	3.459	144.17
	98.08	10	0	0.2600	0.0400	0.1265	0.0160	48.65
	98.15	10	0	0.580	0.247	0.780	0.608	134.49

Variable	Water Content (%)				
	Minimum	Median	Maximum	Range	
Dissolved Oxygen	95.84	0.1000	0.2000	0.4000	0.3000
	97.09	0.1000	0.3000	0.5000	0.4000
	97.82	0.100	0.350	5.400	5.300
	98.08	0.1000	0.3000	0.4000	0.3000
	98.15	0.100	0.200	2.400	2.300

Descriptive Statistics: Dissolved Oxygen (mg/L)

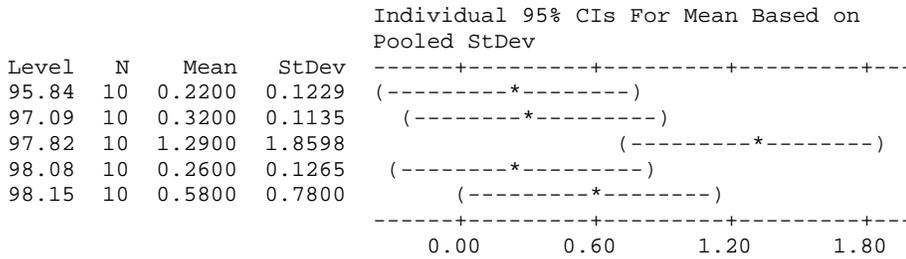
Variable	Sediment Aging Times (Days)		Mean	SE Mean	StDev	Variance	CoefVar	
	N	N*						
Dissolved Oxygen	1	10	0	0.2000	0.0258	0.0816	0.00667	40.82
	15	10	0	0.440	0.170	0.538	0.289	122.25
	30	10	0	1.190	0.582	1.839	3.383	154.57
	45	10	0	0.2900	0.0277	0.0876	0.00767	30.19
	60	10	0	0.550	0.250	0.792	0.627	144.00

Variable	Sediment Aging Times (Days)				
	Minimum	Median	Maximum	Range	
Dissolved Oxygen	1	0.1000	0.2000	0.3000	0.2000
	15	0.100	0.400	1.900	1.800
	30	0.200	0.400	5.400	5.200
	45	0.1000	0.3000	0.4000	0.3000
	60	0.100	0.250	2.400	2.300

One-way ANOVA: Dissolved Oxygen (mg/L) versus Water Content (%)

Source	DF	SS	MS	F	P
Water Content (%)	4	7.931	1.983	2.41	0.063
Error	45	37.001	0.822		
Total	49	44.932			

S = 0.9068 R-Sq = 17.65% R-Sq(adj) = 10.33%

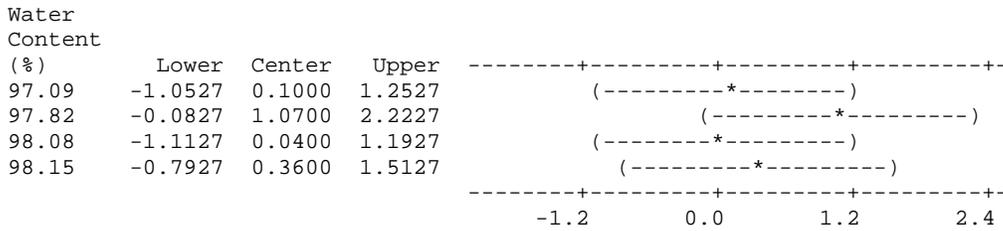


Pooled StDev = 0.9068

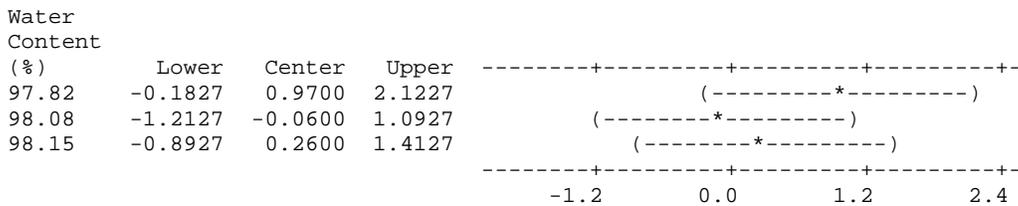
Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of Water Content (%)

Individual confidence level = 99.33%

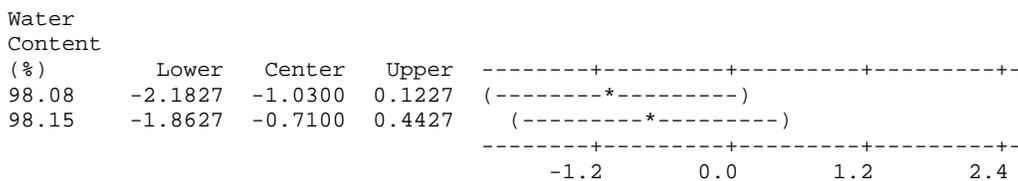
Water Content (%) = 95.84 subtracted from:



Water Content (%) = 97.09 subtracted from:



Water Content (%) = 97.82 subtracted from:



Descriptive Statistics: Total Solid (mg total solid/L)

Variable	Sediment Aging Times (Days)		N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Total Solid	1		10	0	42000	5538	17512	306666667	41.70
	15		10	0	33000	4955	15670	245555556	47.49
	30		10	0	24000	4269	13499	182222222	56.25
	45		10	0	31000	3480	11005	121111111	35.50
	60		10	0	27000	4230	13375	178888889	49.54

Variable	Sediment Aging Times (Days)		Minimum	Median	Maximum	Range
Total Solid	1		20000	40000	60000	40000
	15		10000	30000	60000	50000
	30		10000	20000	50000	40000
	45		20000	30000	50000	30000
	60		10000	30000	40000	30000

General Linear Model: Total Solid (mg total solid/L) versus Sediment Aging Times and Water Contents (%)

Factor	Type	Levels	Values
Sediment Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	5	95.84, 97.09, 97.82, 98.08, 98.15

Analysis of Variance for Total Solid (mg total solid/L), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F
Sediment Aging Times (Days)	4	1892000000	1892000000	473000000	2.55
Water Content (%)	4	1692000000	1692000000	423000000	2.28
Error	41	7618000000	7618000000	185804878	
Total	49	11202000000			

Source	P
Sediment Ageing Times (Days)	0.054
Water Content (%)	0.077
Error	
Total	

S = 13631.0 R-Sq = 31.99% R-Sq(adj) = 18.72%

G.1.5 Statistics Analysis for Total Volatile Solid

Descriptive Statistics: Total Volatile Solid (mg volatile solid/ L)

Variable	Sediment Aging Times (Days)		N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Total Volatile Solid	1		10	0	22000	4667	14757	217777778	67.08
	15		10	0	20000	2981	9428	88888889	47.14
	30		10	0	14000	3055	9661	93333333	69.01
	45		10	0	16000	2211	6992	48888889	43.70
	60		10	0	14000	2211	6992	48888889	49.94

Sediment Aging Times					
Variable	(Days)	Minimum	Median	Maximum	Range
Total Volatile	1	0.000000000	20000	40000	40000
Solid	15	10000	20000	40000	30000
	30	10000	10000	40000	30000
	45	10000	15000	30000	20000
	60	0.000000000	15000	20000	20000

Descriptive Statistics: Total Volatile Solid (mg volatile solid/ L)

Water Content								
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Total Volatile	95.84	10	0	20000	3333	10541	111111111	52.70
Solid	97.09	10	0	13000	2134	6749	45555556	51.92
	97.82	10	0	15000	3416	10801	116666667	72.01
	98.08	10	0	21000	3786	11972	143333333	57.01
	98.15	10	0	17000	3000	9487	90000000	55.80

Water Content					
Variable	(%)	Minimum	Median	Maximum	Range
Total Volatile	95.84	0.000000000	20000	40000	40000
Solid	97.09	0.000000000	10000	20000	20000
	97.82	0.000000000	10000	40000	40000
	98.08	10000	20000	40000	30000
	98.15	10000	15000	40000	30000

General Linear Model: Total Volatile Solid versus Sediment Aging Times (Days) and Water Contents (%)

Factor	Type	Levels	Values
Sediment Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	5	95.84, 97.09, 97.82, 98.08, 98.15

Analysis of Variance for Total Volatile Solid (mg volati, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F
Sediment Aging Times (Days)	4	528000000	528000000	132000000	1.34
Water Content (%)	4	448000000	448000000	112000000	1.14
Error	41	4032000000	4032000000	98341463	
Total	49	5008000000			

Source	P
Sediment Aging Times (Days)	0.271
Water Content (%)	0.352
Error	
Total	

S = 9916.73 R-Sq = 19.49% R-Sq(adj) = 3.78%

G.1.6 Statistics Analysis for Total Kjeldahl Nitrogen

Descriptive Statistics: Total Kjeldahl Nitrogen (%)

Variable	Water Content (%)		N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Total Kjeldahl Nitrogen	95.84		10	0	0.12698	0.00817	0.02585	0.000668	20.35
	97.09		10	0	0.08499	0.00719	0.02273	0.000517	26.75
	97.82		10	0	0.0551	0.0139	0.0438	0.00192	79.51
	98.08		10	0	0.06432	0.00406	0.01283	0.000165	19.95
	98.15		10	0	0.05939	0.00816	0.02579	0.000665	43.42

Variable	Water Content (%)				
	Minimum	Median	Maximum	Range	
Total Kjeldahl Nitrogen	95.84	0.07903	0.12281	0.17575	0.09672
	97.09	0.06323	0.08120	0.12772	0.06449
	97.82	0.0125	0.0423	0.1277	0.1152
	98.08	0.04561	0.06140	0.09210	0.04649
	98.15	0.02956	0.05907	0.10543	0.07586

Descriptive Statistics: Total Kjeldahl Nitrogen (%)

Variable	Sediment Aging Times (Days)		N	N*	Mean	SE Mean	StDev	Variance
Total Kjeldahl Nitrogen	1		10	0	0.09163	0.00961	0.03040	0.000924
	15		10	0	0.05379	0.00861	0.02724	0.000742
	30		10	0	0.0720	0.0122	0.0385	0.00149
	45		10	0	0.0832	0.0101	0.0319	0.00102
	60		10	0	0.0903	0.0160	0.0507	0.00257

Variable	Sediment Aging Times (Days)					
	CoefVar	Minimum	Median	Maximum	Range	
Total Kjeldahl Nitrogen	1	33.18	0.05913	0.08445	0.12772	0.06859
	15	50.64	0.01581	0.05351	0.10850	0.09269
	30	53.56	0.0125	0.0666	0.1187	0.1063
	45	38.34	0.0546	0.0732	0.1438	0.0892
	60	56.10	0.0337	0.0860	0.1758	0.1420

General Linear Model: Total Kjeldahl Nitrogen (%) versus Sediment Aging Times (Days) and Water Contents (%)

Factor	Type	Levels	Values
Sediment Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	5	95.84, 97.09, 97.82, 98.08, 98.15

Analysis of Variance for Total kjeldahl Nitrogen (%), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment Aging Times (Days)	4	0.0098619	0.0098619	0.0024655	3.95	0.008
Water Content (%)	4	0.0350357	0.0350357	0.0087589	14.04	0.000
Error	41	0.0255696	0.0255696	0.0006236		
Total	49	0.0704671				

S = 0.0249729 R-Sq = 63.71% R-Sq(adj) = 56.63%

G.2 Preliminary Test

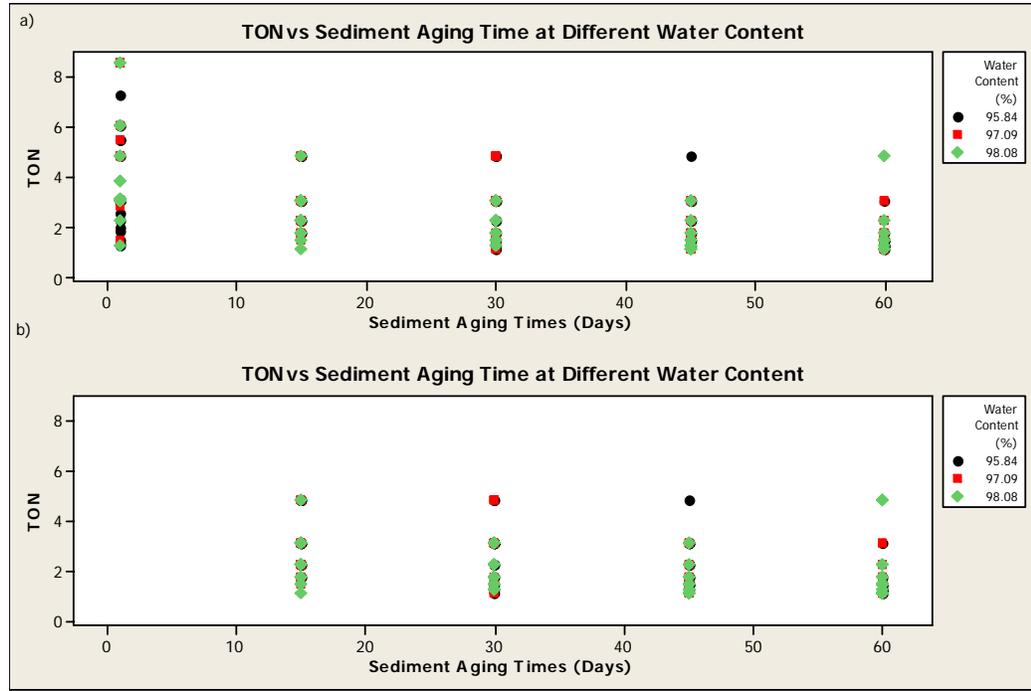


Figure G.2. 1: TON values for a) all odor threshold quantifications and b) 15 to 60 days of aging

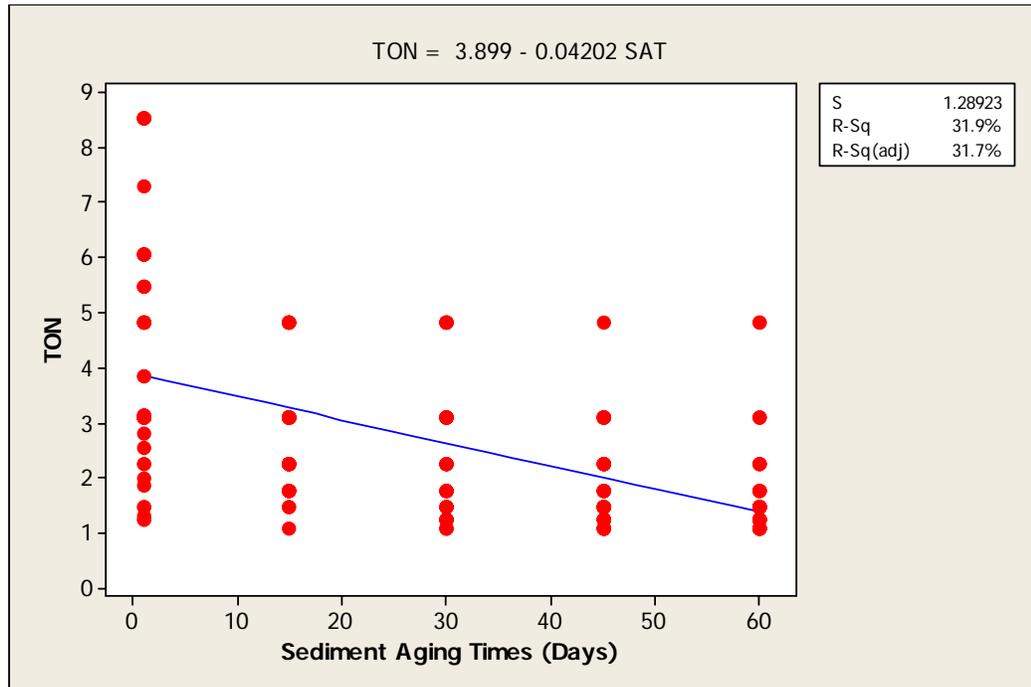


Figure G.2. 2: Relation TON vs Sediment Aging Times

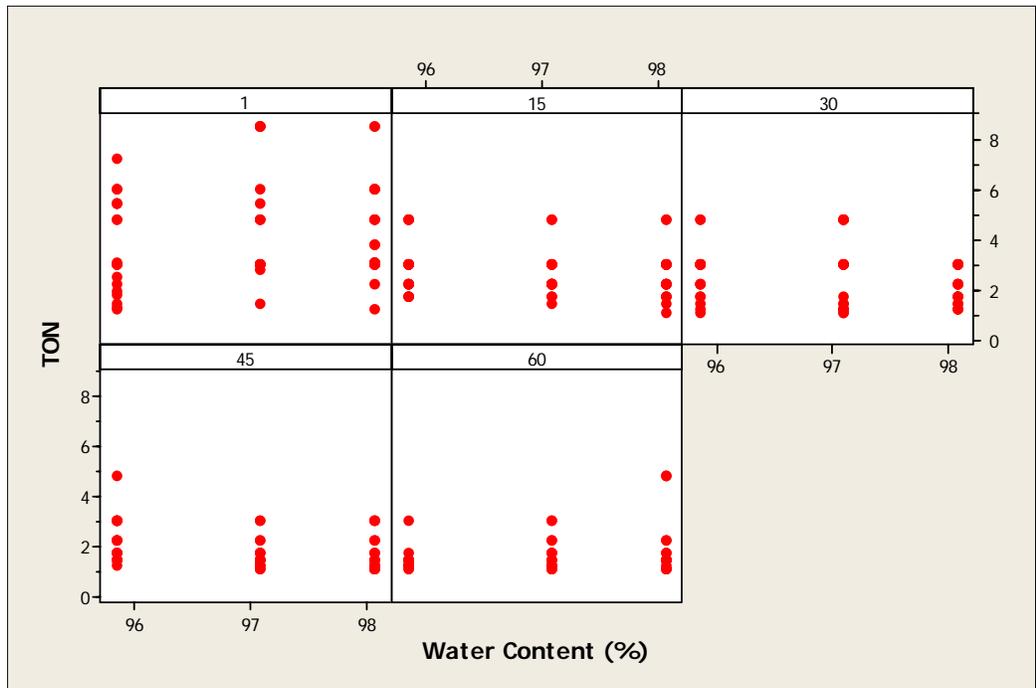


Figure G.2. 3: TON vs Water Contents at different Sediment Aging Times

G.3 Statistics Analysis for TON Tests

G.3.1 Descriptive Analysis for TON Data

Descriptive Statistics: TON

		Sediment Aging Time								
Variable	(Days)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar	Minimum	
TON	1	60	0	4.302	0.272	2.107	4.439	48.97	1.259	
	15	60	0	2.773	0.127	0.981	0.963	35.38	1.106	
	30	60	0	2.574	0.145	1.121	1.256	43.54	1.106	
	45	60	0	1.871	0.101	0.780	0.609	41.71	1.106	
	60	60	0	1.6292	0.0991	0.7674	0.5889	47.10	1.1060	

		Sediment Aging Time		
Variable	(Days)	Median	Maximum	Range
TON	1	3.130	8.566	7.307
	15	2.270	4.856	3.750
	30	2.685	4.856	3.750
	45	1.476	4.856	3.750
	60	1.4760	4.856	3.750

Descriptive Statistics: TON

		Water Content								
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar	Minimum	
TON	95.84	100	0	2.627	0.135	1.352	1.827	51.45	1.106	
	97.09	100	0	2.726	0.181	1.806	3.260	66.24	1.106	
	98.08	100	0	2.537	0.150	1.497	2.242	59.03	1.106	

		Water Content				
Variable	(%)	Q1	Median	Q3	Maximum	Range
TON	95.84	1.476	2.270	3.099	7.306	6.200
	97.09	1.476	2.270	3.099	8.566	7.460
	98.08	1.476	2.270	3.099	8.566	7.460

Descriptive Statistics: TON

Results for Sediment Aging Time (Days) = 1

		Water Content								
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar	Minimum	
TON	95.84	20	0	3.697	0.412	1.843	3.396	49.84	1.259	
	97.09	20	0	4.904	0.540	2.416	5.836	49.27	1.476	
	98.08	20	0	4.306	0.435	1.946	3.786	45.19	1.259	

		Water Content		
Variable	(%)	Median	Maximum	Range
TON	95.84	3.099	7.306	6.047
	97.09	3.978	8.566	7.090
	98.08	3.503	8.566	7.307

Results for Sediment Aging Time (Days) = 15

		Water Content							
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar	Minimum
TON	95.84	20	0	2.981	0.243	1.086	1.178	36.42	1.787
	97.09	20	0	2.689	0.199	0.891	0.794	33.13	1.476
	98.08	20	0	2.648	0.218	0.974	0.948	36.76	1.106

		Water Content		
Variable	(%)	Median	Maximum	Range
TON	95.84	3.099	4.856	3.069
	97.09	2.270	4.856	3.380
	98.08	2.270	4.856	3.750

Results for Sediment Aging Time (Days) = 30

		Water Content							
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar	Minimum
TON	95.84	20	0	2.746	0.225	1.005	1.010	36.59	1.106
	97.09	20	0	2.743	0.330	1.476	2.178	53.80	1.106
	98.08	20	0	2.233	0.163	0.727	0.529	32.57	1.259

		Water Content		
Variable	(%)	Median	Maximum	Range
TON	95.84	3.099	4.856	3.750
	97.09	3.099	4.856	3.750
	98.08	2.270	3.099	1.840

Results for Sediment Aging Time (Days) = 45

		Water Content							
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar	Minimum
TON	95.84	20	0	2.261	0.200	0.895	0.802	39.60	1.259
	97.09	20	0	1.676	0.131	0.588	0.346	35.08	1.106
	98.08	20	0	1.676	0.159	0.710	0.504	42.36	1.106

		Water Content		
Variable	(%)	Median	Maximum	Range
TON	95.84	2.029	4.856	3.597
	97.09	1.476	3.099	1.993
	98.08	1.368	3.099	1.993

Results for Sediment Aging Time (Days) = 60

		Water Content							
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar	Minimum
TON	95.84	20	0	1.4489	0.0941	0.4209	0.1772	29.05	1.1060
	97.09	20	0	1.618	0.139	0.621	0.386	38.42	1.106
	98.08	20	0	1.821	0.244	1.092	1.192	59.96	1.106

		Water Content		
Variable	(%)	Median	Maximum	Range
TON	95.84	1.3675	3.0990	1.9930
	97.09	1.368	3.099	1.993
	98.08	1.476	4.856	3.750

G.3.2 Test for Equal Variance for TON Data

Test for Equal Variances: TON versus Sediment Aging Times (Days)

95% Bonferroni confidence intervals for standard deviations

Sediment Aging Time				
(Days)	N	Lower	StDev	Upper
1	60	1.69918	2.10695	2.74457
15	60	0.79122	0.98109	1.27800
30	60	0.90380	1.12069	1.45985
45	60	0.62935	0.78038	1.01655
60	60	0.61890	0.76742	0.99966

Bartlett's Test (normal distribution)
 Test statistic = 94.01, p-value = 0.000

Levene's Test (any continuous distribution)
 Test statistic = 14.13, p-value = 0.000

Test for Equal Variances: TON versus Water Content (%)

95% Bonferroni confidence intervals for standard deviations

Water Content				
(%)	N	Lower	StDev	Upper
95.84	100	1.15390	1.35151	1.62494
97.09	100	1.54158	1.80557	2.17087
98.08	100	1.27853	1.49748	1.80045

Bartlett's Test (normal distribution)
 Test statistic = 8.67, p-value = 0.013

Levene's Test (any continuous distribution)
 Test statistic = 1.01, p-value = 0.364

G.3.3 ANOVA Analysis for TON Data

ANOVA Analysis using all TON data

General Linear Model: TON versus Water Content (%) and Sediment Aging Times (Days)

Factor	Type	Levels	Values
Water Content (%)	fixed	3	95.84, 97.09, 98.08
Sediment Aging Times (Days)	fixed	5	1, 15, 30, 45, 60

Analysis of Variance for TON, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Water Content (%)	2	1.792	1.792	0.896	0.57	0.567
Sediment Aging Times (Days)	4	263.891	263.891	65.973	41.87	0.000
Error	293	461.691	461.691	1.576		
Total	299	727.374				

S = 1.25528 R-Sq = 36.53% R-Sq(adj) = 35.23%

ANOVA Analysis for TON excluding data of the first aging time

General Linear Model: TON versus Sediment Aging Times (Days), Water Content (%)

Factor	Type	Levels	Values
Sediment Aging Times (Days)	fixed	4	15, 30, 45, 60
Water Content (%)	fixed	3	95.84, 97.09, 98.08

Analysis of Variance for TON, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment Aging Times (Days)	3	54.091	54.091	18.030	21.24	0.000
Water Content (%)	2	2.914	2.914	1.457	1.72	0.182
Error	234	198.655	198.655	0.849		
Total	239	255.660				

S = 0.921385 R-Sq = 22.30% R-Sq(adj) = 20.64%

G.4 Statistic Analysis for H₂S Concentrations

G.4.1 Descriptive Statistics for H₂S Concentrations

Descriptive Statistics: H₂S Concentration (ppm)

Sediment Aging Time							
Variable	(Days)	N	N*	Mean	SE Mean	StDev	Variance
Concentration	1	60	0	0.05203	0.00811	0.06279	0.00394
	15	60	0	0.01318	0.00194	0.01507	0.000227
	30	60	0	0.000333	0.000146	0.001130	0.00000128
	45	60	0	0.000550	0.000155	0.001199	0.00000144
	60	60	0	0.001617	0.000245	0.001896	0.00000360

Sediment Aging Time					
Variable	(Days)	CoefVar	Minimum	Median	Maximum
Concentration	1	120.67	0.000000000	0.02850	0.23000
	15	114.28	0.000000000	0.00700	0.06800
	30	338.99	0.000000000	0.000000000	0.005000
	45	218.04	0.000000000	0.000000000	0.005000
	60	117.30	0.000000000	0.001000	0.006000

Sediment Aging Time		
Variable	(Days)	Range
Concentration	1	0.23000
	15	0.06800
	30	0.005000
	45	0.005000
	60	0.006000

Descriptive Statistics: H₂S Concentration (ppm)

Water Content							
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance
Concentration	95.84	100	0	0.00824	0.00229	0.02295	0.000527
	97.09	100	0	0.02000	0.00471	0.04712	0.00222
	98.08	100	0	0.01239	0.00294	0.02937	0.000862

Water Content							
Variable	(%)	CoefVar	Minimum	Median	Maximum	Range	
Concentration	95.84	278.50	0.000000000	0.000000000	0.16000	0.16000	
	97.09	235.59	0.000000000	0.000000000	0.20000	0.20000	
	98.08	237.01	0.000000000	0.00200	0.23000	0.23000	

Descriptive Statistics: H₂S Concentration (ppm)

Results for Sediment Aging Time (Days) = 1

Water Content								
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Concentration	95.84	20	0	0.02875	0.00964	0.04312	0.00186	149.98
	97.09	20	0	0.0903	0.0157	0.0703	0.00495	77.93
	98.08	20	0	0.0371	0.0124	0.0556	0.00309	149.93

Variable	Water Content (%)	Minimum	Median	Maximum	Range
Concentration	95.84	0.000000000	0.01400	0.16000	0.16000
	97.09	0.000000000	0.0970	0.2000	0.2000
	98.08	0.000000000	0.0200	0.2300	0.2300

Results for Sediment Aging Time (Days) = 15

Variable	Water Content (%)	N	N*	Mean	SE Mean	StDev	Variance
Concentration	95.84	20	0	0.01120	0.00342	0.01532	0.000235
	97.09	20	0	0.00720	0.00210	0.00937	0.0000879
	98.08	20	0	0.02115	0.00370	0.01654	0.000274

Variable	Water Content (%)	CoefVar	Minimum	Median	Maximum	Range
Concentration	95.84	136.75	0.000000000	0.00650	0.06800	0.06800
	97.09	130.18	0.000000000	0.00400	0.03600	0.03600
	98.08	78.22	0.000000000	0.01700	0.05500	0.05500

Results for Sediment Aging Time (Days) = 30

Variable	Water Content (%)	N	N*	Mean	SE Mean	StDev
Concentration	95.84	20	0	0.000000000	0.000000000	0.000000000
	97.09	20	0	0.000850	0.000393	0.001755
	98.08	20	0	0.000150	0.000150	0.000671

Variable	Water Content (%)	Variance	CoefVar	Minimum	Median
Concentration	95.84	0.000000000	*	0.000000000	0.000000000
	97.09	0.00000308	206.52	0.000000000	0.000000000
	98.08	0.000000450	447.21	0.000000000	0.000000000

Variable	Water Content (%)	Maximum	Range
Concentration	95.84	0.000000000	0.000000000
	97.09	0.005000	0.005000
	98.08	0.003000	0.003000

Results for Sediment Aging Time (Days) = 45

Variable	Water Content (%)	N	N*	Mean	SE Mean	StDev	Variance
Concentration	95.84	20	0	0.000800	0.000388	0.001735	0.00000301
	97.09	20	0	0.000250	0.000123	0.000550	0.000000303
	98.08	20	0	0.000600	0.000222	0.000995	0.000000989

Variable	Water Content (%)	CoefVar	Minimum	Median	Maximum
Concentration	95.84	216.89	0.000000000	0.000000000	0.005000
	97.09	220.05	0.000000000	0.000000000	0.002000
	98.08	165.79	0.000000000	0.000000000	0.003000

Variable	Water Content (%)	Range
Concentration	95.84	0.005000
	97.09	0.002000
	98.08	0.003000

Results for Sediment Aging Time (Days) = 60

Variable	Water Content (%)	N	N*	Mean	SE Mean	StDev	Variance
Concentration	95.84	20	0	0.000450	0.000276	0.001234	0.00000152
	97.09	20	0	0.001450	0.000438	0.001959	0.00000384
	98.08	20	0	0.002950	0.000352	0.001572	0.00000247

Variable	Water Content (%)	CoefVar	Minimum	Median	Maximum
Concentration	95.84	274.31	0.000000000	0.000000000	0.004000
	97.09	135.13	0.000000000	0.000000000	0.006000
	98.08	53.29	0.001000	0.003000	0.006000

Variable	Water Content (%)	Range
Concentration	95.84	0.004000
	97.09	0.006000
	98.08	0.005000

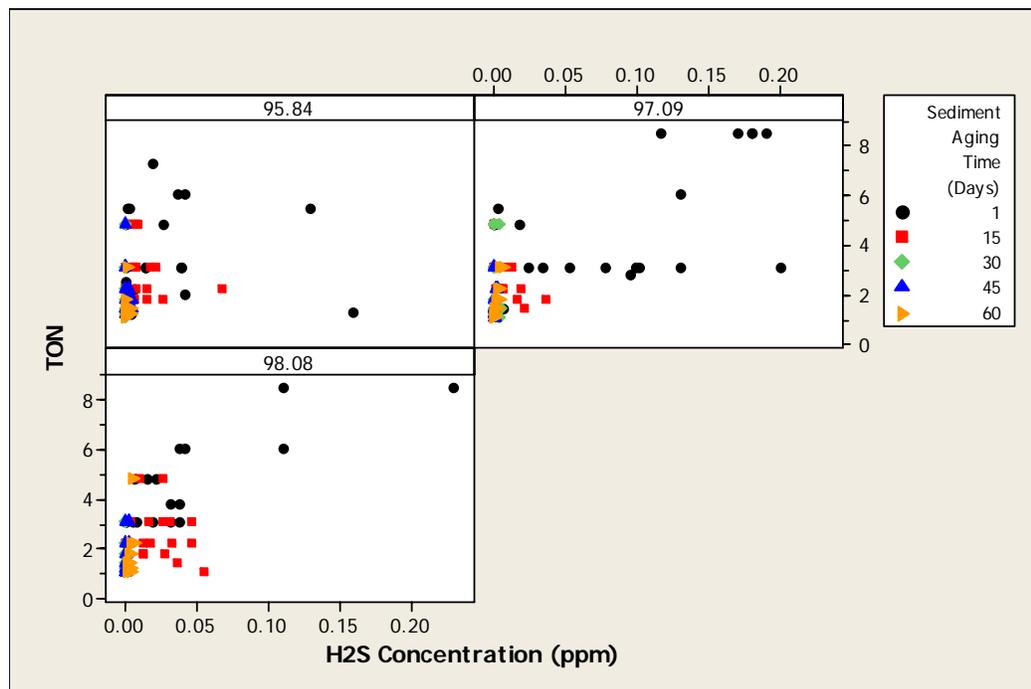


Figure G.4. 1: TON vs H₂S Concentration at different Water Contents and Sediment Aging Times

Descriptive Statistics: H₂S Concentration (ppm)

Results for Sediment Aging Time (Days) = 1

Variable	TON	N	N*	Mean	SE Mean	StDev	Variance
Concentration	1.259	2	0	0.00200	0.00200	0.00283	0.00000800
	1.333	1	0	0.16000	*	*	*
	1.476	2	0	0.00300	0.00300	0.00424	0.0000180
	1.865	1	0	0.000000000	*	*	*
	2.000	1	0	0.042000	*	*	*
	2.270	2	0	0.00300	0.00300	0.00424	0.0000180
	2.563	1	0	0.000000000	*	*	*
	2.835	1	0	0.095000	*	*	*
	3.099	17	0	0.0518	0.0131	0.0542	0.00293
	3.130	4	0	0.01075	0.00691	0.01382	0.000191
	3.875	2	0	0.03500	0.00300	0.00424	0.0000180
	4.856	8	0	0.01063	0.00369	0.01045	0.000109
	5.488	4	0	0.0343	0.0319	0.0638	0.00408
	6.086	6	0	0.0663	0.0172	0.0421	0.00177
	7.306	1	0	0.019000	*	*	*
8.566	7	0	0.1680	0.0160	0.0422	0.00178	

Variable	TON	CoefVar	Minimum	Median	Maximum
Concentration	1.259	141.42	0.000000000	0.00200	0.00400
	1.333	*	0.16000	0.16000	0.16000
	1.476	141.42	0.000000000	0.00300	0.00600
	1.865	*	0.000000000	0.000000000	0.000000000
	2.000	*	0.042000	0.042000	0.042000
	2.270	141.42	0.000000000	0.00300	0.00600
	2.563	*	0.000000000	0.000000000	0.000000000
	2.835	*	0.095000	0.095000	0.095000
	3.099	104.53	0.000000000	0.0380	0.2000
	3.130	128.53	0.000000000	0.00600	0.03100
	3.875	12.12	0.03200	0.03500	0.03800
	4.856	98.32	0.000000000	0.01050	0.02600
	5.488	186.40	0.00100	0.00300	0.1300
	6.086	63.49	0.0360	0.0420	0.1300
	7.306	*	0.019000	0.019000	0.019000
8.566	25.12	0.1100	0.1800	0.2300	

Variable	TON	Range
Concentration	1.259	0.00400
	1.333	0.000000000
	1.476	0.00600
	1.865	0.000000000
	2.000	0.000000000
	2.270	0.00600
	2.563	0.000000000
	2.835	0.000000000
	3.099	0.2000
	3.130	0.03100
	3.875	0.00600
	4.856	0.02600
	5.488	0.1290
	6.086	0.0940
	7.306	0.000000000
8.566	0.1200	

Results for Sediment Aging Time (Days) = 15

Variable	TON	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Concentration	1.106	1	0	0.055000	*	*	*	*
	1.476	2	0	0.02850	0.00750	0.01061	0.000112	37.22
	1.787	9	0	0.01767	0.00341	0.01023	0.000105	57.93
	2.270	20	0	0.01285	0.00395	0.01767	0.000312	137.49
	3.099	20	0	0.01040	0.00286	0.01278	0.000163	122.88
	4.856	8	0	0.00688	0.00308	0.00872	0.0000761	126.91

Variable	TON	Minimum	Median	Maximum	Range
Concentration	1.106	0.055000	0.055000	0.055000	0.000000000
	1.476	0.02100	0.02850	0.03600	0.01500
	1.787	0.00600	0.01500	0.03600	0.03000
	2.270	0.000000000	0.00600	0.06800	0.06800
	3.099	0.000000000	0.00600	0.04700	0.04700
	4.856	0.000000000	0.00450	0.02600	0.02600

Results for Sediment Aging Time (Days) = 30

Variable	TON	N	N*	Mean	SE Mean	StDev
Concentration	1.106	3	0	0.00267	0.00133	0.00231
	1.259	8	0	0.000000000	0.000000000	0.000000000
	1.476	5	0	0.00100	0.00100	0.00224
	1.787	7	0	0.000429	0.000429	0.001134
	2.270	7	0	0.000000000	0.000000000	0.000000000
	3.099	23	0	0.000000000	0.000000000	0.000000000
4.856	7	0	0.000571	0.000571	0.001512	

Variable	TON	Variance	CoefVar	Minimum	Median
Concentration	1.106	0.00000533	86.60	0.000000000	0.00400
	1.259	0.000000000	*	0.000000000	0.000000000
	1.476	0.00000500	223.61	0.000000000	0.000000000
	1.787	0.00000129	264.58	0.000000000	0.000000000
	2.270	0.000000000	*	0.000000000	0.000000000
	3.099	0.000000000	*	0.000000000	0.000000000
4.856	0.00000229	264.58	0.000000000	0.000000000	

Variable	TON	Maximum	Range
Concentration	1.106	0.00400	0.00400
	1.259	0.000000000	0.000000000
	1.476	0.00500	0.00500
	1.787	0.003000	0.003000
	2.270	0.000000000	0.000000000
	3.099	0.000000000	0.000000000
4.856	0.004000	0.004000	

Results for Sediment Aging Time (Days) = 45

Variable	TON	N	N*	Mean	SE Mean	StDev	Variance
Concentration	1.106	9	0	0.000333	0.000167	0.000500	0.000000250
	1.259	8	0	0.000125	0.000125	0.000354	0.000000125
	1.476	15	0	0.000400	0.000335	0.001298	0.00000169
	1.787	9	0	0.001111	0.000655	0.001965	0.00000386
	2.270	8	0	0.000875	0.000350	0.000991	0.000000982
	3.099	10	0	0.000600	0.000400	0.001265	0.00000160
	4.856	1	0	0.000000000	*	*	*

Variable	TON	CoefVar	Minimum	Median	Maximum
Concentration	1.106	150.00	0.000000000	0.000000000	0.001000
	1.259	282.84	0.000000000	0.000000000	0.001000
	1.476	324.59	0.000000000	0.000000000	0.005000
	1.787	176.85	0.000000000	0.000000000	0.005000
	2.270	113.26	0.000000000	0.000500	0.002000
	3.099	210.82	0.000000000	0.000000000	0.003000
	4.856	*	0.000000000	0.000000000	0.000000000

Variable	TON	Range
Concentration	1.106	0.001000
	1.259	0.001000
	1.476	0.005000
	1.787	0.005000
	2.270	0.002000
	3.099	0.003000
	4.856	0.000000000

Results for Sediment Aging Time (Days) = 60

Variable	TON	N	N*	Mean	SE Mean	StDev
Concentration	1.106	12	0	0.000917	0.000434	0.001505
	1.259	14	0	0.000571	0.000388	0.001453
	1.476	19	0	0.001316	0.000325	0.001416
	1.787	6	0	0.002667	0.000715	0.001751
	2.270	4	0	0.004000	0.000816	0.001633
	3.099	3	0	0.00367	0.00145	0.00252
	4.856	2	0	0.005000	0.000000000	0.000000000

Variable	TON	Variance	CoefVar	Minimum	Median
Concentration	1.106	0.00000227	164.19	0.000000000	0.000000000
	1.259	0.00000211	254.20	0.000000000	0.000000000
	1.476	0.00000201	107.64	0.000000000	0.001000
	1.787	0.00000307	65.67	0.000000000	0.003500
	2.270	0.00000267	40.82	0.002000	0.004000
	3.099	0.00000633	68.63	0.00100	0.00400
	4.856	0.000000000	0.00	0.005000	0.005000

Variable	TON	Maximum	Range
Concentration	1.106	0.004000	0.004000
	1.259	0.004000	0.004000
	1.476	0.004000	0.004000
	1.787	0.004000	0.004000
	2.270	0.006000	0.004000
	3.099	0.00600	0.00500
	4.856	0.005000	0.000000000

General Linear Model: Concentration versus Sediment Aging Times, Water Contents

Factor	Type	Levels	Values
Sediment Aging Time (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	3	95.84, 97.09, 98.08

Analysis of Variance for Concentration (ppm), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment Aging Time (Days)	4	0.118031	0.118031	0.029508	36.14	0.000
Water Content (%)	2	0.007114	0.007114	0.003557	4.36	0.014
Error	293	0.239263	0.239263	0.000817		
Total	299	0.364408				

S = 0.0285762 R-Sq = 34.34% R-Sq(adj) = 33.00%

G.5 Statistics Analysis for Average Data

G.5.1 Statistics Analysis for Average TON Data

Descriptive Statistics: Average TON

Sediment Aging Times								
Variable	(Days)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Average TON	1	3	0	4.303	0.348	0.603	0.364	14.02
	15	3	0	2.773	0.105	0.181	0.0329	6.54
	30	3	0	2.574	0.171	0.296	0.0874	11.49
	45	3	0	1.871	0.195	0.338	0.114	18.05
	60	3	0	1.629	0.108	0.186	0.0347	11.44

Sediment Aging Times					
Variable	(Days)	Minimum	Median	Maximum	Range
Average TON	1	3.698	4.306	4.904	1.206
	15	2.649	2.689	2.981	0.332
	30	2.233	2.743	2.747	0.514
	45	1.676	1.677	2.261	0.586
	60	1.449	1.618	1.821	0.372

Descriptive Statistics: Average TON

Water Content									
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar	Minimum
Average TON	95.84	5	0	2.627	0.375	0.838	0.702	31.89	1.449
	97.09	5	0	2.726	0.595	1.330	1.769	48.78	1.618
	98.08	5	0	2.537	0.474	1.059	1.122	41.76	1.676

Water Content				
Variable	(%)	Median	Maximum	Range
Average TON	95.84	2.747	3.698	2.248
	97.09	2.689	4.904	3.286
	98.08	2.233	4.306	2.631

General Linear Model: Average TON versus Sediment Aging Times (Days), Water Contents (%)

Factor	Type	Levels	Values
Sediment Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	3	95.84, 97.09, 98.08

Analysis of Variance for TON Average, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment AgingTimes (Days)	4	13.1949	13.1949	3.2987	22.43	0.000
Water Content (%)	2	0.0896	0.0896	0.0448	0.30	0.746
Error	8	1.1764	1.1764	0.1470		
Total	14	14.4609				

S = 0.383471 R-Sq = 91.86% R-Sq(adj) = 85.76%

G.5.2 Statistics Analysis for Average H₂S Concentrations

Descriptive Statistics: Average H₂S Concentration (ppm)

		Sediment Aging Times					
Variable	(Days)	N	N*	Mean	SE Mean	StDev	Variance
Concentration	1	3	0	0.0520	0.0193	0.0334	0.00111
	15	3	0	0.01318	0.00415	0.00718	0.0000516
	30	3	0	0.000333	0.000262	0.000454	0.00000206
	45	3	0	0.000550	0.000161	0.000278	7.75000E-08
	60	3	0	0.001617	0.000726	0.001258	0.00000158

		Sediment Aging Times			
Variable	(Days)	CoefVar	Minimum	Median	Maximum
Concentration	1	64.11	0.0288	0.0371	0.0903
	15	54.49	0.00720	0.01120	0.02115
	30	136.11	0.000000000	0.000150	0.000850
	45	50.62	0.000250	0.000600	0.000800
	60	77.83	0.000450	0.001450	0.002950

		Sediment Aging Times
Variable	(Days)	Range
Concentration	1	0.0615
	15	0.01395
	30	0.000850
	45	0.000550
	60	0.002500

Descriptive Statistics: Average H₂S Concentration (ppm)

		Water Content						
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Concentration	95.84	5	0	0.00824	0.00554	0.01238	0.000153	150.28
	97.09	5	0	0.0200	0.0176	0.0394	0.00155	196.85
	98.08	5	0	0.01239	0.00730	0.01632	0.000266	131.71

		Water Content			
Variable	(%)	Minimum	Median	Maximum	Range
Concentration	95.84	0.000000000	0.000800	0.02875	0.02875
	97.09	0.000250	0.00145	0.0903	0.0900
	98.08	0.000150	0.00295	0.03710	0.03695

General Linear Model: Average H₂S Concentration versus Sediment Aging Times (Days), Water Contents (%)

Factor	Type	Levels	Values
Sediment Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	3	95.84, 97.09, 98.08

Analysis of Variance for Concentration Average (ppm), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment Aging Times (Days)	4	0.0059016	0.0059016	0.0014754	5.97	0.016
Water Content (%)	2	0.0003557	0.0003557	0.0001779	0.72	0.516
Error	8	0.0019768	0.0019768	0.0002471		
Total	14	0.0082341				

S = 0.0157196 R-Sq = 75.99% R-Sq(adj) = 57.99%

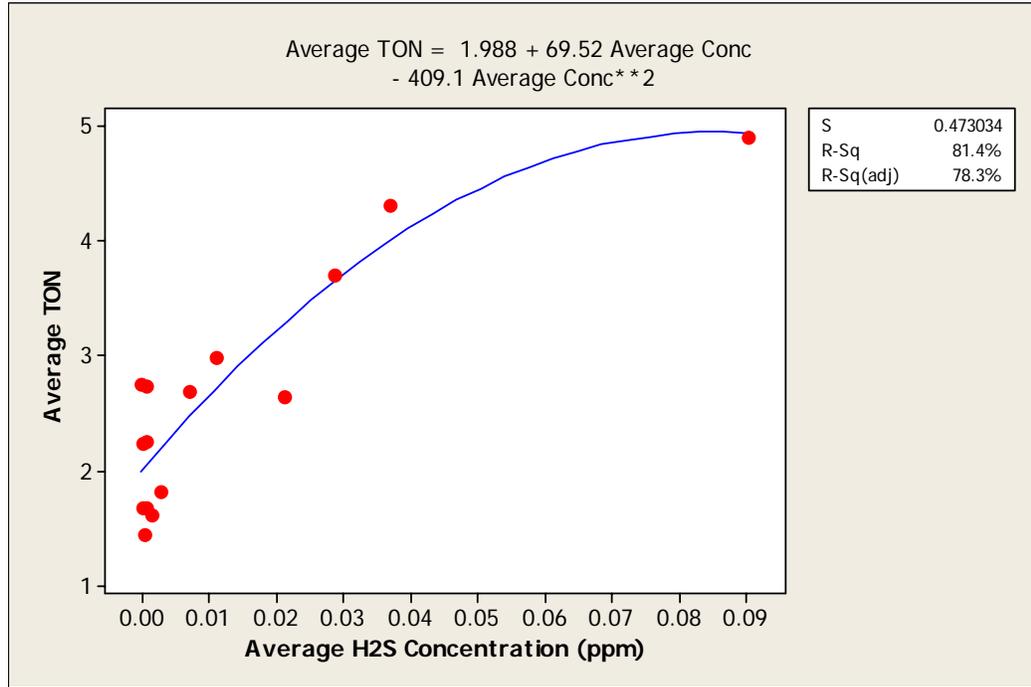


Figure G.5. 1: Average TON vs Average H₂S Concentration

G.5.3 Statistics Analysis for ED₅₀

Descriptive Statistics: ED₅₀

		Sediment AgingTimes						
Variable	(Days)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
ED 50	1	3	0	3.527	0.254	0.440	0.193	12.47
	15	3	0	2.546	0.276	0.479	0.229	18.80
	30	3	0	2.823	0.276	0.479	0.229	16.96
	45	3	0	1.624	0.205	0.354	0.126	21.82
	60	3	0	1.4040	0.0362	0.0626	0.00392	4.46
		Sediment AgingTimes						
Variable	(Days)	Minimum	Median	Maximum	Range			
ED 50	1	3.099	3.503	3.978	0.878			
	15	2.270	2.270	3.099	0.829			
	30	2.270	3.099	3.099	0.829			
	45	1.368	1.476	2.029	0.661			
	60	1.3678	1.3678	1.4763	0.1085			

Descriptive Statistics: ED₅₀

Variable	Water Content (%)		N	N*	Mean	SE Mean	StDev	Variance	CoefVar	Minimum
ED 50	95.84		5	0	2.539	0.359	0.802	0.643	31.60	1.368
	97.09		5	0	2.438	0.495	1.108	1.227	45.42	1.368
	98.08		5	0	2.177	0.382	0.855	0.730	39.24	1.368

Variable	Water Content (%)		Median	Maximum	Range
ED 50	95.84		3.099	3.099	1.732
	97.09		2.270	3.978	2.610
	98.08		2.270	3.503	2.135

General Linear Model: ED₅₀ versus Sediment Aging Times (Days) and Water Content (%)

Factor	Type	Levels	Values
Sediment AgingTimes (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	3	95.84, 97.09, 98.08

Analysis of Variance for ED 50, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment AgingTimes (Days)	4	9.1867	9.1867	2.2967	15.13	0.001
Water Content (%)	2	0.3481	0.3481	0.1741	1.15	0.365
Error	8	1.2147	1.2147	0.1518		
Total	14	10.7495				

S = 0.389663 R-Sq = 88.70% R-Sq(adj) = 80.22%

G.5.4 Statistics Analysis for Dilution₅₀

Descriptive Statistics: Dilution 50

Variable	Sediment AgingTimes (Days)		N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Dilution 50	1		3	0	0.2865	0.0206	0.0356	0.00127	12.44
	15		3	0	0.4012	0.0393	0.0681	0.00463	16.96
	30		3	0	0.3619	0.0393	0.0681	0.00463	18.80
	45		3	0	0.6338	0.0721	0.1249	0.0156	19.71
	60		3	0	0.7132	0.0179	0.0310	0.000962	4.35

Variable	Sediment AgingTimes (Days)		Minimum	Median	Maximum	Range
Dilution 50	1		0.2514	0.2855	0.3226	0.0713
	15		0.3226	0.4405	0.4405	0.1179
	30		0.3226	0.3226	0.4405	0.1179
	45		0.4929	0.6774	0.7311	0.2382
	60		0.6774	0.7311	0.7311	0.0537

Descriptive Statistics: Dilution 50

Variable	Water Content (%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Dilution 50	95.84	5	0	0.4384	0.0803	0.1795	0.0322	40.94
	97.09	5	0	0.4846	0.0950	0.2124	0.0451	43.83
	98.08	5	0	0.5150	0.0827	0.1849	0.0342	35.91

Variable	Water Content (%)	Minimum	Median	Maximum	Range
Dilution 50	95.84	0.3226	0.3226	0.7311	0.4084
	97.09	0.2514	0.4405	0.7311	0.4797
	98.08	0.2855	0.4405	0.7311	0.4456

General Linear Model: Dilution₅₀ versus Sediment Aging Times (Days), Water Contents (%)

Factor	Type	Levels	Values
Sediment Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	3	95.84, 97.09, 98.08

Analysis of Variance for Dilution 50, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment Aging Times (Days)	4	0.406794	0.406794	0.101698	20.69	0.000
Water Content (%)	2	0.014878	0.014878	0.007439	1.51	0.277
Error	8	0.039320	0.039320	0.004915		
Total	14	0.460992				

S = 0.0701071 R-Sq = 91.47% R-Sq(adj) = 85.07%

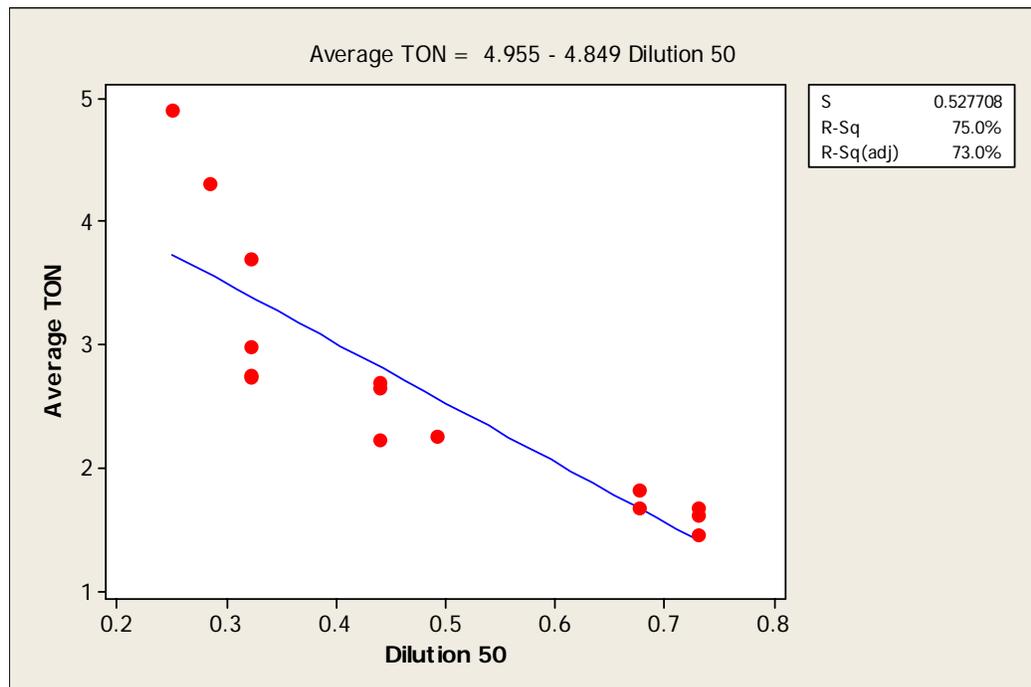


Figure G.5. 2: Relation Average TON vs Dilution₅₀

G.6 Odor Intensity

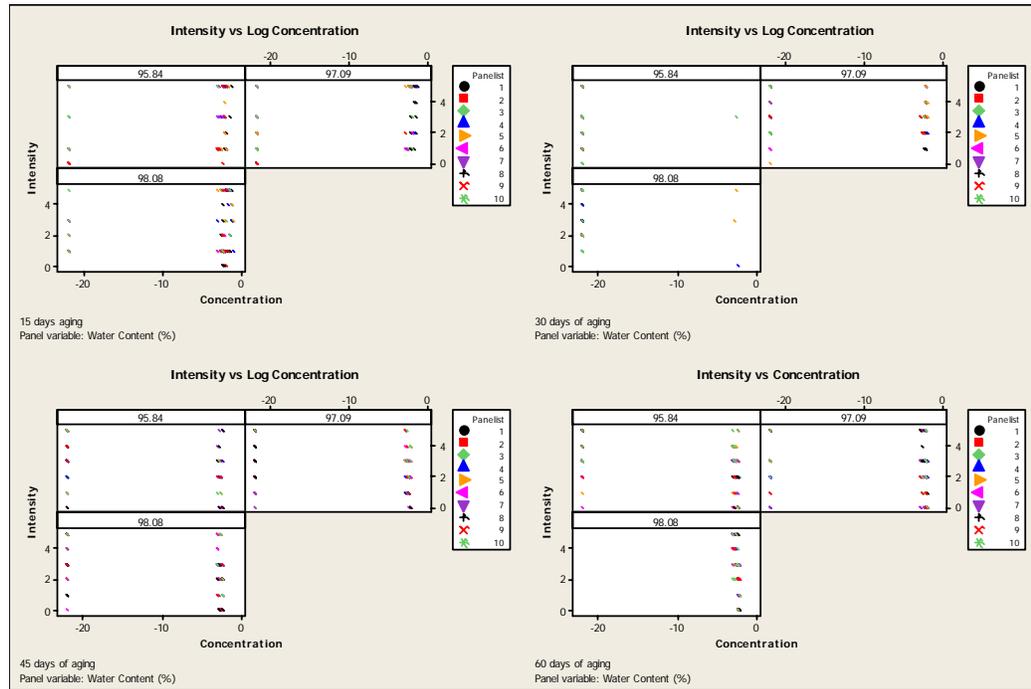


Figure G.6. 1: Behavior of Odor Intensity Test at 15 Days of Aging to 60 Days of Aging

G.7 Statistics Analysis for H₂S Flux Test

G.7.1 Statistics Analysis for Average H₂S Flux Test

Descriptive Statistics: Average Flux (moles H₂S/min)

Variable	Sediment Aging Times					
	(Days)	N	N*	Mean	SE Mean	StDev
Average Flux	1	16	0	0.000000266	6.65020E-08	0.000000266
	15	24	0	0.000000109	2.25602E-08	0.000000111
	30	44	0	2.46273E-08	7.73101E-09	5.12817E-08
	45	44	0	2.97459E-08	7.05050E-09	4.67678E-08
	60	45	0	1.54004E-08	1.11055E-08	7.44977E-08

Variable	Sediment Aging Times				
	(Days)	Variance	CoefVar	Minimum	Median
Average Flux	1	7.07604E-14	100.10	1.68202E-11	0.000000190
	15	1.22151E-14	101.14	0.000000000	8.39139E-08
	30	2.62981E-15	208.23	0.000000000	5.50127E-09
	45	2.18722E-15	157.22	0.000000000	1.35379E-08
	60	5.54991E-15	483.74	0.000000000	9.78279E-11

Variable	Sediment Aging Times		
	(Days)	Maximum	Range
Average Flux	1	0.00000103	0.00000103
	15	0.000000379	0.000000379
	30	0.000000235	0.000000235
	45	0.000000248	0.000000248
	60	0.000000490	0.000000490

Descriptive Statistics: Average Flux (moles H₂S/min)

Variable	Water Content (%)					
	(%)	N	N*	Mean	SE Mean	StDev
Average Flux	97.82	86	0	6.46787E-08	1.18055E-08	0.000000109
	98.15	87	0	5.05452E-08	1.50095E-08	0.000000140

Variable	Water Content (%)				
	(%)	Variance	CoefVar	Minimum	Median
Average Flux	97.82	1.19858E-14	169.27	0.000000000	9.41275E-09
	98.15	1.95997E-14	276.98	0.000000000	5.80464E-09

Variable	Water Content (%)		
	(%)	Maximum	Range
Average Flux	97.82	0.000000520	0.000000520
	98.15	0.00000103	0.00000103

Descriptive Statistics: Average Flux (moles H₂S/min)

		Flow Meter CA				
Variable	(mL/min)	N	N*	Mean	SE Mean	StDev
Average Flux	480.0	12	0	2.37722E-09	8.52368E-10	2.95269E-09
	868.0	13	0	2.72930E-09	1.30544E-09	4.70682E-09
	1145.0	12	0	2.83049E-09	1.22116E-09	4.23024E-09
	2117.0	12	0	1.67722E-08	1.13801E-08	3.94217E-08
	3285.0	20	0	0.000000133	5.49882E-08	0.000000246
	3780.0	12	0	2.69413E-08	2.02578E-08	7.01752E-08
	5131.0	16	0	6.72510E-08	3.12399E-08	0.000000125
	6977.0	20	0	7.50898E-08	2.32567E-08	0.000000104
	8894.5	16	0	5.12450E-08	1.84463E-08	7.37854E-08
	10812.0	20	0	9.00218E-08	3.34334E-08	0.000000150
22698.0	20	0	7.36735E-08	2.58529E-08	0.000000116	

		Flow Meter CA			
Variable	(mL/min)	Variance	CoefVar	Minimum	Median
Average Flux	480.0	8.71837E-18	124.21	2.10773E-12	1.18212E-09
	868.0	2.21541E-17	172.45	0.000000000	6.38105E-10
	1145.0	1.78949E-17	149.45	0.000000000	2.06476E-09
	2117.0	1.55407E-15	235.04	0.000000000	2.79361E-09
	3285.0	6.04741E-14	184.51	0.000000000	3.66234E-08
	3780.0	4.92457E-15	260.48	0.000000000	1.83965E-09
	5131.0	1.56149E-14	185.81	0.000000000	4.84361E-09
	6977.0	1.08174E-14	138.51	0.000000000	2.96904E-08
	8894.5	5.44428E-15	143.99	0.000000000	2.43771E-08
	10812.0	2.23558E-14	166.09	0.000000000	1.90273E-08
22698.0	1.33675E-14	156.93	0.000000000	2.33768E-08	

		Flow Meter CA	
Variable	(mL/min)	Maximum	Range
Average Flux	480.0	1.03293E-08	1.03272E-08
	868.0	1.30653E-08	1.30653E-08
	1145.0	1.52297E-08	1.52297E-08
	2117.0	0.000000138	0.000000138
	3285.0	0.00000103	0.00000103
	3780.0	0.000000248	0.000000248
	5131.0	0.000000379	0.000000379
	6977.0	0.000000359	0.000000359
	8894.5	0.000000239	0.000000239
	10812.0	0.000000620	0.000000620
22698.0	0.000000490	0.000000490	

One-way ANOVA: Average Flux (moles H₂S/min)

Source	DF	SS	MS	F	P
Sediment Aging Times	4	0.0000000	0.0000000	21.53	0.000
Error	168	0.0000000	0.0000000		
Total	172	0.0000000			

S = 0.0000001033 R-Sq = 33.89% R-Sq(adj) = 32.31%

				Individual 95% CIs For Mean Based on Pooled StDev			
Level	N	Mean	StDev	+-----+-----+-----+-----			
1	16	2.65736E-07	2.66008E-07	*			
15	24	1.09275E-07	1.10522E-07	*			
30	44	2.46273E-08	5.12817E-08	*			
45	44	2.97459E-08	4.67678E-08	*			
60	45	1.54004E-08	7.44977E-08	*			
				+-----+-----+-----+-----			
				0.000000	0.000010	0.000020	0.000030

Pooled StDev = 0.0000001033

Fisher 95% Individual Confidence Intervals
 All Pairwise Comparisons among Levels of Sediment Aging Times (Days)
 Simultaneous confidence level = 71.68%

Sediment Aging Times (Days) = 1 subtracted from:

Sediment Aging Times (Days)	Lower	Center	Upper
15	-2.22298E-07	-1.56461E-07	-9.06243E-08
30	-3.00660E-07	-2.41109E-07	-1.81557E-07
45	-2.95542E-07	-2.35990E-07	-1.76438E-07
60	-3.09711E-07	-2.50335E-07	-1.90960E-07

Sediment Aging Times (Days)	+-----+-----+-----+-----			
15	*			
30	*			
45	*			
60	*			
+-----+-----+-----+-----				
	0.000000	0.000010	0.000020	0.000030

Sediment Aging Times (Days) = 15 subtracted from:

Sediment Aging Times (Days)	Lower	Center	Upper
30	-1.36411E-07	-8.46473E-08	-3.28832E-08
45	-1.31293E-07	-7.95286E-08	-2.77645E-08
60	-1.45435E-07	-9.38741E-08	-4.23134E-08

Sediment Aging Times (Days)	+-----+-----+-----+-----			
30	*			
45	*			
60	*			
+-----+-----+-----+-----				
	0.000000	0.000010	0.000020	0.000030

Sediment Aging Times (Days) = 30 subtracted from:

Sediment Aging Times (Days)	Lower	Center	Upper
45	-3.83719E-08	5.11866E-09	4.86092E-08
60	-5.24751E-08	-9.22683E-09	3.40214E-08

Sediment Aging Times (Days)	Lower	Center	Upper
45	*		
60	*		

0.000000 0.000010 0.000020 0.000030

Sediment Aging Times (Days) = 45 subtracted from:

Sediment Aging Times (Days)	Lower	Center	Upper
60	-5.75937E-08	-1.43455E-08	2.89027E-08

Sediment Aging Times (Days)	Lower	Center	Upper
60	*		

0.000000 0.000010 0.000020 0.000030

One-way ANOVA: Average Flux (moles H₂S/min) versus Water Content (%)

Source	DF	SS	MS	F	P
Water Content (%)	1	0.0000000	0.0000000	0.55	0.461
Error	171	0.0000000	0.0000000		
Total	172	0.0000000			

S = 0.0000001258 R-Sq = 0.32% R-Sq(adj) = 0.00%

Level	N	Mean	StDev	Individual 95% CIs For Mean Based on Pooled StDev
97.82	86	6.46787E-08	1.09480E-07	*
98.15	87	5.05452E-08	1.39999E-07	*

0.000000 0.000010 0.000020 0.000030

Pooled StDev = 0.0000001258

Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of Water Content (%)

Individual confidence level = 95.00%

Water Content (%) = 97.82 subtracted from:

Water Content (%)	Lower	Center	Upper
98.15	-5.18805E-08	-1.41336E-08	2.36134E-08

Water Content (%)	Lower	Center	Upper
98.15	*	*	*

0.000000 0.000010 0.000020 0.000030

One-way ANOVA: Average Flux (moles de H2S/min) versus Flow Meter CA (mL/min)

Source	DF	SS	MS	F	P
Flow Meter CA (m	10	0.0000000	0.0000000	1.95	0.042
Error	162	0.0000000	0.0000000		
Total	172	0.0000000			

S = 0.0000001222 R-Sq = 10.76% R-Sq(adj) = 5.25%

Level	N	Mean	StDev
480.0	12	2.37722E-09	2.95269E-09
868.0	13	2.72930E-09	4.70682E-09
1145.0	12	2.83049E-09	4.23024E-09
2117.0	12	1.67722E-08	3.94217E-08
3285.0	20	1.33282E-07	2.45915E-07
3780.0	12	2.69413E-08	7.01752E-08
5131.0	16	6.72510E-08	1.24960E-07
6977.0	20	7.50898E-08	1.04007E-07
8894.5	16	5.12450E-08	7.37854E-08
10812.0	20	9.00218E-08	1.49519E-07
22698.0	20	7.36735E-08	1.15618E-07

Individual 95% CIs For Mean Based on Pooled StDev

Level	Lower	Upper
480.0	*	*
868.0	*	*
1145.0	*	*
2117.0	*	*
3285.0	*	*
3780.0	*	*
5131.0	*	*
6977.0	*	*
8894.5	*	*
10812.0	*	*
22698.0	*	*

0.000000 0.000010 0.000020 0.000030

Pooled StDev = 0.0000001222

Fisher 95% Individual Confidence Intervals
 All Pairwise Comparisons among Levels of Flow Meter CA (mL/min)
 Simultaneous confidence level = 33.34%

Flow Meter CA (mL/min) = 480.0 subtracted from:

Flow
Meter CA

(mL/min)	Lower	Center	Upper
868.0	-9.62867E-08	3.52085E-10	9.69909E-08
1145.0	-9.80994E-08	4.53270E-10	9.90059E-08
2117.0	-8.41577E-08	1.43950E-08	1.12948E-07
3285.0	4.27562E-08	1.30904E-07	2.19053E-07
3780.0	-7.39886E-08	2.45640E-08	1.23117E-07
5131.0	-2.73138E-08	6.48738E-08	1.57061E-07
6977.0	-1.54356E-08	7.27126E-08	1.60861E-07
8894.5	-4.33198E-08	4.88677E-08	1.41055E-07
10812.0	-5.03627E-10	8.76446E-08	1.75793E-07
22698.0	-1.68519E-08	7.12963E-08	1.59444E-07

Flow
Meter CA

(mL/min)	+	+	+	+
868.0	*			
1145.0	*			
2117.0	*			
3285.0	*			
3780.0	*			
5131.0	*			
6977.0	*			
8894.5	*			
10812.0	*			
22698.0	*			
	+	+	+	+
	0.000000	0.000010	0.000020	0.000030

Flow Meter CA (mL/min) = 868.0 subtracted from:

Flow
Meter CA

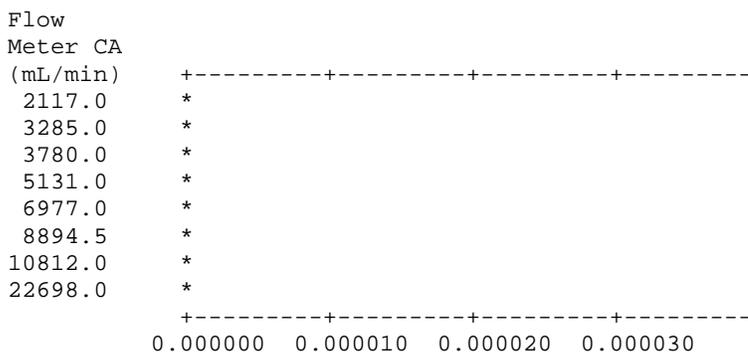
(mL/min)	Lower	Center	Upper
1145.0	-9.65376E-08	1.01185E-10	9.67400E-08
2117.0	-8.25959E-08	1.40429E-08	1.10682E-07
3285.0	4.45492E-08	1.30552E-07	2.16555E-07
3780.0	-7.24269E-08	2.42120E-08	1.20851E-07
5131.0	-2.56170E-08	6.45217E-08	1.54660E-07
6977.0	-1.36427E-08	7.23605E-08	1.58364E-07
8894.5	-4.16230E-08	4.85157E-08	1.38654E-07
10812.0	1.28933E-09	8.72925E-08	1.73296E-07
22698.0	-1.50590E-08	7.09442E-08	1.56947E-07

Flow
Meter CA

(mL/min)	+	+	+	+
1145.0	*			
2117.0	*			
3285.0	*			
3780.0	*			
5131.0	*			
6977.0	*			
8894.5	*			
10812.0	*			
22698.0	*			
	+	+	+	+
	0.000000	0.000010	0.000020	0.000030

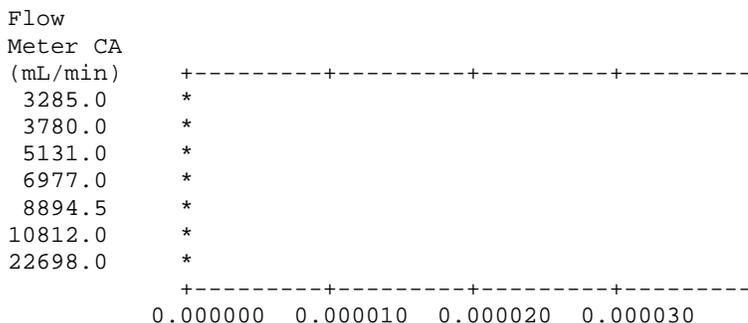
Flow Meter CA (mL/min) = 1145.0 subtracted from:

Flow Meter CA (mL/min)	Lower	Center	Upper
2117.0	-8.46109E-08	1.39417E-08	1.12494E-07
3285.0	4.23029E-08	1.30451E-07	2.18599E-07
3780.0	-7.44419E-08	2.41108E-08	1.22663E-07
5131.0	-2.77671E-08	6.44205E-08	1.56608E-07
6977.0	-1.58889E-08	7.22593E-08	1.60407E-07
8894.5	-4.37731E-08	4.84145E-08	1.40602E-07
10812.0	-9.56897E-10	8.71913E-08	1.75339E-07
22698.0	-1.73052E-08	7.08430E-08	1.58991E-07



Flow Meter CA (mL/min) = 2117.0 subtracted from:

Flow Meter CA (mL/min)	Lower	Center	Upper
3285.0	2.83612E-08	1.16509E-07	2.04658E-07
3780.0	-8.83836E-08	1.01691E-08	1.08722E-07
5131.0	-4.17088E-08	5.04788E-08	1.42666E-07
6977.0	-2.98306E-08	5.83176E-08	1.46466E-07
8894.5	-5.77148E-08	3.44728E-08	1.26660E-07
10812.0	-1.48986E-08	7.32496E-08	1.61398E-07
22698.0	-3.12469E-08	5.69013E-08	1.45049E-07



Flow Meter CA (mL/min) = 3285.0 subtracted from:

Flow Meter CA (mL/min)	Lower	Center	Upper
3780.0	-1.94489E-07	-1.06340E-07	-1.81922E-08
5131.0	-1.47000E-07	-6.60306E-08	1.49386E-08
6977.0	-1.34530E-07	-5.81918E-08	1.81467E-08
8894.5	-1.63006E-07	-8.20366E-08	-1.06737E-09
10812.0	-1.19598E-07	-4.32598E-08	3.30787E-08
22698.0	-1.35947E-07	-5.96081E-08	1.67304E-08

Flow Meter CA (mL/min)	+	+	+	+
3780.0	*			
5131.0	*			
6977.0	*			
8894.5	*			
10812.0	*			
22698.0	*			
	+	+	+	+
	0.000000	0.000010	0.000020	0.000030

Flow Meter CA (mL/min) = 3780.0 subtracted from:

Flow Meter CA (mL/min)	Lower	Center	Upper
5131.0	-5.18778E-08	4.03097E-08	1.32497E-07
6977.0	-3.99997E-08	4.81485E-08	1.36297E-07
8894.5	-6.78839E-08	2.43037E-08	1.16491E-07
10812.0	-2.50677E-08	6.30805E-08	1.51229E-07
22698.0	-4.14160E-08	4.67322E-08	1.34880E-07

Flow Meter CA (mL/min)	+	+	+	+
5131.0	*			
6977.0	*			
8894.5	*			
10812.0	*			
22698.0	*			
	+	+	+	+
	0.000000	0.000010	0.000020	0.000030

Flow Meter CA (mL/min) = 5131.0 subtracted from:

Flow Meter CA (mL/min)	Lower	Center	Upper
6977.0	-7.31305E-08	7.83879E-09	8.88081E-08
8894.5	-1.01355E-07	-1.60060E-08	6.93431E-08
10812.0	-5.81985E-08	2.27708E-08	1.03740E-07
22698.0	-7.45468E-08	6.42249E-09	8.73918E-08

```

Flow
Meter CA
(mL/min)  +-----+-----+-----+-----
 6977.0   *
 8894.5   *
10812.0   *
22698.0   *
          +-----+-----+-----+-----
          0.000000  0.000010  0.000020  0.000030

```

Flow Meter CA (mL/min) = 6977.0 subtracted from:

```

Flow
Meter CA
(mL/min)      Lower      Center      Upper
 8894.5  -1.04814E-07  -2.38448E-08  5.71245E-08
10812.0  -6.14066E-08   1.49320E-08  9.12706E-08
22698.0  -7.77549E-08  -1.41630E-09  7.49223E-08

```

```

Flow
Meter CA
(mL/min)  +-----+-----+-----+-----
 8894.5   *
10812.0   *
22698.0   *
          +-----+-----+-----+-----
          0.000000  0.000010  0.000020  0.000030

```

Flow Meter CA (mL/min) = 8894.5 subtracted from:

```

Flow
Meter CA
(mL/min)      Lower      Center      Upper
10812.0  -4.21925E-08   3.87768E-08  1.19746E-07
22698.0  -5.85408E-08   2.24285E-08  1.03398E-07

```

```

Flow
Meter CA
(mL/min)  +-----+-----+-----+-----
10812.0   *
22698.0   *
          +-----+-----+-----+-----
          0.000000  0.000010  0.000020  0.000030

```

Flow Meter CA (mL/min) = 10812.0 subtracted from:

```

Flow
Meter CA
(mL/min)      Lower      Center      Upper
22698.0  -9.26869E-08  -1.63483E-08  5.99903E-08

```

```

Flow
Meter CA
(mL/min)  +-----+-----+-----+-----
22698.0   *
          +-----+-----+-----+-----
          0.000000  0.000010  0.000020  0.000030

```

Descriptive Statistics: Average Flux/ Area

Variable	N	N*	Mean	SE Mean	StDev	Variance
Average Flux/ Ar	173	0	5.04970E-11	8.37526E-12	1.10159E-10	1.21351E-20

Variable	CoefVar	Minimum	Median	Maximum	Range
Average Flux/ Ar	218.15	0.000000000	5.18744E-12	9.07223E-10	9.07223E-10

Descriptive Statistics: Average Flux/ Area

Sediment Aging Times						
Variable	(Days)	N	N*	Mean	SE Mean	StDev
Average Flux/ Ar	1	16	0	2.33083E-10	5.83304E-11	2.33321E-10
	15	24	0	9.58473E-11	1.97881E-11	9.69415E-11
	30	44	0	2.16012E-11	6.78106E-12	4.49805E-11
	45	44	0	2.60909E-11	6.18417E-12	4.10212E-11
	60	45	0	1.35081E-11	9.74088E-12	6.53438E-11

Sediment Aging Times					
Variable	(Days)	Variance	CoefVar	Minimum	Median
Average Flux/ Ar	1	5.44389E-20	100.10	1.47534E-14	1.66644E-10
	15	9.39765E-21	101.14	0.000000000	7.36029E-11
	30	2.02324E-21	208.23	0.000000000	4.82529E-12
	45	1.68274E-21	157.22	0.000000000	1.18744E-11
	60	4.26981E-21	483.74	0.000000000	8.58071E-14

Sediment Aging Times			
Variable	(Days)	Maximum	Range
Average Flux/ Ar	1	9.07223E-10	9.07208E-10
	15	3.32617E-10	3.32617E-10
	30	2.06331E-10	2.06331E-10
	45	2.17428E-10	2.17428E-10
	60	4.29457E-10	4.29457E-10

Descriptive Statistics: Average Flux/ Area

Water Content						
Variable	(%)	N	N*	Mean	SE Mean	StDev
Average Flux/ Ar	97.82	86	0	5.67313E-11	1.03549E-11	9.60274E-11
	98.15	87	0	4.43343E-11	1.31651E-11	1.22796E-10

Water Content					
Variable	(%)	Variance	CoefVar	Minimum	Median
Average Flux/ Ar	97.82	9.22126E-21	169.27	0.000000000	8.25617E-12
	98.15	1.50789E-20	276.98	0.000000000	5.09138E-12

Water Content			
Variable	(%)	Maximum	Range
Average Flux/ Ar	97.82	4.55946E-10	4.55946E-10
	98.15	9.07223E-10	9.07223E-10

Descriptive Statistics: Average Flux/ Area

		Flow Rate CA				
Variable	(mL/min)	N	N*	Mean	SE Mean	StDev
Average Flux/ Ar	480.0	12	0	2.08512E-12	7.47632E-13	2.58987E-12
	868.0	13	0	2.39394E-12	1.14503E-12	4.12846E-12
	1145.0	12	0	2.48269E-12	1.07111E-12	3.71043E-12
	2117.0	12	0	1.47113E-11	9.98173E-12	3.45777E-11
	3285.0	20	0	1.16904E-10	4.82313E-11	2.15697E-10
	3780.0	12	0	2.36308E-11	1.77687E-11	6.15525E-11
	5131.0	16	0	5.89874E-11	2.74013E-11	1.09605E-10
	6977.0	20	0	6.58631E-11	2.03990E-11	9.12270E-11
	8894.5	16	0	4.49482E-11	1.61797E-11	6.47189E-11
	10812.0	20	0	7.89601E-11	2.93252E-11	1.31146E-10
22698.0	20	0	6.46208E-11	2.26763E-11	1.01411E-10	

		Flow Rate CA			
Variable	(mL/min)	Variance	CoefVar	Minimum	Median
Average Flux/ Ar	480.0	6.70745E-24	124.21	1.84874E-15	1.03686E-12
	868.0	1.70442E-23	172.45	0.000000000	5.59697E-13
	1145.0	1.37673E-23	149.45	0.000000000	1.81105E-12
	2117.0	1.19562E-21	235.04	0.000000000	2.45034E-12
	3285.0	4.65252E-20	184.51	0.000000000	3.21233E-11
	3780.0	3.78871E-21	260.48	0.000000000	1.61360E-12
	5131.0	1.20133E-20	185.81	0.000000000	4.24845E-12
	6977.0	8.32236E-21	138.51	0.000000000	2.60422E-11
	8894.5	4.18854E-21	143.99	0.000000000	2.13817E-11
	10812.0	1.71993E-20	166.09	0.000000000	1.66893E-11
22698.0	1.02843E-20	156.93	0.000000000	2.05042E-11	

		Flow Rate CA	
Variable	(mL/min)	Maximum	Range
Average Flux/ Ar	480.0	9.06008E-12	9.05823E-12
	868.0	1.14599E-11	1.14599E-11
	1145.0	1.33583E-11	1.33583E-11
	2117.0	1.20773E-10	1.20773E-10
	3285.0	9.07223E-10	9.07223E-10
	3780.0	2.17428E-10	2.17428E-10
	5131.0	3.32617E-10	3.32617E-10
	6977.0	3.14676E-10	3.14676E-10
	8894.5	2.09478E-10	2.09478E-10
	10812.0	5.43391E-10	5.43391E-10
22698.0	4.29457E-10	4.29457E-10	

G.7.2 Statistics Analysis for Zero Moment

Descriptive Statistics: Zero Moment

Variable	Sediment Aging Times (Days)							
		N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Moment Zero	1	16	0	152.7	70.6	282.2	79647.3	184.77
	15	24	0	24.31	7.95	38.94	1516.71	160.18
	30	44	0	1.868	0.922	6.115	37.393	327.38
	45	44	0	3.59	1.20	7.94	63.08	221.26
	60	45	0	0.553	0.370	2.484	6.173	448.94

Variable	Sediment Aging Times (Days)				
	Minimum	Median	Maximum	Range	
Moment Zero	1	0.00200	57.9	1114.0	1114.0
	15	0.000000000	7.32	165.91	165.91
	30	0.000000000	0.404	39.049	39.049
	45	0.000000000	0.767	39.68	39.68
	60	0.000000000	0.00200	16.056	16.056

Descriptive Statistics: Zero Moment

Variable	Water Content (%)							
		N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Moment Zero	97.82	86	0	13.96	5.87	54.46	2966.19	390.00
	98.15	87	0	24.0	13.2	123.1	15153.4	512.09

Variable	Water Content (%)				
	Minimum	Median	Maximum	Range	
Moment Zero	97.82	0.000000000	0.544	474.91	474.91
	98.15	0.000000000	0.325	1114.0	1114.0

Descriptive Statistics: Zero Moment

Variable	Flow Rate CA (mL/min)							
		N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Moment Zero (ppm)	480.0	12	0	3.34	1.76	6.10	37.22	182.78
	868.0	13	0	2.12	1.31	4.73	22.38	222.87
	1145.0	12	0	0.696	0.291	1.009	1.017	144.81
	2117.0	12	0	4.00	3.28	11.36	128.96	283.66
	3285.0	20	0	106.7	58.7	262.4	68860.8	245.96
	3780.0	12	0	2.61	2.24	7.77	60.39	297.84
	5131.0	16	0	16.1	10.5	42.2	1779.7	261.82
	6977.0	20	0	13.73	5.94	26.56	705.46	193.46
	8894.5	16	0	5.19	2.89	11.55	133.38	222.57
	10812.0	20	0	15.83	8.31	37.18	1382.23	234.89
	22698.0	20	0	3.56	1.72	7.71	59.38	216.43

Variable	Flow Rate CA (mL/min)	Minimum	Median	Maximum	Range
Moment Zero (ppm)	480.0	0.00100	0.684	21.53	21.53
	868.0	0.000000000	0.0610	16.06	16.06
	1145.0	0.000000000	0.491	3.570	3.570
	2117.0	0.000000000	0.240	39.68	39.68
	3285.0	0.000000000	5.28	1114.0	1114.0
	3780.0	0.000000000	0.0238	27.20	27.20
	5131.0	0.000000000	0.102	165.9	165.9
	6977.0	0.000000000	0.961	86.57	86.57
	8894.5	0.000000000	0.421	43.37	43.37
	10812.0	0.000000000	0.167	153.79	153.79
	22698.0	0.000000000	0.419	31.64	31.64

General Linear Model: Zero Moment versus Sediment Aging Times(Days), Water Content(%) and Flow Meter CA(mL/min)

Factor	Type	Levels	Values
Sediment Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	2	97.82, 98.15
Flow Meter CA (mL/min)	fixed	11	480.0, 868.0, 1145.0, 2117.0, 3285.0, 3780.0, 5131.0, 6977.0, 8894.5, 10812.0, 22698.0

Analysis of Variance for Moment Zero (ppm v)(min), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment Aging Times (Days)	4	325521	287034	71759	10.35	0.000
Water Content (%)	1	4578	4577	4577	0.66	0.418
Flow Meter CA (mL/min)	10	140587	140587	14059	2.03	0.034
Error	157	1089021	1089021	6936		
Total	172	1559706				

S = 83.2853 R-Sq = 30.18% R-Sq(adj) = 23.51%

G.7.3 Statistics Analysis for H₂S Mass

Descriptive Statistics: Hydrogen Sulfide Mass

Variable	Sediment Aging Times (Days)	N	N*	Mean	SE Mean	StDev
H ₂ S Mass	1	16	0	0.0000304	0.00000936	0.0000375
	15	24	0	0.00000598	0.00000166	0.00000812
	30	44	0	0.000000313	0.000000145	0.000000961
	45	44	0	0.000000411	0.000000130	0.000000860
	60	45	0	0.000000137	0.000000100	0.000000671

Sediment Aging Times					
Variable	(Days)	Variance	CoefVar	Minimum	Median
H ₂ S Mass	1	1.40301E-09	123.26	5.71885E-10	0.0000223
	15	6.59634E-11	135.93	0.000000000	0.00000270
	30	9.23180E-13	307.43	0.000000000	3.38890E-08
	45	7.39678E-13	209.26	0.000000000	0.000000110
	60	4.49815E-13	488.28	0.000000000	1.95656E-10

Sediment Aging Times			
Variable	(Days)	Maximum	Range
H ₂ S Mass	1	0.000150	0.000150
	15	0.0000349	0.0000349
	30	0.00000526	0.00000526
	45	0.00000421	0.00000421
	60	0.00000441	0.00000441

Descriptive Statistics: Hydrogen Sulfide Mass

Water Content (%)						
Variable	(%)	N	N*	Mean	SE Mean	StDev
H ₂ S Mass	97.82	86	0	0.00000287	0.000000914	0.00000848
	98.15	87	0	0.00000483	0.00000198	0.0000185

Water Content (%)					
Variable	(%)	Variance	CoefVar	Minimum	Median
H ₂ S Mass	97.82	7.19112E-11	294.97	0.000000000	7.38310E-08
	98.15	3.42377E-10	382.91	0.000000000	3.09713E-08

Water Content (%)			
Variable	(%)	Maximum	Range
H ₂ S Mass	97.82	0.0000639	0.0000639
	98.15	0.000150	0.000150

Descriptive Statistics: Hydrogen Sulfide Mass

Flow Rate CA (mL/min)						
Variable	(mL/min)	N	N*	Mean	SE Mean	StDev
H ₂ S Mass	480.0	12	0	6.56574E-08	3.46435E-08	0.000000120
	868.0	13	0	7.55135E-08	4.66781E-08	0.000000168
	1145.0	12	0	3.26822E-08	1.36619E-08	4.73263E-08
	2117.0	12	0	0.000000347	0.000000284	0.000000985
	3285.0	20	0	0.0000144	0.00000790	0.0000353
	3780.0	12	0	0.000000404	0.000000348	0.00000120
	5131.0	16	0	0.00000339	0.00000222	0.00000887
	6977.0	20	0	0.00000393	0.00000170	0.00000759
	8894.5	16	0	0.00000189	0.00000105	0.00000421
	10812.0	20	0	0.00000701	0.00000368	0.0000165
	22698.0	20	0	0.00000330	0.00000160	0.00000718

Variable	Flow Rate CA (mL/min)	Variance	CoefVar	Minimum	Median
H ₂ S Mass	480.0	1.44021E-14	182.78	1.96721E-11	1.34558E-08
	868.0	2.83250E-14	222.87	0.000000000	2.17000E-09
	1145.0	2.23978E-15	144.81	0.000000000	2.30408E-08
	2117.0	9.70801E-13	283.66	0.000000000	2.07796E-08
	3285.0	1.24814E-09	245.96	0.000000000	0.000000711
	3780.0	1.44933E-12	297.83	0.000000000	3.67930E-09
	5131.0	7.86981E-11	261.82	0.000000000	2.15018E-08
	6977.0	5.76804E-11	193.46	0.000000000	0.000000275
	8894.5	1.77237E-11	222.57	0.000000000	0.000000153
	10812.0	2.71401E-10	234.89	0.000000000	7.40002E-08
	22698.0	5.14858E-11	217.68	0.000000000	0.000000251

Variable	Flow Rate CA (mL/min)	Maximum	Range
H ₂ S Mass	480.0	0.000000424	0.000000423
	868.0	0.000000571	0.000000571
	1145.0	0.000000168	0.000000168
	2117.0	0.00000344	0.00000344
	3285.0	0.000150	0.000150
	3780.0	0.00000421	0.00000421
	5131.0	0.0000349	0.0000349
	6977.0	0.0000248	0.0000248
	8894.5	0.0000158	0.0000158
	10812.0	0.0000681	0.0000681
	22698.0	0.0000294	0.0000294

General Linear Model: Hydrogen Sulfide Mass versus Sediment Aging Times (Days), Water Content (%) and Flow Rate CA (mL/min)

Factor	Type	Levels	Values
Sediment Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	2	97.82, 98.15
Flow Rate CA (mL/min)	fixed	11	480.0, 868.0, 1145.0, 2117.0, 3285.0, 3780.0, 5131.0, 6977.0, 8894.5, 10812.0, 22698.0

Analysis of Variance for Moles of Hydrogen Sulfide, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment Aging Times (Days)	4	0.0000000	0.0000000	0.0000000	21.37	0.000
Water Content (%)	1	0.0000000	0.0000000	0.0000000	1.31	0.255
Flow Rate CA (mL/min)	10	0.0000000	0.0000000	0.0000000	1.21	0.291
Error	157	0.0000000	0.0000000	0.0000000		
Total	172	0.0000000				

S = 0.0000115316 R-Sq = 41.56% R-Sq(adj) = 35.97%

G.7.4 Statistics Analysis for First Moment

Descriptive Statistics: First Moment

		Sediment Aging Times							
Variable	(Days)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar	
First Moment	1	16	0	3471	2191	8764	76803459	252.50	
	15	24	0	213.8	83.6	409.5	167653.9	191.48	
	30	44	0	8.54	5.62	37.31	1392.13	437.03	
	45	44	0	16.80	6.42	42.59	1814.29	253.57	
	60	45	0	3.81	3.46	23.21	538.86	608.54	

		Sediment Aging Times			
Variable	(Days)	Minimum	Median	Maximum	Range
First Moment	1	0.0640	876	35695	35695
	15	0.000000000	26.6	1606.4	1606.4
	30	0.000000000	0.548	245.87	245.87
	45	0.000000000	1.88	196.39	196.39
	60	0.000000000	0.00300	155.83	155.83

Descriptive Statistics: First Moment

		Water Content						
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
First Moment	97.82	86	0	169.4	88.5	820.5	673250.2	484.36
	98.15	87	0	545	411	3834	14702574	704.05

		Water Content			
Variable	(%)	Minimum	Median	Maximum	Range
First Moment	97.82	0.000000000	1.35	6880.1	6880.1
	98.15	0.000000000	0.559	35695	35695

Descriptive Statistics: First Moment

		Flow Rate CA							
Variable	(mL/min)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar	
First Moment	480.0	12	0	24.0	16.1	55.9	3126.0	232.94	
	868.0	13	0	16.0	12.0	43.4	1883.8	272.02	
	1145.0	12	0	1.934	0.723	2.505	6.273	129.51	
	2117.0	12	0	16.8	14.6	50.5	2552.3	300.40	
	3285.0	20	0	2428	1788	7998	63961398	329.44	
	3780.0	12	0	8.12	7.29	25.24	637.27	310.88	
	5131.0	16	0	145	103	413	170806	284.70	
	6977.0	20	0	200	101	452	204083	225.51	
	8894.5	16	0	41.4	32.6	130.2	16960.1	314.39	
	10812.0	20	0	197	131	587	345145	298.89	
	22698.0	20	0	82.8	59.6	266.6	71086.5	321.84	

Variable	Flow Rate CA (mL/min)	Minimum	Median	Maximum	Range
First Moment	480.0	0.00200	1.46	196.4	196.4
	868.0	0.000000000	0.0260	155.8	155.8
	1145.0	0.000000000	1.227	8.192	8.192
	2117.0	0.000000000	0.454	176.2	176.2
	3285.0	0.000000000	14.4	35695	35695
	3780.0	0.000000000	0.00950	88.09	88.09
	5131.0	0.000000000	0.146	1606	1606
	6977.0	0.000000000	1.88	1476	1476
	8894.5	0.000000000	0.644	524.8	524.8
	10812.0	0.000000000	0.163	2555	2555
	22698.0	0.000000000	0.451	1194.6	1194.6

General Linear Model: First Moment versus Sediment Aging Times (Days), Water Content (%) and Flow Rate CA (mL/min)

Factor	Type	Levels	Values
Sediment Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	2	97.82, 98.15
Flow Rate CA (mL/min)	fixed	11	480.0, 868.0, 1145.0, 2117.0, 3285.0, 3780.0, 5131.0, 6977.0, 8894.5, 10812.0, 22698.0

Analysis of Variance for Moment One (ppm V) (min²), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment Aging Times (Days)	4	171667016	151360938	37840235	5.54	0.000
Water Content (%)	1	6223110	6223032	6223032	0.91	0.341
Flow Rate CA (mL/min)	10	77466631	77466631	7746663	1.13	0.340
Error	157	1072379764	1072379764	6830444		
Total	172	1327736521				

S = 2613.51 R-Sq = 19.23% R-Sq(adj) = 11.52%

G.7.5 Statistics Analysis for Average Time of Elution

Descriptive Statistics: Time of Elution (min)

Variable	Sediment Aging Times (Days)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Time of Elution	1	16	0	22.56	3.87	15.49	239.83	68.65
	15	24	0	4.898	0.832	4.074	16.599	83.17
	30	44	0	1.758	0.219	1.455	2.116	82.77
	45	44	0	2.306	0.281	1.865	3.478	80.89
	60	45	0	1.008	0.295	1.979	3.917	196.35

Sediment Aging Times					
Variable	(Days)	Minimum	Median	Maximum	Range
Time of Elution	1	3.28	18.93	55.97	52.70
	15	0.000000000	3.630	13.148	13.148
	30	0.000000000	1.673	6.296	6.296
	45	0.000000000	1.956	9.122	9.122
	60	0.000000000	0.279	9.705	9.705

Descriptive Statistics: Time of Elution (min)

Water Content								
Variable	(%)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Time of Elution	97.82	86	0	3.522	0.751	6.967	48.533	197.79
	98.15	87	0	4.595	0.932	8.692	75.547	189.18

Water Content					
Variable	(%)	Minimum	Median	Maximum	Range
Time of Elution	97.82	0.000000000	1.906	55.973	55.973
	98.15	0.000000000	1.984	44.217	44.217

Descriptive Statistics: Time of Elution (min)

Flow Rate CA								
Variable	(mL/min)	N	N*	Mean	SE Mean	StDev	Variance	CoefVar
Time of Elution	480.0	12	0	3.936	0.869	3.010	9.063	76.48
	868.0	13	0	2.460	0.762	2.747	7.543	111.63
	1145.0	12	0	2.014	0.392	1.357	1.841	67.38
	2117.0	12	0	1.769	0.372	1.290	1.664	72.94
	3285.0	20	0	6.72	1.84	8.23	67.68	122.47
	3780.0	12	0	1.017	0.335	1.160	1.345	114.04
	5131.0	16	0	2.536	0.860	3.440	11.833	135.66
	6977.0	20	0	6.52	2.36	10.57	111.72	162.16
	8894.5	16	0	2.251	0.757	3.029	9.175	134.59
	10812.0	20	0	2.97	1.03	4.59	21.06	154.60
	22698.0	20	0	8.26	3.74	16.73	279.93	202.60

Flow Rate CA					
Variable	(mL/min)	Minimum	Median	Maximum	Range
Time of Elution	480.0	0.0625	2.996	9.122	9.060
	868.0	0.000000000	2.188	9.705	9.705
	1145.0	0.000000000	2.405	3.594	3.594
	2117.0	0.000000000	1.852	4.441	4.441
	3285.0	0.000000000	3.84	32.04	32.04
	3780.0	0.000000000	0.489	3.238	3.238
	5131.0	0.000000000	1.401	11.718	11.718
	6977.0	0.000000000	2.22	36.32	36.32
	8894.5	0.000000000	1.480	12.102	12.102
	10812.0	0.000000000	0.973	16.61	16.61
	22698.0	0.000000000	0.894	55.97	55.97

General Linear Model: Time of Elution (min) versus Sediment Aging Times (Days), Water Content (%) and Flow Rate CA (mL/min)

Factor	Type	Levels	Values
Sediment Aging Times (Days)	fixed	5	1, 15, 30, 45, 60
Water Content (%)	fixed	2	97.82, 98.15
Flow Rate CA (mL/min)	fixed	11	480.0, 868.0, 1145.0, 2117.0, 3285.0, 3780.0, 5131.0, 6977.0, 8894.5, 10812.0, 22698.0

Analysis of Variance for Time of Travel (min), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sediment Aging Times (Days)	4	6279.94	5691.57	1422.89	56.65	0.000
Water Content (%)	1	53.06	52.18	52.18	2.08	0.151
Flow Rate CA (mL/min)	10	395.93	395.93	39.59	1.58	0.118
Error	157	3943.15	3943.15	25.12		
Total	172	10672.07				

S = 5.01155 R-Sq = 63.05% R-Sq(adj) = 59.52%

G.8 Statistics Analysis for H₂S Flux Test with a Water Layer

Descriptive Statistics: Average H₂S Flux (moles H₂S/ min)

Sediment Aging Times						
Variable	(Days)	N	N*	Mean	SE Mean	StDev
Average Flux	15	3	0	7.25886E-09	7.25886E-09	1.25727E-08
	30	2	0	0.000000000	0.000000000	0.000000000
	45	12	0	0.000000000	0.000000000	0.000000000
	60	8	0	2.52433E-11	2.52433E-11	7.13989E-11

Sediment Aging Times						
Variable	(Days)	Variance	CoefVar	Minimum	Q1	Q3
Average Flux	15	1.58073E-16	173.21	0.000000000	0.000000000	0.000000000
	30	0.000000000	*	0.000000000	*	*
	45	0.000000000	*	0.000000000	0.000000000	0.000000000
	60	5.09781E-21	282.84	0.000000000	0.000000000	0.000000000

Sediment Aging Times						
Variable	(Days)	Median	Q3	Maximum	Range	StDev
Average Flux	15	0.000000000	2.17766E-08	2.17766E-08	2.17766E-08	2.17766E-08
	30	0.000000000	*	0.000000000	0.000000000	0.000000000
	45	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000
	60	0.000000000	0.000000000	2.01947E-10	2.01947E-10	2.01947E-10

Descriptive Statistics: Average H₂S Flux (moles H₂S/ min)

Water Content (%)						
Variable	(%)	N	N*	Mean	SE Mean	StDev
Average Flux	97.82	11	0	1.97969E-09	1.97969E-09	6.56589E-09
	98.15	14	0	1.44248E-11	1.44248E-11	5.39725E-11

Water Content (%)						
Variable	(%)	Variance	CoefVar	Minimum	Q1	Q3
Average Flux	97.82	4.31109E-17	331.66	0.000000000	0.000000000	0.000000000
	98.15	2.91303E-21	374.17	0.000000000	0.000000000	0.000000000

Water Content (%)						
Variable	(%)	Median	Q3	Maximum	Range	StDev
Average Flux	97.82	0.000000000	0.000000000	2.17766E-08	2.17766E-08	2.17766E-08
	98.15	0.000000000	0.000000000	2.01947E-10	2.01947E-10	2.01947E-10

One-way ANOVA: Average H₂S Flux (moles H₂S/ min) versus Sediment Aging Times (Days)

Source	DF	SS	MS	F	P
Sediment Aging Times	3	0.0000000	0.0000000	3.07	0.050
Error	21	0.0000000	0.0000000		
Total	24	0.0000000			

S = 3.880244E-09 R-Sq = 30.50% R-Sq(adj) = 20.57%

				Individual 95% CIs For Mean Based on Pooled StDev			
Level	N	Mean	StDev	+-----+-----+-----+-----			
15	3	7.25886E-09	1.25727E-08	*			
30	2	0.00000E+00	0.00000E+00	*			
45	12	0.00000E+00	0.00000E+00	*			
60	8	2.52433E-11	7.13989E-11	*			
				+-----+-----+-----+-----			
				0.000000	0.000010	0.000020	0.000030

Pooled StDev = 0.000000003880

Fisher 95% Individual Confidence Intervals
 All Pairwise Comparisons among Levels of Sediment Aging Times (Days)

Simultaneous confidence level = 80.78%

Sediment Aging Times (Days) = 15 subtracted from:

Sediment Aging Times (Days)				
(Days)	Lower	Center	Upper	
30	-1.46252E-08	-7.25886E-09	1.07467E-10	
45	-1.24676E-08	-7.25886E-09	-2.05008E-09	
60	-1.26966E-08	-7.23362E-09	-1.77060E-09	

Sediment Aging Times (Days)				
(Days)	+-----+-----+-----+-----			
30	*			
45	*			
60	*			
+-----+-----+-----+-----				
	0.000000	0.000010	0.000020	0.000030

Sediment Aging Times (Days) = 30 subtracted from:

Sediment Aging Times (Days)				
(Days)	Lower	Center	Upper	
45	-6.16311E-09	0.00000E+00	6.16311E-09	
60	-6.35419E-09	2.52433E-11	6.40467E-09	

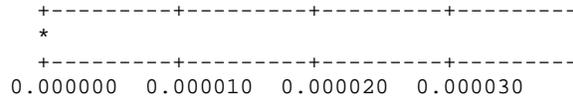
Sediment Aging Times (Days)				
(Days)	+-----+-----+-----+-----			
45	*			
60	*			
+-----+-----+-----+-----				
	0.000000	0.000010	0.000020	0.000030

Sediment Aging Times (Days) = 45 subtracted from:

Sediment Aging Times

(Days)	Lower	Center	Upper
60	-3.65792E-09	2.52433E-11	3.70841E-09

Sediment
Aging
Times
(Days)
60



G. 9 Statistics Analysis for the Effect of Water Layer

Descriptive Statistics: Average Flux (moles H₂S/ min)

Variable	Condition	N	N*	Mean	SE Mean	StDev
Average Flux	Sample	22	0	1.92275E-08	7.47191E-09	3.50464E-08
	Water Layer	22	0	9.99025E-10	9.89451E-10	4.64094E-09

Variable	Condition	Variance	CoefVar	Minimum	Q1
Average Flux	Sample	1.22825E-15	182.27	0.000000000	2.15544E-09
	Water Layer	2.15383E-17	464.55	0.000000000	0.000000000

Variable	Condition	Median	Q3	Maximum
Average Flux	Sample	4.47025E-09	1.45367E-08	0.000000138
	Water Layer	0.000000000	0.000000000	2.17766E-08

Variable	Condition	Range
Average Flux	Sample	0.000000138
	Water Layer	2.17766E-08

One-way ANOVA: Average Flux (moles H₂S/ min) versus Condition

Source	DF	SS	MS	F	P
Condition	1	0.0000000	0.0000000	6.15	0.017
Error	43	0.0000000	0.0000000		
Total	44	0.0000000			

S = 2.470594E-08 R-Sq = 12.51% R-Sq(adj) = 10.48%

Level	N	Mean	StDev
Sample	22	1.92275E-08	3.50464E-08
Water Layer	23	9.55589E-10	4.53902E-09

Individual 95% CIs For Mean Based on Pooled StDev

Level	Lower	Center	Upper
Sample	0.000000	0.000010	0.000020
Water Layer	0.000000	0.000010	0.000030

Pooled StDev = 0.0000002471

Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of Condition

Individual confidence level = 95.00%

Condition = Sample subtracted from:

Condition	Lower	Center	Upper
Water Layer	-3.31303E-08	-1.82719E-08	-3.41348E-09

Condition	Lower	Center	Upper
Water Layer	0.000000	0.000010	0.000020