

ON

RESEARCH, DEVELOPMENT, PRODUCTION AND PROCUREMENT OF CHEMICAL AND BIOLOGICAL DEFENSIVE MATERIEL

## FINAL REPORT OF INTERNATIONAL TASK FORCE-25 HAZARD FROM TOXIC INDUSTRIAL CHEMICALS

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## **EXECUTIVE SUMMARY**

ITF-25 concluded that there is a hazard from the release of industrial chemicals in a military situation. Toxic industrial chemicals are legitimate articles of commerce, are widely produced and traded and are available worldwide. It is highly likely that CANUKUS forces will encounter toxic industrial chemicals in their military missions throughout the world.

The use of industrial chemicals could impact on the following missions: war/conflict, peace-making (enforcing), peace-keeping, humanitarian aid, disaster relief, counter-terrorism, and counter-proliferation.

Several scenarios focusing on production, storage and transport facilities in which industrial chemicals could be either inadvertently or deliberately released have been identified. The major hazard is from massive releases from storage/transport containers of liquified pressurized gases.

ITF-25 defined toxic industrial chemicals as those chemicals which are produced in quantities exceeding 30 tonnes per year at a single facility and have a  $LCt_{50}$  value by inhalation in any mammalian species of less than 100,000 mg.min/m<sup>3</sup>.

Eleven hundred sixty-four chemicals were identified which met the toxicity criterion. This number was reduced by considering only those chemicals that were gases or liquids or solids, with an appreciable vapour pressure at 20°C, or were listed in the U.S. Department of Transportation Emergency Response Guide. By applying the producibility criterion the number was further reduced to 98.

A Hazard Index was developed to rank these 98 toxic industrial chemicals according to their significance in a military situation. Twenty-one chemicals were ranked "high", 41 "medium" and 36 "low". Data sheets for the chemicals ranked "high" and "medium" have been developed and are included in the report.

The chemical industry and national regulatory agencies have developed databases and regulations regarding the safe handling and transport of industrial chemicals. ITF-25 has interfaced with these communities and developed a list of available resources for assistance and additional information.

A formal Memorandum of Understanding with the United States Chemical Manufacturers Association has been established to provide on-call, around-the-clock assistance for emergency response information.

A Guide to Understanding the Hazard from Toxic Industrial Chemicals has been produced and provides an introduction to these hazards. It further provides advice on pre- and post- deployment actions.

Chemicals used in the pesticide industry warrant further consideration.

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The model SLAB was selected as the most appropriate interim heavy gas model for use in the prediction of challenge levels. CA modified SLAB to make it more appropriate for use by ITF-25 and the modified version (CANSLAB) has been provided to all members of the ITF. The model has been applied to numerous typical situations to provide estimations of expected challenge levels and areas of effect.

Lethal hazard zones have been estimated for typical chemical storage sites and hazard distances recommended within which no encampments should be established.

In-service protection equipment has been assessed for effectiveness at the expected challenge levels. In-service respirators should only be used to evacuate the immediate hazard zone resulting from the release of industrial chemicals. Self-contained breathing apparatus must be used in the immediate hazard zone because of the potential lack of oxygen and the very high challenge levels like to be encountered.

Commercially available detection equipment has been identified.

There is a threat from toxic industrial chemicals, but the hazard is manageable provided commanders are educated about and informed as to the extent and nature of the threat. The potential impact of deliberate or accidental releases of industrial chemicals on CANUKUS forces may be lessened, but to do so it is imperative that all elements of training, preparation, prediction, detection, protection, and countermeasures, be considered before deployment to an area.

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## INTRODUCTION

1. International Task Force 25 (ITF-25): Hazard From Industrial Chemicals, was formed at the March 1994 meeting of the Program Officers and Requirements Officers (PO/RO) of the U.S./UK/CA Memorandum of Understanding on Chemical and Biological Defense.

#### **TERMS OF REFERENCE (MARCH 1994)**

2. The Terms of Reference (TOR) of ITF-25, approved by the POs/ROs in March 1994, are given below.

#### **TERMS OF REFERENCE FOR ITF-25: HAZARD FROM INDUSTRIAL CHEMICALS**

#### **Background:**

The statements by combatants in the Bosnian civil war that chlorine might be used a weapon of opportunity has focused the need for an evaluation of the potential battlefield hazard to CANUKUS forces from the use of industrial chemicals or non CWC listed industrial chemicals that could be readily modified for military applications. In peace-making roles, CANUKUS force may operate in countries with well developed chemical industries which are capable of producing large quantities of toxic industrial chemicals. These chemicals or modification thereof could be deliberately used by the combatants against each other or against CANUKUS forces or inadvertently released when production, storage or transport facilities are subjected to attack.

Industrial chemicals are legitimate articles of commerce which are traded in very large volumes and are not subjected to the same regulations or export controls as are chemical warfare agents.

#### **Objective:**

The objective is to determine whether there is a hazard from the release of industrial chemicals in a military situation.

#### **Terms of Reference:**

- a. to develop criteria for assessing the hazard from industrial chemicals and such industrial chemicals that can be readily modified for military applications and to draw up a list of chemicals of concern;
- b. to review existing toxicological data on the chemicals of concern and to develop an agreed set of values;
- c. to review available models required for the simulation of the release of industrial chemicals. Models for the transport and dispersion of neutrally buoyant and heavy gases should be reviewed, their deficiencies noted and the best currently available models selected for interim use;

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- d. to review the adequacy of current protective equipment against expected challenge levels of the chemicals of concern and to recommend commercially available equipment to remedy any deficiencies;
- e. to review commercially available detection methods and equipment for the chemicals of concern; and
- f. to develop a database of industrial groups (e.g., chemical producers) which could provide information in emergency situations.

#### **Guidance:**

The ITF is expected to utilize information available including that in the 1989 NATO LTSS, the UK PO letter (Ptn/IT1202/882/94 dated 23 March 1994) and from civilian emergency planning organizations, chemical producer groups, regulatory agencies, etc.

#### Time Frame:

a. A report will be presented at the September 1994 PO/RO meeting giving a preliminary appreciation of whether there is indeed a hazard including some illustrative examples.

b. If there is indeed a hazard, a program to complete the Terms of Reference should be presented to the POs/ROs at the September 1994 PO/RO meeting.

#### **Composition:**

Since the ITF requires information from very diverse disciplines, i.e., toxicology, modelling, detection and protection, it is envisioned that the members will supply expertise in their own particular area and act in a coordinating capacity to obtain inputs from experts in other areas.

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3. Based on the preliminary report given at the September 1994 PO/RO Meeting (see Appendix Q and paragraphs 70-74 of the Summary Record of the September 1994 PO/RO Meeting) the POs/ROs accepted ITF-25's conclusion that there was a threat and a hazard from the release of industrial chemicals in a military situation and instructed the ITF to complete its Terms of Reference.

#### LIST OF MEMBERS/PARTICIPANTS

4. In addition to the members formally appointed by the POs/ROs and listed in the TOR, the following have made significant contributions to the proceedings of the ITF:

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Mr. James Bowers	U.S. Army Dugway Proving Ground (DPG)
LTC Mark Byers	U.S. Defense Nuclear Agency (DNA)
LTC Michael Coussa	Edgewood Research Development and Engineering Center
Mr. John Wilson	U.S. Army Chemical School (CMLS)
Mr. John C.L. Medhurst	Chemical and Biological Defence Establishment
Dr. Robin Clewley	Defence Research Establishment Suffield
Dr. Eugene Yee	Defence Research Establishment Suffield

5. Many persons and organizations have assisted in the data collection and in collaborative efforts with the ITF-25. These contributors are listed in Appendix T and their help is gratefully acknowledged.

#### **MEETING DATES**

6. The first meeting of ITF-25 was held at the Edgewood Research, Development and Engineering Center (ERDEC) from 16-18 May 1994. The principal objective of the meeting was to review available information to determine whether there was indeed a hazard from the use of industrial chemicals in a military situation. Since the members concluded after their review that a hazard existed, they proceeded to structure the TOR into "doable"pieces and to develop a way forward to present to the POs/ROs at the September 1994 Meeting.

7. A second meeting was held at the ERDEC from 11-14 October 1994 to assess progress and to share data and information. The members greatly benefited from presentations and discussions with Dr Robert Romano of the Chemical Manufacturers Association that took place at this meeting.

8. A third meeting of ITF-25 was held at the Chemical and Biological Defence Establishment (CBDE), United Kingdom, from 24-28 April 1995, to draft a finalized set of data tables, to initiate preparation of the Final Report and to draft the Commander's Guide.

9. A final meeting of ITF-25 was held at the Defence Research Establishment Suffield (DRES), Canada from 25 - 28 July 1995, to complete the data tables, the Commander's Guide and the Final Report.

10. Agendas for the four meetings are given in Appendix U.

## **DEFINITIONS AND CRITERIA**

11. The first TOR instructed ITF-25 to "develop criteria for assessing the hazard from industrial chemicals". The required **definitions** unanimously agreed to by ITF-25 follow. These definitions provided the basic criteria on which existing databases were searched and were used to construct appropriate databases for the findings.

**THREAT**: The ability of an enemy or potential enemy to limit, neutralize, or destroy the effectiveness of a current or projected mission, organization, or item of equipment.

12. The threat definition was extracted from the Glossary section of the 12 March 1986 Update to Army Regulation (AR) 381-11, Threat Support to U.S. Army Force, Combat, and Materiel Development. The ITF noted that the threat from industrial chemicals could involve people and associated materiel or cause an adverse impact on the mission or the organization through delay or diversion. Further, dissemination of hazardous industrial chemicals and the consequential probable deleterious effects on civilian and military populations have potential to alter national policies in a region. A related example is the Lebanon incident where an explosives laden truck crashed into a U.S. Marine Corps troop housing unit resulting in the death of many soldiers. This terrorist action resulted in the withdrawal of the U.S. Forces from the region and world-wide changes in security measures at U.S. facilities. Coincident use of industrial chemicals could have a similar impact.

**INDUSTRIAL CHEMICAL**: A material capable of being produced in quantities exceeding 30 tonnes per year at one production facility. Otherwise, it is considered a speciality chemical.

13. The ITF reviewed the September 1992 version of the Chemical Weapons Convention (CWC) rolling text which deals with the classes of chemicals proposed for control. Schedule 3 chemical activities pertain to chemicals that have been used as or considered as warfare agents but that are manufactured in sufficiently large quantities for legitimate industrial purposes. All facilities that produce more than 30 tonnes of Schedule 3 chemicals and precursor compounds is given in Appendix B. The Chemical Manufacturers Association (CMA), centred in Washington D.C., estimates that over 25,000 commercial facilities worldwide produce, process or stockpile chemicals that fall within the purview of the CWC. Each year, more than 70,000 different chemicals amounting to billions of tonnes of material are produced, processed or consumed by the global chemical industry. A large portion of these chemicals are excluded from the CWC but may exhibit characteristics or be sufficiently hazardous to be a threat in a military situation.

14. Toxic industrial chemicals will be found in practically every region of the world in which CANUKUS forces will operate. Figure  $1^1$  illustrates the number of manufacturers by country that produce chemicals for commercial distribution and sale. Figure  $2^2$  shows that only three countries have declared stockpiles of chemical warfare agents although a few other countries are suspected of having CW capabilities. Practically all countries have the ability to manufacture hazardous chemicals and any industrialized nation will have chemicals that could pose a threat to military forces in their region.

<sup>&</sup>lt;sup>1</sup> Data compiled from listings in the 1995/96 Directory of World Chemical Producers, Chemical Information Services, Inc., P.O. Box 743512, Dallas, Texas.

<sup>&</sup>lt;sup>2</sup> Data given in Burck, G.M. and Flowerre, C.C., International Handbook on Chemical Weapons Proliferation, Greenwood Press, New York, 1991

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15. Industrial chemicals are available in bulk quantities during production, in storage prior to use or shipment, or during their transport from one location to another. Depending on the available routes of movement, and quantity of chemical to be moved, transport can occur by truck or railroad tank cars, over water by barge or boat, over land through above- or below-ground pipelines and sometimes by air.

16. The **CRITERIA** used to draw up the initial list of chemicals of concern are **Toxicity** and **Producibility**.

**PRODUCIBILITY**: producible as an industrial chemical (in quantities exceeding 30 tonnes per year at one production facility).

**TOXICITY**: a LCt<sub>50</sub> value<sup>3</sup> of less than 100,000 mg.min/m<sup>3</sup> (approximately the same as that of ammonia) in the vapour or aerosol phase in any mammalian species.

**TOXIC INDUSTRIAL CHEMICAL (TIC)**: an industrial chemical has a  $LCt_{50}$  value less than 100,000 mg.min/m<sup>3</sup> in any mammalian species and is produced in quantities exceeding 30 tonnes per year at one production facility.

17. The number of compounds of potential importance is enormous. The present study considered only those compounds that produced an acute inhalation effect. Effects from chronic exposures, (e.g., small, long term releases from valves or seal leaks in pipes or storage tanks), or from inhalation of combustion products from fires, (e.g., breakdown products of burning plastics), or of carriers of compounds (e.g., asbestos laden smokes from building insulations) were noted but not considered.

18. An initial screening of the **Registry of Toxic Effects of Chemical Substances** (RTECS) [1] identified 1164 chemicals which met the toxicity criteria. This list of chemicals was reduced by including only those that were gases or liquids or solids, with an appreciable vapour pressure at 20°C, or those that were listed in the U.S. Department of Transportation (DOT) **Emergency Response Guide**. Available producibility data were used to further reduce the list.

19. ITF-25 recognized that the release of large volumes of hazardous chemicals could produce environmental damage that could result in a long term ecological catastrophe to flora, fauna and water resources. It also recognized that antimateriel effects could be caused by corrosive and flammable industrial chemicals. Consideration of both of these effects has been excluded from this study.

<sup>&</sup>lt;sup>3</sup> LCt<sub>50</sub> is the inhalation dosage (vapour concentration of the compound multiplied by the time of exposure) that is lethal to 50 percent of the population of exposed unprotected experimental subjects (animals).



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## MILITARY MISSIONS

20. CANUKUS forces have been deployed throughout the world in a variety of military missions. If deployed in a traditional role of waging war in a highly industrialized area, the deliberate or accidental release of industrial chemicals is practically assured. With limited conflicts and highly sophisticated weapons, such as "smart" bombs, major industrial sites can be targeted selectively to ensure that collateral damage is minimized. However, with the post-Cold War world, the traditional role of the military is being superseded by involvements in Operations Other Than War (OOTW). The ITF analyzed various military missions and noted the OOTW activities in which military presence has been frequently engaged. These missions, shown in Figure 3, include:

- War/Armed Conflict
- Peace-keeping<sup>4</sup>
- Peace-making (Enforcement)<sup>5</sup>
- Humanitarian and Civic Assistance
- Disaster Relief
- Counter-proliferation
- Counter-terrorism

21. As shown in Figure 3, a variety of actions can result in industrial chemicals being deliberately or accidentally released in a military situation. For example, during peace-making operations, the warring factions may deliberately release a hazardous chemical against the opponent, or possibly intentionally disseminate the chemical against the peace-makers. The deliberate actions by terrorists, agitators or opportunists in the field of operations are most difficult to predict or to defend against because the acts can be performed by small groups or non-aligned persons with ill-defined objectives.

22. If the peace-makers determine that the chemicals in question would best be made inaccessible for use, or destroyed, then deliberate release could occur during a preventive or preemptive counterstrike of the facilities/containers by friendly forces.

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<sup>&</sup>lt;sup>4</sup> **Peace-keeping** is defined in general as non-combat military operations undertaken by outside forces with the consent of all major belligerent parties and designed to monitor and facilitate implementation of an existing truce agreement in support of diplomatic efforts to reach settlement of the dispute. Peace-keeping actions are usually conducted under the provisions of Chapter VI of the United Nations Charter.

<sup>&</sup>lt;sup>5</sup> **Peace-making (Enforcement)** constitutes a form of combat or armed intervention, involving all necessary measures, to compel compliance with international sanctions or resolutions; the primary purpose of which is the maintenance or restoration of peace under conditions broadly accepted by the international community.

## **Figure 3: Use of Industrial Chemicals Could Impact on the Following Missions**



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23. During peace-making situations, a quantity of ordnance expended by the warring factions could go off target and impact an industrial site or container of hazardous chemicals. Although not intended, the consequences of misdirected ordnance may include atmospheric release of chemicals or create chemical-fires that produce discharges and residues that deleteriously impact the civilian community and peace-making forces.

24. Industrial chemicals may be released by accident. In the lesser-developed countries, the safety, environmental, maintenance and transportation standards for manufacturing facilities, industrial sites, and shipping containers are usually substantially less stringent than in CANUKUS. Thus, in these areas of the world, it is more likely that an industrial accident will result from human error, poorly-maintained equipment and deteriorating facilities. Natural causes such as earthquakes and atmospheric phenomena, lightning, etc., can be the cause of accidental releases, especially where sub-standard construction codes were followed.

25. In future military situations, a greater emphasis will be placed on ensuring the safety of the indigenous population and assuming more responsibility for maintaining a remediable environment. Identifying who is in charge of the civilian population (police, civil emergency, military, etc.) and determining paths of communication with local officials will be important actions regarding operations in an area. Methods and processes to alert the civilian population of the need to evacuate affected areas must be prepared in advance so as to minimize the impact on the mission caused by blockage and overcrowding of roadways.

26. To lessen the impact of deliberate or accidental releases of industrial chemicals on CANUKUS forces, it is imperative that all elements of training, preparation, prediction, detection, protection, and countermeasures, be considered before deployment.

## SELECTION METHODOLOGY

## DATA SOURCES

27. A variety of sources were used to obtain data on industrial chemical production. *Chemical and Engineering News* publishes annual production figures of the **Top 50 Industrial Chemicals in the U.S.A.** [2]. The **Directory of World Chemical Producers**, 1992/3 Edition [3], includes listings from 59 countries of chemical producers and their products. The 1995/96 Edition [4], which appeared after the initial screening was made, has listings from over 7,000 producers in 81 counties, including limited listings from former USSR. SRI, Inc. produces a series entitled **Directory of Chemical Producers** [5] with volumes for the U.S., Western Europe, Canada and East Asia. STN International producers in 80 countries. The Chemical Daily Co. [7] produces the **Directory of Chemical Products and Producers in China** and the **Japan Chemical Directory**. Some specific information for particular sites can be obtained from the **CHEMPLANT PLUS** database [8] available on DIALOG.

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28. The U.S. Department of Transportation (DOT) **Emergency Response Guidebook** [9] lists hazardous materials commonly shipped in the U.S. This publication is a guidebook for first responders during the initial phase of a hazardous materials incident. The Guidebook highlights especially hazardous materials and provides an index of protective actions and a table of initial isolation and protective action distances for civilians in addition to a guide for emergency measures.

29. The U.S. National Safety Council **Cameo/Aloha/Marplot** [10] package supplies detailed data on over 3,000 hazardous chemicals. This package also permits the calculation of downwind hazard distances.

30. The U.S. Department of Health and Human Services, National Institute for Occupational Health and Safety (NIOSH) **Pocket Guide to Chemical Hazards** [11] provides reference information in a table format which can be used for hazard assessment and management. The information includes chemical names, synonyms, trade names, exposure limits, physical and chemical properties, chemical incompatibilities and reactivities, personal protection measures and health hazards. The NIOSH Pocket Guide is also available through commercial vendors in CD-ROM and floppy diskette electronic formats [12].

31. The Association of American Railroads, Bureau of Explosives, **Emergency Handling of Hazardous Materials in Surface Transportation** book [13] is an information source designed for first responders on the scene of a transportation incident involving hazardous materials. This book provides recommendations for initial responses to an incident involving the various U.S. DOT Hazard Classes of materials. Each compound listed is first described in general terms and action orientated guidance relating to first aid, personnel protection, remediation in the event of fires and environmental considerations is offered.

32. The residue monitoring program of the U.S. Food and Drug Administration provides a list of 325 pesticides in widespread agricultural use [14]. These compounds are listed in Appendix H. Many of the pesticides are organophosphates, carbamates or other compounds with potential or known high toxicity for mammals. However, pesticides have not been included in this study mainly because most, typically, have low vapour pressures. Such toxic compounds with low vapour pressures tend to be principally hazardous by skin contact and by ingestion but fine mists of small droplets could also present a hazard by inhalation. Many of the "banned" chemicals (e.g., DDT) which are no longer found in the CANUKUS commercial markets may still be extensively found and used in developing counties.

33. Thus, pesticides warrant further investigation and should form the basis of a separate study not only to determine whether the chemicals can present an immediate hazard in military situations but also to determine any potential chronic hazard. An entire regulatory and information network exists for these compounds. The Extension Toxicology Network (EXTOXNET), accessible through the Internet [15], provides information profiles on 169 common pesticides, an index of trade names and common names of pesticides and Toxicology Information Briefs (see Appendix N).

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34. Transport Canada in its **Dangerous Goods Regulations** and its **Dangerous Goods Initial Emergency Response Guide** [16] supplies similar information to that contained in U.S. DOT Emergency Response Guidebook.

35. In the UK, the Health and Safety Executive (HSE) publishes information and regulations on hazardous industrial compounds. These include the **Control of Industrial Major Accident Hazards Regulations, 1984** (CIMAH) [17] which forms the basis of the control of major chemical hazards and major toxic hazards in the UK. CIMAH also sets criteria for grouping chemicals into three levels of toxicity depending on the LCt<sub>50</sub> value in rats over a four hour period of exposure.

36. For this study, data on the toxicity of industrial chemicals was obtained primarily from **Registry of Toxic Effects of Chemical Substances** (RTECS) [1] and from publications of the United Kingdom Health and Safety Executive (HSE). ITF-25 accepted toxicological data as given in RTECS and did not attempt to look up original references. Human toxicity estimates are given in reports by the HSE. HSE studies have traced data to the original literature and carefully evaluated all data used. Since HSE data is used for regulatory purposes and, therefore, must consider the entire population, estimates are toward the conservative side.

## **SELECTION OF CHEMICALS**

37. At the first meeting of ITF-25, a preliminary list of 17 hazardous chemicals of concern was drawn up (Table 1). At least six of the chemicals on this list (arsine, chlorine, cyanogen chloride, hydrogen cyanide, phosgene and hydrogen sulfide) were used as war gases during World War I and/or were weaponized by the U.S. or the UK. The other 11 chemicals have been involved in major industrial accidents or were ranked high on the lists of concern by the UK HSE or the U.S. DOT.

38. Each country agreed to search available databases to select additional industrial chemicals which met the toxicity and producibility criteria. The LCt<sub>50</sub> was the toxicity parameter used in the initial screening. Toxicity values were obtained from RTECS and the species considered were rats and mice. These species were selected as they were the most frequently used experimental animals. Although acute toxicity data (e.g., exposure time of 10 minutes or less) were more appropriate, the scarcity of data required that data determined for longer exposure times (e.g., 4 hours or longer) be considered. In estimating a value of the LCt<sub>50</sub>, it was assumed that Haber's rule was obeyed (e.g., the LC<sub>50</sub> value was multiplied by the exposure time). The initial screening identified 1164 candidate industrial chemicals that met the toxicology selection criterion (i.e., had a LCt<sub>50</sub> value of less than 100,000 mg.min/m<sup>3</sup> in either the rat or mouse).

39. Since ITF-25 considered that the principal hazard from industrial chemicals was an inhalation hazard, chemicals which were solids at 20°C were dropped from further consideration, unless the chemical was known to have an appreciable vapour pressure at this temperature (e.g., sulfur trioxide). The number was further reduced by focusing on those chemicals designated as "hazardous" in DOT Emergency Response Guidebook or by the UK HSE. In making this selection, ITF-25 reasoned that the U.S. DOT and the UK HSE would have identified those hazardous

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chemicals which were produced in quantity and routinely transported in either country. This allowed ITF-25 to reduce the number to the 156 chemicals listed in Appendix C.

# TABLE 1: PRELIMINARY LIST OF CHEMICALS OF CONCERN

arsine chlorine cyanogen chloride hydrogen cyanide hydrogen sulfide phosgene allyl alcohol ammonia acrolein bromine formaldehyde hydrogen chloride hydrogen fluoride hydrogen selenide methyl isocyanate oxygen difluoride phosphine

40. Because actual production figures were difficult to obtain except for the "Top 50" to 60 chemicals produced in the U.S., ITF-25 used the number of companies offering a given chemical for sale as an indication of production. This data was obtained primarily 1992/93 edition of the **Directory of World Chemical Producers**. Late in the study, the Chemical Manufacturers Association provided a list of chemical produced in excess of 30 tonnes/year at least one production site. The continents and countries in which manufacturing takes place were also collated (see Appendix V). This additional information reduced the number of chemicals of concern to 98.

#### HAZARD INDEX

41. ITF-25 was asked by the POs/ROs at the September 1994 meeting to develop a **Hazard Index** which would rank the chemicals identified in the secondary screening (see Appendix C). ITF-25 considered that for a given chemical to present a hazard in a military situation, the chemical must be present in sufficient quantity in the area of concern, must exhibit sufficient toxicity by inhalation and must normally exist in a state which could give rise to an inhalation hazard.

42. The probability that a given chemical would be present in an area of concern can be estimated by considering the geographical distribution of countries producing the chemical as well as the number of countries producing it. ITF-25 reasoned that chemicals which have world wide

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production, as indicated by production on all six continents, have a higher probability of being found in a specific area of concern than those chemicals that are produced on only one continent. It similarly reasoned that the larger the number of producers the higher the probability that the chemical would be found in a specific area of concern.

43. The higher the vapour pressure the greater the potential inhalation hazard. Therefore, those chemicals which normally exist as gases present higher potential inhalation hazards than those which exist as low vapour pressure liquids.

44. ITF-25 considered the IDLH value as the most appropriate toxicity value for the hazard index. This value indicates the concentration at which a chemical is deemed to be Immediately Dangerous to the Life and Heath of humans. It is also available for a wide range of chemicals.

45. Using the above reasoning, ITF-25 defined the Hazard Index (HI) as the product of four factors, where a number between 1 and 5 is assigned to each factor according to the ranking scheme given in Table 2. Thus:

HI = f{(toxicity)x(state)x(distribution)x(producers)}

46. The maximum value of the Hazard Index is  $5^4 = 625$ . The Toxic Industrial Chemicals (TIC) were ranked into three categories as an indicator of relative importance and to assist in hazard assessment.

- **High Hazard** indicates a widely produced, stored or transported TIC which has high toxicity and is easily vaporized.
- **Medium Hazard** indicates a TIC which may rank high in some categories but lower in others such as number of producers, physical state or toxicity.
- Low Hazard overall ranking indicates that this TIC is not likely to be a hazard unless specific operational factors indicate otherwise.

47. Chemicals which had a HI of 81 or greater were ranked "high"; those with a HI between 36 and 80, medium and those with a HI less than 36, low. Of the 98 chemicals which met the initial toxicity and producibility criteria, 21 ranked high, 41 medium and 36 low (see Table 3).

48. The Hazard Index ranking provides general guidance to planners. In a given operational situation, it is essential that the planners determine exactly what chemicals are in the area of concern and assess the hazard from any chemical found in quantity that is listed in Appendix C. If a chemical is known to be available (or it's use is threatened), toxicity by any route should be evaluated.

Distribution**		No. of Producers (NP)		Toxicity (IDLH in ppm)		y State in ppm) (VP in torr)	
Continents ≥5	5	NP ≥100	5	IDLH<1	5	Gas	5
Continents = 4	4	50 <u>≺</u> NP <u>&lt;</u> 99	4	1 <u>≤</u> IDLH <u>≤</u> 10	4	Liquid: VP <u>&lt;</u> 400	4
Continents = 3	3	25 <u>≤</u> NP <u>≤</u> 49	3	11 <b>≤</b> IDLH≤100	3	Liquid: 100 <u>&lt;</u> VP<400	3
Continents = 2	2	5 <u>≤</u> NP <u>≤</u> 24	2	101 <u>&lt;</u> IDLH <u>&lt;</u> 500	2	Liquid: 10 <u>&lt;</u> VP<100	2
Continents $= 1$	1	NP<5	1	IDLH>500	1	Liquid : vp<10	1

# TABLE 2:HAZARD INDEX PARAMETERS

\*\* number of continents on which production occurs

49. Appendix D contains a comprehensive listing of the parameter inputs used in developing the respective Hazard Index values for each of the 98 significant chemicals listed in Table 3.

50. Data sheets have been prepared for the industrial chemicals ranked "high" and for some ranked "medium" and "low" (see Appendix F).

## MODEL SELECTION

51. In order to assess the hazard from the release of an industrial chemical, it is necessary to calculate the challenge levels for potential release scenarios. TOR 3 stated that ITF-25 should review available models used to simulate the release of industrial chemicals, note their deficiencies and select the best currently available model for interim use. To complete this TOR, ITF-25 asked The Technical Cooperation Program (TTCP) Technical Panel-9 on Hazard Assessment (TP-9) for guidance. TP-9 formed an Ad Hoc Working Group on Heavy Gas Modelling (HGMWG), led by Mr. J. Bowers of Dugway Proving Ground, to quickly review available models. ITF-25 stated that the interim model must be able to calculate total dosage distance contours and concentration-time profiles at selected positions, run on a PC (486 based) and be available to all participants. Correspondence between the Chairs of ITF-25 and TP-9 are contained in Appendix L.

52. In September 1994, the HGMWG conducted a review of commonly used public domain models and a limited number of proprietary models and concluded that **SLAB** (Sept. 1990 Version) [18], developed by Lawrence Livermore Laboratories, was the best of the public domain models (see Appendix L). For the evaluation of the proprietary models, the HGMWG relied on an independent review of heavy gas models by Hanna, et al. [19] as it was not practical to purchase the models. The one proprietary model that was evaluated, PHAST (version 4.2) [20], was not deemed to be significantly more appropriate for the work of ITF-25 and was dropped from further consideration because of its high purchase price.

HIGH	MEDIUM	LOW
ammonia arsine boron trichloride boron trifluoride carbon disulfide chlorine diborane ethylene oxide fluorine formaldehyde hydrogen bromide hydrogen chloride hydrogen cyanide hydrogen fluoride hydrogen sulfide nitric acid, fuming phosgene phosphorus trichloride sulfur dioxide sulfuric acid tungsten hexafluoride	acetone cyanohydrin acrolein acrylonitrile allyl alcohol allyl amine allyl chlorocarbonate boron tribromide carbon monoxide carbonyl sulfide chloroacetone chloroacetone chloroacetonitrile chlorosulfonic acid crotonaldehyde diketene 1,2-dimethyl hydrazine dimethyl sulfate ethylene dibromide hydrogen selenide iron pentacarbonyl methanesulfonyl chloride methyl bromide methyl chloroformate methyl chloroformate methyl hydrazine methyl isocyanate methyl isocyanate methyl mercaptan n-butyl isocyanate nitrogen dioxide phosphorus oxychloride selenium hexafluoride silicon tetrafluoride silicon tetrafluoride silicon tetrafluoride silicon tetrafluoride tellurium hexafluoride tellurium hexafluoride tetr-octyl mercaptan titanium tetrachloride trichloroacetyl chloride	allyl isothiocyanate arsenic trichloride bromine chloride bromine pentafluoride carbonyl fluoride chlorine pentafluoride chloroacetaldehyde chloroacetaldehyde chloroacetyl chloride cyanogen diphenylmethane-4'-diisocyanate ethyl chloroformate ethyl chlorothioformate ethyl phosphonothioicdichloride ethyl phosphonous dichloride hexachlorocyclopentadiene hydrogen iodide isobutyl chloroformate isopropyl isocyanate n-butyl chloroformate nitric oxide n-propyl chloroformate parathion perchloromethyl mercaptan sec-butyl chloroformate sulfuryl fluoride tert-butyl isocyanate tetraethyl lead tetraethyl pyrophosphate tetramethyl lead toluene 2,4-diisocyanate

## **TABLE 3: HAZARD INDEX RANKING**

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53. The SLAB model has been recognized by the U.S. Environmental Protection Agency (EPA) for modelling toxic air pollutants. SLAB is a general purpose flat terrain model that applies to all types of accidental releases (point or area source, dense or neutrally buoyant gases, continuous or instantaneous releases). It has been extensively compared to experimental data and found to perform well [19]. The principal disadvantages to SLAB are that the source emission rate must be calculated independently and that it is a single source dispersion model.

54. SLAB was commercialized by **Bowman Environmental Engineering** and is available as a BeeLine software package [21]. Since the Bowman version was not entirely suitable for the work of ITF-25, both the UK and CA modified the software for its requirements. The CA modification, done by Dr. Eugene Yee of DRES, extended SLAB to include calculation of the flashing fraction and the probability of lethality contours and made the program more "user friendly". This recoded version of SLAB, entitled CANSLAB [22], was made available to ITF-25 in January 1995. The UK modification, done by Mr John Medhurst of CBDE, which produced output in a format suitable for use in a variety of graphics packages, was made available to ITF-25 in May 1995. Examples of challenge levels for selected scenarios, calculated using SLAB/CANSLAB, are given in Appendix E.

55. TP-9 recognised that ITF-25 required a model which would consider the effects of complex terrain. Since no currently available heavy gas model (which runs on a PC) considers this effect, it would be necessary to select a complex terrain model and modify it to consider heavy gas effects. This was not possible within the time constraints of ITF-25 (delivery of a model by no later than January 1995). TP-9 has recommended that the U.S. Defense Nuclear Agency's complex terrain model, SCIPUFF, be enhanced to consider heavy gas releases. ITF-25 supports this recommendation to develop SCIPUFF as the next generation heavy gas model.

56. The U.S. surveyed commercial software for environmental applications. Trinity Consultants [23] who offer the Breeze Haz suite of air dispersion models for toxic gas release analyses, was identified as potential source of relevant software. Information tables derived from *Pollution Engineering* [24] and *CEP Software Directory* [25] are provided at Appendix P for convenience.

## HAZARD MANAGEMENT

#### PROTECTION

57. Nuclear, biological and chemical (NBC) filtration systems for individual protective equipment (IPE) involve use of a particulate filter for removal of liquid and solid phase aerosols followed by a vapour filter to remove gas phase toxic materials. The particulate filter is of High Efficiency Particulate Air (HEPA) media offering 99.97% filtration efficiency of 0.3 micron diameter aerosol particles (approximating the most penetrating sized particle through HEPA media). The vapour filter consists of activated carbon which has been impregnated with reactive materials. The capture of harmful vapours makes use of two mechanisms, physical adsorption in the pores of the activated carbon and chemical reactions with the impregnants. Low vapour

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pressure chemicals, such as CW nerve and mustard agents, are removed from the airstream by physical adsorption in the microporous structure of the carbon. Higher vapour pressure compounds, such as cyanogen chloride and hydrogen cyanide are not strongly physically adsorbed and rapidly penetrate a nonreactive activated carbon bed. Specific reactive chemicals are impregnated on the activated carbon to chemically decompose high vapour pressure chemical warfare agents and to provide effective filtration of these gases.

58. Although military standard impregnated carbons were developed to specifically filter chemical warfare agents, numerous industrial chemical vapours will be filtered by the sorbents. The filtration performance against chemical vapours are dependent on the vapour pressure and the reaction chemistry of the chemicals. In general, chemicals with a vapour pressure below 10 mm Hg at  $25^{\circ}$ C are effectively removed by physical adsorption in the pores of the activated carbon. Between 10 and 100 mm Hg, some short time protection (filtration) will occur before breakthrough of the filter by the chemical occurs, depending on the challenge concentrations. Chemicals with vapour pressures above 100 mm Hg are ineffectively filtered by the physical adsorption process. The chemical reaction properties of the chemical and the impregnants, thereby, become very important.

59. Many of the important industrial chemicals considered as a potential hazard in this study (e.g., chlorine, ammonia, phosgene) possess high vapour pressures (>100 mm Hg) and undergo poor physical adsorption in the activated carbon beds of military filters. The filtration effectiveness thus depends on the ability of the impregnants to react with these chemicals either to decompose them into nonhazardous gases or to convert them into chemical compounds which are retained on the carbon surface. Military filters have only been tested for their effectiveness against a few of the industrial chemicals of importance and most tests are performed at challenge levels well below that expected following a catastrophic release of bulk supplies.

60. When chemical vapours are removed by chemical reaction with the impregnants, greater protection in terms of concentration time (Ct product) protection levels are observed when the challenge levels to the filter are low. This relationship apparently results because the rate of mass of chemical being fed at high concentrations is often greater than the rate at which the impregnants can react with the chemical. Lower challenge levels provide increased times for reaction resulting in reactions proceeding more nearly to completion.

61. Analysis of typical situations involving release of bulk quantities of toxic industrial chemicals shows that very high concentrations of vapour are expected within the immediate vicinity of the source. In particular, most immediate deaths will take place from exposures or fragmentation effects within 400 m of the release, and lethal concentrations will occur up to 5 km from the source depending on time of day/night and meteorological conditions and the quantities of chemical involved. The dosage levels of chemicals will generally exceed the 100,000 mg.min/m<sup>3</sup> range and there could also be a severe lack of oxygen in the cloud.

62. With these very high concentration feed levels, there is the risk that the heat of reaction in impregnated carbon filtration beds could be sufficiently high so as to cause ignition of the sorbent bed. This effect can become a problem with challenge concentrations that exceed five percent by

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volume. Military filters, therefore, should not be relied upon for protection against reactive vapours at extremely high concentration levels. Further, with high concentration levels, the environment can be devoid of oxygen or have oxygen levels too low to sustain life even if effective filtration should occur. Only a self-contained breathing apparatus is effective in these circumstances.

63. A more thorough discussion and assessment of the performance of CW agent filters for filtering five industrial toxic chemicals from air is found at Appendix I.

64. For fire-fighting, entering any enclosed space where there has been a chemical spill, or spill cleanup work, self-contained breathing apparatus must be used. The military respirator does not afford sufficient protection within the immediate hazard zone where extremely high concentrations of industrial chemicals may occur and where the lack of oxygen requires the use of self-contained breathing apparatus. The military respirator should only be used for emergency protection against the immediate effects of a toxic release and while evacuating from the immediate hazard zone. Military protective suits are not designed for handling toxic industrial chemicals.

65. Insufficient data are available from tests conducted on in-service respirator filtration of toxic industrial chemicals to reliably indicate a safe exposure Ct value if exposed outside the lethal hazard zone. Similarly, commercial industrial respirators are designed to filter low level concentrations of laboratory/plant emissions and usually for particular compounds and are not for use at high and extended concentration levels resulting from massive releases of toxic industrial chemicals. Only self-contained breathing apparatus will suffice in these circumstances.

## DETECTION

66. Some chemical plants, facilities, storage containers, or transport containers may be identified by international HAZCHEM markers (Appendix G). These take the form of a diamond and contain information which can be used to identify the exact industrial chemical. When encountering a suspect industrial chemical the commander should attempt to identify the exact chemical and all possible information before planning any action.

67. Detection of toxic industrial chemicals can in some circumstances be made by in-service military chemical detection systems. Some Chemical Agent Monitors (CAM) were modified for use in the Gulf War to have the capability to detect both hydrogen cyanide and phosgene. With CAM, additional chemicals can, in principle, be added through software modifications and changes in dopant. However, there is a limit to the number of chemicals that CAM can be programmed to detect.

68. Commercial modifications of the CAM are available for environmental vapour monitoring. Femtoscan (Salt Lake City, Utah) in a joint venture with Graseby Ionics offers the EVMII-Environmental Vapour Monitor, capable of analyzing a large variety of volatile organic compounds. This is a hand-portable instrument that combines Ion Mobility Sampling (IMS) technology with Automated Vapour Sampling (AVS)-Transfer Line Gas Chromatography (TLCG)

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sampling and separation capabilities for field applications. This instrument is undergoing Beta phase testing at ERDEC and DRES (see Appendix J).

69. Several generic gas chromatography (GC) or mass spectrometry (MS) based detection systems can be rapidly modified to detect additional toxic industrial chemicals. The U.S. MM1 Mobile Mass Spectrometer is also capable of detecting and identifying volatile organic chemicals. At present it can identify over 100 compounds including the classic chemical warfare agents (see Appendix J). The systems described above could be used as point detection systems to provide an alarm of a toxic industrial chemical presence.

70. Toxic industrial chemicals can be present in very high concentrations such that all respirable oxygen has effectively been displaced. This occurs in confined spaces, low-lying areas, or in storage containers which have not been properly evacuated. Should there be a requirement for entry into or operation in such areas, a respirable air alarm should be used. Several models are available and are commonly found in engineering and maintenance units.

71. Industrial detection systems are available for the rapid detection of specific chemicals such as chlorine, ammonia or hydrogen sulfide. Detection systems such as the Draeger detector system can be used for detecting and determining the concentration of a large number of dangerous chemicals. This system comes in the form of a simple kit which uses individual tubes to detect a variety of specific industrial chemicals. Such systems can be supplied to units operating in areas where there is a known hazard from industrial chemicals. Because of the operation of the detection tubes, they can only provide confirmation/identification of the presence of a toxic industrial chemical and cannot be used for monitoring dangerous concentration levels. A representative list of available detection systems for toxic industrial chemicals is provided in the Appendix K.

72. A comprehensive listing of air sampling instruments for analyzing airborne gases and vapours has been collated by the American Conference of Government Industrial Hygienists, Inc. [26]. This edition describes the various direct reading instruments and provides underlying theories of sampling vapours and particulates.

#### **OPERATIONS AROUND TOXIC INDUSTRIAL CHEMICALS**

73. Most toxic industrial chemicals will be released as vapours. These vapours will tend to remain concentrated downwind from the release point and in low-lying areas such as valleys, ravines or cellars. High concentrations could be found in buildings, woods, or where there is little air circulation. Subject to overriding operational considerations, the preferred positions for locating static military positions are:

## at maximum elevation on open ground upwind or away from the sources of industrial chemicals

74. Military protection and decontamination equipment were not designed for handling toxic industrial chemicals. For proper handling, protection, and hazard management information, the

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Commander should refer to the U.S. Department of Transportation Emergency Response Guidebook and seek assistance from the CHEMTREC Hotline (see Appendix A). Commanders should identify prior to any operations the local civilian authorities who may have additional emergency response procedures and resources which can be used.

75. Personnel or equipment that may have been contaminated with toxic industrial chemicals can be decontaminated by washing with large amounts of cold, soapy water. Contaminated clothing should be immediately removed and disposed of in a safe manner.

#### HAZARD DISTANCES

76. Table 4 shows hazard distances to be observed from chemical production or storage sites. These are distances within which dangerous or lethal exposure levels could be reached if a massive release occurs and were determined by exercising the SLAB program for typical situations. The first figure is for use during the day. The second figure is for use at night and may be more applicable over snow during the day. The distances include a safety allowance to cover variations in terrain effects, meteorological conditions, nature of release and vagaries of the human response. Toxic load values, typically  $LC^{n}t_{10}$  (where these were available or had been estimated from the results of experiments with animals), were used to determine the distances, deliberately erring on the side of caution. However, it should be noted that the distances do not correspond precisely to toxic load values, even  $LC^{n}t_{5}$  or  $LC^{n}t_{1}$ , and that the distances are only intended for guidance during military operations and planning and are not predictive values. Furthermore, the distances may need to be increased where consideration of the dangers to the civilian populace, with a wider range of response and including more hypersensitive individuals than a military force, arises and to ensure that there are no injurious effects of any degree or type to unprotected personnel.

77. Releases of toxic industrial chemicals are most dangerous at night. The downwind hazard distance from a night-time release is much longer than that for a day-time release. Additionally, escape is much more difficult at night. The victims are likely to be asleep and, even if awake, will have difficult seeing the approaching gas cloud. A large night-time release is the scenario most likely to cause heavy casualties.

78. Respirators should always be carried within these hazard distances and troops should be briefed on the hazard and on the actions to be taken in the case of a release. No encampments should be sited within the night-time hazard distance of a chemical plant, storage site, rail depot, etc.

79. The most important action in the case of a massive release of an industrial chemical is immediate evacuation. For example, anyone who sees a storage vessel blow up or clouds of vapour evolving from a chemical site should immediately don his mask and evacuate the area as soon as possible. The greatest risk from a large scale toxic chemical release occurs when the victims of the release are unable to escape and are overcome by fumes or blast effects. This may occur because they are unaware of the release, are trapped, are required to remain at their post or are unable to evacuate in time. It is vitally important that commanders and troops be made aware that the

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best defence against toxic industrial chemicals is to escape the path of the toxic chemical immediately. The respirator can provide limited protection and should only be used to escape the hazard area.

Chemicals	Quantity	Day	Night
Chlorine Phosgene Ammonia Hydrogen Cyanide in Hot Climates Hydrogen Sulphide Methyl Isocyanate	Up to 100 tonnes Up to 50 tonnes Up to 500 tonnes Up to 50 tonnes Up to 50 tonnes Up to 50 tonnes	2.5 km	5 km
Hydrogen Cyanide in Cold Climates Hydrogen Fluoride Sulphur Trioxide Nitrogen Tetroxide Hydrogen Chloride Ammonia Bromine Sulphur Dioxide Acrylonitrile	Up to 50 tonnes Up to 100 tonnes Up to 50 tonnes Up to 50 tonnes Up to 50 tonnes Up to 100 tonnes Up to 50 tonnes Up to 50 tonnes Up to 50 tonnes Up to 50 tonnes	1 km	2.5 km

# TABLE 4: RECOMMENDED HAZARD DISTANCES FROM REPRESENTATIVE CHEMICAL STORAGE SITES

## DELIVERABLES

## AGREEMENT WITH THE CHEMICAL MANUFACTURES ASSOCIATION

80. The Chemical Manufacturers Association (CMA)<sup>6</sup>, founded in 1872, is the oldest trade association in the Western Hemisphere. CMA represents the chemical industry in North America Approximately 185 companies, accounting for more than 90 percent of the productive capacity of basic industrial chemicals in the U.S., are members of CMA. The Association brings together member company experts to help resolve industry-wide public policy, technical and scientific problems. In 1988, CMA embarked on **Responsible Care**, an ambitious and comprehensive environmental improvement effort. Responsible Care commits all members of CMA to:

<sup>&</sup>lt;sup>6</sup> Chemical Manufacturers Association, 2501 M Street, NW, Washington, DC 20037, U.S.A. Note: CMA headquarters will relocate to Commonwealth Building, 1300 Wilson Boulevard, Rosslyn, Virginia, in January 1996.

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- a. continually improve performance in the areas of health, safety and environmental quality, and;
- b. do a better job eliciting and responding to public concerns about products and operations.

81. An important component to the Responsible Care initiative is CHEMTREC, The Chemical Transportation Emergency Center, first established by CMA in 1971. CHEMTREC is a central emergency response service for incidents involving the transportation of hazardous materials. It is a public service resource center provided by the chemical industry and was developed as a means for first responders to emergencies to obtain technical information and assistance on safely mitigating incidents involving chemicals.

82. CHEMTREC maintains the world's largest, continuously updated, database of Manufacturer's Material Safety Data Sheets (MSDS). An MSDS lists health and physical hazard information, emergency response information, physical properties, handling information and appropriate regulatory data about a product. The reference library contains over 1,500,000 MSDSs which can be accessed from the CHEMTREC emergency communicator's workstation in seconds. The emergency center is staffed 24 hours a day, seven days a week by trained communicators.

83. A formal agreement with CMA was prepared and enacted to enable CANUKUS forces in an emergency military situation to receive assistance from CHEMTREC communicators by calling their emergency numbers. For EMERGENCIES ONLY: Within 50 U.S. States; U.S. Virgin Islands; Puerto Rico; Canada: 1-800-424-9300. For International Emergency in locations in Mexico and Outside the Continental U.S. (OCONUS): 1-202 483-7616, collect if need be. A guide to these emergency calls and the completed Memorandum of Agreement between CBDCOM and the Chemical Manufacturers Association is found at Appendix A. Assistance on non-emergency matters and for Manufacturers Material Safety Data Sheets (MSDS) can be obtained from CHEMTREC at 1-800-262-8200.

84. A new training program to educate medical professionals about hazardous chemicals has been developed by CMA. The six-part program, "Medical Response to Chemical Emergencies", includes manuals and videos on overall emergency response programs, emergency medical operations, chemical toxicology and poison control center operations. It was written and produced by hazardous materials experts with input from physicians and occupational health specialists. The program is primarily intended for physicians, toxicologists and emergency room personnel.

# GUIDE TO UNDERSTANDING THE HAZARD FROM TOXIC INDUSTRIAL CHEMICALS

85. Training and instruction on defensive measures to take and operational responses required in a chemical warfare environment are standard practice for CANUKUS forces. Dealing with toxic industrial chemicals and reacting to the associated hazards is not. A Guide to Understanding the Hazard from Toxic Industrial Chemicals has been prepared to acquaint military commanders at various levels with practical concerns and to provide advice and guidance on pre- and post-

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deployment actions to be considered. The Guide is intended to serve as the basis from which each country can prepare a Commander's Guide which is specific to each country's requirement and level of command.

86. The Guide is found at Appendix O. It deals with a general description of the Hazard, Countermeasures and Hazard Management, Operational Planning and provides elements of Immediate Medical Aid.

87. Future military operations will most likely encounter massive quantities of toxic industrial chemicals (TIC) in storage, production or distribution. These TICs, if deliberately or inadvertently released, will pose hazards to the indigent population, the civilian and military contingent and the animal-crop environment of the region. The impact on the mission can be devastating unless extensive preparation, planning and training is accomplished ahead of time. Important elements of consideration are highlighted in the Guide. There is indeed a threat from industrial chemicals in military situations, but with proper planning, intelligence information and preparation, the hazard is manageable.

## CONCLUSIONS

88. There is a threat from the release of industrial chemicals in a military situation. The hazard is manageable provided commanders are educated about and informed to the extent and nature of the threat. To lessen the impact of deliberate or accidental releases of industrial chemicals on CANUKUS forces, it is *imperative* that all elements of training, preparation, prediction, detection, protection, and countermeasures, be considered before deployment to an area.

89. Toxic industrial chemicals are legitimate articles of commerce, are widely produced and traded and are available worldwide. It is highly likely that CANUKUS forces will encounter toxic industrial chemicals in their military missions throughout the world.

90. The use of industrial chemicals could impact on the following missions: war/conflict, peace-making (enforcing), peace-keeping, humanitarian aid, disaster relief, counter-terrorism and counter-proliferation.

91. Several scenarios focusing on production, storage and transport facilities in which industrial chemicals could be either inadvertently or deliberately released have been identified. The major hazard is from massive releases from storage/transport containers of liquified pressurized gases.

92. ITF-25 defined toxic industrial chemicals as those chemicals which are produced in quantities exceeding 30 tonnes per year at a single facility and have a  $LCt_{50}$  value by inhalation in any mammalian species of less than 100,000 mg.min/m<sup>3</sup>.

93. Eleven hundred sixty-four chemicals were identified which met the toxicity criterion. This number was reduced by considering only those chemicals which were gases or liquids or solids, with an appreciable vapour pressure at  $20^{\circ}$ C, or were listed in the U.S. Department of

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Transportation Emergency Response Guide. By applying the producibility criterion the number was further reduced to 98.

94. A Hazard Index was developed to rank these 98 according to their significance in a military situation. Twenty-one chemicals were ranked "high", 41 "medium" and 36 "low". Data sheets for the chemicals ranked "high" and "medium" have been developed and are included in the report.

95. A formal Memorandum of Understanding with the Chemical Manufacturers Association has been established to provide on-call, around-the-clock assistance for emergency response information.

96. A Guide Understanding the Hazard from Toxic Industrial Chemicals has been produced and provides an introduction to these hazards. It further provides advice on pre- and post-deployment actions.

97. Chemicals used in the pesticide industry warrant further consideration.

98. The model SLAB was selected as the most appropriate interim heavy gas model for use in the prediction of challenge levels. The model has been applied to numerous typical situations to provide estimations of expected challenge levels and areas of effect.

99. Lethal hazard zones have been estimated for typical chemical storage sites and hazard distances recommended within which no encampments should be established.

100. In-service protection equipment has been assessed for effectiveness at the expected challenge levels. In-service respirators should only be used to evacuate the immediate hazard zone resulting from the release of industrial chemicals because NBC respirators were not designed to give protection and have not been tested against such chemicals. Self-contained breathing apparatus must be used in the immediate hazard zone because of the potential lack of oxygen and the very high challenge levels like to be encountered.

101. Commercially available detection equipment has been identified.

## RECOMMENDATIONS

102. Determine respirator protection response to high concentrations of selected Toxic Industrial Chemicals listed in the High Hazard Index Category.

103. Determine which in-service detectors could be adapted to detect hazardous concentrations of Toxic Industrial Chemicals listed in the High Hazard Index Category.

104. Conduct a more through analysis of whether releases of low vapour pressure liquids and solids (e.g., pesticides) pose an acute or chronic hazard in a military situation.

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105. Perform a study to assess effects from multiple sources and slow releases of Toxic Industrial Chemicals in a military situation.

106. Develop an Emergency Response Package for NBC officers.

107. Develop the **Guide to Understanding the Hazard from Toxic Industrial Chemicals** for national use by commanders and NBC officers.

## REFERENCES

- 1. U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health (NIOSH), **Registry of Toxic Effects of Chemical Substances (RTECS)**, Division of Standards Development and Technology Transfer, 4676 Columbia Parkway, Cincinnati Ohio, 45226-9966.
- 2. see for example M.S. Reisch, Top 50 Chemicals Production Rose Modestly Last Year, *Chemical & Engineering News*, 11 April 1994, pp. 12-16.
- 3. **Directory of World Chemical Producers**, 1992/93 Edition, Chemical Information Services, Inc., P.O. Box 743512, Dallas, Texas 75374.
- 4. **Directory of World Chemical Producers**, 1995/96 Edition, Chemical Information Services, Inc., P.O. Box 743512, Dallas, Texas 75374; fax, (214) 349-6286; e-mail, cheminfo@connect.net.
- 5. **The Directories of Chemical Producers**, SRI International, Menlo Park, California 94025-3477; phone, (415) 859-4771; fax, (415) 326-5512.
- 6. **Chem Sources U.S.A. and Chem Sources International**, STN International, 2540 Olentangy River Road, P.O. Box 02228, Columbus, Ohio; phone, (614) 447-3600; fax, (614) 447-3713.
- 7. **Directory of Chemical Producers in China and the Japan Chemical Directory**, The Chemical Daily Co., Ltd., 3-16-8 Nihonbashi Hama-cho, Chuo-ku, Tokyo 103, Japan; fax, 81(3)3663-2530. Sold in the U.S. by Tekno-Info Corporation, 500 Trotwood Pl., Louisville, Kentucky 40245-4071; phone (502) 254-5728; fax, (502) 254-9128.
- 8. **CHEMPLANT PLUS**, provided by Reed Information Services, East Grinstead, UK. Available as File 318 on DIALOG, Knight-Ridder Information, Inc., Worldwide Headquarters, 2440 El Camino Real, Mountain View, California, 94040.

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- 9. U.S. Department of Transport, Research and Special Programs Administration, **1993 Emergency Response Guidebook**, ISBN 0-16-042938-2. Order from U.S. Government Printing Office, Washington, D.C.
- CAMEO Dos Version 2.01, Environmental Health Center, National Safety Council, Washington, D.C., May 1994. Information from CAMEO Software Support, 1-800-99CAMEO or (202)293-2273. Order from National Safety Council, P.O. Box 558, Itasca, Illinois 60143-0558; phone, 1-800-621-7619; fax, 1-708-285-0797.
- 11. U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health, **NIOSH Pocket Guide to Hazardous Chemicals**, publication number 94-116, stock number 017-033-00473-1. Order from the U.S. Government Printing Office, Superintendent of Documents, Washington, D.C. 20402; phone, (202) 783-3238.
- 12. CDROM and diskette format vendors for the **NIOSH Pocket Guide to Hazardous Chemicals** include:

**Industrial Hygiene Services, Inc.**, 941 Gardenview Office Parkway, St. Louis, Missouri 63141; phone, 1-800-732-3015 or (314) 993-2236.

**Micromedex, Inc.**, 6200 South Syracuse Way, Suite 300, Englewood, Colorado 80111-4740; phone, 1-800-525-9083 or (303) 486-6400.

**Praxis Environmental Systems, Inc.**, 251 Nortontown Road, Guilford, Connecticut 06437; phone (203) 458-7111.

- 13. Emergency Handling of Hazardous Materials in Surface Transportation, Association of American Railroads, Bureau of Explosives, 50 F Street, Washington, D.C. 20001; phone (202) 639-2222. Order from The Association of American Railroads, P.O. Box 1020, Sewickley, Pennsylvania; phone, (412) 741-1096; fax, (412) 741-0609.
- 14. **Pesticide Program, Residual Monitoring 1993**, U.S. Food and Drug Administration, *J. AOAC Internat.*, 77 (1994) pp. 161A-185A.
- 15. EXTOXNET EXTension TOXicology NETwork, developed by University of California, Davis, Oregon State University, Michigan State University and Cornell University. Accessible on www: http:///www.oes.orst.edu:70/1/ext.
- 16. Transport Canada, Dangerous Goods, **Initial Emergency Response Guide 1992**, ISBN 0-60-14385-2. Order from Canada Communications Group, Ottawa, Ontario.
- 17. Control of Industrial Major Accident Hazards Regulations (CIMAH) 1984, SI 1984/1902 as amended in:

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Control of Industrial Major Accident Hazards (Amendment) Regulations 1988, SI 1988/1462

**Control of Industrial Major Accident Hazards (Amendment) Regulations 1990**, SI 1990/2325

Order from HMSO Publications Center, PO Box 276, London SW8 5DT, England.

- D.L. Ermak, User's Manual for SLAB: An Atmospheric Dispersion Model for Denserthan-air Releases, Lawrence Livermore National Laboratory, Livermore, California 94550, June 1990.
- 19. Hanna, S.R., Chang, J.C. and Strimaitis, D.G., **Hazardous Gas Model Evaluations with Field Observations**, *Atmospheric Environment*, 27A (1993) pp. 2265-2285.
- 20. **PHAST, Version 4.2**, DNV Technica Inc., 40925 Country Centre Drive, Suite 200, Temecula, California 92591.
- 21. Bowman Environmental Engineering, Inc., P.O. Box 59916, Dallas, Texas 75229; phone, (214) BEE-LINE.
- 22. An Atmospheric Dispersion Model for Heavy Gases, CANSLAB Version 1.01, User's Guide, Kosteniuk Consulting Ltd., Saskatoon, Saskatchewan, December 1994. Model and documentation available from Director General, Defence Research Establishment, Suffield, P.O. Box 4000, Medicine Hat, Alberta T1A 8K6, Canada; fax: (403) 544-3388.
- 23. Trinity Consultants, Inc., 12801 N. Central Expwy., Suite 1200, Dallas, Texas 75243; phone, (214) 661-8100; fax, (214) 385-9203.
- 24. Rich, G., Software Strategy, *Pollution Engineering*, pp. 25-34, 1 January 1993.
- 25. **CEP Software Directory**, pp. 59-63, December 1993.
- 26. Air Sampling Instrumentation for Evaluation of Atmospheric Contaminants, 8th Edition, 1994, ISBN 1-882417-08-9. American Conference of Governmental Industrial Hygienists, Inc., 6500 Glenway Avenue, Building D-7, Cincinnati, Ohio 45211-4438.