HETA 95–0044–2561
Metropolitan St. Louis Sewer District
Bissell Point Wastewater Treatment Plant
St. Louis, Missouri

David A. Marlow, B.S.

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from an employer and/or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to federal, State, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

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March 1996
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NIOSH INVESTIGATOR:
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Summary

On November 2, 1994, the National Institute for Occupational Safety and Health (NIOSH) received an employer request for a health hazard evaluation (HHE) at the Metropolitan St. Louis Sewer District Bissell Point wastewater treatment plant in St. Louis, Missouri. The employees reported health problems including periodic headaches, burning sensation in nose, shortness of breath, sore throat, eye irritation, nausea, and diarrhea. In response to this request, an industrial hygiene survey was conducted at the sewage treatment plant on November 21 and 23, 1994.

Personal breathing zone (PBZ) and general area air samples were collected for hydrogen sulfide (H_2S). The maximum H_2S PBZ concentrations ranged from non–detectable (ND) (less than 1 part per million [ppm]) to 2 ppm, all well below the NIOSH ceiling recommended exposure limit (REL) of 10 ppm, and the Occupational Safety and Health Administration (OSHA) ceiling permissible exposure limit (PEL) of 20 ppm. The maximum H_2S concentrations for the general area air samples were all less than 1.0 ppm.

PBZ air sampling results for endotoxin ranged from ND (less than 0.56 endotoxin units per cubic meter of air [EU/m^3]) to 10.9 EU/m^3. While no evaluation criteria have been established for endotoxin, the levels detected were all below a calculated zero pulmonary function effects level for endotoxin of 90 EU/m^3.

Bulk samples of waste activated sewage sludge and wastewater were collected and analyzed qualitatively for headspace volatile organic compounds (VOCs). Major peaks identified in the sewage sludge sample collected from the inlet of a pump under repair included isopropanol, dimethyl sulfide, dimethyl disulfide, and toluene. Major peaks identified in the sewage sludge sample collected from the outlet of a pump under repair included acetone, toluene, butanoic acid, 3–methyl butanoic acid, pentanoic acid, alkyl benzene, n–nonane, n–decane, limonene, n–undecane, cresol, n–dodecane, and n–tridecane. Major peaks identified in the wastewater sample transported to the plant for treatment included dimethyl sulfide, 3–methyl–1–butanol, 1,1,1–trichloroethane, dimethysulfoxide, and n,n–dimethylacetamide. Major peaks identified in the sewage sludge sample collected from a belt press included isopropanol, dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, cresol, and indole.

General area air samples analyzed qualitatively for VOCs had major peaks for n–hexane, chloroform, dimethyl disulfide, toluene, and alkyl benzenes. General area air samples were analyzed quantitatively for 1,1,1–trichloroethane, benzene, toluene, n–hexane, dimethyl sulfide, limonene, and total hydrocarbons. The general area air sampling results for these VOCs ranged

from ND (<0.002 ppm) to 0.059 ppm. All general area air sample results for individual VOCs were below their respective occupational limits where applicable.

Bulk samples of waste activated sewage sludge and incinerator ash were analyzed for elemental composition. Detectable concentrations of 18 different elements were found in these bulk samples. Concentrations of the elements were highest in the incinerator ash samples when compared to the bulk sludge sample results. The eight most abundant elements present in the sludge and ash samples were iron, phosphorous, calcium, aluminum, sodium, magnesium, zinc, and manganese. Twelve of the 18 elements measured in the ash sample have occupational exposure limits. The bulk incinerator ash sample was also analyzed for free crystalline silica content and was found to contain 4% silica.

Based on the PBZ air sampling results, workers in the belt press room were not exposed to H_2S concentrations exceeding the NIOSH ceiling limit REL of 10 ppm or the OSHA ceiling limit PEL of 20 ppm. Daily monitoring for H_2S should continue due to potential seasonal variations in H_2S air concentrations. Historical records indicate that during the summer months H_2S concentrations exceeded 10 ppm in the belt press room. Recommendations are made in the report regarding the use of personal H_2S monitors and respiratory protection when air concentrations equal or exceed 10 ppm.

Keywords: SIC 4952 (Wastewater Treatment) waste activated sludge, incineration, hydrogen sulfide, volatile organic compounds, metals, silica, total particulate, and endotoxin.

Introduction

On November 2, 1994, the National Institute for Occupational Safety and Health (NIOSH) received an employer request for a health hazard evaluation (HHE) at the Metropolitan St. Louis Sewer District Bissell Point wastewater treatment plant in St. Louis, Missouri. The employees reported health problems including periodic headaches, burning sensation in the nose, shortness of breath, sore throat, eye irritation, nausea, and diarrhea. In response to this request, an industrial hygiene survey was conducted at the wastewater treatment plant on November 21 and 23, 1994.

Background and Process Description

The Metropolitan St. Louis Sewer District Bissell Point wastewater treatment plant has been in operation since 1970. The Bissell Point wastewater treatment plant is a secondary treatment facility located on East Grand Avenue in St. Louis, Missouri. Currently, the plant receives an average of 111 million gallons per day (mgd) of wastewater from a 57,000 acre service area covering the northern and eastern parts of the City of St. Louis and portions of North St. Louis County. Over half of the treatment plant's influent biological oxygen demand (BOD) and total suspended solids (TSS) loadings result from industrial sources.

The Bissell Point plant consists of the following sequence of steps: coarse solids removal, grit removal, comminution of coarse floating solids, primary settling to separate effluent wastewater from solids, trickle filtration for rough treatment of chemicals in the wastewater, aeration for the digestion of solids, final settling to separate wastewater effluent from solids, secondary sludge thickening, sludge dewatering, sludge incineration, and ash deposal.

Approximately 100 employees (three shifts per day) work in the sewage sludge dewatering and incineration process at the Bissell Point plant. Of these 100 employees, 40 workers are Operators, 25 workers are Maintenance Mechanics, and 10 workers are Instrument Technicians. During a shift, there are 7 operators: (2) Operator II’s and (1) Operator I in the belt press room, (1) Operator II as the outside incinerator operator, (1) Operator I as the incinerator control room operator, (1) Operator II at the primary clarification, and (1) Operator II at the secondary clarification. The following job titles and descriptions are involved in the operation and maintenance of the wastewater treatment process: Senior Treatment Plant Operator, Treatment Plant Operator I, Treatment Plant Operator II, Stationary Engineer, Maintenance Mechanic, Maintenance Electrician, Instrument Technician, and Treatment Plant Attendant. The Senior Treatment Plant Operator supervises the daily operations at the treatment plant. The Treatment Plant Operator I and II operate the wastewater treatment process including settling and aeration tanks, and sludge dewatering and incineration. The Stationary Engineer stands watch at major pumping stations and operates and performs maintenance on pumps, motors, and related electrical and mechanical equipment. The Maintenance Mechanic maintains, fabricates, installs, repairs, and overhauls mechanical and electro–mechanical equipment throughout the treatment plant. The Maintenance Electrician maintains and repairs wiring and lighting systems, electrical controls, meters, outlets and control panels. The Instrument Technician maintains and installs pneumatic, electrical, hydraulic, and electronic process control systems. The Treatment Plant Attendant sweeps, cleans, dusts, and maintains the treatment plant floors, windows, walls, process equipment, and rest rooms.

In September 1993, the Metropolitan St. Louis Sewer District contracted with private consulting firms to conduct a study to identify the sources and identification of odors being emitted from the Bissell Point plant and to recommend an abatement plan. Odor complaints from the residents living near the plant have occurred yearly since the plant began operations, primarily from June to September. The number of complaints has increased since the secondary treatment facilities began operation in October 1992. Two significant odor episodes occurred on December 14, 1992, and February 4, 1993, resulting in over 100 odor complaints. These episodes were believed to be related to the operation of the new trickling filters. Since that time, domes have been placed on the tops of the filters to prevent emissions from the tops of the filters and all exhaust air from the trickling filters is filtered by scrubbers to remove odorous compounds.

Hydrogen sulfide (H_2S) emissions were determined to be the primary source of odor emissions from the plant. The sources of H_2S sources were: trickling filter quad inlet (43%), primary settling tank weir (30%), trickling filters outlet (13%), pre–aeration basins (5%), grit basin weirs (3%), ash settling basin (1%), and sludge building (1%). Odorous compounds and their emission rates were determined from air samples collected on September 15 and 21, 1993. Air samples were collected at the following locations in the treatment facility: pump station screen room, pump station wet well, grit basins water surface, grit building, comminutor building, pre–aeration basins, primary settling tanks, water surface, trickling filter pump station, trickling filter top, trickling filter quad inlet, trickling filter quad outlet, aeration basins, sludge wells, sludge room ventilation air, trickling filter room ventilation air, incinerators, and ash basins.
Sulfur–containing compounds identified and quantified included H_2S, carbonyl sulfide, methyl mercaptan, dimethyl sulfide, carbon disulfide, and dimethyl disulfide.

H_2S concentrations measured on September 15 and 21, 1993, ranged from ND (grit building) to 32 parts per million (ppm) (trickling filters quad inlet). In the sludge building and thickener room, H_2S concentrations ranged from 0.05 ppm to 0.75 ppm for the two days of sampling. Also during these two sampling days, volatile organic compounds (VOCs) detected by the contractors included acetone, benzene, dichlorobenzene, ethanol, ethyl methyl benzene, ethyl benzene, methyl ethyl ketone, methylene chloride, styrene, tetrachloroethane, toluene, trichloroethane, trichlorofluoromethane, trimethylbenzene, and xylenes. From the VOC sample results, emission rates for total VOCs from the various steps in the wastewater treatment process were calculated. The percent of VOCs emitted from the following steps in the wastewater treatment process were: grit tanks (1%), comminutors (<1%), pre–aeration and influent channel (9%), primary settling tanks (5%), trickling filters (50%), aeration basins and trickling filter effluent channels (4%), final settling tanks and final settling tank effluent channels (2%), thickener room ventilation (1%), belt press room ventilation (4%), sludge well ventilation (1%), and incinerators (13%).

Materials and Methods

Personal breathing zone (PBZ) air samples were collected for H_2S, total particulate, and endotoxin. PBZ air samples for H_2S were collected because H_2S is emitted from wastewater treatment processes due to biodegration of waste materials, and many of the symptoms reported by the employees have been associated with exposure to H_2S. Total particulate PBZ air samples were collected and analyzed for endotoxin because endotoxin is associated with Gram–negative bacteria, and Gram–negative bacteria are present and needed for aerobiotic digestion of solids in wastewater.

PBZ air samples for H_2S were collected with Toxilog Atmospheric Diffusion Monitors manufactured by Biosystems, Inc. Toxilog monitors instantaneously measure H_2S air concentrations using electrochemical sensors and record H_2S concentrations in ppm(s) in the monitor data logger. The limit of detection for the monitors was 1 ppm. The monitors were programmed to record one measurement every minute. At the end of a sampling shift, the dataloggers were downloaded to a computer. Information collected and downloaded to the computer included present H_2S concentration, 10–minute H_2S concentrations, and time–weighted average (TWA) H_2S concentration.

PBZ air samples were collected for total particulate and endotoxin using tared, 5.0-micrometer (µm) pore size, 37–millimeter (mm) diameter, polyvinyl chloride (PVC) filters and connected via tubing to battery powered air sampling pumps calibrated to provide a volumetric air flow rate of 1.5 liters per minute (lpm). Each filter was analyzed gravimetrically according to NIOSH Method 0500 with modifications.[1] Following the final weighing, the filters were extracted in 10–ml of sterile, nonpyrogenic water at room temperature for 60–minutes. The supernatants were decanted into 50–ml centrifuge tubes and centrifuged at 2200 revolutions per minute at 4°C for 10–minutes. Endotoxin analyses were performed in duplicate by the quantitative chromogenic Limulus amebocyte lysate test (QCL–1000; Whittaker Bioproducts, Walkersville, Maryland). Results were reported in terms of endotoxin units (EU) that were compared to the standard, EC–5. For these analyses, 10 EU is equivalent to one nanogram.

General area air samples were collected for H_2S and VOCs. The H_2S general area air sample concentration measurements were obtained with the PhD Atmospheric Diffusion Monitor manufactured by Biosystems, Inc. This monitor uses the same electrochemical sensors as the Toxilog monitors and can also measure oxygen, carbon monoxide, and explosive atmosphere concentrations.

General area air samples for VOCs were collected in pairs; one sample was used as a qualitative screen to identify VOCs and the other was used for quantitative analysis based on the qualitative screening. General area air samples for VOCs were collected on charcoal tubes connected via tubing to battery powered sampling pumps calibrated to provide a volumetric air flow rate of 200 milliliters per minute (ml/min). The qualitative charcoal tubes were desorbed with 1–ml of carbon disulfide and analyzed by gas chromatography with mass spectrometry detection (GC–MSD). The quantitative charcoal tubes were also desorbed with 1–ml of carbon disulfide and analyzed for 1,1,1–trichloroethane, benzene, toluene, n–hexane, dimethyl disulfide, limonene, and total hydrocarbons by GC with flame ionization detection (GC/FID) according to NIOSH Methods 1003, 1500, 1501 and, 1550 with modifications.[1]

Bulk samples of waste activated sewage sludge and wastewater that was hauled to the plant for treatment were collected and analyzed for the presence of different VOCs. The bulk samples were analyzed for VOCs by sampling the headspace air over each sample vial with a thermal desorption tube. Each headspace air sample was collected for 15–minutes at an air sampling flow rate of 50 ml/min. Each thermal desorption tube contained three beds of sorbent materials — a front layer of Carbotrap C (approximately 350 mg), a middle layer of Carbotrap (approximately 175 mg), and a back layer of Carboxen 569 (approximately 150 mg) or Carbosieve S–III (approximately 180 mg). The thermal unit was interfaced directly to a GC/MSD. Samples were analyzed separately by directly inserting each into the thermal desorber unit with no other sample preparation. Each sample tube was desorbed at 300°C for 10–minutes, and compounds present were qualitatively identified by mass spectrometry.

A bulk wastewater sample hauled to the plant for treatment was analyzed quantitatively for the percent present of dimethyl sulfoxide and N,N–dimethylacetamide. The bulk sample was diluted 1:20 in methanol. Aliquots of this dilution mixture were analyzed by GC/FID using NIOSH Method 2004 with modifications.[1]

The sewage sludge and grit samples plus incinerator ash samples were analyzed for the following elements using NIOSH Method 7300[1]: silver (Ag), aluminum (Al), arsenic (As), barium (Ba), beryllium (Be), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), lanthanum (La), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), selenium (Se), strontium (Sr), tellurium (Te), titanium (Ti), thallium (Tl), vanadium (V), yttrium (Y), zinc (Zn), and zirconium (Zr). The incinerator ash samples were also analyzed for silica content using NIOSH Method 7500.[1] Results are reported as percent silica by weight.

Evaluation Criteria

Environmental Criteria

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10–hours per day, 40–hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre–existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criteria. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with skin and mucous membranes, thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs)[2]; (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV®)[3]; and (3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PEL)[4]. In July 1992 the 11th Circuit Court of Appeals vacated the 1989 OSHA PEL Air Contaminants Standard. OSHA is currently enforcing the 1971 standards which are listed as transitional values in the current Code of Federal Regulations; however, some states operating their own OSHA approved job safety and health programs continue to enforce the 1989 limits. Employers are encouraged by NIOSH to follow the 1989 OSHA limits, the NIOSH RELs, the ACGIH TLVs®, or whichever are the more protective criterion. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard and that OSHA PELs included in this report reflect the 1971 values.

TWA exposure refers to the average airborne concentration of a substance during a normal 8–to–10–hour workday. Some substances have recommended short–term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposure over the short–term.

Health Effects

Hydrogen Sulfide

H_2S is a colorless, flammable gas with a strong odor of rotten eggs. In wastewater treatment plants, the majority of the H_2S is present as a result of bacterial decomposition of proteins. Acute exposure to H_2S at airborne concentrations above 10 ppm has been associated with the development of conjunctivitis and keratitis.[5] One–hour exposure to H_2S concentrations between 50 and 100 ppm can produce mild eye and respiratory irritation which becomes markedly worse when the concentrations are in the 200 to 300 ppm range. At H_2S concentrations between 500 and 700 ppm, exposures for 0.5 to 1 hour can result in unconsciousness and death, and between 1000 to 2000 ppm or more, unconsciousness and death can occur within minutes. Conclusive evidence of adverse health effects from chronic exposure to hydrogen sulfide at concentrations below 20 ppm is lacking.[5–8] However, there is some evidence that H_2S alone at low concentrations, or in combination with other chemical substances (e.g., petroleum products or carbon disulfide), is associated with the development of nervous system, cardiovascular, and gastrointestinal disorders, and effects on the eyes.[5] Repeated exposure to H_2S results in increased susceptibility, so that eye irritation, cough, and systemic effects may result from concentrations previously tolerated without effect. Hydrogen sulfide has an odor threshold between 0.002 and 0.003 ppm.[7] The smell is faint but easily perceptible at 0.77 ppm and offensive at 3 to 5 ppm. Up to about 30 ppm, H_2S smells of rotten eggs, but at about 30 ppm the smell is described as sweet or sickening sweet. At 150 ppm, H_2S causes olfactory–nerve paralysis, and the smell is no longer perceptible. The smell of H_2S therefore is not a reliable warning of its presence, especially at high concentrations.

In a recent study, Bhamhani et al.[9] compared the effects of inhalation of 5 ppm H_2S on the physiological and hematological responses of healthy men and women during exercise. Subjects included in the study completed two 30–minute exercise tests on a cycle ergometer at 50% of their predetermined maximal aerobic power while breathing medical air or 5 ppm H_2S from a specially designed flow system. The results indicated that there were no significant differences between the two exposures for the metabolic (oxygen uptake, carbon dioxide production, respiratory exchange ratio), cardiovascular (heart rate, blood pressure, rate pressure production), arterial blood (oxygen and carbon dioxide tensions, pH), and perceptual (rating of perceived exertion) responses in either sex. None of the subjects reported any adverse health effects subsequent to the H_2S exposure. These results suggest that healthy men and women can safely perform moderate intensity work in environments contaminated with 5 ppm H_2S or lower. The device used to deliver H_2S to the subjects fit in their mouths and did not result in exposure to the subjects' eyes. This is important since adverse effects on the eyes are what the NIOSH and OSHA exposure limits are based on.

The NIOSH REL for H_2S is a ceiling limit of 10 ppm, which must not be exceeded during any part of the workday.[2] If instantaneous monitoring is not feasible, the ceiling must be assessed as a 10–minute TWA exposure. When there is a potential for exposure to H_2S at a concentration of 50 ppm or higher, continuous monitoring is recommended by NIOSH. The OSHA standard for H_2S is a ceiling limit of 20 ppm or a maximum allowable peak of 50 ppm for 10–minutes once, if no other measurable exposures occur.[4] The OSHA H_2S ceiling concentration must not be exceeded during any part of the workday; if instantaneous monitoring is not feasible, the ceiling limit must be assessed as a 10–minute TWA exposure. The ACGIH recommends a TLV®–TWA of 10 ppm and a STEL of 15 ppm.[3]

Endotoxin

Bacterial endotoxin is a lipopolysaccharide compound from the outer cell wall of Gram–negative bacteria, which occur abundantly in organic dusts.[10] It has been shown that the biological properties of endotoxin vary depending upon the bacterial species from which they are derived, as well as upon the state of the growth cycle of the bacteria.[11] Endotoxin have a wide range of biological activities involving inflammatory, hemodynamic, and immunological responses. Of most importance in occupational exposures are the activities of endotoxin in the lung.[12] The primary target cell for endotoxin–induced damage by inhalation is the pulmonary macrophage. Human macrophages in particular have been shown to be extremely sensitive to the effects of endotoxin in vitro.[13] Endotoxin, either soluble or associated with particulate matter, will activate the macrophage, causing the cell to produce a host of mediators.[12]

Clinically, little is known about the responses to inhaled endotoxin. Exposure of previously unexposed persons to airborne endotoxin can result in acute fever, dyspnea, coughing, and small reductions in force expiratory volume in one–second (FEV_1), although some investigators have not been able to demonstrate acute changes in FEV_1.[12] The effects of repeated exposure to aerosols of endotoxin in humans are not known. Some animal studies have demonstrated a chronic inflammatory response characterized by goblet cell hyperplasia and increased mucous production. This suggests that repeat exposure may cause a syndrome similar, if not identical, to chronic bronchitis.[12]

Occupational exposure criteria have not been established for bacterial endotoxin by either NIOSH, OSHA, or ACGIH. However, Rylander[14] has reported that sufficient toxicological data is believed to exist for establishing an occupational limit for endotoxin based on acute changes in pulmonary function. Eight–hour (8–hour) TWA concentrations have been suggested for airway inflammation with increased airway reactivity (200 EU/m^3), over–shift decline in FEV_1 (2000 EU/m^3), for chest tightness (3000 EU/m^3), and toxic pneumonitis (10,000 – 20,000 EU/m^3). Castellan[15] has reported a calculated zero pulmonary function effect level for endotoxin of 90 EU/m^3.

Bioaerosols in Sewage Treatment Plants

Laitinen et al.[16] reported endotoxin concentrations that varied from 0.6 to 310 ng/m^3 (7.2 to 3720 EU/m^3, 12 EU = 1 ng) at 10 different wastewater treatment plants. The concentrations of viable bacteria (sampled during the same time) ranged from 10^2 to 10^5 colony–forming units per cubic meter of air (CFU/m^3). The relationships between the bacterial counts and endotoxin concentrations was statistically significant (r= 0.79). A study of sewage workers' exposures to airborne culturable bacteria and inhaled endotoxin was performed at nine wastewater treatment plants in Finland.[17] These plants treated mainly industrial effluents. Endotoxin concentrations measured in the immediate vicinity of the wastewater treatment process ranged from 0.1 to 350 ng/m^3 (1.2 to 4200 EU/m^3). Air concentrations of culturable bacteria ranged from 10 to 10^5 CFU/m^3.

The most common genera of airborne Gram–negative bacteria were *acinetobacter, citrobacter, enterobacter, klebsiella, and pseudomonas*. High levels of exposure to bacteria and bacterial endotoxin usually were related to certain phases of the treatment process. The microbiological contamination of air was highest near the inlets where incoming wastewater entered the basins, in the sludge treatment area, and inside the biofilter tower.

Twenty workers from 15 different municipal sewage treatment plants in eastern Norway participated in another study reported by Melbostad et al.[18] Personal exposures to airborne bacteria, endotoxin, and hydrogen sulfide were evaluated. Endotoxin levels ranged from ND to 370 ng/m^3, median 30 ng/m^3. Total bacteria levels ranged from ND to 9.5×10^6 CFU/m^3, median 5.2×10^5 CFU/m^3. Spherical bacteria levels ranged from ND to 6.9×10^6 CFU/m^3, with a median concentration of 3.3×10^5 CFU/m^3. Rod–shaped bacteria levels ranged from ND to 4.3×10^6 CFU/m^3, median 8.1×10^4 CFU/m^3. Hydrogen sulfide levels were less than 1 ppm as full shift TWAs with peaks of 3, 12, and 45 ppm measured. An association between levels of total bacteria, rod–shaped bacteria, and symptoms such as tiredness and headache, during and after work was found. Endotoxin levels and levels of spherical bacteria were not significantly different in workers reporting headaches or tiredness as compared to workers not reporting these symptoms. No relationship was found between symptoms and average exposure to H_2S during a workshift.

Volatile Organic Compounds

VOC describes a large class of organic chemicals (i.e., containing carbon) that have sufficiently high vapor pressure to allow some of the compounds to exist in the gaseous state at room temperature. Toluene is an example of a VOC which was of concern in this HHE.

Toluene

Inhalation and skin absorption are the major occupational routes of entry for toluene. Toluene can cause acute irritation of the eyes, respiratory tract, and skin. Since it is a defatting solvent, repeated or prolonged skin contact will remove the natural lipids from the skin which can cause drying, fissuring, and dermatitis. The main effects reported with excessive inhalation exposure to toluene are central nervous system depression and neurotoxicity.[19] Studies have shown that subjects exposed to 100 ppm of toluene for six hours complained of eye and nose irritation, and in some cases, headache, dizziness, and a feeling of intoxication (narcosis).[20,21,22] No symptoms were noted below 100 ppm in these studies. The NIOSH REL for toluene is 100 ppm as a TWA for up to a 10–hour work day. NIOSH has also set a recommended 15–minute STEL of 150 ppm. The OSHA PEL for toluene is 200 ppm for an 8–hour TWA. The ACGIH TLV® is an 8–hour TWA of 50 ppm. This ACGIH TLV® carries a skin notation, indicating that cutaneous exposure contributes to the overall absorbed inhalation dose and potential systemic effects.

Benzene

Acute inhalation exposure to high concentrations of benzene can cause drowsiness, fatigue, nausea, vertigo, narcosis, and other symptoms of central nervous system (CNS) depression as noted with excessive exposure to other aromatic hydrocarbons.[3,19,23] However, the most remarkable health effects associated with benzene exposure are chronic effects due to repeated exposure to low concentrations over many years.[19]

Benzene is classified by the International Agency for Research on Cancer (IARC) as a known human carcinogen and has been associated with irreversible bone marrow injury and the development of hematopoietic toxicity, including aplastic anemia and leukemia in humans.[23,24] NIOSH classifies benzene as a human carcinogen, and recommends that occupational exposures be controlled to prevent employees from being exposed to concentrations greater than 0.1 ppm, determined as a TWA concentration for up to a 10-hour work shift in a 40-hour work week. NIOSH further recommends a 15-minute STEL of 1.0 ppm. Although NIOSH has established these guidelines which should not be exceeded, the Institute still urges that exposures be reduced to the "lowest feasible level" (LFL) because it is not possible to establish thresholds for carcinogens which will protect 100% of the population. The OSHA PEL is 1 ppm for an 8-hour TWA with a 15–minute STEL of 5 ppm. However, the PEL does not apply to "... storage, transportation, distribution, dispensing, sale, or use of gasoline, motor fuels, or other fuels containing benzene subsequent to its final discharge from bulk wholesale storage facilities, except operations where gasoline or motor fuels are dispensed for more than four hours per day in an indoor location..." The current ACGIH TLV® is 10 ppm as a suspected human carcinogen. ACGIH has proposed to lower the TLV® to 0.3 ppm and classify it as a confirmed human carcinogen.

1,1,1–Trichloroethane

1,1,1–Trichloroethane causes central nervous system depression. Based on animal studies the following effects are expected in humans: 20,000 ppm for 60–minutes, coma and possible death; 10,000 ppm for 30–minutes, marked incoordination; 2000 ppm for 5–minutes, disturbance of equilibrium. Human subjects exposed to 900 to 1000 ppm for 20–minutes experienced light–headedness, incoordination and impaired equilibrium and transient eye irritation. Textile workers exposed from several months to 6–years to 1,1,1–trichloroethane concentrations sometimes exceeding 200 ppm revealed no evidence of cardiovascular, hepatic, renal, or other effects as a function of exposure.[19,25]

The NIOSH REL for 1,1,1–trichloroethane is a 10–minute ceiling concentration of 350 ppm.[2] The OSHA PEL for 1,1,1–trichloroethane is an 8–hour TWA of 350 ppm.[4] The ACGIH TLV® for 1,1,1–trichloroethane is an 8–hour TWA of 350 ppm and a 15–minute STEL of 450 ppm.[3]

n–Hexane

n–Hexane is an upper respiratory irritant and causes central nervous system depression. Chronic exposure to n–hexane causes peripheral neuropathy. In human subjects, 2000 ppm for 10–minutes produced no effects, but 5000 ppm resulted in dizziness and confusion. Slight nausea, headache, and irritation of the eyes and throat have been reported at 1500 ppm. In industrial practice, mild symptoms of narcosis such as dizziness were observed when concentrations of solvents containing various isomers of hexane exceeded 1000 ppm, but were not seen below 500 ppm. Polyneuropathy has been reported following chronic occupational exposure to vapors containing n–hexane at concentrations typically in the 400 to 600 ppm range, with some ceiling exposure up to 2500 ppm.[19,26,27,28,29]

The NIOSH REL and the ACGIH TLV® for n–hexane is an 8–hour TWA of 50 ppm.[2,3] The OSHA PEL for n–hexane is an 8–hour TWA of 500 ppm.[4]

Results and Discussion

Four PBZ air samples were collected for H_2S using the Toxilog monitors. The monitors recorded the H_2S concentration once a minute throughout the shift. A summary of these data are shown in Table 1. The maximum H_2S air concentration measured on a worker was 2 ppm. This concentration was measured on an Operator I who was working on the press room floor. The other Operator I working on the press room floor had maximum H_2S concentrations of 1 ppm. Two Maintenance Mechanic workers were sampled for H_2S concentrations while they repaired a Schwing pump used to pump sludge from the belt presses to the incinerators. Their maximum H_2S concentrations were ND (<1 ppm) and 1 ppm. The maximum H_2S PBZ concentrations for the two operators and the two maintenance workers were all well below the NIOSH REL and the OSHA PEL.

Two general area air samples were collected for H_2S using the PhD monitors. The PhD monitors recorded the H_2S concentration once a minute throughout the work shift. A summary of these data are shown in Table 1. General area air samples were collected for H_2S on the floor level of the belt press room between G and I belt presses and on the platform level of the belt press room near G belt press. The maximum H_2S concentrations for these two general area air samples were both less than the limit of detection of 1 ppm.

Five PBZ air samples were collected and analyzed for total particulate and endotoxin. The results of these analyses are listed in Table 2. The total particulate and endotoxin PBZ air sample concentrations for the Operator I workers working on the press room floor were 0.12 and 0.07 milligrams per cubic meter (mg/m^3) and 9.44 and 10.9 endotoxin units per cubic meter (EU/m^3), respectively. The Operator II, operating the incinerator, total particulate and endotoxin PBZ air sample concentrations were ND (<0.02 mg/m^3) and ND (<0.56 EU/m^3), respectively. Two PBZ air samples for total particulate and endotoxin were collected on Maintenance Mechanics repairing the #2 Schwing pump. The Schwing pumps pneumatically pump sludge from the belt presses to the incinerator. The total particulate and endotoxin PBZ air sample concentrations for the mechanics were 0.08 and 0.14 mg/m^3 and 2.36 and 6.31 EU/m^3, respectively. All exposures to total particulates are considered very low. All the PBZ endotoxin air sample concentrations were well below 90 EU/m^3, calculated by Castellan to be the zero pulmonary function effects level.[15]

Four bulk samples were analyzed for VOCs by sampling the headspace air above the sample vials. The results of these analyses are shown in Table 3. The bulk samples were collected from waste activated sewage sludge from the #2 Schwing pump inlet and outlet that was under repair, waste activated sludge from the G belt press, and wastewater brought to the plant for treatment. Peaks were considered major if their heights were greater than one half of full scale and minor if the chromatograph peak heights were less than one half of full scale. Major VOCs identified in the headspace air above the sludge sample collected from the inlet to the #2 Schwing pump were isopropanol, dimethyl sulfide, dimethyl disulfide, and toluene. Twenty–seven minor VOCs were identified in the inlet sludge headspace. Major VOCs found in the sludge from the outlet of the #2 Schwing pump included acetone, toluene, butanoic acid, 3–methyl butanoic acid, pentanoic acid, alkyl benzenes, n–nonane, n–decane, limonene, n–undecane, cresol, n–dodecane, and n–tridecane. Twenty minor VOCs were identified in the outlet sludge sample. Major VOCs identified in the headspace of the sludge sample collected from the G belt press included isopropanol, dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, cresol, and indole. Twenty–eight minor VOCs were identified in the sludge sample collected from the G belt press. The major VOCs identified in the headspace air above the wastewater sample from Mallinckrodt were dimethyl sulfide, 3–methyl–1–butanol, 1,1,1–trichloroethane, dimethyl sulfoxide (DMSO), and n,n–dimethylacetamide (DMAC). Twenty–five minor VOCs were identified in the wastewater sample. The wastewater sample was also analyzed quantitatively for DMSO and DMAC. The wastewater samples contained 4.80% DMSO and 6.60% DMAC. The material safety data sheet (MSDS) (provided to NIOSH by the Metropolitan St. Louis Sewer District) specifications for the wastewater were 6% or less for DMSO and 4% or less for DMAC. The concentration of DMAC measured in this sample exceeded the MSDS specification, and the concentration of DMSO in the sample was under the MSDS specifications.

Five general area air samples were collected and analyzed qualitatively for VOCs and are shown in Table 4. The general area air samples were collected outside near an aeration tank receiving the transported wastewater, near repairs being made to #2 Schwing pump, near the G belt press on the platform level of the press room, between the G and I belt presses on the floor level of the press room, and in the grit building near #1 shot. As was the case with the bulk sample analyses for VOCs, peaks were considered major if their heights were greater than one half of full scale, and minor if their heights were equal to or less than one half of full scale. The VOCs identified, all minor, in the general area air sample collected outside near the aeration tank were chloroform, toluene, xylene, and alkyl benzenes. The major VOCs identified in the general area air sample collected near the repair operation on #2 Schwing pump were n–hexane and C_7H_{14}/C_7H_{14} aliphatics. Thirteen minor VOCs were identified in the sample collected near the #2 Schwing pump repairs. The general area air samples collected in the belt press room platform level near the G belt press had four major compounds which were chloroform, dimethyl disulfide, toluene, and alkyl benzenes. Thirteen minor VOCs were identified in the sample collected near the G belt press on the platform level of the press room. One major compound was identified in the sample collected on the floor level of the press room between the G and I belt presses and it was toluene. Fourteen minor VOCs were identified in the general area air sample collected between the G and I belt presses on the floor level of the press room. The general area air sample collected in the grit building near #1 shot had a major VOC of toluene and eleven minor VOCs.

Five general area air samples were collected and analyzed quantitatively for 1,1,1–trichloroethane, benzene, toluene, n–hexane, dimethyl sulfide, limonene, and total hydrocarbons. These results are listed in Table 5. The quantitative general area air samples were collected in the same areas as were the qualitative general area air samples previously reported and shown in Table 4. A trace concentration between 0.002 and 0.006 ppm of 1,1,1–trichloroethane was measured in the general area air sample located in the grit building near #1 shot. A trace concentration between 0.003 and 0.011 ppm of benzene was measured in the general area air sample collected near the G belt press on the platform level in the press room. The general area air samples collected near #2 Schwing pump repair operations, near the G belt press on the platform level in the press room, between the G and I belt presses on the floor level in the press room, and in the grit building near #1 shot had toluene concentrations of trace (between 0.003 and 0.006 ppm), 0.059, 0.012, and 0.011 ppm, respectively. The general area air samples located near #2 Schwing pump repair operations, near the G belt press on the platform level in the press room, and between the G and I belt presses on the floor level in the press room had 0.024 ppm, trace (between 0.003 and 0.010 ppm), and trace concentrations, respectively, of n–hexane.

A trace concentration between 0.009 and 0.030 ppm of dimethyl disulfide was measured in the general area air sample collected near G belt press on the platform level in the press room. Trace concentrations between 0.004 and 0.008 ppm of limonene were measured in the general area air samples collected near the G belt press on the platform level in the press room and in the grit building near #1 shot.

Bulk samples of sludge from #2 Schwing pump inlet, #2 Schwing pump outlet, and the G belt press, and incinerator ash from under #3 incinerator were collected and analyzed for elemental composition. The results of these elemental analyses are listed in Table 6. The bulk samples contained Al, As, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Na, P, Pb, Sr, Ti, and Zn. In addition the ash bulk sample contained La, Mo, and Ni. The five most abundant elements measured in the sludge sample collected from #2 Schwing pump inlet were: Fe, 4950 µg/g; P, 3880 µg/g; Ca, 2930 µg/g; Al, 1790 µg/g; and Na, 785 µg/g. The #2 Schwing pump outlet sludge sample five most abundant elements were: Ca, 20400 µg/g; Fe, 5020 µg/g; P, 2730 µg/g; Al, 1740 µg/g; and Mg, 1110 µg/g. The five most abundant elements found in the sludge sample collected from the G belt press were: Fe, 34000 µg/g; P, 29900 µg/g; Ca, 20900 µg/g; Al, 11200 µg/g; and Na, 6700 µg/g. The five most abundant elements present in the ash sample were: Fe, 56340 µg/g; P, 31400 µg/g; Ca, 29700 µg/g; Al, 15800 µg/g; and Mg, 7510 µg/g. The incinerator ash sample was also analyzed for free crystalline silica and found to have 4.38 % silica.

The belt press room operators at the Bissell Point plant starting in September 1994 began to routinely measure and record the H_2S concentrations around the belt presses and gravity belt thickeners. H_2S measurements made from September 20, 1994, through August 31, 1995, were obtained from the Bissell Point plant. These data were summarized into the following six groups: (1) presses A, C, D, E, and F platform level; (2) presses A, C, D, E, and F floor level; (3) presses G, I, J, K, and L platform level; (4) presses G, I, J, K, and L floor level; (5) presses M, O, P, Q, and R platform level; and (6) presses M, O, P, Q, and R floor level. For the purpose of demonstrating seasonal H_2S concentration patterns, H_2S concentration data were plotted *vs* sample dates for the six summary groups and are illustrated in Figures 1 through 6, respectively. In each of these figures, H_2S concentrations exceeding 10 ppm were measured during the months of July and August 1995. In Figures 2 and 4, H_2S concentrations exceeding 10 ppm were also measured in September 1994 and during March 1995.

On September 15 and 21, 1993, emission tests were conducted at the Bissell Point to determine where and at what rate VOCs and hazardous air pollutants (HAP) are emitted from the plant. The following 27 VOC/HAP compounds were measured: acetone, benzene, carbon disulfide, carbonyl sulfide, chlorobenzene, chloroform, dichlorobenzene, dimethyl sulfide, ethanol, ethyl methyl benzene, ethyl benzene, H_2S, isobutyl mercaptan, isopropanol, methyl ethyl ketone, methyl mercaptan, 3–methyl thiophene, methylene chloride, styrene, tetrachloroethylene, tetrahydrofuran, thiophene, toluene, trichloroethane, trichlorofluromethane, trimethylbenzene, and xylenes. H_2S emission rates were determined to be the highest concentrations of any the compounds emitted from the plant. VOC/HAP emission rate subtotals by treatment process steps are as follows: trickling filters (50%), incinerators (13%), grit tanks (11%), preaeration and influent channel (9%), primary settling tanks (5%), belt press room ventilation (4%), aeration basins (4%), final settling tanks (2%), thickener room ventilation (1%), and sludge well ventilation (1%).

Conclusion

All PBZ and general area air sample results for H_2S were below the NIOSH REL and OSHA PEL ceiling exposure limits. Past H_2S air concentrations measured around the belt presses exceeded both the NIOSH REL and OSHA PEL ceiling limits and have been measured as high as 182 ppm. The H_2S concentration data from 1994 through 1995 shown in Figures 1 through 6 showed that the highest H_2S concentrations occurred during July, August, and September. These data include a potential for overexposure to H_2S. The health problems expressed by the workers have all been previously associated with H_2S overexposure.[5]

Quantitative VOC results ranged from ND to 0.06 ppm in the general area air samples. Detectable concentrations of toluene and n–hexane were measured in these samples, however all measured VOC concentrations were quite low. The qualitative results for all the general area air samples analyzed for VOCs detected were acetone, benzene, chloroform, dichlorobenzene, ethyl methyl benzene, ethyl benzene, tetrachloroethylene, toluene, trichloroethane, and xylenes which were also measured in the emission tests conducted September 15 and 21, 1993. The headspace air samples collected from the sludge and wastewater bulk samples had detectable concentrations of acetone, benzene, carbon disulfide, dichlorobenzene, dimethyl sulfide, ethanol, ethyl, methyl benzene, ethyl benzene, isopropanol, methyl ethyl ketone, methyl mercaptan, methylene chloride, toluene, trichloroethane, trimethylbenzene, and xylenes which were also measured in the emission test measurements made in September 1993. Eleven of the VOCs detected by both the general area air samples and/or headspace air from the bulk samples and the contractor's emission tests have occupational guidelines and standards. Based on these set of VOC data, none of the 11 VOCs with occupational guidelines were measured at concentrations that present a health hazard. While the levels of these VOCs measured were low, these VOCs were present on at least two separate occasions.

No air samples were collected and analyzed for metals. However, incinerator ash was observed to be accumulating under the incinerators and dispersed through out the lower levels of the incinerator portion of the solids handling building. The ash accumulating under the incinerators was the result of back draft air blowing ashes out the bottom of the incinerators. The back drafting can occur from once a week to two or three times per day. Bulk samples of the ash were analyzed and shown to contain 12 metals for which limits of exposure have been established. Thus, the potential exists for exposure to these metals, if the ash were to become airborne.

Recommendations

1. Employees working in areas where H_2S air concentrations are 5 ppm (one half of the NIOSH ceiling REL) or higher should wear continuous direct–reading monitors so that they can be aware of the H_2S concentration at all times. These monitors should be maintained and calibrated according to manufacturers specifications. Daily H_2S measurements should be continued to be made to assure that H_2S levels remain below 10 ppm.

2. Respirators are the least preferred method for protecting workers from respiratory hazards. Respirators can be unreliable if an adequate respiratory protection program is not established by the employer, and they require worker cooperation. Respirators are recommended when exposure to H_2S concentrations exceed recommended ceiling limits (10 ppm) and engineering controls are not technically feasible, or while controls are being installed or repaired, or when emergency or other temporary situations arise. If H_2S concentrations are 100 ppm or less, one of the following types of respirators maybe used: (1) powered air–purifying respirator (PAPR); (2) air–purifying, full–face respirator with a chin–style, front– or back–mounted canister providing protection against H_2S; (3) supplied–air respirator with eye protection; or (4) self–contained breathing apparatus with a full facepiece. For H_2S concentrations greater than 100 ppm the following types of respirators are required: (1) self–contained breathing apparatus with a full facepiece and pressure demand or other positive pressure mode or (2) supplied–air respirator with a full facepiece and is operated in a pressure demand or other positive–pressure mode in combination with a auxiliary self–contained breathing apparatus operated in pressure–demand or other positive pressure mode. Respirators may also be used for operations that require entry into tanks or closed vessels, and in emergency situations. All respirators selected must be approved by NIOSH and Mine Safety and Health Administration (MSHA) under provision of 30 CFR 11.[28] The current list of NIOSH/MSHA certified respirators can be found in the NIOSH Certified Equipment List.[31] A complete respiratory protection program must be implemented and must fulfill all requirements of 29 CFR 1910.134.[32] At a minimum, a respiratory protection program should include regular training, fit–testing, periodic environmental monitoring, maintenance, inspection, cleaning, and storage. Selection of a specific respirator within a given class of recommended respirators depends on the particular situation; this choice should be made by a knowledgeable person. Additional information on the selection and use of respirators can be found in the NIOSH Guide to Industrial Respiratory Protection.[33,34]

3. In the recommended standard for occupational exposure to H_2S, NIOSH recommends that preplacement and periodic examinations (once every three years) be made available to all workers occupationally exposed to H_2S. The following medical procedures should be made available to each employee who is exposed to H_2S at potentially hazardous levels:

    a. *Initial Medical Examination*

A complete history and physical examination to detect pre–existing conditions that might place the exposed employee at increased risk, and to establish baseline for future health monitoring. Examination of the eyes and lungs should be stressed. Hydrogen sulfide is a severe irritant and may cause tissue damage. Those with pre–existing eye problems may be at increased risk from exposure. Hydrogen sulfide may cause human lung damage. Surveillance of the lungs by chest x–ray is indicated. Forced vital capacity (FVC) and force expiratory volume in one second (FEV_1) lung function test should be performed as part of the examination.

b. *Periodic Medical Examination*

The aforementioned medical examination should be repeated once every three years, except that an x–ray is considered necessary only when indicated by results of pulmonary function testing, or by signs and symptoms of respiratory disease.

4. PBZ air samples should be collected by the Metropolitan St. Louis Sewer District and analyzed for metals (those found in the incinerator ash) to determine if the workers are exposed to metals and to what extent. Workers involved in operations, repairs, or cleanup in the incinerator areas where the ash is present should be monitored.

References

1. NIOSH [1994]. NIOSH Manual of Analytical Method. 4th. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health., DDHS (NIOSH) Publication No. 94–113.

2. NIOSH [1992]. Recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92–100.

3. ACGIH [1995]. 1995–1996 threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienist.

4. Code of Federal Regulations [1993]. 29CFR 1910.1000. Washington, DC: U.S. Governmental Printing Office, Federal Register.

5. NIOSH [1977]. Criteria for a Recommended Standard. Occupational Exposure to Hydrogen Sulfide. DHEW (NIOSH) Publication No. 77–158. Washington, DC: U.S. Governmental Printing Office.

6. Beauchamp RO Jr, et al. [1984]. A critical review of the literature on hydrogen sulfide toxicity. CRC Crit Rev Toxicol 13:25–97.

7. Glass DC [1990]. A review of the health effects of hydrogen sulfide exposure. Ann Occup Hyg 34(3):323–327.

8. Schecter MT, Spitzer WO, Hutcheon ME [1989]. Cancer downwind from sour gas refineries: The perception and the reality of an epidemic. Environ Health Perspect 79:283–290.

9. Bhamhani Y, Burnham R, Snydmiller G, MacLean I, Martin T [1994]. Comparative physiological responses of exercising men and women to 5 ppm hydrogen sulfide exposure. Am Ind Hyg Assoc J 55(11): 1030–1035.

10. Hagmar L, Schütz A, Hallberg T, Sjöholm A [1990]. Health effects of exposure to endotoxin and organic dust in poultry slaughter–house workers. Int Arch Occup Environ Health 62:159–164.

11. Rylander R [1987]. The role of endotoxin for reactions after exposure to cotton dust. Am J Ind Med 12:687–697.

12. Jacobs RR [1989]. Airborne endotoxin: an association with occupational lung disease. Appl Occup Environ Health 4:50–56.

13. Olenchock SA [1985]. Endotoxin in occupationally related airborne dust. Govern Lab 1:28–30.

14. Rylander R [1994]. Organic dusts – from knowledge to prevention. Scand J Work Environ Health 20(special issue):116–122.

15. Castellan RM, Olenchock SA, Kinsley KB, Hankinson JL [1987]. Inhalation endotoxin and decreased spirometric values. N Engl J Med 317(10):605–610.

16. Laitinen S, Necalainen A, Kotimaa M, Liesivuori J, Martikainen PJ [1992]. Relationship between bacteria counts and endotoxin concentrations in the air of wastewater treatment plants. Appl Environ Microbiology 58(11): 3774–3776.

17. Laitinen S, Kangas J, Kotimaa M, Liesivuori J, Martikainen PJ, Nevalainen A, Saranitila R, Husman K [1994]. Workers' exposure to airborne bacteria and endotoxin in industrial wastewater treatment plants. Am Ind Hyg Assoc J 55(11): 1055–1060.

18. Melbostad E, Wijnand E, Skogastad A, Sandven P, Lassen J, Sostrand P, Heldal K [1994]. Exposure to bacteria aerosol and work–related symptoms in sewage workers. Am J Ind Med 25: 59–63.

19. Hathaway GJ, Proctor NH, Hughes JP, Fischman MJ [1991]. Proctor and Hughes' Chemical Hazards of the Workplace. 3rd. ed. New York, NY: Van Nostrand Reinhold.

20. WHO [1981]. Recommended health–based limits in occupational exposure to select organic solvents. Geneva: World Health Organization, Technical Report Series No. 664.

21. Benignus VA [1981]. Health effects of toluene. a review. Neurotoxicology 2:567–568.

22. Anderson I, et al. [1983]. Human response to controlled levels of toluene in six–hour exposures. Scand J Work Environ Health 9:405–418.

23. WHO [1989]. IARC monographs on the evaluation of carcinogenic risks to humans: occupational exposures to the petroleum refining; crude oil and major petroleum fuels. World Health Organization *45*: 159–201. 1–8 March 1988.

24. DHHS [1991]. Sixth annual report on carcinogens: summary 1991. Research Triangle Park, NC: U.S. Department of Health and Human Services, Public Health Service, National Institute for Environmental Health Sciences, pp 357–364.

25. Kramer C, et al. [1978]. Health of workers exposed to 1,1,1–trichloroethane: a match–pair study. Arch Environ Health 33: 331–342.

26. Elkins HB [1959]. Chemistry of industrial toxiciology. New York, John Wiley and Sons. p 101.

27. NIOSH [1977]. Recommendation standard: occupational exposure to alkanes, (C_5–C_8). Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77–151

28. Jorgensen NK [1981]. n–Hexane and its toxicological effects. Scand J Work Environ Health 7: 157–168.

29. Spencer PS, et al. [1980]. The enlarging view of hexacarbon and neurotoxicity. CRC Crit Rev Toxicol 7: 279–356.

30. Code of Federal Regulations [1994]. Respiratory protection certification. 30 CFR 11.

31. NIOSH [1994]. NIOSH certified equipment list. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS(NIOSH) Publication No. 94–104.

32. Code of Federal Regulations [1994]. Respiratory protection program. 29 CFR 1910.134.

33. NIOSH [1987]. NIOSH respiratory decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No.87–108.

34. NIOSH [1987]. NIOSH guide to industrial respiratory protection. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87–116.

Authorship and Acknowledgments

Report Prepared By:	David A. Marlow, B.S. Industrial Hygienist Industrial Hygiene Section
Field Equipment Support:	Larry DeArmond Mike King
Analytical Support:	*NIOSH* Ardith A. Grote (qualitative analyses of air samples and bulk sewage sludge samples for volatile organic compounds) Mark B. Millson (quantitative analyses bulk sewage sludge and incinerator ash for metals and silica)

	Stephanie M. Pendergrass (quantitative analyses of bulk wastewater for DMSO & DMAC)
	Data Chem Laboratories Steve Olencheck and Mark Whitmer (quantitative analyses of air samples for endotoxin)
	Robert L. Quigley (quantitative analyses of air samples for total particulate, respirable particulate, quartz, and cristobalite)
	Amy Jo Portlock (quantitative analyses of air samples for selected volatile organic compounds)
Reported Formatted By:	Caren B. Day Office Automation Assistant Industrial Hygiene Section
Originating Office:	Hazard Evaluations and Technical Assistance Branch Division of Surveillance, Hazard Evaluations, and Field Studies

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Copies of this report have been sent to:

1. Director of Wastewater, Metropolitan St. Louis Sewer District.
2. Assistant Director of Wastewater, Metropolitan St. Louis Sewer District, Bissell Point Treatment Plant.
3. Business Manager, International Brotherhood of Electrical Workers, Local No. 1.
4. Employee Representative, Service Employees International Union, Local 50.
5. OSHA Region, VII

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 days.

Table 1

Personal Breathing Zone and General Area Air Sample Results for Hydrogen Sulfide
Metropolitan St. Louis Sewer District
Bissell Point Treatment Plant
St. Louis, Missouri
HETA 95–0044
November 23, 1994

Job Title	Sample Location	Sampling Duration (min.)	Max. 10–min. H_2S Conc. (ppm)	Mean 10–min. H_2S Conc. (ppm)	H_2S TWA Conc. (ppm)	Max. H_2S Conc. (ppm)
Operator I	Press room	450	0.7	0.06	0.06	1
Operator I	Press room	425	0.8	0.07	0.07	2
Maintenance Mechanic	Repairs on #2 Schwing pump	441	ND	ND	ND	ND
Maintenance Mechanic	Repairs on #2 Schwing pump	446	0.1	0.002	0.002	1
General area	Floor level between G & I belt presses in press room	418	ND	ND	ND	ND
General area	Platform level near G belt press in press room	374	ND	ND	ND	ND

H_2S = hydrogen sulfide
ppm = parts per million
limit of detection = 1 ppm
TWA = time–weighted average
ND = non–detectable, less than the limit of detection
STEL = short term exposure limit
NIOSH H_2S REL = 10 ppm ceiling (10–min.)
OSHA H_2S PEL = 20 ppm ceiling (10–min.); 50 ppm (10–minute maximum peak) once, only if no other meas. exp. occurs
ACGIH H_2S TLV® = 10 ppm TWA; 15 ppm STEL (15–min.)

Table 2

Personal Breathing Zone Air Sample Results for Total Particulate and Endotoxin
Metropolitan St. Louis Sewer District
Bissell Point Treatment Plant
St. Louis, Missouri
HETA 95–0044
November 23, 1994

Job Title	Job Location	Sampling Duration (min.)	Total Particulate Conc. (mg/m^3)	Endotoxin Conc. (EU/m^3)
Operator I	Press room	450	0.12	9.44
Operator I	Press room	425	0.07	10.9
Operator II	Incinerator control room	444	ND	ND
Maintenance Mechanic	Repair #2 Schwing pump	445	0.08	2.36
Maintenance Mechanic	Repair #2 Schwing pump	441	0.14	6.31

mg/m^3 = milligrams per cubic meter
EU/m^3 = endotoxin unit per cubic meter
1 EU = 0.1 nanogram of lipopolysaccharide–protein complexes, EC–5
ND = non–detectable, less than the minimum detectable concentration
The minimum detectable concentration for total particulate = 0.02 mg/m^3
The minimum detectable concentration for endotoxin = 0.56 EU/m^3
No occupational exposure criteria have established for bacterial endotoxin by either NIOSH, OSHA, or ACGIH.
Castellan et al.[15] calculated a zero pulmonary function effects level for endotoxin to be 90 EU/m^3.

Table 3

Identification of Headspace Volatile Organic Compounds in Bulk Samples Collected at the Treatment Plant
Metropolitan St. Louis Sewer District
Bissell Point Treatment Plant
St. Louis, Missouri
HETA 94–0044
November 23, 1994

Sample	Headspace Volatile Organic Compounds Present
Sludge from inlet #2 Schwing pump	7,8,9,11,**12**,**14**,17,18,20,21,24,25,27,28,30,**36**,38,**43**,45,46,47,48,51,54,55,57,60,62,63,64,66,68,76
Sludge from inlet #2 Schwing pump	5,6,8,9,**11**,12,13,14,16,17,18,20,21,22,25,36,38,**43**,44,**46**,**47**,48,**51**,**55**,**57**,**60**,**63**,**64**,**66**,**70**,**73**,74,75
Wastewater from Mallinkrodt	3,6,7,8,9,10,11,12,**14**,17,18,20,21,23,24,26,27,32,33,**34**,35,36,**37**,**39**,40,**41**,42,47,54,65,72
Sludge from G belt press	3,5,6,7,8,9,11,**12**,**14**,17,18,20,21,23,24,25,27,34,**36**,38,43,46,47,48,51,**54**,56,62,63,**66**,67,68,71,**76**,77

3 = formaldehyde
5 = propane/dichlorordifluoromethane
6 = methanol/isobutane
7 = methanethiol (mercaptomethane)
8 = trimethylamine
9 = ethanol
10 = acetonitrile
11 = acetone
12 = isopropanol
13 = cyclopropane
14 = dimethyl sulfide
15 = 1,1-dichloroethylene (vinylidene chloride)
16 = methylene chloride
17 = carbon disulfide
18 = 1-propanol
19 = 1,2-dichloroethylene
20 = methyl ethyl ketone
21 = acetic acid
22 = n-hexane
23 = 2-butanol
24 = 2-methyl-1- propanol
25 = propanoic acid
26 = pentanal
27 = benzene/butanol
28 = propyl acetate
29 = 2-pentanone
30 = methylthioacetate
31 = 2-pentanol
32 = trimethylethanediamine
33 = (dimethylamino) acetontrile
34 = 3-methyl-1-butanol
35 = 2-methyl-1-butanol
36 = dimethyl disulfide
37 = 1,1,1-trichloroethane
38 = 2-methylpropanoic acid
39 = dimethylsulfoxide (DMSO)
40 = n-methylacetamide
41 = n,n-dimethylacetamide (DMAC)
42 = sulfonylbismethane
43 = toluene
44 = C_8H_{18}/C_8H_{16} aliphatics
45 = methylpropane thioate, C_4H_8OS
46 = butanoic acid
47 = 3-methylbutanoic acid
48 = 2-methyl butanoic acid
49 = xylene/ethyl benzene isomers
51 = pentanoic acid
52 = methyl heptanone
53 = 4-methylpentanoic acid
54 = dimethyl trisulfide
55 = C_9-C_{12} aliphatics/C_9H_{12}-$C_{10}H_{14}$ alkyl benzenes
56 = C_9H_{12} alkyl benzene
57 = n-nonane
58 = methyl heptanone
59 = phenol
60 = n-decane
61 = dichlorobenzene isomer
62 = $C_{10}H_{14}$, p-cymene
63 = limonene
64 = n-undecane
65 = 2-ethyl-1-hexanol
66 = cresol isomer
67 = dimethyl styrene
68 = 2-piperidenone
69 = naphthalene
70 = n-dodecane
71 = dimethyl tetrasulfide
72 = benzothiazole
73 = n-tridecane
74 = n-tetradecane
75 = n-pentadecane
76 = indole, C_8H_7N
77 = methyl indole isomer

Bold values indicate compound peaks which were higher than half of full scale.

Table 4

Identification of Volatile Organic Compounds in Area Air Samples
Metropolitan St. Louis Sewer District
Bissell Point Treatment Plant
St. Louis, Missouri
HETA 95-0044
November 23, 1994

Sample Location	Volatile Organic Compounds Present
Outside near an aeration tank	4,11,14,17
Near repairs to #2 Schwing pump	2,5,**6**,**7**,11,12,13,14,15,16,17,18,20,22,24
Near G belt press on platform level in press room	2,**4**,9,**10**,**11**,13,14,15,16,**17**,18,19,20,22,23,24,25
Between G & I belt presses on the floor level in press room	4,8,9,10,**11**,13,14,15,16,17,20,22,23,24,25
In grit building near #1 shot	2,4,**11**,12,13,14,15,17,20,22,23,24

2 = ethanol
3 = acetone
4 = chloroform
5 = C_6H_{14}/C_6H_{12} aliphatics
6 = n-hexane
7 = C_7H_{16}/C_7H_{14} aliphatics
8 = 1,1,1-trichloroethane
9 = benzene
10 = dimethyl disulfide
11 = toluene
12 = octane
13 = perchloroethylene
14 = xylene/ethyl benzene isomers
15 = n-nonane
16 = pinenes/C_9H_{16} terpenes
17 = C_9H_{12} alkyl benzenes
18 = C_9-C_{12} aliphatics, C_9H_{12}-$C_{10}H_{14}$ alkyl benzenes
19 = dimethyl trisulfide
20 = n-decane
21 = dichlorobenzene
22 = p-cymene
23 = limonene
24 = n-undecane
25 = n-dodecane

Bold values indicate compound peaks which were higher than half of full scale.

Table 5
General Area Air Sample Results for Selected Volatile Organic Compounds
Metropolitan St. Louis Sewer District, Bissell Point Treatment Plant
St. Louis, Missouri
HETA 95-0044
November 23, 1994

Sample Location	Sample Time (min.)	1 Conc. (ppm)	2 Conc. (ppm)	3 Conc. (ppm)	4 Conc. (ppm)	5 Conc. (ppm)	6 Conc. (ppm)	7 Conc. (ppm)
Near #2 Schwing pump repairs	422	ND	ND	trace	0.024	ND	ND	ND
Near G belt press platform level	411	ND	trace	0.059	trace	trace	trace	ND
Between G & I belt presses floor level	412	ND	ND	0.012	trace	ND	ND	ND
In grit building near #1 shot	439	trace	ND	0.011	ND	ND	trace	ND
Outside near an aeration tank	437	ND	ND	ND	ND	ND	ND	ND

	MDC	MQC	NIOSH REL	OSHA PEL	ACGIH TLV®
1 = 1,1,1-trichloroethane	0.002	0.006	350 ppm ceiling (15–min.)	350 ppm TWA	350 ppm TWA
2 = benzene	0.003	0.011	LFC	1 ppm TWA	10 ppm TWA
3 = toluene	0.003	0.009	100 ppm TWA	200 ppm TWA	50 ppm TWA
4 = n-hexane	0.003	0.010	50 ppm TWA	500 ppm TWA	50 ppm TWA
5 = dimethyl disulfide	0.009	0.030	NA	NA	NA
6 = limonene	0.004	0.008	NA	NA	NA
7 = total hydrocarbons	0.090	0.299	NA	NA	NA

ppm = parts per million
NA = not applicable, no standards or guidelines available
trace = concentration between MDC and MQC
REL = recommended exposure level
PEL = permissible exposure limit
TLV® = threshold limit value
MDC = minimum detectable concentration, assuming an air sample volume of 96 liters
MQC = minimum quantifiable concentration, assuming an air sample volume of 96 liters
ACGIH = American Conference of Governmental Industrial Hygienists
TWA = time-weighted average
ND = non-detectable concentration, less than MDC
NIOSH = National Institute for Occupational Safety and Health
OSHA = Occupational Safety and Health Administration
LFC = lowest feasible concentration

Table 6

Elemental Analyses of Bulk Samples Collected from the Wastewater Treatment Process
Metropolitan St. Louis Sewer District
Bissell Point Treatment Plant
St. Louis, Missouri
HETA 95-0044
November 23, 1994

Analyte (µg/g)	Sample Description			
	Sludge from #2 Schwing pump inlet	Sludge from #2 Schwing pump outlet	Sludge from G belt press	Ash under #3 incinerator
Aluminum (Al)	1790	1740	11200	15800
Arsenic (As)	13.3	ND	97.4	63.9
Barium (Ba)	34.8	394	261	340
Calcium (Ca)	2930	20400	20900	29700
Chromium (Cr)	87.1	68.5	549	245
Copper (Cu)	54.2	134	394	436
Iron (Fe)	4950	5020	34000	56400
Lanthanum (La)	ND	ND	ND	36.6
Magnesium (Mg)	760	1110	5440	7510
Manganese (Mn)	137	143	1030	815
Molybdenum (Mo)	ND	ND	ND	76.4
Sodium (Na)	785	411	6700	7060
Nickel (Ni)	ND	ND	ND	111
Phosphorus (P)	3880	2730	29900	31400
Lead (Pb)	23.6	61.5	140	187
Strontium (Sr)	22.4	33.0	160	209
Titanium (Ti)	46.7	22.8	220	725
Zinc (Zn)	168	468	1160	1280
Limit of Detection	11.6	19.0	72.3	24.2
Silica (Si) (%)				4.38

µg/g = micrograms of analyte per gram of sample

ND = non-detectable, less than the limit of detection