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Predictive Modeling Of Sulfide Removal In Tray Aerators

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PREDICTIVE MODELING OF SULFIDE REMOVAL IN TRAY AERATORS

by

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A Thesis submitted in partial fulfillment of the requirements
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ABSTRACT

Hydrogen sulfide is commonly found in many Florida potable groundwater supplies. Removing sulfur species, particularly hydrogen sulfide is important because if left untreated, sulfide can impact finished water quality, corrosivity, create undesirable taste and odor, and oxidize to form visible turbidity and color. This document presents the results of a study designed to investigate the removal efficiencies of a variety of tray aerators in Central Florida in order to develop a predictive mathematical model that could be used to determine tray effectiveness for sulfide removal. A literature review was performed that indicated there was limited information regarding the removal of hydrogen sulfide using conventional tray aerators, and no information regarding the removal of total sulfide from tray aerators. There was significantly more information available in the literature regarding the usefulness of sulfide removal technologies from water supplies. Consequently, the lack of literature regarding sulfide removal using tray aerators suggested that there was a need for additional research focused on sulfide removal from water flowing thru tray aerators.

Several water purveyors that relied on tray aerators as a part of their water treatment operations were contacted and requested to participate in the study; three water purveyors agreed to allow the University of Central Florida (UCF) to enter their secured sites to collect samples and conduct this study. The three facilities included the UCF's water treatment plant located in Orlando and situated in eastern Orange County, the City of Lake Hamilton's water treatment plant located in west-central Polk County, and the Sarasota-Verna water treatment plant located in western Sarasota County.

An experimental plan was developed and field sampling protocols were implemented to evaluate sulfide removal in commonly used tray aerators at the three drinking water treatment facilities. Total

sulfide concentrations passing through the trays were determined in the field at each site using a standard iodometric analytical technique. In addition, other water quality parameters collected included dissolved oxygen, pH, temperature, conductivity, turbidity, alkalinity, hardness, total dissolved solids and total suspended solids; these samples were collected and analyzed either in the field or at the UCF laboratory.

A first-order empirical model was developed that predicted sulfide removal in tray aerators. The model's constant was evaluated with respect to the water's proton concentration $[H^+]$, the tray aerator's surface area, and hydraulic flow rate thru the trays. The selected model took the form of $C_n = C_0 (10^{-kn})$ where C_n is the sulfide remaining after aeration in mg/L, C_0 is the sulfide entering the distribution tray in mg/L, n is the number of tray stages in the aerator, and $k = (0.00248)(H^+)^{-0.397}(\text{Area})^{0.584}(\text{Flow})^{-1.17}$. From the empirical model, it was shown that sulfide removal was negatively impacted as the proton concentration (H^+) decreased, and flow increased. Conversely, it was observed that increased sulfide removal occurred as the available tray aerator surface area increased. The combined parameters of proton concentration, flow rate, and area were statistically evaluated and used to develop an empirical constant that could be used in a first order model to predict sulfide removal in tray aerators. Using a site-specific derived experimental (empirical) constant, a water purveyor could use the developed model from this work to accurately predict sulfide removal in a tray aerator by simply measuring the total sulfide content in any raw groundwater supply and then providing the desired number of tray stages available for treatment.

This thesis is dedicated to my parents, siblings and friends for all the love and support they have given me.

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LIST OF ACRONYMS AND ABBREVIATIONS

Alk	Alkalinity
APHA	American Public Health Association
ASCE	American Society of Civil Engineers
AWWA	American Water Works Association
°C	Centigrade, degree
Ca	Calcium
CAS	Chemical Abstract Service
CO ₂	Carbon Dioxide
DIC	Dissolved Inorganic Carbon
DO	Dissolved Oxygen
FDEP	Florida Department of Environmental Federation
gpm	Gallon Per Minute
GW	Groundwater
H ₂ S	Hydrogen sulfide
HS ⁻	Hydrogen bisulfide
k, k'	Experimental Constants
MCL	Minimum Contaminant Level
MDL	Method Detection Limit
Mg	Magnesium
Mgd	Million gallons per day
MSE	Mean Square Error
NTU	Number of Transfer Units

Pa	Pascal
ppm	Parts per million
R^2	R-squared (coefficient of variation)
RSD	Relative standard deviation
Sd	Standard deviation
SDWA	Safe Drinking Water Act
SSE	Sum of Squares of Error
S^0	Elemental or Colloidal Sulfur
SO_4^{2-}	Sulfate
Temp	Temperature
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
TRI	Toxic Release of Inventory
UCF	University of Central Florida
UCL	Upper control limit
UWL	Upper Warning limit
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound
WEF	Water Environmental Federation
WHO	World Health Organization
WTP	Water Treatment Plant

CHAPTER 1: INTRODUCTION

Overview

Hydrogen sulfide is commonly found in many Florida potable groundwater supplies. Removing sulfur species, particularly hydrogen sulfide is important because if left untreated, sulfide can create undesirable taste and odor, impact finished water quality including corrosiveness, and oxidize to form visible turbidity and color. Hydrogen sulfide is frequently found in ground water, with as little as 0.5 mg/L of hydrogen sulfide in potable water being noticeable and the odor imparted by 1.0 mg/L of hydrogen sulfide considered offensive (Lim, 1979; Varner *et al.*, 2004). The minimum detectable taste of sulfide in water is approximately 0.05 mg/L. Hydrogen sulfide has a molecular structure similar to that of water, and although sulfur is not as electronegative as oxygen, hydrogen sulfide does exhibit weak polar properties. The melting and boiling points of hydrogen sulfide are much lower than in water; as pure substances, water and hydrogen sulfide boil at 100°C and -60.7°C respectively.

Taste and odors in water supplies are attributed to different elements such as natural forces within the environment and the effect of human activities on the environment. Causes of tastes and odor in groundwater supplies are usually attributed to natural causes, as is the case for sulfide. Additionally, tastes and odor compounds can be caused by bacterial actions within the groundwater aquifers or the through the dissolution of salts and minerals as water percolates through the ground. The microbiological genera *Desulfovibrio* and *Desulfotomaculum* are known to accelerate the reduction of sulfate, and can be a major source of sulfide production in anaerobic environments (Garrels and Naeser, 1958). Odors, color, cloudiness, particulate matter, presence of microorganisms may be

noticed by consumers and can create concerns and complaints about the quality and acceptability of a drinking-water supply from a distribution system.

As indicated previously, as little as 0.5 ppm of hydrogen sulfide in water will cause odor that can be detected by most people; and at concentrations below 1 ppm can impart a "swampy" odor to water. At concentrations between 1 and 2 ppm of hydrogen sulfide in water, a "rotten egg" odor is exhibited and it can also affect the corrosivity of water (Lim, 1979; Varner *et al.*, 2004). Hydrogen sulfide is a common source of customer complaints for consumers of drinking water supplies originating from groundwater in central Florida. Sulfide will also cause significant residual chlorine demand on distributed water, which negatively impacts water quality, and can contribute to corrosion of residential copper tubing and other plumbing appurtenances. Tray aerators were a common selection for water treatment of groundwater because a water purveyor could achieve removal of carbon dioxide and hydrogen sulfide gases (Lochrane 1977, Duranceau *et al.*, 1999).

Tray aerators are usually either natural draft type or forced draft types, in which water in the trays to be treated flow down from the upper trays over the tray sides or weirs into the lower trays by force of gravity (MWH, 2005.) Multiple tray aerators are a series of trays stacked on top of each other over which water falls into collection basin at the bottom of the trays (Scott *et al.*, 1950). Tray aerators are used for taste and odor control primarily through the removal of hydrogen sulfide, in addition to the removal of other gases such as carbon dioxide (MWH, 2005).

Research Scope and Objective

The effectiveness of tray aerators for hydrogen sulfide removal from several Central Florida water treatment plants was evaluated in order to develop a predictive mathematical model that could be used to simulate treatment. The scope of work for this research project was confined to natural-draft cascade type tray aerators. The primary objective of this research was to:

1. Conduct a literature review on sulfide removal by aerators;
2. Identify candidate tray aerators for testing, and collecting hydraulic and physical configuration information regarding the trays;
3. Collect water samples to determine the sulfide content, as well as a few other key water quality parameters in tray aerator of differing configurations;
4. Evaluate overall tray aerator and individual tray efficiencies for sulfide removal ; and
5. Develop a predictive model of sulfide removal in tray aerators.

Three different water treatment facilities in Central Florida were selected for this investigation due to the differing tray aerator configurations they provided. The sites included the water treatment aeration trays at UCF, the aerator trays at the city of Lake Hamilton, Florida, and the aeration facilities at the Verna well field near Sarasota, Florida.

CHAPTER 2: LITERATURE REVIEW

Background

Sulfur Cycle

In order to understand how aeration can be used in reducing H₂S levels in groundwater supplies, an understanding of sulfur chemistry is required. Hydrogen sulfide is a one of the important component of the sulfur cycle and on Earth. As seen in Figure 2-1, sulfur-reducing and sulfate-reducing bacteria convert sulfur or sulfate to hydrogen sulfide. Other bacteria release hydrogen sulfide from amino acids that contain sulfur. Hydrogen sulfide serves a food source for many bacteria oxidizing the hydrogen sulfide to elemental sulfur, or to sulfate where dissolved oxygen, metal oxides (e.g. iron oxyhydroxides and manganese oxides) or nitrate serves as the oxidant (Jorgensen and Nelson, 2004).

The metabolism of species such as *Thiobacillus*, *Thermothrix*, *Thiotrix*, *Beggiato* has been investigated for the oxidation of inorganic (elemental sulfur, hydrogen sulfide, thiosulfate) or organic (methanethiol, dimethylsulfide, dimethyldisulfide) sulfur compounds (Stanier *et al.*, 1986). These microorganisms grow in soil, aquatic habitats, and activated sludge systems under different conditions (Prescott *et al.*, 2003; Postgate 1968).

Sulfates are biologically reduced sulfides by bacteria under anaerobic conditions as presented in Equations (2-1) and (2-2). The ionized state of hydrogen sulfide in groundwater is pH dependent (Faust and Osman, 1983).

Sanyer, McCarty and Parkin, 2003
Figure 2-1: Sulfur Cycle

Hydrogen Sulfide

According to the Hazardous Substances Data Bank (1998), “hydrogen sulfide (H_2S ; CAS No. 7783-06-4) is also known as hydrosulfuric acid, hydrogen sulfuric acid, sulfurated hydrogen, hepatic gas, stink damp, sulfur hydride, sulfurated hydrogen, dihydrogen monosulfide, dihydrogen sulfide, and sewer gas.” Its structural formula is illustrated as $\text{H}-\text{S}-\text{H}$.

Hydrogen sulfide is a colorless and flammable gas with a molecular weight of 34.08 and a vapor pressure of 1929 Pa at a temperature of 21.9 °C. It is soluble in water and other compounds; the solubility of water at 20 °C is 3.93g/L (Camp, 1965). At concentrations lower than 150 mg/m³ in the atmosphere, hydrogen sulfide possesses a deceptively sweet smell; and above 150 mg/m³, hydrogen sulfide affects the sense of smell. Hydrogen sulfide has an offensive "*rotten egg*" odor that is detectable at 8.0 µg/m³.

In water, the taste threshold for hydrogen sulfide in water is between 0.05 and 0.1 mg/liter. Hydrogen sulfide is not listed in the Toxics Release of Inventory (WHO, 1993; Patwardhan and Abhyankar, 1988; National Health and Welfare, 1978; WHO, 1987). The Henry's law constant for hydrogen sulfide at 20 °C is reported as 468 atm per mole fraction as published in the Agency for Toxic Substances and Disease Registry (1999). Even though the relationships of bacteria, algae, other vegetation, and actinomycetes are often interrelated in the production of tastes and odors, as documented by Silvey (1966) and Silvey *et al.*, (1973), there are cases where bacterial activity in aqueous mineral media can be the main causes of tastes and odors. For example, sulfur bacteria and iron bacteria have been responsible for tastes and odors in groundwater and water distribution systems based on different sources of (MacKenthun and Keup, 1973).

Hydrogen sulfide is formed when sulfides are hydrolyzed in water. H₂S dissociates, forming bisulfide (HS⁻) and sulfide ions (S²⁻) ions. Another potential cause of H₂S in water is water heater, which gives hot tap water a bad odor. Formation of hydrogen sulfide can occur by the reduction of sulfates in the water by sulfur bacteria, which can thrive in the warm environment of the hot water heater, or by reaction with the magnesium anode in the water heater (Minnesota Department of Health 2004).

Hydrogen Sulfide in Drinking Water

One of the more common odor problems in groundwater supplies is hydrogen sulfide (H₂S). It is frequently found in groundwater aquifers and sometimes at the bottom of reservoirs (Symons, 1979; Eunpu, 1973). When water moves through the aquifer in the ground, it is exposed to sulfates, and if the water is highly mineralized or there are decomposed materials, these compounds will react with the sulfates to form hydrogen sulfide (H₂S). Hydrogen sulfide (H₂S) gas is toxic at levels exceeding 10 ppm (Roth 1993). The odor threshold concentration of H₂S in water is less than 0.0001 mg/L, and odors from waters containing sulfide above 0.1 mg/L are considered offensive (Lochrane, 1979; Pomeroy and Cruze, 1969).

Hydrogen sulfide dissociates in water according to Equations (2-3) through (2-4):

As seen in Figure 2-2, at pH of about 7, fifty percent of hydrogen sulfide exists as H₂S gas and is available for stripping, so that pH adjustment is normally used to improve removal efficiency. At higher pH of 10, S²⁻ would be the dominant species, thereby preventing the stripping out of H₂S from water. The pK_{a1} for hydrogen sulfide is 6.99, such that the gas can be completely removed at pH values below the pK_{a1} without the formation of turbidity (elemental sulfur). In water that is well aerated with oxygen, hydrogen sulfide is readily oxidized to sulfates and elemental sulfur, while under anaerobic conditions; there is microbial reduction of sulfate to sulfide (Mance *et al.*, 1988).

Oxidation and aeration are effective for controlling hydrogen sulfide, but the effectiveness of these treatment options depends on the hydrogen sulfide concentration and the pH in the water (Sammons, 1959; Dell'Orco *et al.*, 1998; Cotrino *et al.*, 2007). Incomplete chemical reactions in this process, and oxidation of H_2S with oxygen with oxide catalysts, are often responsible for formation of polysulfide complexes and elemental sulfur, which manifest themselves as turbidity in the finished water (Lyn and Taylor 1993; Kovalenko, 2001).

The pH of Florida's groundwater is usually between 7.2 to 7.8 units. In this range approximately fifty to sixty percent of the sulfide present is in the species form of HS^- . HS^- is not volatile and as such it cannot be removed by aeration at high pH values. For effective removal of H_2S , the pH must first be lowered to about a pH of 6. A drawback with this approach to water treatment is that in addition to removing H_2S , the aeration process will also strip form of carbon dioxide from the water, thereby reducing alkalinity in the water. This action results in a finished water that may contribute to the corrosivity of metallic plumbing components. The aerated water must be post-treated for corrosion control and disinfected prior to distribution to the consumer (Duranceau, 2010a). The oxygen content of finished water can impart corrosiveness to the water (AWWA, 1990).

Hydrogen Sulfide Removal from Drinking Water Supplies

Many studies evaluating the removal of hydrogen sulfide from drinking water supplies have been conducted over the years (Cotrino *et al.*, 2007; Thompson *et al.*, 1995; Duranceau *et al.* 2010b).

Figure 2-2: Effect of pH on Hydrogen Sulfide Species as a Fraction of Concentration.

Different methods apart from aeration and oxidation have been used over the years in removing hydrogen sulfide from ground water, especially in Florida. Thompson *et al.* (1995) used chlorine oxidation followed by microfiltration in removing hydrogen sulfide from groundwater in Oviedo, Florida, by first converting hydrogen sulfide to elemental sulfur by oxidation and then subsequently carrying out removal by filtration technique. Cotrino *et al.* (2007) used packed bed anion exchange technology to remove hydrogen sulfide from groundwater. Duranceau and coworkers (2010b) recently demonstrated the use of oxidative manganese filters for targeted removal of sulfide without production of disinfection by-products in a chlorinated groundwater supply.

Hydrogen sulfide is not directly regulated under the Safe Drinking Water Act (SDWA), but it is regulated through the secondary standards for taste and odor. In 2003, the Florida Department of Environmental Protection (FDEP) issued a rule under Section 62-555.315 which addressed the removal of total sulfide in drinking water. The options include the use of chlorine with and without

pH adjustment in groundwater sources with hydrogen sulfide concentration between 0.3 and 0.6 mg/L, forced draft aeration including pH adjustment in hydrogen sulfide concentration in a range between 0.6 and 3.0 mg/L, and packed tower plus pH adjustment for sources with hydrogen sulfide concentrations over 3.0 mg/l as seen in Table 2-1.

Theory and Application

Waterfall and Tray Aerators

Three types of aerators are commonly employed in the treatment of water for sulfide. These include waterfall aerators exemplified by spray nozzles, cascade aerators, and multiple tray aerators; diffusion or bubble aerators, which involve passage of bubbles, compressed air through the water; and mechanical aerators employing motor-driven impellers with or without air injection devices. Waterfall aerators (multiple trays) are the more commonly used aeration devices in water treatment plants. In aeration systems, blow-out towers, slot aerators, and coke trays can be added to maximize the surface-volume ratio of the water (Monscivitz and Ainsworth. 1974; Lin 1977).

For purposes of this document, several terms need to be defined and explained in order to clarify language with regard to mechanical items as related to tray aerators. For example, the term “tray aerators” or “tray aerator system” is used to refer to a complete unit operation comprised of a series of trays arranged in a cascaded format. Also, the term “aerator tray” is used to describe an individual fan-like, trapezoidal or rectangular structure into which water flows through during treatment. The term “tray stage” refers to a grouping of individual aeration trays within a specific stacking level within the aerator system, whereby the collective trays are staged atop each other so that a cascade effect can be achieved.

Table 2-1: FDEP rule- Section 62-555.315

Potential for impacts without Total sulfide removal	Water quality ranges	Potential water treatment
Low	Total sulfide < 0.3 mg/L Dissolved iron < 0.1 mg/L ¹	Direct chlorination ²
Moderate	0.3 mg/L ≤ total sulfide ≤ 0.6 mg/L @pH 7.2 Or 0.3 mg/L ≤ total sulfide ≤ 0.6 mg/L @pH 7.2	Conventional aeration ³ (maximum removal efficiency ≈ 40-50%) or Conventional aeration with pH adjustment ^{4,5} (maximum removal efficiency ≈ 40-50%)
Significant	0.6mg/L ≤ total sulfide ≤ 3.0 mg/L @pH 7.2 Or 0.6 mg/L ≤ total sulfide ≤ 3.0 mg/L @pH 7.2	Forced draft aeration ³ (maximum removal efficiency ≈ 90%) Forced draft aeration with pH adjustment ^{4,5} (maximum removal efficiency ≈ 90%)
Very significant	Total sulfide > 3.0 mg/L	Packed tower aeration with pH adjustment ^{4,5} (maximum removal efficiency ≈ 90%)

¹High iron content raises concern if chlorination is used and significant dissolved oxygen in the source water. Filtration might be required to remove particulate iron prior to water distribution.

²Direct chlorination of sulfide in water in the pH range normally found in potable sources produces elemental sulfur and increased turbidity. Finished water turbidity should not be more than two nephelometric turbidity greater than raw water turbidity.

³Increased dissolved oxygen entrained during aeration may increase corrosivity.

⁴Reduction of alkalinity during pH adjustment and high dissolved oxygen entrained during aeration may increase corrosivity. Corrosion control treatment such as pH adjustment, alkalinity recovery, or use of inhibitors may be required.

⁵High alkalinity will make pH adjustment more costly, and use of other treatment may be in order. Treatment that preserves the natural alkalinity of the source water may enhance the stability of finished water

Source: FDEP, 2003

Hence, water flows at a constant elevation for a grouping of trays prior to trickling into the next level of grouped trays. These grouped trays placed in a sequential level of layers forms the basis for a tray aerator “stage” that offer a low-cost but effective method for removing carbon dioxide and a portion of the sulfide from ground water. Some of the limitations associated with the use of a tray aerator include the following:

1. Water disinfection can be less effective due to chlorine demand exerted by hydrogen sulfide,
2. Corrosion rates in the distribution pipes and the water tanks could increase,
3. The removal is dependent on Henry’s Law,
4. Flooding (excessive loading rates) can occur, causing an improper air and water balance, and
5. Scaling may occur if calcium exceeds 40 mg/L, or magnesium exceeds 10 mg/L; fouling will may also occur if iron exceeds 0.3 mg/L or manganese exceeds a concentration of 0.05 mg/L (US Army Corps of Engineers, 2001).

Multiple tray aerators

Multiple-tray aerators are comprised of multiple levels of slated weirs or perforated trays filled with coke or gravel for maximum removal, a collection basin, and an induced or forced draft ventilation system (Taricska *et al.*, 2009). The water first enters a distributor tray and then falls from tray to tray, finally entering an open collection basin at the base of the tray aerators. The vertical opening between trays usually ranges from twelve inches to thirty inches.

An even distribution of the water over the entire area of each tray is essential for effective sulfide treatment. Perforated distributors should be designed to provide a small amount of head, approximately 2 inches on all holes, in order to provide uniform flow. In aerators with no provision

for forced ventilation, the trays are usually filled with 2- to 6-inch media, such as coke, stone, ceramic or plastic balls to improve water distribution and gas transfer by increasing surface area between the two phases (Taricska *et al.*, 2009). Water application rates range 20 to 30 gpm per square foot (Faust and Aly, 2008; Baumann, 1978).

At locations where icing poses a problem, the aerator must be well protected; additionally, fans or blowers can be provided if necessary to improve efficiency. An increase in the air flow using positive-draft aerators can increase the effectiveness of the addition of oxygen to water, or the removal of hydrogen sulfide, as compared to normal tray aerators (Departments of the Army and Air Force, 1985).

Figure 2-3 depicts a natural draft tray aerator showing four tray stages on top of a CROM storage tank (CROM Corporation, Gainesville, FL). As has been noted, tray aerators have been common place in Central Florida for the intent of removing carbon dioxide and hydrogen sulfide; However, since the FDEP rule 62-555.315 was promulgated, many water purveyors have installed forced-draft aerators in the place of tray aerators. Figure 2-4 depicts a forced-draft packed tower aerator installed by Orange County utilities near Orlando, Florida.

Aeration

Aeration allows for the intimate exposure of water and air by intensely mixing the air and water so that chemical reactions can occur between the air and water in the aerators. The primary objectives of aeration for use to improve water supply quality as stated by Fair *et al.* (1971) and the Departments of the Army and Air Force (1985) are:

Figure 2-3: Natural draft tray aerator [Courtesy of CROM Corporation, Gainesville, FL]

Figure 2-4: Photo representing a packed tower aeration process with odor control scrubbers for removing hydrogen sulfide from groundwater [Courtesy of Orange County Utilities, Orlando, FL]

1. Eliminating tastes and odors producing substances such as hydrogen sulfides and carbon dioxide.
2. Reducing corrosion of metals, cracks in concrete and cement due to the presence of carbon dioxide.
3. Reducing chlorine demand.
4. Addition of oxygen to groundwater for the oxidation of manganese and iron, as groundwater is normally devoid of dissolved oxygen.
5. Carbon dioxide can be partially removed to increase the pH of the water and to reduce the amount of lime required for softening due to losses with reactions that occur with carbon dioxide, thus reducing the overall cost of water softening by precipitation with lime and soda ash.
6. Removal of volatile organic compounds which are suspected cancer-causing compounds.

The use of an aerator allows for water to contact air because of the surface area that the tray provides, and an increase in the surface area of water that comes into contact with the air will allow for mass transfer of dissolved gases to occur between the air and water phases.. By increasing water flow, turbulence can be increased to give better aeration results (Wang *et al.*, 2006). Due to a higher solubility of H_2S than CO_2 in water, when water is aerated, carbon dioxide is removed more rapidly than H_2S during aeration. The removal of CO_2 during aeration increases the pH of the water, thereby causing a shift in the ionization equilibrium, thereby forming more dissolved sulfides (HS^- and S^{2-}) that cannot be removed by aeration (Duranceau, 2004a; Wang *et al.*, 2006). Therefore, the removal of CO_2 or the increase in pH must be controlled to increase the removal efficiency of H_2S by aeration (Duranceau, 1999).

Three basic parameters that must be controlled in the operation of an aeration process are:

- Dissolved oxygen
- pH and
- Temperature

According to Baylar and Batan, (2010), “*oxygen transfer is the process by which oxygen is transferred from the gaseous phase to the liquid phase. The oxygen transfer efficiency depends almost entirely on the amount of surface contact between the air and water.*” The contact between water and air is primarily due to the size of the air bubbles or water droplets in the trays, and the effective surface area of the water available for contact between water and air.

The amount of oxygen that the water can hold is dependent on the temperature of the water. The colder the water, the more oxygen the water can hold. However, water that contains excessive amounts of oxygen can be corrosive to metallic piping components. A surplus of oxygen can also cause some problems in the tray aerators by causing air binding in the filters. In the aeration process, the oxygen from the air is absorbed, increasing the dissolved oxygen in the water as the water cascades down the trays (Minnesota Rural Water Association, 2004).

Gas transfer performance in air strippers has been shown to depend on a number of factors (AWWA 1971; AWWA 1990; ASCE 2005; Speitel and McLay 1993):

1. Characteristics of the volatile material
2. Air and water temperature.
3. Turbulence in liquid and gas/vapor phases.
4. Air-to-volume ratio.

5. Exposure time.
6. Use of a bioreactor on the air waste stream

Chlorine and oxygen oxidation converts hydrogen sulfide to either elemental sulfur or sulfate (Lyn and Taylor 1993). Aeration results in a combination of stripping the volatile fraction of the hydrogen sulfide and oxidizing the hydrogen sulfide to elemental sulfur or sulfate. The volatile fraction is the non-ionized hydrogen sulfide gas form (H_2S), and the concentration of the species depends on the pH. In many cases, aeration systems promote the growth of sulfur oxidizing bacteria that can contribute turbidity to the finished water (Cotrino *et al.*, 2007).

Lochrane (1977) studied natural draft tray aerators for sulfide removal and documented overall removal efficiencies on the order of twenty percent; however, the research did not evaluate individual tray contributions to removal efficiencies nor was a predictive model developed. The work by Lochrane did however indicate the importance of pH, temperature and flow rate to the overall removal efficiencies. Wells (1954) reported 35 to 45 percent removal of sulfide by multiple tray aerators with slat bottoms in Duval County, Florida.

Air-to-Water Ratio

The volumetric air flow to the volumetric water flow ratio (V/L) is known to as the air-to-water ratio. Henry's law is very important in determining the required air-to-water ratio required in a tray aerator. At a given temperature and pH, one can determine the amount of air necessary to provide an adequate flow for the removal of H_2S . Generally, the higher the temperature, the lower the air flow rate and vice versa.

Table 2-2: Characteristics of gas-liquid contacting systems.

Type of contacting device	Process description	Method of gas introduction	Typical applications	Hydraulic head required (ft)
Cascade	Water to be treated flows over the side of sequential pans, creating a waterfall effect to promote droplet-type aeration.	Aeration primarily by natural convection	CO ₂ removal, taste and odor control, aesthetic value, oxygenation	3-10
Multiple tray	Water to be treated trickles by gravity through trays containing media (layers 4-6 inches deep) to produce thin-film flow. Typical media used include coarse stone or coke (2-6 inches in diameter) or wood slats.	Natural or forced draft aeration	H ₂ S, CO ₂ removal, taste and odor control	5-10
Packed tower	Water to be treated is sprayed onto high-surface-area packing to produce a thin-film flow; process configuration typically countercurrent.	Forced draft aeration	H ₂ S, CO ₂ removal, taste and odor control	10-40
Spray aerator	Water to be treated is sprayed through nozzles to form disperse droplets; typically a fountain configuration. Nozzle diameters usually range from 1 to 1.6 inches to minimize clogging.	Natural aeration through convection	H ₂ S, CO ₂ , and marginal VOC removal; taste and odor control, oxygenation	5-25
Low profile (sieve tray)	Water flows from entry at the top of the tower horizontally across series of perforated trays. Large air flow rates are used causing frothing upon air-water contact, which provides large surface area for mass transfer. Units are typically less than 10 ft high.	Air introduced at bottom of tower	VOC removal	-

Source: MWH (2005)

Solubility of gases

The solubility of hydrogen sulfide in water at any given temperature is based on two phenomena: Henry's law and the ionization of hydrogen sulfide as a weak acid. The amount of gas that a liquid can dissolve at a given temperature is determined by Henry's law, which states that the partial pressures of a gas in equilibrium with a solution is equal to a constant times its concentration in the solution.

$$P_a = HX_a \quad (2-5)$$

Where:

P_a = partial pressure in the atmosphere of the hydrogen sulfide

X_a = mole fraction of hydrogen sulfide in the liquid

H = Henry's law constant

Table 2-3 shows the solubility of oxygen, carbon dioxide and hydrogen sulfide at different temperatures in water.

Gas equilibrium and transfer

Mass transfer models are used for gas transfers such as the two-film theory (Whitman, 1923), surface renewal theory (Danckwerts, 1951), the film penetration theory (Toor and Marchello, 1958) and penetration theory (Higbie, 1935). The degree to which the gas-liquid system differs from equilibrium provides the driving force behind diffusion. For diffusion to take place from water to air, there must be a concentration gradient in the direction of transfer.

Higher turbulence can increase the transfer of aqueous H₂S by more rapidly bringing H₂S(aq) molecules into contact with the interface as the transfer processes are controlled by the film in the water phase (Liss and Slater 1974). Increased turbulence can also make the interfacial area larger, thereby giving a higher possibility of aqueous H₂S molecules being transferred.

Table 2-3: Solubility of gases in pure water in contact with the pure gas @ 1 atm

Temp (°C)	Oxygen (O ₂) mg/L	Carbon dioxide (CO ₂) mg/L	Hydrogen sulfide (H ₂ S) mg/L
0	69.8	3360	7100
5	61.2	2790	6040
10	54.3	2345	5160
15	48.7	2000	4475
20	44.3	1720	3925
25	40.4	1495	3470
30	37.2	1305	3090
40	32.9	1040	2520
60	27.8	704	1810
80	25.1	-	1394
100	24.2	-	1230

Source: Camp, 1965.

The kinetics of gas transfer is typically modeled using the two-film theory (MWH 2005). As stated by Kavanaugh and Trussell 1980; Shulka 1984, “*transport requires movement: from the bulk solution, through the liquid film to the interface, from the interface through the gas film, and from the film into the bulk gas. The concentration gradient between the bulk solutions and the interface drives diffusion. If dilute conditions exist, then Henry’s Law applies and mole fraction in liquid is proportional to the mole fraction in air at equilibrium.*” The equilibrium has been shown to be linear and is defined by Henry’s Law.

The basic rate of gas transfer or gas aeration equation is given in Equations (2-6) through (2-8)

$$\frac{dC}{dt} = k_L \left(\frac{A}{V} \right) (C_s - C) \quad (2-6)$$

or

$$\frac{dc}{dt} = k_L a (C_s - C) \quad (2-7)$$

Integrating Equation 2- 8 would yield:

$$K_L a = \frac{(C_s - C_1) - (C_s - C_2)}{t_2 - t_1} \quad (2-8)$$

Where:

C_s - Saturation concentration of gas at interface

C_1, C_2 - Concentration of dissolved gas under aeration after times t_1, t_2

A - Gas-liquid interfacial area

V - Volume of liquid

k_L - Gas transfer coefficient

$K_L a$ - Overall gas transfer coefficient

t_1, t_2 - Time.

Two film theory

Degasification is governed by the principles of gas transfer- Henry's Law and the two-film theory.

The two film theory is regularly employed in determining the mass transfer rates between liquids and gases.

As stated by Whitman (1923), assumptions of the two-film theory are:

1. *"Steady-state: concentrations at any position in the tower do not change with time."*
2. *"Interface between the gas phase and the liquid phase is a sharp boundary."*
3. *"Laminar film exists at the interface on both sides of the boundary."*

4. *“Equilibrium exists at the interface, thus there is negligible resistance to mass transfer across the interface: (x_i, y_i) is the gas and liquid equilibrium concentration.”*
5. *“No chemical reaction: rate of diffusion across the gas-phase film must equal the rate of diffusion across the liquid-phase film and its dependence on operating conditions.”*

The two-film theory of Whitman (1923) helps provide some insight into understanding this concept. According to that theory, equilibrium can be assumed at the interface and the overall resistance to mass transfer can be considered to be made of a gas phase film resistance and a liquid phase film resistance (McCabe, 2005).

When gas is in contact with a liquid, the gas is absorbed by the liquid until the liquid-phase concentration ultimately is in equilibrium with the gas-phase concentration. This equilibrium is described by Henry’s law. The mass-transfer theory comprises of two films; liquid and gas film and their interfaces. The gas and liquid films are assumed to flow as a streamline or laminar flow (Peytavy *et al.*, 1990).

Water quality parameters

This section shows some common water quality parameters and discusses why they are significant in groundwater and how they affect the solubility or dissociation of sulfide in groundwater. Such parameters include pH, temperature, dissolved oxygen, dissolved solids, and alkalinity.

pH

Effect of pH on the solubility of hydrogen sulfide

According to MWH (2005), pH does not affect Henry's constant but it affects the distribution of the species obtained from the dissociation of H_2S in water, which influences the overall gas-liquid distribution of H_2S because only the un-ionized species are volatile.

In Figure 2.5, the effect of pH on the solubility of hydrogen sulfide is shown and the concentration of the S^{2-} ion is not plotted on the graph because in every case it would be off scale (i.e., less than $1 \times 10^{-8} \text{M}$). In addition, the plot only concludes at a pH of 8 because beyond this point the concentration of the HS^- become so large that neglecting the activity coefficients results in significant error.

Carroll, 1998

Figure 2-5: Solubility of Hydrogen Sulfide as a Function of the pH at 25°C

At a low pH below 6, the predominant form of the sulfide species is H_2S , at a pH of about 6 bisulfide ion are present than hydrogen sulfide. A further increase in the pH results in the formation of more bisulfide (Carroll, 1998). As such, hydrogen sulfide gas can be removed effectively at pH less than 6 without forming turbidity (elemental sulfur), but all of the carbon dioxide in the water will also be removed due to the pKa of carbonate system at 6.3. If sulfide removal occurs at pH 6.3, some buffering capacity will remain in the aerated water (Duranceau, 2004a).

At a pH of slightly less than 7, there are equal amounts of bisulfide and hydrogen sulfide in the water (Carroll, 1998) while at a pH of 8, the concentration of the bisulfide ion is higher than H_2S . Equations 2-9 through 2-12 were used in calculating the distribution of the sulfide (H_2S and HS^-) species. At different pH values, the concentration of H_2S and HS^- can be determined using equilibrium expressions.

$$S_T = [H_2S] + [HS^-] \text{ at pH close to neutral} \quad (2-9)$$

$$K_{a1} = 7.94 \times 10^{-8} = \frac{[HS^-][H^+]}{[H_2S]} \quad (2-10)$$

$$K_{a1} = 7.94 \times 10^{-8} = \frac{(S_T - [H_2S])[H^+]}{[H_2S]} \quad (2-11)$$

$$[H_2S] = \frac{S_T[H^+]}{7.94 \times 10^{-8} + [H^+]} \quad (2-12)$$

Where:

S_T = Total sulfide

H_2S - Hydrogen sulfide

H^+ - Hydrogen ion

HS^- -Bisulfide.

Hydrogen sulfide's rate of evaporation depends on temperature, humidity, pH, and the concentration of specific metal ions. At pH levels of less than or equal to 6 pH units, H_2S will cross the air-water interface with kinetics similar to other non-reactive gases, such as oxygen (O_2), nitrogen (N_2), and carbon dioxide (CO_2), (Balls and Slater 1983).

Temperature.

Effect of temperature on the speciation of hydrogen sulfide in water.

Transfer of substances between the air and water is of environmental concern in a number of cases. Important examples are release of odors, emission of substances that affect human health and cause corrosion, and in case of re-aeration and aeration. The effect that pH and temperature have on sulfide speciation in water relative to $\text{H}_2\text{S}/\text{HS}^-$ equilibrium is shown in Figure 2-6 (Yongsiri *et al.*, 2004). Figure 2-6 illustrates the importance of pH as a master variable for evaluating sulfide in water over a range of temperatures.

Yongsiri et al. (2004).

Figure 2-6: Dissociation of hydrogen sulfide ($\text{H}_2\text{S}/\text{HS}^-$ equilibrium) at 15°C , 25°C and 30°C .

Considering the gas-transfer rate across the air-water interface, several investigators such as Streeter, (1926), Elmore and West (1961) and Bewtra *et al.* (1970) used the Arrhenius equation to describe the temperature dependence of O₂ transfer.

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad (2-13)$$

Where:

T= temperature (K);

E_a= activation energy (J mol⁻¹);

k= rate constant (/hr);

R= universal gas constant (8.314 J mol⁻¹ K⁻¹).

Integrating Equation 2.13 between temperatures T₁ and T₂ yields Equation 2-14:

$$\frac{\ln k_2}{\ln k_1} = \frac{E_a(T_2 - T_1)}{RT_2 T_1} \quad (2-14)$$

Introducing $\theta = [E_a(RT_2 T_1)^{-1}]$, the effect of temperature on rate constants can then be reduced to the relationship given in 2-15, as first used by Streeter (1926) for O₂ transfer in the reaeration process, is:

$$K_2 = K_1 \theta^{T_2 - T_1} \quad (2-15)$$

In general, T₁ is at 20°C. Equation 2-15 can be rewritten as follows:

$$k_T = k_{20} \theta^{T - T_1} \quad (2-16)$$

Where

k_T= rate constant at temperature T (°K) and

k₂₀= rate constant at 293°K.

For weak acids such as H₂S, it must be recognized that only the molecular forms of a compound can be removed from water as shown in Equation 2-17. Consequently, when using total sulfide as the reference for H₂S emission, the effect of temperature on the dissociation process must also be considered together with that of the emission process (Yongsiri *et al.*, 2004).

Based on the emission and dissociation processes of H₂S, the mass balance for aqueous H₂S is described in Equation 2-18 as:

$$\frac{d[\text{H}_2\text{S}_{(\text{aq})}]}{dt} = \text{Rate of H}_2\text{S}_{(\text{aq})} \text{ transferred from HS}^- - \text{Rate of H}_2\text{S}_{(\text{aq})} \text{ emitted} \quad (2-18)$$

Dissolved oxygen

Dissolved oxygen (DO) occurs when there is mixing between water and air molecules, such that oxygen is absorbed into the water by gas mass transfer. Factors affecting the DO content include:

- Velocity and volume of flowing water;
- Climate and seasonal factors;
- The number and type of organisms present in the water;
- Total dissolved or suspended solids including the amount of nutrients present; and
- Groundwater inflow (Anchorage Waterways Council 2007; Murphy 2007).

Dissolved solids

Total dissolved solids (TDS) comprises of a sum of mineral compounds dissolved in the water which consist majorly of salts of sodium, calcium, or magnesium usually in the form of sulfates, chlorides, or bicarbonates.

Alkalinity

Alkalinity in water is a measure of the general buffering capacity or stability of the water. Alkalinity is thus directly related to the buffering capacity of water, which is considered an important parameter affecting the pH, and is shown in Equation 2-19.

$$\text{Alkalinity} = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+] \quad (2-19)$$

Alkalinity depends on the concentration of bicarbonate, carbonate, and hydroxide ions in water. According to Lahav and Birnhack (2007) for a given pH value, the higher the alkalinity value, the higher the ability of the water to withstand a change in pH due to release of H^+ and OH^- ions to the water. Duranceau *et al.* (2010) noted that a higher alkalinity at a given pH translates into a higher dissolved inorganic carbon (DIC) concentration of the carbonate species (CO_3^{2-}). However, too high of an alkalinity at higher pH levels may accelerate lead and copper metal release (Duranceau *et al.* 2004b; Taylor *et al.* 2005).

Empirical Model for Predicting Carbon Dioxide in Tray Aerator Effluent

Aeration is largely attributed to the mixing of the air with the falling water in the underlying steps (Taricska *et al.*, 2009). Natural ventilation is a requirement for providing additional improvements in efficiency. Although researchers have explored methods that could be used to develop predictive mathematical models to accurately describe the performance of a drinking water treatment unit operation, a search of the literature indicated that no predictive mathematical models had been developed for sulfide removal in a tray aerator.

Scott *et al.* (1950) demonstrated the successful use of an empirically-derived model for multiple tray aerators designed for natural ventilation. In their model, Scott et al. (1950) developed a simple relationship that was used to estimate carbon dioxide (CO₂) removal in tray aerators:

$$C_n = C_o 10^{-kn} \quad (2-20)$$

Where:

C_n = mg/L CO₂ remaining after aeration.

C_o = mg/L CO₂ present in water in distribution trays.

n = number of trays, including distribution tray.

k = 0.11 to 0.16 depending on, turbulence, ventilation, and pH.

The model shown in Equation 2-20 served as a baseline for the development of a tray aerator model describing sulfide removal in this present research study.

CHAPTER 3: MATERIALS AND METHODS

This chapter will present the experimental methods, laboratory procedures, field operations, and associated quality control procedures employed for this project. Analyses were performed in the University of Central Florida's (UCF's) environmental engineering laboratories on samples taken from the project sites at UCF, City of Lake Hamilton and City of Sarasota, Florida. The methodologies used were in accordance with standard methods and measures were taken to document field and laboratory procedures. Duplicate analyses were utilized for determining precision and accuracy of each test when possible. Sulfide analyses were conducted exclusively in the field because of losses during sampling due to hydrogen sulfide's volatility. Prior studies had indicated that field preservation methods using zinc acetate and subsequent laboratory analysis did not provide reliable and reproducible results as what could be achieved on-site (Duranceau *et al.* 1999; Trupiano 2010).

Description of Sites

The UCF water treatment facility has a capacity of 2.16 MGD and the UCF tray aerators have 24 trays: six trays in each of the four tray stages. UCF operates and maintains its potable water distribution system that serves most of the main campus. The treatment plant has four wells that pump water from the Floridian aquifer to a storage plant at the treatment plant. Each tray aerator has a capacity of approximately 500 gpm. The design capacity of the tray aerator is about 1500 gpm based on using three out of the four well during normal operating conditions. The system uses a series of high service water pumps and an above ground storage tank to maintain constant pressure. Figure 3-1 depicts a view of UCF's tray aerator when off-line, and Figure 3-2 depicts a view of UCF's tray aerator while in operation.

Figure 3-1: A view of the tray aerator at UCF (off-line)

Figure 3-2: A view of the tray aerator at UCF (on-line)

The Lake Hamilton tray aerators also had 24 trays with six trays in each of the four tray stages. The trays were fan-like in design and built on a concrete structure at the top of the water facility covered by perforated nets. This aerator was manufactured by CROM Corporation in Gainesville. The total height of each tray in the aerator was 5.9 inches. The water flowing into the aerator was at a rate of 800 gpm. The aerators were supplied from a well that had a 5-stage vertical turbine pump with an 8-inch pipe for discharge. Figure 3-3 depicts a view of Lake Hamilton tray aerator while in operation.

Figure 3-3: A view of the tray aerator in Lake Hamilton (on-line)

The Sarasota-Verna water treatment facility has a capacity of 12 MGD and the tray aerators have 96 trays with twenty-four racks and four tray stages. The aerators were arranged into three groups with thirty-two trays and eight racks in each group. There are two rows of four trays long and four trays high for a total of 32 trays. Analysis was done on two racks (B and D) in the Sarasota-Verna aerators. A distribution tray with an area of 591 ft² was located at the top of each group which

supplied each of the eight columns. The total surface area of rack B was in the contact with water, but only about one-third of the total surface area was in contact with water because of flow distribution problems. The City of Sarasota had recently retained a design engineering firm to redesign the trays at the Verna wellfield site. That work is expected to be completed in 2011. The trays were arranged horizontally in the aerators with 42 holes in each of the trays for the ease of flow of water from tray to tray. The holes in the trays had an area of 0.54ft^2 . The area of each of the tray was 19.4ft^2 , the height of each tray was 0.33 ft and the volume was 6.5ft^3 . The aerators were run at a flow rate of 2400 gpm. Figure 3-4 depicts front view of trays in the Sarasota-Verna while on-line, and Figure 3-5 depicts a front view of different trays in the Sarasota-Verna aerator while in operation.

Water Quality Methods

The water quality parameters monitored and methods used for samples transported to the UCF laboratory for analysis are shown in Table 3-1. Table 3-2 shows the water quality parameters monitored and methods used for the parameters analyzed in the field laboratory at the testing facility. The method detection limit (MDL) is also shown. Methods noted as standard methods (SM) are from APHA, AWWA, and WEF (1998).

Sample Collection

Water samples were collected and analyzed directly in the field, or packaged and transported to the laboratory for additional analyses. In preparation for a site visit for testing, field equipment was calibrated and the necessary treatment equipment and supplies required for field analyses were transported to the site.

Figure 3-4: Front view of trays in Sarasota-Verna (on-line)

Figure 3-5: Front view of different trays in the Sarasota-Verna aerator (on-line)

Table 3-1: Water quality parameters and methods performed at University of Central Florida water Laboratory.

Parameter	Method Reference	Method Description	MDL
Alkalinity	SM 2320	Titration method	5 ppm
Sulfate	SM 4500E	Turbidimetric method	1mg/L
Calcium	SM 3120B	ICP method	0.1 mg/L
Magnesium	SM 3120B	ICP method	0.1 mg/L
Calcium Hardness	SM 3120B	ICP Method	2.5mg/L as CaCO_3
Total Hardness	SM 3120B	ICP Method	6.6 mg/L as CaCO_3
TDS	SM 2540C	Total Dissolved Solids Dried at 180° C	0 mg/L
TSS	SM2540D	Total Suspended Solids Dried at 103-105°C	0 mg/L

Table 3-2: Water quality parameters and methods performed in the field.

Parameter	Method Reference	Method Description	MDL
Turbidity	SM 2130B	Nephelometric Method	0.01 NTU
Conductivity	SM 2510A	Conductivity	0.01 $\mu\text{s}/\text{cm}$
DO	SM 4500-O G	Membrane probe	0.1 mg/L
pH	SM4500- H ⁺ B	Electrometric Method	0.01 pH Units
Temperature	SM2550B	Temperature	0.01°C
Sulfide	SM4500-S ²⁻ .F	Iodometric method	0.1 mg/L as S ²⁻

The samples were collected in a manner that minimized sample exposure to air. Sealed sample bottles were filled to the brim prior to capping to reduce the potential for exposure to air. The samples were chilled in coolers prior to transportation to the UCF laboratory.

To quantify sulfide at the monitoring stations, water samples were collected from different tray stages in the aerator. In the Sarasota-Verna facility, sampling was done from two racks in the aerator, while at UCF, Lake Hamilton, samples were taken from one tray on each stage. Using a pipette, 200 ml of the water sample was measured into an Erlenmeyer flask with iodine, 1ml of hydrochloric acid and 2-3 drops of starch that was used as the indicator towards the end point. These samples were then titrated against sodium thiosulfate and analyzed for the concentration of sulfide in the trays. Further sulfide analyses were not conducted in the laboratory based on the inconsistent results observed by other researchers.

A total of 4, 7, and 20 samples were taken at the UCF, Lake Hamilton, and Sarasota-Verna sites respectively. The sampling performed at Lake Hamilton and Sarasota-Verna also involved collecting water samples from the distribution tray, water exiting the aerators, and the raw and effluent water flowing in and out of the distribution tray. The sampling at UCF was done on a cloudy, humid day; Lake Hamilton tray aerators were sampled on a hot sunny day and the Sarasota-Verna tray aerators were sampled on a hot windy day. Sulfide concentrations were measured in the field using the iodometric method 4500 I- C dictated by the 20th edition of the Standard Methods for examination of Water and Wastewater. The experiment was slightly modified to meet the need for accuracy and precision. Reagents were prepared the day prior to sampling and analysis in the field.

Development of a First-Order Empirical Model

An empirical model was created to describe sulfide removal in tray aerators. The model was evaluated with the use of MINITAB software using water quality and site-specific tray configuration data obtained from the field experiments. The operating variables (tray area, hydraulic flow rate, H^+ , temperature, and dissolved oxygen) and the response variable (k) were defined and evaluated. A multiple regression analysis was used to establish a dependence of k on the variables area, temperature, flow rate, dissolved oxygen, and H^+ . The experimental data generated was used to fit an equation for the kinetic constant, k , by giving a relationship between the response variable and the operating variables. The statistical model only allowed variables that were statistically significant at the 95 percent confidence level.

Derivation of the First-Order Empirical Model

It is postulated that the sulfide concentration in the water flowing through a tray aerator is a function of the inlet concentration and the number of tray stages in a similar fashion to the model developed by Scott *et al.* (1950) for carbon dioxide:

$$\frac{\partial C}{\partial n} = -k'C \quad (3-1)$$

$$\frac{\partial C}{C} = -k \partial n \quad (3-2)$$

Setting boundary conditions, n is the number of trays from 0 to n and C is the concentration from C_0 as the initial tray to C_n as the concentration of the last tray:

$$\int_{C_0}^{C_n} \frac{\partial C}{C} = -k' \int_0^n \partial n \quad (3-3)$$

Integration yields:

$$\ln \frac{C_n}{C_0} = -k'n \quad (3-4)$$

Algebraic manipulation yields:

$$\frac{\ln \frac{C_n}{C_0}}{2.303} = \frac{-k' n}{2.303} \quad (3-5)$$

Rearrangement:

$$\log \frac{C_n}{C_0} = -kn \quad (3-6)$$

The derivation showing how sulfide can be removed in a tray aerator as given in Equation 3-6 can be modified to yield the expression given in Equation 3-7:

$$C_n = C_0 10^{-kn} \quad (3-7)$$

Where:

C_n = total sulfide remaining after aeration (mg/L).

C_0 = total sulfide present in water in distribution trays (mg/L).

n = number of tray stages.

k' , k = an experimental constant.

Derivation of the Model Experimental Constant

Statistical analysis of the experimental data was conducted to establish if there was a correlation between experimental constant, k (as the dependent variable), and area, pH or H^+ concentration, flow rate, temperature, and dissolved oxygen (as independent variables). Different factors were used in determining the dependence of k on the independent variables in the regression analysis relative to the removal of sulfides from tray aerators. Multiple linear regressions were performed for each expression shown in Equations 3-8 through 3-17 to determine which variables were to be used in formulating a predictive model of the form given in Equation (3-7):

$$k = a(H^+)^b(\text{Area})^c \quad (3-8)$$

$$k = a(H^+)^b(\text{Flow})^c \quad (3-9)$$

$$k = a(H^+)^b(\text{Area})^c(\text{Temp})^d \quad (3-10)$$

$$k = a(H^+)^b(\text{Area})^c(\text{Flow})^d \quad (3-11)$$

$$k = a(H^+)^b(\text{Area})^c(\text{Temp})^d(\text{Flow})^e \quad (3-12)$$

$$k = a(H^+)^b(\text{Area})^c(\text{Temp})^d(\text{Flow})^e(\text{DO})^f \quad (3-13)$$

$$k = a(\text{pH})^b(\text{Area})^c \quad (3-14)$$

$$k = a(\text{pH})^b(\text{Area})^c(\text{Temp})^d(\text{Flow})^e \quad (3-15)$$

$$k = a(\text{pH})^b(\text{Area})^c(\text{Temp})^d \quad (3-16)$$

$$k = a(\text{pH})^b(\text{Area})^c(\text{Temp})^d(\text{Flow})^e(\text{DO})^f \quad (3-17)$$

Where:

k = experimental constant (dimensionless)

$\text{pH} = -\log[H^+]$

$[H^+]$ = hydrogen ion concentration

Temp = temperature ($^{\circ}\text{C}$)

Area = area (ft^2)

Flow = flow rate in the trays (ft^3/min).

These experimental constant relationships were evaluated to determine if a predictive equation could be used to describe sulfide removal in tray aerators, as discussed in the next chapter. Statistical evaluations of the resulting model calculations could be used to specify the specific factors or parameters that would comprise the k in the new tray aerator model.

CHAPTER 4: RESULTS AND DISCUSSION

This chapter presents the results obtained from the study, and discusses the validity of an empirical model developed to predict sulfide removals in tray aerators. Water quality results are also reported herein, and include measurements taken in the field and those analyzed in the UCF laboratory. The water quality parameter such as temperature, pH, turbidity, conductivity, sulfide, alkalinity, sulfate, and hardness are further discussed in this section. Also included in this chapter is an evaluation of a first-order mathematical model to predict the sulfide content found in tray aerators.

Experimental Data Collection

Water samples with unknown sulfide concentrations were collected from three experimental field locations across Central Florida: the University of Central Florida tray aerators; the Lake Hamilton tray aerators; and the Sarasota-Verna tray aerators. Tables 4-1, 4-2, and 4-3 present the temperature, dissolved oxygen, turbidity, pH, sulfate, alkalinity and sulfide at the time of collection at the UCF, Hamilton and the Sarasota-Verna test locations respectively. The results from the field data show that as the pH increases, sulfide concentration decreases with increasing tray stages, and dissolved oxygen increases with increasing tray stages. The oxygen content rises because an aerator serves as an absorber, increasing the oxygen that leaves the air and dissolves in the liquid entering the aerators. When the air comes in contact with water, it serves as a means to strip out the sulfide from the water. The temperature of water flowing through the aeration trays was found to vary slightly, from 21.7°C to 22.1°C for the UCF tray aerators, 28.5°C to 30.3°C for the Lake Hamilton aerators and 27.1°C to 28°C for the Sarasota-Verna tray aerators. The pH ranged from 7.71 to 8.08 for the UCF tray aerators, 7.47 to 8.06 for the Lake Hamilton aerators and 7.04 to 7.76 for the Sarasota-Verna tray aerators, respectively.

Table 4-1: Field and Laboratory data from University of Central Florida Tray aerators

Sample ID	Temp (°C)	pH	DO (mg/L)	Turbidity (NTU)	Sulfide content (mg/L as S ²⁻)	Alkalinity (mg/L as CaCO ₃)	Sulfate (mg/L)
Raw	-	-	-	-	3.0	-	-
1A	22	7.7	2.3	0.52	3.0	150	2.5
1A Dupe	-	-	-	-	-	-	3.1
1B	22	7.9	4.6	0.50	2.8	150	2.6
1C	22	8.0	6.1	0.52	2.3	136	3.5
1CDupe	-	-	-	-	-	-	3.4
1D	22	8.1	7.2	0.52	2.1	136	2.4

Table 4-2: Field and Laboratory data from Lake Hamilton Tray aerators

Sample ID	Conductivity (µS/cm)	Temp (°C)	pH	DO (mg/L)	Turbidity (NTU)	Sulfide content (mg/L as S ²⁻)	Alkalinity (mg/L as CaCO ₃)	Sulfate (mg/L)
Raw	-	27.5	7.2	1.9	0.32	2.5	146	-
Tray 1	314	30.3	7.5	2.0	0.55	2.2	144	5.6
Tray 1D	318	28.6	7.6	2.0	0.32	2.3	144	5.2
Tray 2	304	27.9	7.7	4.6	0.65	2.4	146	4.6
Tray 3	311	29.1	7.7	2.1	0.76	2.2	145	4.2
Tray 4	299	28.5	7.8	4.8	0.58	2.2	146	3.1
Tray 4D	317	-	8.1	4.7	0.47	2.2	-	-
Tray 5	326	-	-	5.0	0.53	2.2	146	4.4
Tray 6	312	-	-	5.8	0.61	2.1	146	4.7
Tray 7	311	-	-	6.0	0.49	2.1	146	4.9
Tray 7D	314	-	-	6.2	0.57	-	146	5.4

Table 4-3: Laboratory and field data from the Sarasota-Verna tray aerators

Sample ID	Conductivity ($\mu\text{S}/\text{cm}$)	Temp ($^{\circ}\text{C}$)	pH	DO (mg/L)	Turbidity (NTU)	Sulfide content (mg/L as S^{2-})	Alk (mg/L as CaCO_3)	Mg (mg/L)	Ca (mg/L)	SO_4^{2-} (mg/L)	TSS (mg/L)	TDS (mg/L)
B1	1177	28	7.2	1.9	0.32	5.5	184	160	349	464	0.0	854
B2	1189	27	7.4	3.0	0.33	5.3	183	163	351	492	0.5	866
B3	1179	27	7.4	4.6	0.55	4.7	183	80	166	479	2.0	850
B4	1159	27	7.5	4.6	0.24	4.3	184	243	529	484	3.5	864
B4D	1187	27	7.6	5.7	0.33	4.3	185	160	345	483	1.5	870
B5	1177	27	7.6	6.1	0.40	3.7	183	237	523	482	0.0	859
B6	1171	27	7.7	6.5	0.87	3.2	187	244	533	491	1.5	898
D1	1189	28	7.4	2.3	0.18	7.4	184	161	349	460	2.0	857
D2	1172	28	7.5	3.2	0.19	6.8	185	160	345	462	1.0	857
D3	1067	28	7.6	4.5	0.24	6.1	187	158	344	437	2.0	881
D3D	1062	28	7.6	5.5	0.34	5.8	184	157	344	480	2.0	847
D4	1065	28	7.6	5.4	0.43	4.7	185	158	344	437	1.5	864
D5	1049	28	7.7	6.0	0.46	4.3	184	152	328	435	1.5	854
D6	1056	28	7.8	6.3	0.82	4.1	185	158	344	467	2.0	859
Run 2							-	-	-	-	-	-
B1	1053	28	7.0	1.8	0.20	5.5	-	-	-	-	-	-
B2	1032	28	7.2	2.7	0.21	5.1	-	-	-	-	-	-
B2D	1050	28	7.3	3.5	0.31	5.2	-	-	-	-	-	-
B3	1042	28	7.5	3.2	0.32	4.9	-	-	-	-	-	-
B4	1041	28	7.6	3.8	0.31	3.5	-	-	-	-	-	-
B5	1044	28	7.7	5.3	0.36	3.7	-	-	-	-	-	-
B6	1048	28	7.7	4.1	0.49	4.5	-	-	-	-	-	-

Table 4-4 depicts the available and total surface area of each tray in the aerators, including the actual area that water occupied in the tray when the aerators were in operation. The area used in the model was the actual or effective area that water occupied in the tray while the aerators were in operation. The UCF tray aerators, Lake Hamilton tray aerators, Sarasota site 2 and Sarasota site 3 were all flowing full while only about one-third of Sarasota site 1 was filled with water during operation as shown in Table 4-4. Table 4-5 shows the operating hydraulic flow rates of the different tray aerators located at UCF, Lake Hamilton and Sarasota-Verna well fields respectively. The hydraulic flow rates at the Sarasota sites were different because the flow rate at Sarasota site 1 was about thirty percent of the total flow rate into the aerators, while Sarasota sites 2 and 3 were about fifty percent of the total flow rate into the aerators. The reason for the difference in the flow rate for Sarasota site 1 as compared to the other Sarasota sites is because only a portion of the wellfield for those trays was in operation at the time of sampling.

Table 4-6 shows the distribution of the sulfide (H_2S and HS^-) species in the tray aerators as a function of pH. The pH was used to calculate the concentration of H_2S in the total sulfide in the tray aerators as described in Chapter 2. The data from Table 4-6 is only applicable where chlorine has not been added prior to aeration. Figure 4-6 shows that as pH increases down the levels, the equilibrium shifts from H_2S to HS^- according to the La Chatelier principle and as such there is less H_2S to be stripped out from the tray aerators. It should be noted that because of sampling limitations and availability of the Lake Hamilton aerators, a few data points in Table 4-6 are absent from the data set; this did not affect the quality of the experiments.

Table 4-4: Available and actual area per tray at different sites

Location	Available ft ² /tray	Actual ft ² /tray
Sarasota site 1	19.51	6.51
Sarasota site 2	19.51	19.51
Sarasota site 3	19.51	19.51
Lake Hamilton	2.15	2.15
UCF	6.63	6.63

Table 4-5: Flow rates of the different tray aerators

Location	Flow rate (gpm)
Sarasota site 1	480
Sarasota site 2	960
Sarasota site 3	960
Lake Hamilton	800
UCF	500

Table 4-6: Distribution of sulfide species in the experimental data

	pH	Total sulfide (mg/L as S ²⁻)	H ₂ S (mg/L as S ²⁻)	HS ⁻ (mg/L as S ²⁻)
Sarasota site 1				
Tray 1	7.4	5.3	1.9	3.4
Tray 2	7.4	4.7	1.6	3.1
Tray 3	7.6	4.3	1.1	3.2
Tray 4	7.6	3.7	0.9	2.8
Sarasota site 2				
Tray 1	7.5	6.8	2.2	4.6
Tray 2	7.6	6.1	1.7	4.4
Tray 3	7.6	4.7	1.2	3.5
Tray 4	7.7	4.3	0.9	3.4
Sarasota site 3				
Tray 1	7.3	5.1	2.1	3.0
Tray 2	7.5	4.9	1.6	3.3
Tray 3	7.6	3.7	1.0	2.7
Tray 4	7.7	3.5	0.7	2.8
Lake Hamilton				
Tray 1	7.7	2.3	0.6	1.8
Tray 2	7.7	2.2	0.5	1.8
Tray 3	-	2.2	-	-
Tray 4	-	2.1	-	-
UCF				
Tray 1	7.7	3.0	0.6	2.4
Tray 2	7.9	2.8	0.4	2.4
Tray 3	8.0	2.3	0.3	2.0
Tray 4	8.1	2.1	0.2	1.9

Laboratory and Field Analytical Quality control results

Laboratory quality control samples were analyzed to assess precision and accuracy of the sample preparation and analytical procedures. During the data collection in the field, various measures were taken to ensure that there was accuracy and precision in the data collected by taking replicates. These measures included proper cleaning of glassware with acid, proper collection and storage of collected samples, procedural blanks, matrix spike samples, laboratory duplicates, and standard reference materials. The data obtained also included the analysis of replicate samples and spiked samples.

Precision and Accuracy

Precision was determined by running duplicate analyses, which was used in calculating an industrial statistic, I-statistic, as described by EPA handbook for Quality control in Water and Wastewater Laboratories (USEPA, 1979). The I-statistic is defined as in Equation 4-1:

$$I = \frac{|A-B|}{[A+B]} \quad (4-1)$$

Where:

I= industrial statistic

A= duplicate value 1

B= duplicate value 2

The average and standard deviation (sd), upper control level (UCL) and upper warning level (UWL) of the data were used to define the acceptable region for duplicate analysis. The upper and lower control limits were set at ± 3 standard deviations from the average mean, thereby exhibiting a normal distribution in which the control limits will capture 99.7 percent of the normal variation.

Values of the data that are above the upper control level were deemed out of control as was data values less than the upper warning level.

Since sulfide was determined by titration, quality control for precision was determined by performing duplicate titrations on some of the sample. Results of the sulfide analysis are given in Table 4-7 which indicates that none of the samples exceeded both the upper control level and upper warning level. The upper control limit and upper warning limits of field measurements of sulfide for Lake Hamilton tray aerators was 2.4 mg/L and 2.0 mg/L respectively. The upper control limit and upper warning limits of sulfide for Sarasota-Verna tray aerators was 5.6 mg/L and 4.3 mg/L respectively.

Table 4-8 presents precision analyses for laboratory measurements of sulfate. The upper control limit and upper warning limits of the laboratory measurements of sulfate for UCF tray aerators was 3.8 mg/L and 2.5 mg/L respectively. The upper control limit and upper warning limits of sulfide for Lake Hamilton tray aerators was 5.6 mg/L and 3.9 mg/L, respectively. The upper control limit and upper warning limits of sulfide for Sarasota-Verna tray aerators was 503 mg/L and 437 mg/L respectively. In addition to sulfate duplicate analyses, sample spikes analyses were also conducted in order to measure the accuracy of the sulfate analyses as shown in Table 4-9. One of the sulfate samples for UCF tray aerators had a RSD of 131%, which was out of range in quality control. This sample was thus excluded from the data set. The percent recovery for the spiked samples were between 90 and 110 and the percent relative standard deviation for the duplicate samples that were included in the data set were also between 80 and 120, thereby indicating adequate accuracy of the data.

Table 4-7: Precision analysis for field measurements of sulfide duplicates

	Duplicate A (mg/L)	Duplicate B (mg/L)
Lake Hamilton	2.2	2.3
	2.2	2.0
Mean I = 0.039		
sd = 0.072		
UCL = 2.4		
UWL = 2.0		
Sarasota	4.7	4.3
	5.8	4.7
	5.1	5.2
Mean I = 0.053		
sd = 0.21		
UCL = 5.6		
UWL = 4.3		

Table 4-8: Precision analysis for laboratory measurements of sulfate duplicates.

	Duplicate A (mg/L)	Duplicate B (mg/L)
UCF	2.5	3.1
	3.5	3.4
Mean I = 0.061		
sd = 0.23		
UCL = 3.8		
UWL = 2.5		
Lake Hamilton	5.6	5.2
	4.3	4.0
	4.7	4.9
Mean I = 0.031		
sd = 0.24		
UCL = 5.6		
UWL = 3.9		
Sarasota	480	437
	479	484
Mean I = 0.026		
sd = 11		
UCL = 503		
UWL = 437		

Table 4-9: Accuracy of sulfate analyses as measured by relative standard deviation and percent recovery

	Sulfate concentration		%	%
	A	B	RSD	Recovery
UCF				
Duplicates	3.1	3.1	118%	
	3.4	3.4	103%	
	2.4	2.4	131%	
Spikes	11.3			94%
Lake Hamilton				
Duplicates	5.6	5.2	93%	
	4.3	4.0	94%	
	4.7	4.9	104%	
Spikes	15.4			108%
	15.1			112%
	13.2			100%
Sarasota				
Duplicates	479	484	101%	
			92%	
Spikes	723			101%
	734			103%

Empirical Model Results

Table 4-10 shows the different non linear regression analyses conducted on the parameters in the different cases to obtain the different experimental constant, k values; it also shows the coefficient of variation (R-squared), mean of square of error and sum of squares of errors of the different cases studied. Mechanistic concepts were employed in eliminating some of the parameters used to determine the model's experimental constant. For example, for the situation where DO was considered, since it was clear that DO was a dependent variable rather than an independent variable, it should not be included in development of the experimental constant. Cases 7 through 10 were discarded since the exponent on the pH parameter was large and hence considered non-representative of the actual working tray, where such contribution was statistically implied to exert a rather large influence over the results. Consequently, the concept of using pH was abandoned and instead the hydrogen ion concentration was evaluated as an experimental constant component. This proved useful as is shown in Cases 1 through 6, which were considered to exhibit a realistic model of the impact of changing pH as expressed as $[H^+]$ across the trays. Case 4 was determined on both a statistical and mechanistic basis to represent an acceptable and accurate form for use as a non-linear regression model experimental constant. The empirical constant form of Case 4 was created using results from the Sarasota tray aerators, resulting in an experimental constant based on hydrogen ion concentration, effective tray area and hydraulic loadings. The 'best-fit' experimental constant was then used for the first-order sulfide removal model as shown in Equation 4-2. It is understood that the Case 4 based empirical model represented mechanistically the tray aerator because as the hydrogen ion concentration and hydraulic flow rate increase, the sulfide removal was negatively impacted and decreased; however, as the available tray surface area increased, sulfide removal was positively impacted and increased.

Table 4-10: Regression analysis of experimental data

Parameters			R^2	SSE	MSE	k values			
Case 1	pH	$k=(2.26 \times 10^{-6})(H^+)^{-0.528}(Area)^{0.275}$	0.07	15.7	1.1		Sarasota site 1	Sarasota site 2	Sarasota site 3
	Area					Level 1	0.031	0.044	0.036
						Level 2	0.031	0.050	0.044
						Level 3	0.038	0.053	0.051
						Level 4	0.039	0.060	0.062
						Weighted average	0.045		
Case 2	pH	$k=(4.99 \times 10^{-3})(H^+)^{-0.258}(Flow)^{-0.503}$	0.06	15.9	1.1	Level 1	7.58E-6	5.19 E-6	5.71 E-6
	Flow rate					Level 2	7.49 E-6	4.89 E-6	5.19 E-6
						Level 3	6.77 E-6	4.72 E-6	4.81 E-6
						Level 4	6.69 E-6	4.48 E-6	4.4 E-6
						Weighted average	5.66 E-6		
Case 3	pH	$k=(7.98 \times 10^9)(H^+)^{0.395}(Area)^{0.24}(Temp)^{-5.96}$	0.25	12.7	0.97	Level 1	0.041	0.048	0.054
	Area					Level 2	0.040	0.044	0.048
	Temp					Level 3	0.035	0.041	0.042
						Level 4	0.035	0.037	0.036
						Weighted average	0.042		
Case 4	pH	$k=(2.49 \times 10^{-3})(H^+)^{-0.397}(Area)^{0.548}(Flow)^{-1.17}$	0.17	14.1	1.0	Level 1	0.045	0.039	0.033
	Area					Level 2	0.046	0.042	0.039
	Flow rate					Level 3	0.054	0.045	0.044
						Level 4	0.055	0.049	0.050
						Weighted average	0.045		

Parameters			R ²	SSE	MSE	k values			
Case 5		$k=(2.17 \times 10^9)(H^+)^{0.355}(Area)^{0.276}$ $(Temp)^{-5.6}(Flow)^{-0.15}$	0.25	12.6	0.97		Sarasota site 1	Sarasota site 2	Sarasota site 3
	pH								
	Area	Level 1				0.042	0.046	0.051	
	Temp	Level 2				0.040	0.042	0.046	
	Flow rate	Level 3				0.036	0.040	0.41	
		Level 4				0.036	0.037	0.036	
		Weighted average				0.041			
Case 6		$k=(0.15)(H^+)^{-0.61}(Area)^{0.733}$ $(Temp)^{-1.89}(Flow)^{-1.21}$ $(DO)^{-1.25}$	0.34	11.2	0.93	Level 1	0.061	0.057	0.041
	pH	Level 2				0.036	0.043	0.057	
	Area	Level 3				0.036	0.038	0.055	
	Temp	Level 4				0.034	0.037	0.046	
	Flow rate	Weighted average				0.045			
		DO							
Case 7	pH	$k=(1.02 \times 10^{-10})(pH)^{9.48}(Area)^{0.277}$	0.07	15.7	1.05	Level 1	0.03	0.043	0.035
	Area	Level 2				0.031	0.049	0.043	
		Level 3				0.038	0.053	0.051	
		Level 4				0.039	0.059	0.061	
		Weighted average				0.044			

Parameters			R ²	SSE	MSE	k values			
Case 8		$k=(2.39 \times 10^{11})(\text{pH})^{-5.6}(\text{Area})^{0.285}$ $(\text{Temp})^{-5.44}(\text{Flow})^{-0.17}$	0.25	12.7	0.91		Sarasota site 1	Sarasota site 2	Sarasota site 3
	pH					Level 1	0.042	0.046	0.051
	Area					Level 2	0.040	0.043	0.046
	Temp					Level 3	0.037	0.041	0.41
	Flow rate					Level 4	0.037	0.038	0.037
						Weighted average	0.042		
Case 9		$k=(2.42 \times 10^{12})(\text{pH})^{-6.4}(\text{Area})^{0.244}$ $(\text{Temp})^{-5.85}$	0.25	12.7	0.91	Level 1	0.041	0.049	0.055
	pH					Level 2	0.04	0.045	0.049
	Area					Level 3	0.036	0.043	0.043
	Temp					Level 4	0.035	0.039	0.038
						Weighted average	0.043		
Case 10		$k=(2.5 \times 10^{-7})(\text{pH})^{11.6}(\text{Area})^{0.752}$ $(\text{Temp})^{-1.71}(\text{Flow})^{-1.26}(\text{DO})^{-1.28}$	0.34	11.1	0.93	Level 1	0.055	0.052	0.036
	pH					Level 2	0.033	0.039	0.052
	Area					Level 3	0.033	0.034	0.051
	Temp					Level 4	0.032	0.034	0.042
	Flow rate					Weighted average	0.041		
	DO								

Equation 4-2 then takes on the form of:

$$k = (0.00248)(H^+)^{-0.397}(Area)^{0.584}(Flow)^{-1.17} \quad (4-2)$$

Where

k= kinetic constant (dimensionless)

$[H^+]$ = hydrogen ion (10^{-pH})

Area= area (ft^2)

Flow= flow rate in the trays (ft^3/min)

Table 4-10 presents the results of regression analyses using the data collection in the study. The model fits with a mean of square error of 1.01 and a sum of square error of 14.1. The kinetic constant obtained from the selected model varied from 0.033 to 0.055 for the conditions encountered in these experiments. For the purpose of this study, a weighted average of 0.045 was used as the kinetic constant in the empirical model. The weighted average was calculated as an average of all the experimental values obtained for the selected ‘best-fit’ model developed from the Sarasota-Verna tray aerator dataset as shown in Table 4-10.

Consequently, considering the experimental methods and taking into account the statistical and mechanistic concepts used in this evaluation, a first-order empirical model that predicts the sulfide content within and across a tray aerator was developed. The model is shown in Equation 4-3, and was used to ascertain how well the mathematical expression predicts sulfide in the outlet of a tray aerator knowing only the number of tray aerator stages and inlet sulfide concentration.

$$C_n = C_o 10^{-0.045n} \quad (4-3)$$

Table 4-11 shows the predicted sulfide concentrations against the actual sulfide concentrations and the differences observed between them are between 0 and 8%. However, there were some percent differences more than 8% that could be due to error in sampling, or impacts of weather.

Table 4-12 shows the total sulfide concentration, overall removal efficiencies and removal efficiencies in each tray derived from the empirical model; it also shows the distribution of H_2S and HS^- based on the predicted sulfide concentration and pH. Figure 4-1 shows a plot of the actual against the predicted sulfide concentrations as provided in Table 4-11 for the three sites analyzed. The diagonal line represents an ideal agreement between the observed and predicted values. This is consistent with the experimental data that suggests that as H^+ concentration and area increases, there is a decrease and increase in the sulfide removal in the tray stages, respectively. The models for the Sarasota 1, Sarasota 2 and Lake Hamilton data sets were predictive, exhibiting correlation coefficients of 0.941, 0.988 and 0.688, respectively.

Figure 4-1 indicated that there was variation in the predicted versus actual model agreement for the UCF and Sarasota 3 data sets, based on coefficient of variation values of 0.550 and 0.734, respectively. This would appear reasonable because the UCF site was sampled on an overcast and humid day, and was the first site evaluated in the study. As such, the UCF data set ended up being a limited effort and a greater chance for error was present because the sampling crew may not have fully understood the details required by the experimental plan.

Table 4-11: Sulfide concentration from first order empirical model and their percent difference.

Location	Tray	Actual measured sulfide concentration	Model	Sulfide concentration predicted by model	% difference
UCF		$C_n = C_0 10^{-0.045n}$			
sulfide inlet					
concentration	1A	3.0		2.7	9.9
3.02 mg/L	2A	2.8		2.7	3.8
	3A	2.3		2.6	12.4
	4A	2.1		2.1	1.6
Lake Hamilton		$C_n = C_0 10^{-0.045n}$			
sulfide inlet					
concentration	2	2.3		2.2	7.2
2.45 mg/L	3	2.2		2.1	4.2
	4	2.2		2.0	8.2
	7	2.1		2.0	4.7
Sarasota site 1		$C_n = C_0 10^{-0.045n}$			
sulfide inlet					
concentration	D2	5.3		5.0	6.5
5.5 mg/L	D3	4.7		4.8	1.7
	D4	4.3		4.2	1.5
	D5	3.7		3.9	4.8
Sarasota site 2		$C_n = C_0 10^{-0.045n}$			
sulfide inlet					
concentration	B2	6.8		6.7	1.9
7.4 mg/L	B3	6.1		6.1	0.5
	B4	5.8		5.5	5.2
	B5	4.3		4.2	1.5
Sarasota site 3		$C_n = C_0 10^{-0.045n}$			
sulfide inlet					
concentration	B2	5.1		5.0	2.8
5.5 mg/L	B3	4.9		4.6	6.2
	B4	3.5		4.4	19.4
	B5	3.7		3.3	4.7

In the case of Sarasota 3 trials, there would be expected variation because at the time that sampling was conducted, strong storms having high winds and unstable atmospheric conditions moved into the area and may have affected data gathering efforts.

Empirical Model Sulfide Variation Analysis

A variation analysis was conducted using the developed model to calculate different experimental constants at different pH or H^+ , tray area and hydraulic flow rate. Table 4-13 presents a result of experimental constants derived from the model when a sensitivity analysis was conducted to determine the changes at a pH between 6 and 8, a hydraulic flow rate between 60 and 140 ft^3/min and a tray area between 2 and 20 ft^2 . Table 4-14 presents the final sulfide outlet concentration obtained from a four tray stage aerator at different pH values (i.e. differing proton concentrations), tray area and hydraulic flow rate as shown in Table 4-13. Table 4-14 shows that a change in pH is more sensitive to the developed model when compared to a change in tray area or change in flow rate. An increase in hydraulic flow rate would impact the model by reducing the sulfide removal in the tray aerators, while an increase in tray area would increase sulfide removal in the trays. The hydrogen ion concentration of the water certainly influences the model as shown in Table 4-14. At a higher pH, there is more sulfide in the form of bisulfide in the water that is non strippable, thereby allowing only a small portion of hydrogen sulfide to be stripped out from the tray aerators.

Table 4-12: Total sulfide concentration and removal efficiencies derived from the empirical model.

Sites	pH	Total sulfide concentration (mg/L as S ²⁻)	H ₂ S concentration (mg/L as S ²⁻)	HS ⁻ concentration (mg/L as S ²⁻)	Sulfide removal efficiency
UCF					
Tray 1	7.7	2.7	0.57	2.2	9.9%
Tray 2	7.9	2.7	0.42	2.3	0%
Tray 3	8.0	2.6	0.32	2.2	6.3%
Tray 4	8.1	2.1	0.21	1.8	19.8%
Overall sulfide efficiency					32.2%
Lake Hamilton					
Tray 1	7.7	2.2	0.51	1.7	9.9%
Tray 2	7.7	2.2	0.44	1.7	2.9%
Tray 3	-	2.0	-	-	5.9%
Tray 4	-	2.0	-	-	1.9%
Overall sulfide efficiency					19.1%
Sarasota site 1					
Tray 1	7.4	5.0	1.6	3.3	9.9%
Tray 2	7.4	4.8	1.3	3.4	3.6%
Tray 3	7.6	4.3	1.1	3.2	11.3%
Tray 4	7.6	3.9	0.83	3.0	8.5%
Overall sulfide efficiency					29.5%
Sarasota site 2					
Tray 1	7.5	6.7	2.4	4.3	9.1
Tray 2	7.6	6.2	2.1	4.0	8.1%
Tray 3	7.6	5.5	1.4	4.1	10.3%
Tray 4	7.7	4.3	1.1	3.2	23.0%
Overall sulfide efficiency					42.7%
Sarasota site 3					
Tray 1	7.3	5.0	2.1	2.9	9.9%
Tray 2	7.5	4.6	1.5	3.1	7.3%
Tray 3	7.6	4.5	1.2	3.2	3.9%
Tray 4	7.7	3.4	0.67	2.7	24.5%
Overall sulfide efficiency					39.4%

Figure 4-1: Predicted versus actual total sulfide concentrations using the first-order empirical model and experimental data

Number of Trays required for Effective Removal

Having developed what appears to be a useful and predictive mathematical expression for evaluating tray aerators for sulfide removal knowing only the inlet sulfide content, a sensitivity analysis was conducted. Most water purveyors in Central Florida utilize three or four stage tray arrays. The model developed in this study was used to evaluate and speculate how an additional number of tray stages could affect sulfide removal effectiveness. Additional work beyond that conducted herein would be required to confirm these speculative projections discussed in this thesis.

Figure 4-2 presents the result of using the developed model to predict concentration levels of sulfide in multiple trays for groundwater supplies having sulfide content as a function of the number of tray stages present. The analyses were bracketed by the highest level of sulfide determined in the field, which was 7.4 mg/L total sulfide at Sarasota-Verna tray aerators. Hence, 8 mg/L of total sulfide was used as the highest inlet sulfide concentration when evaluating the empirical model as shown in Figure 4-2.

Table 4-13: Determination of experimental constants (k) at different pH, hydraulic flow rate and tray area using developed model..

Tray area (ft ²)	<u>Hydraulic flow rate (ft³/min)</u>														
	60	60	60	60	60	100	100	100	100	100	140	140	140	140	140
	<u>pH</u>														
	6	6.5	7	7.5	8	6	6.5	7	7.5	8	6	6.5	7	7.5	8
2	0.007	0.011	0.018	0.028	0.045	0.004	0.006	0.01	0.016	0.025	0.003	0.004	0.007	0.01	0.017
5	0.012	0.019	0.03	0.047	0.074	0.007	0.01	0.016	0.026	0.041	0.004	0.007	0.011	0.017	0.027
10	0.017	0.027	0.043	0.068	0.108	0.01	0.015	0.024	0.038	0.059	0.006	0.01	0.016	0.025	0.04
15	0.022	0.034	0.054	0.085	0.135	0.012	0.019	0.03	0.047	0.074	0.008	0.013	0.02	0.032	0.05
20	0.025	0.04	0.063	0.1	0.158	0.014	0.022	0.035	0.055	0.087	0.009	0.015	0.023	0.037	0.059

Table 4-14: Model sulfide variability analysis used in determining the final sulfide outlet concentration at different pH, hydraulic flow rate and tray area.

		$C_n = C_0 (10)^{-kn}$														
		Hydraulic flow rate (ft ³ /min)														
							pH									
Tray area (ft ²)		60	60	60	60	60	100	100	100	100	100	140	140	140	140	140
		6	6.5	7	7.5	8	6	6.5	7	7.5	8	6	6.5	7	7.5	8
Inlet Conc 1mg/L	2	0.94	0.90	0.85	0.77	0.66	0.96	0.94	0.91	0.87	0.80	0.98	0.96	0.94	0.91	0.86
	5	0.90	0.84	0.76	0.65	0.51	0.94	0.91	0.86	0.79	0.69	0.96	0.94	0.90	0.85	0.78
	10	0.85	0.78	0.67	0.53	0.37	0.92	0.87	0.80	0.71	0.58	0.94	0.91	0.86	0.79	0.69
	15	0.82	0.73	0.61	0.46	0.29	0.90	0.84	0.76	0.65	0.51	0.93	0.89	0.83	0.75	0.63
	20	0.79	0.69	0.56	0.4	0.23	0.88	0.82	0.73	0.6	0.45	0.92	0.87	0.81	0.71	0.58
Inlet Conc 2.5 mg/L	2	2.3	2.3	2.1	1.9	1.7	2.4	2.4	2.3	2.2	2.0	2.4	2.4	2.4	2.3	2.2
	5	2.2	2.1	1.9	1.6	1.3	2.4	2.3	2.2	2.0	1.7	2.4	2.4	2.3	2.1	1.9
	10	2.1	1.9	1.7	1.3	0.93	2.3	2.2	2.0	1.8	1.5	2.4	2.3	2.2	2.0	1.7
	15	2.1	1.8	1.5	1.1	0.72	2.2	2.1	1.9	1.6	1.3	2.3	2.2	2.1	1.9	1.6
	20	2.0	1.7	1.4	1.0	0.59	2.2	2.0	1.8	1.5	1.1	2.3	2.2	2.0	1.8	1.5
Inlet Conc 5 mg/L	2	4.7	4.5	4.2	3.9	3.3	4.8	4.7	4.6	4.3	4.0	4.9	4.8	4.7	4.5	4.3
	5	4.5	4.2	3.8	3.3	2.5	4.7	4.6	4.3	4.0	3.4	4.8	4.7	4.5	4.3	3.9
	10	4.3	3.9	3.4	2.7	1.9	4.6	4.4	4.0	3.5	2.9	4.7	4.6	4.3	4.0	3.5
	15	4.1	3.7	3.0	2.3	1.5	4.5	4.2	3.8	3.3	2.5	4.6	4.5	4.2	3.7	3.2
	20	4.0	3.5	2.8	3.0	1.2	4.4	4.1	3.6	3.0	2.2	4.6	4.4	4.0	3.6	2.9

*Values provided in the table represent sulfide treatments using four tray stages, $C_n = C_0 (10)^{-4k}$.

The data suggests that an additional and beneficial sulfide removal can occur when using more than four tray stages in a design. Figure 4-3 presents the percent sulfide removal anticipated by each tray level. Figures 4-2 and 4-3 suggest that a limiting rate-of-return exists for sulfide removal beyond seven tray stages as sulfide content increased. At approximately 63 percent of the curve, a corresponding fifty percent removal effectiveness could exist in a seven-layer multiple tray design. The result of these limited and speculative analyses suggests that Central Florida purveyors should consider utilizing more than four tray stages, and perhaps as many as seven tray stages, to achieve fifty percent sulfide removal in groundwaters containing less than 8mg/L of total sulfide.

Summary of the Experimentally-Derived Model

The first order empirical model was successfully used in predicting the removal of sulfide from tray aerators. The first order empirical model relied upon a statistically derived experimental constant that was based on pH, tray area, and hydraulic flow rate. The first order empirical model equation used in predicting sulfide removal is given by:

$$C_n = C_o 10^{-kn} \quad (4-4)$$

$$\text{Where } k = (0.00248)(H^+)^{-0.397}(\text{Area})^{0.584}(\text{Flow})^{-1.17}$$

Figure 4-2: Concentration of sulfide (mg/L) in final tray as a function of number of tray stages, n

Figure 4-3: Percent Sulfide Removal by the number of required tray stages.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

Summary

Hydrogen sulfide is commonly found in many Florida potable groundwater supplies. Removing sulfur species, particularly hydrogen sulfide is important because if left untreated, sulfide can impact finished water quality, corrosivity, create undesirable taste and odor, and oxidize to form visible turbidity and color.

The research reported upon herein investigated the removal efficiencies of a variety of tray aerators in Central Florida in order to develop a predictive mathematical model that could be used to predict tray effectiveness for sulfide removal. A literature review was performed that indicated there was limited information regarding the removal of hydrogen sulfide using conventional tray aerators, and no information regarding the removal of total sulfide from tray aerators. There was significantly more information available in the literature regarding the usefulness of sulfide removal technologies from water supplies. Consequently, the lack of literature regarding sulfide removal using tray aerators suggested that there was a need for additional research focused on sulfide removal from water flowing thru tray aerators.

Several water purveyors that relied on tray aerators as a part of their water treatment operations were contacted and requested to participate in the study; three water purveyors agreed to allow the University of Central Florida (UCF) to enter their secured sites to collect samples and conduct this study. The three facilities included the UCF's water treatment plant located in Orlando and situated in eastern Orange County, the City of Lake Hamilton's water treatment plant located in west-central Polk County, and the Sarasota-Verna water treatment plant located in western Sarasota County.

An experimental plan was developed and field sampling protocols were implemented to evaluate sulfide removal in commonly used tray aerators at the three drinking water treatment facilities. Total sulfide concentrations passing through the trays were determined in the field at each site using a standard iodometric analytical technique. In addition, other water quality parameters collected included dissolved oxygen, pH, temperature, conductivity, turbidity, alkalinity, hardness, total dissolved solids and total suspended solids; these samples were collected and determined either in the field or at the UCF laboratory.

Conclusions

Several water purveyors that relied on tray aerators as a part of their water treatment operations were contacted and requested to participate in the study; three water purveyors agreed to allow the University of Central Florida (UCF) to enter their secured sites to collect samples for this study.

The following conclusions were reached during the conduct of this study:

1. Total sulfide concentrations passing through the trays were determined in the field at each site using a standard iodometric analytical technique. Figure 5-1 presents an overview of the results of testing at the three different field locations, and provides a snapshot view of the overall total sulfide removal efficiency for each water plant. Total sulfide removal effectiveness varied between 19.2 percent at Lake Hamilton and 42.7 percent at the Sarasota-Verna location for raw groundwater having a total sulfide content of 2.5 mg/L and 7.4 mg/L, respectively.

Table 5-1: Summary of Overall Total Sulfide Removal Effectiveness for Each Participating Location

Sites	pH	Total sulfide inlet concentration (mg/L as S ²⁻)	Total sulfide outlet concentration (mg/L as S ²⁻)	Overall Sulfide removal efficiency
UCF	8.1	3.0	2.0	32.2%
Lake Hamilton	-	2.5	2.0	19.1%
Sarasota site 1	7.6	5.5	3.9	29.5%
Sarasota site 2	7.7	7.4	4.2	42.7%
Sarasota site 3	7.7	5.5	3.3	39.4%

2. The pH of water flowing through a tray increased and the dissolved oxygen content increased. The largest pH change, from 7.2 to 8.1 pH units at an average temperature of 29 °C, was noted in the Lake Hamilton tray aerators and accompanied a DO rise from 1.9 mg/L to 6.2 mg/L; the Lake Hamilton sulfide removal effectiveness was the lowest of the other sites tested (19.1 percent). In contrast, data collected in the Sarasota-Verna site 2 tray aerator evaluations demonstrated the lowest pH change, from 7.4 to 7.8 pH units at an average temperature of 28 °C, and exhibited a DO increase from 2.3 mg/L to 6.3 mg/L; the Sarasota-Verna site 2 tray aerators exhibited the highest sulfide removal rate at 42.7 percent.
3. An experimental constant was empirically derived based on the data and information collected in this study. The combined parameters of proton concentration, flow rate, and area were statistically evaluated and used to develop an empirical constant that could be used in a first order model to predict sulfide removal in tray aerators. Using statistical analyses and mechanistic concepts, a ‘best-fit’ constant was derived based on the hydrogen ion concentration of the water flowing through the trays, the useable area of the tray, and the hydraulic flow rate of the tray aerator. The empirical constant took the form of:

$$k = (0.00248)(H^+)^{-0.397}(\text{Area})^{0.584}(\text{Flow})^{-1.17} \quad (5-1)$$

where k is the dimensionless kinetic constant, $[H^+]$ is the hydrogen ion concentration ($10^{-\text{pH}}$), area is the amount of useable tray aerator in square feet, and the flow is the hydraulic loading rate to the trays in cubic feet per minute. Based on experimentation conducted at the Sarasota-Verna tray aerator site, k was approximated to equal 0.045.

4. A first-order empirical model was developed that predicted sulfide removal in tray aerators. The model's constant was evaluated with respect to the water's proton concentration $[H^+]$, the tray aerator's surface area, and hydraulic flow rate thru the trays. The selected model took the form of $C_n = C_0 (10^{-kn})$ where C_n is the sulfide remaining after aeration in mg/L, C_0 is the sulfide entering the distribution tray in mg/L and n is the number of tray stages in the aerator and $k = (0.00248)(H^+)^{-0.397}(\text{Area})^{0.584}(\text{Flow})^{-1.17}$. From the empirical model, it was shown that as the pH, and flow increased, sulfide removal was negatively impacted; however, as the available tray aerator surface area increased, sulfide removal also increased. The model was found to be consistent with the experimental data that suggested that as H^+ and area increases, there is a decrease and increase in the sulfide removal in the tray stages respectively. The model was found to be predictive, as shown in Table 5-2.

. Table 5-2: Summary of Model Effectiveness

Location	Number of tray stages	Actual measured sulfide inlet concentration	Actual measured sulfide outlet concentration	Sulfide outlet concentration predicted by model	% difference in sulfide outlet concentration
UCF	4	3.02	2.1	2.05	1.6
Lake Hamilton	4	2.45	2.1	1.98	4.7
Sarasota site 1	4	5.5	3.7	3.88	4.8
Sarasota site 2	4	7.4	4.3	4.24	1.5
Sarasota site 3	4	5.5	3.5	3.34	4.7

5. Using a site-specific derived experimental (empirical) equation, a water purveyor could use the developed model from this work to accurately predict sulfide removal in any tray aerator by simply measuring the total sulfide content in any raw groundwater supply and then providing the desired number of tray stages available for treatment using Tables 4-13 and 4-14. At any given, area, hydraulic flow rate,, and hydrogen ion (H^+), the kinetic constant for the trays can be calculated and the removal of sulfide can be determined from the model.

Recommendations

The data suggests that additional and beneficial sulfide removal can occur when using more than four tray stages in a design of a tray aerator water plant. The result of projecting the model developed in this research would suggest that Central Florida water purveyors should consider utilizing more than four tray stages, and perhaps as many as seven tray stages, to achieve fifty percent sulfide removal in groundwaters containing less than 8 mg/L of total sulfide.

Additional study is recommended to further evaluate atmospheric and meteorological conditions while testing for sulfide removal in tray aerators in order to further develop the model, as it was noted at the UCF and Sarasota-Verna sites, where weather conditions appeared to have an affect on sulfide removal performance.

APPENDIX A: RAW DATA FROM FIELD STUDY

Raw TSS from Sarasota-Verna Tray aerators

Sample Date	Sample ID	Sample Volume (mL)	Initial Weight	Weight 1 (overnight drying)	TSS 1	Weight 2 (1 hr of drying)	TSS 2	%	TSS (mg/L)
7/22/2010	R1D1	200	1.21	1.21	0.0000	1.21	0.0000	0	0.0
	R1D2	200	1.19	1.19	0.0001	1.19	0.0001	0	0.5
	R1D3	200	1.20	1.20	0.0004	1.20	0.0004	0	2.0
	R1D3								
	Dupe	200	1.20	1.20	0.0007	1.20	0.0007	0	3.5
	R1D4	200	1.18	1.18	0.0003	1.18	0.0003	0	1.5
	R1D5	200	1.20	1.20	0.0000	1.20	0.0000	0	0.0
	R1D6	200	1.18	1.18	0.0003	1.18	0.0003	0	1.5
	R1B1	200	1.20	1.20	0.0004	1.20	0.0004	0	2.0
	R1B2	200	1.17	1.17	0.0002	1.17	0.0002	0	1.0
	R1B3	200	1.20	1.20	0.0004	1.20	0.0004	0	2.0
	R1B4	200	1.20	1.20	0.0004	1.20	0.0004	0	2.0
	R1B4								
	Dupe	200	1.17	1.17	0.0003	1.17	0.0003	0	1.5
	R1B5	200	1.19	1.19	0.0003	1.19	0.0003	0	1.5
	R1B6	200	1.18	1.18	0.0004	1.18	0.0004	0	2.0
7/28/2010	Raw	200	1.23	1.23	0.0003	1.23	0.0003	0	1.5
	Effluent	200	1.24	1.24	0.0004	1.24	0.0004	0	2.0

Raw TDS from Sarasota-Verna Tray aerators

Sample Date	Sample ID	Sample Volume (mL)	Initial Weight	Weight 1 (overnight drying)	TDS 1	Weight 2 (1 hr of drying)	TDS 2	%	TDS (mg/L)
7/22/2010	R1D1	100	115	115	0.086	115	0.0854	1	854
	R1D2	100	116	116	0.087	116	0.0866	0	866
	R1D3	100	109	109	0.086	109	0.0850	1	850
	R1D3 Dupe	100	107	108	0.085	108	0.0864	1	864
	R1D4	100	117	117	0.088	117	0.0870	1	870
	R1D5	100	109	109	0.087	109	0.0859	1	859
	R1D6	100	112	112	0.087	112	0.0898	3	898
	R1B1	100	112	112	0.085	112	0.0857	0	857
	R1B2	100	117	117	0.085	117	0.0857	1	857
	R1B3	100	112	112	0.087	112	0.0881	1	881
	R1B4	100	114	114	0.084	114	0.0847	1	847
	R1B4 Dupe	100	113	113	0.085	113	0.0850	1	850
	R1B5	100	113	113	0.085	113	0.0854	1	854
	R1B6	100	110	110	0.086	110.	0.0859	0	859
	Raw	100	112	112	0.081	112	0.0804	1	804
7/28/2010	Effluent	100	107	108	0.082	108	0.0815	0	815

Sulfate data from Lake Hamilton

W/O No:	Sample ID	Dilution For Turbidimetry Method	Turbidity (NTU)	Buffer Type	SO ₄ ²⁻ Conc (ppm) (W/O Adj for Dilution)	SO ₄ ²⁻ Conc (ppm) (With Adj for Dilution)	% RSD	% Recovery
LAK051001	Tray 1	NIL	74.6	B (Low)	5.6	5.6		
	Tray 1D	NIL	73.4	B (Low)	5.2	5.2	93.1	
	Tray 1 Spike (10 mg/L)	NIL	61.6	A (High)	16.5	16.5		107.8
	Tray 2	NIL	71.8	B (Low)	4.6	4.6		
	Tray 3	NIL	70.8	B (Low)	4.3	4.3		
	Tray 3D	NIL	70.0	B (Low)	4.0	4.0	94.0	
	Tray 3 Spike (10 mg/L)	NIL	59.0	A (High)	15.8	15.8		112.3
	Tray 4	NIL	67.3	B (Low)	3.1	3.1		
	Tray 5	NIL	71.3	B (Low)	4.4	4.4		
	Tray 6	NIL	72.1	B (Low)	4.7	4.7		
	Tray 6D	NIL	72.7	B (Low)	4.9	4.9	103.9	
	Tray 6 Spike (10 mg/L)	NIL	55.3	A (High)	14.8	14.8		100.3
	Tray 7	NIL	73.9	B (Low)	5.4	5.4		
	Tray Raw	NIL	74.2	B (Low)	5.5	5.5		

Sulfate data from Sarasota-Verna

W/O No:	Sample ID	Sample Name	Dilution For Turbidimetry Method	Turbidity (NTU)	Buffer Type	SO ₄ ²⁻ Conc (ppm)(W/O Adj for Dilution)	SO ₄ ²⁻ Conc (ppm)(With Adj for Dilution)	% RSD	% Recovery
Tray 0722	R1B1		20:500ml	63.3	A (High)	18.4	459.7		
Tray 0722	R1B2		20:500ml	63.6	A (High)	18.5	462.1		
Tray 0722	R1B3		20:500ml	60.4	A (High)	17.5	436.6		
Tray 0722	R1B4			65.8		19.2	479.5		
Tray 0722	R1B4D		20:500ml	60.5	A (High)	17.5	437.4	91.8	
Tray 0722	R1B4S		99ml sample +1ml of 1000ppm	96.5	A (High)	28.9			102.7
Tray 0722	R1B5		20:500ml	60.2	A (High)	17.4	435.1		
Tray 0722	R1B6		20:500ml	64.2	A (High)	18.7	466.8		
Tray 0722	R1D1		20:500ml	63.9	A (High)	18.6	464.4		
Tray 0722	R1D2		20:500ml	67.4	A (High)	19.7	492.2		
Tray 0722	R1D3		20:500ml	65.7	A (High)	19.1	478.7		
Tray 0722	R1D3D		20:500ml	66.4	A (High)	19.4	484.3	101.0	
Tray 0722	R1D3S		99ml sample +1ml of 1000ppm	97.8	A (High)	29.3			100.95
Tray 0722	R1D4		20:500ml	66.2	A (High)	19.3	482.7		
Tray 0722	R1D5		20:500ml	66.1	A (High)	19.3	481.9		
Tray 0722	R1D6		20:500ml	67.3	A (High)	19.7	491.4		

Raw field data from Sarasota-Verna Tray aerators

Sample ID	Conductivity (mS/cm)	Temp ($^{\circ}C$)	pH	Turbidity (NTU)	Sulfide concentration (mg/L as S^{2-})
Run A	1075	28	7.3	0.30	5.7
Run B	1098	28	7.3	0.31	5.9
Average	1087			0.30	

Effluent field data from Sarasota-Verna Tray aerators

Sample ID	Conductivity (mS/cm)	Temp ($^{\circ}C$)	pH	Turbidity (NTU)	Sulfide concentration (mg/L as S^{2-})
Run A	1059	28	7.7	0.94	3.0
Run B	1061	28	7.8	0.85	3.0
Average	2120			1.80	

Concentration of sulfide (mg/L) in final tray as a function of number of tray stages, n

c_0 (mg/L)	C_n (mg/L)						
	<u>Total number of trays(n)</u>						
	1	2	3	4	5	6	7
1	0.91	0.83	0.75	0.68	0.62	0.56	0.51
2	1.82	1.65	1.5	1.36	1.24	1.13	1.02
3	2.72	2.48	2.25	2.05	1.86	1.69	1.53
4	3.63	3.30	3.00	2.73	2.48	2.25	2.05
5	4.54	4.13	3.75	3.41	3.1	2.81	2.56
6	5.45	4.95	4.5	4.09	3.72	3.38	3.07
7	6.35	5.78	5.25	4.77	4.34	3.94	3.58
8	7.26	6.61	6.00	5.45	4.96	4.50	4.09

APPENDIX B: REGRESSION ANALYSIS RESULTS

Regression Analysis: In K versus In H+, In Area

The regression equation is

$$\text{In K} = -13.0 - 0.528 \text{ In H+} + 0.275 \text{ In Area}$$

Predictor	Coef	SE Coef	T	P
Constant	-12.97	10.20	-1.27	0.223
In H+	-0.5278	0.5638	-0.94	0.364
In Area	0.2752	0.3502	0.79	0.444

$$S = 1.02315 \quad R\text{-Sq} = 7.0\% \quad R\text{-Sq}(\text{adj}) = 0.0\%$$

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	2	1.178	0.589	0.56	0.581
Residual Error	10	15.702	1.047		
Total	12	16.880			

Source	DF	Seq SS
In H+	1	0.531
In Area	1	0.646

Regression Analysis: In K versus In H+, In Q

The regression equation is

$$\text{In K} = -5.3 - 0.258 \text{ In H+} - 0.503 \text{ In Q}$$

Predictor	Coef	SE Coef	T	P
Constant	-5.32	11.74	-0.45	0.657
In H+	-0.2576	0.5681	-0.45	0.657
In Q	-0.5026	0.8042	-0.62	0.541

$$S = 1.03066 \quad R\text{-Sq} = 5.6\% \quad R\text{-Sq}(\text{adj}) = 0.0\%$$

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	2	0.946	0.473	0.45	0.649
Residual Error	10	15.934	1.062		
Total	12	16.880			

Source	DF	Seq SS
In H+	1	0.531
In Q	1	0.415

Regression Analysis: In K versus In H+, InT(C), In Area

The regression equation is

$$\text{In K} = 22.8 + 0.395 \text{ In H+} - 5.96 \text{ InT(C)} + 0.240 \text{ In Area}$$

Predictor	Coef	SE Coef	T	P
Constant	22.82	21.62	1.06	0.309
In H+	0.3949	0.7247	0.54	0.594
InT(C)	-5.964	3.238	-1.84	0.087
In Area	0.2400	0.3258	0.74	0.474

$$S = 0.950187 \quad R\text{-Sq} = 25.1\% \quad R\text{-Sq(adj)} = 9.1\%$$

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	3	4.2402	1.4134	1.57	0.242
Residual Error	9	12.6400	0.9029		
Total	12	16.8801			

Source	DF	Seq SS
In H+	1	0.5313
InT(C)	1	3.2190
In Area	1	0.4899

Regression Analysis: In K versus In H+, In Area, In Q

The regression equation is

$$\text{In K} = -6.0 - 0.397 \text{ In H+} + 0.548 \text{ In Area} - 1.17 \text{ In Q}$$

Predictor	Coef	SE Coef	T	P
Constant	-5.98	11.44	-0.52	0.609
In H+	-0.3967	0.5627	-0.71	0.492
In Area	0.5476	0.4057	1.35	0.199
In Q	-1.1670	0.9249	-1.26	0.228

$$S = 1.00353 \quad R\text{-Sq} = 16.5\% \quad R\text{-Sq(adj)} = 0.0\%$$

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	3	2.781	0.927	0.92	0.456
Residual Error	9	14.099	1.007		
Total	12	16.880			

Source	DF	Seq SS
In H+	1	0.531
In Area	1	0.646
In Q	1	1.603

Regression Analysis: In K versus In H+, In Area, InT(C), In Q

The regression equation is

$$\text{In K} = 21.5 + 0.355 \text{ In H+} + 0.276 \text{ In Area} - 5.60 \text{ InT(C)} - 0.15 \text{ In Q}$$

Predictor	Coef	SE Coef	T	P
Constant	21.51	24.99	0.86	0.405
In H+	0.3550	0.8234	0.43	0.673
In Area	0.2762	0.4553	0.61	0.555
InT(C)	-5.600	4.548	-1.23	0.240
In Q	-0.146	1.230	-0.12	0.907

$$S = 0.985521 \quad R\text{-Sq} = 25.2\% \quad R\text{-Sq(adi)} = 2.2\%$$

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	3	4.2538	1.0635	1.09	0.400
Residual Error	9	12.6263	0.9713		
Total	12	16.8801			

Source	DF	Seq SS
In H+	1	0.5313
In Area	1	0.6464
InT(C)	1	3.0624
In Q	1	0.0137

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