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## I. SUMMARY

In April, 1989, the National Institute for Occupational Safety and Health (NIOSH) received requests from the Laborer's International Union of North America, the Alaska State Health Department, and the U.S. Coast Guard to conduct a health hazard evaluation during the cleanup of more than 10 million gallons of oil spilled in Prince William Sound, Alaska on March 24, 1989.

NIOSH's response focused primarily on industrial hygiene assessment of potential occupational exposures [benzene and other volatile organic compounds, oil mist, polynuclear aromatic hydrocarbons (PNA's), diesel fumes, and noise] during typical tasks performed by the majority of the 11,000 workers involved in the 1989 cleanup activities. In addition, NIOSH efforts also included evaluation of the training provided to new employees; evaluation of the adequacy, availability and decontamination of the personal protective equipment (PPE); and evaluation of the worker decontamination procedures. Also, an attempt was made to evaluate illness and injury issues. Most of the cleanup work force was made up of Alaska residents who were not expecting to engage in such work after the 1989 cleanup effort terminated.

The "weathered" crude oil (WCO), or "mousse" was found to be essentially devoid of the lighter, more volatile, petroleum fractions; therefore, in general, there was no known appreciable health risks from inhalation of these components at the time of this evaluation. Benzene was detected in 12 of 33 full shift personal breathing zone samples in concentrations of up to 0.3 parts per million (ppm); however, the gasoline used as a fuel in the "skiffs" (small flat-bottomed boats) was the likely source, rather than the WCO. Three samples, two at 0.2 ppm and one at 0.3 ppm, were above the NIOSH REL of 0.1 ppm but below the current OSHA PEL of 1.0 ppm. Oil mist was not detected in any of the air samples. The limit of detection (LOD) for oil mist for this evaluation was 0.4 milligrams per cubic meter ( $\text{mg}/\text{m}^3$ ). No mutagenic activity was detected when the original crude and WCO were evaluated via Ames mutagenicity assays.

Seven PNA's (naphthalene, fluorene, phenanthrene, pyrene, chrysene, benzo[b]fluoranthrene, benzo[a]pyrene) were detected at trace concentrations (1 to 34 ppm) in bulk samples of the WCO. Two PNA's (naphthalene, phenanthrene) were detected in 9 of 27 personal breathing zone samples at trace concentrations that

ranged from 50-100 nanograms per cubic meter; however, these exposures were more likely due to diesel fume or environmental tobacco smoke than to the WCO. Results from the use of a Luminoscope, a device which measures induced fluorescence, to evaluate skin contamination with the WCO were not clearly interpretable because of the inability to properly monitor important issues such as the types of soaps and shampoos that were used. The luminoscope does appear to have potential for this type of application and in a situation where a group of workers could be monitored for several days in a row, and where the frequency and use of soaps could be monitored more strictly, the technique would have a better chance of being successful.

Exposures to nitrogen dioxide (NO<sub>2</sub>) which was also used as a surrogate measure of exposure to diesel fumes, ranged from 0.08 to 0.25 ppm in 5 of 14 full shift personal breathing zone air samples. These results, because they represented time-weighted-average exposures for a full shift, are not directly comparable to the short-term OSHA PEL or NIOSH REL of 1 ppm. The results do, however, indicate a potential for overexposure to NO<sub>2</sub> and suggest that there was exposure to diesel fumes. There are no occupational exposure standards for whole diesel fume; however, since it is known to contain numerous toxic chemicals, including carcinogens, exposures should be kept to the lowest feasible level. Water pumps and diesel generators produced the highest noise levels (100 dBA range within 5 feet of the source).

The 4-hour training course, which was reportedly given to all new workers, was judged by the three NIOSH investigators who took it to be adequate in terms of content and delivery. The PPE gear was also judged to be adequate and, except for two cases (temporary shortage of ear plugs and gloves at main supply storage areas), available to the workers. However, the decontamination of PPE gear was not adequate in one of the two Task Forces evaluated, and the wearing of the PPE at the work sites was not consistently enforced: both of these situations resulted in preventable contamination of the skin by WCO.

An unsuccessful attempt was made to conduct a systematic, record-based review of health and injury data in the field. This was not pursued after the 1989 cleanup effort had ended. However, preliminary information on the worker's compensation claims filed with the Alaska State system is discussed in this report.

At the time of this evaluation (about 4 months after the spill), inhalation exposure to volatile components of "weathered" crude oil was insignificant for those work situations evaluated. Certain aspects of the health and safety program designed to minimize skin contamination with crude oil, such as decontamination procedures and the wearing of PPE, were not always effectively and consistently implemented from site to site. Exposures to volatile components of the crude oil at the very beginning of the cleanup operation may have been substantially different.

Keywords: SIC 5172 (petroleum and petroleum products), crude oil, oil, weathered crude oil, mousse, oil spill, benzene, limonene, luminoscope, Valdez, PNA, noise

## II. INTRODUCTION

In April, 1989, NIOSH was asked by the Laborer's International Union of North America, the Alaska State Health Department, and the U.S. Coast Guard to conduct a health hazard evaluation during the cleanup of the oil spill that occurred in Prince William Sound on March 24, 1989. In response, NIOSH investigators made three field trips to Alaska. During the first trip, April 25-30, 1989, two NIOSH investigators, an occupational health physician and an epidemiologist, participated in a meeting convened by the Commissioner of Labor, Alaska Department of Labor (AKDOL) following his announcement that the cleanup was a "hazardous waste operation". The meeting focused on the appropriate content of worker training courses and the amount of training hours necessary to adequately prepare the workers involved in the cleanup. Worker training is one of the required provisions of the Alaska and Federal Hazardous Waste Regulations; these regulations specified 24 hours of training at that time. The NIOSH team also had the opportunity to visit some beach cleanup sites during this trip.

A NIOSH letter containing a discussion of worker training issues, a brief literature review of the toxicity of crude oil, comments on medical testing, recognition of the potential for serious safety related injuries, and preliminary recommendations was forwarded to the requestors on May 24, 1989.

The second NIOSH trip took place on June 5-9, 1989. The itinerary for this visit was prepared jointly by NIOSH and the U.S. Coast Guard, and coordinated with the appropriate agencies in Alaska by the U.S. Coast Guard. The four person team included two officers from the U.S. Coast Guard Headquarters, Safety and Environmental Health Division, Washington, D.C., and two NIOSH investigators; the Director, Division of Safety Research, Morgantown, West Virginia, and the Assistant Chief, Hazard Evaluations and Technical Assistance Branch (HETAB), Division of Surveillance, Hazard Evaluations and Field Studies, Cincinnati, Ohio. Activities focused on a number of occupational safety and health issues, including the general health care of the workers, injury surveillance, and the collection of information necessary to develop an industrial hygiene protocol aimed at evaluating occupational exposures during the oil spill cleanup effort. A NIOSH letter, which detailed trip activities and briefly presented the major components of a proposed follow-up industrial hygiene survey, was forwarded to the requestors on June 16, 1989.

Based on the information obtained during the previous trip, the third NIOSH trip, July 10-24, 1989, focused on the evaluation of four major areas; training, personal protective gear, decontamination, and occupational exposures. The NIOSH team for this trip included two HETAB industrial hygienists and one industrial hygienist from the Protective Technology Branch, Division of Safety Research, Morgantown, West Virginia. Exxon assigned an industrial hygienist to escort the NIOSH team and conduct side-by-side monitoring. A summary of the NIOSH activities and preliminary findings from this trip was given to the requestors by telephone in the last week of July, 1989, and presented at the "Conference on the Alaskan Crude Oil Spill and Human Health", which

was held in Seattle, Washington, on July 28-30, 1989. A synopsis of the conference proceedings was distributed to NIOSH and other conference participants on October 10, 1989.

During July and August 1989, a medical epidemiologist assigned to NIOSH's Division of Safety Research attempted to conduct a systematic record-based review of illness and injury information.

This final report includes the pertinent information contained in earlier letters and presents the industrial hygiene data, including exposure monitoring data obtained during the course of this health hazard evaluation. There is also a brief discussion on illness and injury surveillance; however, attempts to collect this type of information were largely unsuccessful.

### III. BACKGROUND

On March 24, 1989, the Exxon tanker vessel "Exxon Valdez" spilled approximately 10 million gallons of Prudoe Bay crude oil into Prince William Sound in Alaska. As a result of the spill, hundreds of miles of beach were contaminated. Between the time of the spill and September, 1989, when cleanup operations were terminating for the winter, as many as 11,000 workers were involved in the cleanup operations.

The exposure assessment part of this health hazard evaluation focused on evaluation of potential exposures during typical beach cleaning operations, since this was the activity where the majority of the workers were utilized.

During the time period when NIOSH was conducting exposure monitoring, there were six beach cleaning Task Forces. Each Task Force had as many as 600-700 workers who lived on the same berthing vessel (either military vessels or barges modified to serve as housing units) and cleaned beaches in the same general geographic area. The workers were transported to and from the berthing vessel and beach site via military troop transport vessels or fishing boats. Regardless of where the beach cleaning operation was taking place, most of the work being done by most of the workers utilized one of the following three methods.

**Beach Crews** : Crews of up to 30-40 workers used cold (temperature of the bay water) or hot (up to 125-130 degrees F) water via low and high (up to approximately 90 psi) pressure hoses to remove oil from surfaces. The oil was washed into the water where it was contained by booms for subsequent removal using surface skimmers and absorbent materials. This method was used on relatively flat beaches. Workers generally worked 12 daylight hours per day for 14 days straight, and then were to be off for seven days. The majority of workers on these crews were called Oil Recovery Technicians (ORTs). In addition to those assigned to use the hoses, there were also boom tenders (skiff operators), skimmer operators, and support personnel who maintained and operated the hot water heaters and pressure sprayers.

**OMNI Boom:** Hot water under high pressure was remotely applied from a barge platform using a modified concrete pumper. The oil that was washed off the beach was contained with booms for subsequent removal using a surface skimmer. There were typically 10-15 workers involved in this operation; most of these workers were equipment technicians stationed on the barge to maintain and operate the heaters, compressors and other support equipment. There were also at least three ORTs, two boom tenders and a skimmer operator. The work schedules were generally the same as described above for the beach crews. Occasionally, there was a small beach crew (less than 12 workers) assigned to this type of operation; however, this technique was most useful for removing oil from beaches that could not safely be walked on, such as those with steep inclines, large rocks, or cliffs.

**MAXI Barge:** This method utilized a combination of remote application of hot water and beach crews on segments of beaches that had both rugged and moderate terrain. For the remote application, hot water was applied under high pressure from fire hoses being held by two ORTs in a "cherry picker"-type basket on the arm of a crane, which was positioned on a barge. A beach crew worked the low slope beach areas in the same manner as described above. Again, the oil washed off the beach was contained with booms for subsequent collection via a surface skimmer. There were usually less than 10 workers on the barge crew and 10-15 on the beach crew. The barge crew workers were equipment technicians stationed on the barge to maintain and operate the heaters, compressors, crane, and other support equipment. The beach crew was primarily ORTs. Work cycles were the same as described above for beach crews.

Personal protective equipment (PPE) was supposed to be worn by those engaged in the beach cleaning operations. A typical PPE ensemble included rubber boots, 2-piece polyvinyl chloride (PVC) rain suit, hard hat, splash goggles, and oil-resistant gloves. Organic vapor respirators were generally not worn, but were supposed to be available at each beach work site according to the Exxon Safety and Health Plan.

In addition to the beach cleaning operations described above, three other operations, decontamination, boom cleaning, and oily waste handling were also evaluated using air sampling techniques.

**Decontamination:** Decontamination (DECON) of the PPE took place on a barge tethered to the berthing vessel. Workers were issued their PPE on this barge as they left each morning. Upon their return at the end of the day, workers removed their PPE gear and showered in the DECON area of the barge before returning to the berthing vessel. PPE gear was then decontaminated by a crew of six to ten workers in each Task Force during the evening shift so that the cleaned gear would be ready the next morning. The techniques used and the number of PPE items decontaminated was different in the two Task Forces evaluated and is discussed in more detail later in this report. In general, for those items decontaminated, the oil residue was removed using either DeSolv-it®, detergent solutions, or some combination of both. Techniques such as hand wiping, brushing, and soaking in 55 gallon drums of heated cleaner solutions were observed being used.

**Boom Cleaning:** Cleaning of the booms used to contain the oil washed from the beaches for subsequent collection via surface skimmers took place on a barge specifically designed and built for this purpose. Oily boom material, which was stored in a boom corral in the water at one end of the barge, was fed through two wash (containing detergent and brushes) and one rinse machine. High pressure, hot water spray wands were used at two stations between the wash and rinse machines to supplement the oil removal process. The cleaned boom was bundled, banded, and transported on fishing vessels back to sites of use. Eight to ten workers cleaned up to 4500 feet of boom each day during the day shift.

**Oily Waste Handling:** This task was accomplished at a contractor-operated disposal site in Valdez, Alaska. Plastic bags containing oily waste, which were generated during the various phases of the cleanup effort, were processed at this facility. Fishing vessels were used to transport the bags of oily waste to the harbor in Valdez where the bags were loaded into pot ore trucks for transport to the disposal site. At the disposal site, the oily bags were dumped into a pit using a crane that lifted and inverted the pot ore containers. Up to 50 day-shift workers and 20 night-shift workers sorted the bags, separating out those that did not contain oily waste for transport to a sanitary landfill. Those that contained oily waste were double-bagged and moved to a holding area at the site for subsequent destruction by incineration. There were three small incinerators on site that could process 400-500 bags of oily waste per day. However, since the facility received 4000-5000 bags per day, a huge stockpile of bags had accumulated. Other means of disposal, such as transport to other hazardous waste landfills or other incinerator sites, were being explored. The workers sorting the bags wore PPE, including respirators.

#### IV. METHODS

Given the nature of the cleanup operations (e.g. thousands of workers dispersed over hundreds of square miles and the logistical difficulties of getting from work site to work site) a comprehensive evaluation, such as might be accomplished at a single plant site, was not possible. However, based on information obtained during the first two NIOSH field trips (April and June 1989), and communication with other agencies or groups (e.g., union officials, Federal and Alaska State OSHA, Alaska State Department of Health, U.S. Coast Guard), the framework for an investigation was developed in which the following issues were targeted for further evaluation.

##### A. Worker Training

##### B. Personal Protective Equipment (PPE)

- 1 Adequacy, Availability, and Use
- 2 Decontamination

##### C. Exposure Assessment

- 1 Review of Prior Exposure Assessment Data
- 2 Analysis of Bulk Samples
- 3 Inhalation exposures
- 4 Skin exposures

## 5 Noise

### D. Decontamination

### E. Illnesses

### F. Injuries

The methods used to evaluate each of these issues are discussed below.

#### A. Worker Training

As discussed earlier in the Introduction Section, a meeting, which was held in Anchorage in April, 1989, and attended by key government, union, state, and industry personnel, resulted in the development of a 4-hour training course. On July 11, 1989, the three members of the NIOSH industrial hygiene field survey attended the 4-hour Health and Safety Training Course in Anchorage, Alaska, which was intended to acquaint workers with the potential health and safety hazards associated with the oil spill clean-up operations. The NIOSH team's attendance at this training course served two purposes. First, it acquainted the NIOSH industrial hygienists with specific hazards not commonly experienced in general industry so that they would be prepared to live and work under the same conditions as the workers. Secondly, it allowed the three NIOSH team members to critically evaluate the course content and delivery at the end of the 2-week NIOSH field survey, based on the living and working conditions observed first hand.

#### B. Personal Protective Equipment (PPE)

##### 1. Adequacy, Availability, and Use

The adequacy of the PPE was evaluated based on the types of gear being used, protective qualities (e.g. solvent and oil penetration), and suitability for the tasks performed. Availability was evaluated based on inspection of the primary Task Force supply storage and issue points, and random beach cleaning sites. Use of the PPE was evaluated by observing workers in the performance of their tasks.

##### 2 Decontamination

The adequacy of the PPE decontamination procedures were evaluated by observing the decontamination methods used and the condition of the PPE before and after the process.

#### C. Exposure Assessment

##### 1. Review of Prior Exposure Assessment

Industrial hygiene exposure assessment data collected prior to NIOSH involvement were reviewed.

##### 2 Analysis of Bulk Samples

###### a. Crude Oil (Oak Ridge National Laboratory)

The Oak Ridge National Laboratory (ORNL) analyzed samples of both the "weathered" crude oil, provided by NIOSH, and the original "hold" oil, provided by the National Institute of Environmental Health and Science (NIEHS). The ORNL analysis provided information on physical, chemical, and toxicological properties of the original crude and "weathered" crude oils, including; major chromatographable organics, boiling point range, volatile organics, PNA's, elements, and mutagenicity (by Ames testing). The specific ORNL analysis techniques can be found elsewhere [Guerin 1990].

#### b. Crude Oil (NIOSH Analysis)

Four bulk samples of crude oil were submitted to the NIOSH laboratory in Cincinnati for analysis of benzene, other volatile organic compounds (VOC's), and PNA's. Three of the bulk samples were "weathered" crude oil collected about 30, 60, and 90 days after the spill just off three different beaches as they were being skimmed from the water. The fourth bulk was a sample of the original crude oil from the Exxon Valdez tanker. NIOSH received this sample from NIEHS.

For analysis of benzene and other VOC content, charcoal tube samples were obtained in the headspace of a sample of the "weathered" crude oil both a room temperature and at 140 degrees Fahrenheit (60 degrees Centigrade). The 140 degree temperature was believed to be an estimate of the highest temperature that the "weathered" crude could have reached as a result of the use of hot water during the cleanup. All headspace samples were collected using pumps calibrated at 200 cc/min for approximately two hours. Sample volumes ranged from 22-26 liters. The charcoal samples were then desorbed with 1 milliliter (ml) carbon disulfide and analyzed by gas chromatography with flame ionization detection (GC-FID) using a 30-meter DB-1 column (splitless mode). One sample from each bulk was also analyzed by gas chromatography using a mass selector detector (GC-MSD) to confirm component identities. The limit of detection (LOD) for benzene was 0.4 microgram per sample ( $\mu\text{g}/\text{sample}$ ). Other VOC's (toluene,  $\text{C}_5\text{-C}_6$  alkanes, limonene) had LOD's of 1-5  $\mu\text{g}/\text{sample}$ .

The PNA analysis required method development by NIOSH and took about 11 months. The "weathered" crude bulk samples were initially analyzed for 17 PNAs by NIOSH's methods 5506 and 5515 [NIOSH 1984]. The LOD for these methods ranged from 10 to 30  $\mu\text{g}/\text{gram}$ . Since no PNAs were detected using either of these methods, the decision was made to search for a more sensitive method. Information from EPA and Exxon, both of whom had experience with analysis of crude oil, allowed NIOSH to set up a method involving new equipment and new sample

cleanup techniques. EPA Method 3630 was used for cleanup. High resolution mass spectrometry (HRMS) using both the full scan and selected ion monitoring (SIM) modes were used for analysis. The LOD's for the various PNAs monitored with this method were lower, ranging from 0.5 to 4.0 µg/gram. The LOD's for the analysis of PNA's in the air samples using the same techniques ranged from 25 to 200 ng/gram.

c. Decontamination Solution (NIOSH Analysis)

Two bulk samples of decontamination solutions were diluted with carbon disulfide and screened directly by GC-FID and GC-MSD

d. Bulk Air Samples (NIOSH Analysis)

Three Carbotrap® 300 tubes used to collect air samples from the inside of oily waste plastic bags, and two standard charcoal tubes used for the same purpose were submitted for screening analysis. Workers at the Oily Waste Disposal Site, where respirators were mandatory, were potentially exposed to unknown volatile substances as they re-bagged and segregated waste material.

Prior to sampling, the Carbotrap® 300 tubes were cleaned in a Tekmar® Model 5100 Thermal Trap Conditioner by baking at 400 degrees Centigrade for 24 hours with helium flowing through the tubes at 10 cc/min. The Carbotrap® 300 tubes consist of a three-bed sorbent containing Carbotrap C/Carbotrap/Carbosieve S-III materials for trapping organic compounds over a wide range of volatility. The samples were analyzed using a Tekmar® Model 5010 Automatic Desorber interfaced directly to a HP5890A gas chromatograph and HP5791 mass selective detector. A 30-meter DB-1 capillary column was installed in the gas chromatograph. The bulk air charcoal tubes were desorbed with 1 ml of carbon disulfide for subsequent analysis by GC-FID and GC-MSD. A 30-meter DB-1 capillary column was used in each case.

### 3. Inhalation Route

Almost all of the exposure data prior to NIOSH involvement focused on evaluation of worker exposure to volatile organic compounds (e.g., benzene, toluene, xylene) and was predominately collected using passive dosimetry methodology. Information collected during the first two NIOSH field trips (April and June 1989), however, suggested that there were other potential exposures, in addition to volatile organic compounds (VOC's), that warranted evaluation. These included PNAs, diesel fume, oil mist, and noise. The fol-

lowing methods were utilized by NIOSH to assess these exposures during the industrial hygiene field survey in July, 1989.

a. VOC's and Oil Mist

Personal breathing zone (PBZ) and area air samples for VOC's and oil mist were collected using a two stage sampling train comprised of a filter and sorbent tube. A 37-milliliter, glass fiber filter (for the oil mist) was attached to the front end of a standard 150 milligram charcoal tube (for the VOCs). This setup was then attached to a portable, battery-powered sampling pump via Tygon® tubing. The pump was calibrated to sample air at the rate of 200 cc/min. Placing the filter ahead of the charcoal sorbent tube also served to minimize the chance that a direct splash of water would interfere with efficient collection of organic vapors on the sorbent tube.

The oil mist filter samples were extracted with 10 ml of Freon 113® and analyzed by infrared spectrophotometry in accordance with NIOSH Method No. 5026 [NIOSH 1984]. The VOC samples were extracted with 1 ml of carbon disulfide and analyzed by GC-FID in accordance with NIOSH Method No. 1501 [NIOSH 1984].

b. PNA's

Air samples were collected with a 37-milliliter Teflon® pre-filter backed up by a XAD-2 sorbent tube using a flow rate of 1 liter per minute (lpm). Based on prior analysis reports of the PNA content of the "weathered" crude oil, the two laboratory methods routinely used by NIOSH for PNAs (high performance liquid chromatography using fluorescence detection, NIOSH Method 5506 [NIOSH 1984], and gas chromatography using flame ionization detection, NIOSH Method 5515 [NIOSH 1984]), would not likely be sensitive enough for this health hazard evaluation. Therefore, a search for a more sensitive method resulted in the selection of a GC/HRMS/SIM technique which is described above in Section IV-C-2b.

c. Diesel Fumes

Diesel fume is a very complex mixture which contains both gaseous and particulate fractions. Its composition can vary significantly with fuel, engine type, and degree of maintenance. The gaseous components include oxides of sulfur, nitrogen dioxide, nitric acid, carbon monoxide, carbon dioxide, and hydrocarbons (e.g., ethylene, formaldehyde, methane, benzene, phenol, acrolein, and PNAs). The particulate fraction (soot) is

composed of solid carbon cores that are predominantly less than one micron in size. It has been estimated that as many as 18,000 different substances from the combustion process can be absorbed on diesel exhaust particulate [NIOSH 1988]. Due to the large number of potential compounds in the diesel exhaust stream and the constraints of the survey, it was considered impractical to utilize a full-scale, comprehensive sampling protocol. As an alternative, nitrogen dioxide (NO<sub>2</sub>) was selected as a surrogate measure because NO<sub>2</sub> is commonly the most prevalent gas in diesel fume. Samples were collected via passive dosimetry using Palmes tubes, and analysis was by visible absorption spectrophotometry in accordance with NIOSH Method No. 6700 [NIOSH 1984].

#### 4. Skin Route

At the time of the NIOSH field surveys, workers were potentially exposed to "weathered" crude oil rather than the original crude oil. The significance of this is that due to previous evaporation the "weathered" crude oil is almost entirely devoid of volatile components. It follows, therefore, that the expected health risk from inhalation of these substances would be greatly reduced. However, there was still concern that the crude oil, even in its "weathered" state, might still pose a health risk from skin exposure (dermatitis and skin cancer).

There were at least two questions that warranted evaluation. First, was the PPE effective in preventing skin contamination? Second, if the skin became contaminated with the "weathered" crude oil, were the decontamination procedures in place effective in removing the oil?

While patch testing under the PPE gear, skin wiping techniques, and the use of a black light were all considered, none were selected because of a lack of a known "marker" compound to test for, a lack of sensitivity and specificity, or, in the case of the black light technique, problems with the discriminating ability of the operator's eyes. Also, for the black light technique, the intensity of the black light is high enough to cause some concern about the possible synergistic effects with agents on the skin that may be photo-toxic.

A literature search revealed a method that seemed to be better suited for this application [Vo-Dinh 1980, Vo-Dinh 1981, Schuresko 1980]. The method uses a portable instrument called a "luminoscope" which can detect the presence of a compound (e.g., a PNA compound) on a surface, such as skin, using induced fluorescence. Figure 1 presents a schematic of the mode of operation. The instrument uses a bifurcated fiberoptic wave guide that resembles a standard medical stethoscope in appearance. One wave guide transmits ultraviolet (UV) radiation at a specific frequency (360 nanometers from a 125 watt mercury

vapor light) onto the surface being monitored. The other wave guide conveys the fluorescence emitted by compounds on the surface (PNA compounds in this case) back to the detector, where a set of broad band interference filters are used for selecting the spectral region to be monitored. A single photon counting technique utilizing a photomultiplier tube is used by the detection system as a means of quantifying relative contamination levels. It was hoped that this instrument would be particularly useful in evaluating how well the skin was being cleaned once contaminated with "weathered" crude oil.

In preparation for the July, 1989 field survey, the luminoscope was tested in the laboratory with the help of personnel from the Health and Safety Research Division, ORNL. Based on the tasks performed during the cleanup of the oil spill and the type of PPE utilized, four areas of the body were chosen for monitoring. These included the palm of the right hand, the back of the right hand, the inside of the right forearm, and the right side of the neck. These areas would be monitored in the morning before workers donned their PPE, at the end of the work day before they showered, and after they showered. Background laboratory data were collected on two NIOSH investigators before the actual field survey. These data, shown in Figures 2 and 3, indicated that results from day to day on the same location on the body were relatively consistent for each investigator. A sample of the "weathered" crude oil was used to select the frequency that generated the highest level of fluorescence. A "button" containing a stable fluorescence source was used to insure that the instrument was performing consistently from day to day.

## 5. Noise

Noise exposure levels were evaluated using a General Radio 1982 Permissible Sound Level Meter and Analyzer. A General Radio 1562 Sound Level Calibrator was used before and after data collection to insure that proper instrument calibration was maintained.

## D. Decontamination (DECON)

The DECON operations in two of the six Task Forces were evaluated through observation of the procedures being used, visual inspection of the PPE both before and after DECON, and assessment of exposures to the volatile organic components of the DECON solutions. Based on information from MSDS sheets and from qualitative analysis of bulk liquid samples, exposure to DECON VOCs was evaluated using NIOSH Method No. 1501 [NIOSH 1984] which called for the collection of personal breathing zone air samples using a standard 150 milligram charcoal sorbent tube and a sampling rate of 200 cc/min. The charcoal tube samples were then desorbed with 1 ml of carbon disulfide and analyzed by gas chromatography using a 30-meter fused silica capillary column containing the phase SPB-20. A flame ionization detector was used to detect compounds as they eluted from the column.

## E. Illness and Injury

There were numerous locations where workers were seen for health and injury complaints, depending on the severity of the complaint. These included first aid stations at each beach work site, which were usually attended by an emergency medical technician; first aid stations on the various berthing vessels, which were attended by nurses or military medical staff; a floating hospital facility which Exxon put into operation in July 1989; and various clinics and hospitals on land in Valdez and other locations.

A number of these treatment facilities were visited by NIOSH investigators and, in some cases, Coast Guard personnel to interview the medical staff and review available records.

## V. EVALUATION CRITERIA

A general discussion on the toxicity of crude oil, "weathered" crude oil, benzene, limonene (a constituent of De-solv-it®), and nitrogen dioxide is presented below. Brief toxicity and exposure criteria information for some of the other chemicals detected at very low concentrations can be found elsewhere [NIOSH 1990b].

### A. Crude Oil

Crude oil is a complex mixture of various substances including hydrocarbon compounds (alkanes, cycloalkanes, aromatics, polynuclear aromatic compounds) and non-hydrocarbon compounds (sulphur compounds, nitrogen compounds, oxygen compounds, traces of organo-metallic compounds). Health hazards generally associated with crude oils involve the inhalation of the toxic volatile hydrocarbon components, such as benzene, and dermatitis from repeated or prolonged skin contact [ILO 1983]. There is also a concern about the potential for skin contact with crude oil as a cause of skin cancer. This is presumably due to the presence of PNA's, which have been shown in animal studies to have this effect [Bingham et al. 1980]. More information on the chemical makeup of Prudoe Bay crude oil is provided below in Section VI-C2a. While there are occupational exposure standards for individual components of crude oil, there are none for "whole" crude oil itself. Respirators and other personal protective equipment, such as solvent-resistant gloves and other apparel, have traditionally been used to minimize worker exposures.

### B. Weathered Crude Oil

When crude oil is released to the marine environment it is immediately subjected to a wide variety of weathering processes. These processes, which can include spreading, evaporation, dissolution, dispersion of whole oil droplets into the water column, photochemical oxidation, water-in-oil emulsification, microbial degradation, adsorption onto suspended particulate matter, ingestion by organisms, and sinking and sedimentation, are described in detail elsewhere [Jordan and Payne 1980,

Payne and McNabb 1987]. However, one of the most important processes, from the standpoint of health risks to workers, is the evaporation that occurs during the first 24 to 48 hours after the spill. Because of this process, inhalation hazards from the toxic volatile components, such as benzene, are greatly reduced [Payne and McNabb 1987]. The substance remaining after evaporation, called "weathered" crude or "mousse" (even though it contains an appreciable amount of water), is still of concern as a potential dermatitis hazard. However, since the solvent fractions have evaporated, its ability to cause dermatitis may be lessened since it is the solvent fraction that dissolves the protective skin oils. The potency of "weathered" crude as a skin cancer-causing agent is not known; however, for the same reason just discussed, its potency may also be lessened relative to fresh crude oil.

At the time of the NIOSH exposure assessment (about 4 months after the spill), exposure to the volatile components of the original crude oil was not expected to pose a significant hazard, except possibly for confined space tasks or instances when fresh crude had crusted over or been trapped in areas in such a way that evaporation was hampered, and then was disturbed as part of the cleanup operations.

### C. Benzene

Benzene is a colorless, highly flammable, non-polar liquid, with an odor characteristic of aromatic hydrocarbons. Acute exposure causes central nervous system depression as well as headache, dizziness, and nausea. Severe exposures may result in convulsions, coma, and death. Chronic exposure to benzene is well documented to cause an insidious and often irreversible injury to the bone marrow. Long-term exposures to low concentrations have been observed to have an initial stimulant effect on the bone marrow, followed by aplasia (impaired production of blood cells) and fatty degeneration [ACGIH 1986, Proctor et al. 1988, NIOSH 1977]. Both NIOSH and the International Agency for Research on Cancer (IARC) have concluded that recent epidemiologic studies have established the relationship between benzene exposure and the development of acute myelogenous leukemia and that there is sufficient evidence that benzene is carcinogenic to humans [IARC 1982, NIOSH 1986].

NIOSH recommends that occupational exposures to benzene be controlled so that employees are not exposed to concentrations greater than 0.1 parts per million (ppm), determined as a TWA concentration for up to a 10-hour work shift in a 40-hour work week, and 1.0 ppm determined as a 15 minute short-term exposure limit (STEL). Although NIOSH has established these guidelines as levels which should not be exceeded, the Institute still urges that exposures be reduced to their lowest feasible levels because it is not presently possible to establish thresholds for carcinogens which will protect 100 percent of the population. The ACGIH currently has a TLV of 10 ppm and has listed benzene as a suspected human carcinogen. However, the ACGIH has included benzene on its 1990-1991 notice of intended changes which, when adopted, will establish a lower TLV of 0.1 ppm and recognize benzene as a confirmed human carcinogen. The ACGIH has not established a STEL for ben-

zene. OSHA has established a PEL for benzene at 1.0 ppm, as an 8-hour TWA. OSHA has further established a 15-minute exposure limit of 5.0 ppm.

#### D. Limonene

Limonene is one of a general class of chemicals known as terpenes (cyclic olefins). Limonene is highly fragrant and is the main constituent of the terpenoid fraction of many fruits and flowers. It is also present in the leaves and bark of many species of trees and shrubs, especially the orange and lime. Limonene also occurs in the gas phase of tobacco smoke. In addition to its diverse uses as an insect repellent, an aerosol stabilizer, and as a wetting and dispersing agent, limonene is also widely used as an odorant and, to a lesser extent, as a solvent in many products including De-solv-it®. According to several animal and human exposure studies, limonene has low acute toxicity, both orally and dermally. Its odor is detectable in water at a concentration of 10 parts per billion. There are no occupational exposure criteria for this substance.

#### E. Nitrogen Dioxide

Nitrogen dioxide, a gas with a distinctive reddish-brown color, is a respiratory irritant and is capable of causing pulmonary edema. Most of the reported illnesses resulting from NO<sub>2</sub> exposures have resulted from accidental acute exposures. Based on information from human exposures, a concentration of 50 ppm is moderately irritating to the eyes and nose and may possibly cause pulmonary edema and possible subacute or chronic lesions in the lungs [Patty 1981]. The odor of NO<sub>2</sub> is first perceptible to most people in the range of 0.11 to 0.22 ppm [Patty 1981].

The NIOSH Recommended Exposure Limit for NO<sub>2</sub> is 1 ppm for a 15 minute period, the same as the OSHA ceiling limit for this compound. There is no full shift TWA exposure criteria set by either NIOSH or OSHA for this compound. The ACGIH TLV for NO<sub>2</sub> is 3 ppm for an 8-hour TWA, with a STEL of 5 ppm for 15 minutes.

## VI. RESULTS and DISCUSSION

#### A. Worker Training

At the time of the NIOSH Health Hazard Evaluation, worker training sessions were conducted by Exxon contractors in Valdez, Seward, and Cordova, Alaska. The initial 4-hour training session was to take place at the beginning of the employee's tour-of-duty with the cleanup operations; a 1-hour refresher training session was intended for employee's who were returning from rest and relaxation (R&R).

The content of the 4-hour training program is discussed in the Exxon Valdez Cleanup Operations Safety and Health Training Program [Exxon Corporation 1989]. The major topics discussed during the training session attended by NIOSH were

consistent with those identified in the written training program instructions and presented in Appendix A.

The specific content of these types of training courses, which are intended to provide information that will enable the worker to perform his or her tasks free of injury or illness, is always debatable. There is always room for improvements in course content or the manner in which information is presented. This type of training introduces the new employee to potential health and safety hazards. Continued follow-up with on-the-job training efforts and consistent enforcement of all aspects of the safety and health program from work site to work site are also important. Based on the tasks the oil spill clean-up workers were likely to be engaged in, and the environment in which they would be living and working, the training was judged to be adequate by all three NIOSH investigators. No major omissions in subject matter or problems with delivery were noted.

## B. Personal Protective Equipment (PPE)

### 1. Adequacy, Availability, and Use

The following items were considered standard issue for all shoreline cleanup workers. Workers in other job categories were issued PPE consistent with the potential hazards associated with their specific tasks.

- 1 pair heavy cotton work coveralls
- 1 Tyvek® suit
- 1 set of rain gear (pants and jacket)
- 1 pair of deck shoes
- 1 Type III PFD (personal floatation device)
- 1 pair of boots
- 6 pair of wool socks
- 1 hard hat
- 1 laundry bag
- 1 pair of safety glasses
- 5 pairs of oil resistant gloves
- 5 pairs of cotton work gloves

Other PPE items in stock in the major field supply locations included PVC cannery sleeves, barrier creams, ear plugs, ear muffs, hand cleaners (non-solvent type), respirators (3M® 8710 dust/fume/mist and 3M® 5101, 5201, 5301 organic vapor).

PVC was the major type of rain gear and glove material used during shoreline cleanup. A variety of manufactures (Cape Islander, Tingler Web, and Rain

Fair) gear having various quality of construction was noted. Only one permeation study potentially applicable to "weathered crude" was found [Gammage et al. 1988]. Based on the information presented in that study, PVC may allow penetration of the volatile components of crude oil after about two hours, but should offer adequate protection against "weathered" crude oil, which would not be expected to contain significant quantities of volatile components. NIOSH's Division of Safety Research conducted a limited study (see Appendix D) which suggested that the PVC rain gear offered adequate protection against "weathered" crude oil and that eighter ...or De-Solv-It® were appropriate decontaminating agents.

Boots were generally made of a neoprene material, from a variety of manufacturers (e.g. X-Tuff, La Cross, Beta, Helly Hanson, Ranger), and included safety toe and regular toe styles.

The following problems with regard to adequacy, availability and use were noted:

- Task Force II had temporarily run out of gloves at the main supply location.
- Task Force III had temporarily run out of ear plugs.
- There were intermittent problems with maintaining adequate supplies of gloves in a full range of sizes.
- The wearing of PPE was not consistently enforced from work site to work site. When PPE was worn incorrectly, worker's skin became visibly contaminated with "weathered" crude.

-Workers were instructed during their initial training session to use tape to seal the glove/sleeve and boot/pant junctions.

However, this practice was not commonly done at the beach sites, probably due to

the number of times that gear was donned and doffed each day. However, joint taping was strictly enforced at the waste handling facility in Valdez.

-On warm days, some workers wore Tyvek® suits. Before long, however, these garments were heavily soiled and ripped.

-Fogging of glasses and goggles was mentioned as being a safety problem by a number of ORTs.

## 2. Decontamination of PPE

When workers returned from the beaches at the end of the day, potentially reusable PPE gear (e.g. boots, rain suits, chemical resistant gloves, life vests,

hard hats) were left on the DECON barge area for cleaning by second shift workers.

Decontamination of PPE gear in Task Force II was not effective. Several items (life vests, hard hats, boots) were not routinely cleaned. Items that were cleaned were brushed and/or wiped by hand using De-Solv-it®, a petroleum distillate-based cleaner containing a surfactant and limonene. While the decontaminated items were noticeably cleaner, oily residue was still noted on most of the garments inspected, and a few sets of cleaned PVC rain gear were noted to be very stiff. Whether or not multiple cleaning adversely affect the permeability of the garments was not evaluated. The decision on when to discard the garment was left up to the person performing the cleaning.

Decontamination of PPE in Task Force III was judged to be much more effective. There was a good understanding of the necessary work zone concept (dirty to clean work zones). Work boots were brushed clean by each worker as they stepped into a tub partially filled with De-Solv-it®. An attendant then wiped them dry with absorbent pads. Rain gear and life vests were cleaned in a series of scalding solutions. The first was a 55-gallon barrel contained a solution of 50% De-solv-it® and 50% water, the second and third were anionic detergent solutions (Captain's Choice®). The overall decontamination process was much more effective in Task Force III than in Task Force II.

## C. Exposure Assessment

### 1. Review of Prior Exposure Assessment Data

Information on the results of industrial hygiene sampling conducted by Exxon contractors prior to NIOSH involvement was received in June 1989. The data set presented the results of approximately 350 personal breathing zone samples obtained between April 4, 1989, and May 13, 1989. All of the samples were analyzed for VOC's and virtually all were obtained using passive dosimeters. Sampling times ranged from about 1 to 34 hours. About 25 different tasks (e.g. skimmer operator, boom tender, barge deck hand, water pusher, laborer-beach cleaner, DECON barge-cleaning rain gear, and animal rescuer) were monitored. Each sample was analyzed for benzene, toluene, ethyl benzene, total xylenes, and total hydrocarbons (as decane); results were reported as time-weighted-averages for the period of sampling. The LOD varied with sampling time; however, it was reported as 0.03 ppm for the individual hydrocarbons based on a 8-10 hour sampling time.

Statistical analysis of the data was not performed; however, the data indicated that exposures to VOC's were very low. Benzene was not detected in most of the samples; all but seven had concentrations of 0.1 ppm or less. Those above

0.1 ppm were obtained from monitoring two skimmer operators (0.16 and 0.32 ppm), a laborer on a Maxi barge (0.2 ppm), a product pumper (0.25 ppm), a water pusher (0.34 ppm), a boom gate keeper (0.48 ppm), and a laborer-shoreline (0.82 ppm). The results for toluene and ethyl benzene were in the same general range as those for benzene. All but a few of the total hydrocarbon (as decane) results were less than 1 ppm. The highest result, 14 ppm, was obtained from a skimmer operator during the cleaning of the conveyor belt.

## 2. Analysis of Bulk Samples

### a. Crude Oil (ORNL Analysis)

This is a brief presentation of the ORNL data pertinent to this health hazard evaluation. Lower boiling organics were depleted in the "weathered" crude relative to the original crude oil. This was attributed to the weathering process in which low-boiling-point organics evaporated. Volatile organic content, determined by EPA SW846 VOA GC-MSD Method, was 3.14% for the original crude oil and less than 0.01% for the "weathered" crude oil. Benzene made up about 10% of the volatile fraction in the unweathered oil, but was not detected in the "weathered" crude oil. Four PNAs (chrysene, benzo[fluoranthene], benzo[e]pyrene, and benz[ghi]perylene) were detected, ranging in concentrations of 0.2 to 22 ppm in the original crude oil and 1.1 to 13 ppm in the "weathered" crude oil. These concentrations were described as relatively low and comparable to four other common crude oils. No mutagenicity was measured either in the original crude oil or the "weathered" crude oil from Ames tests using strain TA-98 with Arochlor 1254-induced S9 activation or strain TA-100, either with or without S-9 metabolic activation [Guerin 1990]. Low levels of mutagenic activities were detected in two other common crude oils tested at the same time.

### b. Crude Oil (NIOSH Analysis)

The headspace above three different bulk samples of "weathered" crude oil did not contain detectable concentrations of benzene, even when the samples were heated to 140 degrees Fahrenheit (60 degrees Centigrade). The LOD was about 10 parts per billion (ppb). The concentration of total hydrocarbons, which was determined by summing all of the chromatographic peaks, averaged 14 and 290 µg/l for the room and elevated (60 degrees Centigrade) temperature tests respectively, and consisted primarily of C9-C19 aliphatic hydrocarbons.

Table 1 shows the estimated concentrations of the PNA compounds detected in three "weathered" and one original crude oil samples by GC/HRMS/SIM

analysis. Concentrations were determined by comparing peak areas of the identified compounds with those of known internal standards. Results are provided only as rough, semi-quantitative estimations. The major problem encountered with the analysis was the poor extraction efficiencies observed for internal standards and spiked samples. In most cases, the recoveries were less than ten percent. Referring to Table 1, bulk #1, #2, and #3 were "weathered" crude oil samples collected about 30, 60, and 90 days after the oil spill respectively; bulk #4 was a sample of the crude oil left in the tanker and, therefore, represents the original crude oil. Seven PNAs (naphthalene, fluorene, phenanthrene, pyrene, chrysene, benzo[b]fluoranthrene, and benzo[a]pyrene) were detected at trace concentrations, about 1 to 34 ppm in the "weathered" bulks and about 38 to 4732 ppm in the sample of the original crude oil. In addition to the PNA compounds identified by the ORNL analysis, which focused on 4-6 ring PNA compounds, the NIOSH analysis also identified trace concentrations of other compounds, such as C<sub>1</sub>-C<sub>6</sub> alkyl dibenzo thiopenes, alkylated naphthalenes, phenanthrenes, fluorenes, chrysenes, and C<sub>1</sub>-C<sub>6</sub> alkyl carbazoles.

#### c. Decontamination Solutions (NIOSH Analysis)

The two bulk samples of decontamination solutions were obtained during evaluation of the decontamination operation in Task Force II and III. The trade name for the cleaning solution was **De-solv-it**®. Limonene and ntridecane were the largest single components detected. This was consistent with the information on the Material Safety Data Sheet for this product. Based on this analysis, analysis of the air samples obtained during decontamination operations proceeded with limonene and aliphatic hydrocarbons as the main analytes (see Section VI-D).

#### d. Bulk Air Samples (NIOSH Analysis)

Two different sorbents (Carbotrap® 300 and activated charcoal) were used to collect air samples inside two typical plastic bags that contained oily waste. The length of time since the bags were filled was not known; however, there was a strong sulfur smell coming from the inside of each bag at the time of sampling.

The major components identified, using the experimental method (Carbotrap® 300 tubes), included naphthalene, various C<sub>5</sub>-C<sub>7</sub> alkane isomers, dimethyl disulfide, and benzene. Other compounds detected included

methyl naphthalene isomers, some fatty acids, phenol, biphenyl, toluene, indan, indene, methyl trisulfide, indole, and 2-methylbenzofuran. The field blank also contained C<sub>6</sub>-C<sub>14</sub> alkanes, benzene, and toluene but at much lower levels. The individual components were not quantified.

The major volatile components identified on the charcoal samples included limonene, pentanes, hexanes, heptanes, toluene, benzene, xylenes, and numerous other C<sub>8</sub>-C<sub>14</sub> alkanes. Some higher aromatics such as trimethylbenzenes, and tetramethylbenzenes, trichloroethylene, and ethyl ether were also detected. It was likely that breakthrough occurred for the lighter alkanes. These samples were analyzed for limonene, benzene, toluene, C<sub>5</sub>-C<sub>6</sub> alkanes, and total other hydrocarbons. The estimated concentrations of benzene, toluene, and limonene inside the plastic bags were 2.5, 7.5, and 40.4 ppm respectively. The sulfur compounds may have been responsible for the nauseating odor.

At the time of the NIOSH evaluation, all workers at the oily waste handling facility wore organic vapor respirators while handling the oily waste bags in the pit areas.

### 3. Inhalation

#### a. VOC's and Oil Mist

Table 2 presents exposure estimates for 33 workers engaged in either beach cleanup or waste handling operations. Data are presented for benzene, toluene, xylene, and total hydrocarbons (reported as decane).

For benzene, 21 of 33 samples, or 63%, were either non-detectable or below the lower limit of quantitation (approximately 0.01 to 0.1 ppm, depending on the sampling rate and duration). Benzene concentrations in samples that contained quantifiable amounts ranged from 0.01 to 0.30 ppm. Benzene concentrations in three samples, two at 0.2 ppm, and one at 0.3 ppm, exceeded 0.1 ppm NIOSH REL. The OSHA PEL of 1.0 ppm was not exceeded. Although NIOSH has established this numerical REL, the Institute still urges that exposures be reduced to their lowest feasible levels because it is not, at present, possible to establish thresholds for carcinogens which will protect 100 percent of the exposed population. All three samples were from skiff operators. From the analysis of "weathered" crude oil by NIOSH and others, it is unlikely that the benzene vapors were from the "weathered" crude oil. It is more likely that these benzene exposures were the result of other exposures, such as to the volatile components of the gasoline used in the small outboard engines in the skiffs. The composition of gasoline varies with production techniques, seasonal variability, and the addition of proprietary additives, but, is known to typically contain approximately 62% alkanes, 7% alke-

nes, and 31% aromatics [ENVIRON Corporation 1990]. Gasoline can contain as many as 1500 hydrocarbons, although a typical product contains 150 compounds. Benzene is usually present in gasoline in concentrations of about 2 percent. Exposures during self-serve automobile refueling have been estimated to range from 0.23 to 1.1 ppm. [ENVIRON Corporation 1990].

Toluene and xylene exposures were also very low, ranging from non-detectable to 0.4 ppm, except for one sample at 2.0 ppm from an OMNI Barge mechanic. Total hydrocarbon concentrations, reported as decane, ranged from non-detected to about 2.0 ppm. In general, these data supported the fact that the "weathered" crude oil was essentially devoid of volatile organic compounds.

Oil mist (non-volatile and semi-volatile organic compounds in this case) was not detected in any of the air samples. The LOD for oil mist in this evaluation was  $0.4 \text{ mg/m}^3$ . This LOD is higher than normal and due to the fact that the collection filter was mounted on the front of the charcoal tube used to sample volatile organics and the flow rate used for the volatile organics was 200 cc/min. (The usual flow rate for oil mist sampling is 1-2 lpm). This was done to limit the number of sampling trains per individual while maximizing the amount of exposure data collected. Some of the filters were stained which indicated that there may have been oil mist exposure. If there was, it was below  $0.4 \text{ mg/m}^3$ .

#### b. PNA's

Twenty-seven personal breathing zone air samples, obtained from workers engaged in a variety of tasks on the beaches and barges, were analyzed for PNA's using the same technique (GC/SIM) developed for the analysis of the "weathered" crude oil bulk samples. The LOD ranged from 25 to 200 ng/sample, depending on the specific PNA compound. As previously mentioned, the GC/HRMS/SIM analysis was 10 to 100 times more sensitive than NIOSH standard methods 5506 and 5515 [NIOSH 1984].

Detectable levels of two PNA's (naphthalene and/or phenanthrene) were found on nine samples at trace concentrations (50-100 nanograms per cubic meter). However, it is unlikely that the source of the naphthalene and phenanthrene was the "weathered" crude oil because these PNA's were only present at trace concentrations (10-31 ppm) in the "weathered" crude oil (see Table 1). It is more likely that the source of both of these PNA's was either diesel fumes or environmental tobacco smoke. Naph-

thalene and phenanthrene have both been found to be present in diesel fumes and numerous PNA's have been found in environmental tobacco smoke [NIOSH 1980, DHHS 1987].

#### c. Diesel Fumes

For this evaluation, NO<sub>2</sub> was used as a surrogate measure of exposure to diesel fumes since it is commonly the most prevalent constituent gas. Table 4 presents the NO<sub>2</sub> concentrations for members of beach crews, barge crews, and waste handling crews. Five of 14 samples contained quantifiable amounts of NO<sub>2</sub>, ranging from 0.08 to 0.25 ppm. All of the samples were 6-8 hour time-weighted-averages and, therefore, not directly comparable to the OSHA PEL or NIOSH REL (1 ppm), which are short-term or ceiling exposure limits. It is possible that these short term criteria were exceeded, given the intermittent nature of the exposure, however, this could not be determined from these data. This data, as well as the observational data collected during the course of this field study, indicate that there was the potential for significant exposure to diesel fumes from operation of support equipment or, in some cases, ships or tug boats. Another potential, but less potent, source of NO<sub>2</sub> is from environmental tobacco smoke [DHHS 1987].

#### 4. Skin Exposure

It was obvious, from visual observation alone, that many workers returned from the beach work sites each day with their skin (hands and forearms) contaminated with the "weathered" crude oil. The reason was that many workers either did not wear their PPE properly (e.g., did not tape the glove/sleeve joint) or wore gloves and/or PVC jackets intermittently or not at all. Although the Exxon Safety and Health Plan [Exxon Corporation 1989] and the training sessions stressed the importance of wearing the proper PPE ensemble, the enforcement of the plan by both area supervisors and roving safety patrols varied considerably from work site to work site. Showering did seem, at least visually, to remove the visible oil from the skin.

Results from the use the Luminoscope to examine the skin for visible and non-visible contamination with "weathered" crude oil were not interpretable because of the inability to properly monitor important issues such as the types of soaps and shampoos used. Ten workers, all from the same beach work crew, were examined with the Luminoscope pre-shift before they donned their PPE in the morning, post-shift but before cleanup (showering) upon return to the berthing vessel, and post-shift after cleanup. However, the use of the method was terminated due to problems with interpretation of initial field data. The data obtained from three workers, considered typical of that col-

lected, is presented in Figures 4, 5, and 6. Figure 4, data from employee #1, shows that the highest reading was the pre-shift measurement for all four body locations (palm of right hand, back of right hand, right forearm, and right side of neck). The reading on the palm decreased significantly upon return from the beach but increased, almost to the original reading after cleanup. Figure 5, data from employee # 7, shows that the post-shift after cleanup was significantly higher than the pre-shift or the post-shift before cleanup values. Figure 6, data from employee #9, also shows that the the pre-shift was the highest, however, it was expected that the pre-shift reading and the post-shift after cleanup readings would be the lower values, and that the post-shift before cleanup would either be about the same (if the PPE was effective), or higher (if the PPE was not effective or not worn). A possible explanation for the low readings (relative to the pre-shift readings) from skin that was visibly contaminated with "weathered" crude oil may be that there was a "quenching" effect. That is, the UV energy may have been absorbed by the oil. Although there were problems with interpretation of the Luminosope data, the technique deserves more evaluation. A more successful exercise would likely occur in a situation where a group of workers could be monitored for several days in a row and frequency of washing and types of soaps used could be more closely monitored.

## 5. Noise

There were a variety of potentially significant noise sources at each cleanup site. These included water pumps, water heaters (boilers), generators, and engines. Typical noise levels monitored from site to site are presented in Figure 7. Noise levels of 95 to 102 dBA were measured near hot water boilers and diesel generators. In most cases, workers were in these areas intermittently. Ear plugs were available at all the beach sites evaluated and were worn by most, but not all, of the workers when they were in the hazardous noise areas. Hazardous noise areas were not always posted.

### D. Decontamination

The DECON operation in two Task Forces (II and III) was evaluated by observation and air sampling. The DECON operation in Task Force II was not effectively preventing skin contact with contaminated PPE. A number of PPE items (boots, hard hats, goggles, and life vests) were not being decontaminated at all. Worker's street clothes were visibly contaminated. On one day, there was no hot water in the shower area on the DECON barge, requiring workers to shower on board the Navy vessel.

Nearly all facets of the DECON operation in Task Force III were more efficient and effective than in Task Force II. Each item of PPE was more effectively cleaned based on visual observation. On one day, the potable water storage tank ran dry re-

quiring that workers shower on the housing barge. Except for this occasion, entry into the housing barge was strictly controlled to minimize contamination of the living and sleeping areas.

Results of the air sampling conducted to monitor exposure to decon solvent vapors (Desolv-it® contained limonene and petroleum distillates) and is shown in Table 5. Natural ventilation (open doors) was used by both Task Forces to dilute the air concentrations of these vapors in the DECON cleaning areas. Exposures, based on full-shift personal breathing zone sampling, ranged from 0.8 to 5.4 ppm for limonene, and 0.5 to 2.7 ppm for total aliphatic hydrocarbons (reported as dodecane). There are no established exposure standards for limonene; however, based on its low level of toxicity, inhalation exposures at these concentrations would not be expected to cause adverse health effects. PPE was used at both sites to prevent skin contact.

#### E. Illness Data

Medical personnel associated with the oil spill cleanup reported the occurrence of work-related dermatitis. Interviews with nurses in Task Force II and III indicated that the rashes usually occurred on the hands, forearms, face, or neck and were reported by the nurses to be effectively treated using topical steroids. In their opinion, the rashes on the hands and forearms, which were the predominant sites, were related to the improper use, or non-use, of PPE. Upper respiratory infections among workers were reportedly common, their spread presumably facilitated by the crowded living conditions on some of the vessels used for housing. [The awareness of the dramatic increase in upper respiratory tract illnesses among workers and residents of Valdez led to intensified efforts by the Alaska Department of Health to ascertain the viral etiology of this illness and helped to calm fears that these respiratory conditions represented toxic effects of petroleum volatiles and the by-products of incinerated waste collected from the cleanup]. There was at least one reported incident of acute, self-limited, irritant and neurologic symptoms affecting several workers who may have been exposed to incompletely weathered crude oil.

Attempts to survey occupational injuries and illnesses in a systematic way were unsuccessful. A sample of medical records at the hospital in Valdez (the major community provider of health) revealed a variety of injuries and illnesses among oil spill workers, but the relatively low proportion of VECO (the major contractor involved in the cleanup of the oil spill) employees among these workers suggested that the latter were not representative of the workforce. Records at the hospitals in Anchorage were not filed in a way in which those involving visits related to the oil spill could be readily retrieved. A questionnaire survey of a portion of the oil spill workers was planned, but logistic difficulties prevented its timely implementation.

Routine periodic medical testing of the workers was not conducted and did not appear to have been warranted. The available biological tests and medical examinations have little utility for detecting either an episodic exposure or any health effect prior to the occurrence of symptoms. Based on available data, there is no basis for recommending long term medical surveillance of the health of the workers involved in the cleanup of the oil spill.

The possibility of evaluating worker exposure to the "weathered" crude oil, particularly PNA's, using "biomarkers" was explored with other researchers in NIOSH's Division of Biomedical and Behavioral Sciences and in the Center for Disease Control's Center for Environmental Health and Injury Control (CEHIC). Given what was known about the chemical makeup of the "weathered" crude oil, however, no plausible technique was identified. Two biomarkers that were potentially available for use, 1-pyrenol for pyrene, and 1-naphthol for naphthalene, were considered further, but due to the fact that both of these PNA's were present at only trace concentrations (10-31 ppm) in the "weathered" crude oil, and that exposures to either of these could have been from sources other than the oil (e.g., main stream and side stream cigarette smoke and diesel fumes), biological monitoring for these was not pursued.

#### F. Injury Data

Attempts to conduct a systematic, record-based field evaluation of worker's injuries was not successful and was not pursued after the 1989 cleanup operations had ceased.

Jurisdictional issues resulted in the reporting of injuries and illnesses into federal, state, and U.S. Coast Guard systems, depending on whether the incident occurred on land, on the water, on the water but docked, or above or below the high water mark. Reporting requirements and coding of the injury or illness were not always consistent within all three systems. It was possible that the same injury was coded differently from one system to the other.

The Alaska State Worker's Compensation Claim System developed a special data base for oil spill-related claims that allowed entry of a broader range of information than did the standard system. Early data runs on the new system, which were obtained in December 1990, revealed that there was a total of 1,811 state claims filed in 1989 that were related to the oil spill cleanup activities. There were two fatalities (one worker was crushed in a "dumb waiter", and another had a heart attack), 785 non-time-loss, 520 time-loss, 447 "out of jurisdiction", and 60 "other" claims. A listing by "Nature of Injury or Illness" is included as Appendix B. Not unexpectedly, 800 (44%) of the claims were related to sprains/strains, cuts/lacerations, or contusions. Claims related to the respiratory system numbered 264 (14.6%) and consisted primarily of bronchitis-type, rather than chemical-induced, illnesses [Wilson 1991]. There were 44 (2.4%) claims related to dermatitis.

#### VII. CONCLUSIONS

At the time of this evaluation, the content and delivery of the training material was judged to be adequate, considering the tasks the workers were required to perform and the environmental conditions in which they lived and worked.

A wide variety of protective gear from a number of manufacturers was used. The predominant protective garment and glove material was PVC. Available information indicates that this type of gear affords protection.

Wearing of PPE was not consistently enforced from work site to work site. Although many workers were in the proper gear, many exceptions were noted. These usually involved not wearing eye protection, gloves, or PVC garments. The hands and forearms of many workers were contaminated with "weathered" crude oil.

During warm weather ORTs were frequently observed taking off the tops of the PVC rain gear. Impermeable garments impede the loss of body heat. Heat stress under such working conditions is a potentially serious problem that warrants the establishment of contingency plans.

Decontamination of PPE was not consistently effective in the prevention of skin contact with the "weathered" crude oil in the two Task Forces evaluated. For example, in Task Force II, a number of PPE items were not being decontaminated each day, and there was no mechanism for the laundering of potentially contaminated street clothing worn under the protective garments.

Exposures to volatile organic compounds during the beach cleanup operations monitored were very low and were more likely due to sources other than the "weathered" crude oil, since analysis of bulk samples showed the "weathered" crude to be essentially devoid of the lighter petroleum fractions. Benzene was detected in concentrations up to 0.3 ppm, but was more likely due to the gasoline used in the skiffs rather than the "weathered" crude oil.

Trace concentrations (1-31 ppm) of eight PNA's were detected upon analysis of three bulk samples of "weathered" crude oil; however, NIOSH standard methods were not sensitive enough to detect these concentrations. Gas chromatographic analysis incorporating high resolution mass spectrometry and selected ion monitoring (GC/HRMS/SIM) is required. Using the more sensitive method, no significant levels of PNA's were detected in 27 personal breathing zone samples.

The potency of "weathered" crude oil as a skin carcinogen is not known. Its potency may be diminished, relative to fresh crude, due to evaporative loss of the primary solvent fraction. At least one test did not demonstrate mutagenicity activity in either the original or the "weathered" crude oil, although two other common crude oils evaluated at the same time showed mutagenic activity.

## VIII. RECOMMENDATIONS

Since the major cleanup of the Exxon Valdez oil spill terminated soon after this evaluation was conducted, the following recommendations are aimed at the planning and conduct of future oil spill cleanup operations.

Since it would seem prudent to avoid skin contact with crude oil, chemical resistance tests for crude oil and "weathered" crude oil should be conducted on a variety of chemical protective clothing (CPC) in order to select the best type based on need, availability, and environmental conditions. NIOSH recommendations on the total CPC selection process are provided elsewhere [NIOSH 1990a]. The effect that repeated decontamination has on the effectiveness of the protective garment, and the development of criteria for when to discard a garment, should also be evaluated.

For major oil spill cleanup efforts, it is important that a core of key safety and health personnel remain available at the operations headquarters and in each Task Force during the cleanup process rather than rotating personnel in and out. This would promote more consistent training and enforcement of safety and health procedures from work site to work site.

Emergency response plans should include provisions for assessment of exposures to volatile organics in the very early stages of cleanup when exposures would be the greatest.

Exposures to diesel fumes should be minimized through strategic positioning of the sources down wind of the workers where possible or through the use of temporary, vertical exhaust stack extensions. Additional general safety recommendations and a proposed surveillance system for tracking injuries (illness data could also be included) which were prepared by personnel in NIOSH's Division of Safety Research, are presented in Appendix C. There is a need to develop and coordinate an injury/illness surveillance system as soon as possible after work begins.

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- 5 Alaska, Department of Labor
- 6 LIUNA, Local 341
- 7 OSHA, Region 10
- 8 NIOSH, Denver Region

HETA 89-200/273  
Exxon/Valdez Oil Spill

GC/HRMS/SIM Analysis Results for  
PNA Compounds in Sample Bulks

	Detection Bulk #1 Bulk				
	#2 Bulk	#3 Bulk	#4 Bulk	Limit	Compound ( $\mu\text{g/g}$ ) ( $\mu\text{g/g}$ ) ( $\mu\text{g/g}$ ) ( $\mu\text{g/g}$ ) ( $\mu\text{g/g}$ )
Naphthalene	24.1	31.2	20.9	4732.0	0.5
Acenaphthylene	ND	ND	ND	ND	0.5
Acenaphthene	ND	ND	ND	0.5	Fluorene
Fluorene	13.0	11.0	8.8	1033.5	0.5
Phenanthrene	5.9	75.6	33.7	903.7	0.5
Anthracene	ND	ND	ND	ND	0.5
Fluoranthene	ND	ND	ND	ND	0.5
Pyrene	9.9	29.3	15.7	222.3	0.5
Benz[a]anthracene	ND	ND	ND	ND	0.5
Chrysene	6.5	25.3	7.8	406.3	1.0
Benzo[k]fluoranthene	ND	ND	ND	ND	1.0
Benzo[b]fluoranthene	1.4	5.1	1.2	60.9	1.0
Benzo[a]pyrene	5.1	17.4	3.0	37.9	1.0
Benzo[g,h,i]perylene	ND	ND	ND	ND	4.0
Indeno[1,2,3-cd]pyrene	ND	ND	ND	ND	4.0
Dibenzo[a,h]anthracene	ND	ND	ND	ND	4.0

Notes:

Bulk #1: Sample of "weathered" crude oil (WCO) collected off shore about 30 days after the spill

(at skimmer). Bulk #2: Sample of WCO collected off shore about 60 days after the spill (at skimmer). Bulk #3: Sample of WCO collected off shore about 90 days after the spill (at skimmer). Bulk #4: Sample of the original Prudoe Bay Crude oil obtained from the "hold" of the Exxon

Valdez vessel after the spill.  $\mu\text{g/g}$ : micrograms per gram

Table 2

HETA 89-200/89-273

Exxon/Valdez Oil Spill

Personal and General Area Air Samples for Organic Vapors

Sample #	Type	Date	Operation	Time	Ben zen e	Concen- tration, ppm <sub>a</sub> Toluene Xylene	To- tal HC <sub>b</sub>	
200B	PBZ	7/14	ORT (BEACH)-- BLOCK IS- LAND	1006- 1654	ND	ND	ND	(0.4 ) <sub>f</sub>
201B	PBZ	7/14	ORT (BEACH)-- BLOCK IS- LAND	0949- 1534	ND	ND	ND	ND
202B	PBZ	7/14	ORT (BEACH)-- BLOCK IS- LAND	0941- 1745	ND	ND	ND	-0.6
205B	PBZ	7/14	ORT (BEACH)-- BLOCK IS- LAND	1009- 1745	-0	ND	ND	0.7
204B	PBZ	7/15	ORT (SKIFF) OMNI BARGE #2	0900- 1607	0.3	0.4	0.2	1.9
206B	GA	7/15	BOOM PLAT- FORM, OMNI BARGE #2	0924- 1554	-0	ND	ND	ND
207B	PBZ	7/15	OPERATOR, OMNI BARGE #2	0908- 1614	-0	ND	ND	ND
208B	GA	7/16	BOOM PLAT- FORM, MAXI BARGE #3	0905- 1511	ND	ND	ND	ND
209B	PBZ	7/16	ORT (SKIFF) MAXI BARGE #3	0851- 1611	0.2	0.3	0.2	0.8
210B	PBZ	7/16	ORT (BEACH) MAXI BARGE #3	0908- 1614	0	ND	ND	ND
211B	PBZ	7/16	ORT (BASKET) MAXI BARGE #3	0905- 1615	-0	ND	ND	ND

212B	PBZ	7/16	ORT (SKIFF) MAXI BARGE #3	0930- 1625	0	-0.06	-0.1	-0.6
(Table 2 con- tinues on next page)								

Table 2, Continued  
HETA 89-200/89-273  
Exxon/Valdez Oil Spill  
Personal and General Area Air Samples for Organic Vapors

Sample #	Type	Date	Operation	Time	Ben- zen- e	Concen- tration, ppm <sup>a</sup> Toluene Xylene	To- tal HC <sup>b</sup>	
213B	PBZ	7/18	ORT (SKIFF) KNIGHT IS- LAND	0910- 1502	0.2	0.2	0.2	1.1
214B	PBZ	7/18	ORT (BEACH) KNIGHT IS- LAND	0856- 1447	-0	ND	ND	ND
215B	PBZ	7/18	ORT (BEACH) KNIGHT IS- LAND	0912- 1453	-0	ND	ND	-0.6
216B	PBZ	7/18	ORT (BEACH) KNIGHT IS- LAND	0922- 1449	-0	ND	ND	ND
217B	PBZ	7/19	ORT MAXI BARGE	0815- 1500	-0	ND	ND	ND
218B	PBZ	7/19	ORT MAXI BARGE	0755- 1520	-0	ND	ND	ND
219B	PBZ	7/19	ORT MAXI BARGE	0750- 1515	-0	ND	ND	ND
221B	PBZ	7/19	ORT (BEACH) JOB SITE 122	0812- 1526	-0	ND	ND	ND

222B	PBZ	7/19	ORT (BEACH) JOB SITE 122	0719- 1621	0	-0.06	-0	ND
223B	PBZ	7/19	ORT (BEACH) JOB SITE 122	0721- 1556	0	-0.06	-0	0.5
224B	PBZ	7/19	ORT (BEACH) JOB SITE 122	0744- 1622	0	-0.03	ND	0.7
225B	PBZ	7/20	BOOM PLAT- FORM OMNI BARGE #3	1027- 1355	-0	ND	ND	-1.3
226B	GA	7/20	BOOM PLAT- FORM OMNI BARGE #3	0750- 1415	-0	ND	ND	ND
227B	PBZ	7/20	MECHANIC OMNI BARGE #3	0817- 1430	0.1	2.0	-0.1	1.6
(Table 2 con- tinued on next page)								

Table 2, Continued  
HETA 89-200/89-273  
Exxon/Valdez Oil Spill  
Personal and General Area Air Samples for Organic Vapors

Concentration, ppm <sup>a</sup>	Sample #	Type	Date	Operation	Time	Benzene	Toluene	Xylene	Total HC <sup>b</sup>	
	235B	PBZ	7/22	INCINERATOR OPER.	(VALDEZ)	0737-1132	(0.01)	ND	ND	ND
	236B	PBZ	7/22	SANITARY TECH.	(VALDEZ)				0945-1116 (0.04) ND ND (1.7)	
	239B	PBZ	7/22	SANITARY TECH.	(VALDEZ)				0711-1507 0.03 ND ND ND	
	240B	PBZ	7/22	SANITARY TECH.	(VALDEZ)				0711-1524	

	(0.02) ND ND ND
241B PBZ 7/22 SANITARY TECH. (VALDEZ)	0725- 1526 0.03 ND ND ND
242B PBZ 7/22 SANITARY TECH. (VALDEZ)	0715- 1525 0.03 ND ND ND
243B PBZ 7/22 SANITARY TECH. (VALDEZ)	1300- 1524 (0.1) ND ND ND

Evaluation Criteria:

NIOSH Recommended Exposure Limits c 100 100 d ACGIH Threshold Limit  
Values 10<sup>e</sup> 100 100 d OSHA Permissible Exposure Limits 1 100 100 d

- a Parts per million.
- b Reported as decane.
- c NIOSH considers benzene to be a human carcinogen and exposures should be reduced to their lowest feasible levels.
- d None established.
- e The ACGIH considers benzene to be a suspected human carcinogen and recommends that exposures should be kept to a minimum. Worker exposures by all routes (inhalation, skin absorption, and ingestion) should be carefully controlled to levels as low as reasonably achievable below the TLV.
- f Values in parentheses are between Limit of Detection and Limit of Quantitation.

Table 3

HETA 89-200/89-273  
Exxon/Valdez Oil Spill  
Gravimetric Analysis of Zefluor Filters  
for Total Particulates

Sample # Type Date Operation Time Air Volume (liters) Concentration, mg/m<sup>3</sup>

**TASK FORCE II, BLOCK ISLAND, BEACH**

CREW ZF 0005 PBZ 7/14/89 Skimmer and ORT 1007-1505 365 0.6 ZF 2369 PBZ " ORT 1027-1659 317 4.1 ZF 0016 PBZ " ORT 0939-1620 405 0.6 ZF 2360 PBZ " ORT 0948-1642 409 0.7

**TASK FORCE II, OMNI BARGE II** ZF 0010 PBZ 7/15/89 Boom Tender/Skiff 0900-1607 428 0.5 ZF 0021 PBZ " Operator 0913-1617 427 0.4 ZF 0145 GA " Boom Platform 0923-1553 392 0.5

**TASK FORCE III, MAXI BARGE III, KNIGHT ISLAND**

ZF G1 PBZ 7/16/89 ORT 0915-1605 416 \*\*\* ZF 0011 PBZ " Skiff Operator 0850-1558\* 404 0.4 ZF 0148 PBZ " ORT/Boom Operator 0855-1558\* 231 0.5 ZF 0012 GA " On Boom Basket 0905-1512 372 0.5 (Table 3 continues on next page)

Table 3, Continued						
Sample #	Type	Date	Operation	Time	Air Volume (liters)	Concentration, mg/m <sup>3</sup>
HETA 89-200/89-273 Exxon/Valdez Oil Spill Gravimetric Analysis of Zefluor Filters for Total Particulates						
			<b>TASK FORCE III, KNIGHT ISLAND, BEACH CREW</b>			
ZF 2371	PBZ	7/18/89	ORT	0848-*	175	2.5
ZF 0006	PBZ	7/18/90	ORT	0915-1332	257	2.6
ZF 2363	PBZ	"	ORT	0911-1500	349	0.2
ZF 0015	PBZ	"	ORT	1315-1451	96	1.3
ZF 0017	PBZ	"	ORT	1332-1449	77	1.0
			<b>TASK FORCE III, MAXI BARGE</b>			

ZF 0023	PBZ	7/19/ 89	ORT	0750-*	435	0.4
ZF 0037	PBZ	"	ORT	0820-1516	296	0.9
ZF 0031	PBZ	"	ORT	0730-1500*	433	0.6
			<b>TASK FORCE III, KNIGHT IS- LAND, BEACH CREW</b>			
ZF 0036	PBZ	7/19/ 90	ORT**	0817-*	40	3.8
ZF 0022	PBZ	"	ORT**	1017-1530	313	1.3
ZF 0150	PBZ	"	ORT	0716-1555	459	1.4
ZF 2368	PBZ	"	ORT	0737-1600	443	0.4

Table 3, Continued  
HETA 89-200/89-273  
Exxon/Valdez Oil Spill  
Gravimetric Analysis of Zefluor Filters  
for Total Particulates

Sample # Type Date Operation Time Air Volume (liters) Concentration, mg/m<sup>3</sup>

**TASK FORCE III, OMNI BARGE III**

ZF 0024 GA 7/20/89 Boom Operating Plat. 0750-\* 215 0.4

ZF 0149 PBZ " Chemtrack Operator 0810-1442 392 0.3

Comments:

\* Denotes sampling pump failure. Estimated sampling volume obtained from internal pump counter. \*\* Continuation of personal sample. First sampling pump failed after 40 minutes.

New sampling pump and filter connected to oil recovery technician for duration of shift. \*\*\* Sample could not be analyzed.

Table 4					
---------	--	--	--	--	--

HETA 89-200/ 89-273 Exxon/ Valdez Oil Spill Personal and General Area Air Sam- ples For Nitro- gen Dioxide					
Sample #	Type	Date	Operation	Sample Time	Con- centra- tion, ppm
1 2	PBZ PBZ	7/14 7/14	Skimmer, Task Force II, Block Island Skim- mer & ORT, Task Force II, Block Island	1058- 1745 1056- 1422	ND (0.09)

<p>3 4 5 6 7 8 13 14 15 16 18 19</p>	<p>GA PBZ PBZ PBZ PBZ PBZ PBZ PBZ PBZ PBZ PBZ PBZ</p>	<p>7/15 7/15 7/15 7/16 7/18 7/18 7/19 7/19 7/20 7/20 7/22 7/22</p>	<p>Boom Plat- form, Omni Barge II Boom Operator, Omni Barge II Boom Operator, Omni Barge II Boom Operator, Maxi Barge III ORT, Task Force III, Knight Island ORT, Task Force III, LCM Support ORT, Task Force III, Knight Island ORT, Task Force III, Knight Island Operator, Omni Barge III Op- erator, Omni Barge III Sani- tary Tech, Val- ley Disposal Site Sanitary Tech, Valdez Disposal Site</p>	<p>0926- 1557 0906- 1615 0912- 1619 0946- 1619 0848- 1514 0911- 1517 0753- 1635 0825- 1635 0826- 1415 0826- 1415 0726- 1526 0717- 1525</p>	<p>(0.03) (0.03) (0.04) 0.06 0.12 (0.04) 0.11 0.08 0.25 (0.04) (0.03) (0.05)</p>
	<p>Evaluation Cri- teria:</p>				
	<p>ACGIH TLV</p>	<p>3 ppm, 8-hr time weighted average 5 ppm, 15 min short term exposure level</p>			
	<p>OSHA PEL</p>	<p>1 ppm, 15 min short term ex- posure limit</p>			

	NIOSH REL	1 ppm, 15 min ceiling exposure level			
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Table 5  
 HETA 89-200/89-273  
 Exxon/Valdez Oil Spill  
 Personal and Area Air Samples for Limonene and Total Aliphatic Hydrocarbons

SAMPLE #	TYPE <sup>a</sup>	OPERATION	TIME	AIR VOLUME	CONCENTRATION,	ppm <sup>b</sup> (liters) LI-	MONENE ALI-	PHATIC HC <sup>c</sup>																
228B	PBZ	Boom Cleaning	0945-1619	78	1.0	0.9	229B	PBZ Boom Cleaning 0945-1622 71 2.2																
1.8	230B	PBZ Decon, Task Force III	1838-2044	23	0.8	0.6	231B	PBZ Decon, Task Force III																
2125-0120	46	1.0	0.9	232B	GA Decon, Task Force III	2113-0129	49	1.8	1.3	233B	PBZ Decon, Task Force III	1837-2340	60	5.4	2.7	234B	PBZ Decon, Task Force III	2145-0123	43	2.0	2.4			
251B	PBZ	Decon, Task Force II	1835-2333	60	4.2	2.0	252B	GA Decon, Task Force II	1835-2335	59	1.9	1.1	253B	PBZ Decon, Task Force II	1838-2334	58	3.9	1.4	254B	GA Decon, Task Force II	1844-2336	56	0.8	0.5

Limit of Detection (mg per sample) 0.01 0.01 Limit of Quantitation (mg per sample) 0.03 0.03

Evaluation Criteria: NIOSH, ACGIH, OSHA d d

Comments

a Type of air sample. PBZ = personal breathing zone. GA = general area.

b Milligrams per cubic meter of air

c The major hydrocarbons (dodecane, tridecane and tetradecane) had their peak areas summed and these

summed areas were compared to those of the prepared standards. The concentrations reported in this

table for aliphatic hydrocarbons are expressed as ppm of dodecane (this provides the highest [ie. most conservative] reportable concentration).

d None established.

Appendix A

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APPENDICES

Support Materials for Training

State of Alaska-Public Health Advise, April 28, 1989

VECO Safety Manual

Wildlife Information for Clean-Up

Bears and You

MSDS

Hypothermia Cold Water Drowning Guidelines

Respiratory Medical Questions (As Needed)

PPE Issue

10 Person Crew (Gang) Box

Video Tapes

-Material Safety Data Sheets

-"Fisheries Safety and Survival Series"

Cold Water Near Drowning

Hypothermia

Shore Survival

ADDENDUM

Typical Trainer's Presentation Outline Appendix B

INJURY/ILLNESS DATA FROM THE  
ALASKA STATE WORKER'S COMPENSATION  
CLAIM SYSTEM (1989)

Nature of Injury or Illness Frequency

Amputation/Enuclea .....	1
Burn (Heat) .....	26
Burn (Chemical).....	13
Concussion .....	7
Infective/Parasitic .....	49
Contusion, Crushing, .....	144
Cut, Laceration .....	150
Dermatitis .....	44
Dislocation.....	20
Electric Shock .....	4
Fracture.....	47
Exposure to Low Temp .....	6
Hearing Loss/Impairment .....	4
Environmental Heat .....	4
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Pneumoconiosis .....	1
Radiation Effects .....	8
Scratches, Abrasions .....	61
Sprains, Strains .....	506
Hemorrhoids .....	3
Hepatitis .....	3
Multiple Injuries .....	23
Cerebrovascular.....	5
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Mental Disorders .....	2
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Respiratory System .....	264
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Total .....1811

Appendix C

Prepared by:

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The following safety-related recommendations are categorized in three areas:

1. General Safety Recommendations
2. Helicopter Safety Recommendations
3. Occupational Injury Surveillance System Recommendations

General Safety Recommendations

[The recommendations provided in this section were made after reviewing two video tapes of some of the worker tasks involved in the oil spill cleanup operation. It was not possible to conduct a comprehensive review of all worker safety issues via site visits; therefore, an exhaustive list of recommendations could not be provided]

In this section, the term worker(s) pertains to those personnel directly involved in work tasks associated with oil spill cleanup activities.

1 A comprehensive review of existing company safety policies and procedures should be conducted by qualified safety and health personnel to ensure that adequate safety procedures are in place at the time work begins. Written policies should be developed and implemented for all identified safety hazards related to oil spill cleanup tasks.

2 A clearly defined chain of command that establishes responsibility for worker safety should be implemented for all activities related to the cleanup operation. This includes identifying appropriate management staff responsibilities for safety-related matters, such as safety program implementation, worker training, surveillance, incident investigation, provisions for medical personnel and related facilities, etc.

3 At a minimum, all subcontractors should be required to adhere to the established safety and health policies and procedures of the primary unit responsible for the cleanup operation.

4 All workers should be provided with the appropriate tools, equipment, and personal protective devices needed to perform their job tasks.

5 All workers should be trained in safe work procedures germane to their individual work responsibilities and in the proper use and maintenance of appropriate tools, equipment, and personal protective devices.

6 All workers required to operate equipment or machinery should be skilled operators. No one should be required or allowed to operate specific equipment or machinery for which they are not provided sufficient training.

7 All workers should receive training which addresses the control of hazards associated with high pressure water and steam, fire and explosion, and decontamination procedures.

8 First-line supervisors should ensure that workers are:

(1) provided with and wear appropriate personal protective equipment (PPE) (including respiratory protection and protective clothing); (2) are trained in the proper procedures for wearing PPE; and (3) are required to inspect their PPE before beginning work each day. Also, one individual should be assigned the daily responsibility for the proper cleaning, storage, and inspection of PPE.

1 Hard hats equipped with hearing protection should be provided to all workers. These hard hats should be decontaminated and properly stored daily.

2 Full face and eye protection, e.g., face shields, should be provided for all workers, and should be attached to the hard hats noted above. Additionally, workers using high pressure spray nozzles should wear full cover eye goggles to prevent injury or irritation from splash back.

3 Full body personal protective equipment should be utilized which will provide protection from both steam/hot water and oil contamination. This PPE should be properly decontaminated and stored daily.

4 Footwear should have steel toes and shanks and slip and oil resistant soles. Footwear should be cleaned daily.

5 Workers should be provided high efficiency dust/mist respirators during high-pressure spraying operations to prevent ingestion of oil mists present due to splash back. Where vapors are present and airborne concentrations have not been quantified, workers should use organic vapor-rated respirators. Replacement filters and/or cartridges should be available at every work site.

6 Fire extinguishers should be present in fuel transfer and storage areas, and adequate fire fighting equipment should be available in all areas with the potential for fire/explosion.

7 Adequate diking must be provided around aboveground fuel storage tanks to minimize the impact of fuel spills.

8 Grounding/bonding systems should be used to reduce the possibility of explosions due to static electricity generated during fuel transfer operations.

9 Fuel storage and transfer areas should be designated and clearly posted as "No Smoking" areas.

10 Adequate surface transportation (ship-to-shore) should be available to ensure prompt treatment/evacuation of any injured personnel. The capability to utilize two-way radio communication should be present for all crews on shore.

11 Personal flotation devices should be available to all employees working in areas where the potential for drowning exists. All employees should be required to wear flotation devices during ship-to-shore transportation and upon return.

12 Workers should be instructed to exercise extreme caution when working on slippery surfaces (e.g., work on the beach areas), especially during manual materials handling tasks.

13 All workers should be trained in proper lifting techniques/ body mechanics.

- 14 A protocol to minimize heat stress for workers required to wear full body impermeable clothing should be developed and implemented. Sufficient fluid replacement and adequate rest periods should be provided as necessary.
- 15 Workers should be cautioned of the hazards posed by wild animals in the work areas, including those animals that are sick, dead, or dying.
- 16 Trained first-aid personnel and appropriate first-aid equipment should be immediately accessible to all employees. Additionally, first-aid personnel should be trained in CPR.
- 17 Adequate fire protection should be provided for sleeping quarters. Workers should be trained in emergency response procedures, and escapeways should be clearly marked.
- 18 All employees should be trained in the hazards posed by shipboard operations and changing environmental conditions, such as open hatches, tripping hazards, and slippery footing.
- 19 Adequate sanitation facilities should be provided for all employees.

### Helicopter Safety Recommendations

- 1 All Federal Aviation Administration (FAA) regulations should be adhered to during all phases of helicopter operations.
- 2 All personnel who will be riding in helicopters should receive complete training (including emergency simulations) in how to approach, board, and exit the helicopter under normal operating conditions, as well as emergency exits (in or out of the water). Personal flotation devices should be provided for all individuals being transported over water by helicopter.
- 3 All personnel who will be in the vicinity of helicopters should receive complete training in how to approach and work in the vicinity of helicopters.
- 4 All personnel who ride in a helicopter should wear helmets with both hearing and eye protection.
- 5 All personnel who ride in a helicopter should wear seat belts (preferably shoulder and lap belts with multiple attachment points.)
- 6 All helicopter pilots should be instrument rated, have flight hours in the specific make/model of helicopter they are flying, and be experienced flying by instrument flight rules (IFR) in the specific make/model of helicopter. These pilots should have experience flying from visual flight rules (VFR) into IFR conditions.
- 7 All helicopter pilots should have adequate rest between flights and should not be expected to be on call during all 24 hours of the day.
- 8 All helicopter pilots should be familiar with flying in mountainous terrain and over water. These pilots should also have experience landing and taking off from floating helipads on board ships.

9 All helicopter pilots should be granted the final authority to make the decision regarding whether it is "safe" to fly under given environmental conditions--assuming they are complying with FAA regulations.

### Recommendations for Implementing an Occupational Injury Surveillance System

The first step in studying injuries within a population of workers is to enumerate those who are at risk of injury. This enumeration is most effectively accomplished through the collection of data on the energy agents and vehicles/vectors involved in the injury (agent factor); the workers who are injured or are at risk of injury (host factor); and the environmental factors, e.g., physical, social, cultural, etc. involved in the injury (environment factor). These data must be available to identify potential risk factors for injury, to support epidemiologic studies of injury within the worker population, and to target and evaluate intervention efforts. During an emergency situation, such as during an oil spill cleanup, it is important that the surveillance system be implemented as soon as possible after the work activity begins. Additionally, the surveillance system should also be designed to facilitate data entry and data manipulation. Thus, a personal computer-based system, designed such that injury events could be recorded in the field (via a standardized format) and the data transferred electronically to a central location in a timely manner, would be highly useful in monitoring trends, identifying high risk situations, and targeting intervention strategies.

There are three possible options for documenting injury occurrence in a cohort of workers employed on a special work activity, such as an oil spill cleanup. One option is to use existing data sources which are available for other purposes. If existing sources provide accurate, representative data on the event, then, these data would be suitable for developing a surveillance system. If some data are missing or some sub-groups are over- or under-represented in the injury reporting system, then, alternative sources of information need to be considered. One such alternative is to use these existing data sources and supplement them with special studies. If existing sources have limitations which require substantial verification and/or alteration using supplemental studies, then, developing a new surveillance should be considered.

Designing and implementing a customized surveillance system would provide comprehensive coverage, permit linking with other existing records (e.g., company accident/injury reports, vital statistics records, etc.), and include all relevant information (see Table 1). It is also important to ensure comparability with other data sources and surveillance systems by using standardized coding techniques for variables such as industry, occupation, nature of injury, and severity of injury.

Figure 1 provides an example of how a model surveillance system could be structured. Injuries that are so minor that the worker does not seek treatment would not be captured by this system, although it might be possible to study these injuries through a separate worker survey.

Although the third option may be more costly and resource intensive, it provides the most independent, unbiased documentation of injury occurrence, and provides maximum flexibility to ad-

dress different research questions arising under varying circumstances. The surveillance system would be capable of providing accurate data for both the number and types of injuries occurring (numerator data) as well as matching worker exposures (denominator data). Additionally, this special purpose surveillance system would allow monitoring of injury occurrence and could provide baseline data to evaluate intervention efforts.

Once data are available, several descriptive and analytic studies could be conducted. Descriptive data would be used to identify potential risk factors in a timely manner in order to focus safety investigations and intervention efforts. The number, nature, extent, circumstance, type, and severity of injury should be estimated with respect to characteristics of the workers, their place of work, type of work task, and time of injury, etc.

The purpose of analytic studies would be to determine factors causing injuries which could be modified during intervention efforts. To effectively study the injury experience of the population-at-risk, there are three research questions which should be addressed in describing and quantifying risk factors for injury.

First, the extent of injury occurrence should be documented. This involves determining if there is an increase in the number or severity of injuries within the cohort of workers, and includes evaluating whether there is clustering of injuries or changes in the work force, exposure potential, working hours or tasks, etc. It is important to compare the baseline injury experience (or expected injury occurrence) with what is occurring in conjunction with new hazards associated with a unique effort such as a cleanup.

A second research question which should be evaluated is to determine the incidence density (injuries per population-time) of injuries associated with the activity; e.g., cleanup operation. This could be done by conducting a cohort study of all workers involved in the cleanup. This would quantify the occurrence of injuries within the population of workers using person-time at risk as the denominator.

It is also important to evaluate what places a worker at increased risk for injury. This third research question would determine the risk factors for injuries occurring to workers. Factors which increase injury risk could be investigated by comparing injury rates per person-time at risk. This requires that the workers be enumerated and followed during their tasks. Work history information (i.e., job tasks, dates worked, time worked, etc.) should be gleaned from company records or from interviews with workers during the duration of the project. In the event that a prospective study design is too costly, a case-control design could be used; e.g., obtaining work history information on all injured cases and matched controls. In either case, the ratio of injury rates between groups with and without exposure will be estimated.

Whether a prospective or case-control design is used, differences in injury rates could be evaluated with respect to variables such as job experience, age, gender, level of training, use of PPE, different sites within the cleanup area, comparing to other cleanup sites, etc.

These recommendations are included in the context of providing a methodology to document and interpret the injury occurrence in a population of workers involved in a unique work activity such as an oil spill cleanup operation. This methodology is important during all phases of injury prevention within a population, and allows an evaluation of whether the injury occurrence is increased within the population exposed to hazards, especially new hazards. Additionally, such a surveillance system would be useful in preventing injuries during the activity in question, as well as in future incidents of similar populations.

Appendix C - Table 1

## **OCCUPATIONAL INJURY SURVEILLANCE SYSTEM**

### **VARIABLES**

#### Injured Employee

-social security number -gender -race -date of birth -usual occupation -usual industry -occupation at time of injury -industry at time of injury -task at time of injury -employer -experience in task at time of injury -experience in oil spill cleanup effort at time of injury -work shift schedule -time of injury

Injury -body part injured -nature of injury -severity of injury -overall body damage -treatment (all levels) -response time of emergency medical squad -outcome (disability, complete recovery, etc.) -external cause of injury -time injury occurred (date and time) -characteristics of energy agent and vehicle/vector involved -rehabilitation

#### Environment

-weather -work conditions -use of PPE -malfunction of PPE -co-worker activity at time of injury -visibility conditions -geographic location of injury -physical location injury occurred at -noise level

Appendix D

Chemical Resistances of Selected Polyvinyl  
Chloride Rain Gear and Neoprene Boots to  
Weathered Crude Oil, and the Effect of  
Decontamination Agents on Chemical Resistance

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## BACKGROUND

On March 24, 1989, the tanker vessel Exxon Valdez spilled approximately 11 million barrels of crude oil into Prince William Sound. NIOSH became involved as a result of the HHE request and the State of Alaska's request for technical assistance.

Exxon has two contractors conducting oil cleanup operations in Prince William Sound. They are: Veco, which employs nonunion workers, and Norcon, whose employees are represented by Local 341, Laborers' International Union of North America (LIUNA). Employees of the two contractors called oil recovery technicians (ORT) have been hired to manually clean the soiled shoreline.

Weathered crude oil or mousse is a stable water-in-oil emulsion. The lower weight (high vapor pressure) alkanes, such as hexane, and other aromatics, such as benzene, have been previously dissipated via evaporation. Over a 12-day period, for example, an estimated 15-20% loss (by weight) has been attributed to the evaporation process. Weathered crude oil (WCO) is a complex mixture of heavier hydrocarbons which are difficult to qualitatively or quantitatively identify.

## Chemical Protective Clothing (CPC) Issues

1 A variety of polyvinyl chloride (PVC) rain gear brands were being used by the oil recovery technicians, having various quality of construction. Some of the rain gear, the type I used for instance (Cape Islander), permitted water penetration.

2 Many brands of neoprene boots were being used, some with and some without safety toes.

3 Many different brands of PVC gloves were being used.

4 I observed workers' pants legs and boots to be heavily soiled. Gloves were moderately to heavily soiled, depending on the job task. Cross contamination from rain gear to skin was observed when workers removed the contaminated clothing. Some individuals' forearms were soiled due to splashing under loose sleeves.

## Current State of Knowledge for CPC

Weathered crude oil (WCO) is much like tar or asphalt.

- o Materials that have good to excellent degradation ratings for tar or asphalt are:
  - Trell Chem Super® - Viton laminate
  - Neoprene
  - Nitrile
  - Polyvinyl chloride
  - Chlorinated polyethylene

A literature search identified only one permeation study applicable to weathered crude oil: Gammage,

R.B. et al., "Evaluation of Protective Clothing Material Challenged by Petroleum and Synfuel Fluids, Performance of Protective Clothing." Second Symposium, ASTM STP 989, ASTM, Philadelphia, PA (1988), pp 326-338.

Gammage found that volatile organics in crude petroleum had no breakthrough within eight hours for nitrile, Viton®, Tyvek®, or PVC. Neoprene breakthrough time was 240 minutes; butyl was 680 minutes; and PVC was 120 minutes. This weathered crude oil should have no volatile organics, but does have phosphorescing aromatic compounds. Butyl rubber, PVC, nitrile, Viton®, Tyvek®, and PVC have no permeation of phosphorescing aromatic compounds within 24 hours; breakthrough time for neoprene was between 8 and 16 hours. Therefore, PVC is a material suitable for personal protection against WCO. The use of decontamination agents (...or **De-Solv-it®**), however, may cause degradation of PVC.

Neoprene as a boot material to protect workers from WCO contamination needs evaluation. The Gammage study demonstrates that other materials such as PVC are more resistant than neoprene to WCO. This study evaluated the chemical resistance of PVC rain gear and neoprene boots

against weathered crude oil. The effect of the decontamination agent (**De-Solv-it®** and CitriKlean®) on the chemical resistance of these PPE was investigated as well.

### Chemicals

#### Weathered crude oil (WCO)

- o Prudhoe Bay crude oil from the Exxon tanker Valdez was collected on-site. It had weathered approximately three months at the time of collection. A minute amount of biological materials, e.g., algae, were observed to be suspended in the weathered crude oil. The weathered crude oil was used without purification or separation.

#### **De-Solv-It®**

- o **A petroleum distillate solvent mixture of liquids with a light yellow color and citrus odor--this product was used to clean (decontaminate) weathered crude oil from protective equipment.**

#### Other

- o A cleaning mixture which contains ethanolamine, diethylene glycol monobutylether, alkyl acryl sulfonate, alkyl aryl polyether, butylated hydroxytoluene, ethylene diamine tetra acetic acid type cleaning agent and water. This liquid was orange with a distinct citrus odor.

### CPC Materials

1. Edmont 34-500 PVC exam gloves rubber 0.192 mm nominal thickness.
2. Wheeler polyvinyl chloride (PVC) used in total encapsulating suits with a nominal thickness of 0.445 mm.
3. Edmont Wet wear 500® jacket and pants of polyvinyl chloride (PVC) and 0.300 mm nominal thickness.
4. Xtratuf® neoprene boots with a nominal thickness 3.2 mm in the toe area and 1.5 mm in the lower leg area.

### Permeation Cell

An aluminum flange permeation cell with a one-inch internal diameter, was used to challenge the CPC test material. WCO was added to the front or outside material surface. The inner surface was monitored for WCO permeation.

### Analytical Methods

As stated previously, weathered crude oil is a complex mixture of organic chemicals. For the purposes of this study, we did not separate and analyze the components in this mixture. Rather, total fluorescence of the WCO was measured. An Environmental System Corp. L-101A Fiberoptics Luminoscope which is an instrument that detects compounds which fluoresce when excited by ultraviolet (UV) radiation. It uses a bifurcated fiberoptics light pipe to transmit the UV radiation onto the surface being monitored, and to convey the emitted fluorescence signal back into a photomultiplier detector.

A small, lightweight measurement head is mounted on the end of the bifurcated lightguide, and is used to make measurements of selected target areas. A spring operated shutter is located within the measurement head, allowing the target area to be illuminated. A miniature monochromator, with a digital readout of the wavelength (in nm) is used to select the emission wavelengths. A maximum emission wavelength of 420 nm was selected for the purposes of this investigation. The light pipe luminoscope is discussed in detail in an article written by Tuan Vo-Dinh and Richard B. Gammage, "The Light Pipe Luminoscope For Monitoring Occupational Skin Contamination," *Amer. Ind. Hyg. Assoc. J.* (42): 112-120, February 1981. The luminoscope data was stored in an HP computer system.

### Experimental Designs

PVC material from rain gear typically used by the oil recovery technicians and a heavier material used in total encapsulating suits were evaluated for their chemical resistance to WCO. Neoprene boot material was also evaluated.

Initial experiments were designed to evaluate the analytical method for appropriateness, testing commenced with a series of WCO dilutions in hexane. Since hexane does not fluoresce, observed fluorescence was due to the WCO. The lower limit of detection was observed at 2ml of a 1:100 WCO/hexane mixture. Initial WCO permeation tests, used thin PVC examination gloves as the test material. A normal experimental run procedure is as follows:

- 1 The test specimen was mounted in an aluminum flange (permeation cell) using Goretex® expanded PTFE sealant.
- 2 The luminoscope head was positioned on the underside of the cell with the shutter open.
- 3 One-minute background readings from the luminoscope were recorded on an HP computer system for approximately 30 minutes.
- 4 If the baseline did not drift (>10%), then the challenge was added to the permeation cell. The minimum amount of challenge material, to completely coat the test material, was then added.
- 5 The time at which the WCO was added was recorded. One-minute readings were collected.
- 6 Readings were recorded for a minimum of 8 hours.

The primary challenge agent was WCO; however, neat ...and **De-Solv-it®** were also used. Upon completion of a WCO permeation run, the test material was cleaned of WCO by using a rag soaked in ...or **De-Solv-it®**. The test material was wiped dry, washed in a dishwasher, then left in an oven overnight at approximately 60 C to dry.

### Results

Edmont Wet wear 500®, Style 65-515, did not exhibit breakthrough time of WCO, De-Solv-It®, or ...at 8 hours. Also, use of these decontamination agents in cleaning the test sample did not affect breakthrough time.

Xtratuf® neoprene rubber boots did not show WCO, ... or **De-Solv-it®** breakthrough time at 8 hours. Decontamination agents had no effect on permeation.

### Discussion and Conclusion

The immediate breakthrough of WCO and decontamination agents demonstrates that PVC exam gloves are not appropriate for use against WCO or the tested decontamination agents. The long breakthrough time observed in this study strongly suggests that permeation exposure to WCO is minimal during extended usage. **Also, these data demonstrate that ...De-Solv-It® is an appropriate decontaminating agent.**