HETA 94-0182-2519 AUGUST 1995 LITTLE BLUE VALLEY SEWER DISTRICT INDEPENDENCE, MISSOURI NIOSH INVESTIGATORS: David A. Marlow, B.S. Daniel Almaguer, M.S.

SUMMARY

In March 1994 the National Institute for Occupational Safety and Health (NIOSH) received a confidential request to conduct a health hazard evaluation (HHE) at the Little Blue Valley Sewer District wastewater treatment plant in Independence, Missouri. The employees reported gastrointestinal disturbances, sore throats, fatigue, headaches, eye irritation, and unexplained coughing accompanied by hoarseness while working in the belt press room.

An initial site visit, walk-through evaluation, and employee interviews were made at the sewage treatment plant on May 17-18, 1994. On August 2-4, 1994, a return site visit was made to collect personal breathing zone (PBZ) air samples, general area air samples, and bulk sewage sludge and incinerator ash samples. Maximum 10-minute hydrogen sulfide (H_2S) PBZ concentrations ranged from 0.1 parts per million (ppm) to 95 ppm; 8 of the 13 PBZ exceeded the NIOSH 10-minute ceiling recommended exposure limit (REL) of 10 ppm, and 3 of these exceeded the Occupational Safety and Health Administration (OSHA) 10-minute ceiling permissible exposure limit (PEL) of 20 ppm. Maximum 10-minute H_2S concentrations in general area air samples obtained in the belt press room ranged from 46 to 69 ppm. Outside the belt press room, the maximum 10-minute H_2S general area air concentrations ranged from non-detectable to 0.1 ppm.

PBZ air sample results for total particulate and endotoxin ranged from 0.03 to 0.28 milligrams per cubic meter of air (mg/m^3) , and 2.59 to 6.82 endotoxin units per cubic meter of air (EU/m^3) , respectively. While no evaluation criteria has been established for endotoxin, the levels detected were all below the calculated zero pulmonary function effects level for endotoxin of 90 EU/m^3 reported by Castellan, and the levels Rylander has reported causing airway inflammation with increased airway reactivity at 200 EU/m^3 . The general area air sample concentrations of total particulate and endotoxin ranged from 0.03 to 0.19 mg/m^3 and 2.03 to 54.7 EU/m^3 , respectively. The general area air sample containing 54.7 EU/m^3 endotoxin was collected between two gravity concentrators.

Bulk samples of waste activated sewage sludge were collected and analyzed qualitatively for headspace volatile organic compounds (VOCs). The sludge samples containing 40% solids had the highest concentrations and largest variety of VOCs when compared to sludge samples containing 5% solids, which were higher than sludge samples containing 1% solids. Major VOCs identified included toluene, C_{10} - C_{14} aliphatic hydrocarbons, cyclopentanone, methyl ethyl ketone, and acetone. Other VOCs detected included methanol, ethanol, butanol, C_5 - C_{11} aliphatic ketones, furans, limonene, acetic acid, and a few fatty acids.

Pairs of air samples were collected for VOCs in a given location. One sample from each pair was analyzed qualitatively to identify VOCs present. Similar to the results obtained from the sludge headspace air sample results, toluene, limonene, and various aliphatic hydrocarbons, mainly in the

 C_{10} - C_{14} range, were the major compounds identified. Traces of acetone, isopropanol, methyl ethyl ketone, other ketones, furans, and 1,1,1-trichloroethane were also detected on some samples. Based on the qualitative results, the other sample from each pair was analyzed quantitatively for toluene, limonene, and total hydrocarbons. Area air sample results for toluene, limonene, and total hydrocarbons ranged from non-detectable (ND) to 0.39 ppm.

PBZ air sample results for toluene were all below 0.06 ppm, well below the NIOSH REL TWA of 100 ppm and the OSHA PEL TWA of 200 ppm. PBZ air sample results for limonene and total hydrocarbons were all below 0.05 ppm. No evaluation criteria for limonene or total hydrocarbons have been established.

Bulk samples of waste activated sewage sludge and incinerator ash were analyzed for elemental composition. Detectable concentrations of 23 different elements were found. Concentrations of the elements were highest in the incinerator ash samples, followed by sludge samples containing 40% solids. The eight most abundant elements present in the sludge samples were aluminum (Al), calcium (Ca), iron (Fe), phosphorous (P), magnesium (Mg), sodium (Na), barium (Ba), and copper (Cu). The eight most abundant elements present in the ash samples were P, Al, Ca, Fe, Mg, Na, zinc (Zn), and Ba.

General area air samples were collected and analyzed for the following metals: lead (Pb); chromium (Cr); Al; silver (Ag); Zn; Cu; arsenic (As); Be; cadmium (Cd); antimony (Sb); selenium (Se); and titanium (Ti). All results were ND except for a trace concentration of Zn (between 0.9 and 3.0 micrograms per cubic meter of air) present in an air sample collected between the ash and sludge conveyors on the second day of sampling.

Bulk incinerator ash samples were also analyzed for silica content. The concentrations ranged from 3.16 to 5.19% silica. General area air samples were collected and analyzed for respirable particulate and silica (quartz, and cristobalite). The respirable particulate concentrations ranged from 0.01 to 0.08 mg/m³. None of the sample results had detectable concentrations of respirable quartz or cristobalite.

Based on the PBZ air sample results, workers in the belt press room were exposed to H_2S concentrations which exceeded the 10-minute NIOSH ceiling limit of 10 ppm and the 10-minute OSHA PEL of 20 ppm. Recommendations are made to provide continuous H_2S monitors for employees working in or around the belt press room and to implement engineering controls to reduce H_2S concentrations. Respiratory protection is recommended in the interim until work practices and engineering controls can effectively reduce H_2S exposures below recommended levels.

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

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INTRODUCTION

On March 2, 1994, the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a health hazard evaluation (HHE) to evaluate employee exposures at the Little Blue Valley Sewer District wastewater treatment plant. Worker health complaints and symptoms which were believed to be arising from working around the sludge dewatering and incineration processes included gastrointestinal disturbances, sore throats, fatigue, headaches, eye irritation, and unexplained coughing accompanied by hoarseness. An initial site visit was made May 13-14, 1994. During this initial visit, a walk-through survey of the wastewater treatment plant and interviews with some workers involved in process operations were conducted. A return visit was made August 1-4, 1994, during which time an industrial hygiene survey was conducted.

PROCESS DESCRIPTION

Approximately 25 employees (three shifts per day) work in the sewage sludge dewatering and incineration process. The three job categories involved in the operation and maintenance of this process are: operators, mechanics, and electricians. For the purpose of this report, the operators are divided into four categories: head operator, low pressure oxidation (LPO) operator, belt press operator, and outside operator. The head operator oversees the operations in the process and sludge disposal buildings which include the dewatering and incineration of sewage sludge. This person spends a majority of the shift in the control room. The LPO operator is responsible for the operations in the LPO boiler room where low pressure steam is used to reduce the volume of solids present in the sludge prior to dewatering. The belt press operator is responsible for operating the belt presses, gravity concentrators, and ash press, and adding polymers to the sludge. The outside operator is responsible for activities outside the process building, including removing rags from the screens, collecting biochemical oxygen demand (BOD) and chemical oxygen demand (COD) samples, and checking the operations in the raw wastewater pump station, screening building, and aeration and clarification basins.

The Little Blue Valley Sewer District processes approximately 40 million gallons of wastewater per day with a daily peak flow capacity of 100 million gallons. Wastewater enters the plant through a 126-inch pipeline into the raw wastewater pump station where it passes through 3-inch bar screens and grinders, and is then pumped to the screen building. In the screen building, the wastewater passes through 5/16-inch mesh screening to remove debris. The wastewater is then pumped from the screen building to the grit chamber where grit settles out. The wastewater is pumped from the grit chamber to the aeration and clarification splitter box which distributes the wastewater into four aeration and clarification basins. These basins are interchannel clarifiers in which wastewater is circulated around the outside of the basin for aerobic reduction of solids. The middle portion of the basin is kept calm to allow settling of solids. The solids in the middle

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portion of the basin form a blanket at the bottom of the basin. As the blanket of solids builds up, the sludge is drawn off the bottom and is pumped to the process building for dewatering. The clarified effluent water from the middle portion of the basin flows over the top of the basin and is pumped to the Little Blue River. The waste activated sludge drawn from the bottom of the basins is pumped to sludge thickening basins. In the thickening basins, the sludge is mixed with a polymer, and the polymer and sludge flocculate. Two polymers were used: (1) Midfloc PW 1319E, an anionic flocculent emulsion containing petroleum distillates and anionic polyacrylamide; and (2) Magnifloc 1596C, a flocculent containing petroleum distillates and cationic polyacrylamide. After flocculation, the sludge is pumped from the sludge thickening basins to one of five gravity concentrators. The sludge is distributed evenly over the width of rotating drainage belts. As the belt rotates, the sludge goes through plows located in the gravity drainage zone of the belt and churns up the sludge to promote more rapid drainage. The sludge is thickened from approximately 1% solids to 5% solids and is pumped to the sludge storage basin. The belts on the concentrators are cleaned by doctor blades and a high-pressure water wash prior to beginning a new cycle. The sludge is pumped from the sludge storage basins to the LPO room where the sludge is thermally conditioned to reduce the volume of the solids. The thermally conditioned sludge is then pumped to one of two belt presses which further dewater the sludge from approximately 5% solids to 40% solids. The belt is cleaned by doctor blades and a highpressure water wash prior to beginning a new cycle. The dewatered sludge coming from the belt presses drops off the belts onto a conveyor which transports it to an incinerator feed hopper. The sludge is fed from the hopper to the incinerator, and the ash coming from the bottom of the incinerator is slurried with water. The wet ash slurry drops onto a conveyor belt which transports the ash slurry back to the press room where the ash is dewatered using an ash belt press. The dewatered ash coming from the ash belt press is conveyed to a dumpster. When the dumpster is full, the ash is hauled to a landfill.

MATERIALS AND METHODS

An industrial hygiene survey was conducted in and around the process building during the first shift on August 2-4, 1994. Personal breathing zone (PBZ) air samples were collected on the head operator, belt press operator, LPO operator, outside operator, and mechanic. Air samples were collected for hydrogen sulfide (H₂S), volatile organic compounds (VOCs), total particulate, and endotoxin.

PBZ air samples for H_2S were collected with Toxilog Atmospheric Diffusion Monitors manufactured by Biosystems, Inc. Toxilog monitors measure H_2S air concentrations using electrochemical sensors and record H_2S concentrations in parts per million (ppm) in the monitor datalogger. 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-weight average (TWA) H_2S concentration.

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PBZ 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. PBZ 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 toluene, limonene, and total hydrocarbons by GC with flame ionization detection according to NIOSH Methods 1501 and 1550 with modifications.¹

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 H₂S, VOCs, and endotoxin in the belt press room, LPO boiler room, anaerobic building, control room, and polymer pit. General area air samples were collected for metals, respirable particulate, respirable quartz, and respirable cristobalite in the belt press room and near the incinerator ash dumpster. The sample analyses for endotoxin and VOCs were done in the manner previously described. The H₂S 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 metals were collected on 0.8 µm pore size, 37-mm diameter, mixed-cellulose ester filters connected via tubing to battery powered sampling pumps calibrated to provide a volumetric flow rate of 2.0-lpm. The samples were digested and analyzed according to NIOSH Method 73001 modified for microwave digestion and standard matrix matching of samples. Samples were analyzed by inductively coupled plasma emission spectrometry for the following metals: aluminum (Al); antimony (Sb); arsenic (As); beryllium (Be); cadmium (Cd); chromium (Cr); copper (Cu); lead (Pb); selenium (Se); silver (Ag); titanium (Ti); and zinc (Zn). General area air samples for respirable particulate, quartz, and cristobalite were collected using 10-mm nylon cyclones containing 5.0 µm pore size, 37-mm diameter, PVC filters connected via tubing to battery powered sampling pumps calibrated to provide a volumetric flow rate of 1.7-lpm. These samples were analyzed gravimetrically (NIOSH Method 0500), as well as for quartz and cristobalite concentrations. Quartz and cristobalite concentrations were determined by X-ray diffraction using NIOSH Method 7500 with modifications.1

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Bulk samples of sewage sludge and incinerator ash were collected from various steps in the sludge dewatering and incineration processes to determine the concentrations of VOCs and elements present. The bulk incinerator ash samples were also analyzed for silica content. Bulk sewage sludge samples were collected from the following steps in the process: (1) feed to the gravity concentrators (approximately 1% solids), (2) output from the concentrators (approximately 5% solids), (3) feed to the belt press (approximately 5% solids), and (4) belt press output (approximately 40% solids). The incinerator ash was collected from the dumpster where the dewatered wet incinerator ash was disposed. The bulk sludge 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. The sewage sludge samples and the incinerator ash samples were analyzed for the following elements using NIOSH Method 7300: Ag, Al, As, barium (Ba), Be, calcium (Ca), Cd, Cobalt (Co), Cr, Cu, Iron (Fe), lanthanum (La), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus (P), Pb, Sb, Se, strontium (Sr), tellurium (Te), Ti, thallium (Tl), vanadium (V), yttrium (Y), Zn, and zirconium (Zr). The wet 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

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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 and that OSHA PELs included in this report reflect the 1971 values.

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 (H_2S) is a colorless, flammable gas with a strong odor of rotten eggs. In wastewater treatment plants, the majority of the H₂S is present as a result of bacterial decomposition of proteins. Acute exposure to H₂S at airborne concentrations above 10 ppm has been associated with the development of conjunctivitis and keratitis.⁵ One-hour exposure to H₂S 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 H₂S 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 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

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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.⁹ 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 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 H₂S is a 10-minute ceiling concentration of 10 ppm.² 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 10-minute ceiling concentration of 20 ppm or a maximum allowable peak of 50 ppm for 10-minutes once, if no other measurable exposures occur.⁴ 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 Gramnegative 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

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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 (FEV₁), 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 occupation 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). Castellan ¹⁵ has reported a calculated zero pulmonary function effect level for endotoxin of 90 EU/m³.

Bioaerosols in Sewage Treatment Plants

Laitinen et al¹⁶ reported endotoxin concentrations that varied from 0.6 to 310 ng/m³ (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 10² to 10⁵ colony-forming units per cubic meter of air (CFU/m³). The correlation between the bacterial counts and endotoxin concentrations was 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/m³ (1.2 to 4200 EU/m³). Air concentrations of culturable bacteria ranged from 10 to 10⁵ CFU/m³. 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 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 $6.9 \times 10^6 \text{ CFU/m}^3$, with a median concentration of $3.3 \times 10^5 \text{ CFU/m}^3$. Rodshaped bacteria levels ranged from ND to 4.3×10^6 CFU/m³, median 8.1×10^4 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

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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. 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. 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.

Silica (Amorphous, Quartz, Cristobalite)

Amorphous silica does not have a crystalline lattice molecular configuration. Historical toxicity evaluations of amorphous silica suggest that it is of low toxicity, and it has not been reported to produce fibrotic nodules in lung tissue (characteristic of crystalline silica exposure). The NIOSH REL for exposure to amorphous silica is a full-shift, total particulate TWA of 6 mg/m³, providing the silica contains less than 1% crystalline forms. The OSHA PEL is consistent with this NIOSH REL. The ACGIH TLV for amorphous silica containing less than 1% crystalline silica is 10 mg/m³, total particulate TWA over eight hours and a respirable particulate TWA of 3 mg/m³.

Crystalline silica (quartz) and cristobalite have been associated with silicosis, a fibrotic disease of the lung caused by the deposition of fine particles of crystalline silica in the lungs. Symptoms usually develop insidiously, with cough, shortness of breath, chest pain, weakness, wheezing, and non-specific chest illnesses. Silicosis usually occurs after years of exposure,

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but may appear in a shorter period of time if exposure concentrations are very high. The NIOSH RELs for respirable quartz and cristobalite are $50 \,\mu\text{g/m}^3$, as TWAs, for up to 10 hours per day during a 40-hour work week.² These RELs are intended to prevent silicosis. However, evidence indicates that crystalline silica is a potential occupational carcinogen and NIOSH is currently reviewing the data on carcinogenicity.²⁴⁻²⁷ The OSHA PELs and the ACGIH TLVs for respirable quartz and cristobalite are 100 and $50 \,\mu\text{g/m}^3$, as 8-hour TWAs, respectively.

RESULTS AND DISCUSSION

Thirteen PBZ air samples were collected for H₂S using the Toxilog monitors. The monitors recorded the H₂S concentration once a minute throughout the shift, and these data were then downloaded to a computer. A summary of these data are shown in Table 1. The maximum H₂S concentration measured on a worker was 124 ppm. This concentration was measured on a mechanic who was repairing the ash belt press. The maximum 10-minute average H₂S concentration for this mechanic was 95 ppm, and the 8-hour TWA H_2S concentration was 16 ppm. The belt press operators' maximum 10-minute average H₂S concentrations for the three days of sampling were 27, 28, and 19 ppm. The monitor malfunctioned on the third day at 10:16 a.m., therefore this sample was not collected over the full-shift. These 10-minute average H₂S concentrations as well as the one for the mechanic exceeded the NIOSH 10-minute average ceiling REL of 10 ppm and were near or above the OSHA 10-minute average ceiling PEL of 20 ppm. The three maximum 10-minute average H₂S PBZ concentrations for the LPO operator were 18, 17, and 10 ppm; these concentrations were at or exceeded the NIOSH H₂S ceiling REL. The maximum 10-minute average H₂S concentrations for the head operator were 0.1, 5.0, and 16 ppm; the H₂S concentration on August 4th exceeded the NIOSH ceiling REL. The maximum 10-minute average H₂S concentrations for the Outside Operator were 1.0, 0.7, and 1.1 ppm, with all concentrations below applicable guidelines and standards.

Six general area air samples were collected for H₂S using the PhD monitors. The PhD monitors recorded the H₂S concentration once a minute throughout the work shift. Following the sampling shift, these data were then down loaded to the computer. A summary of these data are shown in Table 2. General area air samples were collected for H₂S in the belt press room, LPO boiler room, anaerobic building, and polymer pit. The general area air samples collected in the belt press room were collected on the cat-walk between #5 gravity concentrator and #1 belt press on the first two days of sampling and on the floor between #1 and #2 gravity concentrators on the third day of sampling. The maximum 10-minute average H₂S concentrations in the belt press room for the three days were 46, 51, and 69 ppm, respectively. Any worker spending at least tenminutes at these locations would potentially be exposed to H₂S concentrations in excess of the OSHA PEL and NIOSH REL. The belt press operator and the mechanic (Wednesday only) spent a significant portion of their work day in these locations. The maximum 10-minute average H₂S concentrations for the LPO boiler room, anaerobic building, and polymer pit were ND, ND, and 0.1 ppm, respectively.

The results of five PBZ air samples collected and analyzed for total particulate and endotoxin are listed in Table 3. The belt press operator had PBZ air sample concentrations of 0.12 and

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0.07 mg/m³ for total particulate and 2.75 and 6.82 EU/m³ for endotoxin. The LPO operator had PBZ air sample concentrations of 0.03 and 0.28 mg/m³ for total particulate and 3.55 and 2.67 EU/m³ for endotoxin. The outside operator had a PBZ air sample concentration of 0.16 mg/m³ for total particulate and 2.59 EU/m³ for endotoxin. None of these results exceeded any evaluation criteria, where applicable, and all exposures are considered very low. All the PBZ endotoxin air sample concentrations were well below 90 EU/m³, calculated by Castellan to be zero pulmonary function effects level. 15 The results of seven general area air samples which were collected and analyzed for total particulate and endotoxin are listed in Table 4. The general area air samples were collected in the belt press room, LPO boiler room, control room, anaerobic building, and polymer pit. Three general area air samples were collected in the belt press room for total particulate and endotoxin. Total particulate concentrations ranged from 0.11 to 0.19 mg/m³. All general area air sample results for total particulate were very low. The three air sample results for endotoxin collected in the belt press room were 4.45, 6.27, and 54.7 EU/m³. Endotoxin concentrations in the LPO boiler room, control room, anaerobic building, and polymer pit were 5.27, 2.23, 2.03, and 2.39 EU/m³, respectively. All general area air sample results for endotoxin were considered low except for the concentration measured between the #1 and #2 concentrator, which was 54.7 EU/m³. This concentration of endotoxin is approximately 60% of the concentration calculated to be the zero pulmonary function effects level of 90 EU/m³. 15

The results of the qualitative analyses for VOCs in the headspace air of the sewage sludge samples collected at various steps in the dewatering process are listed in Table 5. Major compounds found in the sludge headspace samples were toluene, limonene, C_{10} - C_{14} aliphatic hydrocarbons, cyclopentanone, methyl ethyl ketone, and acetone. Other compounds detected included alcohols (methanol, ethanol, and butanols), C_5 - C_{11} aliphatic ketones, furans, acetic acid, and a few fatty acids. Overall, the belt press output sludge produced the highest concentrations and the largest variety of VOCs. The headspace of the belt press feed sludge bulk samples contained similar compounds as identified in the belt press output sludge. Toluene was the major VOC detected in the headspace samples collected from both the concentrator feed and output sludge bulk samples.

General area and PBZ air sample results for VOCs are shown in Table 6. Qualitative sample results showed toluene, limonene, and various aliphatic hydrocarbons, mainly in the C_{10} - C_{14} range, were the major compounds identified, these sample results were similar to the headspace sewage sludge sample results shown in Table 5. Traces of acetone, isopropanol, methyl ethyl ketone, furan, 1,1,1-trichloroethane, and other ketones and alkyl furans were also detected on some samples.

Four full-shift PBZ charcoal tube air samples were collected and analyzed quantitatively for toluene, limonene, and total hydrocarbons (total hydrocarbon analyses were performed against standards of n-dodecane). These results are listed in Table 7. The PBZ air sample results for toluene ranged from trace (between 0.003 and 0.009 ppm) to 0.06 ppm. All the toluene concentrations were well below the NIOSH REL-TWA of 100 ppm and the OSHA PEL-TWA of 200 ppm. The PBZ air sample results for limonene ranged from trace (between 0.002 and

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0.006 ppm) to 0.05 ppm. There are no occupational exposure limits for limonene. The PBZ air sample results for total hydrocarbons ranged from non-detectable (ND) (less than 0.04 ppm) to trace (between 0.04 and 0.14 ppm). The molecular weight of n-dodecane, 170.34 g/mole, was used to calculate air concentrations for total hydrocarbons. There are no evaluation criteria with which to compare these results, however the concentrations detected are all very low.

Eight general area air samples were collected and analyzed for toluene, limonene, and total hydrocarbons, and the results are listed in Table 8. Three of these general area air samples were collected in the belt press room, two in the control room, and one each in the LPO boiler room, anaerobic building, and the polymer pit. Overall the concentrations of toluene, limonene, and total hydrocarbons were very low, ranging from ND to 0.4 ppm, well below existing occupational exposure limits.

Bulk sewage sludge samples collected from various points in the dewatering process and incinerator ash collected from the ash dumpster were analyzed for elemental composition. The results of these elemental analyses are listed in Table 9. On each of the three sampling days, bulk samples of sewage sludge were collected from the gravity concentrator feed, gravity concentrator output, belt press feed, and belt press output, and incinerator ash samples were collected from the incinerator ash dumpster. Detectable concentrations of 23 different elements were found in some of the sludge and ash samples. The elements not detected in any of the bulk samples were Be, Cd, Co, Se, Te, Tl, and Y. As expected, higher concentration of elements were found in the incinerator ash when compared to belt press output sludge samples which were higher than concentrator output samples. The eight most abundant elements present in descending concentrations in the sludge samples were Al, Ca, Fe, P, Mg, Na, Ba, and Cu. The most abundant elements present in descending concentration in the ash samples were P, Al, Ca, Fe, Mg, Na, Zn, and Ba.

General area air samples for metals were collected near the incinerator ash dumpster and between the conveyor belts used to move wet ash from the bottom of the incinerator to the ash belt press and sludge from the belt press to the incinerator. The metals analyzed for included Pb, Cr, Al, Ag, Zn, Cu, As, Be, Cd, Sb, Se, and Ti. The minimum detectable concentration for these metals ranges from 0.1 to $10~\mu g/m^3$. None of the samples contained detectable concentrations of these metals except a trace concentration of Zn (between 0.9 and $3.0~\mu g/m^3$) was measured in the general area air sample collected between the ash and sludge conveyors on the second day of sampling.

The incinerator ash samples were also analyzed for silica content. For the three days of sampling the silica contents were 3.16, 4.70, and 5.19%. Six general area air samples were collected and analyzed for respirable particulate, respirable quartz, and respirable cristobalite. These samples

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were collected near the incinerator ash dumpster and between the conveyors moving incinerator ash from the bottom of the incinerator to the ash belt press and sludge from the belt press to the incinerator. The results for these samples are shown in Table 10. The respirable particulate concentrations ranged from 0.01 to 0.08 mg/m³. No detectable concentrations of quartz or cristobalite were measured in these samples.

CONCLUSIONS

Eight of the 13 PBZ air samples for H₂S had maximum 10-minute concentrations exceeding the NIOSH ceiling REL of 10 ppm, and four of these results exceeded the OSHA ceiling PEL of 20 ppm. The results indicate that workers were overexposed to H₂S on the days of sampling. In examining the general area air sampling results for H₂S, all maximum 10-minute sample results from the belt press room exceeded both NIOSH and OSHA occupational exposure limits for H₂S while none of the measurements for H₂S made in other areas of the plant exceeded these levels. This indicates that significant exposure to H₂S occurs in the belt press room. Workers reported health complaints including gastrointestinal disturbances, sore throats, fatigue, headaches, eye irritation, coughing, and hoarseness. Many of these symptoms have been associated with exposure to H₂S.⁵

PBZ air sample results for endotoxin were low with no concentrations approaching those previously associated with adverse health effects. Rylander reported airway inflammation with increased airway reactivity with endotoxin concentrations of $200 \, \text{EU/m}^3$. Castellan at al calculated a zero-change FEV threshold for endotoxin of $90 \, \text{EU/m}^3$. One area air sample collected between #1 and #2 concentrators had an endotoxin concentration of $54.7 \, \text{EU/m}^3$, which is approximately 60% of $90 \, \text{EU/m}^3$.

Analyses of the headspace air above the sludge samples indicated that a wide variety of VOCs were present. Analysis of charcoal tube air samples showed that similar VOCs were present. However, the quantitative air sample results for toluene, limonene, and total hydrocarbons (the major compounds detected) indicated their presence at trace or very low levels, below those expected to cause adverse health effects. Analyses of the ash for silica content showed that the percent silica in the ash ranged from 3.16 to 5.19%. Respirable particulate concentrations, in areas where the ash was present, ranged from 0.01 to 0.08 mg/m³. Quartz and cristobalite were not detected in the area air samples.

The sludge and ash samples contained 22 different elements (including such metals as Cu, Li, Mg Ni, and Pb). However, none of the area air samples contained quantifiable levels of these or other metals indicating that current procedures used to handle sludge and ash do not pose a hazard with respect to inhalation of these elements.

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RECOMMENDATIONS

- 1. Operators working in the belt press room where the airborne H₂S concentrations approach 10 ppm or higher should wear continuous direct-reading monitors so that they can be aware of the H₂S concentration at all times. These monitors should be maintained and calibrated according to manufacturers specifications. In addition, a continuous area air monitor for H₂S should be installed in the belt press room. Continuous monitoring is recommended when there is a potential for exposure to H₂S at a concentration of 50 ppm or higher. Concentrations exceeding 50 ppm were measured in the belt press room during this survey.
- 2. Engineering controls such as the addition of a ventilation system designed to keep H₂S levels below the NIOSH ceiling REL of 10 ppm in the belt press room should be designed and installed.
- 3. 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 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 may be 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 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 selfcontained 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. 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.²⁹ A complete respiratory protection program must be implemented and must fulfill all requirements of 29 CFR 1910.134.30 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.³²

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4. 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 force 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.

- 5. Operating procedures, such as the length of time sludge is held before being incinerated, should be investigated to determine if there are operations which may reduce the amount of H₂S being produced or emitted into the workplace.
- 6. When workers are hosing down the belt press room floor or unplugging drains, faceshields or goggles should be worn to protect against splashing of sludge in the face.

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- 2. Project Engineer, Little Blue Valley Sewer District
- 3. 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.

Table 1 Personal Breathing Zone Air Sample Results for Hydrogen Sulfide Little Blue Valley Sewer District Independence, Missouri HETA 94-0182

Sample Date	Job Title	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)
8/2/94	Belt Press Operator	436	27	4.7	4.8	44
8/3/94	Belt Press Operator	451	28	7.1	7.0	49
8/4/94	Belt Press Operator	120	19	5.0	4.6	29
8/2/94	Head Operator	456	0.1	ND	ND	1.0
8/3/94	Head Operator	477	5.0	0.2	0.2	11
8/4/94	Head Operator	472	16	0.5	0.5	21
8/2/94	LPO Operator	452	18	0.4	0.4	36
8/3/94	LPO Operator	451	17	0.4	0.4	51
8/4/94	LPO Operator	476	10	0.2	0.2	21
8/2/94	Outside Operator	409	1.0	0.1	0.1	3.0
8/3/94	Outside Operator	463	0.7	0.1	0.1	3.0
8/4/94	Outside Operator	473	1.1	0.1	0.1	8.0
8/3/94	Mechanic	449	95	16	16	124

 H_2S = hydrogen sulfide ppm = parts per million TWA = time-weighted average

STEL = short term exposure limit

LPO = low pressure oxidation ND = non-detectable

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_2 S TLV = 10 ppm TWA; 15 ppm STEL (15-min.)

Table 2 Area Air Sample Results for Hydrogen Sulfide Little Blue Valley Sewer District Independence, Missouri HETA 94-0182

Sample Date	Sample Site	Sample Time (min.)	Max. 10-min. H ₂ S Conc. (ppm)	Mean 10-min. H ₂ S Conc. (ppm)	TWA H_2S Conc. (ppm)	Max. H_2S Conc. (ppm)
8/2/94	Belt press room	387	46	17	17	48
8/3/94	Belt press room	340	51	24	25	59
8/4/94	Belt press room	428	69	52	51	78
8/2/94	LPO boiler room	375	ND	ND	ND	ND
8/3/94	Anaerobic building	425	ND	ND	ND	ND
8/4/94	Polymer pit	419	0.1	ND	ND	1.0

 H_2S = hydrogen sulfide

TWA = time-weighted average

STEL = short term exposure limit

ppm = parts per million

LPO = low pressure oxidation

ND = non-detectable

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_2 S TLV = 10 ppm TWA; 15 ppm STEL (15-min.)

Table 3 Personal Breathing Zone Sample Results for Total Particulate and Endotoxin Little Blue Valley Sewer District Independence, Missouri HETA 94-0182

Sample Date	Job Title	Sample Time (min.)	Air Sample Volume (liters)	Total Particulate Conc. (mg/m ³)	Endotoxin Conc. (EU/m³)
8/2/94	Belt Press Operator	436	654	0.12	2.75
8/4/94	Belt Press Operator	450	675	0.07	6.82
8/2/94	LPO Operator	451	676	0.03	3.55
8/4/94	LPO Operator	475	713	0.28	2.67
8/3/94	Outside Operator	463	695	0.16	2.59

LPO = low pressure oxidation

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

 EU/m^3 = endotoxin unit per cubic meter

OSHA Total Particulate PEL = 15 mg/m³ TWA

ACGIH Total Particulate TLV = 10 mg/m³ TWA

No occupational exposure criteria have established for bacterial endotoxin by either NIOSH, OSHA, or ACGIH. Castellan¹⁵ has calculated a zero pulmonary function effects level for endotoxin of 90 EU/m³.

TWA = time-weighted average

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

Table 4 Area Air Sample Results for Total Particulate and Endotoxin Little Blue Valley Sewer District Independence, Missouri HETA 94-0182

Sample Date	Sample Site	Sample Time (min.)	Air Sample Volume (liter)	Total Particulate Conc. (mg/m³)	Endotoxin Conc. (EU/m³)
8/2/94	Belt press room (between #5 concentrator & #1 belt press)	389	584	0.15	4.45
8/3/94	Belt press room (between #5 concentrator & #1 belt press)	436	654	0.11	6.27
8/4/94	Belt press room (between #1 & #2 concentrators)	419	629	0.19	54.7
8/2/94	LPO boiler room (on top of Clayton boiler)	367	550	0.07	5.27
8/3/94	Control room	419	629	0.11	2.23
8/3/94	Anaerobic building (in the middle of the main room)	425	638	0.03	2.03
8/4/94	Polymer pit (next to #1 mixing tank)	419	629	0.05	2.39

LPO = low pressure oxidation

TWA = time-weighted average

mg/m³ = milligrams per cubic meter

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

 EU/m^3 = endotoxin unit per cubic meter

OSHA Total Particulate PEL = $15 \text{ mg/m}^3 \text{ TWA}$

ACGIH Total Particulate TLV = 10 mg/m³ TWA

No occupational exposure criteria have been established for bacterial endotoxin by either NIOSH, OSHA, or ACGIH. Castellan¹⁵ has calculated a zero pulmonary function effects level for endotoxin of 90 EU/m³.

Identification of Headspace Volatile Organic Compounds in Sewage Sludge Little Blue Valley Sewer District Independence, Missouri

HETA 94-0182

Sample Date		nple iption		Headspace Volatile Organic Compounds Present	
8/2/94	Feed to concentrate	ors, 1% solids	1,6,25		
8/3/94	Feed to concentrate	ors, 1% solids	25,42		
8/4/94	Feed to concentrate	ors, 1% solids	6,7,9,19,36,	,42	
8/2/94	Output from conce	ntrators, 5% solids	1,5,6,25,34		
8/3/94	Output from conce	ntrators, 5% solids	19,22,25,18	3,38,42	
8/4/94	Output from conce	ntrators, 5% solids	1,19,25,38		
8/2/94	Feed to belt press,	5% solids	1,3,8,7,11,1	2,14,19,23-28,29,32,33,38,39,42,45	
8/3/94	Feed to belt press,	5% solids	6,11,22,25,26,28,32,38,39,42		
8/4/94	Feed to belt press,	5% solids	1,3,5,6,7,11,12,14,19,20,22,25-28,29,32,33,39,42		
8/2/94	Belt press output, 4	40% solids	1-8,11-15,17-20,22,23,25-28,29-35,37,39-44,46		
8/3/94	Belt press output, 4	40% solids	4,6,8,11,14,16,17,19,21,22,25,28,30,32-34,39,41,43-45		
8/4/94	Belt press output, 4	40% solids	6,8,10,11,14,19,22,25-28,29,32-34,39,41,43,44,46		
2 = Ace 3 = Met 4 = Bute 5 = Etha 6 = Ace 7 = Isop 8 = Fura 9 = Met 10 = 1-Pr	1 = Formaldehyde 17 = n-Butanol 2 = Acetaldehyde 18 = 2-Pentanon 3 = Methanol 19 = Acetic acid 4 = Butene 20 = 3-Methyl-1 5 = Ethanol 21 = 2-Ethyl furz 6 = Acetone 22 = Propanoic a 7 = Isopropanol 23 = Dimethyl so 8 = Furan 24 = Methyl program 9 = Methylene chloride 25 = Toluene 10 = 1-Propanol 26 = Cyclopenta		n rid fide anoic acid one	33 = 2-Pentyl furan 34 = C ₁₀ -C ₁₄ aliphatic hydrocarbons, terpenes, methyl decalin, C ₉ H ₁₂ alkyl benzenes 35 = n-Decane 36 = Octamethylcyclotetrasiloxane 37 = Limonene 38 = Cresol isomer 39 = 2-Nonanone 39 = 2-Nonanone 40 = Hexyl furan	
11 = Met	hyl ethyl ketone	27 = 2-Hexanone	(MBK)	41 = n-Undecane	

42 = Decamethylcyclopentasiloxane

43 = n-Dodecane

44 = n-Tridecane

45 = Undecanone

46 = n-Tetradecane

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28 = Fatty acids/esters

32 = Methyl heptanones

29 = 2-Heptanone

30 = 2-Butyl furan

31 = n-Nonane

12 = 2-Butanol

13 = 2-Methyl furan

15 = Vinyl acetate

16 = Formic acid

14 = 2- Methyl-1-propanol

Identification of Volatile Organic Compounds in Personal Breathing Zone and

Area Air Samples

Little Blue Valley Sewer District Independence, Missouri HETA 94-0182

Sample Date	Sample Description	Volatile Organic Compounds Present
8/2/94	Outside Operator	3,6,7,8,9,14
8/4/94	Outside Operator	6,8,12,13,14,18
8/3/94	LPO Operator	1,3,8,14,16,18,19
8/3/94	Belt Press Operator	2,8,14,16,18,19,20,21
8/2/94	Control room near Head Operator	3,8,14
8/4/94	Control room near Head Operator	8,13,14,17
8/2/94	Belt press room between #5 concentrator & #1 belt press	2,3,4,5,8,10,11,16,18,19,20,21
8/3/94	Belt press room between #5 concentrator & #1 belt press	2,5,8,11,15,16,18,18,20,21
8/4/94	Belt press room between #1 & #2 concentrators	8,16,18,19,20,21
8/2/94	LPO boiler room on top of Clayton boiler	8
8/3/94	Anaerobic building	8
8/3/94	Polymer pit near #1 mixing tank	6,8,16,18,19,20,21

1 = Butane 8 = Toluene 15 = Ketone (nonanone)

2 = Acetone $9 = C_8$ alkanes 16 = n-Undecane

3 = Isopropanol 10 = Ketone (methyl heptanone) 17 = Decamethylcyclopentasiloxane

4 = Furan 11 = Pentyl furan 18 = n-Dodecane 5 = Methyl ethyl ketone 12 = Xylenes/ethyl benzene 19 = n-Tridecane 13 = Pinene 13 = Pinene 20 = n-Tetracane 14 = Limonene $21 = C_{10}-C_{14}$ aliphatics

LPO = low pressure oxidation

Personal Breathing Zone Air Sample Results for Toluene, Limonene, and Total Hydrocarbons

Little Blue Valley Sewer District Independence, Missouri HETA 94-0182

Sample Date	Job Title	Sample Time (min.)	Sample Volume (liters)	Toluene Conc. (ppm)	Limonene Conc. (ppm)	Total Hydrocarbons Conc. (ppm)
8/2/94	Outside Operator	458	91.6	0.01	0.05	trace
8/4/94	Outside Operator	448	89.6	trace	0.05	ND
8/3/94	Belt Press Operator	451	90.2	0.06	0.03	trace
8/3/94	LPO Operator	452	90.4	trace	trace	ND

ppm = parts per million

LPO = low pressure oxidation

trace = trace concentration (between MDC and MQC)

ND = non-detectable concentration, less than MDC

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

Toluene: MDC = 0.003 ppm; MQC = 0.009 ppm Limonene: MDC = 0.002 ppm; MQC = 0.006 ppm

Total Hydrocarbons: MDC = 0.04 ppm; MQC = 0.14 ppm

Total Hydrocarbons analyses were performed against standards of n-dodecane.

NIOSH toluene REL = 100 ppm TWA; 150 ppm STEL (15-min.) OSHA toluene PEL = 200 ppm TWA, 300 ppm ceiling (10-min.)

ACGIH toluene TLV = 50 ppm TWA

No occupation exposure criteria have been established for limonene or total hydrocarbons by either NIOSH, OSHA, or ACGIH.

Table 8 Area Air Sample Results for Toluene, Limonene, and Total Hydrocarbons

Little Blue Valley Sewer District Independence, Missouri HETA 94-0182

Sample Date	Sample Site	Sample Time (min.)	Sample Volume (liters)	Toluene Conc. (ppm)	Limonene Conc. (ppm)	Total Hydrocarbons Conc. (ppm)
8/2/94	Belt press room between #5 concentrator & #1 belt press	387	77.4	0.09	trace	trace
8/3/94	Belt press room between #5 concentrator & #1 belt press	436	87.2	0.10	ND	trace
8/4/94	Belt press room between #1 and #2 concentrators	309	61.8	0.39	ND	0.3
8/2/94	Control room near Head Operator	458	91.6	trace	0.09	ND
8/4/94	Control room near Head Operator	472	94.4	trace	0.12	ND
8/2/94	LPO boiler room on top of Clayton boiler	376	75.2	trace	ND	ND
8/3/94	Anaerobic building in the middle of the main room	425	85.0	trace	ND	ND
8/4/9	Polymer pit near #1 mixing tank	419	83.3	trace	ND	0.39

ppm = parts per million

trace = trace concentration (between the MDC and MQC)

ND = non-detectable concentration, less than the MDC

Toluene: MDC= 0.003 ppm; MQC = 0.009 ppm

Total Hydrocarbons: MDC = 0.04 ppm; MQC = 0.14 ppm

Total Hydrocarbons analyses were performed against standards of n-dodecane

NIOSH toluene REL = 100 ppm TWA; 150 ppm STEL (15-min.)

OSHA toluene PEL = 200 ppm TWA, 300 ppm ceiling (10-min.)

ACGIH toluene TLV = 50 ppm TWA

No occupation exposure criteria have been established for limonene or total hydrocarbons by either NIOSH,

OSHA, or ACGIH.

LPO = low pressure oxidation

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

MQC = minimum quantifiable concentrations, assuming

an air sample volume of 96 liters

Limonene: MDC = 0.002 ppm; MQC = 0.006 ppm

Elemental Analysis Results for Sewage Sludge and Incinerator Ash Little Blue Valley Sewer District Independence, Missouri HETA 94-0182

		Element Concentration (µg/gram of sample)							
Sample Date	Sample Description	Ag	Al	As	Ba	Ca	Cr	Cu	Fe
8/2/94	Concentrator feed, 1% solids	ND	240	ND	6.2	392	ND	4.4	158
8/3/94	Concentrator feed, 1% solids	ND	281	ND	7.5	441	ND	5.6	180
8/4/94	Concentrator feed, 1% solids	ND	275	ND	7.2	432	ND	4.6	184
8/2/94	Concentrator output, 5% solids	ND	310	ND	8.1	487	ND	5.3	196
8/3/94	Concentrator output, 5% solids	1.5	384	ND	10.8	586	ND	6.9	251
8/4/94	Concentrator output, 5% solids	1.5	375	ND	10.2	559	ND	6.5	242
8/2/94	Belt press feed, %5 solids	19.6	5456	ND	147	5147	11.4	73.4	3603
8/3/94	Belt press feed, %5 solids	18.7	5016	ND	149	5105	9.4	70.1	3358
8/4/94	Belt press feed, %5 solids	17.2	4581	ND	133	4739	8.5	64.6	3080
8/2/94	Belt press output, 40% solids	54.1	15040	7.0	433	14646	30.3	204	10168
8/3/94	Belt press output, 40% solids	48.2	13334	6.0	376	12390	24.4	176	8612
8/4/94	Belt press output, 40% solids	53.8	14316	ND	410	13836	27.0	198	9166
8/2/94	Wet incinerator ash	51.2	27427	ND	604	29851	51.3	282	38374
8/3/94	Wet incinerator ash	76.9	35481	ND	898	29157	76.0	370	25647
8/4/94	Wet incinerator ash	78.0	33582	ND	893	29876	68.1	383	23016

Ag = silver; Al = aluminum; As = arsenic; Ba = barium; Ca = calcium; Cr = chromium; Cu = copper;

Fe = iron; ND = non-detectable

Table 9 Cont.

Elemental Analysis Results for Sewage Sludge and Incinerator Ash Little Blue Valley Sewer District Independence, Missouri HETA 94-0182

G 1		Element Concentration (µg/gram of sample)							
Sample Date	Sample Description	La	Li	Mg	Mn	Mo	Na	Ni	P
8/2/94	Concentrator feed, 1% solids	ND	ND	68.8	12	1.7	324	ND	396
8/3/94	Concentrator feed, 1% solids	ND	ND	77.5	13	1.7	337	ND	468
8/4/94	Concentrator feed, 1% solids	ND	ND	72.9	11	2.2	287	ND	456
8/2/94	Concentrator output, 5% solids	ND	ND	86.1	14	1.4	328	ND	546
8/3/94	Concentrator output, 5% solids	ND	ND	104	18	ND	335	ND	686
8/4/94	Concentrator output, 5% solids	ND	ND	90.7	15	2.2	295	ND	603
8/2/94	Belt press feed, %5 solids	ND	ND	2157	415	45.4	594	16.9	19760
8/3/94	Belt press feed, %5 solids	ND	ND	1861	372	35.6	575	14.8	17613
8/4/94	Belt press feed, %5 solids	ND	ND	2020	435	42.8	626	15.7	20014
8/2/94	Belt press output, 40% solids	ND	ND	830	146	24.7	423	ND	6829
8/3/94	Belt press output, 40% solids	ND	ND	815	147	20.8	552	5.2	6902
8/4/94	Belt press output, 40% solids	ND	ND	717	146	14.3	413	ND	6510
8/2/94	Wet incinerator ash	27.3	ND	3602	665	57.7	2269	56.9	30089
8/3/94	Wet incinerator ash	27.2	ND	4405	839	89.9	2445	49.6	42716
8/4/94	Wet incinerator ash	25.3	10	4318	880	84.7	2220	47.8	43671

 $La = lanthanum; \quad Li = lithium; \quad Mg = magnesium; \quad Mn = manganese; \quad Mo = molybdenum; \quad Na = sodium;$

Ni = nickel; P = phosphorus; ND = non-detectable

Table 9 Cont.

Elemental Analysis Results for Sewage Sludge and Incinerator Ash Little Blue Valley Sewer District Independence, Missouri

HETA 94-0182

G 1		Elemental Concentration (µg/gram of sample)							
Sample Date	Sample Description	Pb	Sb	Sr	Ti	V	Zn	Zr	LOD
8/2/94	Concentrator feed, 1% solids	0.9	ND	3.5	2.4	ND	11.7	ND	1.1
8/3/94	Concentrator feed, 1% solids	1.0	ND	4.0	2.4	ND	94.2	ND	1.1
8/4/94	Concentrator feed, 1% solids	1.0	ND	3.7	2.3	ND	9.5	ND	1.2
8/2/94	Concentrator output, 5% solids	1.2	ND	4.2	2.6	ND	10.7	ND	1.3
8/3/94	Concentrator output, 5% solids	1.7	ND	5.3	2.8	ND	13.5	ND	1.3
8/4/94	Concentrator output, 5% solids	1.3	ND	4.9	3.3	ND	12.9	ND	1.3
8/2/94	Belt press feed, %5 solids	87.1	ND	144	156	ND	509	49.2	12.0
8/3/94	Belt press feed, %5 solids	67.8	ND	129	141	ND	432	44.6	10.0
8/4/94	Belt press feed, %5 solids	65.5	12.5	145	145	ND	457	46.4	11.4
8/2/94	Belt press output, 40% solids	24.1	ND	50.3	65.2	ND	181	12.6	7.0
8/3/94	Belt press output, 40% solids	25.5	ND	51.3	44.3	ND	169	19.2	4.0
8/4/94	Belt press output, 40% solids	19.5	ND	49.1	50.8	ND	147	14.2	5.0
8/2/94	Wet incinerator ash	126	50.7	223	618	17.7	994	43.0	11.7
8/3/94	Wet incinerator ash	155	21.9	293	425	20.0	1102	58.1	11.5
8/4/94	Wet incinerator ash	144	26.9	303	338	17.0	1024	54.3	10.4

 $Pb = lead; \quad Sb = antimony; \quad Se = selenium; \quad Sr = strontium; \quad Ti = titanium; \quad V = vanadium; \quad Zn = zinc; \\$

Table 10 Area Air Sample Results for Respirable Particulate, Quartz, and Cristobalite Little Blue Valley Sewer District Independence, Missouri HETA 94-0182

Sample Date	Sample Site	Sample Time (min.)	Sample Volume (liters)	Respir. Part. Conc. (mg/m³)	Respir. Quartz Conc. (mg/m³)	Respir. Cristobalite Conc. (mg/m³)
8/2/94	Between sludge & ash conveyors	369	627	0.04	ND	ND
8/2/94	Near wet ash dumpster	344	585	0.03	ND	ND
8/3/94	Between sludge & ash conveyors	428	728	0.08	ND	ND
8/3/94	Near wet ash dumpster	437	743	0.04	ND	ND
8/4/94	Between sludge & ash conveyors	405	689	0.04	ND	ND
8/4/94	Near wet ash dumpster	425	723	0.01	ND	ND

 mg/m^3 = milligrams per cubic meter of air ND = non-detectable sample results, less than MDC Respirable dust: MDC = 0.01 mg/m^3 ; MQC = 0.02 mg/m^3 Respirable Quartz = MDC = 0.01 mg/m^3 ; MQC = 0.04 mg/m^3 Respirable Cristobalite = MDC 0.02 mg/m^3 ; MQC = 0.04 mg/m^3 NIOSH silica, amorphous, REL = 6 mg/m^3 TWA NIOSH silica, quartz, REL = 0.05 mg/m^3 TWA

NIOSH silica, cristobalite, REL = $0.05 \text{ mg/m}^3 \text{ TWA}$ OSHA silica, amorphous, PEL = $80 \text{ mg/m}^3 \text{ %SiO}_2 \text{ TWA}$ OSHA silica, quartz, PEL = $10 \text{ mg/m}^3 \text{ %SiO}_2 + 2 \text{ TWA}$ OSHA silica, cristobalite, PEL = $5 \text{ mg/m}^3 \text{ %SiO}_2 + 2 \text{ TWA}$ ACGIH silica, amorphous, TLV = $3 \text{ mg/m}^3 \text{ TWA}$ ACGIH silica, quartz, TLV = $0.1 \text{ mg/m}^3 \text{ TWA}$ ACGIH silica, cristobalite, TLV = $0.05 \text{ mg/m}^3 \text{ TWA}$