IV. ENVIRONMENTAL DATA

Sampling and Analytical Methods

Few reports of methods studied for their efficiency in collecting DNOC in air have been found. Kurchatova [48] suggested the use of a cotton filter, designated as FPP-15, in series with an absorber containing 5 ml of a 1% solution of sodium hydroxide. He did not provide information regarding the efficiency of the sampling method.

Methods that have been tested for their effectiveness in the determination of DNOC in air samples include spectrophotometry, thin-layer chromatography, and gas chromatography. Kurchatova [48] suggested using spectrophotometry in the visible range to quantitatively determine DNOC from an air sample. A peak wavelength of 370 nm was obtained from an alkaline solution of DNOC. Separate measurements were made for the quantity of DNOC vapor absorbed in sodium hydroxide and for the DNOC on the filter. The material on the filter was eluted with hot sodium hydroxide before it was analyzed. The author did not discuss the possibility of interfering substances and provided no data that permit assessment of the accuracy of the method.

Kurchatova [48] recommended thin-layer chromatography for separating dinitrophenolic compounds and for qualitatively determining the presence of DNOC. After separation of the compounds, quantitative measurement of DNOC could be done spectrophotometrically.

In addition to the sampling and analytical procedures described above, NIOSH has investigated alternative methods. Two air sampling methods for DNOC have been tested. Activated charcoal tubes, as described in NIOSH Method No. P and CAM 127 [49], have been used as a collection medium. The precision of this method for collecting DNOC was not discussed, but it is expected that desorption of DNOC would be a difficult procedure. Further work by NIOSH indicated that, in the experiment conducted at room temperature, DNOC existed as a mixture of 75-80% particulate and 20-25% vapor [50]. However, under other experimental conditions or in the workplace, the proportions could be entirely different. Imprecise results were obtained from attempts to sample this type of environment at a rate of 1.5 liter/minute with a glass-fiber filter attached to the inlet of a midget bubbler containing 10 ml of 0.1 M sodium hydroxide. However, the investigators [50] did not determine whether the problem was in the sampling method itself or in the method used to generate the DNOC sample.

NIOSH evaluated two methods for determining the concentration of DNOC in air samples [50]. After sampling by adsorption on charcoal, desorption with acetone and analysis by gas chromatography with a flame ionization detector gave clearly defined peaks but lacked adequate sensitivity. Analysis by gas chromatography with an electron-capture detector might provide increased sensitivity. For this analysis, desorption from charcoal with a suitable solvent, such as 10 ml of 99:1 benzene-methanol (v/v), would be required.

NIOSH found that a spectrophotometric method based on a spectral absorption at 395 nm yielded satisfactory results [50]. The NIOSH Validation Report [50] indicated that the coefficient of variation for the analytical phase of the test, CV1, was 0.027 at the 0.2 mg/cu m level. The coefficient of variation of the sampling phase, CV2, was 0.169 (with no mention of sampling bias error). Assuming a coefficient of variation of the sampling pump to be 0.05, the calculated coefficient of variation of the total sampling and analytical procedure, CV6, is 0.177. Therefore, the absolute total error at the 95% confidence limit, would be at least ±35% based on the formula:

$$CV6 = \frac{\text{total error (\%)}}{1.96}$$

Although the method involving sampling by glass-fiber filter and midget bubbler and analysis by spectrophotometry has not been fully evaluated by NIOSH and the sampling bias has not been accurately determined, NIOSH believes this method is the best available. Therefore, pending further research, these are the recommended sampling and analytical methods, and they are fully described in Appendices I and II.

Biologic Monitoring Methods

Experimental techniques have been developed that permit accurate determination of the DNOC levels in the blood. Mikolajek [51] described a polarographic method. A standard solution containing DNOC in a buffer at pH 7.0 was mixed with 1 ml of blood, and then 0.01 N potassium chloride, methanol, and a buffer solution of pH 7.0 were added. One drop of n-octanol was added, and oxygen was purged with nitrogen before DNOC was determined polarographically in a range of potentials from -0.2 to 1.2 volts. The sensitivity of the method to interference from other compounds was not discussed.

Parker [52] first described a colorimetric procedure for the quantitative determination of DNOC in biologic fluids, including blood and urine. The method was based on a determination of the absorbance of the yellow color obtained when a methyl ethyl ketone extract of DNOC was treated with sodium carbonate.

Fenwick and Parker [53] found that beta-carotene could interfere with the ketone extract and modified the original Parker method [52] accordingly. The methyl ethyl ketone extract of DNOC was yellow in alkaline solution and colorless in acid, while the extract of beta-carotene retained the same color in acid and in alkali. Therefore, concentrated hydrochloric acid was added to the alkaline extract, and the amount of DNOC was determined from the difference in the absorbance before and after the acid was added.

Edson [54] suggested a simplified method for field measurements, which was similar to that of Parker [52] except that, instead of the absorbance being measured in a spectrophotometer, the color of the extract was visually compared to a series of nine standards containing various concentrations of DNOC. The lower limit of sensitivity of the method was 5 μg of DNOC/ml of whole blood.

NIOSH recommends that the method described in Appendix III, which is based on the techniques described by Parker [52] and Fenwick and Parker [53], be used for the biologic monitoring of DNOC.

Environmental Levels

Only a few reports were found in which investigators [18,25,26] recorded the concentrations of DNOC in workplace air. However, the sampling and analytical procedures used were discussed in none of these, and the reports provided no information that could be of value in making recommendations for the environmental monitoring of DNOC.

Engineering Controls

Engineering controls should have as their main objective keeping concentrations of airborne DNOC vapor and aerosol as low as possible, minimizing skin contact, and preventing explosions. In DNOC manufacturing and formulating areas, closed systems under negative pressure, when properly operated and maintained, are the best method of controlling concentrations of airborne DNOC and preventing exposure. When closed systems are not feasible, well-designed local exhaust ventilation systems are also effective. Ventilation systems are needed at loaders, blenders, mixers, mills, packaging equipment, and at all other potential sources of vapor, spray, or dust containing DNOC. Recommendations for appropriate ventilation systems are found in NIOSH *Recommended Industrial Ventilation Guidelines* [55], *Industrial Ventilation-A Manual of Recommended Practice* [56], published by the American Conference of Government Industrial Hygienists, and in *Fundamentals Governing the Design and Operation of Local Exhaust Systems*, Z9.2-1971 [57], published by the American National Standards Institute. In addition, since DNOC dust can form explosive mixtures with air, the National Fire Protection Association Codes on combustible dusts (NFPA N. 63-1971) and blower and exhaust systems (NFPA N. 91-1973) should be followed. Ventilation systems should be inspected and maintained regularly to ensure effective operation. Changes in process that may affect the ventilation system should be assessed promptly to make certain that workers are adequately protected.

Since closed systems and local exhaust ventilation are not feasible for field application of DNOC, other engineering controls should be employed to prevent or minimize exposure. The use of air conditioned spray rig cabs with temperature and contaminant control, spraying equipment that produces coarse droplets instead of finely atomized sprays, and agitators that keep DNOC in suspension to prevent nozzle clogging will reduce the likelihood that workers will come in contact with DNOC.

V. WORK PRACTICES

Experience indicates that the major routes of worker exposure to DNOC are by inhalation and dermal absorption [6,14,17-25]. Work practices should therefore be implemented to prevent or minimize exposure by these routes. Because the sources of DNOC and the likelihood of exposure will vary, depending on whether DNOC is being manufactured, formulated, or applied in agriculture, the work practices should fit the exposure situation.

(a) Work Practices for Manufacture and Formulation of DNOC

Exposure by inhalation can lead to adverse respiratory and systemic effects. Compliance with the recommended permissible exposure limit should protect workers against adverse health effects from inhalation of DNOC. Whenever feasible, operations, processes, and materials should be enclosed to reduce the accumulation of airborne concentrations of DNOC. These systems should be inspected frequently for leaks or damage, and any needed repairs should be made promptly. Although enclosure of systems is the recommended means of protection, during certain operations when the environmental limit is temporarily exceeded, respirators with suitable particulate canisters may be permitted. Any devices provided must meet the specifications of Table I-1.

A respiratory protective program in accordance with 29 CFR 1910.134 must be followed to ensure that respirators are routinely inspected and properly cleaned, maintained, and stored. Respiratory protective devices should be decontaminated after each use and discarded when signs of deterioration are evident.

DNOC can also irritate the skin and eyes and cause severe systemic effects when it is absorbed through the skin [16,23]. Therefore, protective clothing must be worn by workers who handle these compounds. The degree of protection required depends on the severity of the potential exposure. Operations in which an aerosol may be generated require coveralls, gloves, and face shields (8-inch minimum) with goggles to prevent contact of DNOC with any part of the body, including the eyes. For jobs in which there is a possibility of the body being wetted with DNOC, full-body suits are necessary to adequately protect skin and eyes. Employees involved in operations in which splashes to the face or body may occur can be adequately protected with face shields (8-inch minimum), coveralls, aprons, and gloves. When exposure is limited to the handling of contaminated equipment or to handling small amounts of material that are unlikely to be splashed, coveralls and gloves should afford sufficient protection.

In one report [21] it was stated that rubber and plastic gloves afford protection from DNOC, but a case was cited of high blood DNOC levels in one worker even though he used such gloves. Therefore, protective equipment made of rubber or plastic should be used only if the manufacturer of the equipment states, or experience has shown, that it will offer sufficient protection from DNOC. Protective clothing and equipment should be decontaminated before reuse, and any protective apparel showing signs of deterioration should be discarded in clearly labeled, closed containers.

Emergency showers and eyewash fountains must be available in all work areas where DNOC is manufactured or formulated. Severe injury to the eyes can be prevented by immediate use of eyewash fountains. DNOC is also absorbed through the skin and will produce systemic effects [16,23]. Therefore, it is important that emergency showers be readily available so that DNOC can be immediately removed from the skin.

Ingestion of DNOC can be fatal [14]. A good sanitation program, safe work practices, and good personal hygiene will reduce the risk of exposure by this route. If eating areas are provided, they should be separate from all areas where DNOC is manufactured, formulated, used, or stored. Food and beverage consumption and smoking must be prohibited in any area where there is occupational exposure to DNOC.

DNOC should be stored in closed containers in cool, well-ventilated areas away from heat and strong oxidizing agents. Damaged drums or other containers for storage or transportation should be repaired only after they have been thoroughly purged with steam, flushed with water, and air dried.

DNOC is a combustible solid, and its dust may form explosive mixtures with air [4]. The National Fire Protection Association Code on combustible dusts (NFPA N.63-1971) should be followed. Because of the possibility of fire or dust explosion, all ignition sources must be controlled wherever DNOC is present. Foam, dry chemical, or carbon dioxide extinguishers should be used in the event of fire.

Spills of DNOC must be cleaned up immediately. Only properly trained and adequately protected employees should take part in cleanup operations. The area of a spill should be posted and secured to prevent entry by unauthorized personnel. Liquid DNOC formulations can be absorbed in vermiculite, dry sand, earth, or other suitable material. If sufficient drainage to a suitable collection basin is available, spilled liquid can be hosed away with large quantities of water. Spilled solid material should be collected and deposited in a sealed container, and the area of a spill should be ventilated to remove any vapor or aerosol. Methods of waste disposal must comply with federal, state, and local regulations.

Maintenance and repair workers, especially those working on ventilation systems or in enclosed environments, have a high risk of exposure. To minimize or prevent exposure, they must be familiar with the hazards of the materials and with proper work practices, and they must have adequate supervision. Special precautions must be taken when work is to be performed in confined spaces. Entry into confined spaces should be controlled by a permit system. Prior to entry, all sources of DNOC must be sealed off and the equipment used for handling DNOC must be purged and tested for oxygen deficiency and for the presence of flammable vapors and toxic gases. Purging should be done with steam and followed by flushing with water. Continuous ventilation of the confined space should be maintained throughout the entry period. Personnel entering confined spaces should wear protective clothing, be equipped with a safety harness and lifeline, and use either a self-contained, pressure-demand mode breathing apparatus or a combination supplied-air suit with an auxiliary self-contained air supply. Anyone entering a confined space should be observed by a properly trained and equipped standby worker familiar with emergency procedures, in case rescue is necessary. A communication system should be set up among workers involved in the operation.

(b) Work Practices in the Application of DNOC

Agricultural spraying is a major source of occupational exposure to DNOC. Due to the nature of the spraying process, relatively high concentrations of airborne DNOC may be generated. Such concentrations may be hazardous, and spray personnel must be protected. Therefore, unless it can be shown by frequent industrial hygiene surveys that the DNOC air concentration does not exceed the permissible exposure limit, respiratory devices as specified in Table I-1 should be used to protect against inhalation of airborne DNOC. Full facepieces, helmets, or hoods may be used only if adequate coverage of exposed portions of the head and face is assured by the use of supplemental headgear. Half-mask respirators or other respiratory protective devices that do not afford eye protection must not be used because DNOC may irritate the eyes.

Wolfe [58] has stated that over 97% of most pesticides that contact the body during occupational exposure are deposited on the skin. Investigations of spray operators who used DNOC as a blossom-thinning agent showed that the average dermal exposure was 63.2 mg/hour [27]. Because of this demonstrated deposition of DNOC on skin surfaces and because it has been shown that skin contact with DNOC can lead to adverse health effects [16,23], protective clothing and equipment should be used by DNOC applicators.

All personnel occupationally exposed to DNOC should wear freshly laundered coveralls or work uniforms (long pants and long-sleeved shirts) [59]. If the coveralls or uniforms might become wetted by mist or spray use of a waterproof raincoat should provide the best protection for the upper back, shoulders, and forearms [58], but this may cause discomfort or even heat stress in a hot environment. In such environments, wearing long-sleeved, water-repellant or waterproof clothing that will not be easily penetrated by the pesticide should provide a significant measure of protection [58].

Protection of the lower trunk and legs from contamination is important where the potential exists for liquid spillage, soaking by continued contact with sprays or sprayed foliage, or penetration of clothing through excessive contact with DNOC. Waterproof trousers will provide the best protection for the lower trunk and legs [58]. Even though the coveralls or uniforms are covered by waterproof protective clothing, daily bathing after work and daily changes to freshly laundered clothing are important for minimizing percutaneous absorption [58].

The head and neck should also be protected from contact with DNOC. Therefore, some type of protective headgear, such as waterproof rainhats and washable safety hardhats and caps, should be worn. Waterproof or water-repellant parkas may also be used to protect the head and neck at the same time [59]. Personnel potentially exposed to downward drifts of DNOC should wear wide-brimmed, water-repellant or waterproof hats to obtain additional protection for the head and neck areas [58].

Workers handling concentrated wettable powders, concentrated liquids, or finely divided dust formulations should wear protective gloves of natural rubber, neoprene, or plastic, although the permeability of these materials to DNOC remains to be determined. Contact of wet skin with DNOC should be avoided to minimize absorption.

If an employee comes in contact with concentrated formulations, his hands will often receive the highest exposure. Because they cover the wrist area not normally protected by the sleeve, unlined rubber gauntlet gloves provide the best protection [58]. These gloves can be turned wrong side out for proper cleaning of the inside surface.

Use of waterproof footwear is necessary to minimize exposure when the DNOC formulation may wet the feet [58]. Footwear should be washed and dried thoroughly, inside and out, as frequently as necessary to remove DNOC.

Although development of cataracts following ingestion of DNOC has been reported [7,11,12], there is no evidence to suggest that eye exposure to DNOC causes cataracts. However, because DNOC can be irritating to the eyes [4], it is recommended as a minimum that all employees engaged in spraying DNOC or who might encounter DNOC spray or dust drift wear safety goggles. Face shields (8-inch minimum) with goggles should provide adequate protection for employees who handle the liquid pesticide.

To minimize absorption of DNOC through ingestion, employees should not eat, drink, or smoke in any area where there is a potential for occupational exposure to DNOC.

The employer is responsible for proper disposal of surplus pesticides and pesticide containers [60]. The Environmental Protection Agency has established regulations defining prohibited procedures pertinent to the disposal of surplus pesticides and containers (40 CFR 165, published in the Federal Register 39:3686 7-70, October 15, 1974). Specifically, open dumping is prohibited, and water dumping is generally prohibited. Open burning is also prohibited, except for small quantities, in combustible containers, not to exceed 50 pounds or the quantity emptied in a single workday, whichever is less. Such open burning may be performed only where it is consistent with federal, state, or local ordinances. "Open burning" means the combustion of a pesticide, pesticide container, or pesticide-related waste in any fashion other than by incineration in a pesticide incinerator (40 CFR 165, published in the Federal Register 39:3686 7-70, October 15, 1974). Applicable local, state, and federal regulations should be consulted; if such regulations do not exist, suggested precautions include disposing of DNOC by incineration or burial. Incineration or burial should be performed in a manner not contributing to air or water pollution.

Since agricultural spraying often occurs during hot weather when full-body protective clothing might cause discomfort to workers, controls other than respiratory devices and full-body suits that are equally effective may be employed. If spraying can be done by aircraft or by other motorized vehicles, such as tractors with enclosed air-conditioned cabins, full-body protection is not necessary. The air-conditioned cabins should be frequently monitored to ensure that DNOC air levels are not exceeding the permissible occupational exposure limit. When air or ground vehicles are used to apply DNOC to fields, employees should not direct them through the drift of the spray or operate them where wind creates a drift hazard to themselves or others.

(c) Employee Education

Employee education on the safe handling of DNOC and its hazards is essential if injury and disease are to be prevented. It is particularly important that employees be informed of the dangers of skin contact with these compounds. The importance of the immediate removal of contaminated clothing and the use of liberal amounts of water to remove the compound from the skin or eyes must be stressed. Workers potentially exposed to DNOC must be made aware of the signs and symptoms associated with DNOC intoxication and of the similarity of these effects to those produced by hot weather. Employees should be encouraged to contact medical personnel immediately if symptoms occur. Workers must also be informed that, because the toxicity of DNOC is increased in hot weather, extra care is necessary under these conditions to prevent injury.

In all workplaces where there is occupational exposure to DNOC, written instructions informing employees of the particular hazards of these chemicals, proper handling methods, procedures for cleaning up spilled material, personal protective equipment to be worn, and procedures to be used in emergencies must be on file and available to employees. The Material Safety Data Sheet shown in Appendix IV may be used as a guide for employers in providing the required information.