WASTEWATER TREATMENT PLANTS:
ENVIRONMENT, HUMAN HEALTH, AND AIR QUALITY ASSESSMENT

by

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PH.D. THESIS

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To my mother for caring me with unceasing love, patience, and wisdom.
I would like to dedicate this dissertation, my final fruits of seven-year of work, to her who truly dedicated her entire life to me. I love you.

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CHAPTER I

INTRODUCTION

Occupational health studies typically focus on assessments of health problems and their causes, and they are designed to produce recommendations to control the adverse health effects. This study, which focuses on wastewater treatment plants (WWTPs), can be similarly characterized. It was initiated by a fatality at a WWTP in Iowa in 2000, when a worker checking sludge levels manually inside a tank was exposed to an excessive level of hydrogen sulfide. Several studies have found that the majority of human deaths from exposures to hydrogen sulfide occurred in WWTPs or similar industries [Adelson & Sunchine, 1966; Hendrickson et al., 2004; Smith & Cummins, 2004; NIOSH, 2000]. Although average levels of hydrogen sulfide in WWTPs are considered low (less than 20 ppm), the risk of fatal injuries remains and investigations to minimize exposures are warranted, particularly those related to WWTP job duties and procedures since exposures to excessive levels can occur in this occupational setting. For example, job duties or unit operations associated with water agitation can enhance the contaminants' dispersion to the air quickly and increase the risks [Laitinen et al., 1994; Lundholm & Rylander, 1983]. These potential risks have not been sufficiently monitored or investigated in previous studies. Levels of airborne contaminants change by, for example, season, time of day, location of contaminant sources, and features of the unit operation, all of which challenge the accuracy of measurements. Accurate measurements were considered an important subject for this study and prediction of airborne contaminants in a given condition was therefore included as a chapter of the study. Because many engineering studies have shown that computer software is capable of predicting contaminant levels in a given space under a particular condition, it was worth exploring whether one of those software programs could be used as a tool to increase the the efficienty of monitoring contaminant levels.

This study had three aims. The first aim was to evaluate levels of contaminants, particularly hydrogen sulfide and endotoxin, by area monitoring at different workplaces. The second aim was divided into three parts: (1) to survey workers' health in comparison to a control group, (2) to report levels of the two contaminants by personal monitoring during different job tasks, as well as (3) to estimate workers' health risks associated with the job tasks. This study's third aim was to investigate gas concentrations determined by computer simulation to examine whether they were in agreement with concentrations measured by gas tracer analysis. This comparison was made to make recommendations for future use of computer simulation as an air quality assessment technique in complicated indoor environments like those that exist in wastewater treatment plants.

A review of the literature related to these three aims is presented below. Typical wastewater treatment procedure and air quality in WWTPs are discussed, followed by a description of WWTP workers' health and the contaminants associated with health problems. Finally, general principles of computer simulation will be briefly discussed. Chapters II, III, and IV will fully describe the three studies.

Aim 1: Indoor and Outdoor Air Quality Assessment of Four Wastewater Treatment Plants

The entire wastewater treatment procedure involves sequential steps that are different. Wastewater is treated physically, chemically, and biologically in several sequential steps associated with different levels of water agitation. After those procedures, about 0.06% of solid materials remain in the wastewater, including inorganic and organic materials as well as disease-causing organisms (Figure 1-1) [Mancl, 1995].

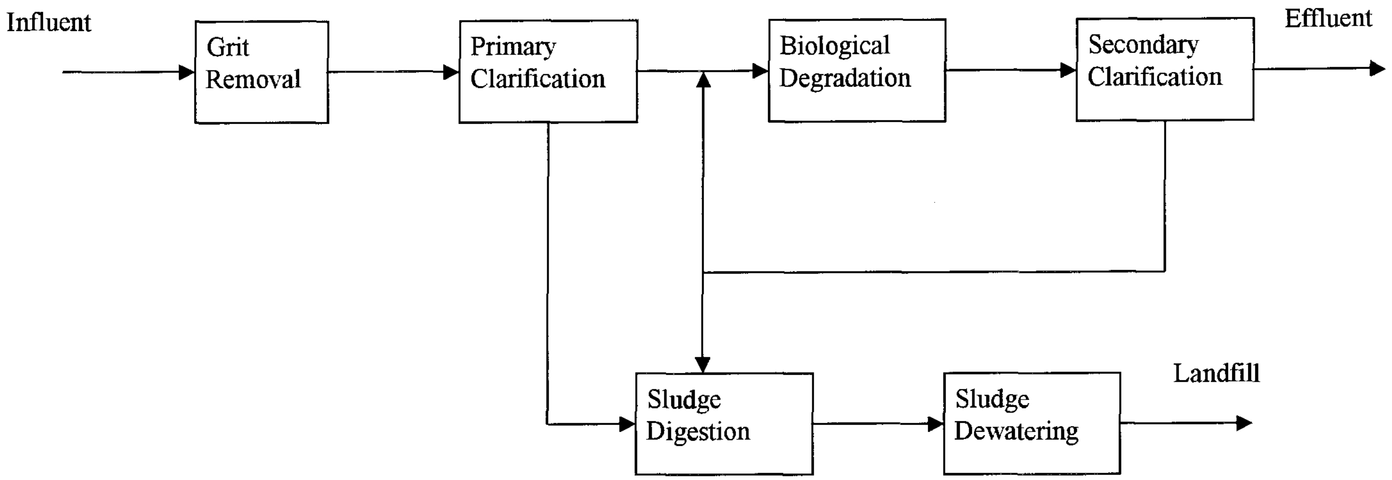

Figure 1-1. Diagram for Wastewater Treatment Process

Once wastewater is collected in sewage pipes, large pieces of debris are first separated out at the WWTP, using bar screens and/or a grit chamber. For the primary clarification step, the water flows to large tanks where it is stored for hours until solids either float to the top or settle down. Chemical polymers are often used to speed the sedimentation of small debris.

Next, the wastewater undergoes bacterial digestion to remove organic compounds; aerobic microorganisms are commonly used for this step. Typically, three types of biological treatment systems are used: fixed film, suspended film and lagoon systems. In fixed-film systems, the wastewater is spread over certain support materials, such as rock-like structures, sand, or plastics, where microorgasms can grow to degrade organic materials in the wastewater. Trickling filters, rotating biological contactors, and sand filters are examples of fixed-film systems. Suspended-film systems mix the microorganisms with the wastewater, and biological degradation occurs in the wastewater itself, as with activated sludge, oxidation ditches, and sequential batch reactors. Lagoon systems hold wastewater in a shallow basin(s) for several months for natural biodegradation, and the effluent from the biological digestion passes through a secondary clarification tank for further sedimentation of suspended materials produced by the bacterial digestion.

The sludge generated from the physical, chemical and biological processes contains highly putriscible organic materials and consists of 97% water by volume. The two main goals of sludge treatment, therefore, are dewatering and stabilization. For the dewatering process, sand drying beds, vacuum filters, filter presses and centrifuges are used in many WWTPs. To transform the putriscible matters into stable or inert organic and inorganic materials, anaerobic digestion is typically used, providing an advantageous net energy gain in the form of methane gas and minimizing the amount of final sludge disposal. After the anaerobic treatment, the sludge is dewatered and sent for either incineration or conversion to fertilizer. The purified water is discharged to a river with or without having undergone a disinfection procedure [Mancl, 1996].

Since the mechanisms of each step in the wastewater treatment process are different, the characteristics and levels of contaminant production are also different. For example, levels of endotoxin, Gram-negative and total culturable bacteria have been found to be higher for unit operations involving grit removal, biological treatment and sludge dewatering; whereas, the levels were low for unit operations that involved less water agitation, such as sedimentation basins [Laitinen et al., 1994; Lundholm & Rylander, 1983; Thorn et al., 2002a]. Many different agents are involved in the treatment process, such as bacterial agents including endotoxin; gases from digestion such as methane, carbon dioxide, volatile organic compounds (VOCs), hydrogen sulfide; and chemicals such as polymers, chlorines, and heavy metals that typically come from industries [McCunney, 1986]. However, levels of the various contaminants in different unit operations have not been sufficiently investigated; the range of contaminants for air quality assessments has been limited to biological agents [Laitinen et al., 1994; Lundholm & Rylander, 1983; Smit, et al., 2005; Thorn et al., 2002a]. After a careful review of the literature, no studies of hydrogen sulfide levels in different unit operations were found. The study described in Chapter II was designed to overcome this lack of information by measuring hydrogen sulfide and endotoxin in various unit operations. Factors potentially associated with contaminant levels such as biological oxygen demand (BOD), total incoming flows, and temperature and relative humidity were also investigated.

Nonetheless, many different agents remain uninvestigated, as previously mentioned, and the need for more information on contaminant levels has increased as the range of health problems becomes broader. Pulmonary symptoms, gastrointestinal symptoms and infection were typically reported in other WWTP studies, while neurological and reproductive symptoms have more recently become critical issues among potentially exposed populations [Gross et al., 2001; Jobling et al., 2002; Jonhson & Sumper, 2001; Kraut et al., 1988; Schiffman et al., 2000; Thorn & Kerakes, 2001; Thorn et al., 2002]. Also, identifying specific causes for symptoms in WWTPs is more difficult because exposures typically occur simultaneously, at low levels, over a long term, and with many other agents. Lung-function decrement, for example, is associated with exposures not only to hydrogen sulfide but also endotoxin. For better decision making on health policies, air quality assessments should be followed by identification of risks and levels of health effects in occupational settings.

Aim 2: Monitoring Risks in Association with Occupational Health in Wastewater Treatment Plants

Typically, many different types of contaminants exist together in wastewater treatment plants. Accordingly, the spectrum of reported symptoms that WWTP workers experience is broad, including gastrointestinal (GI) symptoms, infectious disease, respiratory symptoms/lung function decrement, skin/mucosal irritations and systemic symptoms, such as fever [Thorn & Kerakes, 2001]. Symptoms are often reported to be potentially work-related; prevalence rates of the symptoms among the WWTP workers have been shown to be higher than those for control groups, and several symptoms have been associated with common contaminants (Table 1-1) as well as WWTP workers' job tasks or unit operations. Also, some of the symptoms are directly related to exposure to several contaminants, such as hydrogen sulfide, endotoxin and infectious pathogens like the hepatitis A virus [Bonnani et al., 2001].

Table 1-1. Common Symptoms Associated with Contaminants in WWTP Workers

Symptoms/ disease	Specific Symptoms	Associated contaminants	Reference
Respiratory symptoms	Respiratory function changes	Endotoxin	Rylander, 1985
	Airway and intestinal inflammation	Endotoxin	Rylander, 1999
	Pulmonary edema	Hydrogen sulfide	Milby & Baselt, 1999
	Lung function reduction	Hydrogen sulfide	Richardson, 1995
GI symptoms	Diarrhea, stomach cramps, nausea	Cryptosporidium, giardia lamblia	CDC, 2004
	Stomach pain	Ascariasis	CDC, 2004
	General GI symptoms	Endotoxin	Lundholm & Rylander, 1983
CNS symptoms	Tiredness	Rod-shaped bacteria	Melbostrad et al., 1994
		Hydrogen sulfide	Beauchamp et al., 1984
		Benzene	Kraut et al., 1988
	Headache	Rod-shaped bacteria, total bacteria	Melbostrad et al., 1994
		Hydrogen sulfide	Beauchamp et al., 1984
		Benzene	Kraut et al., 1988
	Fatigue, forgetfulness	volatile organic compounds	Douwes et al., 2001
		Hydrogen sulfide	Beauchamp et al., 1984
	Lightheadedness, increase of sleep requirement	Benzene	Kraut et al., 1988
	Neurobehavioral changes	Hydrogen sulfide	Beauchamp et al., 1984
Ocular symptoms	Eye irritation/ conjunctivitis	Hydrogen sulfide	IPCS, 1981; Ruffat et al., 1999
	Olfactory deficits	Hydrogen sulfide	Hirsch & Zavala, 1999
	Acute eye and throat irritation	Hexaachlorocyclopentadiun (HCCPD)	Morse et al., 1979
Systemic symptoms	Fever/Flu-like symptoms	Endotoxin	Lundholm, 1983; Rylander, 1999
	Runny nose	Aspergillus	CDC, 2004
Infections	Hepatitis A	Hepatitis A virus	Clerk, 1987
	Lung infection	Aspergillus	CDC, 2004
Others	Postural sway	Total volatile organics	Kuo et al., 1996

Common GI symptoms among WWTP workers are diarrhea, stomach pain, indigestion, nausea, constipation and vomiting; these symptoms show moderate to high prevalence rates (13 – 45%) [Douwes et al., 2001; Friis, 1998; Mattsby & Rylander, 1983; Thorn & Kerakes, 2001]. In several studies, gastrointestinal infections and cancers such as gastroenteritis, gastritis and stomach cancers were suspected to result from an unspecific inflammation, infection or a toxic effect by exposures to viral (e.g. Norwalk Agent, *Helicobacter pylori*) and/or bacterial agents (Gram negative bacteria, enterotoxin, endotoxin) [Clark, 1987; Friis et al., 1996; Jeggli et al., 2004; Lundholm & Rylander, 1983].

Increased risks of acquiring hepatitis A among WWTP workers have been well documented in a number of studies that used blood tests or comparison to control groups [Brugah et al., 1998; Cadihac & Roudat-Thorval, 1996; Heng et al., 1994; Shakespeare & Poole, 1993; Skinhoj et al., 1981; Weldon et al., 2000]. In these studies, 30–60% prevalence rates of hepatitis A were indicated and the adjusted odds ratio ranged from 2 to 2.6. Also, occurrences of hepatitis B, leptospirosis, *Entamoeba histolytica* infection, *Giardia Lamblia* infection, gastroenteritis, Pontiac fever, and hepatitis C among WWTP workers were reported, although the number of cases were few [Arvanitidou et al., 1998; Brautbar & Navizadeh, 1999; Clark, 1987; De Serres et al, 1995; Gregersen et al., 1999; Khuder et al. 1998].

Because wastewater is a good source for the growth of numerous bacteria, viruses, and worm eggs, poor hygiene and unit operations involving high water agitation have been highlighted as potentially increasing health risks [Lundholm & Rylander, 1983; McCunney, 1986; Shakespeare & Poole, 1993]. A particular outcome showed that GI illnesses occurred in early years of employment, supporting the possibility that inexperienced workers' practices, such as having poor hygiene, might increase the risk of symptom development [Clark, 1987; Clark et al., 1979]. In contrast to the studies discussed above, other studies have shown no risk of increased infections, including gastroenteritis; however, those studies still stressed immunization for this occupational population to prevent the transmission of infection [Bonanni et al., 2001; Cadihac & Roudat-Thorval, 1996; Glas et al., 2001; Lerman et al., 1990; Levin et al., 20001; Shakespeare & Poole, 1993].

Health effects involving respiratory organs of WWTP workers are well documented with questionnaire surveys and/or lung function measurements with spirometry [Nethercott & Holness, 1988; Rylander, 1990; Thorn et al., 2002b; Juskin et al., 1993]. Common respiratory symptoms are chronic bronchitis, chest tightness, cough, phlegm, wheezing, breathlessness, and upper airway irritations. Prevalence rates of respiratory symptoms were 10 – 27% and the range of odds ratios was between 1.2 and 5.4 [Khuder et al., 1998; Thorn et al., 2002b]. These symptoms are thought to occur from acute and/or prolonged exposures to irritants (e.g. total reduced sulfur and hydrogen sulfide), inflammatory agents (e.g. endotoxin) and high percentage of dust with aerodynamic diameter less than 5 μm particulate [EPA, 2003; Harrison, 2000; Lundholm & Rylander, 1983; Milby & Baselt, 1999; NIOSH, 1994; Nethercott & Holness, 1988; Richardson, 1995; Rylander, 1987; Skerrett et al., 2004]. Typically, these agents that target respiratory organs exist together in WWTPs and are believed to cause workers' respiratory symptoms even at low concentrations [EPA, 2003]. Also, susceptible individuals, such as workers with asthma or those exposed to excessive levels of hydrogen sulfide, showed hyper-responsiveness of the respiratory track at low levels (e.g. 2 ppm). Thus, estimating dose-response relationships for WWTP workers' respiratory symptoms is not as simple as in other occupational populations [Jappinnen et al., 1999; Milby & Baselt, 1999; Toren et al., 1996].

Headache, fatigue/unusual tiredness, and dizziness are central nervous system (CNS) symptoms commonly reported by workers in WWTPs or similar industries [Ahlborg, 1951; Douwes et al., 2001; Kilburn, 1997; Thorn et al., 2002b]. The reported prevalence rate of these symptoms has been 15 to 50%. Generally, hydrogen sulfide, VOCs, malodorous smell, and total/rod-shaped bacteria are known agents associated with these types of neurological/psychological dysfunction [Kilburn, 1997; Kraut et al., 1988; Melbostad et al., 1994; Schiffman et al., 2000]. Hydrogen sulfide was specifically identified in clinical reports as causing brain damage by a single exposure and/or prolonged exposure, and has been suspected as a key element in the occurrence of neurological symptoms [Albin, 2000; Gaitonde et al., 1987; Kilburn, 1997; Matsuo et al., 1979]. In addition, skin/ocular irritations and systemic symptoms are commonly found among WWTP workers, with skin/ocular irritations believed to be attributable to hydrogen sulfide exposure (IPCS, 1981; Hirsch & Zavala, 1999; Ruffat et al., 1999).

Hydrogen sulfide, which is the most acutely toxic gas in WWTPs, can cause sudden unconsciousness and/or death (knockdown) by even a single exposure at levels of 1,000 ppm [IPCS, 2003]. An occupational death poll (the Census of Fatal Occupational Injuries, CFOI) revealed that 52 deaths from 1993 to 1999 were related to hydrogen sulfide poisoning. The major industries in which the fatalities occurred were waste management and petroleum/natural gas industries (at 42%); workers in WWTPs, which have occupational settings similar to those industries, are at high risk for death by hydrogen sulfide exposure [Hendrickson et al., 2004].

The toxic mechanism of hydrogen sulfide for ‘knockdown’ is intracellular inhibition of cytochrome oxidase by sulfide ion on the brain tissue [ATSDR, 1999; WHO, 2000]. However, brain damage from exposure to non-fatal levels of hydrogen sulfide is caused by hypoxia followed by either hydrogen sulfide-induced respiratory failure or by obstruction of oxygen intake, such as pulmonary edema [Milby & Baselt, 1996]. Once inhaled, hydrogen sulfide is rapidly absorbed into the lungs and GI, and broken down into hydrogen sulfide anion, which is believed to be the absorbed form in the body. The gas is then metabolized by 1) oxidation (the major metabolic pathway), 2) methylation, and 3) reactions with metalloproteins or disulfide-containing proteins. In particular, the reaction with metalloenzymes results in toxicity by inhibiting cytochrome oxidase, the final enzyme in the respiratory chain. Disruptions of oxidative metabolism lead to consequent damage on nervous and cardiac tissues, which have the highest demand for oxygen [EPA, 2003].

Many case reports show that human death occurred by a single exposure at levels of 500 ppm or higher of hydrogen sulfide [EPA 2003; Beauchamp. et al., 1984]. Exposure to levels in the range of 100 to 200 ppm can cause olfactory paralysis, so the "rotten-egg odor" typically associated with hydrogen sulfide gas is not an appropriate warning indicator of exposure [Reiffenstein et al., 1992; Hirsche & Zavala, 1999; Sostrand et al., 2000]. At a 20 ppm level, central nervous system symptoms, such as fatigue, loss of appetite, headache, irritability, poor memory and dizziness, were experienced among the exposed group [Ahlborg, 1951]. Eye irritations and metabolic effects were found among the exposed group at levels in the range of 5 to 20 ppm [Bhambhani et al., 1997; IPCS, 1981]. Even at lower levels, such as 2 ppm, bronchial constrictions among asthmatic individuals and spontaneous abortions were indicated in two studies [Jappinen et al., 1990; Hemminiki &Niemi, 1982]. As animal studies noted, hydrogen sulfide was found in the heart, kidney, spleen, brain, liver, lung and blood; given this information, it is assumed that a wide range of human body organs are also affected by exposure to hydrogen sulfide at different concentrations [Kohno et al., 1991].

Various toxic effects by short-term (a few minutes to 14 days) and mid-term (14 to 30 days) exposure at different ranges of hydrogen sulfide concentration were found in animal studies. In a several-hour exposure, death (500 ppm or higher), pulmonary function decrease (200 ppm or higher), cardiac arrhythmia and eye tissue damage (80 ppm), cytotoxic effects on nasal and bronchoalveolar lavage (10 ppm), and behavioral changes (200 ppm) were found [EPA, 2003; Riffat et al., 1999]. Exposure to levels of 20 ppm of hydrogen sulfide for one hour during 11 days caused eye irritation, fatigue, drowsiness, dizziness, and itching to the animals [Haider et al., 1980]. Nasal and olfactory systems were affected by mid-term (10 to 12 weeks) exposure to an 80 ppm level of hydrogen sulfide; mild inflammation and neuron loss on the nasal and olfactory regions were found when the animals were exposed at the 80ppm level for 5-6 hours/day, 5-7 days/week. Also, a decreased rate of weight gain, lack of response to artificial light stimulus, and an irregular gait were shown in the experimental animals [Brenneman et al., 2000; CIIT 1983]. No animal studies have experimented with long-term exposure to hydrogen sulfide.

Endotoxin, which is one of the major contaminants monitored in this study, is regarded as a potential attributor of common symptoms among WWTP workers, such as flu-like symptoms [Thorn et al., 2002b]. The lipopolysaccharide complex, which is part of the outer membrane of Gram-negative bacteria, is referred to as endotoxin [Milton, 1999]. Acute exposure to endotoxin by inhalation can create inflammation in the blood and lungs as well as flu-like symptoms such as fever and chills, acute airflow obstruction by bronchoconstriction, and nonspecific bronchial hypersensitivity [Michel et al., 1997]. The lowest exposure level of endotoxin associated with acute airflow obstruction was 0.7 EU/m^3, as measured by personal monitoring [Kateman et al., 1990]. Chronic exposure—even at low levels of endotoxin (e.g. 45 EU/m^3)—was found to be associated with non-atopic chronic obstructive pulmonary diseases and severity of domestic asthma. Also, fatigue and mucosal irritations were found among individuals exposed to endotoxin at a level of 2 EU/m^3 [Milton, 1997; Michel et al., 1997].

From a practical standpoint, identifying the health risks of job tasks and work spaces is important to minimize detrimental changes in workers' health in WWTPs. Specific health problems have been found to be associated with particular unit operations and/or job tasks; for example, a symptom of "soft stools" was related to pump stations and sludge handling [Thorn et al., 2002b]. Reduced lung function or other chronic respiratory symptoms were associated with "closed channel," "drainage," and "incineration" work practices [Nethercott et al., 1988; Juskin et al. 1993]. Occurrences of gastrointestinal symptoms were related to "cleaning basins" and "servicing pumps," as well as unit operations involving water agitation, such as aerated basins, sprinkler systems, incoming water tunnels and sludge dewatering devices [Lundholm et al., 1983]. Studies in WWTPs have concluded that different characteristics and levels of risks exist in various unit operations and job duties, and induce distinctive health problems. As a result of these conclusions, providing different medical surveillance devices for health problems posed by different job tasks or in different unit operations has been suggested [McCunney, 1986].

Levels of hydrogen sulfide and endotoxin in WWTPs were measured in several studies since these contaminants are considered major attributors for workers' common symptoms. The typical ranges reported were 1 ppm and 1–2000 EU/m^3 for hydrogen sulfide and endotoxin, respectively [Lidwien et al., 2005; Melbostad et al., 1994; Praźmo et al., 2003; Thorn et al., 2002a]. In particular, personal monitoring showed that the majority of the levels were less than 200 EU/m^3 [Lidwien et al. 2005]. A job task of "repair work in sedimentation basin" and unit operations for biological treatments showed higher exposure levels compared to other tasks and unit operations; those levels were 185 EU/m^3 and 30–60 EU/m^3, respectively [Prazmo et al., 2003; Thorn et al., 2002a]. Although two studies showed concentrations of endotoxin associated with specific health problems in WWTPs, the amount of scientific research on hydrogen sulfide and endotoxin related to different job tasks and unit operations is low [Lidwien et al. 2005; Thorn et al., 2002a].

Therefore, the primary goals of this study were 1) to evaluate potential risks associated with characteristics of WWTP workers' jobs by investigating levels of hydrogen sulfide and endotoxin for different unit operation and job tasks, and 2) to make possible recommendations to increase the efficiency of intervention programs to minimize exposure. A final goal aimed to determine relationships between exposure levels and workers' health outcomes. Several limitations exist in this study, such as insufficient sample size; these are described in Chapter III. Nonetheless, the information provided by this study is believed to fill certain gaps of knowledge regarding this occupational setting and will eventually be used to help implement better safety and hygiene plans in WWTPs.

Aim 3: Computer Simulation—A Tool for Air Quality Assessment

TWA is an abbreviation used frequently by Industrial Hygienists when reporting air quality of an occupational workplace. It indicates the "time-weighted average" air concentration of contaminants during a given period, typically eight hours. As an average, a concentration is assumed to be constant over the sampling (measuring) period, and any concentration changes during the period are not detectable unless direct-reading instruments are used. Erroneous results are, therefore, produced when contaminants are changing over time as demonstrated in a study by Nicas [Nicas, 1996]. At the same time, several studies have concluded that mathematical modeling and computer simulation based on Computational Fluid Dynamics (CFD) provide more reliable predictions than real-time monitoring which averages measured concentrations over time (TWA) [Belsley et al., 1980; Feigley et al., 2002; Lee et al., 2002; Nicas, 1996].

With an ultimate goal of minimizing exposure levels and improving workers' occupational health, it was appropriate for this study to investigate the accuracy of methods to monitor airborne contaminants. The mathematical modeling and computer simulations calculated theoretical concentrations at a given time or a given space using a material balance equation and Navier-Stokes equations. The following analysis describes the formulation of models to predict contaminant concentration from the simple "completely-mixed" model to the more complex CFD. The concentration of a contaminant at a given time can be calculated by mathematical manipulation of a differential material balance equation (eq. 1-1) [Gressel et al., 1992].

Accumulation Rate = Generation Rate – Removal Rate

$$VdC = Gdt - \frac{QC}{K}dt \qquad \text{(eq. 1-1)}$$

where V is volume of the room, C is concentration at time t, G is the contaminant's generation rate, Q is flow (ventilation) rate and K is the "mixing factor" that incorporates deviations between the model and actual systems. For estimating the concentration changes between time t_1 and t_2, eq. 1-1 is rearranged in an integration form as follows:

$$\int_{C_{t1}}^{C_{t2}} \frac{dC}{G - QC/K} = \frac{1}{V}\int_{t_1}^{t_2} dt \qquad \text{(eq. 1-2)}$$

where C_{t1} is concentration at t_1 and C_{t2} is the concentration at t_2. Solving the equation yields the following:

$$\ln\left[\frac{G - \frac{QC_{t2}}{K}}{G - \frac{QC_{t1}}{K}}\right] = -\frac{Q}{KV}(t_2 - t_1) \qquad \text{(eq. 1-3)}$$

When the generation rate is zero, the equation becomes

$$\ln\left[\frac{C_{t2}}{C_{t1}}\right] = -\frac{Q}{KV}(t_2 - t_1) \qquad \text{(eq. 1-4)}$$

or

$$\ln C_{t2} = \ln C_{t1} - \frac{Q}{KV}(t_2 - t_1) \qquad \text{(eq. 1-5)}$$

When C_{t0} is replaced for C_{t1} as an initial concentration (t_1=0) and C_t as a concentration at any time, t, eq. 1-5 becomes

$$\ln C_t = \ln C_0 - \frac{Q}{KV}(t) \qquad \text{(eq. 1-6)}$$

As shown, equation 1-6 describes a linear relationship between time and $\ln C_t$ with an intercept, $\ln C_0$, and slope, Q/KV. In an actual system, Q and V are given conditions and concentrations at time *t* can be measured or calculated by real-time monitoring or computer simulations. The mixing factor, K, is a function of the degree of mixing;

therefore, in a perfectly mixed room, the mixing factor is equal to 1. Air in a room with K-factors within the range of 1.5 to 2.0 is regarded as well mixed and 2 or higher as poorly mixed [Koholoff & Scholz, 2004]. If K increases, the effective ventilation rate is decreased and the decay of the contaminant is much slower. An estimation of K from a gas-tracer experiment can be obtained by plotting the relationship between time and lnC measured by real-time monitoring and calculating the resulting slope. Given eq. 1-6 and knowing V and Q, K can be back-calculated.

Recently, multi-zone modeling has been suggested to illustrate imperfectly mixed conditions [Nicas, 1996]. The simplest multi-zone model is a two-zone model in which a room is conceptually divided into upper and lower zones (Figure 1-2). This two-zone model can occur in cases where both the inlet and outlet are located on the ceiling of a room. When air is supplied to the upper zone with a rate of Q and air is exchanged between the two zones at a rate of β, the true ventilation rate in the lower zone (Q_L) is described as:

$$Q_L = \left(\frac{\beta}{\beta + Q}\right) Q \qquad \text{(eq. 1-7)}$$

Because β is always greater than 0, therefore, under most circumstances, Q_L is smaller than Q. When the exchange rate, β, is high enough (in other words, the room is very well mixed) the term in the brackets will approach unity and $Q_L = Q$ (eq. 1-7) and the room is essentially a one-zone, completely-mixed system.

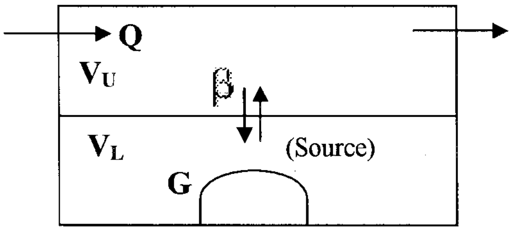

Figure 1-2. Schematic for the Two-Zone Model

Based on this two-zone scenario, Nicas established a formula to calculate decaying concentrations over time when Q, β, and the upper and lower volumes of the space are given [Nicas, 1996]. Although the two-zone model is widely used for airflow investigations, the exchange rates (β), is poorly understood and subsequent studies are needed to explain many factors existing in the real world, including the exchange rate.

Most software packages developed for CFD analysis are based on multi-zone modeling. A CFD software package used in this study, Airpak 2.1 (Fluent. Inc, Lebanon, NH), utilizes a control-volume-based technique for multi-zone modeling. The control-volume-based technique consists of three steps; 1) division of the domain into discrete control volumes using a computational grid, 2) integration of the governing equations on the individual control volumes to construct algebraic equations for the discrete unknown variables (flow properties) such as velocity, pressure, temperature and conserved scalars, and 3) linearization of the discretized equations and solution of the resultant linear equation system to yield updated values of the unknown variables. In Airpak, the governing equations are linearized implicitly; a single variable in all cells is solved at the same time and the next variables are solved at the same time, and so on until variable solution converge to a steady-state value despite further iterations [Fluent, 2001].

In several studies simulating airflows, the reliability of the simulated models was investigated by comparing them to tracer analysis performed by real-time monitoring and to predicted concentrations from mathematical models [Bennett et al., 2000; Feigley et al., 2002; Lee et al., 2002]. Simulation methods using CFD have been reported to estimate the concentrations with less error than simpler approaches, suggesting CFD modeling is a powerful method to evaluate true exposure levels and provide significant information for engineering controls [Flowe et al., 2001; Gilham et al., 2000; Lee et al., 2002; Nicholson et al., 2000; Yang et al., 2001]. This study, therefore, aimed to validate prediction of concentrations from computer simulation and a mathematical modeling by comparing them to measured concentrations from tracer analysis.

Hydrogen sulfide was chosen specifically for the investigation, rather thaninert gases, such as sulfur hexafluoride (SF_6) or carbon dioxide (CO_2) that are typically used as tracer gases in indoor air quality studies, because the behavior of hydrogen sulfide gas is believed to be associated with changes of exposure levels. Since hydrogen sulfide is heavier than air, the gas is anticipated to settle on the floor until an air disturbance occurs. For example, hydrogen sulfide gas was assumed to be contained on the bottom of a sludge dewatering unit and dispersed into the breathing zone when workers sprayed water on the machine for cleaning.

This study aimed to investigate the behavior of hydrogen sulfide gas by using computer simulation and mathematical modeling to depict concentration changes in a given space. Experimental conditions were devised for a chamber fitted with different ventilation rates and different configurations (e.g., locations, number of openings). To compare accuracy, decaying curves of two tracer gases (carbon dioxide, CO_2, and hydrogen sulfide, H_sS) were calculated by computer simulation and mathematical modeling and then compared to the results of tracer analysis; the mathematical modeling used was developed by Nicas [Nicas, 1996]. The outcome of this work, which is discussed in Chapter IV, validates these approaches to estimating hydrogen sulfide and warrants further studies to estimate concentrations of contaminants in unit operations of WWTPs.

CHAPTER II

INDOOR AND OUTDOOR AIR QUALITY ASSESSMENT OF FOUR WASTEWATER TREATMENT PLANTS

Abstract

The study assessed the air quality of four wastewater treatment plants (WWTPs) by monitoring levels of hydrogen sulfide (H_2S) and endotoxin. Samples were taken over a 1-year period (2001– 2002). The unit operations at each WWTP were categorized as: a) grit removal, b) primary clarification, n) biological treatment, d) secondary clarification, e) sludge dewatering, and f) digestion. Temperature and humidity were monitored simultaneously, whereas airborne H_2S and endotoxin were monitored at each of the six unit operations in each plant. Carbonaceous biochemical oxygen demand (CBOD) and total incoming flow of the day of visit were also recorded. The geometric means of H_2S concentration were less than 1 ppm and endotoxin ranged from 6 to 1247 EU/m^3. A mixed-model analysis of covariance (ANCOVA) was used for the statistical analysis. While temperature was not associated with the levels of both contaminants, humidity was influential on the level of H_2S ($p < 0.01$) but not of endotoxin. CBOD did not affect the levels of either contaminant; however, incoming flows showed an association with the levels of H_2S ($p < 0.05$). The concentrations of H_2S in the six unit operations were statistically different, whereas endotoxin did not show any differences in concentrations between units. Individual comparisons proved that concentrations of H_2S in the grit removal and sludge dewatering unit operations were statistically higher than the other operations. Overall, the concentrations of H_2S varied depending on total

incoming flow, humidity, and different unit operations. This trend was not observed for endotoxin. The results showed that the factors analyzed affected concentrations of H_2S and endotoxin differently. Therefore, different control methods for endotoxin and H_2S need to be considered to effectively reduce their concentrations at WWTPs.

Introduction

Wastewater treatment plants (WWTPs) are typical work environments where airborne contaminants such as hydrogen sulfide (H_2S) and microorganisms exist. Particularly, H_2S and endotoxin are believed to cause various health problems even at low levels, and several epidemiologic studies showed high prevalence rates of respiratory health problems among workers in WWTPs and similar industries [Astrakianakis et al., 1998; Laitinen et al., 1994; Lundholm & Rylander, 1983; Melbostad et al., 1994; Schiffman et al., 2000; Thorn et al., 2002]. Although theories regarding a connection between workers' health problems and exposure to contaminants were posed in these studies, adequate information on concentration levels for evaluating the risks has not been sufficiently provided. Concentrations of both H_2S and endotoxin, particularly in WWTPs, have been rarely determined.

The levels of contaminants common to WWTPs have been reported; endotoxin ranged from below detection levels to 4000 EU/m^3 and H_2S levels were reported as less than 2 ppm (Table 2-1) [Laitinen et al., 1994; Laitinen et al., 1992; Liesivuori et al., 1994; Melbostad et al., 1994; Sostrad et al., 2000]. Previous studies have also suggested that the levels of various contaminants, such as endotoxin and total bacteria are related to WWTP procedures– the workplaces containing water agitation, such as aeration basins, inlet tunnels, or water sprinkling systems, showed the highest contaminant levels [Lundholm & Rylander, 1983]. Furthermore, the exposure levels in outdoor workplace areas were lower than indoor areas [Laitinen et al., 1994]. Likewise, concentrations of airborne bacteria and fungi were correlated with the quantity of sewage treated [Brandi et al., 2000]. However, there were a few limitations with these studies: a) precise levels of H_2S were not provided, b) concentration measurements from area sampling devices were rarely reported, and c) potential factors in association with the contaminants' generation rates were seldom investigated.

Table 2-1. Summery of Exposure Levels of Airborne Contaminants Common to WWTPs

	Total Bacteria ($10^3/m^3$)	Spherical Bacteria ($10^3/m^3$)	Rod-shaped bacteria ($10^3/m^3$)	Gram-negative rods ($10^3/m^3$)	Endotoxin (EU/m^3)	Hydrogen Sulfide (ppm)
Typical Levels	520	300	81	NR*	300– 1000	NR*
Ranges	0– 9500	0– 6900	0– 4300	0.01– 100	0– 4000	< 1

* Not reported in literature.

The aim of this study was to characterize the levels of H_2S and endotoxin in WWTPs in a comprehensive manner by monitoring different unit operations at WWTPs and evaluating the influences of other operational and environmental factors on the levels of these airborne contaminants. Specifically, this study investigated three aims: (1) determine whether there is an association between contaminant levels and both qualitative (carbonaceous biochemical oxygen demands) and quantitative (total incoming flow per day) characteristics of wastewater, (2) determine if environmental factors such as temperature and relative humidity affect concentration levels, and (3) determine if the detected levels are different among the various unit operations.

Methods

Site Description

Four wastewater treatment plants in Iowa were chosen for this study. The four plants received both residential and industrial sewage. Total incoming flows varied from 15,140 m^3/day to 143,830 m^3/day and carbonaceous biochemical oxygen demand (CBOD), which is an indicator of the degree of organic contamination of incoming wastewater, ranged from 188 to 550 mg/l (Table 2-2). The unit operations associated with each wastewater treatment plant were categorized as: grit removal, primary clarification, biological treatment, secondary clarification, sludge dewatering, and digestion, although one plant did not have a unit for sludge digestion. The specific operating techniques associated with each unit operation in the four plants are summarized in Table 2-3. Unit operations for grit removal, sludge dewatering, and sludge digestion were located indoors in all four plants and all other units were outdoors.

Table 2-2. Average Levels of CBOD and Total Incoming Flows

Plant	CBOD (mg/L)	Total incoming flow (m^3/day)
Plant I	197	15,140
Plant II	188	18,925
Plant III	550	143,830
Plant IV	208	75,700

Table 2-3. Treatment Techniques

Unit Operation	Plant I	Plant II	Plant III	Plant IV
Grit Removal*	Bar Screening	Bar Screening, Grit removing chamber	Bar Screening	Bar Screening
Primary Clarification	Settling Tank	Settling Tank	Settling Tank	Settling Tank
Biological Degradation	Trickling Filter	Roughing filter, Aeration Basin	Trickling filter (Not accessible)	Aeration Tank (Not accessible)
Secondary Clarification	Settling Tank	Settling Tank	Settling Tank	Settling Tank
Sludge Dewatering*	Sludge Pressing	Dissolved Air Floatation (DAF)	Incinerator	Sludge Pressing
Sludge Digestion*	Digestion	Digestion	N/A	Digestion

* Located indoors.

Sampling and Sample Analysis

Each of the four plants was visited multiple times during the time period between August 2001 and October 2002. At each of the six unit operations, area samples for H_2S and endotoxin were taken over a 4- to 5-hour time period along with temperature and relative humidity measurements. Measurement instruments were placed on a large cart (1.2 m high) and placed within 1 m, and downwind of the edge of a tank associated with the outdoor unit operations (primary and secondary clarification and biological degradation). The cart was placed as near to the source of open water in indoor operations as possible (grit removal and sludge dewatering). The sludge digestion operation involves enclosed tanks; therefore, sampling took place within the control room for this operation at each plant. However, the biological degradation operation in one plant was not available for sampling and one plant did not have a sludge digestion operation. Therefore, a total of 22 unit operations were sampled, and a total of 105 samples for hydrogen sulfide and 104 samples for endotoxin were collected, with 2 to 8 samples taken per unit operation per plant.

H_2S was measured using a direct-reading instrument (Jerome 631-X; Arizona Instrument, Phoenix, AZ). An annual calibration from the manufacturer was completed for the instrument just prior to the initiation of this study. The instrument was also examined using a functional test module (FTM) to check the accuracy of measurements before each visit. As reported by the manufacturer, the limit of detection (LOD) of the instrument was 3 ppb with an accuracy of ± 3 ppb at the level of 50 ppb. The instrument monitored the air for 30 sec at 5-min intervals, with a 0.15 L/min flow rate during the sampling period. The concentrations measured during each sampling period were averaged for the statistical analysis.

Endotoxin was collected using pumps (GilAir; Sensidyne, Clearwater, FL) with 37-mm glass-fiber filters housed in 3-piece cassettes (SKC Inc., Eight Four, PA). The sampling flow rate was 2 L/min and pumps were calibrated using a soap-bubble flow meter (Gilibrator, Sensidyne). The concentration of endotoxin in the air was determined using the *Limulus* amoebocyte lysate (LAL) assay (QCL-1000; BioWhittaker Inc., Walkersville, MD) and reported in endotoxin units per cubic meter (EU/m^3). A 0.05% solution of Tween 20 in pyrogen-free water was used for the filter-extraction. The LOD for the analysis was 0.049 EU/ml of elute solution [Thorne et al., 2003].

Temperature and relative humidity were monitored over the sampling period using a direct reading instrument (Q-trak; model # 5881, TSI Incorporated, Shoreview, MN). The accuracy of the temperature and humidity readings were ±0.6 °C and ± 3% respectively and were calibrated with a sling psychrometer (Bacharach, Inc, Pittsburgh, PA).

Statistical Analysis

Statistical analyses were performed using SAS 9.1 (SAS Institute, Cary, NC). To investigate whether specific unit operations produced higher contaminant concentrations than others, a mixed model ANCOVA for repeated measurements was used. The variable "six unit operations" was considered as a fixed effect and the variable "plants" was a random effect in the mixed model. Also, CBOD, total incoming flow rates, temperature, relative humidity and indoor/outdoor were included as covariants to test their influences on the contaminant levels. A normal distribution was required for satisfying criteria needed to use the repeated mixed model; however the datasets for both contaminants were not normally distributed and a log-transformation was attempted to normalize the H_2S and endotoxin concentrations. This effort did not make the datasets normally distributed and they were then rank-transformed as a nonparametric approach. The six unit operations were grouped as indoor and outdoor units and differences in the levels were tested with the mixed design. As a part of the analysis, an option for a Tukey comparison was applied to identify specific unit operations showing high concentration levels compared to others. A z-test with normal approximation was also used in order to test the difference in contaminant levels between indoor and outdoor units.

The correlations between factors were analyzed with Pearson correlation coefficients. Significant correlations among the factors were detected; therefore, collinearity was suspected to affect the estimate value of each factor. Hence, the values of the model coefficients were compared with and without variables having correlation to see if there were significant changes in the coefficient values. The results of this analysis indicated that there were no significant changes, and collinearity was assumed to have little effect on the results of the regression analysis.

Results

In general, geometric means (GMs) of the H_2S levels at 22 unit operations in the four plants were less than 1 ppm (Figure 2-1, Table 2-4), whereas endotoxin showed a very broad range of GMs among the unit operations, ranging from 6–1248 EU/m^3 (Figure 2-1, Table 2-5). Coefficients of variation (CVs) were calculated to determine seasonal variations. The contaminant levels showed broad ranges in CV values for both contaminants: <0.001 to 1.72 and 0.01 to 0.97 for H_2S and endotoxin, respectively.

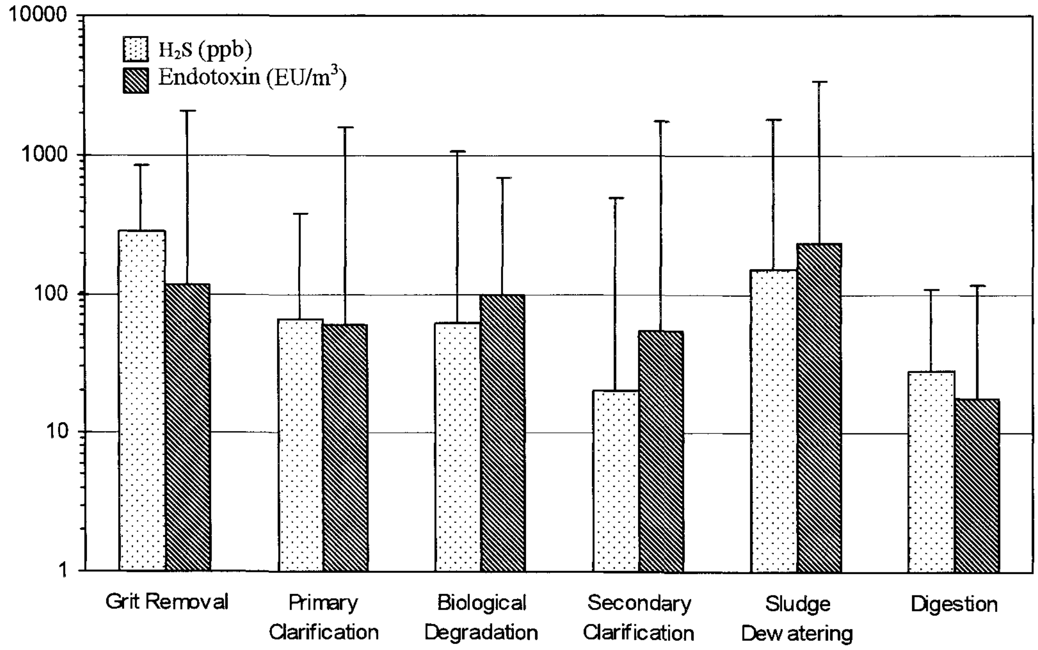

Figure 2-1. Geometric Means and 95% Confidence Intervals of Hydrogen Sulfide (ppb) and Endotoxin Levels (EU/m^3) in Unit Operations

Table 2-4. Hydrogen Sulfide Concentrations Associated With the Unit Operations at the Selected Plants

	Plant I			*Plant II*			*Plant III*			*Plant IV*		
	N	GM(ppb) (range, ppb)	CV	N	GM(ppb) (range, ppb)	CV	N	GM(ppb) (range, ppb)	CV	N	GM(ppb) (range, ppb)	CV
Grit Removal	5	140.9 (3.5 – 544.6)	0.06	8	940.8 (344.0 – 3518.6)	<0.01	4	300.8 (35.5 – 3018.0)	0.04	8	173.8 (3.3 – 4659.0)	0.08
Primary Clarification	4	11.0 (5.5 – 44.0)	0.24	5	76.1 (11.2 – 667.0)	0.07	4	314.0 (51.1 – 2718.5)	0.02	4	73.4 (54.8– 145.4)	0.02
Biological Degradation	4	5.6 (2.9 – 11.6)	0.35		N/A*		6	506.6 (76.8 – 7000.0)	0.01	4	30.5 (5.0 – 76.1)	0.11
Secondary Clarification	2	4.9 (4.0 – 5.9)	0.27	4	2.0 (0.4 – 7.3)	1.72	4	134.3 (11.6 – 676.4)	0.04	4	66.0 (3.3 – 3432.3)	0.28
Sludge Dewatering	5	640.2 (89.1 – 2834.7)	0.01	7	31.6 (1.0 – 1800.0)	0.40	6	940.8 (46.0 – 19022.2)	0.01	5	38.8 (5.0 – 840.0)	0.18
Sludge Digestion	4	27.1 (9.1–76.8)	0.09	4	49.6 (13.8 – 515.9)	0.11		N/A†		4	16.4 (11.5 – 28.4)	0.09

Note: N=sample size; GM= geometric mean; CV= coefficient of variation.

* Area not accessible for sampling.

† No unit operation of this type at this plant.

Table 2-5. Endotoxin Concentrations Associated With the Unit Operations at the Selected Plants

	Plant I			*Plant II*			*Plant III*			*Plant IV*		
	N	GM (EU/m^3) (Range, EU/m^3)	CV	N	GM (EU/m^3) (Range, EU/m^3)	CV	N	GM (EU/m^3) (Range, EU/m^3)	CV	N	GM (EU/m^3) (Range, EU/m^3)	CV
Grit Removal	5	40.70	0.11	8	103.06	0.12	4	534.21	0.01	8	58.59	0.04
		(3.94– 162.57)			(31.81 – 22281.46)			(244.15 – 2139.82)			(17.09 – 319.52)	
Primary Clarification	4	66.82	0.22	5	60.87	0.04	4	35.59	0.06	4	88.79	0.39
		(2.43 – 1585.70)			(14.18 – 155.20)			(16.38 – 82.69)			(3.02– 12983.02)	
Biological Degradation	4	89.07	0.10		N/A*		6	147.77	0.04	4	62.37	0.09
		(6.53 – 1394.90)						(29.00 – 4097.26)			(6.40 – 312.64)	
Secondary Clarification	2	66.00	0.02	4	38.61	0.03	4	68.17	0.04	4	55.85	0.97
		(65.42 – 66.58)			(32.65 – 51.00)			(14.44 – 168.09)			(0.90 – 12234.14)	
Sludge Dewatering	5	308.47	0.01	6	1247.65	0.01	6	393.37	0.02	5	15.45	0.19
		(70.98 – 2261.91)			(87.1 – 34727.85)			(26.13 – 3201.115)			(2.60 – 49.67)	
Sludge Digestion	4	34.14	0.22	4	27.40	0.08		N/A†		4	6.29	0.27
		(5.28 – 594.67)			(14.58 – 82.47)						(3.30 – 11.09)	

Note: N=sample size; GM= geometric mean; CV= coefficient of variation.

[*] Area not accessible for sampling.

[†] No unit operation of this type at this plant.

After including temperature, relative humidity, CBOD and total incoming flow rates into the statistical analysis, the results showed the concentrations of H_2S were significantly affected by the three factors: unit operations, total incoming flow, and relative humidity (p-values< 0.05) (Table 2-6). However, none of the factors of interest in this study were associated with endotoxin concentrations. Individual comparisons of the six different unit operations were analyzed in the mixed model to detect specifically which units contained high levels of contaminants compared to the others. According to the results of the Tukey analysis, concentrations of H_2S in the grit removal unit were statistically higher than all other unit operations except sludge dewatering unit (p-values <0.05). Furthermore, H_2S levels in the sludge dewatering unit were significantly higher than the monitored levels in the secondary clarification and digestion units (p-values <0.05). Concentrations of endotoxin were not statistically different among the six unit operations (Table 2-7).

Table 2-6. Mixed Model Analysis

Effect	Num DF[*]	Den DF[†]	F Value	PR >F
Unit Operations	5	76	4.45	0.0017
Total Flow	1	76	12.98	0.0006
Relative Humidity	1	76	6.27	0.0144

Note: Mixed Model Analysis: the association between h₂s concentrations and different unit operations and environmental factors.

[*] Numerator degree of freedom (k-1).

[†] Denominator degree of freedom (n-1).

Relative humidity was generally constant for both indoor and outdoor unit operations over the four different sampling visits whereas temperatures at outdoor units varied as expected (Table 2-8). Pearson correlation analysis revealed that relative humidity and CBOD were significantly correlated ($r = 0.31$, $p < 0.01$). The association between CBOD and incoming flow rates also proved to be significant ($r = 0.87$, $p < 0.01$). Furthermore, a z-test revealed that H_2S concentrations were higher indoors than outdoors ($p < 0.001$) (Table 2-9).

Table 2-7. Paired Comparison of Hydrogen Sulfide and Endotoxin Concentrations Among the Six Unit Operations

Unit Operation		Hydrogen sulfide		Endotoxin	
		df	*t*	*df*	*t*
Grit removal	Primary Clarification	70	2.63*	62	-0.57
Grit removal	Biological Degradation	70	2.69*	62	-0.78
Grit removal	Secondary Clarification	70	3.82**	62	-0.40
Grit removal	Sludge dewatering	70	0.40	62	-0.51
Grit removal	Digestion	70	2.51*	62	0.22
Primary Clarification	Biological Degradation	70	0.10	62	-0.27
Primary Clarification	Secondary Clarification	70	1.22	62	0.16
Primary Clarification	Sludge dewatering	70	-2.22*	62	0.09
Primary Clarification	Digestion	70	0.13	62	0.66
Biological Degradation	Secondary Clarification	70	1.11	62	0.41
Biological Degradation	Sludge dewatering	70	-2.29*	62	0.32
Biological Degradation	Digestion	70	0.04	62	0.83
Secondary Clarification	Sludge dewatering	70	-3.42**	62	-0.06
Secondary Clarification	Digestion	70	-0.97	62	0.52
Sludge dewatering	Digestion	70	2.15*	62	0.65

* p-value < 0.05; ** p-value <0.01.

Table 2-8. Geometric Means of Temperature and Relative Humidity for Indoor and Outdoor Unit Operations

Unit Operations	Period of visits	Temperature (°C)	Relative Humidity (%)
Indoor[*]	Aug-Sep, 01	23.3	57.5
	Oct-Nov, 01	18.9	52.3
	Feb-Mar, 02	10.5	49.8
	Sep-Oct, 02	20.5	56.5
Outdoor[†]	Aug-Sep, 01	24.1	50.1
	Oct-Nov, 01	16.2	57.6
	Feb-Mar, 02	1.4	52.8
	Sep-Oct, 02	23.5	49.0

[*] Grit remover, sludge dewatering and digestion units.

[†] Primary and secondary clarifications and biological degradation units.

Table 2-9. Least Square Means Estimate of Hydrogen Sulifde Levels

Effect	Estimate	Standard Error	DF	t Value	Pr >|t|
Indoor/Outdoor	1.7076	0.5877	67	2.91	<.005

Discussion

The statistical analysis to compare the concentrations taken from the different unit operations was performed under two assumptions: (1) the chosen four plants were homogeneous, and (2) that each designated unit operation in each of the four plants involved the same treatment technique.

As shown in Table 2-3, the chosen plants used a variety of treatment techniques for the same unit operation. For example, a trickling filter, roughing filter, and aeration tank were utilized for the biological degradation unit operation. However, one of our aims was to detect whether certain unit operations produced statistically different contaminant concentration levels from the others regardless of technique; thus, the effect of different treatment plants on concentration levels was not considered as a factor of interest but rather taken as a random effect in the statistical analysis for the study. Therefore, the comparison between different unit operations involved a comparison between the combinations of different treatment techniques associated with each unit operation rather than each treatment technique separately.

From the comparison of H_2S concentrations among unit operations, the levels associated with grit removal and sludge dewatering were statistically higher than the levels of the other units. Normally, grit removal, biological degradation and sludge dewatering involve a large amount of water movement and resulting turbulence whereas water is retained in primary and secondary clarification tanks for hours with minimal agitation. Therefore, the physical nature of the unit operations influenced the different levels of contaminants measured during this study. In addition, the significant difference between concentrations of H_2S at indoor and outdoor units supports the effect of locations. Compared to indoor units which include grit removal and sludge dewatering, contaminants at outdoor units are likely to be diluted by air dispersion. This outcome suggests that the level of control needed to minimize H_2S levels should be different depending on unit operation type and that the level of control needed to reduce H_2S exposures is related to the amount of wastewater flow through a plant. In this study, endotoxin outcomes showed no difference between different unit operations while such a difference was found in another study [Laitinen et al., 1994]. The lack of an association between unit operation and endotoxin levels in this study may be due to the wide range of variability among the observations.

There are potential health concerns associated with the H_2S levels measured during this study. In this study, 17% of the 105 measurements were higher than the proposed Threshold Limit Value (TLV) of 1 ppm for H_2S. Furthermore, chronic exposures to low levels of H_2S have been associated with health problems such as neurological and respiratory symptoms [Gaitonde et al., 1987; Kilburn, 1997; Richardson, 1995]. Likewise, considering suggested levels of 50 EU/m^3 for endotoxin, the results from this study showed that 60.9% of overall endotoxin levels exceeded the suggested occupational exposure limit level [Heederik & Douwes, 1990]. Therefore, further investigations regarding health problems associated with exposures to hydrogen sulfide and endotoxin among wastewater treatment plant workers are warranted.

CHAPTER III

MONITORING RISKS IN ASSOCIATION WITH EXPOSURE LEVELS AMONG WASTEWATER TREATMENT WORKERS

Abstract

This study investigated the exposure of workers at wastewater treatment plants (WWTPs) to hydrogen sulfide and endotoxin in relation to job tasks and health symptoms. A symptom questionnaire was filled out by 93 workers, of which 49 also carried personal monitoring devices. As a control group, 54 drinking water treatment plant workers responded to the questionnaire. Individual symptoms and four categorized symptoms were used for data analysis: 1) respiratory, 2) neurology, 3) gastro-intestine, and 4) mucosal & skin irritations. The job tasks were classified into ten categories and eight unit operations. Logistic regression analysis was performed to compute statistical associations while controlling for age, gender, smoking, employment-years, asthma and use of respiratory protection.

The prevalence rates of surveyed symptoms were typically higher in WWTP workers compared to the control group. Symptom occurrence rates at work showed the work-relatedness of the symptoms. All four categorized symptoms showed significant odds ratios among WWTP workers compared to the controls. Hydrogen sulfide was less than 1 ppm for all monitored tasks and the averaged endotoxin level was 1071 EU/m^3. Among the tasks, workers were exposed to hydrogen sulfide to the greatest extent during plant inspection and cleaning-workstation tasks (geometric means: 0.23 and 0.27 ppm, respectively). However, hydrogen sulfide levels over 100 ppm maximum were detected

near sludge-related locations or performing sludge-transportation. Several tasks showed statistically significant associations with varied symptoms. This information suggests that health protection programs are required for those tasks associated with the highest contamination levels.

Introduction

A wide range of contaminants are generated as part of the wastewater treatment process: noxious gases (e.g. sulfur containing compounds and volatile organic compounds), chemicals (e.g. PCBs, polymers, and heavy metals), organic agents (e.g. pathogens, fungi, parasites, and viruses), and non-infectious biological agents (e.g. endotoxins and mycotoxins). Studies have associated these contaminants with common health symptoms among workers in waste water treatment plants (WWTPs) or similar industries; where these symptoms are often related to exposure to more than a single contaminant (Table 1-1). The range of symptoms is broad and extends from respiratory, central nervous system and gastrointestinal symptoms to infection and skin/eye irritations. Although fewer studies have investigated the prevalence of reproductive problems and cancers, it is suspected that WWTPs or similar industries' environments are associated with an increase in those conditions as well [Heminnik & Niemi, 1983; IPCS, 2003; Xu et al., 1998].

Respiratory symptoms, which are commonly found in WWTP workers, are associated with exposure to hydrogen sulfide, endotoxin and fine dust. Hydrogen sulfide is a particularly well-known causal agent for respiratory symptoms and lung function decrement [Friis et al., 1999; National Research Council, 1979; Nethercott & Holness, 1988; Richardson, 1995; Rylander, 1990; Thorn & Kerakes, 2001; Thorn et al., 2002b; Juskin et al., 1993]. For example, pulmonary edema can occur by exposure to hydrogen sulfide at a nonfatal level (e.g. 200 ppm or higher) [EPA, 2003]. As an inflammatory agent, inhaled endotoxin also induces obstruction of airflow by bronchoconstriction even at a very low level (0.7 EU/m^3) [Kateman et al., 1990]. This pulmonary failure can lead to obstruction of oxygen intake; consequently, damage to the brain and cardiac system may take place due to oxygen deficiency, as those organs have the highest demand for oxygen [EPA, 2003; Milby & Baselt, 1996].

Central nervous system (CNS) symptoms are known to be related to hydrogen sulfide exposure at a level of 20 ppm [Ahlborg, 1951; Bhambhani et al., 1997]. Common CNS symptoms found among WWTP workers are fatigue, loss of appetite, dizziness, headache, poor memory and psychological change, such as depression and irritability [Bhambhani et al., 1997; IPCS, 1981]. The symptom of 'tiredness' was the most frequently found CNS symptom in WWTPs and the prevalence rates were 33 to 55% [Rylander, 1999; Thorn et al., 2002]. Although the causal mechanisms of psychological symptoms have not been fully understood, animal studies and case reports suggest that behavioral changes are related to hydrogen sulfide exposure [Brenneman et al., 2000; CIIT 1983; Tvedt et al., 1991]. The psychological symptoms, such as depression, among WWTPs are also suspected to relate to hydrogen sulfide exposure. In addition to hydrogen sulfide, volatile organic compounds or rod-shaped bacteria were also found to be associated with CNS symptoms (e.g. headache and fatigue) (Douwes et al., 2001; EPA, 2003; Kilburn, 1997; Kraut et al., 1988; Melbostrad et al., 1994).

Ocular/skin irritations were shown in animal experiments at levels between 5 and 80 ppm by short-term or prolonged exposure to hydrogen sulfide; however, these symptoms can occur in WWTP workers at even lower levels because other agents having similar toxic effects (e.g. endotoxin) also exist in the occupational environment [Brenneman et al., 2000; CIIT 1983; Haider et al., 1980]. Endotoxin, which is ubiquitous in WWTPs, can cause ocular irritation by exposures at a level of 2 EU/m^3 [Milton, 1997; Michel et al., 1997]. Exposure to endotoxin and airborne microorganisms was shown to cause gastrointestinal (GI) symptoms such as nausea, vomiting and diarrhea in many WWTP studies [Clark, 1987; Dean, 1978; Friis et al., 1998; Khuder et al., 1998;

Lundholm & Rylander, 1983; National Research Council, 1979]. In addition, influenza-like symptoms, which were often found among WWTP workers, are strongly suspected to result from endotoxin exposure [Gregersen et al., 1999, Lundholm & Rylander, 1983; National Research Council, 1979; Thorn et al., 2002b].

Although many different contaminants exist in WWTPs, hydrogen sulfide, endotoxin, and bacterial agents were the major concern in past studies because of their high toxicity. For example, a single exposure at 500 ppm or higher of hydrogen sulfide can cause sudden unconsciousness and human death. In addition, an occupational death poll (the Census of Fatal Occupational Injuries, CFOI) indicated that industries similar to WWTPs were the main occupational workplaces where hydrogen sulfide related fatalities occurred [Hendrickson et al., 2004]. For these reasons, more scientific research needs to characterize hydrogen sulfide exposures in WWTPs. Hydrogen sulfide levels at various unit operations or job tasks were rarely reported, whereas information on other agents, such as endotoxin and bacterial organisms, has been provided by other studies (Table 3-1) [Koe, 1985; Prażmo et al., 2003; Sostrand et al., 2000; Thorn et al., 2002a].

Given the results in Table 3-1 indicating different risk levels in the unit operations, other factors associated with job performance, such as job tasks, exposure levels, and employment periods, are suspected to be potentially related to workers' health problems. For example, a proportional relationship with the length of employment period was detected in neuro-behavioral abnormalities [Kraut et al, 1988]. The prevalence of neuro-behavioral symptoms was also related to specific job tasks and unit operations [Khuder et al., 1998; National Research Council, 1979; Zuskin et al., 1993]. "Cleaning basin" and "servicing pumps" areas were, for example, related to occurrences of gastrointestinal symptoms; workers in "closed channel," "drainage," and "incinerator" areas showed high prevalence rates of chronic respiratory symptoms or reduced lung function [National Research Council, 1979; Thorn et al., 2002b; Zuskin et al., 1993]. Hence, distinctive medical surveillance devices have been suggested for various jobs [McCunney, 1986].

However, the volume of information on concentrations of toxic contaminants for various job tasks/unit operations, and the relationship between contaminant levels and workers' symptoms, is insufficient and more investigation is needed.

Table 3-1. Typical Range of Concentrations of Contaminants in WWTPs

	Total mesophilic bacteria	Gram-negative bacteria	Thermophilic actinomycetes	Fungi	Total microorganisms	Endotoxin (personal sampling)	Hydrogen sulfide
Units	cfu/m^3	cfu/m^3	cfu/m^3	cfu/m^3	cfu/m^3	EU/m^3	ppm
Grit sedimentation	2400 – 7100	200– 500	10– 40	20– 50	2400– 7100	2– 180 (2– 300)	-
Pump station	1900	200	20	20	2000	0– 180 (6– 130)	-
Primary clarifier	1700	600	20	30	1800	2	1.0 – 2.0
Biological treatment unit	1500– 2200	100	20	10– 150	1400– 2300	10– 2060	-
Secondary clarifier	600	20	20	10	640	10	-
Sludge dewatering	800	60	50	80	900	2– 20(10)	-
Personal monitoring*	-	-	-	-	0– 9500	0– 4100	<1ppm

* Levels reported without specifying unit operations.

This study was initiated by the need to investigate airborne exposure levels of workers at WWTPs. Hydrogen sulfide and endotoxin were chosen for assessment during this study not only because they are highly toxic but also because information regarding the exposure levels of these contaminants at WWTPs is lacking. Furthermore, workers' job characteristics were investigated in terms of exposure levels of individual job tasks/unit operations and workers' health associated with the job characteristics. Based on the study's outcome, practical suggestions for better safety strategies to reduce the exposure were also made. Specifically, this study aimed to 1) investigate health symptoms among WWTP workers in comparison to a control group, 2) assess exposure levels of hydrogen sulfide for different job tasks and unit operations, and 3) investigate job tasks, unit operations, and population characteristics as risks associated with health symptoms. In the second aim, endotoxin levels were measured during hydrogen sulfide monitoring although the levels were not measured for job tasks and unit operations separately.

Methods

Participants

For this investigation, questionnaires were completed and personal monitoring was conducted in wastewater treatment plants (the exposed group) and water treatment plants (the control group). The exposed group was made up of workers from four WWTPs in Iowa who participated from August 2001 to April 2004. Workers in 21 drinking water treatment plants (WTPs) in Iowa were invited to participate as a control group in 2005. Participation in the exposed group involved both questionnaire and personal monitoring, whereas the subjects in the control group completed the questionnaire only. Except for the questions regarding job performance (see Appendix I), the questionnaire used for the exposed and the control groups was identical; control group subjects were not asked to provide information on job performance since this aspect of WTP workers was not within the scope of the study.

The total numbers of workers in the four participating WWTPs were 140 and 109 for the 21 WTPs respectively. All workers were invited to participate in this study. Out of 140 exposed workers, a total of 93 completed the questionnaire (response rate: 66.4 %) and 67 participated in personal monitoring (response rate: 47.9 %). Among the 67, thirty-seven workers volunteered for personal monitoring more than once (two to twelve times); a total of 125 hydrogen sulfide and 76 endotoxin samples were collected. The number of exposed workers providing both questionnaire data and exposure levels was 49. The response rates in the four plants were different: in one plant the response rates were 45% and 11% for the questionnaire and personal sampling respectively, whereas rates at the other three plants were from 88 to 100%. A reason for the low response rates in the one plant was that plant supervisors did not allow the study to be explained to workers or to study staff to encourage workers' participation. Of the WTP workers (the control group), 66 out of 109 (response rate: 60.6 %) agreed to fill out the survey. Among the 66, twelve control workers had a history of working in WWTPs longer than a year. Therefore, the questionnaires from those workers were discarded.

Health Survey and Questionnaire

The questionnaire used in this study was based on a questionnaire developed for an investigation of endotoxin exposure in agricultural environments [Rylander et al., 1990]. The questionnaire obtained information regarding demographic characteristics, health symptoms, and work activities. The demographic characteristics were age; gender; race; smoking status; respirator use; employment period at the present work site; and physician-diagnosed health conditions, such as asthma, allergies, eczema, and hay fever. Questions were posed on airway and gastrointestinal symptoms; joint pain; skin and eye irritation; fever; and central nervous system symptoms, including headache, unusual tiredness, and memory or concentration difficulties.

The questions for each symptom consisted of occurrence at work, frequency of symptoms, improvement of symptoms during time off work, and increase of symptoms on the first day of the work week. Chronic bronchitis was defined as having a history of cough with phlegm for at least three months a year for a period of at least two consecutive years. A subject was coded as having had ODTS if (s)he answered yes to the following questions; "Have you, during the last year, had episodes of influenza-like symptoms (fever, shivering, malaise, cough, tiredness, weakness, muscle and joint pains) in connection with work?" [Rylander, 1997; Thorn et al., 2002b]. The Center for Epidemiologic Studies Depression Scale (C-ESD, 11 items) was used to define depression [Radloff, 1977]. Getting a score of greater than eight in the C-ESD was defined as having depression.

WWTP workers were asked to fill out an activity log in which a list of unit operations and job tasks were written (Table 3-2). Since there were seasonal variations in performing job tasks for WWTP workers, the workers were asked to characterize their year-round work activities based on a list of job tasks (Table 3-2); percentage of time spent for each task was recorded under the assumption that all work activities during a year totaled 100%. Eighty seven of 93 survey participants provided their year-round work activities. The questions regarding job activities were not asked of water treatment workers since their job performance was not within the scope of this study.

Table 3-2. Unit Operations and Job Tasks of the Activity Logs

Unit Operations	Job Tasks
A. Grit room	1. Cleaning a workstation
B. Primary clarification	2. General building maintenance
C. Biological treating facilities	3. Sample collection and simple chemical analysis
D. Secondary clarification	4. Plumbing &/or sewer duct repair
E. Sludge dewatering, storage	5. Electric work
F. Digester	6. Plant inspection*
G. Disinfection	7. Office work including computer surveillance for processing in office
H. Office/others (e.g. on the road for transportation)	8. Sludge transportation and/or application
	9. Handling chemicals other than hydrogen sulfide†
	10. Break (Lunch)

[*] For this job task, workers tour the plant and check the operation in each unit.

[†] Health effects of chemicals such as chlorine or polymers were evaluated with this job task; exposure to hydrogen sulfide was assumed to be associated with handling sludge or wastewater.

Personal Monitoring

Personal monitoring for airborne endotoxin analysis was performed using pumps (GilAir; Sensidyne, Clearwater, FL) and 37-mm glass-fiber filters housed in three-piece-cassettes (SKC Inc., Eighty Four, PA). The pump was set to collect air with a flow rate of 2 L/min and calibrated using a soap-bubble flow meter (Gilibrator; Sensidyne, Clearwater, FL) before each sampling episode. Endotoxin analysis was performed using the kinetic chromogenic Limulus Amoebocyte Lysate (LAL) assay (QCL-1000; Biowhittaker Inc., Walkersville, MD). The collected filters were extracted using 0.05% Tween 20 in pyrogen-free water. The limit of detection (LOD) was 0.056 EU/ml of elute solution [Thorne et al., 2003].

Personal monitoring for hydrogen sulfide was accomplished with ToxiUltra (Biosystems, Middletown, CT) and Logic 600 Series (Ist-Aim Inc., Horseheads, NY) meters, which have a sensitivity of 0.1 and 1 ppm respectively. They were calibrated before sampling with calibration gases (25 ppm). The concentrations were measured every five minutes for seven to eight hours and recorded using data loggers.

The workers participating in personal monitoring were asked to record their work activity in logbooks. They recorded job tasks and locations every 30 minutes during the monitoring period. When performing multiple tasks, workers were asked to record all job tasks for that period of time in the list. The duration of each task was assumed to be equal during a period of time; for example, if tasks 3 and 4 were performed in the 30-minute period, 15 minutes were assumed to be devoted to each task. Job tasks and unit operations are listed in Table 3-2.

Data Analysis

All data analysis was performed with statistical analysis software (SAS 9.1, Cary, NC). Logistic regression analysis was used to compute odds ratios (OR) of symptoms in the case and control groups with the use of 95% confidence intervals corresponding to a 5% significance level. The percentage of respirator use when the workers were exposed to gases or dust, the type of respirators primarily being used, and the years of using respirators were among the confounding variables. They were coded as follows: (0) if the percentage of respirator used was 0 %, (1) for less than 50% of the time, (2) for 50–80% of the time, and (3) for 80–100 % of time. Likewise coding for personal protective equipment was (0) for no use, (1) for dust mask, (2) for powered air purifying respirator (PAPR), and (3) for self-contained breathing apparatus (SCBA). Duration of respirator use was recorded in years. Smoking was coded as follows: (0) never smoked, (1) used to smoke, and (3) currently smoking. If a worker had any diagnosed allergy, such as food, animals, dust, metal, etc, (1) was used for the coding whereas no allergy was coded as (0).

The surveyed symptoms were categorized into four groups: “respiratory,” “neurology,” “gastro-intestine” and “ocular & skin irritations.” “Respiratory” consisted of dry cough, cough with phlegm, chest tightness, breathlessness, wheeze and chronic bronchitis. “Neurology” included depression, dizziness, unusual tiredness, memory or concentration difficulties, and headache. “Gastro-intestine” included indigestion, diarrhea, constipation, nausea, vomiting, and stomach pains. Throat, nasal, eye and skin irritations as well as sinus troubles composed the “ocular & skin irritations” category. The data of categorized and individual symptoms were used in the logistic regression analysis.

In order to calculate odds ratios (ORs) of symptoms, maximum R-square (MAXR) and Mallow’s Cp were examined to determine variables (age, smoking, years of employment, respirator use, and physician-diagnosed health problems, such as hay fever and allergy). Variables showing the MAXR and lowest Cp were considered in the final models [Belsley et al. 1980]. The ORs were calculated using exact logistic regression adjusting for significant variables associated with symptoms. Smoking was adjusted for ORs of “respiratory” symptoms; years of respirator use was adjusted for “neurology;”

respirator type in use was adjusted for "ocular & skin irritation;" allergy was adjusted for ORs of "gastro-intestine."

Among the variables, collinearity in regression was suspected to exist. Hay fever was associated with asthma, smoking, and allergy in Pearson's Chi-square tests (p-values<0.001). Also, length of employment was associated with age and years of respirator use in the correlation tests (p-value <0.0001 and 0.05 respectively). Therefore, parameter estimates of variables in models with and without the interaction terms were compared. No significant changes in the estimates were shown by adding the terms; therefore, the model was concluded to be insignificantly influenced by correlations among the variables. Variance inflation factors (VIF) in linear regression analysis were also calculated for diagnoses of collinearity in the final models; exceeding a VIF value of 10 is suggested as indicating collinearity and none of the final models had 10 or greater [Belsley et al., 1980].

Associations between health symptoms and job tasks were tested with logistic regression analysis where the risks associated with job tasks were reported with ORs and 90% confidence interval because the sample size was relatively small (n=87). The confounding variables as well as a "plant" variable were controlled in the model because the health symptoms were surveyed in four different plants. All "job tasks" are continuous variables except task 8 (sludge transportation and land application) and task 9 (handling chemicals other than hydrogen sulfide). Those two job tasks were made into a binary variable (0: never work, 1: spending a certain proportion of work hours), because the data distributions showed many 0's for the tasks in the continuous variables. Procedures for choosing variables and diagnosis for collinearity were done in the same fashion as described above.

The correlation between the concentrations of two contaminants was tested with a Pearson correlation test. Tukey comparisons as part of ANOVA tests were performed to compare concentrations of different tasks and locations. Because four different plants participated in this study, a "plant" variable was controlled by addition of the variable in the statistical model.

Results

Population Characteristics

Both of the study populations consisted primarily of males with 91% and 98% for the exposed and control groups, respectively. For the two groups, the average ages were 45 and 49 years, and average employment was 12 and 16 years. Smoking history, respiratory-related health conditions, and use of respirators are summarized in Table 3-3.

Symptoms

Prevalence rates of symptoms questioned were varied (0–44%), with sinus trouble being the highest in the exposed group among the individual symptoms (Figure 3-1). In the symptom categories, the odds of "neurological symptoms" for both groups were the highest, followed by "ocular & skin irritation," whereas "GI symptoms" showed odds of only 0.3 and 0.1 for the exposed and control groups respectively (Table 3-4). Compared to the exposed group, the control group showed lower prevalence rates for all symptoms analyzed. The prevalence rates of the questioned symptoms were typically less than 10%, except mucosal irritations and neurological symptoms, which showed rates of 10–24%.

Chronic symptoms (those persisting longer than three months) were reported in the workers currently having symptoms; these symptoms included cough, breathlessness, stomach pain, mucous irritations, unusual tiredness, headache, and memory or concentration difficulties. However, the numbers of workers with each chronic symptom were low (less than three). Among the control workers, only two workers reported that their current symptoms (tiredness and headache) had lasted for longer than three months. Prevalence rates of chronic bronchitis and ODTS were 3.6% and 12.7% respectively.

Table 3-3. Population Characteristics: Smoking, Respiratory Condition and Use of Respirators

Characteristics	Exposed (%) (N=93)	Control (%) (N=54)
Smoking Status		
Smoker	25.8	20.4
Ex-smokers	36.6	31.5
Never-smokers	36.6	46.3
Respiratory-related condition (Physician diagnosed)		
Asthma	10.8	0
Allergy	23.7	16.7
Hay fever	17.2	16.7
Use of Respirators*		
% of using a respirator when exposed to gases or dusts		
None	49.5	46.3
Less than 50% of the time	24.7	22.2
50-80% of the time	9.7	9.3
80-100% of the time	16.1	22.2
The major respirator type in use		
No use	49.5	48.1
Dust mask	21.5	35.2
Powered Air Purifying Respirator	7.5	1.9
Self Containing Breathing Apparatus	21.5	14.8
Years of using respirators	9.4	7.4

* The percentages were calculated out of the total population of each group.

Table 3-4. Numbers of Symptoms in Four Categories for Exposed and Control Group Workers

Symptoms (list of individual symptoms)	Number of symptoms	Number of workers	
		Exposed (n=93)	Control (n=54)
Respiratory Symptoms *Breathlessness*† *Chest tightness* *Chronic bronchitis* *Cough with phlegm* *Dry cough* *Wheeze*	0	61	46
	1	12	6
	2	10	1
	3	4	1
	4	4	0
	5	1	0
	6	1	0
	Odds [frequency]*	0.5 [32/61]	0.2 [8/46]
GI Symptoms *Constipation* *Diarrhea* *Indigestion* *Nausea* *Stomach pain* *Vomiting*	0	71	50
	1	11	3
	2	6	0
	3	3	1
	4	2	0
	5	0	0
	6	0	0
	Odds [frequency]	0.3 [22/71]	0.1 [4/50]
Ocular & Skin Irritation *Eye irritation* *Nasal irritation* *Sinus trouble* *Skin problem* *Throat irritation*	0	42	43
	1	15	3
	2	15	5
	3	10	2
	4	6	1
	5	5	0
	Odds [frequency]	1.2 [51/42]	0.3 [11/43]
Neurological Symptoms *Depression* *Dizziness* *Headache* *Forgetfulness* *Tiredness*	0	35	33
	1	17	13
	2	14	5
	3	17	2
	4	9	1
	5	1	0
	Odds [frequency]	1.7 [59/35]	0.6 [21/33]

* The ratio of workers having symptoms (at least one) to no-symptom workers.

† Individual symptoms within categories.

Among the exposed workers, prevalence rates of chronic bronchitis and ODTS were 12.9% and 36.6 % respectively. Depression, which was measured by the CES-D depression scale, was indicated in 45.2% of the exposed workers. Of the control subjects, 23.6% were indicated to have depression.

ORs for the four symptom categories changed appreciably among the exposed group (Table 3-5). Among the exposed group, increased risks for most of the individual "neurology" and "ocular & skin irritations" symptoms were found after adjusting use of respirator, hay fever, and allergies. The risks of categorized "gastro-intestine" and "respiratory" symptoms were increased in the exposed workers; however, none of the individual symptoms of these categories showed significant changes in ORs. The OR for ODTS was higher in the exposed group as well, and the exposed group showed a tendency to have higher risks of chronic bronchitis and joint pain compared to the control group (p-values of OR were 0.054 and 0.066 respectively).

Most of the symptoms among the exposed group were potentially work related; symptom-occurrence rates during work shifts were high (75% on average) and the symptoms occurred an average of 3.3 days in 5 workdays (Table 3-6, Figure 3-1). Ocular/skin irritations, which occur instantly from exposure to contaminants, showed high rates of improvement after work-shifts (77–100%), whereas symptoms that take longer to overcome, such as GI problems (stomach pains, indigestion and diarrhea), showed relatively low improvement rates (0–37%). In addition, the improvement rates of the symptoms after the work in the exposed workers were lower than the rates in the controls. The work-relatedness of the symptoms was not apparent in the control group because the number of workers reporting health symptoms was very low, and most workers having symptoms reported that the symptoms occurred at work.

Table 3-5. Adjusted Odds Ratio and Confidence Interval (CI) for Statistically Significant Symptoms

Symptoms	Adjusted variables[‡]	Number of Cases Exposed (n=93)	Number of Cases Controls (n=54)	Odds Ratio	95% CI
Respiratory[†]	Smoking	32	8	2.7^{*}	1.1 – 7.7
Gastro-intestinal[†]	Allergy	22	4	3.3^{*}	1.0 – 14.3
Neurological[†]	Years of respirator use	58	21	3.1^{**}	1.4 – 6.9
Depression	Years of respirator use	43	13	3.0^{**}	1.3 – 7.3
Memory or concentration difficulties	Percentage of respirator use	24	6	3.1^{*}	1.1 – 10.4
Headache	Years of respirator use	32	6	4.8^{**}	1.7 – 16.2
Tiredness	-	33	8	3.1^{*}	1.3 – 8.6
Ocular & skin irritations[†]	Types of respirator in use	51	11	4.6^{***}	2.0 – 11.4
Eye irritation	Types of respirator in use	20	2	6.8^{**}	1.5 – 62.9
Nasal irritation	Types of respirator in use	27	6	1.1^{*}	0.1 – 2.3
Skin Problems	Allergy	17	1	10.0^{**}	1.5 – 435.8
Sinus Trouble	Percentage of respirator use	41	10	3.8^{**}	1.6 – 9.8
Throat irritation	Hay fever	19	4	3.4^{*}	1.0 – 14.8
ODTS (past year)	Employment period in WWTPs	34	7	5.1^{***}	1.8 – 16.1

* p-value <0.05; ** p-value <0.01; *** p-value <0.001.

[†] Symptom categories.

[‡] Adjusted variables in logistic regression analysis.

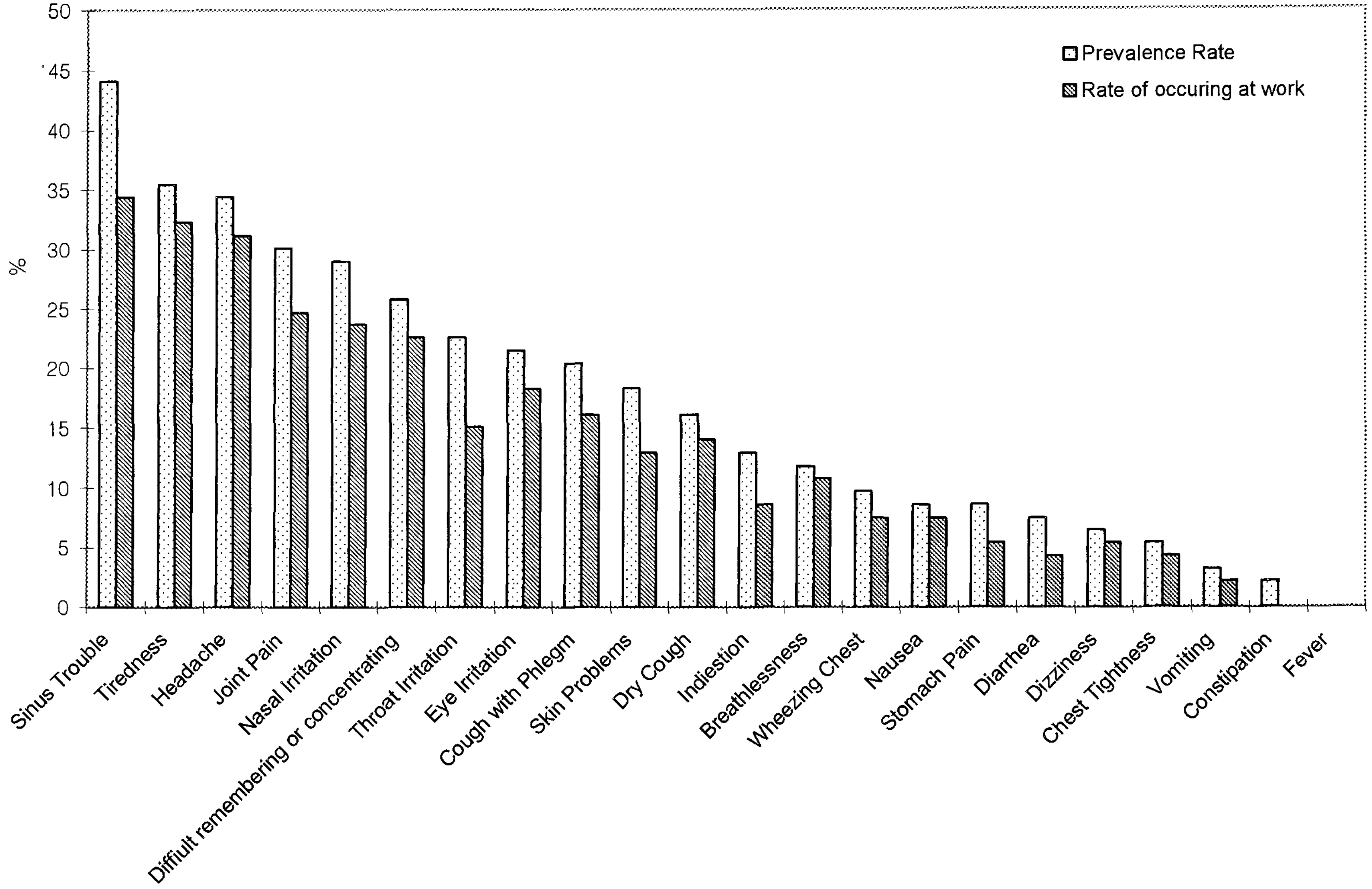

Figure 3-1. Prevalence Rates of Current Symptoms and Occurrence Rates at Work for the Exposed Workers

Table 3-6. Prevalence Rates [and At-work Occurrence Rates], Duration of Symptom Occurrence at Work and Rates of Symptom Improvement after Work among Exposed and Control Group Workers

	Exposed (N=93)			Control (N= 54)		
	Prevalence Rate (%)	*Days occurring during work week*	*Rates of symptom improves (%)*[*]	*Prevalence Rate (%)*	*Days occurring during work week*	*Rates of symptom improves (%)*[*]
Respiratory[†]	12.7 [10.8]	3.2	55.4	3.0 [2.5]	2.9	25.0
Dry Cough	16.1 [14.0]	3.3	69.3	5.5 [3.6]	2.0	0
Cough with Phlegm	20.4 [16.1]	3.6	53.4	5.5 [5.5]	3.7	0
Wheezing Chest	9.7 [7.5]	3.7	42.7	1.8 [1.8]	1.0	0
Chest Tightness	5.4 [4.3]	2.2	51.2	0 [0]	.	.
Breathlessness	11.8 [10.8]	3.4	60.2	1.8 [1.8]	5.0	100.0
Ocular &skin irritation[†]	27.1 [20.9]	3.4	79.4	9.2 [3.7]	1.7	27.1
Nasal Irritation	29 [23.7]	3.6	77.2	10.9 [7.3]	1.5	33.3
Throat Irritation	22.6 [15.1]	2.8	100.0	7.3 [7.3]	2.0	50.0
Sinus Trouble	44.1 [34.4]	3.4	56.4	18.2 [10.9]	2.5	10.0
Skin Problems	18.3 [12.9]	3.6	75.2	1.8 [1.8]	1.0	0
Eye Irritation	21.5 [18.3]	3.7	88.0	3.6 [1.8]	5.0	50
Neurology[†]	25.6 [22.9]	3.4	72.3	9.2 [3.7]	1.7	27.1
Headache	34.4 [31.2]	2.2	79.2	10.9 [7.3]	1.33	16.7
Dizziness	6.5 [5.4]	3.7	79.6	0 [0]	.	.
Memory or concentration difficulties	25.8 [22.6]	3.6	57.1	10.9 [0]	.	.
Tiredness	35.5 [32.3]	4.0	73.4	14.5 [7.3]	2.0	37.5
GI[†]	7.2[4.7]	3.0	56.2	1.8 [1.5]	2.5	0
Vomiting	3.2 [2.2]	2.0	100.0	0 [0]	.	.
Indigestion	12.9 [8.6]	2.8	37.2	3.6 [3.6]	3.5	0
Stomach Pain	8.6 [5.4]	4.3	20.4	1.8 [1.8]	2.0	0
Diarrhea	7.5 [4.3]	3.4	51.2	3.6 [3.6]	2.0	0
Constipation	2.2 [0.0]	-	-	0 [0]	-	-
Nausea	8.6 [7.5]	2.6	72.0	1.8 [0]	-	-
Joint Pain	30.1 [24.7]	4.3	56.7	16.4 [9.1]	2.1	22.2
Fever	0 [0]	-	-	0 [0]	-	-

[*] Calculated among the workers having the symptoms.

[†] Symptom categories.

Concentration of Hydrogen Sulfide and Endotoxin

Average levels of hydrogen sulfide were typically less than 1 ppm and ranged from 0 to 42.50 ppm with a peak level of 122 ppm (Table 3-7, 3-8). Of the collected samples, 95.2% were less than the proposed Threshold Limit Value (TLV) of 1 ppm; the current TLV level of hydrogen sulfide is 10 ppm. The average concentration of endotoxin was 1071.39 EU/m^3, which ranged from 0.59 to 39742.18 EU/m^3. Among the 76 endotoxin samples, 67.1% of the concentrations exceeded 30 EU/m^3, an occupational limit proposed by Heederik & Douwes [Heederik & Douwes, 1990]. Also, no correlation in concentrations of hydrogen sulfide and endotoxin was detected by a t-test.

Hydrogen Sulfide Exposure: Job Tasks and Unit Operation

The job tasks performed during a shift were investigated using data-loggers installed in the hydrogen sulfide monitors (Figure 3-2). Hydrogen sulfide levels were measured every 5 minutes and the averaged concentrations for each job task and unit operation were calculated based on the logbooks that were kept by workers participating in personal monitoring. Geometric means (GMs) of the averaged concentrations for each job tasks/unit operations were calculated; GMs for all job tasks were less than 1 ppm, which is a proposed TLV level (Table 3-7).

Of a total of 355 averaged concentrations for all tasks, ten averages exceeded 1 ppm and the excessive levels were found most frequently in the plant inspection task (n=5). Among the tasks surveyed, the highest GM concentrations were obtained when cleaning a workstation and handling chemicals other than hydrogen sulfide (0.27 and 0.32 ppm respectively) whereas break and office-work hours were the tasks showing the lowest concentrations (0.1 ppm). The maximum average for the task of plant inspection was 42.5 ppm, which is the highest level among all average concentrations. The highest peak levels were found in the task of plant inspection and cleaning workstation, 122.0 ppm and 95.8 ppm respectively.

Concentrations for different job tasks were compared using ANOVA tests with Tukey comparisons. The results demonstrated that the job task of plant inspection was significantly higher than other tasks (p-value = 0.049). Also, plant inspection was the most frequently performed job task of the WWTP workers (n=84). The average duration to perform a job task was about two hours and the workers took more time to perform general building maintenance and electric work than other job tasks. Sewage duct repair, electric work, and handling chemicals other than hydrogen sulfide were the least frequently performed tasks.

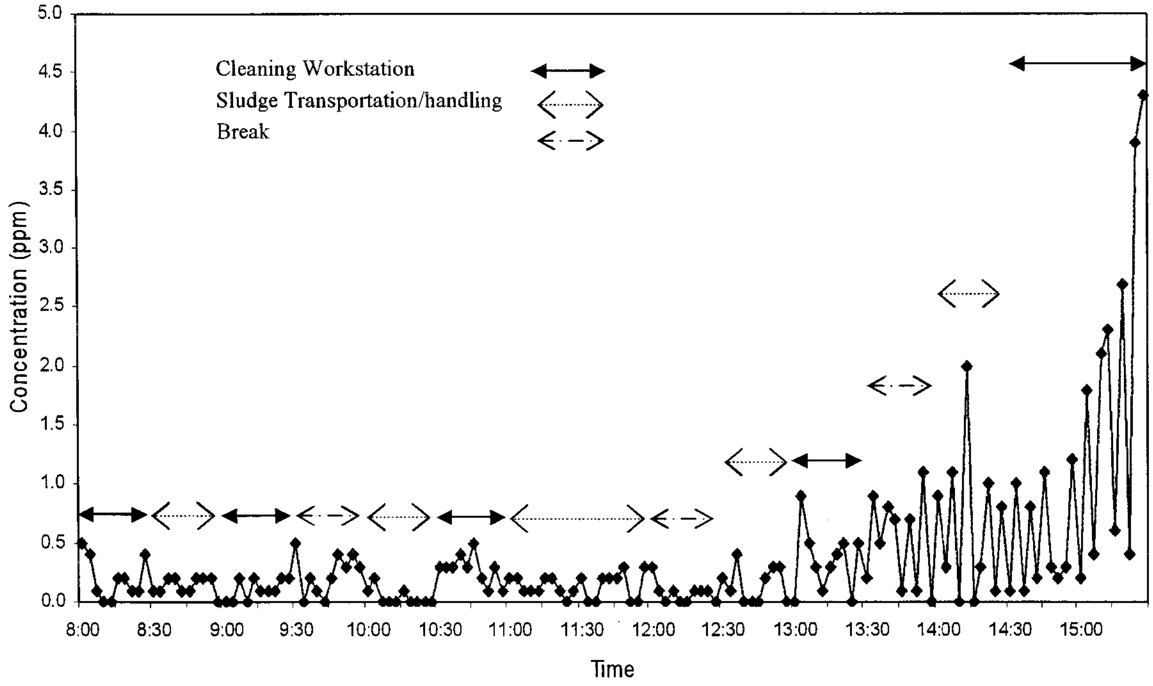

Figure 3-2. Example of Concentrations of Hydrogen Sulfide Measured During a Work Shift

Table 3-7. Average Concentrations of Hydrogen Sulfide during Tasks

Tasks	N[*]	Levels (ppm)	Duration (min)	Tasks	n	Levels (ppm)	Duration (min)
Cleaning a workstation	6	0	117.5	Plant inspection	22	0	166.3
	6	≤0.1	106.5		23	≤0.1	157.6
	7	≤0.2	93.0		10	≤0.2	130.8
	3	≤0.3	69.1		14	≤0.3	142.4
	3	>0.3	114		9	>0.3	139.9
	[2][†]	Max: 14.9			*[5]*	Max: 42.5	
		Peak: 95.8				Peak: 122.0	
(Total) GM[§]	**(25)**	**0.27**	**101.8**	(Total) GM	**(78)**	**0.23**	**151.8**
General building maintenance	11	0	194.5	Office work	11	0	60.9
	6	≤0.1	208.3		18	≤0.1	138.4
	5	≤0.2	262.3		9	≤0.2	117.6
	7	≤0.3	154.3		7	≤0.3	106.6
	6	>0.3	108.3		4	>0.3	168.5
	[0]	Max: 0.6			*[0]*	Max: 0.9	
		Peak: 3.7				Peak: 3.7	
(Total) GM	**(35)**	**0.13**	**183.7**	(Total) GM	**(49)**	**0.11**	**115.1**
Sampling collection and simple chemical analysis	8	0	59.8	Sludge transportation & land application	2	0	202.5
	9	≤0.1	75.6		6	≤0.1	136.3
	13	≤0.2	73.4		4	≤0.2	72.3
	7	≤0.3	71.4		5	≤0.3	113.0
	4	>0.3	81.3		2	>0.3	30.0
	[1]	Max: 1.2			*[0]*	Max: 3.5	
		Peak: 28.0				Peak: 65.0	
(Total) GM	**(41)**	**0.15**	71.7	(Total) GM	**(19)**	**0.21**	**112.5**
Plumbing & sewage duct repair	2	0	115.0	Handling chemicals other than hydrogen sulfide	1	0	70
	2	≤0.1	99.5		1	≤0.1	139
	2	≤0.2	186.0		0	≤0.2	.
	0	≤0.3	.		0	≤0.3	.
	2	>0.3	144.0		3	>0.3	23.3
	[0]	Max: 0.5			*[1]*	Max: 1.0	
		Peak: 5.0				Peak: 1.0	
(Total) GM	**(8)**	**0.15**	**136.1**	(Total) GM	**(5)**	**0.32**	**67.3**
Electric work	1	0	210.0	Break (Lunch)	29	0	59.5
	2	≤0.1	160.0		28	≤0.1	69.5
	0	≤0.2	.		7	≤0.2	85.7
	0	≤0.3	.		14	≤0.3	77.6
	1	>0.3	240.0		9	>0.3	75.5
	[0]	Max: 0.7			*[1]*	Max: 1.0	
		Peak: 4.0				Peak: 7.0	
(Total) GM	**(4)**	**0.17**	**192.5**	(Total) GM	**(87)**	**0.10**	**69.3**
Overall averages	92	0	110.7				
	101	≤0.1	119.9				
	60	≤0.2	115.4				
	57	≤0.3	108.4				
	43	>0.3	107.0				
	[10]	Max: 42.5					
		Peak : 122.0					
(Total) GM	**(355)**	**0.15**	**113.2**				

Notes: Max = Maximum average concentration for the task; Peak = Peak concentration. for the task; GM = Geometric mean.

[*] Number of averaged concentrations for the corresponding range of concentrations.

Table 4-7. Continued

[†] Number of averaged concentrations exceeding the proposed TLV level of hydrogen sulfide (1 ppm).

In a total of 284 average concentrations, seven exceeded 1 ppm and five of the seven were detected in the unit operation of sludge collection & dewatering (Table 3-8). Sludge collection & dewatering was the unit operation with the highest GM (0.42 ppm); GMs of hydrogen sulfide concentrations for the other unit operations were less than 0.2 ppm. The unit operation of sludge collection & dewatering also showed the highest average concentration and peak level (42.5 ppm and 122 ppm respectively).

The unit operations most frequently visited were office/others (n=98), sludge collection & dewatering (n=43), and grit room (n=39). In addition, office/others and sludge collection & dewatering were the unit operations in which WWTP workers spent more time (190 and 150 minutes). Statistical comparisons of exposure levels across unit operations showed the concentrations of hydrogen sulfide in the sludge collection & dewatering were higher than in primary clarification, biological degradation, disinfection, and office/others (p-value = 0.026).

In this study, endotoxin was measured along with hydrogen sulfide by personal monitoring. However, the individual levels associated with different job tasks and unit operations could not be monitored because results of the measurements were integrated over the entire sampling periods. A regression analysis was performed to see if there were significantly contributing tasks or unit operations for endotoxin levels; however, no significance in tasks and unit operations was found.

Table 3-8. Average Concentrations of Hydrogen Sulfide at Unit Operations

Unit Operations	n[*]	Level (ppm)	Duration (min)	Unit Operations	n	Level (ppm)	Duration (min)
Grit room	13	0	81.8	Sludge collection & dewatering	14	0	79.8
	6	≤0.1	137.5		8	≤0.1	210.3
	7	≤0.2	70.4		6	≤0.2	213.8
	6	≤0.3	99.0		4	≤0.3	214.5
	7	>0.3	51.0		11	>0.3	133.0
	[0][†]	Max: 0.63			*[5]*	Max:42.50	
		Peak: 10.0				Peak: 122	
(Total) GM[§]	**(39)**	**0.14**	**85.4**	(Total) GM	**(43)**	**0.42**	**148.9**
Primary clarification tank	5	0	38.1	Digestion	11	0	87.1
	1	≤0.1	75.0		4	≤0.1	271.1
	7	≤0.2	53.5		6	≤0.2	150.6
	4	≤0.3	63.4		1	≤0.3	240.0
	4	>0.3	38.0		4	>0.3	219.3
	[0]	Max: 0.63			*[1]*	Max:1.00	
		Peak: 28.0				Peak: 3.7	
(Total) GM	**(21)**	**0.18**	**49.8**	(Total) GM	**(26)**	**0.12**	**156.3**
Biological degradation unit	6	0	130.4	Disinfection	4	0	24.4
	6	≤0.1	85.9		1	≤0.1	199.0
	7	≤0.2	66.7		0	≤0.2	.
	3	≤0.3	176.0		0	≤0.3	.
	2	>0.3	48.8		1	>0.3	45.0
	[0]	Max: 0.37			*[1]*	Max: 1.00	
		Peak: 4.2				Peak: 1.0	
(Total) GM	**(24)**	**0.12**	**99.6**	(Total) GM	**(6)**	**0.14**	**56.9**
Secondary clarification tank	4	0	27.1	Office/others (e.g. transportation)	24	0	195.5
	9	≤0.1	110.8		39	≤0.1	204.9
	6	≤0.2	89.6		15	≤0.2	174.6
	4	≤0.3	142.3		13	≤0.3	137.4
	4	>0.3	115.5		7	>0.3	209.6
	[0]	Max: 0.41				Max: 0.87	
		Peak: 4.2				Peak: 7.0	
(Total) GM	**(27)**	**0.13**	**99.0**	(Total) GM	**(98)**	**0.10**	**189.4**
Overall averages	81	0	111.2				
	74	≤0.1	180.7				
	50	≤0.2	129.0				
	37	≤0.3	130.5				
	42	>0.3	122.6				
	[7]	Max: 42.50					
		Peak:122					
(Total) GM	**(284)**	**0.16**	**136.6**				

Notes: Max = Maximum average concentration for the task; Peak = Peak concentration for the task; GM = Geometric mean.

[*] Number of averaged concentrations for the corresponding range of concentrations.

[†] Number of averaged concentrations exceeding the proposed TLV level of H_2S (1 ppm).

The percentage of time each worker spent for different tasks during the days associated with this study did not coincide with that devoted to year-round tasks reported in the questionnaire. For instance, workers reported in the questionnaire that they spent the most time annually in plant inspection (27.2%) whereas time spent doing electric work was the highest reported during the day a particular worker was tracked as part of this study (15.78%) (Figure 3-3). Hence, workers' symptoms were analyzed only with the year-round percentages reported in the questionnaire.

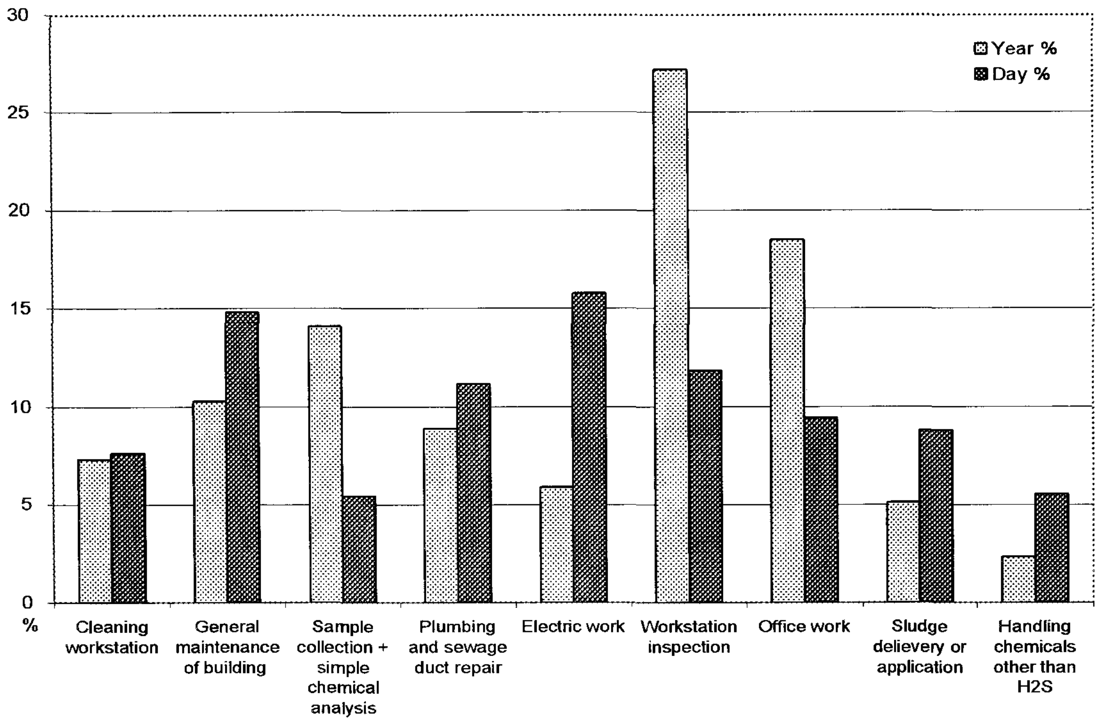

Figure 3-3. Percentages of Time Spent per Day during the Study Period and Year-Round for Job Tasks as Reported in the Questionnaire

Risks Associated with Symptoms

In this study, job tasks, respirator uses and employment period (year) in WWTP plants were considered as risks associated with workers' symptoms, and the information on job task was based on year-round job performance as described previously. The year-round tasks showed statistically significant associations with several symptoms among the questioned WWTP workers, such as neurological symptoms, throat irritations, and stomach pain (Table 3-9).

The three variables regarding respirator use (type of respirator in use; percentage of respirator use when exposed to dust or gases; years of respirator use) were significantly associated with most of the ocular/skin irritation and neurological symptoms.

The higher the protection level of the respirators used by the exposed workers, the more they reported headaches and eye irritations (p-values < 0.05 and < 0.01 respectively). Increased risks of acquiring memory or concentration difficulties and nasal irritation were also associated with a higher percentage of respirator use (p-value < 0.01 and < 0.05 respectively). The more years the exposed workers used respirators, the more they had depression and flu-like symptoms (p-values < 0.01 for both symptoms). In the statistical analysis, smoking history and physician-diagnosed health problems were adjusted; smoking history was adjusted for respiratory symptoms.

The number of workers reporting from 0 to up to 6 specific symptoms in each general symptom category, as well as the concentrations of contaminants (hydrogen sulfide and endotoxin), are summarized in Table 3-10. GMs of both contaminants in the category of respiratory symptoms show the exposure levels of workers with no symptoms were lower than those of most workers having more than one symptom. The GM levels of endotoxin in workers with no symptoms versus more than one symptom show a tendency of increase in Table 3-10. A t-test was performed to compare the exposure levels in two groups (with no symptom, with more than one symptom); however, any significant differences between exposures levels in the two groups were not indicated in the statistical analysis.

Table 3-9. Job Tasks and Significantly Associated Symptoms: Adjusted Odds Radios and 95% Confidence Intervals (CI)

Risks associated with Job Performance	Associated symptoms	Coefficients‡	Odds Ratio (90% CI)
Job Tasks			
Plumbing & sewage duct repair	Neurological Symptoms†	-2.1095	0.12 (0.02 – 0.90)*
Plant inspection	Respiratory Symptoms†	1.7376	5.68 (1.21 – 26.69)*
	Memory or concentration difficulties	3.2013	24.56 (4.31 – 139.92)***
	Throat irritation	1.9538	7.06 (1.43 – 34.75)**
Sludge transportation and land application	Memory or concentration difficulties	-1.3657	0.26 (0.08 – 0.86)*
Handling chemicals other than hydrogen sulfide	Stomach Pain	1.8047	6.08 (1.69 – 21.93)**
Respirators			
Type of respirator in use	Neurological Symptoms†	0.3548	1.43 (1.00 – 2.02)*
	Headache	0.4748	1.61 (1.16 – 2.23)**
	Ocular/skin irritation†	0.5644	1.76 (1.19 – 2.61)**
	Throat irritation	0.4608	1.59 (1.1 – 2.28)**
	Sinus trouble	0.6087	1.84 (1.29 – 2.61)***
	Eye irritation	0.7939	2.21 (1.51 – 3.25)***
Percentage of time using respirator when exposed to dusts and gases	Memory or concentration difficulties	0.6988	2.01 (1.35 – 3.01)***
	Nasal irritation	0.4877	1.63 (1.08 – 2.49)**
Years of respirator uses	Tiredness	0.0942	1.10 (1.03 – 1.17)**
	Dizziness	0.1602	1.17 (1.05 – 1.32)**
Employment period (years) in WWTPs			
	Depression	0.1641	1.18 (1.10 – 1.26)***
	Chronic Bronchitis	0.1094	3.64 (1.90 – 7.00)**
	Ocular/skin irritation†	0.1429	1.15 (1.08 – 2.61)***
	Eye irritation	0.0599	1.06 (1.00 – 1.13)*
	Sinus trouble	0.0569	1.06 (1.01 – 1.11)**
	Skin irritation	0.0664	1.07 (1.01 – 1.13)**
	Flu-like symptoms	0.0735	1.08 (1.03 – 1.13)***
	Joint Pains	0.0907	1.76 (1.13 – 2.74)***

* p-value <0.10; ** p-value <0.05; *** p-value <0.01.

† Symptom categories.

‡ This coefficient represents the linear increment in log odds per unit. For example, the value 1.8037 for the binary variable "handling chemical other than hydrogen sulfide" is the estimated difference in the log odds of stomach pain between workers with and workers without the job task ($e^{\wedge 1.8037}$ = 6.08). As another example of continuous variables, the value of 0.1641 for "employment period in WWTPs" represents the adjusted estimated increase in log odds of depression per one year increment of employment period [Szklo & Nieto, 2000].

Table 3-10. Exposure Levels of Hydrogen Sulfide and Endotoxin in Workers Having Symptoms

			H_2S (ppm)		Endo (EU/m^3)	
	N_s[*]	N_w[**]	GM	Range	GM	Range
Respiratory Symptoms *Breathlessness*[†] *Chest tightness* *Chronic bronchitis* *Cough with phlegm* *Dry cough* *Wheeze*	0	28	0.13	(0–4.12)	16.65	(1.08 – 14583.50)
	1	7	0.23	(0–1.29)	93.52	(6.21–3540.35)
	2	5	0.23	(0–0.95)	43.55	(2.48–277.07)
	3	4	0.49	(0.02–3.02)	495.93	(10.61–3551.91)
	4	3	0.03	(0–0.08)	66.34	(48.17–83.33)
	5	1	0	0	3.25	3.25
	6	1	0.11	0.11	24.36	24.36
GI Symptoms *Constipation* *Diarrhea* *Indigestion* *Nausea* *Stomach pain* *Vomiting*	0	35	0.18	(0–4.12)	33.83	(1.08 – 14583.50)
	1	4	0.04	(0–0.16)	41.09	(10.61–277.07)
	2	6	0.04	(0–0.16)	109.94	(6.21–3236.29)
	3	2	0.01	(0–0.01)	3.01	(1.49–6.09)
	4	2	1.11	(0.11–3.02)	294.15	(24.36–3551.91)
	5	0	N/A	N/A	N/A	N/A
	6	0	N/A	N/A	N/A	N/A
Ocular & Skin Irritation *Eye irritation* *Nasal irritation* *Sinus trouble* *Skin problem* *Throat irritation*	0	22	0.20	(0–4.12)	26.33	(1.08 – 14583.50)
	1	9	0.07	(0–0.18)	88.14	(5.26–1451.30)
	2	8	0.05	(0–0.12)	33.20	(1.49–2503.49)
	3	6	0.23	(0.02–0.95)	77.21	(2.48–3236.29)
	4	3	0.01	(0–0.02)	5.95	(3.25–1061)
	5	1	3.02	3.02	3551.91	3551.91
Neurological Symptoms Depression Dizziness Headache Forgetfulness/ Tiredness	0	17	0.24	(0–4.12)	49.98	(1.68 – 3540.35)
	1	9	0.22	(0–0.18)	23.38	(1.08–3551.91)
	2	9	0.05	(0–0.17)	35.60	(1.49–14583.50)
	3	8	0.22	(0–0.95)	29.05	(2.48–298.39)
	4	5	0.05	(0.02–0.11)	81.01	(3.25–1061)
	5	1	0	0	83.33	83.33

[*] Number of symptoms; [**] number of workers.

[†] Individual symptoms in the symptom categories.

Discussion

The outcome of the analysis of symptom data reflect that the symptoms were potentially work related - a high percentage of workers reported that most symptoms occurred during work hours, and the duration of symptoms was 3.3 days out of 5 workdays. In particular, symptoms occurring soon after exposure, such as "ocular/skin irritations" disappeared after the shifts at high rates (56-100%), whereas GI symptoms, which typically develop with repeated exposures, did not readily disappear; up to 37 % of workers with symptoms reported the symptoms cleared after the work shift (Table 3-6).

The work-relatedness of symptoms was further investigated in terms of job tasks, respirator use, and years of employment in WWTPs. As Table 3-7 and 3-8 indicate, a certain job performance or unit operation changed the exposure levels. Through statistical analysis, workers were found to be highly exposed to hydrogen sulfide during plant inspection and in sludge dewatering/transportation compared to other job tasks and unit operations. Also, plant inspection and sludge dewatering/transportation showed all peak levels exceeding or close to 100 ppm of hydrogen sulfide. These different risk levels in job performance may explain how the association between plant inspection and throat irritation and memory/concentration difficulties occurred; even though the exposure levels were relatively low (0.23 ppm in GM), the symptoms are highly suspected to result from hydrogen sulfide exposure.

Characteristics of job performance were also assumed to be significant factors in changing risk levels. When workers' job activities are associated with a lot of water agitation, or if a worker's job task location is close to contaminant sources, exposure levels will be increased. For example, "cleaning workstations" was associated with significantly higher levels of hydrogen sulfide. The job task is typically associated with water spraying and might increase a worker's chance to inhale the gas; hydrogen sulfide is a heavier gas and would subside (or be stabilized) on the floor. Once workers spray water to remove sludge from the station, the gas can be stirred up to the breathing zone and thus cause the high level of exposure. As shown in Table 3-11, the levels from personal samplings were relatively higher than those from area sampling. At the participating WWTPs, area monitoring was conducted by placing the measuring instruments about one or two feet away from the operating station. Hence, the workers were assumed to be closer to an operation station and potentially taking in more airborne contaminants before they dispersed to the ambient air.

Table 3-11. Comparison of Concentrations of Hydrogen Sulfide from Environmental and Personal Monitoring (ppm)

	Area monitoring			Personal monitoring		
	n	GM (ppm)	GSD	n	GM (ppm)	GSD
Grit removal	25	0.284	0.008	39	0.138	0.138
Primary clarification	17	0.067	0.005	21	0.176	0.188
Biological digestion	14	0.063	0.010	24	0.120	0.104
Secondary clarification	14	0.020	0.011	27	0.131	0.114
Sludge collection & dewatering	23	0.151	0.013	43	0.421	1.076
Digestion	12	0.028	0.003	26	0.117	0.031
Disinfection		-		6	0.137	0.109
Others		-		98	0.096	0.120

Respirator use, which was monitored in terms of type of respirator, percentage of time using respirator, and years of respirator use, were largely related to neurological symptoms and ocular irritations (Table 3-9). The association was assumed to occur due to fatigue from wearing the respirators and use of respirators incorrectly when entering highly contaminated unit operations because an increased risk of "ocular/skin irritations" was found among the workers using respirators with higher protection levels. The only types of respirators currently available for protection against hydrogen sulfide exposure over an eight-hour shift are the powered air purifying respirator (PAPR) and self-contained breathing apparatus (SCBA), the uncomfortable features of available respirators may discourage workers from wearing them. Therefore, periodic training on appropriate respirator use is important for WWTP workers, and manufacturers should be encouraged to develop lighter, more comfortable respirators.

The employment period was also a significant factor associated with workers' symptoms, such as depression, chronic bronchitis, ocular/skin irritations and flu-like symptoms. This association is similar to results shown in a couple of studies, in which the length of employment was associated with "neuro-behavioral abnormality" and "lower respiratory & skin symptoms" [Kraut et al., 1988; Smit et al, 2005]. Given that the present study also showed a potential increase of the health problems from exposures over an extended period, two suggestions are particularly relevant for long-term employees. First, they should be trained in precautionary work practices (even though exposure levels of contaminants are relatively low). This may pose a challenge with this particular group. For example, WWTP workers at the facilities associated with this study wear a monitor to indicate exposure levels when they enter unit operations where contaminant levels are highly contaminated; once the monitor alarm sounds they are mandated to vacate the location. However, participating workers often continued to work when they thought the indicated levels were not dangerously high. The second recommendation is for WWTP workers to receive enhanced medical surveillance, in particular, periodic surveillance and prevention programs for depression. The prevalence rate of depression (about 45%) among the largely male WWTP worker population was noticeably higher than that of the general population (18% for males) [Merchant et al., 2002]

This study contains limitations that requires further investigation, especially in relation to the time-integrated endotoxin measurements and repeated measurements of exposure levels. As this study found different exposure levels of hydrogen sulfide for various job performances, a comparable result would be expected for endotoxin. Changes of endotoxin levels in different unit operations have been found in other studies; for instance, higher levels of Gram-Negative Bacteria (GNB) were detected at water-agitated unit operations such as aeration basins with sprinkler systems [Lundholm & Rylander, 1983; Thorn et al., 2002b]. Although endotoxin monitoring was conducted in this study, individual levels of endotoxin associated with different job tasks and unit operations were not measured. This type of investigation into endotoxin is important, to increase the amount of basic information and to provide specifics on risk levels in various jobs, which can lead to better safety plans.

The single measurement of hydrogen sulfide for each worker weakened the rationale for connecting exposure levels with worker symptoms. Statistical analysis showed insignificant association between the exposures and symptoms; however, uncertainty about the association remains because a single measurement cannot represent a typical exposure level throughout a year. The dose-response relationship of hydrogen sulfide exposure in WWTPs needs to be evaluated through further investigation with repeated measurements because the unique WWTP environment can result in health problems even at lower doses, as mentioned previously.

Having WTP workers as a control group provided the advantages of a similar population background and controlled background variables: socio-economical status, physical activities for job performance, and education levels. However, use of the WTP workers as a control group could have created a confounding factor. WTP workers are potentially exposed to chlorine, which is typically used for disinfecting water. As chlorine gas is a well-known agent causing pulmonary irritations and lung injuries, the respiratory symptoms this study investigated might be associated with exposure to chlorine in this population. Smit used office staff in participating WWTPs as a control group [Smit et al., 2005]. Compared to that study, lower prevalence rates of respiratory symptoms in the WTP workers were found. One possible reason for the lower prevalence rates among WTP workers in this study is a "healthy worker effect;" because job performance for WTPs needs a certain amount of physical health and workers with physical limitations will more likely leave employment. Another possible reason is the baseline exposure of WWTP office staff whose occupational environment would be identical to the exposed workers who are involved with wastewater treatment procedure.

The approaches to distributing questionnaire were different in the WWTP workers and water treatment workers. The researchers visited the participating WWTP plants in person and introduced the study, whereas WTP workers agreed to participate through a phone contact and questionnaires were collected by mail. Although this difference existed between the two groups, the approach to preventing researcher bias was identical: 1) participants were not specifically informed of what the researchers expected to find from this study, 2) the signed human subject consent forms and anonymous questionnaires were collected separately, and 3) sufficient time was allowed to pass before deata entry so that the workers who turned in questionnaires could not be identified. In addition, the questionnaire began with general information such as age, race, education, etc. so as not to emphasize health issues (Appendix I). The researchers also emphasized the confidentiality of any information the workers provided on the questionnaire, explaining that 1) the questionnaire did not contain any questions to identify individuals, 2) the answers on questionnaires would not be revealed, especially to the employers, managers, or supervisor, and 3) two envelopes were provided for the separate return of questionnaires and consent forms, and both had to be sealed before they were turned in. Through these procedures, the study attempted to minimize bias and misleading data collection.

CHAPTER IV

COMPUTER SIMULATION: A TOOL FOR AIR QUALITY ASSESSMENT

Abstract

This study was conducted to investigate whether numerical modeling techniques, such as computer simulation and mathematical modeling, can be used as an alternative to real-time monitoring for air quality assessments. To determine the consistency among two measurement techniques (numerical modeling and real time monitoring), the exponential decay of a gas in a room was analyzed and a ratio of comparison, K, was calculated from concentrations measured by CFD software (K_{CFD}), mathematical modeling ($K_{Two\text{-}Zone}$), and gas tracer analysis (K_{Tracer}). For this comparison, hydrogen sulfide and carbon dioxide were released in a chamber with three different airvent configurations and two levels of airflow rates. Five cases (combinations of configurations and airflow rates) were designed, and three or five trials were completed for each case. In each trial, two and four measurement locations were chosen for hydrogen sulfide and carbon dioxide concentrations respectively. The results showed the Ks from two of the measurement techniques (K_{Tracer} and K_{CFD}) were statistically different, depending on the given conditions of airflow level, configuration, gas, and measuring location. Those findings were consistent with outcomes of comparisons between K_{Tracer} and $K_{Two\text{-}Zone}$ in two-zone model cases. In summary, gas concentration predictions differed from real-time monitoring results; however, the differences could be explained by several features of the experiment (e.g. gas behavior). With further research to control for these features, concentration prediction using numerical techniques could

be a powerful technique for air quality assessment in industries, providing a comprehensive view of contaminant distribution over time and space.

Introduction

In wastewater treatment plants (WWTPs), hydrogen sulfide typically exists at low levels; however that exposure can still pose a great health risk. To estimate risk levels, it is important to establish dose-response relationships, which demand accurate measurements of exposure levels. However, an accurate assessment of these relationships is difficult to determine when uneven distributions of airborne contaminants occur in throughout a workplace. "Area" samples taken at various locations throughout a workplace can be used to give a general indication of spatial variability with accuracy increasing with an increase in the number of samplers. Numerical modeling of indoor airflows using Computational Fluid Dynamics (CFD) can provide a comprehensive map of contaminants' distribution that would be achieved only with enormous time and effort using a network of integrated samplers. For this reason, numerical modeling has been utilized, for example, to predict atmospheric dispersions of contaminants from a smokestack or to validate the performance of ventilation systems [Bennett et al., 2000; Flowe et al., 2001; Lee et al., 2002].

Numerical modeling typically includes complex equations, such as the Navier-Stokes Equations [Gerhart & Gross, 1992]; however, commercially manufactured software that provides appropriate Computational Fluid Dynamics (CFD) codes enables users to build their desired models with relative ease. Taking advantage of software developed for airflow simulations, this research aimed 1) to describe how changes of concentrations in an experimental space over time were represented by tracer analysis, computer simulation, and mathematical modeling developed by Nicas [1996], 2) to validate the predicted concentrations from computer simulation and mathematical modeling by comparing them to measured concentrations from tracer analysis, and 3) to investigate if airflow rates, ductwork configurations, chemicals (gases), and location of measurements were associated with changes of concentrations over time and with different concentrations from the three assessment techniques. For Aim 3, two levels of ventilation rates and three airvent configurations were established in an experimental space. One of the airvent configurations was built for a two-zone room scenario, which is used in mathematical modeling. In addition, concentrations of both carbon dioxide and hydrogen sulfide, which are commonly found in WWTPs, were measured at four different locations in the experimental space. Generally, this investigation estimated concentrations using numerical modeling and compared them to actual concentrations in order to validate the use of a CFD modeling approach to estimating concentrations throughout a workplace.

Methods

Software and Equations

Transient concentrations of hydrogen sulfide and carbon dioxide were computed using commercially available computational fluid dynamic (CFD) software, (Airpak 2.1, Fluent Inc. Lebanon, NH) (Figure 4-1). In this study, an indoor zero-equation model for airflows designed by Chen was used to solve fluid equations [Chen & Xu, 1998]. According to his theory, the turbulence viscosity term (μ_t) in momentum equations was expressed with a local mean velocity, *V*, and a length scale, *l*, instead of unknown parameters such as turbulent kinetic energy parameter (κ) and a turbulence dissipation rate(ε) (eq. 4-2). The following equations were used to solve momentum of gas flows and concentrations of species in the CFD software.

Momentum equation:

$$\frac{\partial \rho V_i}{\partial t} + \frac{\partial \rho V_i V_j}{\partial x_j} = -\frac{\partial P}{\partial x_i} + \frac{\partial}{\partial x_j}\left[(\mu_t + \mu)\left(\frac{\partial V_i}{\partial x_j} + \frac{\partial V_j}{\partial x_i}\right)\right] \qquad \text{(eq. 4-1)}$$

$$\mu_t = 0.03874\rho Vl \qquad \text{(eq. 4-2)}$$

Species concentrations:

$$\frac{\partial \rho C_i}{\partial t} + \frac{\partial \rho V_i C}{\partial x_j} = \frac{\partial}{\partial x_j}\left[\Gamma_{c,eff}\frac{\partial C}{\partial x_j}\right] + S_c \qquad \text{(eq. 4-3)}$$

where ρ=air density; $V_{i(j)}$=velocity component in $x_{j(j)}$ direction; P=pressure, μ_t = turbulence viscosity; μ=laminar viscosity; β= thermal expansion coefficient of air; T=temperature; $g_{i(j)}$=gravity acceleration in i(j) direction; V=local mean velocity; l=distance from wall; $\Gamma_{c,eff}$=effective turbulent diffusion; S_c=source term of C .

The majority of airflows are assumed to be turbulent, in other words characterized by random fluctuations in fluid velocity [Gilham et al., 2000]. The fluctuations in velocity and pressure are associated with the motion of lump (eddies) that carries fluid properties like mass, momentum, and energy. There are several models to solve turbulence cases and, eddy-viscosity models, which are based on the lump motion theory, are popular for simulating turbulent flows. Of the eddy-viscosity models, the κ-ε model is regarded as the most accurate; however, it requires large computer memory capacity and drive-space to solve equations. Alternative, simpler models are therefore recommended.

In Chen's study, the outcomes of air velocity, temperature and gas concentration using the zero-equation model with eq. 4-2 showed relatively good agreements with κ-ε model simulations, and the use of the computer's memory was reduced greatly by using a simplified equation to solve the turbulence term [Chen & Xu, 1998]. Even though there are few studies of accuracy levels in predicting indoor airflows using this model, the savings in cost and time justify its use from an industrial hygienist's perspective.

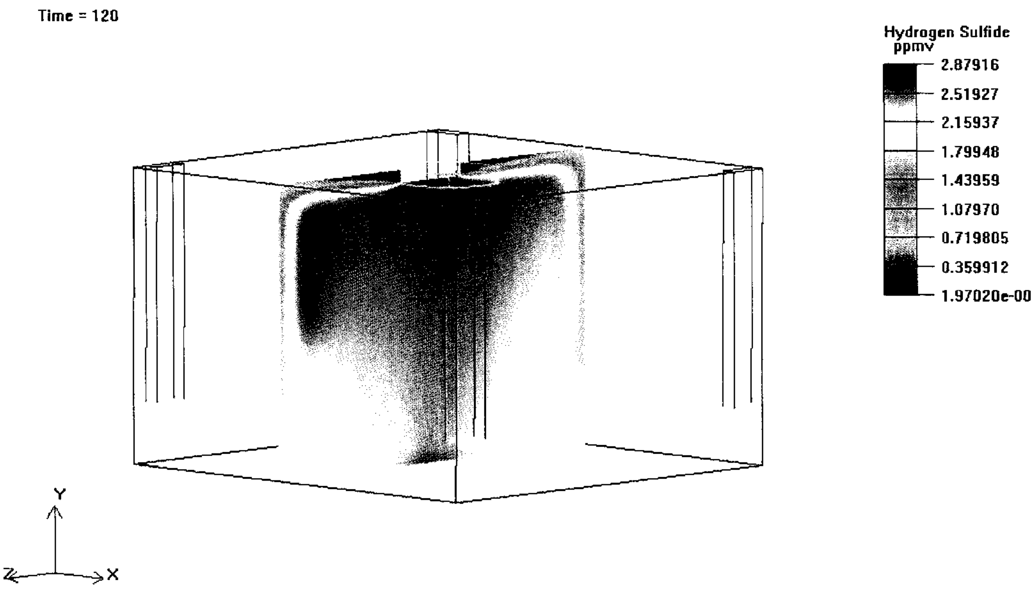

Figure 4-1. Hydrogen Sulfide Concentration Distribution at 120 Second for Case 1

Experimental Chamber

A stainless steel environmental chamber in the University of Iowa Hospitals and Clinics was used as the test site for this study. In this facility, airflow rates, temperature and humidity could be controlled and monitored by a computerized system. The temperature and relative humidity were set to 21.1 C° and 24.2% respectively. The dimension of the chamber was 3.40 m wide, 3.44 m long and 2.29 m high; the room volume was 26.78 m^3. For Configuration 1, a circular airflow inlet with no diffuser attached was located at the center of the ceiling and four rectangular exhaust airvents were located at each corner of the chamber and approximately 0.5 m from floor level (this and the other configurations are represented in Figure 4-1). This configuration was designed to maximize mixing throughout the chamber. For Configuration 2, only one exhaust airvent located in one corner was used so as to decrease ventilation efficiency decrease ventilation efficiency compared to Configuration 1 (a poorly-mixed volume). For the two-zone room cases (Configuration 3), a cylindrical duct was connected to one of the four exhaust airvents and, using a 180° connector and additional straight pipe, the inlet was brought up to near ceiling height while the other three exhaust vents were closed (a two-zone volume). During a trial, a gas was injected into a port located in the room supply duct and mixed with clean air by a static mixing device located immediately downstream of the injection port.

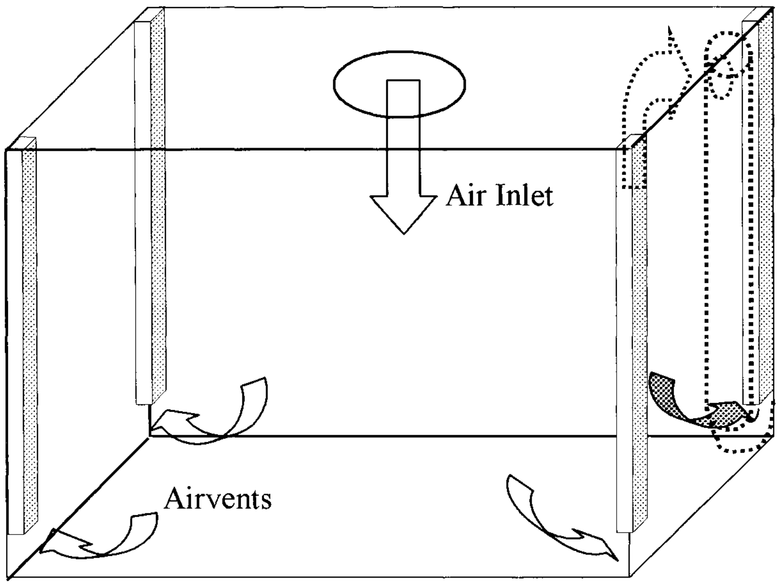

Figure 4-2. Experimental Chamber
Notes: the four lower arrows indicate Configuration 1; the gray arrow indicates Configuration 2; the dotted lines show the structure and upper airflow of Configuration 3.

Mesh

A hexahedral mesh was used for CFD analysis consisting of 38,548 cells and 42,857 nodes. For diagnosis of the mesh, the element aspect ratio, the face alignment, and the element volume were checked in the software, which indicated distortion of the elements and the minimum element volumes in the mesh. The smallest element aspect ratio and the face alignment were 0.6 and 0.65; 0.15 was recommended for mesh quality and 1 indicates the best element aspect ratio and the perfect alignment. The minimum element volume was 7.9×10^{-6}; much smaller elements, e.g. 10^{-12} or lower, were recommended to be avoided [Fluent, Airpak manual]. Reynolds numbers for the cases with low air flows were approximately 45000 (Case 1 and Case 4). For the high air flows, Reynolds numbers ranged between 77000 and 91000.

Gas Release Condition

For the experiments, pure hydrogen sulfide and carbon dioxide gases were used. The air flowing into the chamber was HEPA filtered and contained 330 to 370 ppm of carbon dioxide. The gases were injected into the supply duct to yield levels of 5 ppm of hydrogen sulfide and 1000 ppm of carbon dioxide before they entered the chamber. A steady-state concentration was obtained for at least 10 minutes and then the source gas was shut off. The resulting decay curves were measured for 10 to 20 minutes.

Gas Detection Instruments

Direct-reading instruments were used for the gas measurements. Two Jerome 631-Xs (Arizona Instrument, Phoenix, AZ) and four Q-traks (TSI Incorporated, Shoreview, MN) were used for hydrogen sulfide and carbon dioxide respectively. The Jerome was calibrated using a function test module (FTM) which produced 0.2 to 0.3 ppm of hydrogen sulfide gas. As the manufacturer recommended, ten readings of the instruments after exposure to the FTM were taken and averaged; the average levels fell into the recommended range and therefore the instrument was assumed to be reading concentrations correctly. The limit of detection (LOD) of the instrument was 3 ppb with an accuracy of ±3 ppb at the level of 50 ppb. The Jerome sampled the air for 30 seconds with 0.15 L/min flow rate at one-minute intervals during the entire sampling period. The Q-Traks were calibrated with a reference gas (1000 ppm of carbon dioxide) prior to the experiments and instrument readings of the gas were also taken to check if the instruments were properly functioning during the experiments. This instrument measured every minute and recorded results in a data-logger. The accuracy and LOD of carbon dioxide measurement were ± 1.5 ppm at a level of 50 ppm and 0 ppm respectively.

Experimental Design

In this study, three different configurations and two air flow rates (high and low) were applied (Table 4-1). In Configuration 1, the four airvents at each corner of the chamber were open (Figure 4-2); this configuration was used for Cases 1 and 2. For Configuration 2 (Case 3), one airvent close to Locations 1 and 3 was open and the other airvents were closed (Figure 4-3 and 4-4). For Configuration 3, a cylinder-shaped duct was connected to the airvent near Locations 1 and 3, and the other three airvents were closed. Connecting the duct changed the location of the airvent and the airflow direction was therefore changed from lower to upper part of the chamber, establishing uneven airflow distribution (Cases 4 and 5). Three experimental trials were completed for each case except Case 3. In Configuration 2, low airflow rates were not achieved, and trials were run for two different airflow rates (870m^3/hr—three trials and 1030 m^3/hr—two trials). A total of 34 hydrogen sulfide measurements at two different locations for hydrogen sulfide and 68 carbon dioxide measurements at four different locations were collected; further description of measuring locations follow.

Table 4-1. Experimental Designs for Five Cases

Case	Configurations	Number of Trials	Flow Rates (m^3/hr)	Number of Airvents	Location of Airvents
1	1	3	509.8 (low)	4	Lower
2	1	3	930.3 (high)	4	Lower
3	2	3/2	870.8 / 1030.0 (high)	1	Lower
4	3	3	509.3 (low)	1	Upper
5	3	3	1018.1 (high)	1	Upper

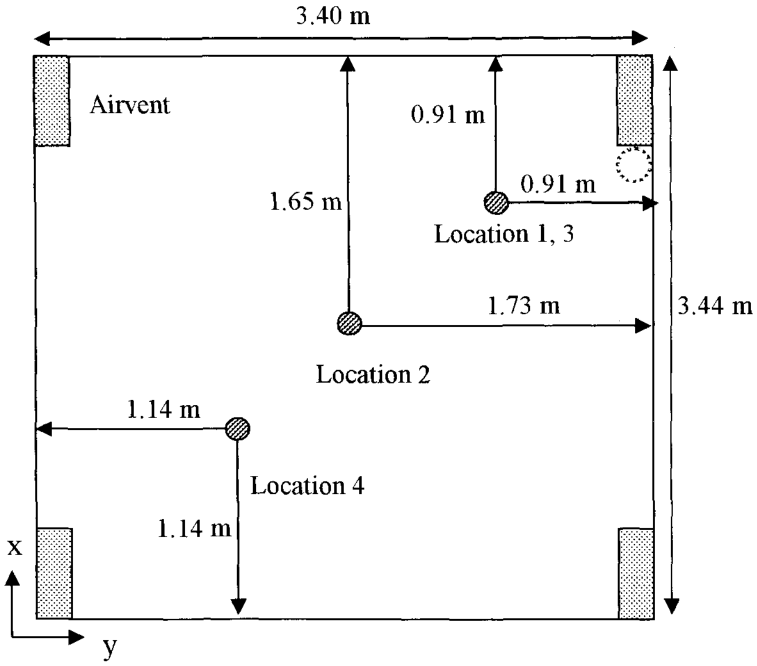

Figure 4-3. Top View of the Chamber with Locations of Gas Monitors
Note: dotted circle is the location of the airvent for Cases 4 and 5

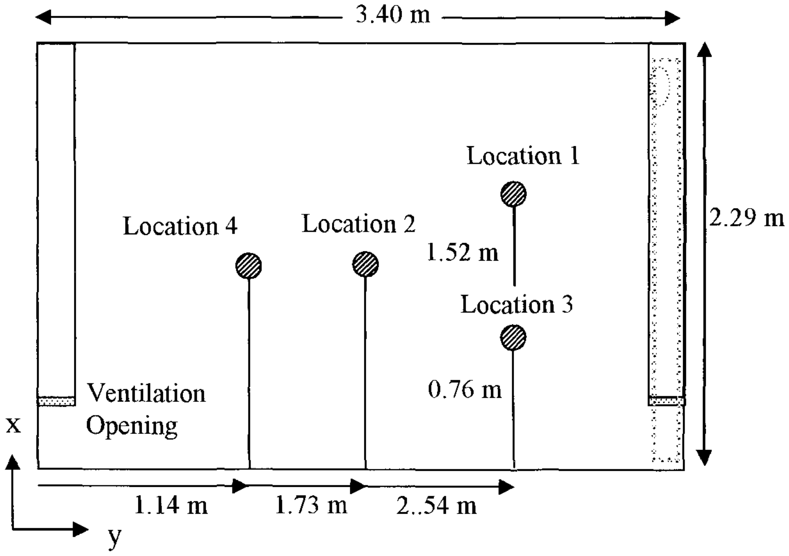

Figure 4-4. Side View of the Chamber with Locations of Gas Monitors
Note: dotted line is the duct location of the airvent for Cases 4 and 5

Location of Gas Detection Instruments

The gas monitors were placed at four locations in the chamber (Figure 4-3, 4-4). The hydrogen sulfide monitors were placed at Locations 1 and 2 only and the carbon dioxide monitors were at all four locations.

Comparison of Ks from Three Techniques

The retention time of a gas to be decayed out in a given volume, τ, was determined for each configuration. The theoretical retention time is equal to the time required to replace the entire air volume, V, in a volume (chamber) for a given airflow rate, Q (eq. 4-4).

$$\tau_{theory} = \frac{V_{Chamber}}{Q_{FlowRate}} \qquad \text{(eq. 4-4)}$$

However, when an incomplete mixing situation occurs (e.g., due to complex configurations of the chamber), the actual time needed to ventilate the entire air volume of the chamber is increased. A ratio of actual retention time (τ_{actual}) over theoretical (τ_{theory}) is expressed as K, in which K is equal to 1 when a space is perfectly mixed (eq. 4-5); therefore, K becomes an indicator of ventilation efficiency.

$$K = \frac{\tau_{actual}}{\tau_{theory}} \qquad \text{(eq. 4-5)}$$

The τ_{actual} and resulting K value can be calculated from an exponentially decaying curve of concentrations. For these calculations, a material balance differential equation must be introduced (eq. 1-1) [Gressel et al., 1992].

Material balance differential equation:

Accumulation Rate = Generation Rate – Removal Rate

$$VdC = Gdt - \frac{QC}{K}dt \quad \text{(eq. 1-1)}$$

where V is volume of a room, C is concentration at time t, G is the contaminant's generation rate, Q is flow (ventilation) rate and K is an indicator of ventilation efficiency as explained previously. In this equation, concentration changes are assumed to occur only based on generation rate G and ventilation Q; hence, chemical reactions, decompositions, or absorptions of chemicals into any materials in the space are assumed not to be taking place in the space V. For estimating the concentration changes between some time t_1 and t_2, eq. 1-1 can be integrated as follows:

$$\int_{C_{t1}}^{C_{t2}} \frac{dC}{G - QC/K} = \frac{1}{V}\int_{t_1}^{t_2} dt \qquad \text{(eq. 1-2)}$$

where C_{t1} is the concentration at t_1 and C_{t2} is the concentration at t_2. Performing the integration yields the following:

$$\ln\left[\frac{G - \frac{QC_{t2}}{K}}{G - \frac{QC_{t1}}{K}}\right] = -\frac{Q}{KV}(t_2 - t_1) \qquad \text{(eq. 1-3)}$$

Furtherfmore, when the generation rate is zero, the equation becomes

$$\ln\left[\frac{C_{t2}}{C_{t1}}\right] = -\frac{Q}{KV}(t_2 - t_1) \qquad \text{(eq. 1-4)}$$

or

$$\ln C_{t2} = \ln C_{t1} - \frac{Q}{KV}(t_2 - t_1) \qquad \text{(eq. 1-5)}$$

When C_{t0} is replaced with C_{t1} as an initial concentration (t_1=0) and C_t as a concentration at any time, t, eq. 1-5 becomes

$$\ln C_t = \ln C_0 - \frac{Q}{KV}(t) \qquad \text{(eq. 1-6)}$$

or

$$\ln\left[\frac{C_t}{C_0}\right] = -\frac{Q_{FlowRate}}{K \times V_{Chamber}}(t) \qquad \text{(eq. 4-6)}$$

where C_t and C_0 are the concentration at time t and 0.

$V_{chamber}$ and $Q_{flowrate}$ are given for the experimental designs described in Table 4-1. C_0 and C_t were each determined by either tracer analysis, computer simulations, or mathematical modeling. Ks, therefore, could be calculated from the graph of $\ln(C_t / C_0)$ versus t ; a sample graph of Case 3 is shown in Figure 4-4 and 4-5. $V_{chamber}$ was 26.78 m^3 and $Q_{flowrate}$ was 870.8 m^3/hour in Case 3; hence, τ_{theory} was 1.85 minutes. In the graphs, the slope ($-Q_{Florrate}/KV_{chamber}$), -0.3558 is equal to $- 1/ \tau_{actural}$ as follows;

$$-0.3558 = -\frac{Q_{FlorRate}}{K \times V_{Chamber}} = -\frac{\tau_{theory}}{K} = -\frac{1}{\tau_{actual}}$$

Hence, actual retention time becomes 2.81 minutes.

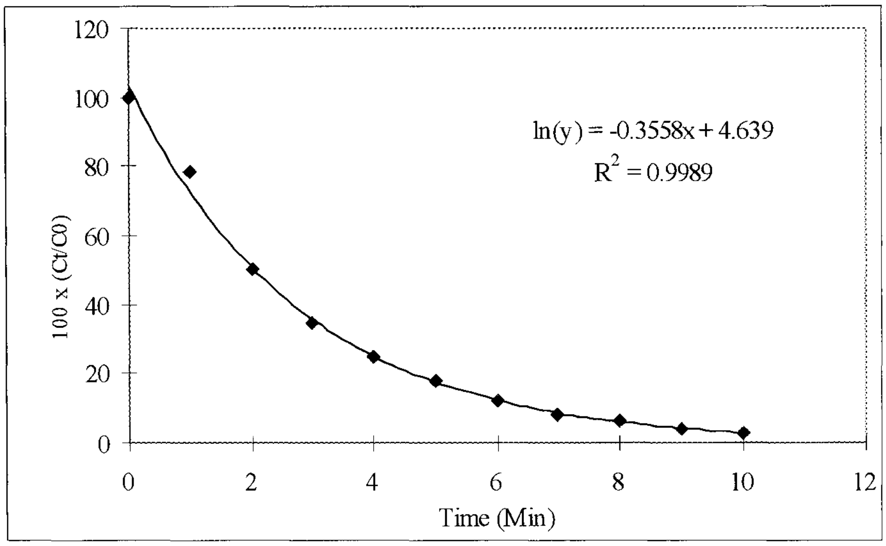

Figure 4-5. A Decaying Curve from Tracer Analysis for Case 3 Showing Regression Line

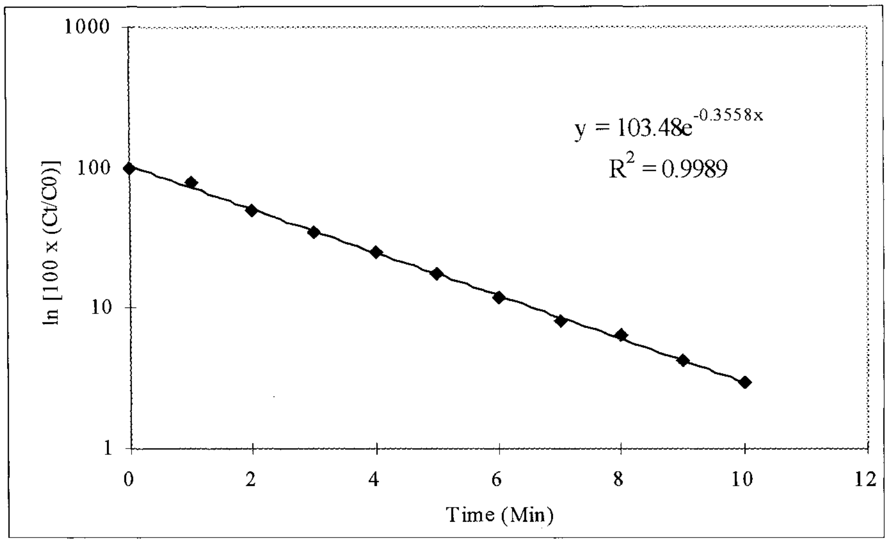

Figure 4-6. The Decay Curve of Figure 4-5: Y-Axis was Log-Transformed

In this study, K was either measured by tracer analysis or calculated by computer simulation and mathematical modeling, and denoted as follows: K_{Tracer} is from tracer analysis, K_{CFD} is from computer simulation, and $K_{Two\text{-}Zone}$ is from mathematical modeling (eq. 4-7, 4-8, and 4-9). These three Ks were used to compare the three assessment methods.

$$K_{tracer} = \frac{\tau_{tracer}}{\tau_{theory}} \qquad \text{(eq. 4-7)}$$

$$K_{CFD} = \frac{\tau_{CFD}}{\tau_{theory}} \qquad \text{(eq. 4-8)}$$

$$K_{Two-Zone} = \frac{\tau_{Two-Zone}}{\tau_{theory}} \qquad \text{(eq. 4-8)}$$

Data Analysis

Individual comparisons among K_{Tracer} and comparisons between K_{CFD} and K_{Tracer} were all done by non-parametric method; when the variables had two different levels, such as hydrogen sulfide versus carbon dioxide or high airflow versus low airflow, Wilcoxon signed rank sum tests were used. Comparisons among more than two levels, such as four measuring locations, were performed with a Kruskal-Wallis test. One-sample t-tests with null hypothesis of no differences in Ks for overall comparisons were used (H_0: K_{Tracer} - K_{CFD} = 0, K_{Tracer} for hydrogen sulfide- K_{Tracer} for carbon dioxide = 0). The associations between K_{Tracer} (or the difference between K_{Tracer} and K_{CFD}) and four different conditions—different airflows, configurations, gases and measuring locations—were investigated using general linear models (GLM).

The variable of airflow rate was dichotomized with as "high" and "low;" Cases 1 and 4 were "low" and the others were "high." Individual comparisons for the three configurations were performed with a Tukey comparison. A paired t-test was used to test whether the degree of difference in the two Ks (K_{Tracer} and K_{CFD}) was related to the different gases. This test used concentrations of carbon dioxide at Locations 1 and 2 only because concentrations of hydrogen sulfide were not measured at the other locations. A 5% significance level was applied for all data analysis. Statistical analysis software used for this study was SAS 9.1 (SAS Institute, Cary, NC).

Using mathematical modeling of a "two-zone" ventilated room, which was proposed by Nicas, $K_{Two\text{-}Zone}$ were calculated with given values of Q, V, C_l and C_u, where C_l and C_u are concentrations in the lower and upper zone of the room [Nicas, 1996]. As explained by Nicas, the concentrations in a room where air is partially circulated by ventilation are different. In this study, the concentrations of hydrogen sulfide at Locations 1 and 2 were calculated with the equations Nicas developed to explain concentrations in a two-zone room. $K_{Two\text{-}Zone}$ values were calculated from the concentrations for each minute in the same fashion as described above (detailed calculations are provided in Appendix II). Comparisons of $K_{\text{Two-Zone}}$ with K_{CFD} and K_{Tracer} for Cases 4 and 5 (in which partial air distributions were designed to occur) were reported as the result.

Results

Concentrations Derived from Tracer Analysis, Computer Simulation, and Mathematical Modeling

K_{Tracer} and K_{CFD} calculated from decaying concentrations derived by tracer analysis and computer simulation are summarized in Table 4-2 and Figure 4-7. Figures 4-8 to 4-11 show the contour of hydrogen sulfide gas distributions in a computer simulation using the CFD software. Given initial concentrations, decaying concentrations at four measurement locations were modeled. Concentrations for carbon dioxide were modeled in the same way as for hydrogen sulfide. K_{CFD} and $K_{\text{Two-Zone}}$ were then calculated from decay concentrations, as described earlier in "Comparison of Ks from Different Techniques."

Table 4-2. K_{Tracer} and K_{CFD} for Different Airflows, Configurations, Chemicals, and Measuring Locations

Case	Flow Rates (m^3/hr)	Configurations	Chemical	Location	$K_{Tracer}{}^*$	K_{CFD}
1	509.8	1	H_2S	1	1.75	1.23
				2	1.68	1.18
			CO_2	1	1.47	1.24
				2	1.41	1.18
				3	1.49	1.22
				4	1.55	1.31
2	930.3	1	H_2S	1	1.72	1.27
				2	1.60	1.25
			CO_2	1	1.27	1.27
				2	1.23	1.25
				3	1.24	1.25
				4	1.30	1.35
3	870.8/ 1030.0	2	$H_2S^†$	1	1.46	1.26
				2	1.52	1.24
			$CO_2{}^†$	1	1.31	1.26
				2	1.25	1.24
				3	1.30	1.25
				4	1.29	1.35
4	509.3	3	H_2S	1	1.26	1.04
				2	1.32	1.05
			CO_2	1	1.09	1.05
				2	1.10	1.06
				3	1.09	1.05
				4	1.10	1.05
5	1018.1	3	H_2S	1	1.65	1.07
				2	1.47	1.01
			CO_2	1	1.29	1.07
				2	1.28	1.01
				3	1.32	1.05
				4	1.30	1.01

* Averages of three trials for each case.

† Averages for K_{Tracer} were made from five trials.

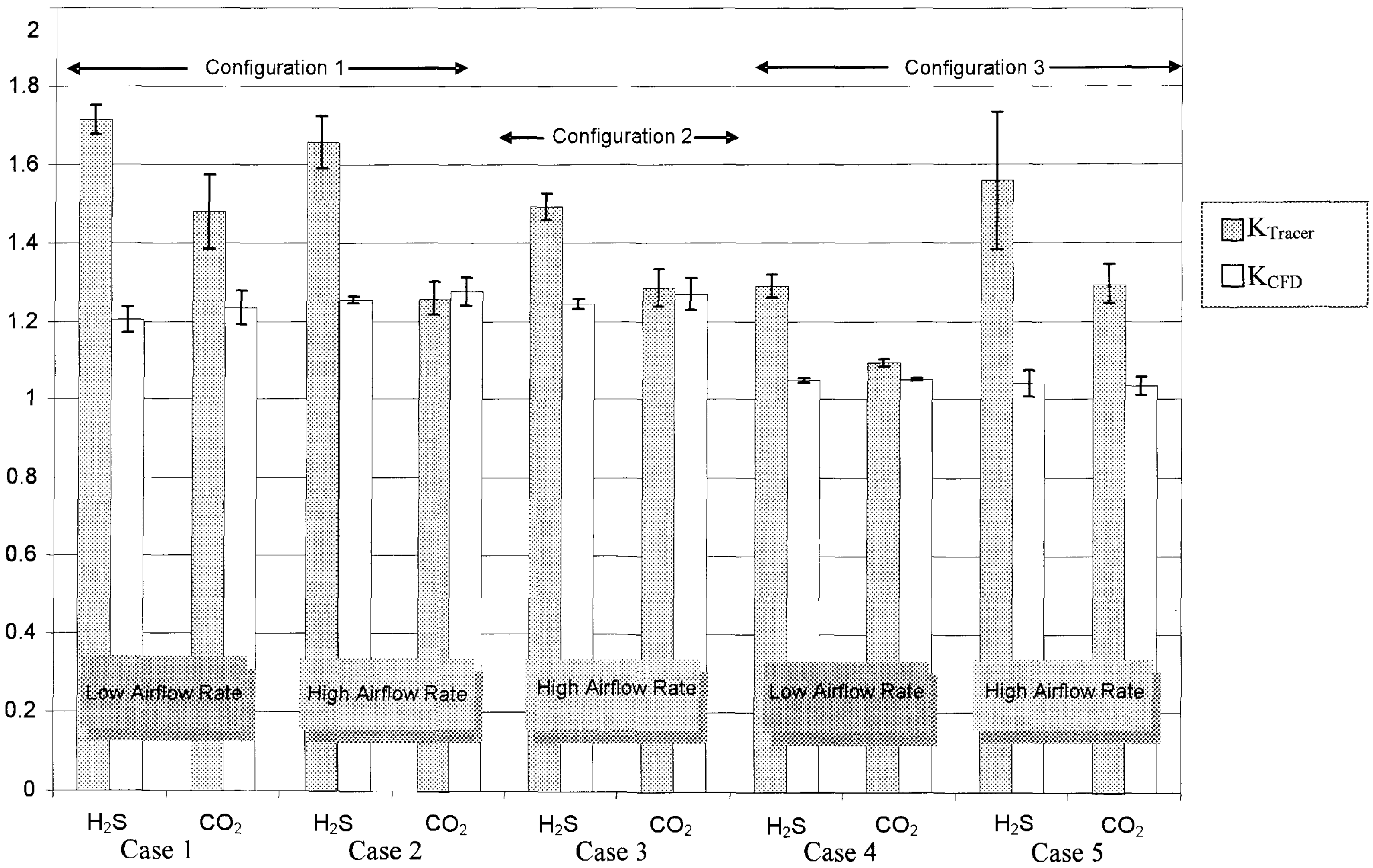

Figure 4-7. K_{CFD} an K_{Tracer} with Error Bars Showing 95% Confidence Intervals for Different Airflow Rates, Configuration, Chemicals, and Location

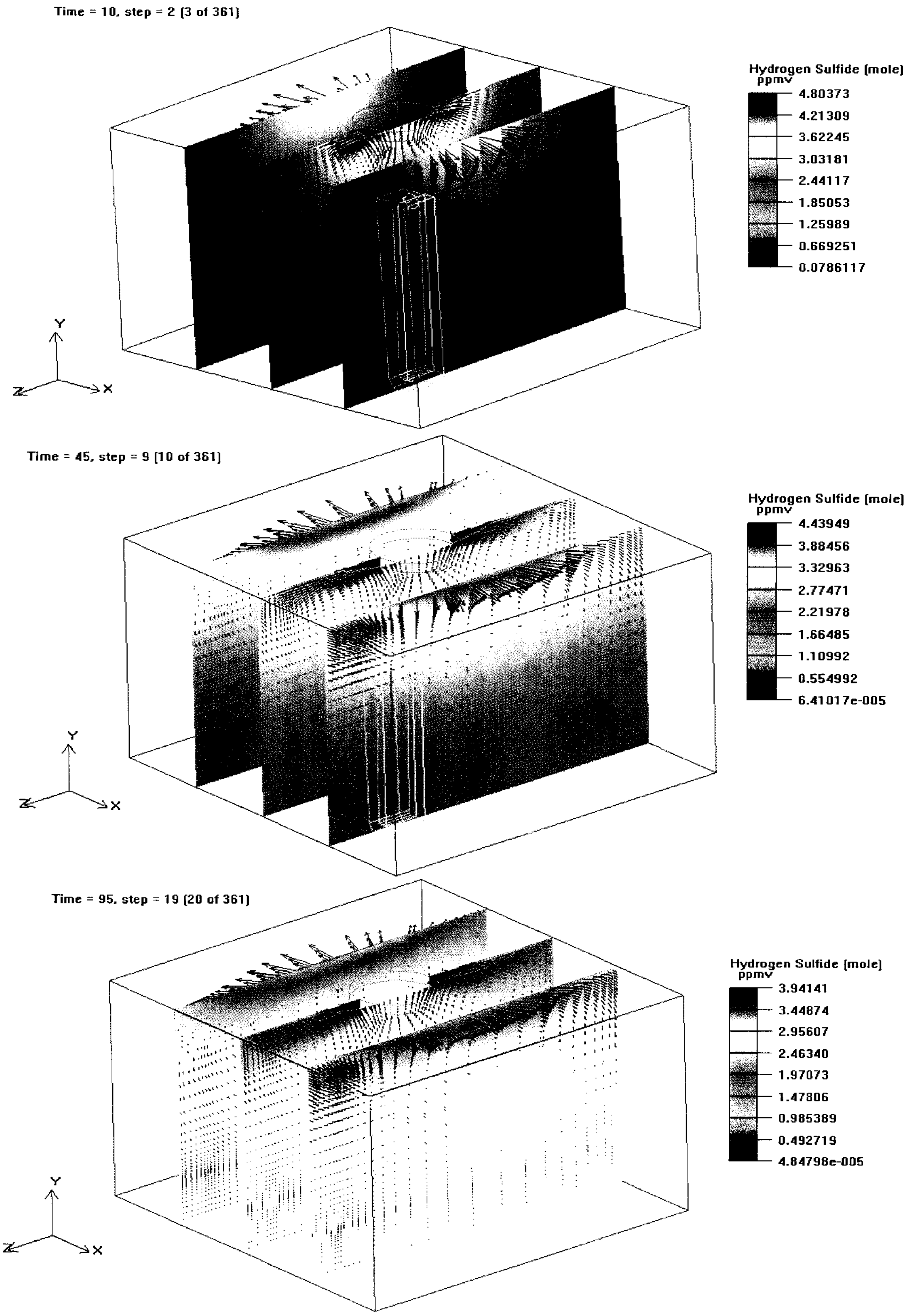

Figure 4-8. Concentration Distribution of Hydrogen Sulfide for Configuration 3 at Location 1- 4, and 10, 45, and 95 Second

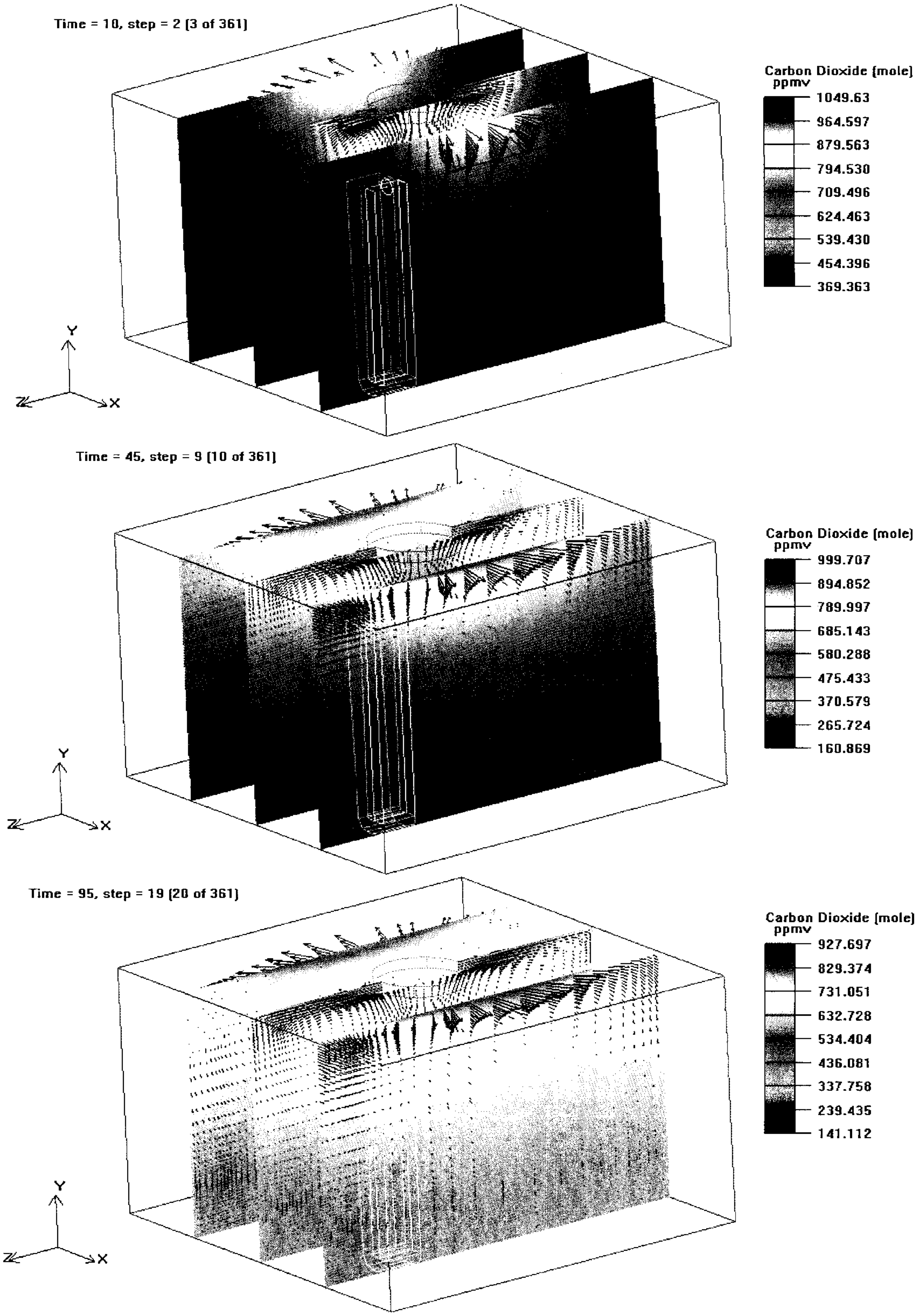

Figure 4-9. Concentration Distribution of Hydrogen Sulfide for Configuration 3 at Location 1- 4, and 10, 45, and 95 Second

To determine $K_{Two\text{-}Zone}$, coefficients for decaying curves were calculated using formulas for a two-zone volume; the coefficients are summarized in Table 4-3 [Nicas, 1996]. Figures 4-12 and 4-13 depict decay curves and eq. 4-9 to eq. 4-12 represent the decay equations for the two different airflow rates in Configuration 3. Using the decay equations, K_{CFD} were calculated and the results are summarized in Table 4-4. The detailed calculation procedure is described in Appendix II.

Table 4-3. Coefficients for Decay Equations for the Two Zone Model

Case	Flow Rate, Q (m^3/hr)	Exchange Rate, β (m^3/hr)	Volume (m^3)		Initial Concentrations, C(0) (ppm)		Lambda, λ (/hr)		Delta, δ (/hr)	
			Lower Room, Vl	Upper Room, Vu	Lower Room Cl (0)	Upper Room Cu (0)	λ_1	λ_2	δ_1	δ_2
4	509.3	3935.79	17.78	9.01	4.80	4.25	-17.96	-697.00	4.75	0.05
5	1018.1	6845.35	17.78	9.01	2.70	2.35	-35.65	-1227.70	2.67	0.03

Table 4-4. K_{Tracer}, K_{CFD}, and $K_{Two\text{-}Zone}$ for Case 4 and 5 in Upper and Lower Zones

Case	Air Flow Rate(m^3/hr)	Location (Zone)	K_{Tracer}^{*}	K_{CFD}	$K_{Two\text{-}Zone}$
4	509	1 (Upper)	1.2562	1.0437	1.0577
		2 (Lower)	1.3165	1.0529	1.0518
5	1018	1 (Upper)	1.6464	1.0701	1.0672
		2 (Lower)	1.4716	1.0109	1.0598

* Averaged K values from repeated trials for each case.

Case 4 (lower flow rates, 509 m^3/hr):

Lower zone decay equation

$$Cl : 4.748 \times e^{-17.96 \times t} + 0.0523 \times e^{-697.0 \times t} \qquad \text{(eq. 4-9)}$$

Upper zone decay equation

$$Cu: 4.362 \times e^{-17.96\times t} - 0.112 \times e^{-697.0\times t} \qquad \text{(eq. 4-10)}$$

Case 5 (higher flow rate, 1018 m^3/hr):

Lower zone decay equation

$$Cl: 2.668 \times e^{-35.65\times t} + 0.003 \times e^{-1222.7\times t} \qquad \text{(eq. 4-11)}$$

Upper zone decay equation

$$Cu: 2.421 \times e^{-35.65\times t} - 0.071 \times e^{-1222.7\times t} \qquad \text{(eq. 4-12)}$$

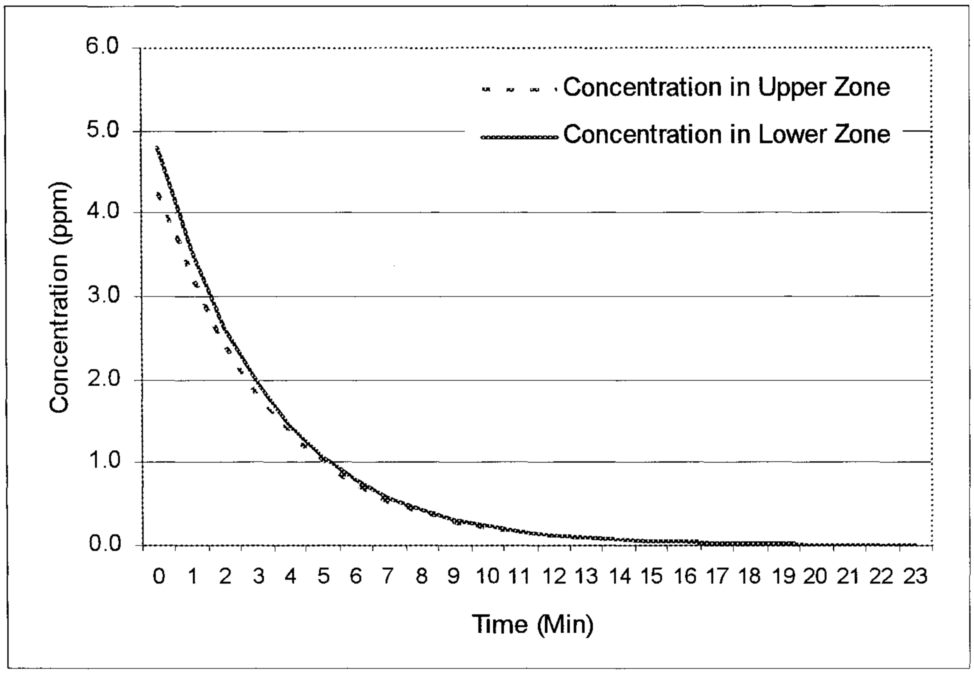

Figure 4-10. Decaying Curves of Hydrogen Sulfide Concentration in Upper and Lower Zones at a Low Flow Rate (509 m^3/hr)

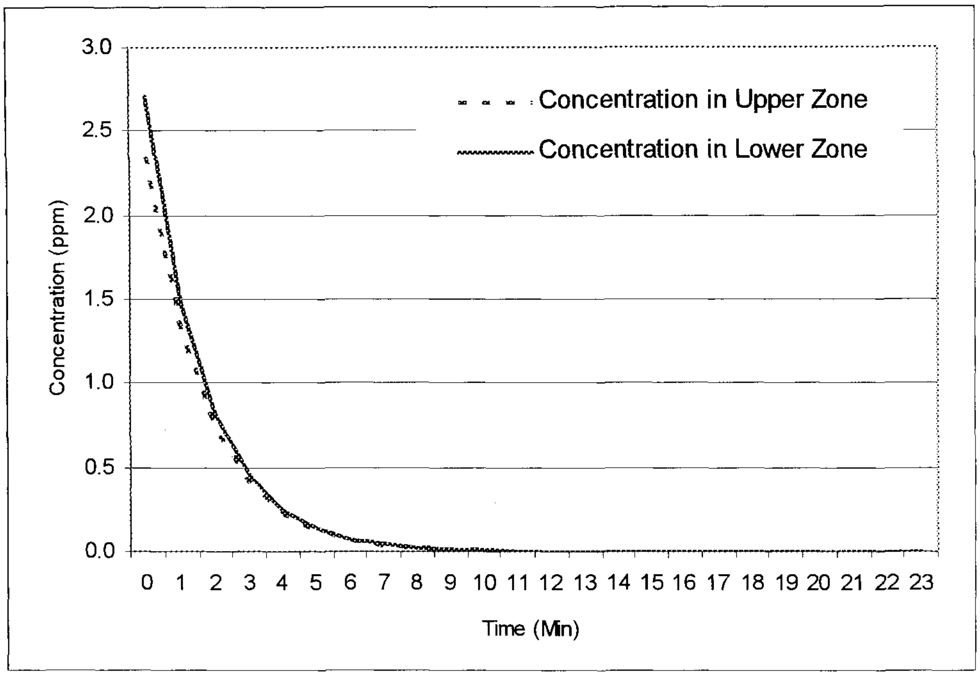

Figure 4-11. Decaying Curves of Hydrogen Sulfide Concentration in Upper and Lower Zones at a High Flow Rate (1018 m^3/hr)

Validation of Concentration Predictions Derived from Computer Simulation and Mathematical Modeling

As shown in Figure 4-7, K_{CFD} were typically smaller than K_{Tracer} except for Case 2. The ranges of differences within K_{CFD} for each case were relatively smaller than the ranges of Ks within the tracer analysis. Statistical analysis (t-test) revealed that K_{CFD} and K_{Tracer} were different overall, and the two Ks also differed when the different levels of airflow, measurement location, and gases were compared. Further discussion of these comparisons between the two Ks will follow in the next section.

$K_{Two\text{-}Zone}$ values were calculated and reported in comparison to K_{CFD} and K_{Tracer} (Figure 4-12 and Table 4-3). $K_{Two\text{-}Zone}$ and K_{CFD} showed a similarity whereas the differences between $K_{Two\text{-}Zone}$ (or K_{CFD}) and K_{Tracer} were relatively greater. Also, differences between calculated Ks ($K_{Two\text{-}Zone}$ and K_{CFD}) and measured K (K_{Tracer}) were greater for Case 5 with a high airflow rate compared to the differences in Case 4 with a low flow rate (Figure 4-13 to 4-16). Ranges of the differences among the three K-factors were approximately 0.19 and 0.48 for the low and high flow rates, respectively.

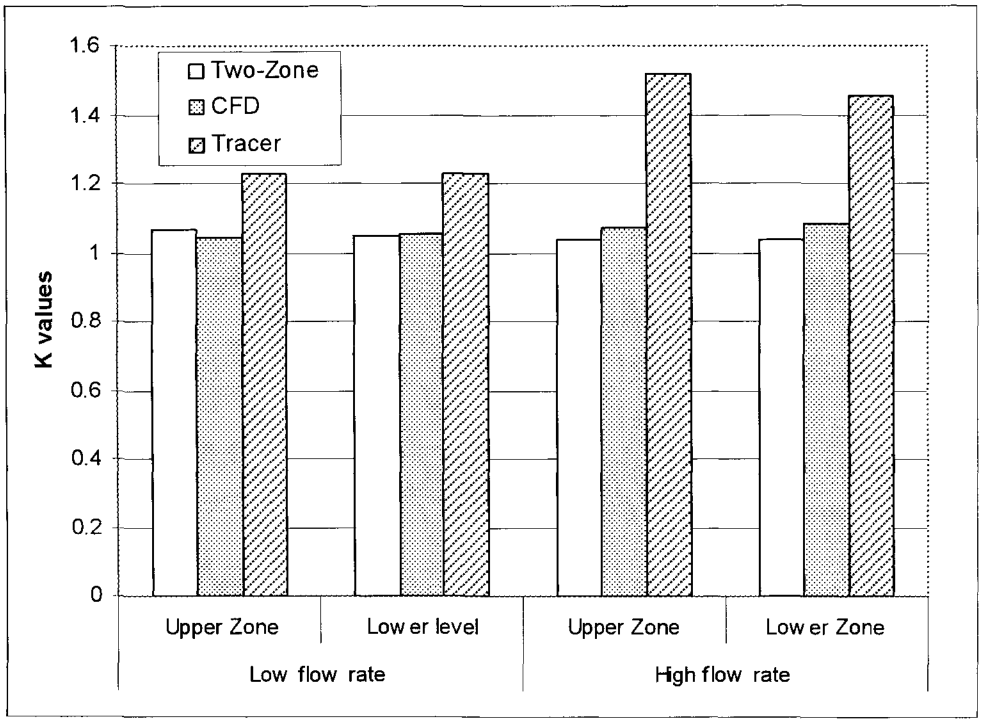

Figure 4-12. Comparisons of $K_{\text{Two-Zone}}$, K_{CFD} and K_{Tracer} for Low and High Flow Rate Cases

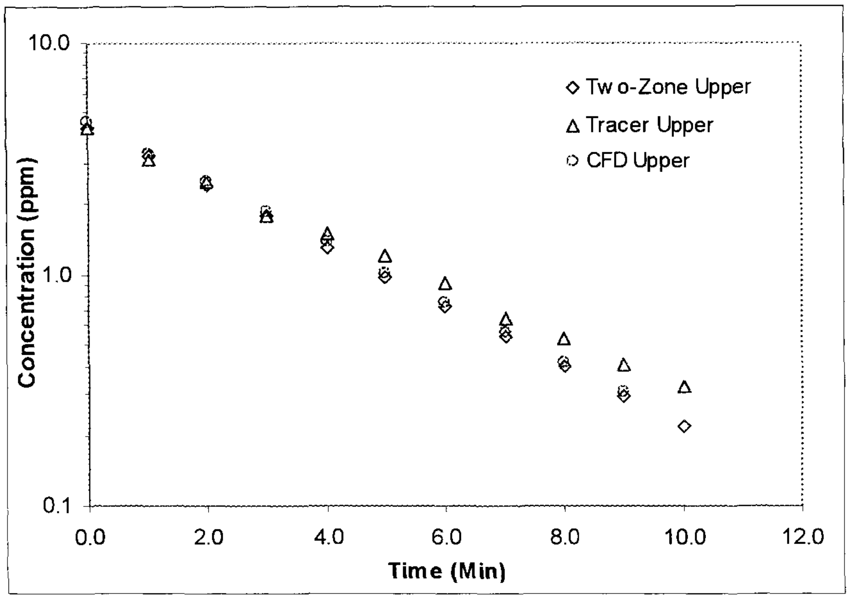

Figure 4-13. Decay Curves of Hydrogen Sulfide in the Upper Zone at Low Flow Rate Calculated with the Nicas Formula, Computer Simulation and Tracer Analysis

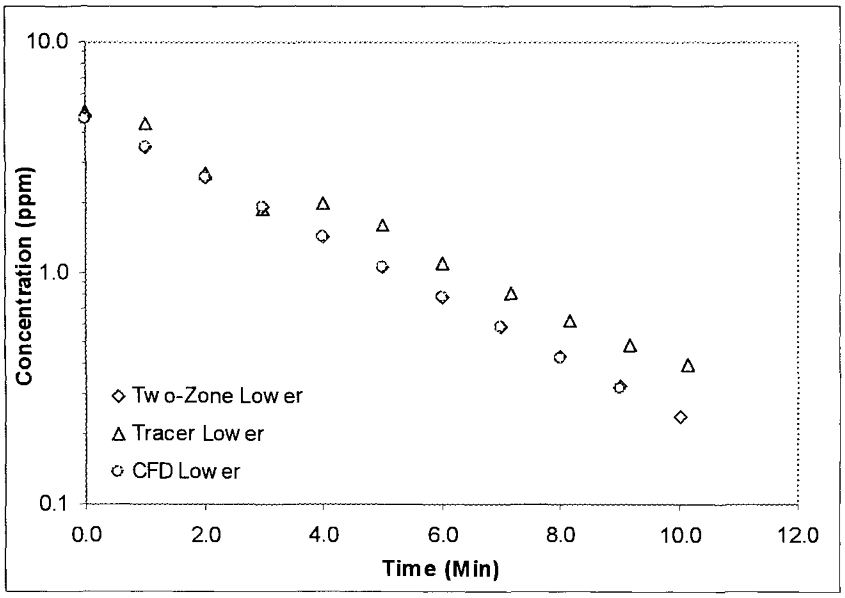

Figure 4-14. Decay Curves of Hydrogen Sulfide in the Lower Zone at Low Flow Rate Calculated with the Nicas Formula, Computer Simulation and Tracer Analysis

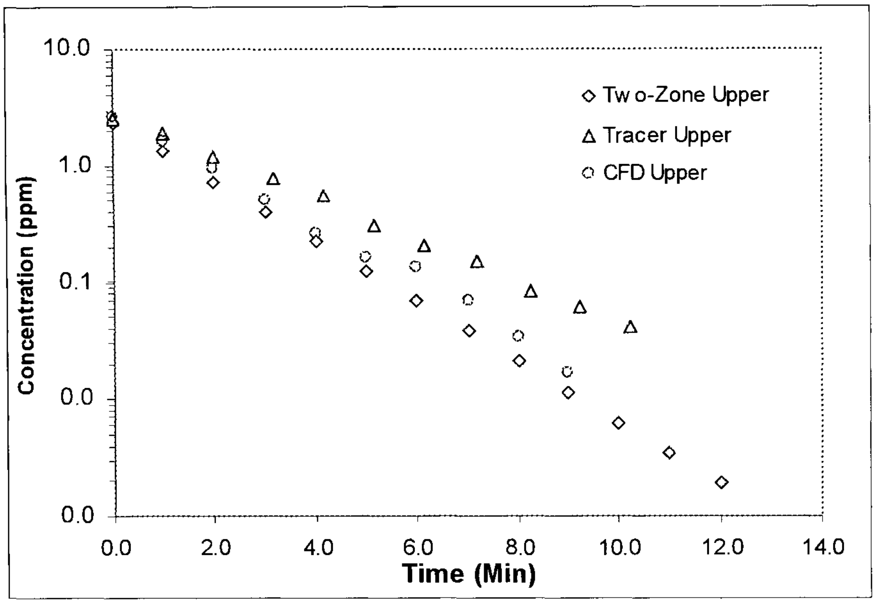

Figure 4-15. Decay Curves of Hydrogen Sulfide in the Upper Zone at High Flow Rate Calculated with the Nicas Formula, Computer Simulation and Tracer Analysis

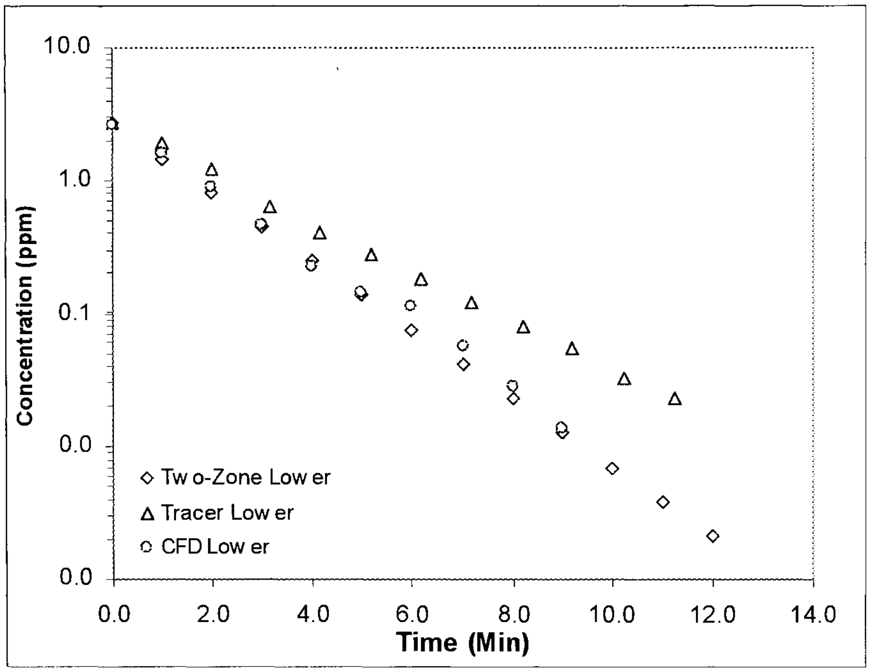

Figure 4-16. Decay Curves of Hydrogen Sulfide in the Lower Zone at High Flow Rate Calculated with the Nicas Formula, Computer Simulation and Tracer Analysis

Association of Ks and Different Conditions: Flow Rates, Configurations, Gases, and Measurement Locations

K_{Tracer} results were compared across different conditions: airflows, configurations, gases and measuring locations (Figure 4-7). Airflow rates achieved statistical significance in association with changes in K_{Tracer} (Table 4-5); specifically, differences of K_{tracer} were found in Configuration 3 (Cases 4 & 5) for both carbon dioxide and hydrogen sulfide while K_{Tracer} showed a significant difference in Configuration 1 for carbon dioxide only. Directions of the differences, however, were not consistent in the two configurations; K_{Tracer} for high airflow rates were smaller in Configuration 1 (well-ventilated condition) and larger in Configuration 3 (two-zone condition). K_{Tracer} in Configuration 1 were greater than those in Configuration 2 and 3 for hydrogen sulfide (p-value <0.0001). K_{Tracer} for carbon dioxide showed greater K_{Tracer} in Configuration 1 and 2 compared to those in Configuration 3.

For the cases overall, differences in K_{Tracer} between hydrogen sulfide and carbon dioxide were found in a paired t-test (p-value <0.001). Specifically, at high flow rates no differences in K_{Tracer} were detected between the two gases but a significant difference was shown at low airflow rates in the overall comparison (p-value=0.0219). In addition, the differences in K_{Tracer} between the two gases were found only in Configuration 1 (p-value < 0.001); K_{Tracer} for hydrogen sulfide were greater than carbon dioxide K_{Tracer}. Different measuring locations also contributed significantly to changes of K_{Tracer} for hydrogen sulfide; K_{Tracer} at Location 2 (center) were higher than those at Location 1 (upper). Location, however, made no difference in K_{Tracer} for carbon dioxide.

K_{Tracer} and K_{CFD} were compared statistically in terms of airflows, configurations, gases and measuring locations. Using regression analysis, a difference between overall K_{Tracer} and K_{CFD} was significantly associated with gases (p<0.001) whereas airflows, configurations and locations were shown to be insignificant. The difference between the two Ks was greater for hydrogen sulfide than carbon dioxide. The influence of airflows, configurations, and locations on the difference between Ks varied for individual gases.

For hydrogen sulfide, the difference between the Ks was significantly greater at the lower measuring location (center) compared to those measured at the higher location ($p=0.0003$); airflows and configurations were not significant contributors to differences across Ks. For carbon dioxide, no association of airflows, configurations or measuring locations was found with the K_{Tracer} /K_{CFD} difference.

Table 4-5. Statistical Analysis Outcome of GLM Procedure

Dependent Variable	N	R^2	Source	Sum of squares (Type III)	F Value
H_2S K_{Tracer}	33	0.5341	Airflow Configuration Location	0.0033 0.4021 0.4735	0.12 14.65*** 17.26***
H_2S $K_{Tracer} - K_{CFD}$	33	0.3259	Airflow Configuration Location	0.0753 0.0435 0.3920	2.16 1.25 11.24**
CO_2 K_{Tracer}	68	0.2129	Airflow Configuration Location	0.0314 0.3588 0.0171	1.34 15.25*** 0.02
CO_2 $K_{Tracer} - K_{CFD}$	68	0.0175	Airflow Configuration Location	0.0064 0.0209 1.19 E-5	0.27 0.87 0.00

Note: N= Number of observation.
* p-value <0.05; ** p-value <0.01; *** p-value <0.001.

Discussion

In this study, concentrations of hydrogen sulfide and carbon dioxide were predicted by computer simulations (K_{CFD}) and mathematical modeling ($K_{Two\text{-}Zone}$). In general, these predictions varied from concentrations measured by tracer analysis (K_{Tracer}); however, certain conditions of the experiments, such as airflow rates, configurations, gases, and measurement locations were associated with the variability. As shown by statistical analysis, the measured Ks (K_{Tracer}) were different in three configurations of the experimental chamber, and those differences were associated with different airflow rates. Configuration 1 created a "well-ventilated" space compared to Configuration 3, which had two imaginary zones with uneven gas distribution. In the well-ventilated condition (Configuration 1) and at high flow rates, K_{Tracer} values were smaller; in the poorly ventilated condition (Configuration 3) at high flow rates they were greater for both gases. In other words, ventilation efficiency increased in a volume with good ventilation structure and decreased in a volume with poor ventilation even under the same (high) airflow conditions. That result could be attributed to turbulence generation from higher airflows, which might be associated with structural features that cause uneven airflow distribution. This important outcome proves that structural features themselves (in this study, the location of vents) can reduce ventilation efficiency regardless of other factors like furniture or human activity within the space. It is also assumed that turbulence flow generation under conditions of uneven airflow distribution may decrease the accuracy of prediction with computer simulation or mathematical modeling. In Figure 4-16, K_{CFD} or $K_{Two\text{-}Zone}$ differ more from K_{Tracer} at high airflow rates than at low flow rates.

Behavior of the two gases was also assumed to influence ventilation efficiency. A t-test indicated that at low flow rates K_{Tracer} values for hydrogen sulfide were greater than carbon dioxide K_{tracer} ($p=0.0219$) although no difference was present with high flow rates. This outcome reflects that, under conditions of high airflow, hydrogen sulfide molecules are floating and sufficiently mixed for their concentration decays to be similar to carbon dioxide decays, but when airflow is insufficient, hydrogen sulfide gases tend to sink, being heavier than air. The initial concentrations at different locations also revealed the variable gas behavior. As shown in Table 4-6, the initial concentrations of hydrogen sulfide in the lower zone were smaller than upper zone concentrations. No statistical differences were found for carbon dioxide K_{Tracer} at four different locations. Variability may also be related to the instrument used to measure hydrogen sulfide, which took sampled the air for 30 seconds and reported the average levels during that period, whereas the computer simulation showed a "snapshot" of the corresponding time.

Table 4-6. Initial Concentrations (ppm) of Hydrogen Sulfide and Carbon Dioxide in Configuration 1 and 3

Configuration	Case	H_2S (n=3) Location 1 (upper) Average (STD)	H_2S (n=3) Location 2 (lower) Average (STD)	CO_2 (n=3) Location 1 (upper) Average (STD)	CO_2 (n=3) Location 2 (lower) Average (STD)
1 (Well-mixed)	1 (low airflow)	4.60 (*)	6.80 (0.36)	1306.33 (23.18)	1300.00 (30.35)
	2 (high airflow)	2.83 (0.06)	3.17 (0.06)	770.00 (27.73)	761.33 (5.03)
3 (Two-zone)	4 (low airflow)	2.35 (0.21)	2.70 (0.10)	748.33 (8.39)	723.67 (8.96)
	5 (high airflow)	4.25 (0.07)	4.80 (0.20)	1032.00 (0.00)	1026.33 (0.58)

Note: STD=Standard Deviation.

* The hydrogen sulfide measuring instrument had regeneration procedures when decay steps started in two of three trials; hence, initial concentrations were missing although Ks from the rest of decay curves were calculated.

To calculate $K_{Two\text{-}Zone}$ for the upper and lower zones, the volume occupied by the upper and lower zones needed to be determined. As shown in Figure 4-4, hydrogen sulfide was measured at Locations 1 and 2, and K values changed depending on where the zones were partitioned [Nicas, 1996]. When the zones were arbitrarily divided at Location 1, the sizes of the upper and lower zones were 9.0 $m^3$and 17. 78 m^3 respectively, while the size of both zones was 13.39 m^3 when divided at Location 2. The two $K_{Two\text{-}Zone}$ values with partitioning at Location 1 and 2 are summarized in Table 4-7. As the results shows, $K_{Two\text{-}Zone}$ for two partitioning locations were found to have only minor differences, especially at a low flow rate; in this study, Location 1 was used for the partitioning.

Table 4-7. $K_{Two\text{-}Zone}$ with Zone Partitions

Room Partitioning Location	$K_{Two\text{-}Zone}$ Low flow rate (509 m^3/hr)		High flow rate (1018 m^3/hr)	
	Upper zone	Lower zone	Upper zone	Lower zone
Location 1	1.0381	1.0202	1.0225	1.0213
Location 2	1.0681	1.0503	1.0378	1.0370

It is unclear how different conditions influence each other, changes in K_{Tracer} or the accuracy of the concentration prediction. Although this study found an inconsistency between concentration prediction by CFD and measured results, the reasons for the difference between the two techniques can be explained by configurations, airflows, gases, and measuring locations. This study's comparison between the two gases is especially significant since most of indoor air quality research on computer simulations use SF_6 or CO_2 which behave more like ideal gases than does hydrogen sulfide. Computer simulation software for estimating airborne contaminant concentrations may need to be modified to adjust for those differences. In addition, this study's results were based on experiments in controlled conditions; further research is required before numeric techniques can be used for air quality assessment in real occupational environments.

CHAPTER V

OVERVIEW AND RECOMMENDATION

While "recognition," "evaluation," and "control" of exposures are the tools Industrial Hygienists use to achieve safer occupational environments, this study focused on the "evaluation" of the occupational environment of WWTPs in terms of environment, human health, and air quality assessment. Although many studies in the last few decades have provided limited information about exposure agents and workers' health problems, few have linked risk levels with performance of specific jobs. Studies that investigated hydrogen sulfide levels for specified job tasks are even rarer. Such information is important because typically each wastewater treatment procedure in a plant involves unique toxic agents and risk levels, and by applying the knowledge of varying risk levels related to the environment and job performance, control of those risks can be more practical and effective.

Indoor and Outdoor Air Quality Assessment of Four Wastewater Treatment Plants

To investigate the environment and workers' health, unit operations and job tasks need to be classified in an appropriate manner. Most of the research on WWTPs has reported levels of contaminants or prevalence rates of health symptoms without consideration of the different unit operations or work activities. In some cases, very simple classifications have been used, such as high or low levels of contamination or indoor versus outdoor unit operations [Brandi et al., 2000; Khuder et al., 1998; Laitinen et al., 1994; Laitinen et al., 1992; Melbostad et al., 1994]. While there are two studies reporting endotoxin levels in various unit operations, none has investigated hydrogen sulfide levels in different unit operations [Smit, et al., 2005; Thorn et al., 2002a].

As described in Chapter II, changes in hydrogen sulfide levels were found in association with different unit operations and other conditions, such as total amount of incoming flows and relative humidity. Temperature was not associated with the levels of hydrogen sulfide. Given this outcome, several suggestions can be made: 1) plants receiving large amounts of incoming flows should put more effort into reducing levels of hydrogen sulfide compared to small plants; 2) efforts to reduce exposures, such as ventilation, should be maintained during hot weather because the levels of hydrogen sulfide were not changed by temperature; and 3) efforts to minimize hydrogen sulfide exposure should be more intensive for particular unit operations, such as grit removal and sludge dewatering, based on the varying levels of different unit operations. Also, it is suggested that workers need to be trained to wear appropriate personal protective equipment when they perform unit operations for sludge handling.

Monitoring Risks in Association with Exposure Levels among Wastewater Treatment Workers

As shown in Table 5-1 below, exposure levels measured by area and personal samplings were different. The differences were assumed to be influenced by the characteristics of the job task in different unit operations, as well as by individuals' work behavior, so a systematic job classification was crucial to this study. In other studies, job tasks were divided in accordance with workers' job titles, such as "maintenance/operation," or "no-exposure/partially exposed/exposed." More recent studies have begun to investigate individual unit operations in association with health symptoms and contaminant levels; however, the sample numbers are few and systematically classified job tasks were not discussed [Thorn et al., 2002a; Thorn et al., 2002b]. In the process of evaluating workers' exposure for this study, ten job categories were created based on discussions with the participating workers and observation of workers' duties [Conrad & Soule, 2001].

Classification by job title was not appropriate for this study since workers in two of the four participating plants were involved with all job duties, as is common in WWTPs. Also, in the other two plants the duties of maintenance/operation workers were not identical. Acquiring accurate information regarding workers' time spent on job tasks was challenging as well. Participants varied in the accuracy of their job-task/unit operation logs. For example, when workers recorded job tasks at the end of the day, some wrote down only major tasks and omitted detailed information. Nonetheless, the job classification used in this study is believed to be an improved means for evaluating these data and useful for future research as well.

The research described in Chapter III demonstrated different risk levels among job tasks and identified associations between health symptoms and particular job tasks, respirator use, and employment period. Based on the findings, the following suggestions should be considered: 1) periodic medical surveillance and prevention programs, especially for depression, 2) training on appropriate use of respirators, 3) education on precausionary work practices, and 4) development of user-friendly respirators to reduce exposure to hydrogen sulfide needs. In addition, this study suggests the development of follow-up studies. The association of health symptoms with contaminant levels of different job tasks and unit operations needs further investigation with repeated measurments for determination of exposure levels. Also, measurements of endotoxin levels in unit operations and job tasks need further investigation since this study found no difference in endotoxin levels across unit operations, whereas other studies demonstrated a difference [Laitinen et al., 1994; Thorn et al., 2002a].

Computer Simulation, a Tool for Air Quality Assessment

In scientific research, outcomes are assumed to be based on accurate measurements, although accuracy is typically reported as a range of errors since it is agreed that no instrument is capable of presenting absolutely true values. To achieve a higher level of accuracy in measuring airborne contaminants, it is necessary not only to use highly sensitive instruments; careful sampling plans must also be developed in which outcomes representing general exposure levels can be generated regardless of time and location of measurement. To determine the location, duration and schedule of a sampling plan, Industrial Hygienists need to consider the worst-case scenario, the typical work-schedule that most workers have, and the locations workers stay at or visit frequently. However, information from real-time monitoring will necessarily be limited by the number of measuring locations and length of sampling duration; the fewer the samples and the shorter the length of the sampling period, the coarser the map of air contaminants' distribution in a given space.

Using computer simulation as an air quality assessment tool is a reasonable approach for Industrial Hygiene practice because numerical modeling (computer simulation as well as mathematical modeling) gives a distribution of concentration comprehensively in space and time. At present, it requires profound knowledge to build scenarios of real work spaces in a computer simulation system, and much experimental work is needed to simplify complicated Navier-Stokes equations. However, using computer simulation methods is undeniably attractive for Industrial Hygienists since the outcome is a comprehensive view of contaminants' distribution within the boundary conditions of the space. Although computer simulations in this study showed inconsistency compared to the outcomes from tracer analysis, the inconsistency was explained by several features of the experiment. With more research to reduce the difference between concentrations from prediction and from real-time monitoring, use of numerical techniques could be an alternative technique for air quality assessment.

Final Statement

The background and initial purpose of this study was simple: to prevent unexpected exposure to dangerous levels of hydrogen sulfide in wastewater treatment plants. To achieve that purpose, the WWTP environment, workers and IH assessments were closely examined, and I believe the findings and practical suggestions from the study represent meaningful steps toward achieving this prevention goal. I hope the limitations of this work will inspire other researchers to initiate further studies to achieve healthy and safe occupational environments in WWTPs.

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APPENDIX A

QUESTIONNAIRES USED FOR HEALTH STATUS MONITORING AMONG WWTP AND WTP WORKERS

Low Level Exposure to Hydrogen Sulfide among Wastewater Treatment Employees

ID No. _______ (data entry number) ___ Date ___________________________

Facility ________________________ Job Title ________________________

Male ____ Female ____ Birth Date _____ _____ _____
Mo. Day Yr

Race: ___White ___ African American ___ Native American ___ Hispanic ___ Other

QUESTIONS ABOUT PREVIOUS WORK

1. Before this work, did you work in any other environments with exposure to gases and/or dusts?

____ Yes
____ No ➔ Proceed to question 3.

2. What type of work?	Number of Years
____	_____________
____	_____________
____	_____________
____	_____________
____	_____________

QUESTIONS ABOUT PRESENT WORK (Wastewater Treatment)

3. How many years have you worked at your present job? ___ Yr ___ Mo.
4. How many days per week do you usually work? ___ Days
5. How many hours per day do you usually work? ___ Hours

6. What are your primary tasks?	Hours worked (%)
_______________	_______
_______________	_______
_______________	_______
_______________	_______
_______________	_______

7. What types of work or tasks are you exposed to gases (e.g. hydrogen sulfide) or dusts?	hours worked (%)
_______________	_______
_______________	_______
_______________	_______
_______________	_______
_______________	_______

8. How many hours have you worked today? ____ Hours

9. Do you ever wear breathing protection (respirator) at work?
___ Yes ➔ Proceed to question 10
___ No ➔ Proceed to question 13

10. What kind of respirator do you wear?
____Self-Containing Breathing Apparatus (SCBA)
____ Powered Air Purifying Respirator (PAPR)
___ Dust mask
____Others Specify________________

11. How often do you wear this when exposed to gases or dusts?
____ 80 – 100 % of the time
____ 50 – 80 % of time
____ Less than 50%
____ No use

12. How many years have you used a respirator? _____ Years

QUESTIONS ABOUT CURRENT SYMPTOMS

13. Do you have any of the following symptoms *at least one day per work week* (for more than one hour)?

			Occurs at work			How many days per work week (1-5)	Improves during time off work		Worse first day of work week		
	Yes	No	Yes	No	Don't know		Yes	No	Yes	No	Don't know
A. Symptoms from Chest											
Dry cough											
Cough with phlegm											
Wheezing chest											
Chest tightness											
Breathlessness											
Nasal irritation											
Throat irritation											
Sinus trouble											
B. General Symptoms											
Fever											
Headache											
Dizziness											
Nausea											
Tiredness											
Joint pains											
Vomiting											
Indigestion											
Stomach pain											
Diarrhea											
Constipation											
Skin problems											
Eye irritation											
Difficulty remembering things or concentrating											

14. Are any of the symptoms worse on a specific day of the week?

_____ Yes ➔ What kind of symptoms? ________________

Which day? ___________

_____ No

15. Have any of the symptoms caused sick leave?

_____ Yes ➔ What kind of symptoms? __________________

How long? ____________

_____ No

16. Do you use medicine regularly for any of the symptoms?

_____ Yes ➔ What kind of medicine? __________________

_____ No

17. Have you ever experienced unconsciousness because of hydrogen sulfide exposure or been admitted in a hospital when you worked?

_____ Yes _____ No

18. For each statement below, think about how often you felt or behaved that way *during the past week.*

0 Rare/None = less than 1 day
1 Some/a little = 1 to 2 days
2 Occasionally = 3 to 4 days
3 Most/All the time = 5 to 7days

1) I did not feel like eating; my appetite was poor	0	1	2	3
2) I felt depressed.	0	1	2	3
3) I felt that everything I did was an effort	0	1	2	3
4) My sleep was restless.	0	1	2	3
5) I was happy.	0	1	2	3
6) I felt lonely.	0	1	2	3
7) I felt that people were unfriendly	0	1	2	3
8) I enjoyed life.	0	1	2	3
9) I felt sad.	0	1	2	3
10) I felt that people disliked me.	0	1	2	3
11) I could not get "going"	0	1	2	3

QUESTIONS ABOUT LONG TERM SYMPTOMS

19. Do you have any other symptoms that you think can be related to you work?
_____ Yes ➔ What kind of symptoms ? ____________________
_____ No

20. Do you usually have cough with phlegm?
_____ Yes ➔ ____ Less than 3 months per year
____ More than 3 months per year
_____ No ➔ Proceed to question 22

21. How long have you had cough with phlegm?
_____ Less than 2 years
_____ More than 2 years

22. Does your chest ever feel tight in connection with work?
_____ Yes
_____ No ➔ Proceed to question 24

23. Does the chest tightness occur on any particular day?
_____ Yes ➔ _____ Most of the first days back at work only
_____Other day(s) or _____only other days
_____ No

24. Have you, during the last year, had episodes of influenza-like symptoms (fever, shivering, malaise, cough, tiredness, weakness, muscle and joint pains) in connection with work?
_____ Yes ➔ How many times? _____ times
_____ No ➔ Proceed to question 27

25. What were you doing when this occurred? ______________________________
_____ Don't know

26. How long did it last?
_____ To the next day
_____ Several days
_____ Don't know

27. Have you ever got (eye irritation, conjunctivitis) in connection with work? (Circle anything related)
_____ Yes ➔ How frequently? _________________
_____ No

28. Do you have any of the following condition? (Specify in parenthesis)

			Verified by physician	
	Yes	No	Yes	No
Hay fever				
Eczema				
Asthma				
Food allergy (____________________)				
Allergy to house dust (____________________)				
Allergy to animals (____________________)				
Allergy to metals (____________________)				
Allergy to something else in your environment (____________________)				

SMOKING

29. Have you ever smoked cigarettes?

_____ Yes
_____ No ➔ Proceed to question 35

30. How old were you when you first started regularly smoking cigarettes?

_____ Age in years
_____ Does not apply

31. Do you now (within the past month) smoke cigarettes?

_____ Yes
_____ No
_____ Does not apply

32. If you have completely stopped smoking cigarettes, how old were you when you stopped smoking?

_____ Age in years
_____ Still smoking
_____ Does no apply

33. How many cigarettes do you smoke per day now?

_____ Number of cigarettes
_____ Does no apply

34. On the average of the entire time you smoked. How many cigarettes did you smoke a day?

_____ Number of cigarettes

_____ Does not apply

35. Is there anything else you wish to tell us concerning your symptoms or your work?

____

____

____

____

____

____

____

____

____

Thank you for your time.

All responses will remain confidential and data will be reported only in aggregate form.

Low Level Exposure to Hydrogen Sulfide among Water Treatment Employees

ID No. _______ (data entry number) ___ Date ____________________________

Facility _________________________ Job Title _________________________

Male ____ Female ____ Birth Date _____ _____ _____
Mo. Day Yr

Race: ___White ___ African American ___ Native American ___ Hispanic ___ Other

QUESTIONS ABOUT PREVIOUS AND PRESENT WORK

1. Have you worked at water pollution control facilities (wastewater treatment plants) before? Yes _________ years, No ________

How many years have you worked at your present job? ___ Yr ___ Mo.

2. Do you ever wear breathing protection (respirator) at work?
___ Yes ➔ Proceed to question 3
___ No ➔ Proceed to question 6

3. What kind of respirator do you wear?
____Self-Containing Breathing Apparatus (SCBA)
____ Powered Air Purifying Respirator (PAPR)
___ Dust mask
____Others Specify_________________

4. How often do you wear this when exposed to gases or dusts?
____ 80 – 100 % of the time
____ 50 – 80 % of time
____ Less than 50%
____ No use

5. How many years have you used a respirator? _____ Years

QUESTIONS ABOUT CURRENT SYMPTOMS

6. Do you have any of the following symptoms *at least one day per work week* (for more than one hour)?

			Occurs at work			How many days per work week (1-5)	Improves during time off work		Worse first day of work week		
	Yes	No	Yes	No	Don't know		Yes	No	Yes	No	Don't know
A. Symptoms from Chest											
Dry cough											
Cough with phlegm											
Wheezing chest											
Chest tightness											
Breathlessness											
Nasal irritation											
Throat irritation											
Sinus trouble											
B. General Symptoms											
Fever											
Headache											
Dizziness											
Nausea											
Tiredness											
Joint pains											
Vomiting											
Indigestion											
Stomach pain											
Diarrhea											
Constipation											
Skin problems											
Eye irritation											
Difficulty remembering things or concentrating											

7. Are any of the symptoms worse on a specific day of the week?
_____ Yes → What kind of symptoms? __________________
Which day? ____________
_____ No

8. Have any of the symptoms caused sick leave?
_____ Yes → What kind of symptoms? ___________________
How long? _____________
_____ No

9. Do you use medicine regularly for any of the symptoms?
_____ Yes → What kind of medicine? ___________________
_____ No

10. Have you ever experienced unconsciousness because of hydrogen sulfide exposure or been admitted in a hospital when you worked?
_____ Yes _____ No

11. For each statement below, think about how often you felt or behaved that way *during the past week.*

1 Rare/None = less than 1 day
2 Some/a little = 1 to 2 days
3 Occasionally = 3 to 4 days
4 Most/All the time = 5 to 7days

1) I did not feel like eating; my appetite was poor	0	1	2	3
2) I felt depressed.	0	1	2	3
3) I felt that everything I did was an effort	0	1	2	3
4) My sleep was restless.	0	1	2	3
5) I was happy.	0	1	2	3
6) I felt lonely.	0	1	2	3
7) I felt that people were unfriendly	0	1	2	3
8) I enjoyed life.	0	1	2	3
9) I felt sad.	0	1	2	3
10) I felt that people disliked me.	0	1	2	3
11) I could not get "going"	0	1	2	3

QUESTIONS ABOUT LONG TERM SYMPTOMS

12. Do you have any other symptoms that you think can be related to you work?

_____ Yes ➔ What kind of symptoms ? ____________________
_____ No

13. Do you usually have cough with phlegm?

_____ Yes ➔ ____ Less than 3 months per year
____ More than 3 months per year
_____ No ➔ Proceed to question 15

14. How long have you had cough with phlegm?

_____ Less than 2 years
_____ More than 2 years

15. Does your chest ever feel tight in connection with work?

_____ Yes
_____ No ➔ Proceed to question 17

16. Does the chest tightness occur on any particular day?

_____ Yes ➔ _____ Most of the first days back at work only
_____Other day(s) or _____only other days
_____ No

17. Have you, during the last year, had episodes of influenza-like symptoms (fever, shivering, malaise, cough, tiredness, weakness, muscle and joint pains) in connection with work?

_____ Yes ➔ How many times? _____ times
_____ No ➔ Proceed to question 20

18. What were you doing when this occurred? ______________________________

_____ Don't know

19. How long did it last?

_____ To the next day
_____ Several days
_____ Don't know

20. Have you ever got (eye irritation, conjunctivitis) in connection with work? (Circle anything related)

_____ Yes ➔ How frequently? _________________
_____ No

21. Do you have any of the following condition? (Specify in parenthesis)

			Verified by physician	
	Yes	No	Yes	No
Hay fever				
Eczema				
Asthma				
Food allergy (____________________)				
Allergy to house dust (____________________)				
Allergy to animals (____________________)				
Allergy to metals (____________________)				
Allergy to something else in your environment (____________________)				

SMOKING

22. Have you ever smoked cigarettes?

_____ Yes
_____ No ➔ Proceed to question 28

23. How old were you when you first started regularly smoking cigarettes?

_____ Age in years
_____ Does not apply

24. Do you now (within the past month) smoke cigarettes?

_____ Yes
_____ No
_____ Does not apply

25. If you have completely stopped smoking cigarettes, how old were you when you stopped smoking?

_____ Age in years
_____ Still smoking
_____ Does no apply

26. How many cigarettes do you smoke per day now?

_____ Number of cigarettes
_____ Does no apply

27. On the average of the entire time you smoked. How many cigarettes did you smoke a day?

_____ Number of cigarettes
_____ Does not apply

28. Is there anything else you wish to tell us concerning your symptoms or your work?

____
____
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Thank you for your time.
All responses will remain confidential and data will be reported only in aggregate form.

APPENDIX B

CALCULATION FOR CONCENTRATIONS IN UPPER AND LOWER ZONES

The equations for contaminant concentration decay in the two-zone room.

When a room in Figure 1-1 is considered, the differential mass balance equations for the Lower and upper zone are expressed as follows:

$$V_L \cdot dC_l = -\beta \cdot C_L(t) \cdot dt + \beta \cdot C_U(t) \cdot dt \qquad \text{(A-1)}$$

$$V_U \cdot dC_U = \beta \cdot C_L(t) \cdot dt - (Q+\beta) \cdot C_U(t) \cdot dt \qquad \text{(A-2)}$$

where $V_{L(U)}$ is volume of the lower(upper) zone, $C_{L(U)}(t)$ is concentration in the lower (upper) zone at time t, G is contaminant's generation rate, β is exchange rate between two zones and Q is flow rate.

When arrange them again, the equations are written as:

$$\frac{dC_L}{dt} = C_L'(t) = -\frac{\beta}{V_L} \cdot C_L(t) + \frac{\beta}{V_L} \cdot C_U(t) \qquad \text{(A-3)}$$

$$\frac{dC_U}{dt} = C_U{}'(t) = \frac{\beta}{V_U} \cdot C_L(t) - \frac{(Q+\beta)}{V_U} \cdot C_U(t) \qquad \text{(A-4)}$$

In matrix form, the mass balance can be rewritten as:

$$\begin{pmatrix} C_L{}'(t) \\ C_U{}'(t) \end{pmatrix} = \begin{pmatrix} -\beta/V_L & \beta/V_L \\ \beta/V_U & -(Q+\beta)/V_U \end{pmatrix} \begin{pmatrix} C_L(t) \\ C_U(t) \end{pmatrix} \qquad \text{(A-5)}$$

The general solution of the equation A-5 is:

$$\begin{pmatrix} C_L(t) \\ C_U(t) \end{pmatrix} = \delta_1 \cdot e^{(\lambda_1 \cdot t)} \cdot X_1 + \delta_2 \cdot e^{(\lambda_2 \cdot t)} \cdot X_2 \qquad \text{(A-6)}$$

where λ_1 and λ_2 are the eigenvalues of matrix A, which is denoted for the 2 by 2 coefficient matrix in A-5; X_1 and X_2 are the corresponding 2 by 1 eigenvectors; and δ_1 and δ_2 are coefficients.

To simplify A-5, the components are replaced by a, b, and c as follows:

$$\begin{aligned} a &= \beta / V_L \\ b &= \beta / V_U \\ c &= (Q+\beta)/V_U \end{aligned}$$

Then, A-5 will be:

$$\begin{pmatrix} C_L{}'(t) \\ C_U{}'(t) \end{pmatrix} = \begin{pmatrix} -a & a \\ b & -c \end{pmatrix} \begin{pmatrix} C_L(t) \\ C_U(t) \end{pmatrix} \qquad \text{(A-7)}$$

To solve for the eigenvalues, λ of A, the 2 by 2 matrix A-λI should be zero, although eigenvectors are not zero. I is the identity matrix.

$$\begin{pmatrix} -a & a \\ b & -c \end{pmatrix} - \lambda \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} -a & a \\ b & -c \end{pmatrix} - \begin{pmatrix} \lambda & 0 \\ 0 & \lambda \end{pmatrix} = \begin{pmatrix} -a-\lambda & a \\ b & -c-\lambda \end{pmatrix} = 0 \qquad \text{(A-8)}$$

The characteristic polynomial equation of A-8 is:

$$(a+\lambda)\cdot(c+\lambda) - ab = 0$$

or

$$\lambda^2 + (a+c)\lambda + ac - ab = 0 \qquad \text{(A-9)}$$

Eigenvectors X_1 and X_2 are can be calculated as follows:

$$\begin{pmatrix} -a-\lambda & a \\ b & -c-\lambda \end{pmatrix} X = \begin{pmatrix} -a-\lambda & a \\ b & -c-\lambda \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = 0$$

$$-(a+\lambda)x_1 + ax_2 = 0$$

$$x_2 = \frac{(a+\lambda)}{a} x_1$$

$$X = \begin{pmatrix} x_1 \\ \dfrac{(a+\lambda)\,x_1}{a} \end{pmatrix} = x_1 \begin{pmatrix} 1 \\ \dfrac{a+\lambda}{a} \end{pmatrix}$$

Therefore, the eigenvectors are:

$$X_1 = \begin{pmatrix} 1 \\ \dfrac{a+\lambda_1}{a} \end{pmatrix}$$

$$X_2 = \begin{pmatrix} 1 \\ \dfrac{a+\lambda_2}{a} \end{pmatrix} \qquad \text{(A-10)}$$

From the A-9, the eigenvalues are:

$$\lambda_{1,2} = \frac{-(a+c) \pm \sqrt{(a+c)^2 - 4(ac-ab)}}{2} \qquad \text{(A-11)}$$

By replacing eigenvector X to equation A-6 the general solution for $C_l(t)$ and $C_u(t)$ are written as:

$$C_L(t) = \delta_1 \cdot e^{(\lambda_1 \cdot t)} + \delta_2 \cdot e^{(\lambda_2 \cdot t)} \qquad \text{(A-12)}$$

$$C_U(t) = \delta_1 \cdot (\frac{a+\lambda_1}{a}) \cdot e^{(\lambda_1 \cdot t)} + \delta_2 (\frac{a+\lambda_2}{a}) \cdot e^{(\lambda_2 \cdot t)} \qquad \text{(A-13)}$$

For this study, exchange rate, β and generation rate G were calculated indirectly using Nicas theory, $C_L(0)=G(\beta + Q)/\beta Q$, and $C_U(0)=G/Q$.

With his theory, $C_L(0)$ and $C_u(0)$ of A-12 and A-13 can be re-written:

$$C_L(0) = \delta_1 + \delta_2 = \frac{G(\beta+Q)}{\beta Q} \qquad \text{(A-14)}$$

$$C_U(0) = \delta_1 \cdot (\frac{a+\lambda_1}{a}) + \delta_2 (\frac{a+\lambda_2}{a}) = \frac{G}{Q} \qquad \text{(A-15)}$$

By mathematical manipulation, δ_1 and δ_2 of the equation A-14 and A-15 will be:

$$\delta_1 = G\left(\frac{\beta \cdot Q + \lambda_2 \cdot V_L(\beta+Q)}{\beta \cdot Q \cdot V_L(\lambda_1 - \lambda_1)} \right) \qquad \text{(A-16)}$$

$$\delta_2 = G\left(\frac{\beta \cdot Q + \lambda_1 \cdot V_L(\beta + Q)}{\beta \cdot Q \cdot V_L(\lambda_1 - \lambda_1)}\right) \qquad \text{(A-17)}$$

To calculate concentration at each time from equation A-12 and A-13, δ_1, δ_2, λ_1, and λ_2 need to be calculated first. For example, in Case 4, $C_L(0)$ was 4.80 ppm and $C_U(0)$ was 4.25 ppm which were measured by tracer analysis and Q was 509.338 m^3/hr. Using A-14 and A-15, β and G can be calculated as follows:

$C_L(0)$= 4.80 ppm = G (β + 509.338 m^3/hr)/ (β x 509.338 m^3/hr) (A-18)

$C_U(0)$= 4.25 ppm = G/509.338 m^3/hr (A-19)

From A-19, G becomes 0.00216 m^3/hr and β can be calculated as follows:

$$C_L(0) = 4.80 \text{ ppm} = 4.8 * 10^{-6} = \frac{0.00216\, m^3/hr\, (\beta + 509.338\, m^3/hr)}{(\beta \text{ x } 509.338\, m^3/hr)}$$

Finally, β becomes 3935.786 m^3/hr.

With the G and β, the constants a, b, and c for A-11 can be calculated. The two zone volumes were determined by partitioning at location 1: V_L=17.778 m^3, V_U=9.006 m^3.

$$a = \beta / V_L = \frac{3935.786 m^3 / hr}{17.778 m^3} = 221.386$$

$$b = \beta / V_U = \frac{3935.786 m^3 / hr}{9.006 m^3} = 437.022$$

$$c = (Q + \beta) / V_U = \frac{509.338 m^3 / hr + 3935.786 m^3 / hr}{9.006 m^3} = 493.578$$

Now, λ_1, and λ_2 can be calculated from equation A-11 and they are:

λ_1= -17.964, and λ_2= -697.000

δ_1 and δ_2 from A-16 and A-17 become:

δ_1= 4.748, and δ_2= 0.052

Then, concentrations for lower and upper zone at time t will be:

$$\boxed{C_L(t) = 4.748 \cdot e^{(-17.964 \cdot t)} + 0.052 \cdot e^{(-697.000 \cdot t)}}$$

$$C_U(t) = 4.748 \cdot (\frac{221.386 - 17.964}{221.386}) \cdot e^{(-17.964 \cdot t)} + 0.052(\frac{221.386 - 697.000}{221.386}) \cdot e^{(-697.000 \cdot t)}$$

Or $$\boxed{C_U(t) = 4.362 \cdot e^{(-17.964 \cdot t)} - 0.112 \cdot e^{(-697.000 \cdot t)}}$$