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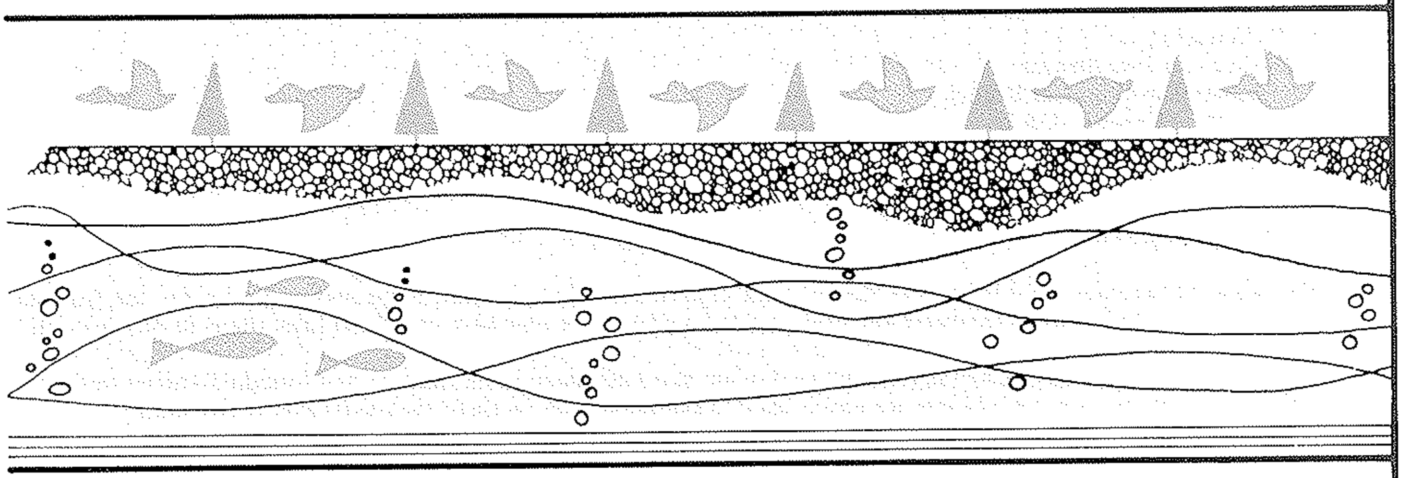
SPILL TECHNOLOGY NEWSLETTER



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The Spill Technology Newsletter was started with modest intentions in 1976 to provide a forum for the exchange of information on spill countermeasures and other related matters. We now have over 2000 subscribers in over 40 countries.

To broaden the scope of this newsletter, and to provide more information on industry and foreign activities in the field of spill control and prevention, readers are encouraged to submit articles on their work and views in this area.

INTRODUCTION

The first article of this issue is by Dave Smith and Susan Herunter who provide details of a situation in which birds were harmed by Canola oil. The article is a general review of the damage caused by oil and presents the thesis that vegetable oils are just as harmful to birds as mineral oils. The second article is by Merv Fingas, one of the newsletter's editors, who presents a review of protective equipment used to respond to chemical spills.

Good reading!

BIRDS AFFECTED BY A CANOLA OIL SPILL IN VANCOUVER HARBOUR, FEBRUARY, 1989

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Introduction

Non-petroleum oil spills can affect waterbirds to a greater extent than spills of petroleum oils (McKelvey et al., 1980). Both oils affect aquatic birds by soiling the feathers and destroying their waterproofing qualities (Thorne, 1987; Hartung, 1967). Once this happens, water penetrates to the skin and the insulation and buoyancy afforded by the trapped air in the underlying down feathers is lost. In this condition birds suffer exposure and ultimately death, especially in winter and during harsh weather. Because vegetable oils are edible, they may not be considered as threatening to aquatic birds as petroleum oils when spilled. However, the end result is the same; birds die.

The purpose of this paper is to document the number of each aquatic bird species involved in a small spill of rapeseed oil (canola) which occurred in Vancouver Harbour on February 26, 1989.

Spill Description

From approximately 2300 to 2340 h, February 26, 1989, a partially open bleeder valve on a dockside manifold, at Neptune terminals, allowed an estimated 1818 L (400 gal) of rapeseed oil to spill into Vancouver Harbour during a product transfer operation. The spill site was located on the north shore of the harbour about 2 km west of the Second Narrows bridge (Figure 1). An aerial reconnaissance approximately 10 hours after the accident located the spilled oil and bird numbers in the inner harbour. At that time, a patchy slick of yellow oil stretched from the spill site to the centre of the harbour and a thin film of oil covered the entire harbour from Stanley Park to the Second Narrows bridge. No initial effort was made to contain the spill with booms and an attempt to disperse the oil with multiple passes of a small tug through the slick proved ineffective. At first light, Neptune contracted Sprayaway Marine Services to recover the spilled oil. Sprayaway deployed two self-propelled skimming vessels to recover oil and set up booms to contain oil for subsequent recovery.

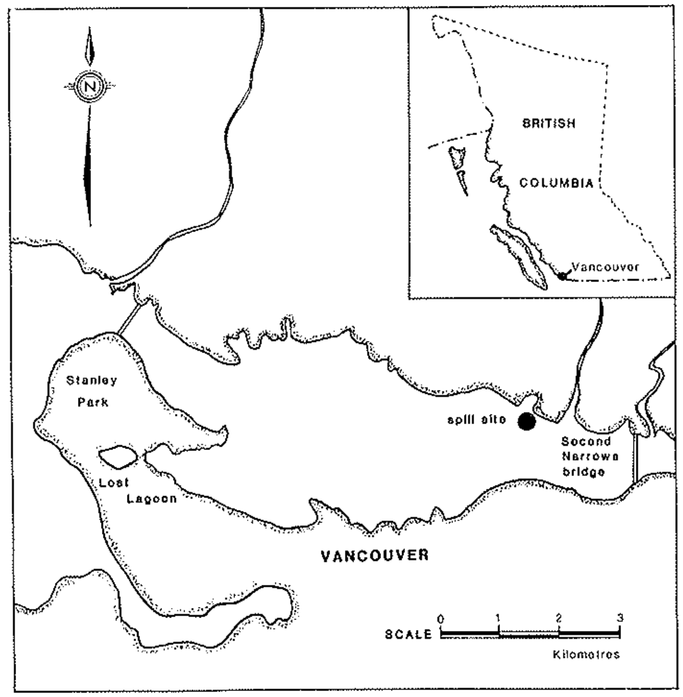

Figure 1 Vancouver Harbour, Showing the Site of the Rapeseed Oil Spill

Cleanup Operations

Sprayaway concluded their cleanup operations at 1430 h on February 27th, some 15 hours after the spill was discovered. The skimmer boats pumped the effluent to tanker trucks which transported the oil/water mixture to a disposal site where it was mixed with sawdust and incinerated.

The Wildlife Rescue Association of B.C. (WRA), Society for the Prevention of Cruelty to Animals (SPCA), and Stanley Park Zoo were informed of the spill and began preparations to receive, clean, and rehabilitate oiled birds.

Birds submitted for cleaning and rehabilitation were treated primarily at the WRA facility in Burnaby. Cleaning procedures followed that of A. Berkner (1988, pers. com. - oiled bird cleaning workshop). A continual supply of hot water, maintained at a specific temperature, is essential in an operation to clean oiled birds. A portable, propane-fueled, hot water heating system developed and described by McKelvey (1988) was loaned to the WRA, by the Canadian Wildlife Service, for this purpose.

Impact

The aerial reconnaissance estimated that at least 700 birds were present in the harbour after the spill: 500

diving ducks (scoters, scaups, and goldeneyes), 100 gulls, and 100 other divers (grebes and cormorants). At 1600 h, February 27th, about 2000 birds were counted around Stanley Park, of which 20 appeared to be oiled (J. Vanderhoven, pers. com.). On February 28th, over 300 oiled goldeneyes (mostly Barrow's - *Bucephala islandica*) were seen crowded on islands in Lost Lagoon and remained there for two days (L. Lesage, pers. com.). Their numbers decreased over the next four days, presumably as birds cleaned themselves and returned to feeding areas around the harbour. A survey of the north shore of the harbour by boat, on March 1, 1989, revealed over 1040 birds of 12 species; only five individuals appeared to be oiled.

Oiled birds are usually not recovered until about three days after an oil spill. It generally takes that long for birds to become weakened to the point where they can be captured. The numbers of birds found in days subsequent to the spill are shown in Figure 2. The second peak which appeared on the seventh day after the spill, was largely composed of several Mallards which were secondarily oiled from an open reservoir on the spill site property which held some spilled oil. A total of 88 birds of 14 species were recovered from Vancouver waters after this spill (Table 1).

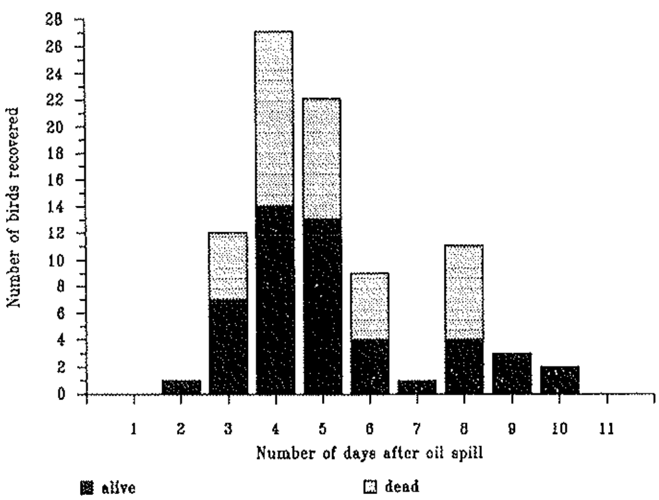

Figure 2 Numbers of Oiled Birds Found Each Day

Discussion

When aquatic birds are oiled, their daily activity patterns are interrupted and more time is devoted to preening in an attempt to clean feathers. In winter birds normally spend a great portion of their time feeding (Paulus, 1988). Alteration of normal feeding patterns might affect survival, especially in winter when food resources are limited and energy requirements are high. Reduced feeding may increase recovery time or weaken the bird to the point of no return. In the state of thermoregulatory stress that an oiled bird experiences, energy requirements are higher than normal just to maintain body heat (Hartung, 1967). Distraction from feeding for increased preening will accelerate metabolic draw on stored resources and weaken birds further. In this weakened state, birds also become more susceptible to disease.

Even if a bird survives the initial oiling, the long-term effect of ingested oil and physiological stress may severely inhibit its longevity and reproductive ability. Ingestion of petroleum oil has been shown to inhibit fecundity in birds prior to egglaying (Ainley et al., 1981; Fry et al., 1986). Hartung (1966) tested the toxicity of a variety of industrial oils ingested by waterfowl and found the effects were: lipid pneumonia, gastrointestinal irritation, fatty changes of the liver, and adrenal cortical hyperplasia. The physical effects of the ingestion of vegetable oils is not known; however, subsequent deaths of recovering oiled birds was unexpected. Some other factor related to ingestion of vegetable oil may have been responsible.

Over 144 000 tonnes of grain oils were shipped through Vancouver Harbour in 1988 (Vancouver Port Corp.). The spill of 1818 L (400 gal) on February 26th accounted for a negligible portion of the volume handled. Nevertheless, effects of such a small spill could be observed on aquatic birds. This may be of particular concern to Barrow's Goldeneye as more than 80% of the world population breeds in B.C. (Savard, 1988) and Vancouver Harbour is one of the more important wintering sites within the Strait of Georgia (Savard, 1989). Almost 24% of birds recovered from this spill were Barrow's Goldeneye.

The bulk of spilled oil was in the harbour for about 15 hours, which resulted in at least 88 aquatic birds being oiled. Many of these birds were found dead and over half of the birds found alive subsequently died during treatment. The number of casualties is likely higher than recorded for various reasons. Predator pressure is high in winter and dead and dying birds would quickly be taken by raptors and scavengers. Long-term effects of ingested oil, manifested later, makes it difficult to relate to this spill. Heavily oiled birds may sink once oiled and would not be recorded.

Rehabilitation is one way to mitigate the effects of oil spills on aquatic birds. However, the percentage of birds that can be released is small and their chance of survival is unknown.

Containing and recovering oil as soon as possible after it is spilled is the best alternative. Ships transferring any such product should be surrounded by booms that would prevent any spilled oil from escaping into the harbour. Transfer lines should be tested before use to check for leaks. The system should be monitored during transfers and spill detection equipment should be in place to alert the operators to any problem. On-site personnel should be trained and prepared to initiate an emergency/contingency plan in the event of a spill. This would include the immediate reporting of any spill to Environment Canada,

Table 1 Species Composition of Aquatic Birds Recovered

Species		Number of Bird Recovered			
		Dead	Alive	Released*	Totals
1.	Western Grebe	2	3	1	5
2.	Red-necked Grebe	0	3	2	3
3.	Horned Grebe	4	8	7	12
4.	Pelagic Cormorant	1	1	0	2
5.	Mallard	5	12	7	17
6.	American Wigeon	5	0	0	5
7.	Ring-necked Duck	2	0	0	2
8.	Greater Scaup	0	2	0	2
9.	Lesser Scaup	2	0	0	2
10.	Surf Scoter	0	1	0	1
11.	Barrow's Goldeneye	8	13	4	21
12.	Common Goldeneye	7	4	1	11
13.	Bufflehead	1	1	1	2
14.	Red-breasted Merganser	0	1	0	1
15.	Unidentified	2	0	0	2
Totals		39	49	23	88

*birds released after rehabilitation

the Coast Guard, and the Harbour Commission. Edible, non-toxic vegetable oils pose environmental hazards which may not be considered as dangerous as petroleum oil products. These hazards must nevertheless be emphasized.

Acknowledgements

We thank Paul Ross of Environment Canada, for his role in coordination and communication among all groups involved. We also thank the Vancouver Police Department for providing the crew and boat VPD-99 to conduct the survey of Vancouver Harbour. We thank W.S. Boyd, A. Breault, R. Butler, R. McKelvey, and J-P.L. Savard for reviewing previous drafts of this paper and for their numerous suggestions for improvement.

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REVIEW OF PERSONAL PROTECTIVE EQUIPMENT FOR SPILLS

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Introduction

Personal protective equipment is very important in spill situations because the user faces a multitude of safety and health concerns that could result in serious injury or illness. These hazards are accentuated by the unknown nature of the spill site and the random nature of spills. The multiple hazards of spill sites distinguish such incidents from occupational situations involving hazardous materials. Those in spill response cannot always predict which chemicals they will encounter. Responders entering a site are not only subject to the hazards of chemical exposure, but also to the dangers posed by the unknown and disorderly physical environment of a spill site. There is also a notable lack of standards and guidelines for the selection and operation of spill emergency equipment.

Preventing exposure to toxic chemicals is a primary concern at spill sites. Substances can enter the unprotected body by inhalation, skin absorption, and ingestion. Ingestion can occur by transferring adsorbed contaminant during eating, smoking, or by other forms of contact with the mouth. Chemical exposures are generally divided into two categories: acute and chronic. Acute exposures are short-term contact with the contaminant, (e.g., one-hour or one-day exposures). The term "chronic" implies long-term exposure, usually for weeks or years. Acute exposure is the main concern in spill situations.

The most common categories of protection equipment necessary for spill response are clothing and respirators. Totally-encapsulated or gas-tight suits are used when the contaminant is unknown or when a skin-penetrating or skin-corroding chemical is present. The self-contained breathing apparatus (SCBA) is the most commonly-used form of respiratory protection in the initial phases of a spill and provides the highest protection against the inhalation of chemical contaminants. The use of equipment at a spill scene is summarized in Table 1. The levels illustrated here are commonly accepted among spill response organizations including: Environment Canada, United States Environmental Protection Agency, and the United States Coast Guard.

TABLE 1 SPILL PROTECTION LEVELS

LEVEL	SITUATION	PROTECTIVE EQUIPMENT
A	ENTRY INTO UNKNOWN OR SKIN-PENETRATING CHEMICALS PRESENT	SCBA AND GAS-TIGHT SUIT
B	HIGH CONCENTRATIONS - NO SKIN-PENETRATING CHEMICALS PRESENT	SCBA AND SPECIAL CLOTHING
C	KNOWN LEVELS OF NON-PERCUTANEOUS CHEMICALS	RESPIRATOR AND CLEANUP CLOTHING
D	CHEMICALS WELL BELOW DANGER LEVELS	OVERALLS OR STREET CLOTHING

Level A is the first-response or entry level. The SCBA and totally-encapsulated suit are used to protect against high or unknown levels of chemicals. Chemical substances that permeate or otherwise attack the skin may be present and the totally-encapsulated suit must protect against these. Level B involves the use of the SCBA with standard chemical-protection clothing in situations where it is known that no skin-penetrating or corroding chemicals are present, or where high levels of contaminant may be present that a standard air-purifying device would not offer sufficient protection for. The clothing constitutes a variety of acceptable options, but usually consists of coveralls or rain-type gear and rubber boots. Gloves are used throughout the first three protection levels.

Level C includes respirators and standard clothing, which most typically consists of liquid-repellant coveralls. This level of response is very commonly used by cleanup crews when the situation has stabilized and concentrations are known and are not likely to rise above the capability of the respirator. No skin-penetrating materials are present. Level D is applicable to spills where there are no air-borne contaminants of concern and where the likelihood of harm by contact with the spilled material is minimal. Many organizations provide cotton coveralls for working in such frequently-occurring situations.

The Spill Situation

The most important consideration for protection equipment selection is the target chemical. The nature of spills becomes an important topic because one cannot be prepared for all spills but can be prepared for the most frequent spills.

A national data base has been in existence in Canada for a number of years and is useful in assessing priorities.[1,2] Table 2 is a list of the most common chemicals spilled, their frequency and volume over the ten-year period of 1974 to 1984. Only 35 materials have been involved in over ten instances and 105 materials have been spilled more than three times. The list shows that about 5% of the incidents are single or one-time incidents with a low probability of repeat. About 90% of the incidents are spills of common industrial materials. Fifty substances account for about 90% of the spills and 100 substances for about 95% of the spills.

Table 3 is a summary of the protection requirements necessary for the materials that have been spilled twice or more during the ten-year survey period. The assessments are given in terms of whether SCBA's or encapsulated suits are required or not. Some listings are rated as "possible" for normal cleanup, this means that sufficient concentration of material may remain to require the use of the SCBA rather than the air-purifying respirator. Use of Tables 1 and 2 will enable the potential spill responder to be prepared for most of the potential chemical spills, even without specific knowledge of the production and transportation of material in that region.

Selection of Respiratory Protection Equipment. Selection of respiratory protection equipment in the workplace has been the topic of several well-known references.[3,4,5] Selection of this equipment for spill situations has been described in three references.[6,7,8] The differences between normal workplace respirator selection and selection for spills hinges on the certainty with which both the actual substances present and their concentrations, are known. In spill situations maximum protection must often be used because of the possible presence of high chemical concentrations.

Respiratory protective devices consist of a face-piece connected to either an air-source or an air-purifying device. There is a wide variety of devices on the market, some of these are listed in Table 4. This table also lists a protection factor which is the ratio of the concentration of the contaminant outside the facepiece versus the concentration inside the facepiece. The protection factors presented in the table represent an average value for a large number of individuals. Such values can be much lower in the case of an individual with a poor face-piece fit. Beards, for example, can cause leakage around a face-piece, reducing the protection factor by as much as a factor of 10.

TABLE 2 SPILLS OF CHEMICALS 1974-1984

CHEMICAL	NUMBER OF SPILLS	VOLUME (t)
Polychlorinated biphenyls	334	89
Sulphuric acid	155	13 362
Hydrochloric acid	123	3 335
Ammonia, anhydrous	107	466
Sodium hydroxide	92	8 225
Sulphur	68	69 720
Ammonium nitrate	63	4 237
Fenitrothion	49	100
Nitric acid	40	139
2,4-D	37	129
Chlorine	36	120
Ethylene glycol	31	593
Potassium chloride (potash)	31	11 836
Vinyl chloride	31	183
Styrene	24	5 001
Sodium chlorate	23	7 676
Calcium chloride	20	3 678
Methanol	18	734
Calcium hydroxide	17	360
Phosphorus	16	45
Sulphur dioxide	16	89
Ammonium hydroxide	15	127
Asbestos	15	310
Xylenes	14	46
Toluene	13	105
Aminocarb	12	55
Benzene	12	13
Calcium oxide	12	530
Phosphoric acid	12	36
Mercury	11	19
Sodium hypochlorite	11	58
Phenol	10	14
Perchloroethylene	10	15
Formaldehyde	10	41
Acetic acid	9	73
Aluminum sulphate	9	122
Trifluralin	9	4
Acetic anhydride	8	1
Ammonium sulphate	8	261
Ferric chloride	8	1 004
Phosphamidon	8	15
Vinyl acetate	8	7
Chromic acid	7	8
Cyanides	7	2
Hydrogen peroxide	7	0.5
Malathion	7	0.3
Toluene diisocyanate	7	2
Ethyl mercaptan	6	0.01
Ammonium phosphate	5	144
Copper sulphate	5	22
Ferric oxide	5	22
Hexane	5	8
Hydrofluoric acid	5	0.7
Lignin sulphonate	5	181
MCPA	5	1
Oxygen, liquified	5	24
Acetone	4	9
Calcium hypochlorite	4	17
Carbofuran	4	0.05
Diazinon	4	0.2
Ethyl benzene	4	0.8
Isopropanol	4	9
Methyl ethyl ketone	4	7
Methylene chloride	4	6
Potassium permanganate	4	9
Sodium sulphite	4	29
Tetraethyl lead	4	71
Trichloroethane	4	0.8
Aluminum phosphate	3	8
Calcium phosphate	3	103
Cesium 137	3	0.000003
Diallate	3	0.08
Ethanol	3	50
Ethyl acrylate	3	1
Flamprop-methyl	3	0.2
Hydrazine	3	4
Methyl methacrylate	3	3
Naphthalene	3	6
Nitrogen	3	1
Nitrogen dioxide	3	0.001
Phthalic anhydride	3	7
Picloram	3	0.5
Sodium carbonate	3	25
Sodium cyanide	3	82
Sulphur chloride	3	3
Trichlorfon	3	2
Uranyl nitrate	3	0.2
Zinc oxide	3	54
Zinc sulphate	3	68

TABLE 3

	REQUIREMENTS FOR PROTECTIVE EQUIPMENT			
	SCBA's		ENCAPSULATED SUITS	
	EXTREME SITUATIONS	NORMAL CLEANUP	EXTREME OR ENTRY	NORMAL CLEANUP
Acetic acid	YES	POSSIBLE	YES	NO
Acetic anhydride	YES	POSSIBLE	YES	NO
Acetone	YES	POSSIBLE	YES	NO
Aldrin	YES	NO	YES	NO
Aluminum phosphate	YES	NO	NO	NO
Aluminum sulphate	YES	NO	NO	NO
Aminocarb	YES	POSSIBLE	YES	NO
Ammonia,anhydrous	YES	YES	YES	NO
Ammonium hydroxide	YES	POSSIBLE	YES	NO
Ammonium nitrate	YES	NO	NO	NO
Ammonium phosphate	YES	NO	NO	NO
Ammonium sulphate	YES	NO	NO	NO
Asbestos	YES	NO	NO	NO
Atrazine	YES	NO	YES	NO
Benzene	YES	POSSIBLE	YES	NO
Benzoic acid	YES	NO	YES	NO
Calcium chloride	YES	NO	NO	NO
Calcium hydroxide	YES	NO	NO	NO
Calcium hypochlorite	YES	NO	YES	NO
Calcium oxide	YES	NO	NO	NO
Calcium phosphate	YES	NO	NO	NO
Carbaryl	YES	NO	YES	NO
Carbofuran	YES	NO	YES	NO
Cesium 137	YES	NO	NO	NO
Chlordane	YES	NO	YES	NO
Chlorine	YES	YES	YES	POSSIBLE
Chlorine dioxide	YES	POSSIBLE	YES	POSSIBLE
Chromic acid	YES	NO	YES	NO
Copper sulphate	YES	NO	NO	NO
Cresols	YES	NO	YES	NO
Cyanides	YES	NO	YES	NO
Diallate	YES	NO	YES	NO
Diazinon	YES	NO	YES	NO
Dicamba	YES	NO	YES	NO
Diethylamine	YES	NO	YES	NO
Dimethyl amine	YES	NO	YES	NO
Dinitroamine	YES	NO	YES	NO
Diquat	YES	NO	YES	NO
Ethanol	YES	NO	NO	NO
Ethyl acrylate	YES	NO	YES	NO
Ethyl benzene	YES	NO	YES	NO
Ethyl chloride	YES	NO	YES	NO
Ethyl mercaptan	YES	YES	YES	NO
Ethylene	YES	NO	NO	NO
Ethylene glycol	YES	NO	NO	NO
Fenitrothion	YES	NO	YES	NO
Ferric chloride	YES	NO	NO	NO
Ferric hydroxide	YES	NO	NO	NO
Ferric oxide	NO	NO	NO	NO
Flamprop-methyl	YES	NO	YES	NO
Formaldehyde	YES	POSSIBLE	YES	NO
Heavy water	NO	NO	NO	NO
Hexane	YES	NO	NO	NO
Hydrogen peroxide	YES	NO	YES	NO
Hydrazine	YES	NO	YES	NO
Hydrochloric acid	YES	POSSIBLE	YES	POSSIBLE
Hydrofluoric acid	YES	POSSIBLE	YES	POSSIBLE
Isopropanol	YES	NO	NO	NO
Lead oxide	YES	NO	NO	NO
Lignin sulphonate	YES	NO	NO	NO
Malathion	YES	NO	YES	NO
MCPA	YES	NO	YES	NO
Mercury	YES	NO	YES	NO
Methanol	YES	NO	YES	NO
Methyl chloride	YES	NO	YES	NO
Methyl ethyl ketone	YES	NO	YES	NO
Methyl methacrylate	YES	NO	YES	NO
Methylene chloride	YES	NO	YES	NO
Naphthalene	YES	NO	YES	NO
Nitric acid	YES	POSSIBLE	YES	POSSIBLE
Nitrogen	YES	NO	NO	NO
Nitrogen dioxide	YES	POSSIBLE	YES	NO
Nonylphenol	NO	NO	NO	NO
Oxygen,liquified	YES	NO	NO	NO
Paraquat	YES	NO	YES	NO
Pentachlorophenol	YES	NO	YES	NO
Perchloroethylene	YES	NO	YES	NO
Phenol	YES	NO	YES	NO
Phenolsulphonic acid	YES	NO	YES	NO
Phosphamidon	YES	NO	YES	NO
Phosphoric acid	YES	NO	YES	NO
Phosphorus	YES	NO	YES	NO
Phthalic anhydride	YES	NO	YES	NO
Picloram	YES	NO	YES	NO
Polychlorinated biphenyls	YES	NO	YES	NO
Potassium chloride	POSSIBLE	NO	NO	NO
Potassium hydroxide	POSSIBLE	NO	NO	NO
Potassium permanganate	YES	NO	NO	NO
Propylene oxide	YES	NO	YES	NO
Pyridine	YES	NO	YES	NO
Sodium carbonate	POSSIBLE	NO	NO	NO
Sodium chlorate	POSSIBLE	NO	NO	NO
Sodium chloride	NO	NO	NO	NO
Sodium cyanide	YES	NO	YES	NO
Sodium dithionite	YES	NO	YES	NO
Sodium hydrosulphite	YES	NO	YES	NO
Sodium hydroxide	YES	NO	YES	NO
Sodium hypochlorite	YES	NO	YES	NO
Sodium sulphite	NO	NO	NO	NO
Styrene	YES	NO	YES	NO
Sulphuryl chloride	YES	NO	YES	NO
Sulphur	YES	NO	NO	NO
Sulphur chloride	YES	NO	YES	NO
Sulphur dioxide	YES	NO	YES	NO
Sulphuric acid	YES	NO	YES	NO
Terphenyl	YES	NO	YES	NO
Tetraethyl lead	YES	POSSIBLE	YES	POSSIBLE
Titanium dioxide	NO	NO	NO	NO
Toluene	YES	NO	YES	NO
Toluene 2,4-diamine	YES	NO	YES	NO
Toluene diisocyanate	YES	NO	YES	NO
Trichlorfon	YES	NO	YES	NO
Trichloroethane	YES	NO	YES	NO
Trifluralin	YES	NO	YES	NO
Uranyl nitrate	YES	NO	NO	NO
Vinyl acetate	YES	NO	YES	NO
Vinyl chloride	YES	POSSIBLE	YES	NO
Xylenes	YES	NO	YES	NO
Zinc oxide	NO	NO	NO	NO
Zinc sulphate	NO	NO	NO	NO
2,4-D	YES	NO	YES	NO
2,4,5-T	YES	NO	YES	NO

TABLE 4 RESPIRATORY PROTECTION EQUIPMENT AND ASSOCIATED PROTECTION FACTORS	
RESPIRATOR	PROTECTION FACTOR
AIR-PURIFYING PARTICULATE	
SINGLE-USE DUST MASK	5
QUARTER MASK	5
HALF MASK	10
FULL FACEPIECE MASK	50
POWERED DUST MASK	1000
AIR-PURIFYING GAS-ABSORBING	
HALF MASK	10
FULL FACEPIECE	50
SUPPLIED AIR RESPIRATORS	
DEMAND HALF MASK	10
DEMAND FULL FACEPIECE	50
PRESSURE-DEMAND HALF MASK	1000
PRESSURE-DEMAND FULL FACEPIECE	2000
CONTINUOUS FLOW HELMET OR SUIT	2000
SCBA's *(SELF-CONTAINED BREATHING APPARATUS)*	
OPEN-CIRCUIT DEMAND	50
OPEN-CIRCUIT PRESSURE DEMAND	10000
CLOSED-CIRCUIT, OXYGEN TANK-TYPE *(ALL ARE FULL FACEPIECE)*	50

Protection factors are important criteria for the selection of respiratory protection equipment. The protection factor must be sufficiently high to reduce the contaminant to an acceptable level inside the facepiece. This acceptable level is usually taken as the TLV or Threshold Limit Value. The TLV values for the commonly-spilled materials are listed in Table 5. These data are used in the following manner. Suppose we had a spill of a substance with a TLV of 5 ppm and by our calculations, the concentration at the spill scene could rise as high as 5000 ppm. We would require a respirator with a protection factor of at least 1000. If we wanted a safety factor of 2, we would need a protection factor of 2000. Pressure-demand SCBA's have a protection factor of about 10 000; therefore, they represent the ultimate in safety and are generally used at spill scenes because the exact type of substance and concentration is not known for certain until careful testing has been completed.

Air-purifying respirators have limitations on the concentration which they can handle or absorb. The top level at which an air-purifying respirator is useful is at the IDLH or the "Immediately Dangerous to Life and Health" level. This is also the level at which a chemical can cause severe damage. The IDLH value represents the value at which one must switch from an air-purifying respirator to an air-supplying respirator, or escape from the environment. Table 5 lists the IDLH values for commonly-spilled chemicals.

To simplify the selection process for respiratory protection at a spill scene, the following rules can be set:

- for entry into an unknown situation or where unknown or high levels of a toxic chemical are used, the SCBA should be used; and

- where the situation is stable and where the levels of chemicals are below the IDLH and have a very low possibility of rising, the air-purifying respirator can be used.

In both cases, the selection should be verified by making measurements and calculating concentrations inside the facepiece.

Clothing Selection

Clothing, gloves, goggles, boots and other such items are required to prevent contact of the chemical with the skin or eyes. The use of these protection devices is summarized in Table 6. In the case of vapours which can be absorbed through the skin, gas-tight protection is required. In the case of chemicals that are corrosive or absorbed as liquids through the skin, protection is required to prevent contact with the substance. Some chemicals pose both dangers.

Chemicals can gain access to the wearer or can affect clothing material in three ways:

1. **Degradation:** This is the deterioration of clothing material caused by the action of the chemical. Degradation may change bulk properties such as tensile strength or may result in the dissolution of small areas of the material. In previous years, the lack of standards for the measurement of other types of chemical intrusion meant that most data were for degradation. Many different measurements were known as "chemical compatibility". As will be shown later, degradation data, although important, are not usually as crucial as permeation data.

2. **Permeation:** This is the process by which liquid or gaseous chemical moves through clothing material on a molecular basis. It is the most important indicator of the usefulness of a particular clothing material. Some chemicals can pass through clothing material in only a few seconds by permeation. If these chemicals are toxic, then the clothing material is not useful for chemical protection.

3. **Penetration:** Penetration is the flow of the liquid or gaseous chemical through closures, seams, pin holes or other similar types of openings. Penetration does not pertain to the type of material selected, although certain types of materials are more or less resistant to puncture mechanisms (e.g., abrasion, pin-holing) depending on how the clothing is used or abused.

TABLE 5 THRESHOLD CONCERN VALUES FOR FREQUENTLY SPILLED CHEMICALS

CHEMICAL	TLV	IDLH
Acetic acid	10	1 000
Acetic anhydride	5	1 000
Acetone	750	20 000
Aldrin	0.25 m	
Aluminum phosphate	2 mg	
Aluminum sulphate	2 mg	
Ammonia	20	500
Asbestos	0.5-2f/cc	
Carbaryl	5 m	600 m
Carbofuran	0.1 m	
Chlordane	0.5 ms	500 m
Chlorine	1	30
Chlorine dioxide	0.1	10
Chromic acid	0.5 mg	30 m
Copper sulphate	1 mg	
Cresol	5 s	250
Cyanides	5 mgs	50 m
Diazinon	0.1 ms	
Diethylamine	10	2 000
Dimethylamine	10	2 000
Diquat	0.5 m	
Ethanol	1000	
Ethyl acrylate	5	2 000
Ethyl benzene	100	2 000
Ethyl chloride	1000	20 000
Ethyl mercaptan	0.5	
Ethylene	a	
Ethylene glycol	50	80
Ferric chloride	1 mg	
Ferric hydroxide	1 mg	
Ferric oxide	1 mg	
Formaldehyde	1	
Hexane	50-500	5 000
Hydrazine	0.1 s	
Hydrogen peroxide	1	75
Hydrogen sulphide	10	300
Hydrochloric acid	5	100
Hydrofluoric acid	3	30
Isopropanol	500	12 000
Lead oxide	0.15 mg	
Malathion	10 ms	5 000 m
Mercury	0.05 ms	28 m
Methanol	200 s	25 000
Methyl chloride	50	
Methyl ethyl ketone	200	
Methyl methacrylate	100	4 000
Methylene chloride	50	
Naphthalene	10	500
Nitric acid	2	100
Nitrogen dioxide	3	50
Paraquat	0.1 m	1.5 m
Pentachlorophenol	0.5 s	150 m
Perchloroethylene	50	
Phenol	5 s	250
Phosphoric acid	1 m	
Phosphorus	0.1	
Phthalic anhydride	1	10 000
Picloram	10	
Polychlorobiphenyls	1 s	
Potassium hydroxide	2 m	
Propylene oxide	20	2 000
Pyridine	5	3 600
Sodium cyanide	5 mgs	50 mg
Sodium hydroxide	2 m	250 m
Styrene	50 s	5 000
Sulphur dioxide	2	100
Sulphuric acid	1 m	80 m
Terphenyls	0.5	3 500 m
Tetraethyl lead	0.1 mgs	40 m
Titanium dioxide	10	
Toluene	100	2 000
Toluene diisocyanate	0.005	10
Trichloroethane	10 s	
Uranyl nitrate	0.2 mg	30 m
Vinyl acetate	10	
Vinyl chloride	5	
Xylene	100	1 000
Zinc oxide	5 m	
2,4-D	10 m	
2,4,5-T	10 m	

NOTES ALL VALUES IN PPM EXCEPT AS NOTED
m - designates value in mg/m^3
f/cc - designates value in fibres per cc
g - indicates a generic value used
s - indicates that the value is for skin contact
a - asphyxiant

TABLE 6 CLOTHING USED FOR SPILL EMERGENCIES		
TYPE OR ACCESSORY	DESCRIPTION	USE protects against:
FULL BODY PROTECTION ITEMS		
fully-encapsulating suit	one-piece gas tight suit	most hazards
non-encapsulating suit	not gas-tight	splashes
fire-fighters gear	bunker gear including pants	splashes, heat
proximity garment	heat-resistant garment	heat and flame
TORSO PROTECTION ITEMS		
aprons	aprons of resistant material	splashes
coats	bunker or rain coats	splashes,spray
bib overalls	standard or special material	splashes
overalls	standard or special material	splashes
floatation coat or overalls	floatation material built in	drowning
HEAD PROTECTION ITEMS		
hard hat	standard hard hat	blows,projectiles
helmet liner		cold
hood	liquid-tight hood	contact
EYE AND FACE PROTECTION ITEMS		
face shield	plastic semi-circle	projectiles
splash hood	liquid tight hood	splashes
safety glasses		projectiles
goggles	standard	splashes
goggles, gas-tight		chemicals
EAR PROTECTION ITEMS		
ear plugs		noise
headphones	with communication	noise
ARM AND HAND PROTECTION		
gloves	standard and chemical	chemicals
sleevelets or armlets		splashes
FOOT PROTECTION		
boots	standard or chemical	chemical contact
disposable shoe covers		contact
OTHER ITEMS		
safety harness		falls
life preserver or belt	floation device	drowning
life-line		high-hazard areas

Permeation is the most important of the entry mechanisms in terms of spill response. It is chemical dependent and often variable with a number of conditions including material thickness, temperature, and the presence of other solvents. It has been found, for example, that mixtures of chemicals can sometimes penetrate the clothing material much faster than any of the substances by themselves.

Existing data on permeation, for the most part, is measured using the American Society for Testing and Materials (ASTM) procedure.[9,10] This prescribes the use of a standard test cell consisting of two spherical halves. The clothing material forms the divider between these two halves. The challenge liquid is placed on one side, with air in the other side. The air is monitored for the presence of the chemical. Breakthrough is said to occur when the chemical can be measured in the air space. As the clothing material is completely immersed in the challenge liquid, the test does provide a conservative measure.

Permeation data for commonly spilled chemicals through common clothing material are presented in Table 7. Data are compiled from the American Conference of Industrial Hygienists (ACIH) collection and from two data bases.[11,12,13] The clothing materials represented here are those commonly used for totally-encapsulated suits or gloves. In both cases permeation data are very important for selection. Permeation times of less than 30 minutes imply that the material has little application to spills as this is the usual time spent in an encapsulated suit. In some cases, however, there is no material with a long permeation time and the best available suit would be used.

Specific permeation data on the clothing material actually used in the manufacture should be obtained whenever possible. There exist, as noted before, large variances in permeation times, even with similar, but not identical materials. Much of the variance is due to the thickness of the material. The thicker the material, the longer the permeation time. In fact, thickness is so important that even materials that show significant permeation in thin sheets of typically 0.05 cm as used in light clothing, can have immeasurable permeability in thicknesses of about 0.5 cm. Permeation through very thick synthetic materials such as on SCBA facepieces, therefore, may not be a serious concern. One must also be cautious of spurious or erroneous numbers. It is important to verify the data used with more than one source.

A few cautions should be noted in selecting totally-encapsulated suits:

1. There are no standards governing the construction of such equipment, extra care must be taken by the buyer to ensure that any purchase decision is correct;

2. One must ensure that any permeation data are that measured for the actual suit material and are generated by a standard method, preferably the ASTM method;

3. Suits that interfere with the face-seal of the SCBA should not even be considered for purchase; such practice is against most occupational health laws and is dangerous;

4. Gas-tight suits sometimes have several materials, so permeation of the weakest material is the limiting factor. Permeation of each material should be measured, as well as the joint between them. Because of the complexity of such data, it may be wise to avoid multiple-material suits;

5. The suits should allow access to the controls of the SCBA, irrespective of whether the SCBA is worn inside or outside the suit. It is for this reason that many responders prefer that the SCBA be worn outside the suit;

6. Caution should be observed in dealing with sales staff for totally-encapsulated suits; many are not aware of the intricacies of spill response, respiratory protection, safety at spill scenes, and permeation data and may provide incorrect information or information of marginal value; and

7. A survey of other users should be made to ensure that any potential purchase has performed well in actual use.

The selection of boots and gloves should be made on the basis of permeation data as well. The selection of other clothing material is less critical. Coveralls and such clothing are not worn when there is a skin-penetrating

TABLE 7 **PENETRATION TIME INTO CLOTHING MATERIALS (min.)**

CHEMICAL	BETEX	BUTYL	CPE	RUBBER	NEOPRENE	NITPVC	NITRILE	PVC	VITON
Acetic acid	>360	180	180	120	360	360	360	180	120
Acetic anhydride	>360	>240	60	3	210			4	
Aminocarb									
Ammonia,anhydrous	>360		105						
Ammonium hydroxide	>360	>480		120	360	180	360	180	>60
Ammonium nitrate	>360								
Benzene	15	30V	20	3V	12V	15V	15V	1V	9V
Chlorine	>360	>480	>180	>480	>480		>480	30	>480
Chromic acid	100	>480		70	75	360	360	360	
Cyanides	>360			480	480		480	480	
Ethyl mercaptan	15								
Ethylene glycol	>360			360	360	360	360	360	
Fenitrothion									
Formaldehyde	>360	>480	>180	60	120	30	>360	70V	>480
Hexane	15	15V	180	5	50V	90	360	30	>480
Hydrogen peroxide	>360			>480	6		>360	>360	
Hydrochloric acid	300	>480	>180	360	>360	200	360	360	>480
Hydrofluoric acid	>480	>480	66	150V	360	65	120V	360	>480
Malathion									
MCPA									
Mercury	>360								
Methanol	100	>480	>180	15	10	180V	180V	2	60
Nitric acid	>360	>480		360	150	270	100V	240	60
Pentachlorophenol					6		>360	180	>480
Perchloroethylene	10								
Phenol	>360	>480	190	60	180	120	60	20V	>480
Phosphamidon									
Phosphoric acid	>360			>360	>360	>360	>360	>360	
Phosphorus (tri-cl)	>360		45		60	30		1	25
Polychlorinated bp's		>480	>180	60	>480		150V		>480
Sodium hydroxide	>360	>480	>180	360	360	>360	360	>360	>480
Sodium hypochlorite	>360			360	360	360	360	360	
Styrene	10	30V	60	10	12	30V	30	30	>180
Sulphur dioxide	>360								
Sulphuric acid	>360	>480	>180	80	125	220	360	105	>480
Toluene	10	20V	60	5V	10V	20	20V	10V	>180
Toluene diisocyanate		>480	>120	7			240	480	>480
Trifluralin									
Vinyl acetate									
Vinyl chloride			>180				300		260
Xylenes	10	30V	60V	2V	6V	4V	60	1V	>480
2,4-D									

NOTES * BETEX=BUTYL ON NEOPRENE
* RUBBER=NATURAL RUBBER
* NITPVC=NITRILE ON PVC
* CPE=CHLORINATED POLYETHYLENE
* V - INDICATES HIGHLY VARIABLE DATA

material spilled. Disposable coveralls are now frequently used at spill scenes and are very useful for minimizing contact with the substance. Treated cellulose fabrics are now more popular than Tyvek because of their greater comfort. Goggles are used occasionally at the spill scene if there is a danger of material getting into eyes. Splash guards are also occasionally used, but their use is not encouraged. They were originally designed for spark and projectile protection for grinders, welders, and construction workers. They protect from flying objects when they are directly projected at the guard. In the case of liquids and in the case of spills, the materials can be at ground level and can actually be directed to the face by the "splash-guard" because of the open area at the bottom of the device. Hard-hats and ear protectors should be used as required.

The Protection Program

Response to chemical spills requires a complete program involving the elements of medical testing, training, retraining, and practice. The equipment-related phases of acquisition, maintenance, upgrade, and replacement are also a part of the program. Someone in the organization should be designated to supervise, coordinate, and develop the program. A body of literature exists to help with establishing a recognized and systematic program. The program should be based on a carefully-developed policy regarding spill-site entry procedures and minimum training/equipment requirements. Organizations such as Environment Canada and the U.S. Environmental Protection Agency have had programs and policies for many years. For example, these organizations have policies which state that everyone must have a minimum of one week of training in the equipment used before entering a spill scene and that a refresher course of at least one-day must be undertaken every year. Environment Canada, for example, has issued their responders with an SCBA and a totally-encapsulated suit with all the accessories. This equipment is signed out by the individual and is his (hers) until he (she) leaves the program. The equipment is repaired and replaced at regular time intervals.

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