This Health Hazard Evaluation (HHE) report and any recommendations made herein are for the specific facility evaluated and may not be universally applicable. Any recommendations made are not to be considered as final statements of NIOSH policy or of any agency or individual involved. Additional HHE reports are available at http://www.cdc.gov/niosh/hhe/reports

HETA 94-0405-2551 METROPOLITAN ST. LOUIS SEWER DISTRICT LEMAY 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.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 94-0405-2551 JANUARY 1996 METROPOLITAN ST. LOUIS SEWER DISTRICT LEMAY WASTEWATER TREATMENT PLANT ST. LOUIS, MISSOURI

NIOSH INVESTIGATORS: DAVID A. MARLOW, B.S.

SUMMARY

On September 16, 1994, the National Institute for Occupational Safety and Health (**NIOSH**) received requests from employer and employee reprentatives to conduct a health hazard evaluation (**HHE**) at the Metropolitan St. Louis Sewer District Lemay wastewater treatment plant in St. Louis, Missouri. The employees reported health problems including periodic headaches, burning sensation in the nose, loss of breath, sore throat, eye irritation, nausea, and diarrhea. In response to this request, a site visit and industrial hygiene survey was conducted at the sewage treatment plant on November 21 and 22, 1994.

Personal breathing zone (**PBZ**) and general area air samples were collected for hydrogen sulfide (**H**₂**S**) using continuous H₂S monitors. The maximum H₂S PBZ air sample concentrations ranged from non-detectable (**ND**) (less than 1 part per million) to 20 parts per million (**ppm**). The maximum H₂S PBZ air sample for a maintenance mechanic was 20 ppm. This concentration exceeds the NIOSH ceiling recommended exposure limit (**REL**) of 10 ppm, and is at the Occupational Safety and Health Administration (**OSHA**) ceiling permissible exposure limit (**PEL**) of 20 ppm. All other PBZ air sample results for H₂S were below the NIOSH REL and OSHA PEL ceiling values. All general area air sample results for H₂S were <1.0 ppm.

PBZ air sample results for endotoxin ranged from 1.08 to 5.51 endotoxin units per cubic meter of air (**EU/m³**). While no evaluation criteria have been established for endotoxin, the levels detected were all below the calculated zero pulmonary function effects level for endotoxin of 90 EU/m³ reported by Castellan.

Bulk samples of waste activated sewage sludge, grit, and wastewater brought to the plant for treatment were collected and analyzed qualitatively for headspace volatile organic compounds (VOCs). Major VOCs identified in the sewage sludge sample included acetone, isopropanol, dimethyl sulfide, methyl ethyl ketone, 2-butanol, dimethyl disulfide, dimethyl trisulfide, cresol isomer, and indole. Thirty other VOCs were identified in the sludge headspace sample. Major VOCs identified in the wastewater headspace air sample included dimethyl sulfide, 3-methyl-1-butanol, 1,1,1-trichloroethane, dimethyl sulfoxide, and n,n-dimethylacetamide. Twenty-seven other VOCs were identified in the wastewater sample. Cresol isomer was the major substance identified in the grit sample which had 17 other VOCs.

General area air samples analyzed qualitatively for VOCs had major compounds including 1,1,1-trichloroethane, toluene, and limonene. General area air samples were analyzed quantitatively for 1,1,1-trichloroethane, benzene, toluene, n-hexane, dimethyl disulfide, limonene, and total hydrocarbons based on the qualitative area air sample results. General area air sample results for 1,1,1-trichloroethane, toluene, n-hexane, and limonene ranged from ND (<0.002 ppm) to 0.04 ppm. All general area air sample results for individual VOCs were below respective occupational exposure limits, where applicable. General area air sample results for benzene, dimethyl disulfide, and total hydrocarbons were all ND.

Bulk samples of waste activated sewage sludge, grit, and incinerator ash were analyzed for elemental composition. Detectable concentrations of 20 different elements were found in these bulk samples. Concentrations of the elements were highest in the incinerator ash samples when compared to the sludge and grit bulk samples. The eight most abundant elements present in the sludge and ash samples were calcium (Ca), phosphorous (P), aluminum (Al), iron (Fe), magnesium (Mg), sodium (Na), manganese (Mn), and zinc (Zn). The eight most abundant elements present in the grit sample were Ca, Fe, P, Mg, Al, Na, lead (Pb), and Mn. The incinerator ash sample was also analyzed for free crystalline silica content and contained 2.54% silica, of which none was crystalline.

One worker's maximum H_2S concentration exceeded the NIOSH REL ceiling value of 10 ppm and was at the OSHA PEL ceiling value of 20 ppm. All the other PBZ air sample results for H_2S were below these exposure limits. Daily monitoring for H_2S should continue due to seasonal variations in H_2S concentrations. Historical records indicate that during the summer months H_2S concentrations approach 10 ppm on the press room floor where operators regularly work. Recommendations are made in the report regarding the use of personal H_2S monitors and respiratory protection when H_2S concentrations approach or exceed 10 ppm.

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

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INTRODUCTION

On September 16, 1994, the National Institute for Occupational Safety and Health (**NIOSH**) received requests from employer and employee representatives to conduct a health hazard evaluation (**HHE**) at the Metropolitan St. Louis Sewer District Lemay wastewater treatment plant in St. Louis, Missouri. The employees reported health problems including periodic headaches, burning sensation in the nose, loss 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 22, 1994.

BACKGROUND AND PROCESS DESCRIPTION

The Lemay treatment plant is located adjacent to the Mississippi River just south of River des Peres and receives wastewater from the southern and western parts of the city of St. Louis, and portions of St. Louis County. The treatment plant began operation in 1968 with primary clarification, and in 1985, secondary clarification was added. Currently, the treatment plant receives an average of 115 million gallons of wastewater per day (**mgd**). The treatment plant's biological oxygen demand (**BOD**) and total suspended solids (**TSS**) loadings result from primarily residential sources, though some industrial contribution is present. In addition, some industrial wastewater is brought into the plant for treatment.

The Lemay Wastewater Treatment Plant consists of the following sequence of steps: grit removal, comminutor shredding of rags, primary settling, aeration, final settling, scum thickening, sludge dewatering, and sludge incineration.

There are 101 employees at the Lemay treatment plant. The breakdown is: maintenance, 30; operators, 43; janitors, 5; management, 13; instrument technicians, 8; and chemists, 2. There are three shifts per day. There are six operators per shift: one for the primary settling tanks, one for the final settling tanks, two for the belt filter press room, one for the incinerator, and one senior operator. The following job categories are used 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 Operators 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-mechnical equipment throughout the treatment plant. The Maintenance Electrician maintains and repairs wiring and

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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 June 1994 the Metropolitan St. Louis Sewer District contracted with private consulting firms to identify the sources and composition of odors emitted from the Lemay plant and to recommend an abatement plan. This study was initiated in response to odor complaints from people in the surrounding communities. Odor complaints were relatively infrequent until the secondary treatment facilities were added in 1985. A significant odor episode occurred in June 1992. Dozens of odor complaints were received at the plant over a period of several days, primarily in the evening hours. Some odor complaints continued to be received for the remainder of 1992. The flood of 1993 significantly disrupted treatment operations and very few odor complaints were received. With the hot dry summer of 1994, odor complaints were once again reported.

In October 1994 a final report was issued by the consultant. A review of the complaints made by people living around the plant during 1992 showed that complaints were made in all months except November. Most complaints were registered between the months of May and October, with the majority occurring during the month of June. The contractors determined that H₂S was the most prevalent odorous compound detected in the samples collected. Starting in August 1994 hydrogen sulfide concentrations have been routinely monitored on the press room floor of the incinerator and filter house building, and near the belt filter press. During the peak odor generating months (i.e., warm summer months when the plant is receiving normal wastewater flows), concentrations of H₂S are typically below 2 parts per million (**ppm**) on the press floor, but localized readings up to 10 ppm have been recorded. Concentrations of H₂S at the V-section of the belt presses during the peak odor months are typically in the range of 10 to 125 ppm. During other times of the year and when the influent flow is high due to rainfall or high river stages, much lower concentrations of H₂S are noted.

During June 20 and 22, 1994, the contractors collected samples to determine what compounds were being emitted and what those emission rates were. Concentrations of H₂S ranged from ND around the aeration basins to 18 ppm at the incineration and filter building exhaust fans. Nineteen VOCs and hazardous air pollutants (HAPs) were detected and measured as part of the contractor's emission study. The compounds measured included acetone, benzene, bromomethane, carbon disulfide, carbonyl sulfide, chloroform, dichlorobenzene, dimethyl sulfide, ethyl-benzene, methyl ethyl ketone, methyl mercaptan, methylene chloride, styrene, tetrachloroethylene, toluene, trichloroethane, vinyl chloride, and xylenes. Recommendations made to reduce odor emissions included collecting and treating air being emitted from the sludge well and from the grit tank weirs. Reducing odor emissions from the plant could also reduce worker exposures to these compounds (i.e., H₂S) since the workers work around the sources of these odor emissions.

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MATERIALS AND METHODS

Personal breathing zone (**PBZ**) air samples were collected for hydrogen sulfide ($\mathbf{H_2S}$), total particulate, and endotoxin. PBZ air samples for $\mathbf{H_2S}$ were collected because it is emitted from wastewater treatment processes due to biodegradation of waste materials and many of the symptoms reported by employees have been associated with exposure to $\mathbf{H_2S}$. Total particulate PBZ air samples were collected and analyzed for endotoxin because endotoxin is present in gram-negative bacteria and gram negative bacteria are needed for the aerobatic digestion of wastewater solids.

PBZ air samples for H_2S were collected with Toxilog Atmospheric Diffusion Monitors manufactured by Biosystems, Incorporated. Toxilog monitors instantaneously measure H_2S air concentrations using electrochemical sensors and record H_2S concentrations in **ppm** in the monitor datalogger. 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 current H_2S concentration, 10-minute average 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. The filters were 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, lipopolysaccharide-protein complexes, EC-5. For these analyses, 10 EU is equivalent to one nanogram of endotoxin.

General area air samples were collected for H₂S and VOCs. The H₂S general area air samples 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 volatile organic compounds (**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

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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. Analysis was performed 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, grit, and wastewater that was brought to the plant for treatment were collected and analyzed for VOCs. The bulk samples were analyzed for VOCs by covering each sample vial with aluminum foil and inserting a disposable pipette connected to an air source to aerate the sample. The headspace air was then sampled with a thermal desorption tube. Each headspace air sample was collected for 15-minutes at a 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.

The bulk wastewater sample was analyzed quantitatively for the presence of dimethyl sulfoxide (**DMSO**) and N,N-dimethylacetamide (**DMAC**). The bulk samples were 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 an incinerator ash sample, were analyzed for the following elements using NIOSH Method 7300¹: 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 free crystalline 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

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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 increasing 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 (**TLVs**)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.

A time-weighted average (**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

Hydrogen sulfide ($\mathbf{H}_2\mathbf{S}$) is a colorless, flammable gas with a strong odor of rotten eggs. In wastewater treatment plants, the majority of the $H_2\mathbf{S}$ is present as a result of bacterial decomposition of proteins. Acute exposure to $H_2\mathbf{S}$ at airborne concentrations above 10 ppm has been associated with the development of conjunctivitis and keratitis. One-hour exposure to $H_2\mathbf{S}$ 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 $H_2\mathbf{S}$ 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

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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 H₂S 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 H₂S 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, H₂S smells of rotten eggs, but at about 30 ppm the smell is described as sweet or sickening sweet. At 150 ppm, H₂S causes olfactory-nerve paralysis, and the smell is no longer perceptible. The smell of H₂S therefore is not a reliable warning of its presence, especially at high concentrations.

In a recent study, Bhambhani et. al. compared the effects of inhalation of 5 ppm H₂S 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 H₂S 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 H₂S exposure. These results suggest that healthy men and women can safely perform moderate intensity work in environments contaminated with 5 ppm H₂S or lower. The device used to deliver H₂S to the subjects fits 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 H₂S is a ceiling concentration of 10 ppm which must not be exceeded during any part of the work day.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 H₂S at a concentration of 50 ppm or higher, continuous monitoring is recommended by NIOSH. The OSHA standard for H₂S is a ceiling concentration of 20 ppm or a maximum allowable peak of 50 ppm once, if no other measurable exposures occur.⁴ The OSHA H₂S ceiling concentration must not be exceeded during any part of the workday; if instantaneous monitoring is not feasible, the ceiling must be assessed as a 10-minute exposure. The ACGIH recommends a TLV-TWA of 10 ppm and a STEL of 15 ppm.³

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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 Endotoxins 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 forced expiratory volume in one-second (**FEV**₁), although some investigators have not been able to demonstrate acute changes in FEV₁. 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, Rylander¹⁴ 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-hr**) TWA concentrations have been suggested for airway inflammation with increased airway reactivity (200 EU/m₃), over-shift decline in FEV₁ (2000 EU/m³), for chest tightness (3000 EU/m³), and toxic pneumonitis (10,000-20,000 EU/m³). Castellan¹⁵ has reported a calculated zero pulmonary function effect level for endotoxin of 90 EU/m³.

Bioaerosols in Sewage Treatment Plants

Laitinen et al. 16 reported endotoxin concentrations that varied from 0.6 to 310 ng/m³ (7.2 to 3720 EU/m³, 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/m³**). The correlation between the bacterial counts and endotoxin concentrations was r = 0.79 indicating high correlation. A study of sewage workers' exposures to airborne culturable bacteria and inhaled endotoxin was performed at nine wastewater treatment plants in Finland. 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

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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 non-detectable (ND) to 370 ng/m³, median 30 ng/m³. Total bacteria levels ranged from ND to 9.5x10⁶ CFU/m³, median 5.2x10⁵ CFU/m³. Spherical bacteria levels ranged from ND to 6.9x10⁶ CFU/m³, with a median concentration of 3.3x10⁵ CFU/m³. Rod-shaped bacteria levels ranged from ND to 4.3x10⁶ CFU/m³, median 8.1x10⁴ CFU/m³. 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 H₂S during a work shift.

Volatile Organic Compounds

Volatile organic compounds describe 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. The following are health effects and evaluation criteria for VOCs which were quantitated in this HHE.

Toluene

Inhalation and skin absorption are the major occupational routes of entry. 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. 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). 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.

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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. 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. The current ACGIH TLV® is 10 ppm and it is considered 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. Human subjects exposed to 900 to 1000 ppm for 20-minutes experienced lightheadedness, incoordination and impaired equilibrium, and transient eye irritation. Textile workers exposed from several months to 6-years sometimes exceeding 200 ppm revealed no evidence of cardiovascular, hepatic, renal, or other effects as a function of exposure.²⁶

The NIOSH REL for 1,1,1-trichloroethane is a 10-minute average 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-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. Mild symptoms of dizziness have been noted when concentrations of isomers of hexane exceeded 1000 ppm, but were not seen below 500 ppm.²⁷ Chronic occupational exposures to n-hexane concentrations in the 400 to 600 ppm range have been shown to cause polyneuropathy.²⁸⁻³⁰ Dermal exposure to n-hexane caused immediate irritation characterized by erythema and hyperemia.²⁸

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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 DISCUSSIONS

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 is shown in Table 1. The maximum H_2S concentration measured on a worker was 20 ppm. This concentration was measured on a maintenance mechanic who was repairing the feed gate for the #1 incinerator. This H_2S concentration exceeds the NIOSH REL of 10 ppm and is at the OSHA PEL of 20 ppm. The maximum 10-minute average H_2S concentration for this mechanic was 3.5 ppm, and the 8-hour TWA H_2S concentration was 0.08 ppm. The operators working on the press floor had maximum H_2S concentrations of <1.0 and 1.0 ppm. The incinerator operator had a maximum H_2S concentration of <1.0 ppm. The maximum H_2S concentrations for the three operators were all below the NIOSH and OSHA guidelines and standards.

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 is shown in Table 1. General area air samples were collected for H_2S near the feed gate for the #2 incinerator and between #2 and #3 belt press on the press room floor. No H_2S was detected in these air samples.

Four 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 operators working on the press room floor were 0.03 and 0.04 milligrams per cubic meter (**mg/m³**) and 1.29 and 1.50 endotoxin units per cubic meter (**EU/m³**), respectively. The operator operating the incinerators had total particulate and endotoxin PBZ air sample concentrations of 0.02 mg/m³ and 1.08 EU/m³, respectively. Two PBZ air samples for total particulate and endotoxin were collected on maintenance mechanics, one on an outside mechanic working on #6 aeration tank and the other on a mechanic working on the press room floor repairing the feed gate to #1 incinerator. The total particulate and endotoxin PBZ air sample concentrations for the mechanic working outside were 0.01 mg/m³ and 5.51 EU/m³, respectively. The total particulate and endotoxin concentrations for the mechanic working on the press room floor were 0.08 mg/m³ and 3.53 EU/m³, respectively. These particulate exposures are considered very low. All the PBZ endotoxin air sample concentrations were well below 90 EU/m³, calculated by Castellan to be the zero pulmonary function effects level. ¹⁵

Three 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 waste activated sewage sludge from the #3 belt press, grit from the #4 incinerator feed, and wastewater brought to the plant from Mallinckrodt, Inc. Compounds identified were considered major if their chromatograph peak height was greater than one half of full scale, and minor if the

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chromatograph peak height was less than one half of full scale. Major VOCs identified in the headspace air above the sludge sample were acetone, isopropanol, dimethyl sulfide, methyl ethyl ketone, 2-butanol, dimethyl disulfide, dimethyl trisulfide, cresol isomer, indole, and methyl indole isomer. Thirty minor VOCs were identified in the sludge headspace air. The grit sample had one major compound identified, cresol, and 15 minor VOCs. 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, DMSO, and DMAC. Twenty-six minor VOCs were identified in the Mallinckrodt wastewater sample. The wastewater brought to the treatment plant from Mallinckrodt was also analyzed quantitatively for DMSO and DMAC content. The bulk wastewater samples from Mallinckrodt contained 3.80% DMSO and 3.40% DMAC which were both under the material safety data sheet (provided to NIOSH) specifications of 6% or less for DMSO and 4% or less for DMAC.

Four general area air samples were collected and analyzed qualitatively for VOCs as shown in Table 4. The general area air samples were collected in the press room near the grit shooting operation, in the press room on an instrument panel between #2 and #3 belt presses, in the press room near the feed gate to the #2 incinerator, and in the grit building near a conveyor dumping grit. The major VOCs identified in the general area air sample collected near the grit shooting operation were 1,1,1-trichloroethane, toluene, and limonene. Sixteen minor VOCs were identified in the general area air sample collected near the grit shooting operation. The major VOCs identified in the general area air sample collected between #2 and #3 belt presses were toluene and limonene. Twelve minor VOCs were identified in the sample from between the belt presses. Both the general area air samples collected in the belt press room near the feed gate to the #2 incinerator and the grit building near the conveyor dumping grit did not have any major compounds. Thirteen minor VOCs were identified in the sample collected near the feed and six minor VOCs were identified in the sample collected in the grit building.

Five general area air samples were collected and analyzed for 1,1,1-trichloroethane, benzene, toluene, n-hexane, dimethyl sulfide, limonene, and total hydrocarbons. These results are listed in Table 5. The general area air samples were collected in the same areas as the qualitative VOCs shown in Table 4 and at the aeration tank where Mallinckrodt wastewater was being pumped into an aeration tank. Detectable concentrations of 1,1,1-trichloroethane were found in the press room. Trace concentrations of 1,1,1-trichloroethane, between 0.002 and 0.006 ppm, were measured between #2 and #3 presses and near the feed gate to #2 incinerator. An air concentration of 0.013 ppm 1,1,1-trichloroethane was measured during the grit shooting operation. Also found on the general area air sample collected near the grit shooting operation were trace concentrations between 0.003 and 0.012 ppm of toluene and n-hexane and a concentration of 0.040 ppm of limonene. Detectable concentration of toluene (0.015 ppm) and a trace concentration of limonene (between 0.004 and 0.009 ppm) were found in the general area air sample collected between #2 and #3 belt presses.

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Bulk samples of sludge from the #3 belt press, grit being fed to the #4 incinerator, and incinerator ash from under the #2 incinerator were collected and analyzed for elemental composition. The results of these elemental analyses are listed in Table 6. The sludge sample contained Al, Ba, Ca, Cu, Fe, Mg, Mn, Na, P, Pb, Sr, Ti, and Zn. The eight most abundant elements measured in the sludge sample were: Ca, 4170 µg/g; P, 3290 µg/g; Al, 3110 µg/g; Fe, 3060 µg/g; Mg, 766 µg/g; Na, 724 µg/g; Mn, 339 µg/g; and Zn, µg/g. The grit sample contained Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Na, P, Pb, Sr, Ti, and Zn. The eight most prominent elements present in the grit sample were Ca, 50000 µg/g; Fe, 7170 µg/g; P, 4390 µg/g; Mg, 2570 µg/g; Al, 2010 µg/g; Na, 622 µg/g; Pb, 306 µg/g; and Mn, 224 µg/g. The incinerator ash sample contained Ag, Al, Ba, Ca, Cr, Cu, Fe, La, Li, Mg, Mn, Na, Ni, P, Pb, Sr, Ti, Zn, and Zr. The eight most prominent elements present in the ash sample were Ca, 55300 µg/g; P, 42600 µg/g; Al, 39700 µg/g; Fe, 36000 µg/g; Mg, 10500 µg/g; Na, 7920 µg/g; Mn, 3410 µg/g; and Zn,

 $1730 \,\mu\text{g/g}$. The bulk incinerator ash sample was also analyzed for free crystalline silica and was found to contain 2.54% silica, but not crystalin silica.

Press room operators at the Lemay plant in August 1994 began to routinely measure and record the H₂S concentrations using H₂S monitors at various locations throughout the wastewater treatment process. H₂S measurements made from August 1 through November 19, 1994, were collected from the Lemay plant by a NIOSH investigator. H₂S measurements were taken on the press room floor, near the high press drain, in the control room, at the V-section of the belt presses, near the belt press control panels, and above the rising well. For the purpose of demonstrating seasonal H₂S concentration patterns, H₂S concentration data from the belt presses (V-section), high press drain, rising well, and press room floor were plotted and are shown in Figures 1 through 4, respectively. In each of the figures, higher H₂S concentrations were measured in late August early/September and lower H₂S concentrations were measured in late October/early November. These patterns shown in Figures 1 through 4 are consistent with the patterns of odor complaints reported by residents near the plant in 1992.

CONCLUSIONS

A maintenance mechanic had a maximum H₂S concentration of 20 ppm while repairing a feed gate to incenerator #1. This result exceeds the NIOSH REL ceiling of value of 10 ppm and is at the OSHA PEL ceiling value of 20 ppm. All other PBZ and area air sample results for H₂S were below the NIOSH REL and OSHA PEL ceiling values. Past measurements have shown low concentrations of H₂S during November, the month that the NIOSH survey was conducted. Past measurements of H₂S indicate that the higher H₂S concentrations occur from May through October, and during these months H₂S concentrations approach the NIOSH REL ceiling limit for H₂S of 10 ppm (see Figure 4, press floor H₂S concentration of 10 ppm on August 28, 1994). Therefore, the potential exists for overexposure to H₂S. The employees' complaints of burning sensation in the nose, loss of breath, sore throat, eye irritation, nausea, and diarrhea have all been associated with H₂S exposure.⁵

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VOC results ranged from ND to 0.40 ppm in general area air samples. Detectable concentrations of 1,1,1-trichloroethane, toluene, n-hexane, and limonene were measured in these samples, however all measured VOC concentrations were quite low. Comparing the NIOSH qualitative general area air sample results with the contractor's emission study results show that 8 VOCs were common to both. The common VOCs were acetone, chloroform, 1,1,1-trichloroethane, benzene, toluene, perchloroethylene, ethyl benzene, and dichlorobenzene.

No air samples were collected and analyzed for metals. However, incinerator ash was observed to be accumulating under the incinerators and dispersed through the lower floors of the incinerator areas. The ash accumulating under the incinerators was the result of a back draft of air blowing ashes out of the bottom of the incinerator. This event reportedly occurs from once a week to two or three times a day. Samples of this ash were analyzed and shown to contain 13 metals for which occupational exposure limits have been established. Thus, the potential exists for exposure to these metals, if the ash were to become airborne.

RECOMMENDATIONS

- 1. Employees working in the incinerator and filter building should wear personal H₂S monitors when the H₂S concentrations approach 5 ppm (one half of the NIOSH REL) or higher in the press room area or near the belt presses. Daily H₂S measurements should continue to be made to assure that the H₂S levels in these work areas in and around the incinerator and filter building are maintained below 10 ppm.
- Respirators are the least preferred method of worker protection from respiratory hazards because they can be unreliable if an adequate respiratory protection program is not established by the employer and because they require worker cooperation. Respirators are recommended when exposures exceed recommended levels (10 ppm) and engineering controls are not technically feasible, while controls are being installed or repaired, or when emergency or other temporary situations arise. If H₂S 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 H₂S; (3) supplied-air respirator with eye protection; or (4) self-contained breathing apparatus with a full facepiece. For H₂S 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 an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations.

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All respirators selected must be approved by NIOSH and the Mine Safety and Health Administration (**MSHA**) under provision of 30 CFR 11.³¹ The current list of NIOSH/MSHA certified respirators can be found in the NIOSH Certified Equipment List.³² A complete respiratory protection program must be implemented and must fulfill all requirements of 29 CFR 1910.134.³³ 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.³⁴ Additional information on the selection and use of respirators can be found in the NIOSH Guide to Industrial Respiratory Protection.³⁵

3. In the recommended standard for occupational exposure to H₂S, NIOSH recommends that preplacement and periodic examinations (once every three years) be made available to all workers occupationally exposed to H₂S. The following medical procedures should be made available to each employee who is exposed to H₂S 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 forced expiratory volume in one second (FEV₁) 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 metals found in incinerator ash samples) to determine if the workers are exposed to the metals which are present in the ash. Workers involved in the operation, repair, or clean-up of the incinerator areas where the ash is present should be monitored.

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- 3. Union Shop Steward, IBEW #1
- 4. OSHA Region VII
- 5. Confidential Requestor

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.

Personal Breathing Zone and General Area Air Sample Results for Hydrogen Sulfide

Metropolitan St. Louis Sewer District

Lemay Treatment Plant St. Louis, Missouri HETA 94-0405 November 22, 1994

Job Title	Sample Location	Sample Time (min.)	Max. 10-min. H ₂ S Conc. (ppm)	Mean 10-min. H ₂ S Conc. (ppm)	H ₂ S TWA Conc. (ppm)	Max. H ₂ S Conc. (ppm)
Operator II	Press Room Floor	466	ND	ND	ND	ND
Operator II	Press Room Floor	462	0.1	0.004	0.004	1
Maintenance Operator II	Incinerator Control Room	464	ND	ND	ND	ND
Mechanic	Feed Gate for #1 Incinerator	467	3.5	0.08	0.08	20
General area air	Feed Gate for #2 Incinerator	431	ND	ND	ND	ND
General area air	Instrument Panel Between #2 & #3 Belt Presses	395	ND	ND	ND	ND

 H_2S = hydrogen sulfide

STEL = short term exposure limit

TWA = time-weighted average

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

ppm = parts per million

limit of detection = 1 ppm

NIOSH H₂S 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 and General Area Air Sample Results for Total Particulate and Endotoxin

Metropolitan St. Louis Sewer District Lemay Treatment Plant St. Louis, Missouri HETA 94-0405 November 22, 1994

Job Title	Job Location	Sample Time (min.)	Total Particulate Conc. (mg/m³)	Endotoxin Conc. (EU/m³)
Operator II	Press Room Floor	486	0.03	1.29
Operator II	Press Room Floor	476	0.04	1.50
Operator II	Incinerator Control Room	470	0.02	1.08
Maintenance Mechanic	Outside in #6 Aeration Tank	349	0.01	5.51
Maintenance Mechanic	Feed Gate for #1 Incinerator	440	0.08	3.53

TWA = time-weighted average

1 EU = 0.1 nanogram of lipopolysaccharide-protein complexes, EC-5

 $mg/m^3 = milligrams per cubic meter$

 EU/m^3 = endotoxin unit per cubic meter

No occupational exposure criteria have been 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/m³.

Identification of Headspace Volatile Organic Compounds in Bulk Samples Collected at the Treatment Plant

Metropolitan St. Louis Sewer District Lemay Treatment Plant

St. Louis, Missouri HETA 94-0405

November 22, 1994

Sample	Headspace Volatile Organic Compounds Present			
Sewage Sludge from #3 Belt Press	3, 11 , 12 , 14 ,17,21, 20 , 23 ,24,26,28,29,30,31,34, 36 ,38,43,45,46,47, 48,51,52,53, 54 ,56,58,60,61,62,63, 66 ,67,68,69,70,71, 76,77			
Wastewater from Mallinckrodt	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			
Grit from Feed to #4 Incinerator	9,11,12,20,21,25,38,46,47,48,51,53,59,	61,62,63, 66 ,69		
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 = methylthioacetonitrile 31 = 2-pentanol 32 = trimethylethanediamine 33 = (dimethylamino)-acetonitrile 34 = 3-methyl-1-butanol 35 = 2-methyl-1-butanol (methyl heptanone) 36 = dimethyl disulfide 37 = 1,1,1-trichlororethane 38 = 2-methylpropanoic acid (isobutyric acid) 39 = dimethylsulfoxide (DMSO) 40 = n-methylacetamide 41 = n,n dimethylacetamide (DMAC) 42 = sulfonylbismethane 43 = toluene 44 = C ₈ H ₁₈ /C ₈ H ₁₆ aliphatics 45 = methylpropane thioate 46 = butyric acid 47 = 3-methylbutanoic acid 48 = 2-methylbutanoic acid 49 = xylene/ethyl benzene isomer 51 = valeric acid (pentanoic acid) 52 = M.W. 114 ketone (methylheptanone) 53 = 4-methyl pentanoic acid	54 = dimethyl trisulfide 55 = C ₉ -C ₁₂ aliphatic/C ₉ H ₁₂ - C ₁₀ H ₁₄ alkyl benzene 56 = C ₉ H ₁₂ alkyl benzene 57 = n-nonane 58 = M.W. 128 ketone 59 = phenol 60 = n-decane 61 = dichlorobenzene isomer 62 = C ₁₀ H ₁₄ aromatic (p-cymene) 63 = limonene 64 = n-undecane 65 = 2-ethyl-1-hexanol 66 = cresol isomer 67 = C ₁₀ H ₁₄ (dimethyl styrene) 68 = 2-piperidinone 69 = napthalene 70 = n-dodecane 71 = dimethyl tetrasulfide 72 = benzothiazole plus hexamethylenetetramine 73 = n-tridecane 74 = n-tetradecane 75 = n-pentadecane 76 = indole 77 = methyl indole isomer		

Bold values indicate compound peaks which were higher than half of full scale of the mass spectrometer chromatograph.

Identification of Volatile Organic Compounds in Area Air Samples

Metropolitan St. Louis Sewer District Lemay Treatment Plant St. Louis, Missouri

HETA 94-0405

November 22, 1994

	•		
Sample Location	Volatile Organic Compounds Present		
In Belt Press Room Near Grit Shooting Operation	2,3,4,7, 8 ,9, 11 ,13,14,15,16,17,18,20,21,22, 23 ,2 4,25		
In Belt Press Room Near Instrument Panel Between #2 & #3 Belt Presses	7,8,9, 11 ,13,14,17,18,20,21,22, 23 ,24,25		
In Belt Press Room Near Feed Gate to #2 Incinerator	8,9,11,14,15,17,18,20,21,22,23,24,25		
In Grit Building Near Conveyor Dumping Grit	11,14,18,22,23,24		
2 = ethanol $10 = dimethyl disulfid$	e $18 = C_9 - C_{12}$ aliphatic, $C_9 H_{12}$		

2 = ethanol	10 = dimethyl disulfide	$18 = C_9 - C_{12}$ aliphatic, $C_9 H_{12}$
3 = acetone	11 = toluene	C ₁₀ H ₁₄ alkyl benzene
4 = chloroform	12 = octane	19 = dimethyl trisulfide
$5 = C_6H_{14}/C_6H_{12}$ aliphatic	13 = perchloroethylene	20 = n-decane
6 = n-hexane	14 = xylene/ethyl benzene isomers	21 = dichlorobenzene
$7 = C_7 H_{16} / C_7 H_{14}$ aliphatic	15 = n-nonane	22 = p-cymene
8 = 1,1,1-trichloroethane	$16 = pinenes/C_9H_{16}$ terpenes	23 = limonene
9 = benzene	$17 = C_9 H_{12}$ alkyl benzene	24 = n-undecane
	, •	25 = n-dodecane

Bold values indicate compound peaks which were higher than half of full scale of the mass spectrometer chromatograph.

General Area Air Sample Results for Selected Volatile Organic Compounds Metropolitan St. Louis Sewer District, Lemay Treatment Plant St. Louis, Missouri

HETA 94-0405 November 22, 1994

Sample Time (min.)	1 Conc. (ppm)	2 Conc. (ppm)	3 Conc. (ppm)	4 Conc. (ppm)	5 Conc. (ppm)	6 Conc. (ppm)	7 Conc. (ppm)
439	trace	ND	0.015	ND	ND	trace	ND
434	trace	ND	ND	ND	ND	ND	ND
448	ND	ND	ND	ND	ND	ND	ND
425	ND	ND	ND	ND	ND	ND	ND
385	0.013	ND	trace	trace	ND	0.040	ND
	Time (min.) 439 434 448 425	Time (min.) Conc. (ppm) 439 trace 434 trace 448 ND 425 ND	Time (min.) Conc. (ppm) Conc. (ppm) 439 trace ND 434 trace ND 448 ND ND 425 ND ND	Time (min.) Conc. (ppm) Conc. (ppm) Conc. (ppm) 439 trace ND 0.015 434 trace ND ND 448 ND ND ND 425 ND ND ND	Time (min.) Conc. (ppm) Conc. (ppm) Conc. (ppm) Conc. (ppm) Conc. (ppm) Conc. (ppm) 439 trace ND 0.015 ND 434 trace ND ND ND 448 ND ND ND ND 425 ND ND ND ND	Time (min.) Conc. (ppm) ND ND	Time (min.) Conc. (ppm) ND ND ND ND ND ND ND <t< td=""></t<>

	<u>MDC</u>	<u>MQC</u>	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

MDC = minimum detectable concentration, assuming an air sample volume of 96 liters

MQC = minimum quantifiable concentration, assuming an air sample volume of 96 liters

NIOSH = National Institute for Occupational Safety and Health

OSHA = Occupational Safety and Health Administration

ACGIH = American Conference of Governmental Industrial Hygienists

LFC = lowest feasible concentration

TWA = time-weighted average

trace = concentration between MDC and MQC

ND = non-detectable concentration, less than MDC

 $REL = recommended \ exposure \ level$

 $PEL = premissible \ exposure \ limit$

TLV = threshold limit value

Elemental Analyses of Bulk Samples Collected from the Wastewater Treatment Process Metropolitan St. Louis Sewer District

Lemay Treatment Plant St. Louis, Missouri HETA 94-0405 November 22, 1994

	Sample Description				
Analyte (µg/g)	Sludge from	Grit feed to	Ash collected		
	#3 belt press	#4 incinerator	under #2		
Silver (Ag)	ND	ND	67.4		
Aluminum (Al)	3110	2010	39700		
Barium (Ba)	67.0	48.1	835		
Calcium (Ca)	4170	50000	55300		
Chromium (Cr)	ND	49.5	138		
Copper (Cu)	42.6	94.5	450		
Iron (Fe)	3060	7170	36000		
Lanthanum (La)	ND	ND	42.5		
Lithium (Li)	ND	ND	34.0		
Magnesium (Mg)	766	2570	10500		
Manganese (Mn)	339	224	3410		
Molybdenum (Mo)	ND	ND	105		
Sodium (Na)	724	622	7920		
Nickel (Ni)	ND	ND	89.9		
Phosphorus (P)	3290	4390	42600		
Lead (Pb)	21.3	306	297		
Strontium (Sr)	25.7	54.0	280		
Titanium (Ti)	21.8	55.4	501		
Zinc (Zn)	111	168	1730		
Zirconium (Zr)	ND	ND	32.9		
Limit of Detection	13.4	17.3	23.5		
Silica (Si) (%)			2.54		

 $\mu g/g = micrograms$ of analyte per gram of sample

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

Figure 1Belt Presses Hydrogen Sulfide Conc.

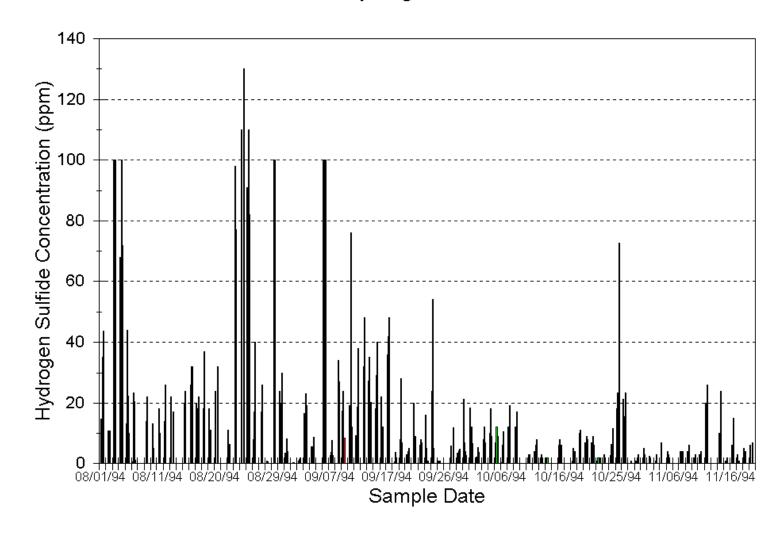


Figure 2
High Press Drain Hydrogen Sulfide Conc

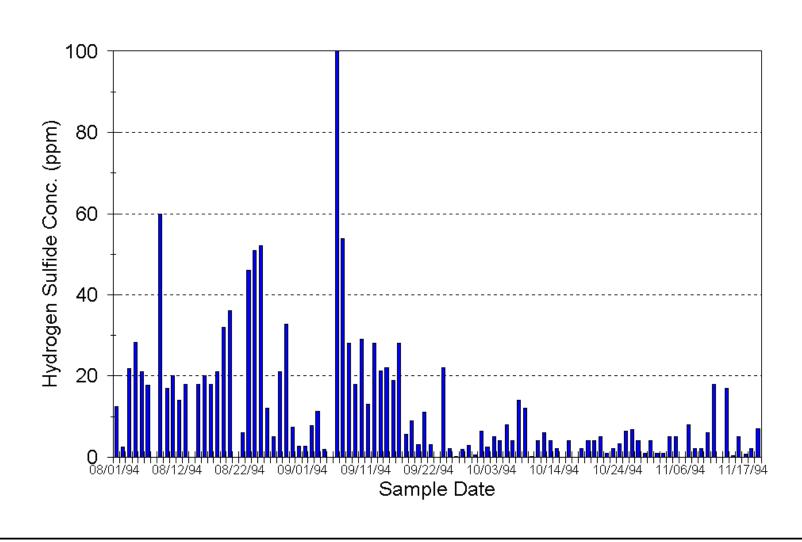


Figure 3Rising Well Hydrogen Sulfide Conc.

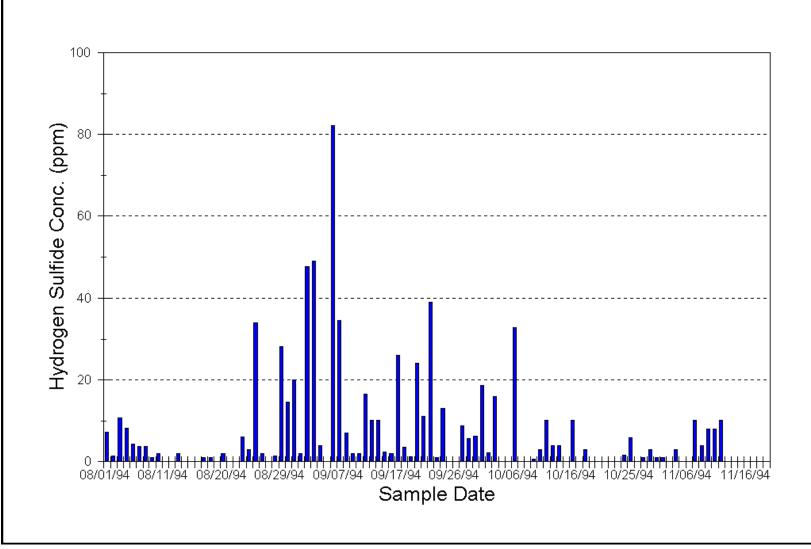


Figure 4Press Floor Hydrogen Sulfide Conc.

