DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service

National Institute for Occupational Safety and Health
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Keith E. Laurie
Superintendent of Safety & Environmental Affairs
Unocal Corporation, Chemicals Division
P.O. Box 575
Kenai, Alaska 99611

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Dear Mr. Laurie:

Enclosed please find a copy of the prepublication version of the report of the health hazard evaluation (HHE) conducted by the National Institute for Occupational Safety and Health (NIOSH) at the Unocal Corporation urea fertilizer facility located in Kenai, Alaska. After we have received the final publication version of the report from the printer, we will provide you with a copy.

This prepublication version will close the current HHE file for this project. Please note the posting requirements in the section entitled, "*Distribution and Availability of Report,*" which are required by law. Thank you for your cooperation during the duration of this project. If you have any questions regarding our investigation or this report, please call me at (513) 841-4374.

Sincerely yours,

Gregory M. Kinnes, MS, CIH, RS
Industrial Hygienist
Hazard Evaluations and Technical Assistance Branch
Division of Surveillance, Hazard Evaluations and Field Studies

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Unocal Corporation
Kenai, Alaska

Gregory M. Kinnes, MS, CIH, RS
Alan S. Echt, MPH, CIH, RS
Ruth A. Shults, RN, MPH

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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.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, technical and consultative assistance to Federal, State, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease. Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Gregory A. Kinnes, Alan S. Echt, and Ruth A. Shults, of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Kenneth F. Martinez, MSEE and Teresa A. Seitz, MPH, CIH. Desktop publishing by Ellen E. Blythe and Caren B. Day.

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Health Hazard Evaluation Report 91-0153-2581
Unocal Corporation
Kenai, Alaska
June 1996

Gregory M. Kinnes, MS, CIH, RS
Alan S. Echt, MPH, CIH, RS
Ruth A. Shults, RN, MPH

SUMMARY

On March 19, 1991, the National Institute for Occupational Safety and Health (NIOSH) received a request for a health hazard evaluation (HHE) from the Oil, Chemical, and Atomic Workers International Union (OCAW) on behalf of members employed at the Unocal Corporation urea fertilizer facility located in Kenai, Alaska. The Kenai facility produces urea fertilizers through ammonia intermediaries in both prill and granular forms. The request was prompted by concerns about potential health effects from the use of a formaldehyde-based additive to improve the handling characteristics of the urea. These concerns were related to whether formaldehyde is present in the final product or whether it reacts to form methylenediurea (MDU). On August 7-9, 1991, and April 13-14, 1992, NIOSH investigators collected environmental samples for ammonia, total and respirable dust, formaldehyde vapors, and formaldehyde on dust during the manufacture of the prill and granular forms of the urea fertilizer. Private employee interviews were also conducted during the initial site visit to determine if any adverse health effects were being experienced by the workers.

Personal breathing zone (PBZ) and general air samples were collected during the manufacture of both the prill and granular forms of the urea fertilizer, during the loading of the product for sea transport, and during other plant operations. Airborne formaldehyde vapor concentrations ranged from less than 0.006 to 2.2 parts per million (ppm), with the highest concentrations encountered during the unloading of a tanker containing the formaldehyde-based additive (UF-85). A PBZ sample collected from the operator performing this unloading operation had a concentration of 0.25 ppm, which exceeds the NIOSH ceiling limit of 0.1 ppm. Two area samples collected during this operation had concentrations that also exceeded the NIOSH limit and the American Conference of Governmental Hygienists (ACGIH) Threshold Limit Value (TLV™) ceiling limit of 0.3 ppm. The concentrations of inhalable dust ranged from 0.3 to 78.6 milligrams per cubic meter (mg/m^3), while the corresponding airborne concentrations of particulate formaldehyde equivalents (FE) ranged from 0.6 to 1110 micrograms per cubic meter ($\mu g/m^3$). Airborne total dust concentrations ranged from 0.1 to 76 mg/m^3, while two area respirable dust samples had concentrations of 4.33 and 0.09 mg/m^3. The highest concentrations of inhalable and total dust occurred during the daily blow-down operation in the granulation plant. Inhalable and total dust concentrations during this operation exceeded the relevant evaluation criteria, as did two full-shift PBZ concentrations for samples collected from individuals performing other operations in the granular plant.

Airborne concentrations of ammonia ranged from less than 0.02 to 276 ppm. One full-shift, PBZ sample collected from a prill tower operator had an ammonia concentration that equaled the NIOSH and ACGIH limits of 25 ppm, while the concentrations for all the short-term samples collected during the prill tower inspection rounds exceeded the NIOSH and ACGIH short-term exposure limits (STEL) of 35 ppm.

Twenty-one employees were interviewed during the medical evaluation. The most commonly reported symptoms experienced by these employees were throat irritation (47%), nose irritation (43%), runny nose (43%), and eye irritation/tearing (33%). Six of the 21 employees reported having at least two symptoms consistent with a diagnosis of asthma (shortness of breath, chest pain or tightness, cough, or wheeze).

Environmental sampling indicated that employees may be exposed to low concentrations of formaldehyde vapor during the manufacture and loading of urea. However, formaldehyde concentrations during the unloading of the tankers containing UF-85 can exceed both the NIOSH and ACGIH ceiling limits. The analysis of the urea and MDU bulk samples indicated that MDU will produce positive results for formaldehyde when analyzed by the formaldehyde on dust method (NIOSH Method #5700). When using an analysis technique that employs milder, non-acidic conditions, only low levels of free formaldehyde (0.02%) in the urea dust were analytically determined during this investigation. However, the formaldehyde on dust samples still indicated that inhalable dust concentrations could exceed the ACGIH TLV for inhalable particulates. Total, inhalable, and respirable dust concentrations may periodically exceed their relevant evaluation criteria, but the use of respiratory protection and the relatively short amount of time spent in areas with higher concentrations limited worker exposures. Ammonia concentrations in the prill tower can exceed both the time-weighted average and short-term exposure limits; however, only one PBZ sample collected from a prill tower operator had an ammonia concentration that reached the NIOSH and ACGIH limit of 25 ppm for an 8-hour TWA. Although some employees may be experiencing symptoms consistent with occupational asthma, a specific diagnosis could not be made without further medical evaluation. Recommendations to reduce exposures are presented in this report.

Keywords: SIC 2873 (Agricultural chemicals, nitrogenous fertilizers) urea, formaldehyde, ammonia, formaldehyde-based additives, methylenediurea, inhalable and total particulates, asthma.

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INTRODUCTION

On March 19, 1991, the National Institute for Occupational Safety and Health (NIOSH) received a request for a health hazard evaluation (HHE) from the Oil, Chemical, and Atomic Workers International Union (OCAW) on behalf of members employed at a Unocal Corporation urea fertilizer facility located in Kenai, Alaska. The Kenai facility produces urea fertilizers through ammonia intermediaries in both prill and granular forms. During the process, a urea-formaldehyde concentrate (UF-85) is added to improve the handling characteristics of the urea fertilizer. The UF-85 additive reportedly reacts to form methylenediurea and a combination of urea-formaldehyde polymers. OCAW was concerned about the potential health effects of the urea-formaldehyde reaction products and if any free formaldehyde is released during the final stages of production, storage, or transportation.

On August 7-9, 1991, NIOSH investigators conducted an initial site visit at the Kenai facility. An opening conference was held with representatives from both Unocal and OCAW to discuss the scope of the request and the proposed investigation. A walk-through survey of the facility was conducted, and additional process information and records were gathered. Environmental samples were collected for ammonia, total and respirable dust, and formaldehyde vapors during the manufacture of both the prill and granular forms of the urea fertilizer. Since the final product is in solid form and produces dust during handling, samples were collected to determine the formaldehyde content on particulates using a method developed by NIOSH's Division of Physical Sciences and Engineering. The analyses were used to estimate the formaldehyde dose from inhalable dust at the point of particle retention in the breathing passages. Private interviews were also conducted with 21 employees to determine if any adverse health effects were being experienced.

On April 13-14, 1992, NIOSH investigators returned to the facility to conduct additional environmental sampling, primarily during operations that were not performed during the initial site visit. Environmental samples were collected for ammonia, total dust, formaldehyde vapors, and formaldehyde on dust during the manufacture of the urea fertilizer, as well as during the loading of the product on a freighter for sea transport. Environmental sampling was also performed during the unloading of a truck tanker containing the UF-85 additive and the daily "blow-down," or cleaning, of the #5 urea granulation plant.

BACKGROUND

The Unocal Corporation manufactures solid urea at its Kenai facility for use as a nitrogen fertilizer. Urea also has other commercial applications which include an animal food additive and a constituent of some cosmetic and consumer products, such as body creams, liquid soaps, and shampoos. Several characteristics of urea make it particularly attractive as a fertilizer material, including its nitrogen content of 46.6% which is considerably higher than other solid nitrogen fertilizers, its better storage and handling properties, and its cheap production costs.[1] Also, urea presents no burning or explosion hazard, which is a significant advantage over ammonium nitrate. The Kenai facility employs approximately 200 employees and consists of five plants, two (Plants #2 & #5) of which produce the urea fertilizer.

Urea is manufactured from liquid ammonia and gaseous carbon dioxide (CO_2) at elevated pressures and temperatures; both reactants are typically obtained from an ammonia-synthesis plant.[2] Urea plants are usually located adjacent to ammonia production facilities which conveniently furnish not only the ammonia but also the CO_2, because CO_2 is a by-product of ammonia production and purification. Plants #1 and #4 at the Kenai facility are ammonia-synthesis plants that supply the reactants to the urea producing plants. The remaining plant (Plant #3) generates power for the entire Kenai facility. The Kenai facility produces

approximately 1 million tons of urea and 1 million tons of ammonia per year. The ammonia and CO_2 are fed to a high pressure reactor at temperatures of about 200 degrees Celsius (°C) where ammonium carbamate is formed as an intermediate compound, which is simultaneously dehydrated to form urea:

$$2\,NH_3 + CO_2 \rightleftharpoons \underset{\text{Ammonium carbamate}}{NH_2CONH_4} + \text{heat}$$

$$NH_2CONH_4 + \text{heat} \rightleftharpoons \underset{\text{Urea}}{NH_2CNH_2} + H_2O$$

Although, the reaction to form the ammonium carbamate is complete at elevated pressures, the reaction to form the urea is incomplete under all practical conditions. Because an excess of ammonia (typically a 4:1 ratio) is fed to the reactor, and because the reactions are reversible, ammonia and CO_2 exit the reactor along with the ammonium carbamate and urea. The ammonia, CO_2, and ammonium carbamate are then recycled back into the reaction process. Purification of the ammonia, CO_2, and ammonium carbamate in the liquid stream from the reactor achieves a urea solution of about 72%. After the reaction process and the removal of the by-products for recycling, the urea in solution is crystallized, centrifuged, dried, melted, and finished by either prilling or granulation.

Of the two plants that produce the urea, one produces urea in the prill form while the other produces granular urea. Worldwide, prilling is the most widely used method of solidifying urea, but the use of granulation is increasing rapidly.[1] Urea prilling is the more economical method for finishing, but the prills have low strength and are generally too small for use in blending with granular materials such as diammonium phosphate.[1] Also, the prilling operation is a serious polluter, the abatement of which is costly because of the large volume of dust-laden air that must be treated. For these reasons, there is a strong trend toward granulation of urea. Although prilling is still the most widely used method worldwide, granulation is now the leading method of finishing urea in the United States.[1]

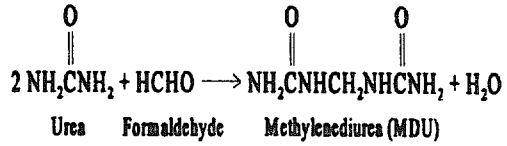
Plant #2 was built in 1968 and produces from 1250 to 1450 tons of the prill urea per day. In prilling, molten urea that is almost anhydrous is forced through spray heads or spinner buckets at the top of a tower to produce droplets that fall through a countercurrent stream of air in which they solidify to form prills.[1] The prills are collected at the base of the prill tower by a rotating rake and dumped onto a conveyor that feeds the prill bucket elevator. The prills are then elevated to the prill screens where undersized and oversized prills are removed. The undersized and oversized prills are collected and returned to the crystal melt tanks for reprocessing. The final product is then transported to a storage building by a series of conveyors.

The granular urea is produced in Plant #5 which became operational in 1978. Plant #5 typically produces from 1700 to 1800 tons of the granular urea per day. In this process, granules are formed by the successive spraying and drying (layering) of concentrated urea 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 urea seed passes through the granulator, the sprayed molten urea impinges on them and the granules are grown. The final product is then transported to a storage building.

The finished granules and prills are stored in separate warehouses while awaiting shipment. Most of the urea fertilizer is transported from the Kenai plant by ocean freighter. The urea storage warehouses are equipped with overhead conveyor systems to distribute the finished urea in the warehouse and

subfloor conveyor systems to transport the product to the wharf for loading. The conveyors are located in the center and run the length of both warehouses. The floors of the warehouses are equipped with a series of grates that open to the subfloor conveyor system. The urea falls from the overhead conveyor onto the warehouse floor forming large mounds of the finished product. The urea then falls through the opened grates onto the subfloor conveyor that transports it to the wharf where it is loaded into the holds of a freighter. Both the conveyors and the grates are controlled so that the warehouses are filled evenly. Two large loaders are used in the warehouses to aid the loading operations by moving the urea over the floor grates and dislodging urea that has caked together.

During both the prilling and granulation processes, UF-85 is added to the molten urea prior to finishing. The UF-85 is a liquid mixture containing 60% formaldehyde, 15% water, and 25% urea. Formaldehyde, such as in the UF-85, has been widely used in the production of urea since the mid-1970's as a conditioning agent to harden the product, reduce dust generation during handling, and provide anti-caking properties in storage.[3] Approximately 95% of the domestic urea fertilizer producers condition their urea with a formaldehyde-based additive (ureaforms) and virtually all solid urea producers employ some type of conditioning agent to improve product handling.[4] The fertilizer industry has conducted extensive research concerning the use of formaldehyde and its chemical characteristics during fertilizer production. The Tennessee Valley Authority (TVA) conducted a research project to determine if formaldehyde is present in the finished urea fertilizer or if it is a reaction product and if formaldehyde can be released from the finished product during either handling or storage. The TVA concluded that it was reasonable to assume that no exposure risk to formaldehyde existed since no formaldehyde vapors were detected from ureaform-containing urea products at both ambient temperature and 54°C.[5] Because formaldehyde was not detected from a spiked sample of urea, the TVA assumed that formaldehyde added to urea under production conditions combines with the urea to form some type(s) of ureaform, and that if formaldehyde does evolve, it is more likely to recombine with the urea than to escape from the mass.[5] Another study conducted by The Fertilizer Institute (TFI) determined that formaldehyde reacts immediately and irreversibly with molten urea to form, principally, methylenediurea (MDU).[4,6] This reaction is only reversible in the presence of strong acids:



This TFI study also determined that MDU is the actual conditioning agent for urea and not formaldehyde, as had been historically reported by the fertilizer industry, and that the traditionally-used chromotropic acid analysis method actually measures the equivalent amount of formaldehyde added to the process and not the amount of "free" or gaseous formaldehyde in the product. Regarding potential employee exposures to formaldehyde, TFI concluded that even though the formaldehyde-based additives can release formaldehyde gas, such additives can be safely used in urea fertilizer production, and that the evolution of gaseous formaldehyde, if any, from the solid urea only approaches the analytical limits of detection during any phase of their storage, handling, or use.[4] Unocal has also conducted its own research regarding the use of formaldehyde. Unocal conducted a detailed trace formaldehyde species analysis using polarography in the presence of 3-methyl-2-benzothiazolinone hydrazone (MBTH).[7] This study determined that, in addition to the major component (MDU) formed by the formaldehyde, significant amounts of methylolurea, aminomethylurea, and apparent free formaldehyde were shown to be present in the urea.[7] The identification of free formaldehyde, as well as the other reaction products, in the prill and granular urea was the primary reason OCAW requested this HHE. OCAW was concerned about potential employee exposures to formaldehyde and the components formed by the formaldehyde-based additives.

METHODS

Environmental Evaluation

NIOSH investigators visited the Unocal Kenai facility on August 8-9, 1991, and April 13-14, 1992. Environmental samples were collected to determine the airborne concentrations of ammonia, total and respirable dust, formaldehyde vapors, and formaldehyde on inhalable particulates during the manufacture of both the prill and granular forms of the urea fertilizer. The second site visit was needed to collect environmental samples during plant operations that were not performed during the initial site visit. The environmental samples were collected during the manufacture of the urea fertilizer, as well as during the loading of the product on a freighter for sea transport. Environmental sampling was also performed during the unloading of a truck tanker containing the UF-85 additive and during the cleaning or "blow-down" of the #5 urea granulation plant.

The formaldehyde (or formaldehyde equivalent) on particulate samples were collected using a method developed by NIOSH's Division of Physical Sciences and Engineering. This method was originally developed to estimate the formaldehyde dose from inhalable textile or wood dust at the point of particle retention in the breathing passages. Bulk samples of both the prill and granular fertilizers were collected, and a sample of analytically pure MDU synthesized by Unocal's Science and Technology Division was also obtained. These bulk samples were analyzed to determine if the particulate method measured actual formaldehyde or the formaldehyde equivalents, such as MDU. Unocal contended that the method measured the formaldehyde equivalent content since the method involved the use of perchloric acid which would catalyze the reverse reaction from these reaction products back to formaldehyde. Therefore, both this method and the traditionally-used chromotropic acid (basis for NIOSH method 3500[8]) method would actually determine the equivalent amount of formaldehyde originally added to the process and not the amount of "free" formaldehyde in the product.

Initial Site Visit - August 8-9, 1991

During this visit, four area samples for formaldehyde were collected and analyzed in accordance with NIOSH Method 3500.[8] Samples were collected at the second and third decks in the granular plant, and above the prill melt box and at the screens in the prill plant (Table 1). The samples were collected with two midget impingers in series, each of which contained approximately 15 milliliters (mL) of 1% sodium bisulfite solution. The first impinger in each set was preceded by a tared 37-millimeter (mm) diameter, 5-micrometer (µm) pore-size polyvinyl chloride (PVC) filter in order to exclude formaldehyde-containing particulate from the impinger, and thus prevent a positive bias. Tygon® tubing was used to connect the filter cassette to the first impinger, to connect that impinger to the second impinger, and to connect the second impinger to a battery-powered sampling pump calibrated at a flow rate of 0.5 liter per minute (L/min). The analytical limit of detection (LOD) for this set of samples was 2 micrograms (µg)/sample, which equates to a minimum detectable concentration (MDC) of 0.006 ppm, based upon the maximum sample volume of 256 L for this set of samples. The minimum quantifiable concentration (MQC) for this sample set was 0.018 ppm, based upon an analytical limit of quantitation (LOQ) of 5.6 µg/sample, and a maximum sample volume of 256 L.

Ten area samples and nine personal breathing zone (PBZ) samples were also collected for formaldehyde on dust. The locations of the area samples and the job titles of the sampled employees are provided in Table 2. Samples for formaldehyde on dust were collected on tared 25-mm diameter, 5 µm pore size PVC filters placed in personal samplers for inhalable dust. These samplers collect inhalable (inspirable) particles in the size range the worker takes in through the nose and mouth during the act of breathing, i.e., particles with an aerodynamic diameter up to

100 µm.[9,10] Inhalable particles have been described as those that can be deposited anywhere in the respiratory tract.[10] The samplers were connected via Tygon® tubing to battery-powered sampling pumps operating at a flow rate of 2 L/min Samples collected in this manner were analyzed using NIOSH Method 5700.[8] The LOD for this sample set was 0.4 µg/sample, or a MDC of 0.32 micrograms (µg/m³) for a sample volume of 1244 L, the maximum sample volume for this set of samples. The MQC for this sample set was 0.88 µg/m³, based upon a LOQ of 1.1 µg/sample and a sample volume of 1244 L.

Three area, partial period consecutive samples for total dust were collected at the granulation plant on the third deck. Two other area, partial period consecutive samples for total dust were collected at the prill tower melt box in the prill plant. In addition, one full-shift PBZ sample was collected in the breathing zone of the granulation plant's control operator. These samples are described in Table 3. The six samples were collected on 37-mm diameter, 5-µm pore size PVC filters in two-piece cassettes, using personal sampling pumps calibrated at a flow rate of 1 L/min. The sampling media were analyzed for total dust by gravimetric analysis according to NIOSH Method 0500, with the following modifications: (1) the filters were stored in an environmentally controlled room (21 ± 3 °C and 40 ± 3% relative humidity) and were subjected to the room conditions for a long duration for stabilization. Therefore, the method's eight- to sixteen-hour time for stabilization between tare weighings was reduced to five to ten minutes; (2) the filters and backup pads were not vacuum desiccated.[8]

Two area samples were also collected for respirable dust, one on the third deck of the granulation plant, and the other above the melt box in the prill tower. Samples were collected on 37-mm diameter, 5-µm pore size PVC filters using 10-mm nylon cyclones and personal sampling pumps calibrated to 1.7 L/min. Samples were analyzed for respirable dust according to NIOSH Method 0600 with the same modifications noted above for NIOSH Method 0500.[8]

Air sampling for ammonia was also performed during the site visit. Nine PBZ samples, which included two short-term samples, and three area samples were collected and analyzed by visible spectroscopy in accordance with NIOSH Method S347.[11] The location and duration of these samples is presented in Table 4. Samples were collected on silica gel tubes in plastic holders connected via Tygon® tubing to battery-powered sampling pumps calibrated to operate at a flow rate of 0.2 L/min (one of the short-term samples was collected at a flow rate of 1.0 L/min to ensure that ammonia was detected because the higher sample volume would provide a lower MDC). The LOD for this set of samples was 0.3 µg/sample, which resulted in MDCs of 0.003 ppm and 0.05 ppm, based upon maximum sample volumes of 125 L for the long-term samples, and 9 L for the short-term sample collected using the higher flow rate. The LOQ for these samples was 1.0 µg/sample, which equates to an MQC of 0.01 ppm for the long-term samples, and 0.16 ppm for the short-term samples, based upon these sample volumes.

Second Site Visit - April 13-14, 1992

Six area samples were collected and analyzed for formaldehyde in accordance with NIOSH Method 3500.[8] One sample was collected during UF unloading, two were collected near the melt box in the prill tower, one was collected in the prill warehouse, and the remaining two samples were collected in the granular warehouse. Each sample was collected with one midget impinger which contained approximately 15 mL of 1% sodium bisulfite solution. Each impinger was preceded by a tared 37-mm diameter, 5-µm pore-size PVC filter in order to exclude formaldehyde-containing particulate from the impinger, and thus prevent a positive bias. The sample trains were constructed in the same manner as during the first visit, except that a flow rate of 1 L/min was used. The LOD for this set of samples was 0.6 µg/sample, which equates to a MDC of 0.001 ppm, based upon the maximum sample volume of 388 L for this set of samples. The MQC for this sample set was 0.004 ppm, based upon

an LOQ of 1.7 µg/sample, and a maximum sample volume of 388 L.

Two short-term, 35-minute samples (one PBZ sample and one area sample) for formaldehyde were also collected during UF unloading and analyzed using NIOSH Method 2541 with modifications.[8] These samples were collected on solid sorbent tubes (10% 2-[hydroxymethyl] piperidine on XAD-2 resin) in plastic holders connected via a length of Tygon® tubing to battery-powered personal sampling pumps operating at a flow rate of 200 mL/min. The LOD for this sample set was 0.5 µg/sample, which equates to a MDC of 0.06 ppm, based upon the maximum air sampling volume for this set of samples, 7 L. The LOQ for this sample set was 1.7 µg/sample, which equates to a MQC of 0.2 ppm, based upon a maximum sample volume of 7 L.

Six PBZ samples and eight GA samples were collected and analyzed for formaldehyde on dust. The locations of the area samples and the job titles of the employees sampled are provided in Table 2. These samples for formaldehyde on dust were collected and analyzed in the same manner as during the initial visit. However, one of the PBZ samples was lost at the laboratory during analysis. The LOD for this sample set was 3 µg/sample, or a MDC of 3.7 µg/m^3 for a sample volume of 818 L, the maximum sample volume for this set of samples. The MQC for the NIOSH method for this sample set was 10.4 µg/m^3, based upon a LOQ of 8.5 µg/sample and a sample volume of 818 L.

In addition, ten partial period samples for total dust were collected (Table 3). These included four PBZ samples (one on a loader in the granular warehouse, one on a loader in the prill warehouse, one on an operator in the granulation plant during blow-down, and one on a NIOSH investigator who accompanied that operator) and six area samples (including one in the prill tower, two in the prill warehouse, and three in the granular warehouse). The ten samples were collected in the same manner as the total dust samples from the initial visit and analyzed according to NIOSH Method 0500, with modifications.[8]

During this visit, 22 air samples were collected and analyzed for ammonia (Table 4). Sample collection was the same as the first visit, but the sample preparation and analysis was conducted according to EPA Method 350.1, which is similar to NIOSH Method S347.[11,12] The LOD for this set of samples, 0.5 µg/sample, is equal to an MDC of 0.007 ppm, based upon a maximum sample volume of 108 L for this sample set. The MQC for this set of samples was 0.02 ppm, based on an LOQ of 1.5 µg/sample and the 108 L sample volume.

Medical Evaluation

The medical evaluation consisted of interviews with 21 employees, review of the Occupational Safety and Health Administration (OSHA) 200 Logs, and informal discussions with management. The purposes of the interviews were (1) to identify any adverse health effects of primary concern to the labor force, and (2) to obtain information on potential past and current chemical and physical exposures in the work environment. NIOSH investigators requested that all employees who were working in the urea plants and on the wharf during the NIOSH visit participate in the interviews, and employees from other work areas were interviewed upon their request.

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),[13] (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs™)[10] and (3) the U.S. Department of Labor, OSHA permissible exposure limits (PELs).[14] 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 or the NIOSH RELs, 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 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.

Formaldehyde

Formaldehyde is a colorless gas with a strong odor. Exposure to formaldehyde can occur through inhalation and skin absorption. The acute effects associated with formaldehyde are irritation of the eyes and respiratory tract and sensitization of the skin. The first symptoms associated with formaldehyde exposure, at concentrations ranging from 0.1 to 0.3 ppm, are burning of the eyes, tearing, and general irritation of the upper respiratory tract. Variations have been noted in individual tolerance and susceptibility to the effects of formaldehyde exposure.[15,16]

NIOSH has identified formaldehyde as a suspected human carcinogen and recommends that exposures be reduced to the lowest feasible concentration. NIOSH has also established RELs of 0.016 ppm as an 8-hour TWA and 0.1 ppm as a ceiling limit. The OSHA PEL is 0.75 ppm as an 8-hour TWA and 2 ppm as a STEL.[17] ACGIH considers formaldehyde a suspected human carcinogen and therefore recommends that worker exposure by all routes should be carefully controlled to levels "as low as reasonably achievable" below the TLV™.[10] ACGIH has also set a ceiling limit of 0.3 ppm.

Particulates Not Otherwise Regulated

Particulates not otherwise regulated (nuisance dusts) have a long history of little adverse effect on lungs and do not produce significant organic disease or toxic effect when exposures are kept under reasonable control. The lung tissue reaction caused by inhalation of nuisance dusts has the following characteristics: (1) the architecture of the air spaces remains intact; (2) scar tissue is not formed to a significant extent; and (3) the tissue reaction is

potentially reversible.[18] Respirable particulate refers to materials that are able to reach the gas-exchange region of the lung.

The current OSHA PEL for particulates not otherwise regulated is 15 mg/m^3 for total dust and 5 mg/m^3 for the respirable portion.[19] The ACGIH TLV for particulates not otherwise classified is 10 mg/m^3 for inhalable particulate and 3 mg/m^3 for respirable particulate.[10] These criteria were established to minimize mechanical irritation of the eyes and nasal passages, and to prevent visual interference. NIOSH has not developed specific criteria for total particulates.

Formaldehyde on Dust

In two mortality studies dealing with occupational exposure to formaldehyde, a difference in results has brought into question the source of formaldehyde exposure in each study. In a study by Stayner *et al.*, in which statistically significant elevations in proportionate mortality were observed for cancers of the parotid gland, gallbladder, and multiple myeloma, formaldehyde measurements revealed low levels, assumed to be in a vapor-phase due to off gassing of formaldehyde from cloth used in garment manufacture.[20] In a reanalysis of data from an earlier study, Blair *et al.*, stated that "the pattern for nasopharyngeal cancer suggests that simultaneous exposure to formaldehyde and particles may be a risk factor for this tumor."[21] The factories in the Stayner study and the Blair study where excess nasopharyngeal cancers were found were noted to be dusty. Therefore, the particulate matter to which employees were exposed may have contained either adsorbed or chemically-bound formaldehyde, the latter of which could be released in the warm, moist environment of the upper respiratory tract.[22] Much work remains to be done in this area to better assess the effect of formaldehyde-containing dust on the incidence of cancers of the upper respiratory tract. There are currently no workplace evaluation criteria for formaldehyde-containing dust.

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.[15,23] The NIOSH REL for ammonia is 25 ppm for a 10-hour TWA. The NIOSH STEL is 35 ppm. ACGIH has established a TLV™ of 25 ppm TWA and an STEL of 35 ppm. The OSHA PEL for ammonia is 50 ppm.

Occupational Asthma

Asthma, a lung disorder characterized by reversible obstruction of the lung airway system (called the bronchial tubes) causes intermittent respiratory symptoms, including shortness of breath, wheezing, chest tightness, and cough. In occupational asthma, airway obstruction is caused or made worse by workplace exposure to dusts, fumes, gases, or vapors.[24] In the U.S., asthma occurs in about 5% of the general population; 2% of these cases are thought to be occupational.[25] Common mechanisms of occupational asthma include direct airway irritation (reflex bronchoconstriction), inflammatory bronchoconstriction, and allergic bronchoconstriction (Type I hypersensitivity).

Direct airway irritation (reflex bronchoconstriction)

In this type of occupational asthma, the airways of the lung are irritated by many nonspecific agents such as cold air, dust particles, gases, and fumes. It does not involve the body's immune system, and in most cases, the individual has a history of asthma prior to any occupational exposure. These people are considered to have abnormally reactive airways, and they generally develop symptoms of shortness of

breath, chest tightness, cough, and wheezing immediately after exposure to occupational or other agents. Symptoms can occur following exposure to extremely low concentrations of the irritant.

Inflammatory bronchoconstriction

Asthma of this type results from inhalation of irritant gases and vapors in very high concentrations. The irritant gases cause damage to the cells lining the bronchial airways and result in an inflamed airway. The individual has symptoms of shortness of breath, wheezing, chest tightness, and cough. Symptoms usually resolve within several weeks, but in some individuals the symptoms can persist following exposure (over extended periods) to low levels of many non-specific irritants.

Allergic bronchoconstriction or Type I hypersensitivity

Allergic bronchoconstriction is the most common type of occupational asthma. Susceptible workers develop antibodies after being exposed to substances at work, and repeated exposure causes asthma to develop. The time between developing asthma symptoms after exposure to the workplace substance can vary from weeks to years. Once asthma has developed, symptoms may occur immediately after exposure, following a delay of several hours, or in a pattern with both early and late components.

RESULTS

Environmental Evaluation

Sample results for gaseous formaldehyde ranged from non-detected to 2.2 ppm (Table 1). Of the four samples collected during the initial visit, only one had a detectable amount of formaldehyde. This sample had only a trace amount of formaldehyde that was between the analytical LOD and LOQ and was collected on the third deck of the granular urea plant. The airborne formaldehyde concentrations for the samples collected during the second visit ranged from 0.004 to 2.2 ppm. Two of these samples were collected from the same area, near the prill tower melt box, as two of the samples collected during the first visit. The formaldehyde concentrations determined for these samples were 0.024 and 0.028 ppm, as compared to the non-detectable concentrations on the samples from the first visit. The remaining six samples were collected from locations different than those sampled during the initial visit. Three were collected from the storage warehouses during the freighter loading operations and three during the unloading of a UF-85 tanker. Of the three samples collected in the warehouses, the two collected from the granular warehouse both had formaldehyde concentrations of 0.004 ppm, while the concentration for the sample collected in the prill warehouse was 0.007 ppm.

Because the formaldehyde exposure potential was most likely greatest during the unloading of the UF-85 tanker, two of the three samples were collected using a sorbent tube method. This method has a higher LOD than the impinger method, but is more practical for collecting PBZ samples. Therefore, a PBZ sorbent tube sample was collected from the operator performing the unloading operation, in addition to two area samples from the same location using both methods for comparison. The formaldehyde concentrations determined for the area samples were 1.6 and 2.2 ppm for the sorbent tube and impinger methods, respectively. The PBZ sample collected using a sorbent tube was determined to have a concentration of 0.25 ppm. The sampling duration for all three of these samples was only 35 minutes, which was the duration of the unloading operation.

Unocal had also conducted limited sampling for airborne formaldehyde prior to the NIOSH visits. Unocal's samples were collected in the prill warehouse and near the prill tower melt box using both the impinger and sorbent tube methods discussed above. Adjacent samples using the two methods were collected from both locations. Since no pre-filter was used on the impinger samples, this method would measure both free formaldehyde as

well as the urea-formaldehyde reaction products, including MDU, in particulate form while the sorbent tube method would specifically measure free formaldehyde vapor. For the two adjacent samples collected in the prill warehouse, the concentrations were 0.09 ppm for the impinger method and 0.01 ppm for the sorbent tube method while concentrations of 0.011 and less than 0.01 ppm were determined for the samples collected near the prill tower melt box using the impinger and sorbent tube methods, respectively. Two subsequent impinger samples were also collected from the prill warehouse with one of these samples collected using a pre-filter so that only the free formaldehyde vapor would be measured. The resultant concentrations for these samples were 0.02 with the pre-filter and 0.018 ppm without it.

The airborne formaldehyde concentrations in both the prill and granular manufacturing areas were below the relevant evaluation criteria and were consistent with the Unocal results for the samples collected in the prill tower. The formaldehyde concentrations found in the warehouses were lower than the two detectable concentrations (0.024 and 0.028 ppm) found in the prill tower and were also consistent with the concentrations determined by Unocal with the exception of an impinger sample with a concentration of 0.09 ppm. This sample was collected without a pre-filter; therefore, the higher concentration may be attributable to urea-formaldehyde reaction products on dust present during the sample collection. The other two Unocal samples collected from this location were consistent even though one was also collected without a pre-filter. These results may also indicate that less airborne dust containing the urea-formaldehyde reaction products was present when these samples were collected.

One area sample collected during the unloading of the UF-85 tanker was above the OSHA STEL of 2 ppm. Both area samples collected during this 35-minute unloading operation had formaldehyde concentrations that also exceeded the ceiling limits of 0.1 and 0.3 ppm established by NIOSH and ACGIH, respectively. The PBZ sample collected from the operator performing the unloading operation had a concentration of 0.25 ppm which exceeded the NIOSH ceiling limit. Operators unloading the tanker are required to wear Tyvek® suits coated with polyethylene, rubber gloves, and a face shield with chemical goggles. When there is the possibility of exposure to formaldehyde vapor, such as during this operation, the Unocal safety procedures dictate that a MSA full face piece chest mounted respirator with yellow GMC-SS supersize canisters should be worn.

The results of the bulk sample analysis indicated that the formaldehyde on dust method actually measures the concentration of both free formaldehyde and the urea-formaldehyde reaction products, such as MDU. Positive results for formaldehyde were obtained for both the bulk samples of urea and the analytically pure MDU, which indicated that MDU hydrolyzes to form formaldehyde and urea due to the addition of perchloric acid during the analytical procedure. Therefore, the results of the samples collected using the inhalable cassettes will be presented as formaldehyde equivalents. A more detailed description of the bulk sample analysis is provided in the "Discussion" section of this report.

The airborne concentrations of inhalable dust, particulate formaldehyde equivalent, and percent, by weight, formaldehyde equivalents are presented in Table 2. The concentrations of inhalable dust ranged from 0.3 to 78.6 mg/m^3 while the equivalent airborne concentrations of particulate formaldehyde equivalents (FE) ranged from 0.6 to 1110 µg/m^3. The determined percentages, by weight, of FE ranged from not detected to 4.06%. Inhalable dust concentrations ranged from 0.3 to 28.3 mg/m^3 for full-shift PBZ samples collected during normal operations. Area samples were also collected from several locations in both plants during normal operations. The samples collected from the prill plant had inhalable dust concentrations ranging from 7.7 to 46.9 mg/m^3. In the granular plant, partial shift consecutive area samples were collected from two locations. The time-weighted average concentrations for these samples were 1.9 and 18.1 mg/m^3. Seven area and PBZ samples were

collected from both warehouses during the loading of a freighter, and the inhalable dust concentrations for these samples ranged from 1.2 to 17.1 mg/m^3.

Samples were also collected during the daily blow-down operation in the granulation plant. During this operation, an operator uses a compressed air hose to clean settled dust off equipment in the plant. The operator, who wears a half-face respirator equipped with HEPA cartridges, starts on the top deck and cleans each deck in successive order until all the dust is accumulated on the ground floor, where it can be swept up. The samples that were collected from the operator performing the blow-down had inhalable dust concentrations of 21.9 and 78.6 mg/m^3, while an area sample had an inhalable dust concentration 29.7 mg/m^3. A sample simulating the exposure of the operator was also collected on a NIOSH investigator following as close as possible to the operator throughout the procedure. This sample had an inhalable dust concentration of 31.0 mg/m^3. Three of the samples collected during the blow-down and one in the prill warehouse were overloaded with dust. Therefore, the concentrations presented most likely underestimate the actual concentrations and are noted in Table 2.

The highest concentrations of inhalable dust occurred during the daily blow-down operation. The 8-hour time-weighted averages, calculated assuming no further exposures for these samples, ranged from 3.7 to 12.3 mg/m^3. One of these concentrations was above the ACGIH TLV of 10 mg/m^3 for inhalable particulates; those particulates that can be deposited anywhere in the respiratory tract. Two of the full-shift PBZ samples collected from an operator and helper in the granular plant also exceeded this limit. The corresponding FE concentrations were highest for the inhalable dust samples collected during the blow-down operation and the warehouse loading operations, and the FE percentages were also greatest during these two operations. If the results of the Unocal MBTH study which showed that free formaldehyde may be present in the urea is accurate, there would be a potential for some exposure to formaldehyde because there is the potential for exposure to high concentrations of the urea dust.

The results for total and respirable dust are presented in Table 3. Airborne total dust concentrations ranged from 0.1 to 45 mg/m^3 during operations in both plants and warehouses, while two samples collected during the blow-down operation in the granulation plant had estimated concentrations of 64 and 76 mg/m^3. Respirable dust concentrations were 4.33 and 0.09 mg/m^3 near the prill tower melt box and the third deck of the granulation plant, with the higher concentration being determined for the sample from the prill tower. Both of the respirable dust samples were collected during the initial visit in the same locations as consecutive, partial shift total dust samples. The time-weighted total dust concentration near the prill tower melt box was 5.49 mg/m^3, while the concentration in the granulation plant was 1.44 mg/m^3. One total dust sample collected from near the prill tower melt box during the second visit was found to be overloaded with dust, but the estimated concentration was determined to be 45 mg/m^3.

The total dust samples from both warehouses were collected during the loading of a freighter. PBZ samples were collected from the loader operators, and area samples were collected on the loaders, both inside and outside of the cab. The concentrations for these samples ranged from 0.1 to 1.6 mg/m^3. As expected, the concentrations determined for the samples collected from inside the cabs of the loaders were lower than outside of the cabs. The concentrations were reduced from 1.9 to 0.5 mg/m^3 on a loader in the prill warehouse while the reduction was from 1.3 to 0.1 mg/m^3 in the granular warehouse. However, the concentrations experienced by the loader operators were higher than the concentrations determined inside the loader cabs sampled in both warehouses. The loader operators were exposed to 1.1 and 1.6 mg/m^3 in the prill and granular warehouses, respectively. An area sample with a concentration of 0.7 mg/m^3 was also collected from a location on the granular warehouse floor. The concentrations determined during the blow-down operation in the granulation plant were 76 mg/m^3 for the operator and 64 mg/m^3 for a sample which was carried as closely as possible to the operator. Both these samples were also

overloaded with dust, so the determined concentrations most likely underestimate the actual concentrations. The duration of this operation is approximately 95 minutes, so the 8-hour time weighted averages calculated, assuming no further exposure, for these samples were 15 and 13 mg/m^3, respectively.

The highest exposures to total dust also occurred during the blow-down operation in the granulation plant. The 8-hour time-weighted averages for both samples collected during this operation exceeded the ACGIH TLV of 10 mg/m^3, and one was equal to the OSHA PEL of 15 mg/m^3. These total dust concentrations were compared to the ACGIH TLV for inhalable particulates because this classification includes particulates with the greatest aerodynamic diameters, up to 100 micrometers. In addition, the total dust results would actually underestimate the actual inhalable concentrations due to the lower collection efficiencies of the total dust sampling method, as compared to the inhalable dust method, for particulates greater than 15 micrometers in size. However, the use of the half-face respirator with HEPA cartridges seemed to provide adequate protection for this operation. The area respirable dust sample collected from near the prill tower melt box had a concentration that was above the ACGIH TLV of 3 mg/m^3. However, operators only spend short periods of time at this location during their normal inspection rounds so their personal exposures would not be expected to exceed this limit. Actual exposures may also be higher because operators often blow dust off their uniforms using compressed air.

Airborne concentrations of ammonia ranged from less than 0.02 to 276 ppm and are presented in Table 4. Full-shift PBZ samples for ammonia were collected from operators, maintenance personnel, and an electrician. These ammonia concentrations ranged from 0.3 to 25 ppm with the highest exposures being experienced by prill plant front end compression and prill tower operators. The concentrations experienced by these workers ranged from 5.2 to 25 ppm. The remaining samples were collected on two maintenance workers in the prill plant and two operators and an electrician in the granular plant. These concentrations ranged from 0.3 to 2.9 ppm. Short-term PBZ samples were also collected from the prill tower operator during both visits. This operator conducts routine inspection rounds in the prill tower throughout the entire shift. The concentrations determined for these samples ranged from 75 to 103 ppm with sampling durations of 16 to 21 minutes. During the initial visit, two short-term samples for ammonia were collected by a NIOSH investigator who followed the operator during the routine rounds. These samples were collected to simulate the exposures experienced by the operator during the inspection rounds and were not worn by the operator because he was already wearing a full-shift sample. The concentrations determined for these samples were 156 and 276 ppm with a 9 minute sample duration. Area samples for ammonia were also collected from locations near the prill tower melt box. Consecutive partial samples were collected at three locations to prevent breakthrough in the sorbent tubes. The time-weighted averages for the three sets of consecutive samples collected were 106, 115, and 190 ppm with the highest partial period concentration of 203 ppm. One additional area sample was also collected in the prill plant control room for comparison. This sample had an ammonia concentration of 5.3 ppm.

Ammonia samples were also collected in both warehouses during the loading of a freighter. These samples were collected in the same locations as the total dust samples collected during this operation, as previously described. The concentrations for the samples collected in the prill warehouse ranged from 13 to 22 ppm. Two PBZ samples collected from the loader operators working in the prill warehouse had ammonia concentrations of 13 and 20 ppm. The area sample collected outside the loader had a concentration of 22 ppm, while the area sample inside was 20 ppm. The ammonia concentration on the prill warehouse floor was 27 ppm. The ammonia concentrations in the granular warehouse were lower than the concentrations found in the prill warehouse. The concentrations in the granular warehouse ranged from less than 0.02 ppm to 1.9 ppm. The sample with the less than 0.02 ppm concentration was an

underestimate of the actual concentration because the hose attaching the sorbent tube to the sampling pump had disconnected at some point during the sampling period. This sample was collected from outside the loader and had only a trace amount of ammonia that was between the analytical LOD and LOQ. The loader operator in the granular warehouse was exposed to an ammonia concentration of 1.4 ppm, while the concentration inside the loader was 1.9 ppm. The ammonia concentration on the granular warehouse floor was found to be 0.6 ppm.

The highest ammonia concentrations were found in the prill tower. Area concentrations near the prill tower melt box were well above the evaluation criteria established by NIOSH, OSHA, and ACGIH. However, the operators only spend a limited amount of time during their routine inspection rounds exposed to these high concentrations. However, one of the full-shift, PBZ samples collected from a prill tower operator had an ammonia concentration which equaled the NIOSH and ACGIH limit of 25 ppm. This concentration could also be considered at the OSHA action limit which is half the PEL of 50 ppm. NIOSH and ACGIH have also established a STEL of 35 ppm. The short-term samples collected during the prill tower inspection rounds all exceeded this limit. The operators performing this operation typically wear half-face respirators which may not provide adequate protection because ammonia is irritating to the eyes. Also, one prill tower operator was observed using a half-face respirator equipped with only HEPA cartridges which do not provide protection against ammonia vapors. The respirators should be equipped with approved cartridges that provide protection against ammonia. Airborne concentrations of ammonia were considerably higher in the prill warehouse than in the granular warehouse. The concentrations in the prill warehouse approached the NIOSH and ACGIH criteria of 25 ppm. Also, the loader cab did not provide significant protection since the concentrations inside the cab approached the concentrations measured outside the cab.

Medical Evaluation

Health effects were considered to be occupational in origin if an employee identified them as occurring exclusively or predominately at work, or specified plausible and specific work conditions related to the symptom(s) at work. Employees were asked if they had experienced any of the following symptoms within the past month: irritation of the eyes, nose, or throat; tearing of the eyes; headache; nasal discharge or bleeding; sneezing; shortness of breath; cough; wheeze; and chest pain/tightness.

Twenty-one male employees were interviewed. Their ages ranged from 31 to 51 years old, with an average age of 41 years. Duration of employment at Unocal ranged from 2 to 16 years, with an average duration of 10 years. Job titles of those interviewed included operator, loader, welder, mechanic, electrician, instrument technician, utility operator, and unit coordinator.

The occurrence of symptoms among the 21 employees is presented in Table 5. Six of the 21 employees reported having at least two symptoms consistent with a diagnosis of current asthma (shortness of breath, chest pain or tightness, cough, or wheeze).[28-31] Given the potential for intermittent exposure to ammonia throughout the plant and the high concentrations of ammonia documented in the prill tower, some employees may be experiencing these symptoms in response to their individual exposures. Although these symptoms could be present in persons with respiratory illnesses characterized by hyper-reactive airways, such as asthma, diagnosis of these illnesses cannot be made based on the occurrence of symptoms alone.

DISCUSSION

To address concerns that positive results for the formaldehyde on dust method (NIOSH Method 5700[5]) would not accurately reflect free formaldehyde in the samples, but rather, formaldehyde formed from the acid hydrolysis of the MDU in the samples due to the required acidification with dilute perchloric acid, bulk samples of the prill urea, granular urea, and MDU were analyzed. Two samples of each the prill and granular bulk samples were analyzed in the same manner as the samples collected with the inhalable cassettes. The average percent formaldehyde determined for the two prill and granular samples was 0.37% and 0.58%, respectively. The granular urea was shown to have approximately 50% more formaldehyde than the prill urea. These results were consistent with the percentages reported by Unocal. Unocal reported that the percentage of MDU in the final urea products range from approximately 1.3 to 1.9%, with the percentages greater in the granular forms than the prill forms. This would correspond to equivalent formaldehyde percentages of 0.30 to 0.43% by dividing the percentage of MDU by the conversion factor of 4.4 stated in the TFI report.[4] The TFI report also states that formaldehyde-based additives are typically present in urea at a "formaldehyde equivalent" level of 0.3 to 0.5% as determined by the chromatropic acid test.[4]

Four samples of the bulk MDU, four samples of MDU spiked with formaldehyde, and two additional samples of formaldehyde standard solution were also analyzed concurrently in the same manner as inhalable air samples. The recovery of formaldehyde from both the spiked and unspiked samples of MDU was consistent with the amount of formaldehyde which would be theoretically produced if all MDU were converted to urea and formaldehyde as a result of the analytical procedure. An average of 92.0% ± 2.9% of the theoretical was obtained after correction for the experimentally determined recovery of formaldehyde in the absence of MDU. There were at least two possible explanations for this observation. The MDU may hydrolyze under the conditions of the extraction step in which the samples are placed in 10 mL of deionized water for 4 hours at 41°C, or the MDU may be undissociated in the extraction step and react with the perchloric acid added in the derivatization step to produce formaldehyde which then forms the hydrazone derivative with 2,4-dinitrophenylhydrazine (2,4-DNP), the derivatizing agent. If the MDU hydrolyzes during the extraction step, it could be assumed that the potential for exposure to formaldehyde exists because this method was designed to measure the potential for formaldehyde availability upon inhalation or ingestion of particulate containing bound formaldehyde. If the MDU hydrolyzes during the derivitization step, the potential for exposure to formaldehyde would be dependent on the body's ability to hydrolyze the MDU.

Bulk samples of the urea fertilizer were also analyzed by the Elia and Messmer method which also uses an aqueous extraction procedure and colorimetric analysis, but with acetylacetone (ACE) as the reagent.[26] This method was not published until October 1992, and was used for comparison during the validation of the final version for NIOSH method 5700. As part of this comparison, the Elia-Messmer method was also used to analyze samples collected during a 1993 field study at a fiberboard manufacturing facility which utilized urea-formaldehyde resins as the fiberboard binding materials.[27] Comparison of results from 2,4-DNP analyses with those from ACE analyses indicated that there was a significant difference between the two methods. The ACE analyses used much milder conditions and appeared to be reacting only with released formaldehyde, whereas the 2,4-DNP analysis required the addition of perchloric acid and may be reacting with both the released formaldehyde and formaldehyde equivalents (e.g., the small oligomeric pieces of formaldehyde-containing, partially hydrolyzed resin) present in more acidic hydrolysis solutions. Although the 2,4-DNP analyses yielded formaldehyde concentrations that were from 2 to 18 times higher than the ACE analyses, the field study air sample results for these two methods were highly correlated (r=0.98).[27] To

investigate the performance of these analytical methods on various matrices other than wood or textile dust, bulk samples of the urea fertilizer remaining from the Unocal site visits were reanalyzed using both the 2,4-DNP and ACE methods. Four samples of varying weights were analyzed by both the methods. The formaldehyde percentages in these urea fertilizer samples averaged 0.02% using the ACE method and 0.9% using the 2,4-DNP method. These results supported the previous contention that the acidic conditions of the 2,4-DNP analytical procedure hydrolyzes both the formaldehyde oligomers and, in the case of the urea fertilizer, urea-formaldehyde reaction products such as MDU. Therefore, these results also supported the theory that the 2,4-DNP analyses actually measures the concentration of both free formaldehyde and formaldehyde equivalents, while the ACE analyses only measured free formaldehyde.

The analysis of the fertilizer bulk samples by both the ACE and 2,4-DNP methods indicated that the MDU or other urea-formaldehyde reaction products are most likely hydrolyzed during the derivitization step of the 2,4-DNP analytical procedure. The results also tend to confirm the findings of the previous Unocal polarography/MBTH study that free formaldehyde is present only at low levels (0.02%) in the urea fertilizer.[7] Although there was the potential for exposure to free formaldehyde from the inhalable urea dust, most of the formaldehyde detected on the inhalable dust samples was probably due to the hydrolysis of the urea-formaldehyde reaction products such as MDU. Therefore, the greatest overall potential for exposure to formaldehyde would be dependent on the body's ability to hydrolyze the MDU, the determination of which is beyond the scope of this investigation. Since the analysis of the bulk samples indicated that a significant percentage of the positive results for formaldehyde were most likely due to the hydrolysis of the MDU and a definitive conclusion regarding the potential for actual formaldehyde exposure could not be made, the results of the samples collected using the inhalable cassettes were presented as formaldehyde equivalents. It should be noted that more epidemiologic studies are needed to relate the potential for any adverse health outcomes to exposure from either the free formaldehyde or urea-formaldehyde reaction products on inhalable urea fertilizer dust.

CONCLUSIONS

The environmental sampling indicated that employees may be exposed to low concentrations of formaldehyde vapor during the manufacture and loading of urea. Because formaldehyde has been identified as a suspected human carcinogen, NIOSH recommends that exposures be reduced to the lowest feasible level. The greatest potential for exposure to formaldehyde occurred during the unloading of the tankers containing UF-85. Environmental samples collected during this operation determined that formaldehyde concentrations can exceed both the NIOSH and ACGIH ceiling limits of 0.1 and 0.3 ppm, respectively. The analysis of the urea and MDU bulk samples indicated that MDU will produce positive results for formaldehyde when analyzed by the formaldehyde on dust method (NIOSH Method 5700). When using an analysis technique that employs milder, non-acidic conditions, such as the ACE method, only low levels of free formaldehyde (0.02%) in the urea dust were analytically determined during this investigation. This confirms the prior studies conducted by Unocal using the MBTH method. However, the formaldehyde on dust samples still indicated that inhalable dust concentrations could exceed the ACGIH TLV for inhalable particulates. The results for the total and respirable dust samples indicated that these concentrations may periodically exceed their relevant evaluation criteria, but the use of respiratory protection and the amount of time spent in areas with higher concentrations limit worker exposures. The environmental sampling for ammonia indicated that concentrations in the prill tower do exceed both the time-weighted and short-term exposure limits. However, only one PBZ sample collected from a prill tower operator reached the NIOSH and ACGIH limit of 25 ppm. The short-term concentrations for ammonia also exceeded the

NIOSH and ACGIH STEL of 35 ppm during the prill tower inspection rounds, and an operator conducting these rounds was wearing a respirator that was not approved for protection against ammonia. In addition, although employees noted symptoms during the medical evaluation which could be consistent with occupational asthma, further medical evaluations would be necessary to confirm any specific diagnosis.

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 all employees at the Unocal Kenai facility.

1. Unocal should promote further studies concerning the potential for employee exposures to formaldehyde from the urea dust. Even though the presence of only small amounts of formaldehyde (0.02%) in the dust could be analytically determined during this investigation, further studies should be conducted to determine the potential for exposure from the apparent free formaldehyde determined using the Elia and Messmer method (ACE) or polarography in the presence of MBTH and whether or not MDU can be hydrolyzed by the human body to form formaldehyde when deposited in the upper respiratory tract.

2. Unocal should consider establishing a joint management and union committee to address health and safety issues at the facility. The committee can address the feasibility of using engineering controls and work practices to reduce worker exposures to the urea dust, ammonia, and other compounds.

3. Unocal should review its current respiratory protection program to ensure that it complies with the requirements described in 29 CFR 1910.134.[32] Publications developed by NIOSH which should also be referenced include the NIOSH Guide to Industrial Respiratory Protection and NIOSH Respirator Decision Logic.[33,34] It is recommended that the written program be revised to 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. The respirator program should also reference the requirements contained in the confined space program to assure that employees are adequately protected when working in these areas. 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.

4. The use of compressed air to perform the blow-down operation in the granular plant and clean off individual uniforms should be eliminated. The feasibility of alternative methods, such as wet methods or vacuuming, should be investigated. Requiring employees to frequently change dirty work uniforms or the use of a vacuum systems equipped with HEPA filters to remove dust are possible alternatives to reduce worker exposures. Until alternative methods for cleaning are implemented, any compressed air used for the purposes of cleaning should have a pressure of less than 30 pounds per square inch (psi) and be used in accordance with 29 CFR 1910.242.[35]

5. Unocal should investigate the use of HEPA filters, in conjunction with filters approved for ammonia, on the loaders used in the warehouse operations. Use of these types of filters in the loader ventilation systems would reduce the potential for exposures to both dust and ammonia.

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TABLE 1
Airborne Concentrations of Formaldehyde
Unocal Urea Fertilizer Plant
Kenai, Alaska
HETA 91-0153
August 8-9, 1991 & April 13-14, 1992

Sample Description	Date	Sample Duration (minutes)	Sample Volume (liters)	Concentration (ppm)
Plant #2 - Area Near Prill Tower Melt Box	8/8/91	510	255	ND
Plant #2 - Area Near Sizing Screens	"	512	256	ND
Plant #5 - Area on second Deck	"	485	242	ND
Plant #5 - Area on third Deck	"	479	240	trace
Plant #2 - Area Near Prill Tower Melt Box	4/14/92	295	295	0.024
Plant #2 - Area Near Prill Tower Melt Box	"	295	295	0.028
Area samples collected during warehouse operations (loading of freighter)				
Prill Warehouse - Area Near Wall	4/14/92	252	252	0.007
Granular Warehouse - Area Near Grizzly	4/13/92	388	388	0.004
Granular Warehouse - Area at South End	"	373	373	0.004
Unloading of UF-85 tanker				
Area Between Tanker & Transfer Pipes	4/14/92	35	35	2.2
Area Between Tanker & Transfer Pipes (sorbent tube)	"	35	7	1.6
Unloading Operator (sorbent tube)	"	35	7	0.25
Evaluation Criteria (8-hour TWA unless otherwise noted)			*NIOSH* *ACGIH* *OSHA*	*0.016 LFC* *0.1 C* *0.3 C* *0.75* *2.0 STEL*

Note - All samples were collected for formaldehyde using impingers (NIOSH method #3500) unless otherwise indicated as using sorbent tubes (NIOSH method #2541).
ppm - parts per million
ND - not detected
trace - detected value was between the minimum detectable concentration (MDC) and minimum quantifiable concentration (MQC) of 0.006 and 0.018 ppm, respectively, calculated for formaldehyde samples collected during the 1991 visit assuming a sampling volume of 256 liters.
LFC - Even though NIOSH has established a REL, NIOSH recommends that exposures be reduced to the lowest feasible concentration because formaldehyde has been identified as a suspected human carcinogen.
C - ceiling limit
STEL - short-term exposure limit

TABLE 2
Airborne Concentrations of Inhalable Dust and Particulate Formaldehyde Equivalent
Unocal Urea Fertilizer Plant
Kenai, Alaska
HETA 91-0153
August 8-9, 1991 & April 13-14, 1992

Sample Description	Date	Sample Volume (liters)	Total Inhalable Weight (mg/m^3)	Particulate Formaldehyde Equivalent ($\mu g/m^3$)	Percent Formaldehyde Equivalent (by weight)
Personal breathing zone samples collected from the prill and granular plants					
Plant #2 - Operator (back end)	8/8/91	1244	6.7	2.0	0.03
Plant #2 - Prill Tower Operator	"	1010	4.7	2.3	0.05
Plant #2 - Maintenance	8/9/91	744	0.93	3.6	0.39
Plant #2 - Maintenance	"	188	2.2	9.0	0.41
Plant #5 - Process Operator	8/8/91	1064	0.3*	(0.6)*	0.20
Plant #5 - Helper (building scaffolds)	"	1048	28.3	11.5	0.04
Plant #5 - Operator	"	1108	15.3	2.9	0.28
Plant #5 - Electrician	"	366	5.4	7.4	0.14
"	"	550	3.0	5.8	0.19
TWA for above 2 consecutive samples	"	*916*	*4.0*	*6.4*	*0.17*
Area samples collected from the prill and granular plants					
Plant #2 - Near Sizing Screens	8/8/91	454	4.4	7.9	0.18
"	"	570	10.3	5.6	0.05
TWA for above 2 consecutive samples	"	*1024*	*7.7*	*6.6*	*0.11*
Plant #2 - Prill Tower Melt Box	"	468	10.9	7.9	0.07
"	"	556	16.5	5.6	0.03
TWA for above 2 consecutive samples	"	*1024*	*14.0*	*6.7*	*0.05*
Plant #2 - Prill Tower Melt Box	4/14/92	590	26.6	16.2	0.06
Plant #2 - Prill Tower Melt Box	"	332	46.9	28.0	0.06
Plant #5 - Third Deck	8/8/91	350	30.9	20.3	0.07
"	"	406	12.2	7.1	0.06
"	"	286	11.0	42.0	0.38
TWA for above 3 consecutive samples	"	*1042*	*18.1*	*21.1*	*0.15*

TABLE 2 (Continued)
Airborne Concentrations of Inhalable Dust and Particulate Formaldehyde Equivalent

Sample Description	Date	Sample Volume (liters)	Total Inhalable Weight (mg/m^3)	Particulate Formaldehyde Equivalent ($\mu g/m^3$)	Percent Formaldehyde Equivalent (by weight)
Plant #5 - Second Deck	"	360	2.8	8.3	0.30
"	"	416	1.3	6.0	0.47
"	"	296	1.6	4.7	0.30
TWA for above 3 consecutive samples	"	*1072*	*1.9*	*6.4*	*0.36*
Warehouse operations during loading of freighter					
Prill Warehouse - Area Outside Loader	4/14/92	534	17.1‡	397‡	2.32
Prill Warehouse - Area Inside Loader	"	546	1.2	48.4	4.06
Prill Warehouse - Area on Floor	"	504	5.6‡	115‡	2.07
Granular Warehouse - Area Inside Loader	4/13/92	770	1.4	13.8	0.98
Granular Warehouse - Area on Floor	"	776	1.6	ND	ND (<0.2)
Granular Warehouse - Loader Operator	"	738	2.8	12.4	0.44
Granular Warehouse - Loader Operator	"	818	5.5	31.2	0.57
Daily blow-down operation in Plant #5 - Granulation					
Area on third Deck	4/13/92	118	29.7‡	641‡	2.16
Operator Performing Blow-Down	"	190	21.9**	363**	1.65
Followed Operator Performing Blow-Down	"	186	31.0‡	984‡	3.18
Operator Performing Blow-Down	4/14/92	88	78.9‡	1511‡	1.92
"	"	62	78.1	1052	1.35

* - Sampling pump faulted, so sample volume was estimated; therefore, concentrations may underestimate actual concentrations.

‡ - Filters for these samples were overloaded; concentrations presented most likely underestimate actual concentrations.

** - Filter for this sample was damaged due to overloading; concentrations presented most likely underestimate actual concentrations.

mg/m^3 - milligrams per cubic meter

$\mu g/m^3$ - micrograms per cubic meter

<0.2 - less than 0.2%

TABLE 3
Airborne Concentrations of Total and Respirable Dust
Unocal Urea Fertilizer Plant
Kenai, Alaska
HETA 91-0153
August 8-9, 1991 & April 13-14, 1992

Sample Description	Date	Sample Duration (minutes)	Sample Volume (liters)	Concentration (mg/m^3)
Plant #5 - Granulation Control Operator	8/8/91	555	555	0.34
Area samples collected from the prill and granular plants				
Plant #2 - Near Prill Tower Melt Box (Resp)	8/8/91	227	386	4.33
Plant #2 - Near Prill Tower Melt Box	"	229	229	2.79
"	"	277	277	7.73
TWA for above 2 consecutive samples	"	*506*	*506*	*5.49*
Plant #2 - Near Prill Tower Melt Box	4/14/92	295	590	45*
Plant #5 - Granulation third Deck (Resp)	8/8/91	522	887	0.09
Plant #5 - Granulation third Deck	"	179	179	0.56
"	"	200	200	2.75
"	"	143	143	0.70
TWA for above 3 consecutive samples	"	*522*	*522*	*1.44*
Warehouse operations during loading of freighter				
Prill - Area outside loader	4/14/92	267	534	1.9
Prill - Area inside loader	"	273	546	0.5
Prill - Loader operator	"	270	540	1.1
Granular - Area outside loader	4/13/92	385	770	1.3
Granular - Area inside loader	"	385	770	0.1
Granular - Loader operator	"	414	890	1.6
Granular - Area on warehouse floor	"	388	776	0.7
Daily blow-down operation in Plant #5 - Granulation				
Operator performing blow-down	4/13/92	95	190	76*
Followed operator performing blow-down	"	93	186	64*
Evaluation Criteria			*ACGIH* *OSHA*	*10, 3 (Resp)* *15, 5 (Resp)*

* - Filters for these samples were overloaded; concentrations presented most likely underestimate actual concentrations.
mg/m^3 - milligrams per cubic meter
Resp - Respirable Dust Sample

TABLE 4
Airborne Concentrations of Ammonia
Unocal Urea Fertilizer Plant
Kenai, Alaska
HETA 91-0153
August 8-9, 1991 & April 13-14, 1992

Sample Description	Date	Sample Duration (minutes)	Sample Volume (liters)	Concentration (ppm)
Plant #2 Maintenance	8/9/91	373	75	2.4
Plant #2 Maintenance	"	371	74	1.5
Plant #5 Process Operator	8/8/91	447	89	2.2
Plant #5 Compression Operator	"	573	115	2.9
Plant #5 Electrician	"	458	92	0.3
Plant #2 Front End Compression Operator	"	615	123	5.2
Plant #2 Prill Tower Operator	"	607	121	25
Plant #2 Prill Tower Operator	4/13/92	538	108	13
Plant #2 Prill Tower Operator	"	538	108	12
Evaluation Criteria (8-hour TWA)			*NIOSH, ACGIH* *OSHA*	*25* *50*

STEL samples collected from the prill tower operator during routine rounds

Plant #2 Prill Tower Operator*	8/9/91	9	9	156
Plant #2 Prill Tower Operator*	"	9	1.8	276
Plant #2 Prill Tower Operator (morning)	4/14/92	21	4.2	96
"	"	21	4.2	75
Plant #2 Prill Tower Operator (afternoon)	"	16	3.2	85
"	"	16	3.2	103
Evaluation Criteria (STEL)			*NIOSH, ACGIH*	*35*

Area samples collected in the prill tower

Plant #2 - Control Room Desk	8/8/91	627	125	5.3
Plant #2 - Near Prill Tower Melt Box	"	230	46	181
"	"	146	29	203
TWA for above 2 consecutive samples	"	*376*	*75*	*190*

TABLE 4 (Continued)
Airborne Concentrations of Ammonia

Sample Description	Date	Sample Duration (minutes)	Sample Volume (liters)	Concentration (ppm)
Plant #2 - Near Prill Tower Melt Box	4/14/92	120	24	102
"	"	90	18	103
"	"	95	19	143
TWA for above 3 consecutive samples	"	*305*	*61*	*115*
Plant #2 - Near Prill Tower Melt Box	"	120	24	102
"	"	90	18	103
"	"	95	19	113
TWA for above 3 consecutive samples	"	*305*	*61*	*106*
Warehouse operations during loading of freighter				
Prill - Area Outside Loader	4/14/92	267	53	22
Prill - Area Inside Loader	"	273	55	20
Prill - Loader Operator	"	270	54	20
Prill - Loader Operator**	"	258	52	13**
Prill - Area on Warehouse Floor	"	252	50	27
Granular - Area Outside Loader**	4/13/92	385	77	trace**
Granular - Area Inside Loader	"	385	77	1.9
Granular - Loader Operator	"	409	82	1.4
Granular - Area on Warehouse Floor	"	388	78	0.6
Evaluation Criteria (8-hour TWA)			*NIOSH, ACGIH* *OSHA*	*25* *50*

* - These samples were collected to simulate ammonia exposures during the routine inspection of the melt box and tanks at the top of the prill tower; the samples were carried by the NIOSH industrial hygienist who followed, as close as possible, the prill tower operator.

** - Estimated concentrations which underestimate true concentrations; hoses attaching sorbent tubes to the sampling pumps had disconnected at some point during sampling period.

trace - detected value was between the minimum detectable concentration (MDC) and minimum quantifiable concentration (MQC) of 0.007 and 0.02 ppm, respectively, assuming a sampling volume of 108 liters.

ppm - parts per million

TWA - time-weighted average

STEL - short-term exposure limit

TABLE 5
Symptom Occurrence Among Interviewed Unocal Employees
Unocal Urea Fertilizer Plant
Kenai, Alaska
HETA 91-0153
August 8-9, 1991

Symptom	Number Reporting	Percentage Reporting (%)
Throat Irritation	10	47
Nose Irritation	9	43
Runny Nose	9	43
Eye Irritation/Tearing	7	33
Sneeze	5	24
Headache	4	19
Shortness of Breath	6	29
Cough	5	24
Wheeze	4	19
Chest Pain/Tightness	4	19

Note: Employees interviewed were asked if they had experienced specific symptoms within the past month.

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