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HETA 96–0089–2657
Agrium, Inc. (Formerly Cominco Fertilizers)
Beatrice, Nebraska

Gregory M. Kinnes
Kevin W. Hanley

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 any employer 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.

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ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Gregory M. Kinnes and Kevin W. Hanley, of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Desktop publishing by Ellen E. Blythe.

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Health Hazard Evaluation Report 96–0089–2657
Agrium, Inc. (Formerly Cominco Fertilizers)
Beatrice, Nebraska
October 1997

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SUMMARY

On February 21, 1996, the National Institute for Occupational Safety and Health (NIOSH) received a request for a health hazard evaluation (HHE) from the International Chemical Workers Union (ICWU) on behalf of members employed at Agrium U.S., Incorporated, Homestead Nitrogen Operations (formerly Cominco Fertilizers, Inc.), located in Beatrice, Nebraska. The request concerned the adverse employee health effects attributed to exposure to the chemical additives used in the boiler feed water. Prior to this investigation, the use of alternative chemical additives was initiated in an effort to eliminate the problem. Therefore, environmental sampling for the constituents of the additives that were eliminated could not be conducted. Two of these additives contained diethylhydroxylamine, N–isopropylhydroxylamine, cyclohexylamine (CHA), and diethylaminoethanol (DEAE). As a result of the use of alternative chemical additives, most of the employee symptoms had been alleviated at the time of the NIOSH investigation. However, the union was still concerned about potential employee exposures to oxides of nitrogen (NO_x), components of the new additives, and other compounds present during this manufacturing process. On April 8–9, 1996, investigators from NIOSH visited the Agrium facility and evaluated potential employee exposures to NO_x, nitrosamines, ammonia, inorganic acids, and volatile organic compounds (VOCs) in the boiler house and nitric acid plant.

Adjacent full shift samples for nitrogen dioxide (NO_2) and nitric oxide (NO) were collected using two different analytical methods at eight locations in the acid plant. The NO_2 concentrations ranged from 0.09 to 9.7 parts per million (ppm) using an active sampling method with triethanolamine–treated sorbent tubes (NIOSH Method #6014) and from 0.09 to 5.8 ppm using a passive sampling method with Palmes tubes (NIOSH Method #6700). Airborne concentrations of NO ranged from 0.02 to 8.7 ppm and from 0.06 to 11 ppm using the sorbent and Palmes tubes, respectively. Two personal breathing zone (PBZ) samples were also collected on the acid plant operators using the active sampling method. The NO_2 concentrations for these samples were 0.41 and 0.28 ppm, while the respective NO concentrations for these samples were 0.45 and 0.20 ppm.

One of the area samples had NO_2 concentrations, measured by both methods, which exceeded the 5 ppm ceiling limit established by the Occupational Safety and Health Administration (OSHA). In addition, the area samples also indicated that airborne NO_2 concentrations can exceed both the NIOSH short–term exposure limit (STEL) of 1 ppm and the 5 ppm STEL established by the American Conference of Governmental Industrial Hygienists (ACGIH). Although these area samples were collected during the course of a full shift, the time–weighted average (TWA) concentrations still exceeded the exposure limits established to prevent symptoms from short–duration peak exposures. Therefore, NO_2 concentrations must have exceeded these criteria at some point during the sampling period.

Since one of the replacement boiler feed water additives being used at the time of this investigation contained morpholine, samples were collected and analyzed for nitrosamines because morpholine can react under certain conditions with NO_x to form N–nitrosomorpholine (NMOR). One sample had a confirmed NMOR concentration of 0.26 micrograms per cubic meter ($\mu g/m^3$). Airborne nitric acid concentrations ranged from not detected to 0.05 ppm, while the ammonia concentrations ranged from 1.5 to 11 ppm. The only compounds identified during the qualitative analysis for VOCs were traces of propane, pentane, and a nitrogen compound, possibly an aliphatic amine.

The use of alternative boiler feed water additives initiated prior to this investigation seemingly alleviated most of the symptoms being experienced by the employees. In addition, one of the additives that had been eliminated contained both DEAE and CHA, which have been previously associated with the occurrence of symptoms similar to those experienced by the Agrium employees. Since the use of the boiler feed water additives that were most likely associated with the employee symptoms had been discontinued, the primary scope of this investigation was to determine potential employee exposures to chemical agents currently present. The results of the environmental sampling indicated that, although full–shift PBZ concentrations for NO_2 collected from the acid plant operators did not exceed the 8–hour TWA evaluation criteria, the operators may still at times encounter NO_2 concentrations which exceed both the NIOSH recommended ceiling limit and the OSHA and ACGIH STEL. The environmental sampling also indicated that the potential for NMOR formation existed during this process. All the air concentrations determined for NO, nitric acid, and ammonia were below their relevant exposure limits.

Keywords: SIC 2873 (Nitrogenous Fertilizers) ammonium nitrate, boiler additives, oxides of nitrogen, nitrogen dioxide, nitric oxide, nitric acid, ammonia, nitrosamines, morpholine, N–nitrosomorpholine, cyclohexylamine, diethylaminoethanol, respiratory irritation.

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INTRODUCTION

On February 21, 1996, the National Institute for Occupational Safety and Health (NIOSH) received a request for a health hazard evaluation (HHE) from the International Chemical Workers Union (ICWU) on behalf of their Local 815 members employed at Agrium U.S., Incorporated, Homestead Nitrogen Operations (formerly Cominco Fertilizers, Inc.), located in Beatrice, Nebraska. The request concerned the adverse health effects being reported among the employees at the facility. These adverse health effects included the occurrence of rashes, headaches, upper respiratory irritation, skin irritation, vomiting, and disorientation which were attributed to exposure to the chemical additives used in the boiler feed water. Both the Agrium management and the union had been involved in an effort to eliminate the problem by using alternative chemical additives, and prior to this investigation, the use of alternative chemical additives was initiated. As a result of the use of alternative chemical additives, most of the employee symptoms had been alleviated at the time of the NIOSH investigation. However, the union was still concerned about potential employee exposures to oxides of nitrogen (NO_x), components of the new additives, and other compounds present during this manufacturing process.

On April 8–9, 1996, investigators from NIOSH visited the Agrium facility to conduct environmental sampling in the areas of the plant where employees could be potentially exposed to airborne contaminants. On April 8, 1996, an opening conference was held with management and union representatives to discuss the request and conduct a walk–through inspection of the facility to familiarize the NIOSH investigators with the manufacturing process and worker responsibilities. On April 9, 1996, the NIOSH investigators evaluated potential employee exposures to NO_x, nitrosamines, ammonia, inorganic acids, and volatile organic compounds (VOCs) in the boiler house and nitric acid plant.

BACKGROUND

The Agrium U.S., Inc. facility started operations in 1965 and produces approximately 260,000 tons of dustless, free–flowing, agricultural grade ammonium nitrate annually for distribution throughout the Midwest. In addition, 50,000 tons of anhydrous ammonia, which is received for processing via pipeline from an anhydrous ammonia plant located in Texas, is distributed annually from the plant location.

Ammonium nitrate is manufactured by first combining anhydrous ammonia with oxygen, in the presence of a catalyst, to make oxides of nitrogen. These oxides of nitrogen are then absorbed in water to produce nitric acid, which when neutralized with anhydrous ammonia creates ammonium nitrate liquor. The liquor is evaporated and the material is formed into granules. In this process, the ammonium nitrate granules are formed by the successive spraying and drying (layering) of concentrated ammonium nitrate solution on recycled granules in a rotating drum. Special design of the drum and sprays, together with the control of air flow, results in hard granules of particle sizes favorable for blending and other use. Spraying occurs primarily in the first third of the granulator, the remaining portion is used mainly as a rotary cooler. The cooled granules discharge from the drum and are screened into oversize, undersize, and product size. The oversized granules are crushed and returned to the front of the granulator as recycle, along with the undersized, to form seed. As the recycled ammonium nitrate seed passes through the granulator, the sprayed ammonium nitrate impinges on them, and the granules are grown. The granules are then coated to prevent caking, and the final product is transported via conveyor systems to one of two bulk storage buildings with total storage capacities of 40,000 tons.

This investigation focused on the areas of the facility, the acid plant and boiler house, where employees could be potentially exposed to the boiler additives and NO_x. The acid plant contains the processes where ammonia is converted to nitric acid and where the nitric acid is subsequently reacted with ammonia to form the ammonium nitrate. The boiler house provides feed water to the acid plant where heat recovery and steam production from the exothermic reaction of the ammionia and nitric acid is used to power a turbine which generates compressed air for the process. During typical daily operations, there are two operators stationed in the acid plant and one operator in the boiler house. The acid plant operators' duties include monitoring the process controls in the control room, conducting walk–through inspections of the process equipment every two hours, and performing any corrective activities. The walk–through inspections are typically 20 to 30 minutes in duration and include recording information from several process gauges in the plant. During each of these inspections, one of the operators collects a sample of the nitric acid from the sample station and measures the specific gravity and temperature to determine the concentration of the resultant nitric acid. The operator in the boiler house monitors the feed water process used in the steam production and condensate recovery processes. This operator ensures proper conditions are maintained in the feed water by controlling the addition of the additives.

Boiler feed water additives are used to inhibit the formation of boiler scale, scavenge oxygen, and raise the pH in the steam and condensate to prevent the formation of carbonic acid. In October 1994, Agrium initiated the use of new additives to the boiler feed water. After the use of the new additives was initiated, operators had complained of skin rashes, severe headaches, and respiratory irritation. In an effort to eliminate the adverse employee effects that were being reported by the employees, Agrium began using alternative boiler feed water additives, including some of the additives that were initially replaced. These efforts to find alternative additives that would alleviate employee complaints led the company and union officials to believe that two of the additives were most likely responsible. One of these additives contained diethylhydroxylamine and N–isopropyl hydroxylamine, while the other consisted of cyclohexylamine, diethylaminoethanol, and morpholine. Prior to the NIOSH investigation, the use of these two additives was discontinued and most of the symptoms being reported by the employees had been alleviated. However, the union was still concerned about potential employee exposures to NO_x, components of the new additives, and other compounds present during this manufacturing process.

METHODS

Since the use of the boiler feed water additives that were most likely associated with the employee symptoms had been discontinued, the primary scope of this investigation was to determine potential employee exposures to chemical agents currently present. Personal breathing zone (PBZ) and general area air samples were collected from various areas throughout the nitric acid plant and boiler house on April 9, 1996. These environmental samples were collected to determine the air concentrations of ammonia, NO_x, nitrosamines, and nitric acid. Qualitative samples to identify other VOCs were also collected. In addition, informal employee interviews were conducted with several employees during the investigation.

Potential employee exposures to NO_x in the acid plant were determined using two NIOSH analytical methods. These two methods were used so that the NIOSH investigators could conduct a field comparison of the methods. One method utilized solid sorbent tubes attached to a personal sampling pump (active sampling method) while the other utilized Palmes tubes (passive sampling method). Eight locations where the potential for NO_x exposure existed were chosen as sampling sites (Table 1). Samples for NO_x were collected using both the active and passive methods from each location. Two additional PBZ samples were collected from the acid plant operators using the active sampling method.

The active sampling method, NIOSH Method 6014[1], utilizes two triethanolamine (TEA)–treated molecular sieve sorbent tubes in series, separated by a chromate oxidizer tube, attached via Tygon® tubing to a battery–powered sampling pump, calibrated to operate at a flow rate of 0.2 liters per minute (L/min). Nitrogen dioxide (NO_2) is collected on the first TEA sorbent tube, and is thereby separated from nitric oxide (NO), which is oxidized by the chromate oxidizer tube and is then collected on the second TEA sorbent tube (adjacent to the sampling pump). The samples were prepared for analysis by visible absorption spectrophotometry according to NIOSH Method 6014. Absorbances were measured using a Hitachi 100–20 spectrophotometer at a wavelength of 540 nanometers.

NIOSH Method 6700[2] uses a passive dosimeter (Palmes tube) with TEA–treated screens to measure concentrations of NO_2. A modified version of NIOSH Method 6700, which is based on a method originally described by Palmes and Tomczyk,[3] measures concentrations of both NO_2 and NO. This sampling device does not, however, collect NO directly; the NO is converted to NO_2 before it can be collected. Therefore, two Palmes tubes are required to quantitate both NO_2 and NO. One dosimeter directly measures NO_2 concentrations while the other tube, with the addition of a chromic acid disc, captures NO_2 and converts and captures NO as well. The NO concentration is then determined by calculating the difference obtained from the two dosimeters. The Palmes tube samples were prepared for analysis by visible absorption spectrophotometry according to NIOSH Method 6700. Absorbances were also measured using a Hitachi 100–20 spectrophotometer at a wavelength of 540 nanometers.

Eight area samples for nitrosamines were collected from various locations in the acid plant utilizing Thermosorb™/N tubes attached via Tygon® tubing to battery–powered sampling pumps calibrated to operate at a flow rate of 2 L/min and analyzed for the presence of seven nitrosamine analytes: N–nitrosodimethylamine (NDMA), N–nitrosodiethylamine (NDEA), N–nitrosodipropylamine (NDPA), N–nitrosodibutylamine (NDBA), N–nitrosopyrrolidine (NPYR), N–nitrosopiperidine (NPIP), and N–nitrosomorpholine (NMOR). Each tube was backflushed with 2 mL of desorbing solution (80% dichloroethane, 20% methanol) into scintillation vials and prepared for analysis. The N–nitrosamine analysis was performed using gas chromatography with detection by mass spectroscopy (GC/MS). The GC was equipped with a 30–meter by 0.25–millimeter HP–INNOWAX capillary column, while the mass spectrometer was operated in the high–resolution selected–ion–monitoring (HRSIM) mode. The samples were screened for nitrosamines by monitoring the characteristic NO^+ ion during the expected chromatographic retention time of each analyte. For confirmation, the mass spectrometer is set to monitor the molecular ions of the nitrosamines during analysis; a positive response at the correct molecular weight and retention time confirms the presence of the nitrosamine.

Two PBZ and five area samples were collected in the acid plant and analyzed for inorganic acids using NIOSH Method 7903.[1] The two PBZ samples and two of the area samples were collected over a full shift, while the remaining three area samples were collected as 15–minute short–term exposure limit (STEL) samples. The location and duration of these samples are presented in Table 2. Samples were collected using 600 milligram (mg), ORBO™ 53 washed silica gel sorbent tubes connected via Tygon® tubing to a battery–powered sampling pump calibrated to operate at a flow rate of 0.2 L/min. The samples were then analyzed for the nitrate ion concentration by a Dionex DX300 ion chromatograph equipped with a Waters 717 Plus autosampler.

Air sampling for ammonia was also performed during the site visit. Four area samples were collected and analyzed by automated visible spectroscopy in accordance with NIOSH Method 6015.[1] The location and duration of these samples are presented in Table 2. Samples were collected on sulfuric acid–treated silica gel tubes connected via Tygon® tubing to a battery–powered sampling pump calibrated to operate at a flow rate of 0.2 L/min. The samples were analyzed using a TRAACS 800 spectrophotometer with the absorbance measured at 660 nanometers.

Three area samples were collected using thermal desorption tubes to qualitatively identify any airborne VOCs that may originate from the boiler feed water additives. Stainless steel tubes configured for the Perkin–Elmer ATD 400 thermal desorption system were connected via Tygon® tubing to battery–powered sampling pumps calibrated to operate at a flow rate of 0.05 L/min. Each thermal desorption tube contained three beds of sorbent materials: a front layer of Carbopack Y (~90 mg), a middle layer of Carbopack B (~115 mg), and a back section of Carboxen 1003 (~150 mg). The sorbent tubes were dry purged with helium for 30 minutes at 0.1 L/min prior to analyses to remove any excess water from the samples. Samples were then analyzed using the ATD 400 automatic thermal desorption system containing an internal focusing trap packed with Carbopack b/Carboxen 1000 sorbents. The thermal unit was interfaced directly to a HP5890A gas chromatograph and HP5970 mass selective detector (TD–GC–MSD).

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the 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 health 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 criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH recommended exposure limits (RELs),[4] (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs®),[5] and (3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs).[6] 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. NIOSH encourages employers to follow the 1989 OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criteria. 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 the 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 exposures over the short-term. A STEL is defined as a 15–minute TWA exposure which should not be exceeded at any time during a workday even if the 8–hour TWA criterion is not exceeded.[5] Exposures above the 8–hour TWA up to the STEL should not be longer than 15 minutes and should not occur more than four times per day with at least 60 minutes between successive exposures in this range.[5] A ceiling limit is a concentration that should not be exceeded during any part of the working exposure. In conventional industrial hygiene practice if instantaneous monitoring is not feasible, then the ceiling limit can be assessed by sampling over a 15–minute period except for those substances that may cause immediate irritation when exposures are short.[5]

Oxides of Nitrogen (NO and NO_2)

Nitric oxide (NO) is a colorless gas with a reported odor threshold in the range of 0.3 to 1 parts per million (ppm).[7] NO is converted spontaneously in air to nitrogen dioxide (NO_2); hence, some of the latter gas is invariably present whenever NO is found in the air.[8] Nitric oxide causes cyanosis (blue color of mucous membranes and skin) in animals, apparently from the formation of methemoglobin.[9] No effects in humans have been reported from NO alone.[9] However, intoxication of two patients from the use, as an anesthetic, of 75% nitrous oxide in oxygen that was contaminated with more than 1.5% NO resulted in both individuals suffering cyanosis and methemoglobinemia, as well as respiratory distress and pulmonary edema (fluid in the lungs) attributed to NO_2.[10] It is likely that the effects of concomitant exposure to NO_2 will become manifest before the methemoglobin effects due to NO can occur.[9] In 1968, experimental animal data indicated that NO is about one–fifth as toxic as NO_2.[10]

NO_2 is a reddish–brown gas; in high concentrations, it is partially associated to nitrogen tetroxide (N_2O_4).[10] The odor threshold is on the order of 0.12 ppm.[9] NO_2 is a respiratory irritant which can cause pulmonary edema.[9] Many deaths from pulmonary edema, induced by the inhalation of high concentrations of NO_2, have been reported.[10] Brief exposure of humans to concentrations of about 250 ppm causes cough, production of mucoid or frothy sputum, and increasing dyspnea (shortness of breath).[8,11] Within 1 to 2 hours, the person may develop pulmonary edema with tachypnea (rapid breathing), cyanosis, and tachycardia (rapid heart beat). The condition then may enter a second stage of abruptly increasing severity; fever and chills precede a relapse, with increasing dyspnea, cyanosis, and recurring pulmonary edema. Death may occur in either the initial or the second stage of the illness; a severe second stage may follow a relatively mild initial stage. The person who survives the second stage usually recovers over 2 to 3 weeks; however, some persons do not return to normal, but experience varying degrees of impaired pulmonary function.[9] Humans exposed to varying concentrations of NO_2 for 60 minutes can expect the following effects: 100 ppm, pulmonary edema and death; 50 ppm, pulmonary edema with possible residual lung damage; and 25 ppm, respiratory irritation and chest pain.[12] The incidence of chronic effects from long–term exposures is less well defined.[10]

On the basis of information from animal and human studies, the ACGIH has established a TLV for NO_2 of 3 ppm as a TWA and 5 ppm as a STEL. The NIOSH REL for NO_2 is 1 ppm as a STEL, while the OSHA PEL is a 5 ppm ceiling limit. The NIOSH REL, ACGIH TLV, and OSHA PEL for NO are all 25 ppm as a TWA.

N–nitrosamines

Nitrosamines are compounds characterized by the -N--N=O functional group. They result from the combination of primary, secondary, or tertiary amines with nitrite. These reactions can occur in the laboratory; in various food, household, or industrial products; in industrial processes; and in vivo. Because of the variety of amines and reaction conditions possible, there are hundreds of nitrosamines; and because of the large number of exposure sources, including formation in vivo, there is a complicated matrix of total nitrosamine exposure. Occupational exogenous exposures have been observed in rubber industries, leather tanning industries, metal working industries, chemical industries, mining, pesticide production, detergent production, and fish factories.

Most nitrosamines are suspected to be human carcinogens, but direct causal associations have not yet been proven. The suspected mechanism of carcinogenesis of nitrosamines is that nitrosamines are metabolized into reactive intermediates, which can then covalently bind to macromolecules, including DNA. Although a causal association between nitrosamine exposure and human cancer has not yet been firmly established, there is circumstantial evidence that nitrosamines could cause cancer in humans.[13,14,15] A few human DNA adduct studies have revealed higher levels of nitrosamine–related DNA adducts in cancer cases than in controls.[16,17] Studies in experimental animals have shown similar DNA adduct formation to those detected in the human studies.[18,19,20]

Only one nitrosamine, nitrosodimethylamine, is regulated in the United States. Both OSHA and NIOSH considers NDMA to be an occupational carcinogen. NIOSH recommends that its exposure be reduced to the lowest feasible concentration.[4] OSHA requires certain controls and work practices for handling NDMA. There are no established *numerical* exposure limits in this country.

Germany has strict regulations for occupational exposures to nitrosamines. In general industry, the total exposure to all nitrosamines present may not exceed 1 microgram per cubic meter of air ($\mu g/m^3$). In special cases, such as the tire storage warehouses, exposures to all nitrosamines present may not exceed 2.5 $\mu g/m^3$. In addition to these regulations, eight nitrosamines are regulated individually—nitrosodimethylamine, nitrosomorpholine, nitrosopiperidine, phenyl-ethylnitrosamine, phenyl–methylnitrosamine, di–N–butylnitrosamine, di-iso-propylnitrosamine, and diethylnitrosamine.

Nitric Acid

Nitric acid is a colorless or yellowish liquid with a suffocating odor. It is a primary irritant and is corrosive in high concentrations. Nitric acid causes corrosion of the skin and other tissues from topical contact, and acute pulmonary edema or chronic obstructive pulmonary disease from inhalation.[9] When nitric acid is exposed to air or comes in contact with organic matter, it decomposes to yield a mixture of oxides of nitrogen, including NO and NO_2, the latter being more hazardous than nitric acid.[9] Prolonged exposure to low concentrations of the acid vapor may lead to chronic bronchitis and/or loss of appetite. Discoloration or erosion of the teeth may also occur in exposed workers.[21] Ingestion of the liquid will cause immediate pain and burns of the gastrointestinal tract. When in contact with the eyes, the liquid produces severe burns, which may result in permanent damage and visual impairment.[9] On the skin, the liquid or concentrated vapor produces immediate, severe and penetrating burns; concentrated solutions cause deep ulcers and stain the skin a bright yellow or yellowish–brown color.[22] Dilute solutions of nitric acid produce mild irritation of the skin and tend to harden the epithelium without destroying it.[9] The TWA exposure limit established for nitric acid by NIOSH, OSHA, and ACGIH is 2 ppm. In addition, both NIOSH and ACGIH have established a STELs of 4 ppm for nitric acid.

Ammonia

Ammonia is a severe irritant of the eyes, respiratory tract, and skin. It may cause coughing, burning, and tearing of the eyes; runny nose; chest pain; cessation of respiration; and death. Symptoms may be delayed in onset. Exposure of the eyes to high gas concentrations may produce temporary blindness and severe eye damage. Exposure of the skin to high concentrations of the gas may cause burning and blistering. Repeated exposure to ammonia gas may cause chronic irritation of the eyes and upper respiratory tract.[9,23] Tolerance to usually irritating concentrations of ammonia may be acquired by adaptation, a phenomenon frequently observed among workers who became acclimated to the effects of exposure.[9] Both NIOSH and ACGIH have established a 25 ppm TWA exposure limit and 35 ppm STEL for ammonia. The OSHA PEL for ammonia is 50 ppm for an 8–hour TWA.

RESULTS AND DISCUSSION

Adjacent full–shift samples for NO_2 and NO were collected using two different analytical methods at eight locations in the acid plant (Table 1). The NO_2 concentrations ranged from 0.09 to 9.7 ppm using sorbent tubes and from 0.09 to 5.8 ppm using the Palmes tubes. Airborne concentrations of NO ranged from 0.02 to 8.7 ppm and from 0.06 to 11 ppm using the sorbent and Palmes tubes, respectively. Two full–shift PBZ samples were also collected on the acid plant operators. The NO_2 concentrations for these samples were 0.41 and 0.28 ppm, while the respective NO concentrations for these samples were 0.45 and 0.20 ppm.

The TWA concentrations of NO_2 and NO for both of the PBZ samples collected from the acid plant operators were below the ACGIH TLV of 3 ppm for NO_2 and the 25 ppm criterion established for NO. However, one of the area samples had NO_2 concentrations, by both methods which exceeded the 5 ppm ceiling limit established by OSHA. In addition, the area samples also indicated that airborne NO_2 concentrations can exceed both the NIOSH STEL of 1 ppm and the 5 ppm ACGIH STEL. Although these NO_2 concentrations were determined with full–shift samples, periods of the peak NO_2 concentrations exceeding the STELs must have occurred in these areas since the full–shift TWA concentrations exceeded the STELs. This indicates that the operators may encounter NO_2 concentrations in these areas which exceed both the ceiling limit and STEL evaluation criteria. The greatest potential for operator exposure to NO_2 would occur during the operator inspection rounds and any maintenance activities where the operators are required to remain in the acid plant (outside of the control room) for any extended periods of time. All of the NO concentrations determined from the area samples were below the 25 ppm evaluation criterion. However, one sample collected using a Palmes tube had a NO concentration of 11 ppm, which approached the OSHA action limit (half of the PEL). However, the NO concentration determined using the TEA tubes at this location was only 6.3 ppm. Since exposure to both NO_2 and NO can cause respiratory irritation, exposures to these compounds may have been a contributing factor to the earlier reported employee symptoms.

The NO_x concentrations determined using the two analytical methods were compared using the Wilcoxon matched–pairs test.[24] NO_2 concentrations obtained from the two methods were statistically different ($p = 0.012$), but the concentrations for NO were not statistically different ($p = 0.844$). The NO_2 concentrations determined by the sorbent tube method were statistically greater than the concentrations determined by the Palmes tube method. This observation contradicts previously reported results which indicated that the Palmes tube method gives higher results for NO_2 than the sorbent tube method.[25]

Since one of the boiler feed water additives being used at the time of this investigation contained morpholine, eight samples were collected and analyzed for nitrosamines. Morpholine can react under certain conditions with NO_x to form N–nitrosomorpholine (NMOR). Screening of the samples using the VG 70–S mass spectrometer indicated that NMOR was detectable on five samples. However, concentrations could only be estimated, and the results could not be confirmed due to instrument problems. Two of the high–level samples were then examined using a Hewlett–Packard 5890 GC equipped with a Hewlett–Packard 5971 mass selective detector. These samples were chosen because they represented the highest quantity of the suspected analyte at levels which might be detected by this instrument. The chromatograms showed peaks which were consistent with the presence of NMOR based on the full–scan mass spectra (at unit resolution). In addition, the highest level sample was sent to an analytical contract laboratory for analysis by GC–HRSIM. This laboratory reported the presence of NMOR at a concentration of 0.24 micrograms per sample (µg/sample). This translates to an air concentration of 0.26 $\mu g/m^3$ using an air volume of 940 L that was collected for this sample. Therefore, the presence of NMOR (0.26 µg/m^3) was confirmed on only one sample, while the presence of trace amounts of NMOR could be assumed on the other four samples.

The sample with a confirmed NMOR concentration of 0.26 µg/m^3 was collected from a location at the north end of the steam turbine near a steam vent. This concentration was below the German standard of 1 µg/m^3 for exposure to all nitrosamines in general industry. There is no established numerical exposure limit for NMOR in this country, but OSHA has strict control requirements, and NIOSH recommends exposures be kept as low as feasible.[4] The other four samples with trace amounts of NMOR were collected from the south end of the steam turbine near a steam vent, from two locations near the ground floor condensate drain in the southeast corner of the plant, and from under the blow–down drum near a ladder. The concentrations for these samples were determined from area samples and do not represent operators' exposures. Employees would not routinely spend significant time at these locations unless repairs or other maintenance operations were being conducted. Further sampling for nitrosamines would be need to be conducted to determine if potential employee exposures to NMOR could actually occur.

The results of the samples for both nitric acid and ammonia are reported in Table 2. PBZ samples for nitric acid were collected from both acid plant operators. The airborne nitric acid concentrations determined for these samples were a trace concentration, defined as between the analytical limit of detection (LOD) and limit of quantitation (LOQ), and 0.04 ppm. Two area samples collected from the acid sample station and near the condensate drain in the southeast corner of the acid plant building were 0.05 and 0.03 ppm, respectively. These TWA concentrations determined for the full shift were well below the relevant evaluation criterion (2 ppm). The LOD and LOQ for nitric acid were 2.0 and 6.8 µg/sample, respectively, which equate to a minimum detectable concentration (MDC) and minimum quantifiable concentration (MQC) of 0.01 and 0.03 ppm, respectively, assuming a sampling volume of 95.0 liters. Three short–term samples for nitric acid were also obtained during the collection of nitric acid samples at the acid sample station. This station is a small area where an operator obtains an acid sample from a process valve to determine the nitric acid concentration. This operation is typically performed during the periodic rounds conducted by the operators. A storage box containing an air–purifying respirator and face shield is located near this sample station. This personal protective equipment (PPE), available for use during this operation, was not used during the sample collections that the NIOSH investigators observed. The operator, who was wearing goggles, visibly experienced some discomfort during the collection of the samples. Only one sample had a detectable amount of nitric acid, which was determined to be a trace concentration well below the 4 ppm STEL established by both NIOSH and ACGIH. For the short–term samples, the MDC and MQC were 0.3 and 0.9 ppm, respectively, assuming a sampling volume of 3 liters.

Four full–shift area samples were collected for ammonia from various areas in the acid plant. The ammonia concentrations determined for these samples ranged from 1.5 to 11 ppm. These concentrations were also below the relevant evaluation criteria for ammonia.

Since the use of the boiler additives which contained diethylhydroxylamine, N–isopropylhydroxylamine, cyclohexylamine, and diethylaminoethanol had been discontinued at the time of the investigation, and different additives were being used, two samples were collected using thermal desorption tubes to qualitatively identify any VOCs that may be present. One of these samples was collected in the acid plant while the other was collected in the boiler house. One additional sample for VOCs, to be used as a background sample, was also collected from a location near the laboratory building. The only compounds identified were traces of propane, pentane, and a nitrogen compound, possibly an aliphatic amine, on the sample collected in the acid plant.

One of the boiler feed water additives eliminated before the NIOSH investigation contained both diethylaminoethanol (DEAE) and cyclohexylamine (CHA). Diethylaminoethanol and CHA are two common amines used as additives in steam boilers and, to a lesser extent, humidification systems for corrosion control. The NIOSH REL and OSHA PEL for both of these chemicals are 10 ppm, measured as a TWA. In sufficient concentrations, these chemicals are irritants of the skin, eyes, and respiratory system. CHA is also listed as a sensitizing agent which is capable of producing allergic reactions in some sensitive individuals following repeated exposure. There is very limited information regarding human health effects of chronic, low–level exposure to DEAE and CHA.[26,27] Based on available information, the most significant effect is from acute exposure, which produces irritation of the mucous membranes and skin.[28] Since DEAE and CHA were no longer being added to the boiler feed water, and most of the employee symptoms had been alleviated, it seems plausible that these compounds may have had some role in the occurrence of respiratory and skin irritation among employees.

CONCLUSIONS

Prior to the NIOSH investigation, the use of alternative boiler feed water additives had been initiated, and most of the symptoms experienced by the employees had been alleviated. One of the additives that had been eliminated contained both DEAE and CHA, which have been previously associated with the occurrence of symptoms similar to those experienced by the Agrium employees. Since the use of the boiler feed water additives that were most likely associated with the employee symptoms had been discontinued, the primary objective of this investigation was to determine potential employee exposures to chemical agents currently present in the facility.

The results of the environmental sampling indicated that, although full–shift PBZ concentrations for NO_2 collected from the acid plant operators did not exceed the relevant evaluation criteria, the operators may at times encounter NO_2 concentrations which exceed both the ceiling limit and STEL. The environmental sampling also indicated the potential for NMOR formation during this process. All the air concentrations determined for NO, nitric acid, and ammonia were below their relevant evaluation criteria.

RECOMMENDATIONS

The following recommendations are based on the environmental sampling results and observations made during this investigation and are offered in the interest of improving health and safety conditions for employees at this Agrium facility.

1. An environmental sampling program which includes the evaluation of full–shift and short–term exposures during both routine operations and maintenance activities should be developed to determine the extent of exposures and proper control measures that should be implemented. An initial goal of this program should be an in–depth assessment of the potential for employee exposures to both NO_2 and NMOR.

2. Agrium and ICWU should continue their joint efforts to eliminate any adverse employee health effects from the use of boiler feed water additives. A continuing monitoring program should be developed to identify and track any employee health complaints associated with the use of these additives. This program should evaluate the constituents of any new additive to identify any chemicals that might be of concern, such as DEAE and CHA. This program should also evaluate all chemical handling procedures and process delivery systems to minimize potential employee exposures during these phases of the operation. If a formal agreement for the establishment of a joint management and union committee to address this and other health and safety issues at the facility has not already been reached, both Agrium and ICWU should draft a formal agreement to ensure that both parties actively address the feasibility of using engineering controls and work practices to reduce worker exposures.

3. The preventive maintenance program should be evaluated to ensure that it adequately addresses the need to eliminate leaks and perform other repairs which reduce the potential for employee exposures. The condition of all gaskets, joints, valves, etc. should be evaluated to reduce the potential for leaks where NO_x gases could escape the nitric acid production system. The acid plant boilers and steam production system should be evaluated and repaired so that any feed water leaks are minimized, thereby reducing the potential for NMOR or other nitrosamine formation. This preventive maintenance program should also include environmental sampling to ensure that any control measures are actually reducing potential employee exposures.

4. The joint management and union health and safety committee should investigate alternative ways to obtain nitric acid process samples from the production system. The use of engineering controls at the sample collection stations or other design modifications of these stations should be investigated. In the interim, the committee should address the use of proper work practices and PPE used during sample collection to ensure that they minimize potential employee exposures or risks of injury. The use of proper work practices and PPE should be strictly enforced.

5. Agrium should review its current respiratory protection program to ensure that it complies with the requirements described in 29 CFR 1910.134.[28] Publications developed by NIOSH which should also be referenced, include the NIOSH Guide to Industrial Respiratory Protection and NIOSH Respirator Decision Logic.[29,30] The written program should designate one individual with the responsibility for administering the respiratory protection program. The written respirator program should also contain information on the following topics: (a) the departments/operations which require respiratory protection; (b) the correct respirators required for each job/operation; (c) specifications that only NIOSH/MSHA approved respiratory devices shall be used; and (d) the criteria used for the proper selection, use, storage and maintenance of respirators, including limitations. A respiratory protection program should include the following elements:

a. written operating procedures
b. appropriate respirator selection
c. employee training
d. effective cleaning of respirators
e. proper storage
f. routine inspection and repair
g. exposure surveillance
h. program review
i. medical approval
j. use of approved respirators

All of these elements are discussed in more detail in the referenced materials.

REFERENCES

1. NIOSH [1994]. Eller PM, ed. NIOSH manual of analytical methods. 4th rev. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94–113.

2. NIOSH [1984]. Eller PM, ed. NIOSH manual of analytical methods. 3rd ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84–100.

3. Palmes ED and Tomczyk C [1979]. Personal sampler for NO_x. Am Ind Hyg Assoc J 40:588591.

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

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

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

7. NIOSH [1995]. Occupational health guideline for nitric oxide. In: Occupational health guidelines for chemical hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95–121.

8. NIOSH [1976]. Criteria for a recommended standard: occupational exposure to oxides of nitrogen (nitrogen dioxide and nitric oxide). Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 76–149.

9. Hathaway GJ, Proctor NH, Hughes JP, Fischman ML [1991]. Proctor and Hughes' chemical hazards of the workplace. 3rd ed. New York, NY: Van Nostrand Reinhold.

10. ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists, with supplements through 1994.

11. Morgan WKC, Seaton A [1975]. Occupational lung diseases. Philadelphia, PA: WB Saunders, pp. 330–335, 344–345.

12. Anonymous [1964]. Emergency exposure limits: nitrogen dioxide. Am Ind Hyg Assoc J 25:580–582.

13. Magee PN and Barnes JM [1956]. The production of malignant primary hepatic tumors in the rat by feeding dimethylnitrosamine. British Journal of Cancer 10:114–122.

14. NIOSH [1983]. N–nitroso compounds in the factory environment. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 83–114.

15. Bartsch H and Montesano R [1984]. Relevance of n–n–nitrosamines to human cancer. Carcinogenesis 5(11):1381–1393.

16. Umbenhauer D, Wild CP, Montesano R, Saffhill R, Boyle JM, Huh N, Kirstein U, Thomale J, Rajewsky MF, Lu SH [1985]. O^6–methylguanosine in oesophageal DNA among individuals at high risk of oesophageal cancer. International Journal of Cancer 37: 661–665.

17. Saffhill R, Badawi AF, Hall CN [1988]. Detection of O^6–methylguanine in human DNA. In: Methods for detecting DNA damaging agents in humans: applications in cancer epidemiology and prevention, IARC Scientific Publications No. 89 (H. Bartsch, K. Hemminki, and I.K. O'Neill, Eds.). International Agency for Research on Cancer, Lyon. pp. 301–305.

18. Boucheron JA, Richardson FC, Morgan PH, Swenberg JA [1987]. Molecular dosimetry of O^4–ethyldeoxythymidine in rats continuously exposed to diethyl–n–nitrosamine. Cancer Research 47: 1577–1581.

19. Deal FH, Richardson FC, Swenberg JA [1989]. Dose response of hepatocyte replication in rates following continuous exposure to diethyl–n–nitrosamine. Cancer Research 49:6985–6988.

20. Belinsky SA, Foley JF, White CM, Anderson MW, Maronpot RR [1990]. Dose–response relationship between O^6–methylguanine formation

in Clara cells and induction of pulmonary neoplasia in the rat by 4–(methylnitrosamino)–1–(3–pyridyl)–1–butanone. Cancer Research 50:3772–3780.

21. NIOSH [1995]. Occupational health guideline for nitric acid. In: Occupational health guidelines for chemical hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95–121.

22. NIOSH [1976]. Criteria for a recommended standard: occupational exposure to nitric acid. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 76–141.

23. NIOSH [1995]. Occupational health guideline for ammonia. In: Occupational health guidelines for chemical hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95–121.

24. Daniel WW [1991]. Biostatistics: a foundation for analysis in the health sciences. 5th ed. New York, NY: John Wiley & Sons, pp. 586–589.

25. Jones W, Palmes ED, Tomczyk C, Millson M [1979]. Field comparison of two methods for the determination of NO_2 concentration in air. Am Ind Hyg Assoc J 40:437–438.

26. ACGIH [1990]. Case studies. Workplace exposures to corrosion–inhibiting chemicals from a steam humidification system. Cincinnati, OH: American Conference of Governmental Industrial Hygienists. Applied Occupational and Environmental Hygiene, 5(10):672.

27. NIOSH [1996]. NEG and NIOSH basis for an occupational health standard for 2–diethylaminoethanol. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 96–104.

28. Code of Federal Regulations [1993]. 29 CFR 1910.134. Respiratory protection. Washington, DC: Occupational Safety and Health Agency, U.S. Department of Labor, U.S. Government Printing Office.

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

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

Table 1
Airborne Concentrations of NO_2 and NO
Agrium, Inc. (formerly Cominco Fertilizers)
HETA 96–0089
Beatrice, Nebraska
April 8, 1996

Sample Description	**Duration (minutes)**	**Nitrogen Dioxide**		**Nitric Oxide**	
		TEA	**Palmes**	**TEA**	**Palmes**
Area samples, concentrations expressed as parts per million					
Acid plant control room	478	0.23	0.26	0.16	0.15
Convertor – air valve wheel	476	1.2	0.8	1.5	1.5
Convertor – b/w NH_3 valve & air intake	472	4.2	2.4	4.1	4.1
Main level – above tail gas exhaust	478	9.7	5.8	8.7	6.5
Ground level – SE condensate drain	456	0.35	0.22	0.24	0.23
Acid sample station	461	0.09	0.09	0.02	0.06
Above super heater flanges	333	0.32	0.22	0.12	0.14
Control panel – near convertor	332	4.8	3.1	6.3	11
Personal Breathing Zone samples, concentrations expressed as parts per million					
Acid plant: A–operator	492	0.41	n/a	0.45	n/a
Acid plant: B–operator	397	0.28	n/a	0.20	n/a

Evaluation Criteria			
	ACGIH	**3 ppm, 5 ppm STEL**	**25 ppm**
	NIOSH	**1 ppm STEL**	**25 ppm**
	OSHA	**5 ppm Ceiling**	**25 ppm**

NO_2 = nitrogen dioxide
NO = nitric oxide
TEA = triethanolamine–treated sorbent tube method
ppm = parts per million
STEL = 15–minute short–term exposure limit

b/w = between; NH_3 = ammonia; SE = Southeast

Table 2
Airborne Concentrations of Nitric Acid and Ammonia
Agrium, Inc. (formerly Cominco Fertilizers)
HETA 96–0089
Beatrice, Nebraska
April 8, 1996

Sample Description	Duration (minutes)	Sample Volume (liters)	Nitric Acid Concentration (ppm)
Acid plant: A–operator PBZ	492	98.4	trace
Acid plant: B–operator PBZ	492	98.4	0.04
Ground level – SE condensate drain	456	91.2	0.03
Acid sample station	461	92.2	0.05
Short–term exposure limit samples			
Acid sample station	5	1	ND
Acid sample station	15	3	trace
Acid sample station	15	3	ND
Evaluation Criteria	**NIOSH & ACGIH**		**2 ppm, 4 ppm STEL**
	OSHA		**2 ppm**

Sample Description	Duration (minutes)	Sample Volume (liters)	Ammonia Concentration (ppm)
Acid plant control room	478	95.6	1.5
Convertor – air valve wheel	476	95.2	1.8
Convertor – b/w NH_3 valve & air intake	472	94.4	6.7
Acid plant burn tank	444	88.8	11
Evaluation Criteria	**NIOSH & ACGIH**		**25 ppm, 35 ppm STEL**
	OSHA		**50 ppm**

ppm = parts per million
trace = detected value was between the minimum detectable concentration (MDC) and minimum quantifiable concentration (MQC) of 0.01 and 0.03 ppm for the full–shift samples, respectively, assuming a sampling volume of 95.0 liters. For the short–term samples, the MDC and MQC were 0.3 and 0.9 ppm, respectively, assuming a sampling volume of 3 liters.
ND = not detected: value was below the MDC of 0.3 ppm, assuming a sample volume of 3 liters.
PBZ = personal breathing zone sample
STEL = 15–minute short–term exposure limit

SE = Southeast; b/w = between; NH_3 = ammonia

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