Ecological Risk Assessments of Priority Substances Under the Canadian Environmental Protection Act

Resource Document

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Chemicals Evaluation Division
Commercial Chemicals Evaluation Branch
Environment Canada

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Chapters

Introduction

This resource document provides supplementary material on the approaches and methods described in the manual entitled *Ecological Risk Assessments of Priority Substances Under the Canadian Environmental Protection Act: Guidance Manual.* To do this, we discuss the advantages and disadvantages of key methods and their underlying assumptions, describe how they may be applied to assessments of priority substances, and provide case studies and references to the scientific literature. Thus, the resource document serves as a teaching tool for assessors and other participants in the Priority Substances Assessment Program. Each chapter in this document covers the same subject areas as the corresponding chapter in the guidance manual, with the exception that this document does not expand upon the overview chapter in the guidance manual (*i.e.*, Chapter 1). In addition, several detailed appendices are included with this document that were not included in the guidance manual.

Requests for additional copies of this resource document, guidance manual, or Priority Substances Assessment Program publications may be sent to:

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Data Collection and Generation

This chapter provides an overview of information sources available to collect and generate data required for ecological risk assessments of priority substances under the Canadian Environmental Protection Act. Chapter 2 of the accompanying guidance manual provides guidance on the approach or strategy which should be used to collect and generate this data. The information sources described in this chapter have been selected to provide assessors with the resources required to begin a successful search for required data. While these resources will be sufficient to obtain most types of data required for assessments of priority substances, information gathering will need to be customized and expanded to new and additional resources on a substance-by-substance basis. Efforts will be made to coordinate data collection at the program level for all substances being assessed to ensure efficient use of resources.

For details on how to obtain or use the information presented in this chapter, if not provided below, please telephone the Chemicals Evaluation Division, Commercial Chemicals Evaluation Branch of Environment Canada (Headquarters) at (819) 997-3201.

Data used when conducting assessments of Priority Substances must be of acceptable quality. All key data must be verified by consulting its primary source. Assessors should obtain original references to critically and scientifically evaluate the data. In cases where sources of information are incomplete (*e.g.*, information on detection limits, sample sizes, measured concentrations, etc. are not reported), assessors should contact individual authors or the primary source to obtain the data necessary to evaluate the data. Also, erroneous data may result from transcription or typographical errors during the process of publication or database development. Since published data varies in quality, assessors should become familiar with issues of data quality. Specific QA/QC issues are addressed where applicable throughout this document and the accompanying guidance manual.

2.1 Desk References

Listed below are several desk references (*e.g.*, textbooks, encyclopedias, dictionaries, reports) that can provide useful environmental information. The sources and a brief description of the contents of each are provided.

Atmospheric Chemical Compounds: Sources, Occurrence, and Bioassays (Graedel *et al.* 1986) - sources and releases

Canadian Water Quality Guidelines (CCREM 1987 and updates) - production, uses, physical-chemical properties, fate information, effects information

Chemical Economics Handbook (SRI International 1951 to present) - uses, imports, production, trade information

Fundamentals of Aquatic Toxicology (Rand 1995) - effects, environmental fate, risk assessment

Fundamentals of Environmental Chemistry (Manahan 1993) - fate, effects, toxicology

Handbook of Ecotoxicology (Hoffman *et al.* 1995) - fate, effects, ecotoxicology

Handbook of Environmental Fate and Exposure Data for Organic Chemicals - Large Production and Priority Pollutants, Volume I (Howard 1989) - sources, quantities released and environmental levels (occasionally Canadian data)

Handbook of Environmental Fate and Exposure Data for Organic Chemicals - Solvents, Volume II (Howard 1990) - sources, quantities released and environmental levels (occasionally Canadian data)

Handbook of Environmental Fate and Exposure Data for Organic Chemicals - Solvents 2, Volume IV (Howard 1993) - sources, quantities released and environmental levels (occasionally Canadian data)

Handbook of Chemical Property Estimation Methods (Lyman *et al.* 1982, 1990) - physical-chemical properties, definitions, estimation methods and uncertainties

Handbook of Environmental Degradation Rates (Howard *et al.* 1991) - degradation information in various media

Illustrated Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals - Volatile Organic Chemicals, Volume III (Mackay *et al.* 1993) - physical-chemical properties, fate information

Illustrated Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals - Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs, Volume I (Mackay *et al.* 1992a) - physical-chemical properties, fate information

Illustrated Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals - Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins and Dibenzofurans, Volume II (Mackay *et al.* 1992b) - physical-chemical properties, fate information

Kirk-Othmer Encyclopedia of Chemical Technology (Kirk and Othmer 1991) - production statistics, transport information, properties and uses, analytical and test methods

The Merck Index (Budavari *et al.* 1989) - uses, alternative names for substances

The Condensed Chemical Dictionary (Hawley 1981) - uses, alternative names for substances, containers commonly used to transport product

Additional sources of environmental information can be found by consulting the *Encyclopedia of Environmental Information Sources* (Balachandran 1993), a more detailed description can be found in Section 2.5.

2.2 Non-Canadian National and International Organizations

This section provides resources required to collect ecological assessments that have been conducted by other organizations or countries. These assessments may provide valuable scientific data and references. They may also provide assessors with an overall picture of the key issues in the assessment.

2.2.1 OECD Chemicals Programme

The OECD Chemicals Program has become a forum for the international exchange of information and data on chemicals. One focus of the existing chemicals activities is *High Production Volume (HPV)* chemicals (*i.e.*, chemicals produced at >10000 $t \cdot yr^{-1}$ in at least one country, or >1000 $t \cdot yr^{-1}$ in at least two countries). HPV chemical dossiers or *Screening Information Data Sets (SIDS)* provide the minimum data elements essential for conducting an initial assessment to determine whether or not a chemical requires further investigation or risk management. If data gaps are identified, research is initiated by member countries. When an initial assessment is completed, the results are made available worldwide through the *International Register of Potentially Toxic Chemicals (IRPTC)*. Although the existing chemicals activities will continue to centre on HPV chemicals, the OECD Secretariat will assist Member countries in identifying opportunities for co-operative collection, generation or assessment of data on chemicals of mutual interest that may not be produced in high volumes.

Information exchange systems among the 25 member countries are another vital component of the OECD Chemicals Programme. These systems have been designed to support the management of chemical risks by member countries. One such system is the *Complimentary Information Exchange Procedure (CIEP)*, a network of contact points through which Member countries exchange information on their chemical assessment, management and control policies. These contact points can suggest appropriate experts in their organization for priority substances of interest.

The *EXICHEM database* is another information exchange mechanism. Member countries provide information on current and planned activities for existing chemicals to the EXICHEM database. EXICHEM is a useful tool to collect information; however, be aware that the database has not been kept up-to-date by all countries. Searches can be done using chemical IUPAC name or CAS number. The information provided in the database is a description of the activity and is identified by code, the date, the country contact and the current status of the activity. Since the activity is identified by a general description rather than a document title, it can be difficult to determine the exact nature of each activity.

The Commercial Chemicals Evaluation Branch of Environment Canada is the Canadian contact point for the Chemicals Group of the OECD. The resources listed above can be obtained from CCEB by calling (819) 997-1499 or faxing (819) 953-4936.

2.2.2 European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC)

ECETOC, located in Brussels, produces two series of reports that contain data useful for the assessment of priority substances: *Technical Reports* and *Joint Assessment of Commodity Chemicals.* These reports evaluate human health effects, experimental toxicology, environmental effects, ecotoxicology and exposure levels. For additional information or to order reports call (32) 2 675 36 00 or fax (32) 2 675 36 25.

2.2.3 Commission of the European Community (CEC)

Located in Luxembourg, the CEC produces several report series. The most useful for PSL assessments is the series entitled *Classification and Labelling of Dangerous Substances in the EC.* These reports evaluate human health effects, experimental toxicology, ecotoxicology and physico-chemical properties. For additional information or to order reports call (352) 49 928 or fax (352) 49 00 03.

2.2.4 International Programme on Chemical Safety (IPCS)

The IPCS, located in Geneva, produces a valuable report series for assessors entitled *Environmental Health Criteria Documents* that evaluate human health effects, experimental toxicology, environmental effects, ecotoxicology and exposure levels. For

additional information or to order reports call (41) 22-791 35 88 or fax (41) 22-788 19 49.

2.2.5 United Nations Environment Programme (UNEP)

Located in Geneva, Switzerland, UNEP provides access to many resources including the *International Register of Potentially Toxic Chemicals (IRPTC)* mentioned previously (Section 2.2.1) which operates a global network for information exchange on chemicals. The IRPTC database has a series of files on all aspects of a chemical that are deemed important to conducting a hazard assessment, including information on regulatory control. The database for use on a PC can be ordered from the Programme Activity Centre in Geneva. More information about additional resources available from UNEP can be found at the UNEP World Wide Web site on the Internet (URL: http://www.unep.ch).

2.2.6 Unites States Environmental Protection Agency (U.S. EPA)

The U.S. EPA has several headquarters offices and many regional offices. The regional offices are mainly concerned with regional issues including permits, monitoring and clean-up activities. Each region is responsible for setting regional environmental standards. The headquarters are divided into five offices, each dealing with different legislated issues: Office of Water, Office of Solid Waste and Emergency Response, Office of Air and Radiation, Office of Prevention, Pesticides and Toxic Substances, and Office of Research and Development. The headquarters offices are mainly responsible for developing guidance documents and policy. The Office of Prevention, Pesticides and Toxic Substances is split into new chemicals and existing chemicals; the work involved includes the development of ecological risk assessment guidelines and conducting risk assessments for substances of concern.

The U.S. EPA Headquarters Telephone Directory can be purchased by contacting the Superintendent of Documents, P.O. Box 371954, Pittsburgh, PA 15250-7954, or by fax at (202) 512-2233. The directory contains both an organizational directory and an alphabetical directory with information on both headquarters and the regions. In addition, a directory entitled *ACCESS EPA* which is a pathfinder to many major information resources, such as clearinghouses, hotlines, records, databases, models, documents and contacts can be ordered via the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161, or by telephone (703)487-4650 or fax at (703) 321-8547.

The U.S. EPA has an extensive Internet site on the World Wide Web which provides access to many up to date information resources (URL: http://www.epa.gov). Environment Canada also has a list of useful contacts that may be obtained from the Chemicals Evaluation Division.

2.2.7 Agency for Toxic Substances and Disease Registry (ATSDR)

The ATSDR in Atlanta, GA, offers several resources to the assessor. They have produced over 200 *Toxicological Profiles* to date and continue to produce new profiles and update older ones as required. For more information or to order publications call (404) 639-6312 or fax (404) 639-6324. Information about ATSDRs other resources can be found on their Internet site (URL: http://atsdr1.atsdr.cdc.gov:8080/atsdrhome.html).

2.2.8 German Chemical Society (GDCh) Advisory Committee on Existing Chemicals of Environmental Relevance (BUA)

Located in Frankfurt, Germany, the BUA produces *Toxicological Evaluations* which cover human health effects, experimental toxicology, environmental effects, ecotoxicology and exposure levels. To order reports or to get more information call (49) 69-7917 331 or fax (49) 69-7917 322

2.2.9 Verband Der Chemischen (VCI)

The VCI in Frankfurt, Germany produces standardized data sets (Grunddatensätze) for most chemicals produced in Germany. These data sets cover health effects, experimental toxicology and ecotoxicology. For more information or to order reports call (49) 69-255 60 fax (49) 69-255 6471.

2.2.10 Health Council of The Netherlands (GR)

The Netherlands Health Council in Den Haag produces *Criteria Documents* on existing chemicals. These reports evaluate human health effects, experimental toxicology, environmental effects and ecotoxicology. For more information or to order reports call (31) 70-347 14 41 or fax (31) 70-383 71 09.

2.2.11 The Netherlands National Institute of Public Health and Environmental Protection (RIVM)

RIVM produces a series of *Integrated Criteria Documents* which evaluate human health effects, experimental toxicology and environmental effects. For additional information or to order reports call (31) 30-74 91 11 or fax (31) 30-742971.

2.2.12 United Kingdom Department of the Environment (DOE)

The Toxic Substances Division of the UK DOE in London produces a series of assessments on individual chemicals called *Environmental Hazard Assessments.* These assessments focus on effects on organisms (excluding man) in the environment. For details or to order reports call (44) 0171 276 8047 or fax (44) 0171 276 8333.

2.2.13 Additional International Organizations

Contacting the following organizations may also be useful in obtaining more information on priority substances:

- World Health Organization (WHO), Geneva
- UN Food and Agriculture Organization (FAO), Rome
- Monitoring and Assessment Research Centre (MARC), University of London
- International Maritime Organization (IMO), London

2.2.14 Additional Resources

In addition to the organizations covered thus far, the following resources may be useful in locating additional existing assessments:

- Technical Report 30(5) - *Existing Chemicals: Literature Reviews and Evaluations* (ECETOC 1994) which provides an overview of the various environmental assessments performed on approximately 3000 existing chemicals by 20 international organizations
- *Programs in Ecological Risk Assessment - Directory of Organizations* (ILSI Risk Science Institute (RSI) and the Society of Environmental Toxicology and Chemistry (SETAC) 1995). The directory includes information on government, business, academic, non-profit, and public interest organizations conducting work in ecological risk assessment. The directory has over thirty entries world-wide, although most of this volume is focused on organizations located in the United States. Each entry includes information on organizational mission, on-going and future activities in ecological risk assessment, pertinent publications, and contacts. For a free copy of the directory, send requests to Dr. Jeffrey Foran, Executive Director, ILSI Risk Science Institute, 1126 16th. St., NW, Washington, D.C. 20036.

2.3 Canadian Federal Government Departments

A group of Federal Government Department contacts has been established for to help assessors locate necessary contacts and information for the assessment of priority substances. Requests to this group will be managed by the Priority Substances Assessment Program Manager (819) 953-1667.

The inventory entitled *"Databases for Environmental Analysis: Government of Canada"* is a result of the combined effort of Environment Canada and Statistics Canada (1994). Over 370 databases were identified in 13 Government of Canada departments and agencies. This inventory of databases includes information on levels of chemicals in biota, atmospheric pollutants, habitat information, effluents/emissions, spill incidents, and manufacturers. A complimentary diskette version of the report is included with each purchase (Statistics Canada Catalogue number 11-527E, telephone (800) 267-6677, fax (613) 951-1584).

The remainder of this section is organized by federal department.

2.3.1 Environment Canada

Information related to entry and exposure of a substance to the Canadian environment are available at headquarters, regional offices and research institutes. Government telephone directories including regional offices can be obtained through Renouf Publishing Co. Ltd., 1294 Algoma Rd., Ottawa, Ontario, K1B 3W8, (613) 741-4333.

The *Envirosource - Reference Directory to Information Holdings* (Environment Canada 1991a) is a comprehensive document, updated regularly, used to access information within Environment Canada including contacts.

Headquarters

The *Domestic Substances List* (Environment Canada 1991b) has both confidential and non-confidential information from 1984-86 on the use(s) of substances in Canada, whether they were imported or exported and the quantities used. The data are catalogued by CAS number. Information that is confidential can only be used in a manner that ensures that its status will be protected.

The Pesticide Registrant Survey: 1990 Report (Environment Canada and Agriculture Canada 1991) contains information on pesticides, and sales figures for substances used as active ingredients in Canada. Such information is protected and, therefore, data from this source must be used in compliance with the requirement of confidentiality.

The *Use Patterns Section of the Commercial Chemicals Evaluation Branch* has a set of chemical fact sheets on substances of commercial importance produced by *Camford Information Services*, previously known as Corpus Information Service (CPI) spanning roughly a ten year period from the late 1970s. The most recent editions should be used. The sheets summarize uses, production, import and export statistics, market trends and predictions. If data are not available for a substance of interest,

Camford Information Services, (416) 291-3215, will generate the information required for a fee.

The *Use Patterns Section* also has data from *The International Trade Division of Statistics Canada*, the most recent year is available on microfiche. This is a good source for import data. Statistics Canada will charge a fee to release additional data from this source. Substances are listed by "Tariff Codes". Sometimes a substance of interest is grouped with others by Statistics Canada, which makes it impossible to extract information on that substance only.

There are two databases that deal with industrial emissions to air, water and land, the *National Emissions Inventory (NERM)*(industry driven), and the *National Pollutant Release Inventory (NPRI)*(government driven). These databases were developed cooperatively. Protocols have been developed to measure emissions from industrial sites into various environmental media. Environment Canada has established the NPRI for use beginning in April 1995. The data can be accessed through the general NPRI number (613) 953-1656; alternatively the NPRI may be accessed via the Internet (URL: http://www.doe.ca/pbd/npri.html). For information regarding NERM see Section 2.6.

The *NATES database* contains spills information and is operated by the Pollution Data Analysis Division of Environment Canada. These data are reported on a voluntary basis only, hence it may not provide a complete picture of the spills situation in Canada. The percent of spills recovered may also be available.

ENVIRODAT is a database on levels of substances in various media (mostly water) in the Canadian environment. Regional Environment Canada offices collect the samples. The samples are sent to federal government, provincial government or private laboratories for analyses, then the results are compiled in the regional offices where they are entered on ENVIRODAT. QA/QC information on the data is difficult to obtain. Interpretation of the output data is aided by the *ENVIRODAT Dictionary of Codes (Provisional)*(Environment Canada 1994).

ARET stands for the Accelerated Reduction/Elimination of Toxics. The purpose of this voluntary program is to reduce adverse effects of substances on health and the environment by accelerating the reduction and elimination of selected substance emissions. Over 160 companies participate in ARET. Administrative support is provided by Environment Canada. The first report, *Environmental Leaders 1, Voluntary Commitments to Action on Toxics through ARET* (Environment Canada 1995) was published in March 1995. Reports are to be produced annually and contain emission data from participating facilities. Copies of ARET reports are available from: ARET Secretariat, Environment Canada, 11th floor, 351 St. Joseph Boulevard, Hull, Quebec. K1A 0H3. For more information on ARET, call (819) 953-7832, or fax (819) 953-7970.

Regional Offices and Research Institutes

In 1993, the Pacific and Yukon region compiled a list of 82 available databases/publications in their region. It contains names of databases, contact persons and types of information available. Quebec Region has a database called *Répertoire informatisé des bases de données environnementales sur le Fleuve Saint-Laurent (REPEN)* which is a collection of 175 databases administered by 60 organizations in Quebec. Other information available in that region include chemical characteristics and some toxicity testing of marine sediments, environmental effects of some effluents and an inventory of federal contaminated sites. Atlantic Region has put together a report entitled *1990 Catalogue of Environmental Data in Atlantic Canada* (Spencer 1991) which contains information on 112 environmental databases.

The *Canadian Centre for Inland Waters* (CCIW) in Burlington, Ontario is one of the world's leading centres for water research, generating environmental information and knowledge about the Great Lakes. The organizations within the Centre are concerned with environmental research and development, as well as monitoring, resource management, charting, and coastal harbour engineering. The Centre is a useful resource for information and expertise for ecological risk assessments of priority substances.

The *National Water Research Institute* (NWRI), in Burlington, Ontario conducts a comprehensive program of research and development in the aquatic sciences, which it undertakes in partnership with water management agencies and water science communities in Canada and around the world. This research creates knowledge pertaining to ecological effects of substances that would be useful for priority substance assessments. The institute has expertise on water quality issues important for sustainable water resource use and the preservation of freshwater ecosystems.

The *National Hydrology Research Institute* (NHRI), located in Saskatoon, Saskatchewan, conducts research on environmental issues related to the integrity and sustainability of Canada's aquatic ecosystems. In collaboration with many national and international partners in universities, government agencies, other research facilities, and the private sector, NHRI participates in interdisciplinary research programs addressing regional, national and international environmental problems. The Institute's support to CEPA focuses on the impacts of chemicals on Canadian aquatic resources, principally on river, lake and wetland ecosystems in western and northern Canada.

The *National Wildlife Research Centre* (NWRC) is located at in Hull, Quebec maintains a database entitled *The National Registry of Toxic Chemical Residues* which contains collection and chemical residues data on over 40,000 specimens collected by Canadian Wildlife Service biologists since the 1970s. The specimens are mostly avian species, with some mammalian and amphibian species. The collections are from

various parts of Canada. The chemical residues catalogued are restricted to organochlorine pesticides and metabolites, PCB congeners, metals, dioxins, furans and non-ortho PCBs. The contact officer's number is (819) 997-6122.

The *Environmental Technology Centre* at River Road in Ottawa, Ontario houses monitoring data for many substances in the Canadian environment which can be used in assessments.

2.3.2 Fisheries and Oceans Canada

Data on levels of substances in fish tissues and Canadian fish habitats, and effects data for specific substances are available from Fisheries and Oceans Canada.

2.3.3 Transport Canada

Transport Canada's *Transport of Dangerous Goods Directorate* can provide spill statistics by mode of transport (road, rail, marine, etc.). The information is collected from a variety of sources, but may not give a complete picture of the spills situation in Canada. United Nations transport codes, which can be located in the CCINFO/ CHEMINFO database, are used to search for data.

2.3.4 Agriculture Canada

Agriculture Canada has information on concentrations of metals in Canadian soils, and contacts to provide advice on soil-related problems. The *Inventory of Canadian Agricultural Research (ICAR)* is a comprehensive and up-to-date database for agriculture and food research in Canada and is a product of the Canadian Agri-food Research Council. ICAR contains detailed information on research projects in agriculture, food, human nutrition, aquaculture and related areas of biotechnology. Currently, ICAR describes over 4000 projects from industry, universities, and provincial and federal establishments. For each project, ICAR provides the title, objectives, known and anticipated impact of research, a status report and the names of the researchers and the research establishment. ICAR is available on the AGRISEARCH CD-ROM (1-800-343-0064), online via CISTI, online via FIND, on Internet via Suranet (ag1360000@ncccot2.agr.ca), and through the ICAR office, Room 1135, K.W. Neatby Bldg., 960 Carling Ave., Ottawa, Ontario K1A 0C6, (613) 995-7084.

2.3.5 Department of Indian and Northern Affairs Canada

The Natural Resources and Economic Development Branch of the Department of Indian Affairs and Northern Development has an online Northern Information Network (NIN). Data can be obtained on levels of various chemicals and a list of media (animal or plant tissue, eggs, etc.) from which the measurements were obtained. The

sampling, storage and analytical methods are included. The data are on a Bulletin Board System (BBS) and can be accessed throughout North America without long distance charges (time limits apply) at (800) 567-6935, or in the Ottawa area at (613) 994-2557 or (613) 994-2622. A NINBBS User's Manual is available. This data can also be accessed via Internet through the department's site on the World Wide Web (URL: http://www.inac.gc.ca).

A published document entitled *Environmental Studies No. 72 - Synopsis of Research Conducted Under the 1993-94 Northern Contaminants Program* (Indian and Northern Affairs Canada 1994) summarizes the results of research and monitoring studies on chemicals in northern Canada. The project topics include sources, substance transport, and contamination of marine, freshwater and terrestrial ecosystems.

2.3.6 Natural Resources Canada

A large database on major and trace elements in Canadian streams, lakes and marine sediments, soils and glacial tills is available from the Geological Survey of Canada (GSC). Most data for these media represent total concentrations, although limited information is available on labile (*i.e.*, relatively soluble) forms of some metals. Many samples have been collected beneath potentially contaminated surface layers of sediment (*e.g.*, NGR program lake sediments) and soil (*i.e.*, C horizon soils and glacial tills), and thus GSC data can be especially useful in characterizing natural background concentrations. Data are also available from the GSC on element concentrations in samples of bedrock, surface and ground water, peat, and ice cores from selected regions of Canada, as well as on concentrations of natural organic compounds in some Canadian crude oils and sedimentary rocks.

Information on metallurgical processes used by Canadian metal producing industries (*e.g.*, smelters) can be obtained from the Canada Centre for Mineral and Energy Technology (CANMET).

2.3.7 Statistics Canada

In addition to the data available from the *International Trade Division* mentioned previously (Section 2.3.1), Statistics Canada also has an *Environmental Information System* that contains a wide variety of geographically referenced information including biophysical conditions, land use, cultivation practices (including pesticide, fertilizer and irrigation use), and industrial establishments and activity.

2.4 Canadian Provincial and Territorial Government Information and Contacts

An inventory entitled "*Databases for Environmental Analysis: Provincial and Territorial Governments*" (Statistics Canada and the Canadian Council of Ministers of the Environment 1994) lists over 800 databases from 94 departments and ministries. This inventory of provincial and territorial governments databases includes information on surface and groundwater quality, spills, fish populations, air pollution monitoring, geochemistry, contamination of the northern aquatic food chain, biomonitoring and community inventories. Database holdings are organized into subject matter categories and by keywords to facilitate searches for information on a particular topic. A complimentary diskette version of the report is included with each purchase (Statistics Canada Catalogue number 11-529E, telephone (800) 267-6677, fax (613) 951-1584).

The Federal-Provincial Advisory Committee (FPAC) can be used to identify appropriate contacts and locate information. To obtain information from the provinces through the (FPAC), contact the manager of the Program Integration Directorate of Environment Canada at (819) 953-2672. Please inform the Priority Substances Assessment Program Manager (819) 953-1667 before making such a request.

A list of many useful contacts in the provinces and territories is continuously updated at the Chemicals Evaluation Division, Environment Canada (819) 997-3201, and is available. In addition, provincial government telephone directories may be ordered via Faxon/SMS Canada, Book Division, P.O. Box 103, Routledge Street, Hyde Park, Ontario, N0M 1Z0, telephone (800) 263-2966, fax (519) 472-1072.

2.5 Commercial Databases

Listed in table 3.1 are commercial databases recommended for routine searching for ecological risk assessments of priority substances.

Table 3.1. Databases recommended for routine searching for ecological risk assessments of priority substances.

Database	*Subject / Producer*
AQUALINE	water, environment, hydrology, pollution / Water Research Centre, Buckinghamshire, 0491-571531
AQUAREF	water resources, hydrology, environmental impact assessment / Environment Canada, Inland Waters Directorate, (819) 997-2324

Database	***Subject / Producer***
AQUIRE	environment, toxicology, chemical properties, pollution / Office of Toxic Substances, Environmental Research Laboratory, Duluth, (218) 720-5602
ASFA	fisheries, aquaculture, oceanography, biology / Cambridge Scientific Abstracts, (301) 961-6750
BIOSIS	biology, medicine, botany, agriculture, environment / Biosciences Information Services (BIOSIS), (800) 523-4806
CAB ABSTRACTS	agriculture, environment, biology, forestry / CAB International, North American Representative, (800) 528-4841
CAS Online	chemistry, toxicology / (1987+) Chemical Abstracts Service, American Chemical Society, (614) 421-3600
CESARS	toxicology, chemical properties, environment / Environmental Assessment Section, Michigan Dept. of Natural Resources, Chemical Information Specialist, (517) 373-2190
CHEMICAL ABSTRACTS SOURCE INDEX	chemistry, chemical engineering / Chemical Abstract Services, American Chemical Society, (614) 447-3600
CODOC	government publications - Canada, U.S., U.K., France, Germany / Ms. Virginia Gillham, Head Librarian Wilfred Laurier University, Waterloo, (519)884-1970 ext. 3380
CURRENT CONTENTS SEARCH	chemistry, biology, geosciences, agriculture / Institute for Scientific Information, (800) 523-1857 ext. 1591
ELIAS	environment - library holdings / Environment Canada Library, Manager, (819) 997-1767
ENVIROFATE	chemical properties, environment / U.S. Environmental Protection Agency, Office of Toxic Substances, (202) 382-3524

Database	***Subject / Producer***
ENVIROLINE	environment, chemistry, geology, biology / R.R. Bowker Publishing Co. (800) 323-3288
ENVIRONMENTAL BIBLIOGRAPHY	environment, pollution, toxicology / Environmental Studies Institute, International Academy at Santa Barbara, Editor, (805) 965-5010
FATERATE	environmental fate / Office of Toxic Substances, U.S. EPA, (202) 382-3912 / U.S. EPA
GEOREF	geology, earth sciences, geosciences / GeoRef Information System, American Geological Institute, (703) 379-2480
HSDB	toxicology, hazardous waste, chemistry, environment / National Library of Medicine, U.S. Dept. of Health and Human Services, (800) 638-8480
IRIS	physical and chemical properties, toxicology, health risk, US regulations / Environmental Criteria and Assessment Office, U.S. Environmental Protection Agency, (513) 569-7254
IRPTC	environmental fate, toxicology / Bureau of Chemical Hazards, Health Canada, (800) 267-3364 / Health Canada
LIFE SCIENCES COLLECTION	biology, toxicology, zoology, biochemistry / Cambridge Scientific Abstracts, (800) 843-7751
LOGKOW	LOG Kow values / Sangster Laboratories, Montreal
MICROLOG: CANADIAN RESEARCH INDEX	Canada - Government Publications / Micromedia Ltd., Toronto, Canada, (416) 362-5211
NTIS	science, technology, government publications / National Technical Information Service, U.S. Dept. of Commerce, Product Manager, (703) 487-4929

Database	***Subject / Producer***
PHYTOTOX	toxicity, plants / Office of Toxic Substances, Environ. Research Laboratory, Duluth, (218) 720-5602
POLLUTION ABSTRACT	pollution, environment, science, oceanography / Cambridge Scientific Abstracts, (800) 843-7751
RTECS	toxicology / Canadian Centre for Occupational Health and Safety
TOXLINE	toxicology, environment, chemicals, biochemistry / National Library of Medicine, U.S. Dept. of Health and Human Services (800) 638-8480
TRI (TOXIC CHEMICAL RELEASE INVENTORY)	toxicology, wastes, chemicals / U.S. Environmental Protection Agency, Office of Toxic Substances, (202) 554-1404 / (202) 382-3524
WATER RESOURCES ABSTRACTS	water, engineering, environment / U.S. Geological Survey, U.S. Dept. of the Interior, Chief, (703) 648-6821

Additional information on the databases in table 3.1 and information on other databases can be found in Csenge *et al.* (1994), Balachandran (1993), Cosmides (1990), Haines and MacDonald (1992) and Environment Canada (1992).

In Csenge *et al.* (1994), database descriptions are arranged in alphabetical order by name. Database descriptions include the database name, subjects, a summary, producer, time coverage and file data, corresponding printed sources, language, vendor and price information. A vendor index, a producer index, a database alternate names index and a subject index are also available.

Balachandran (1993) is divided into two sections: the subject section and the sources cited section. In the first section, entries are arranged alphabetically by subject (*e.g.*, air chemistry, bioavailability, natural resources, etc.) and further subdivided by type of source (*e.g.*, abstracting and indexing services, encyclopaedias and dictionaries, general works, online data bases, etc), and by publication title or organization name. About 1100 environmental subjects are covered by 13 different types of information sources. In the second section, all of the sources cited in the subject section are arranged in alphabetical order.

The Cosmides (1990) source is the first part of a series of papers that describe some of the databases on toxicology information, their content, and their accessibility. The series is a project of the Information Handling Committee of the Society of Toxicology.

2.6 Canadian Industry Information and Contacts

The resources listed in this section can be used to identify useful contacts and information from Canadian industry.

The Industry Coordinating Group (ICG) includes 22 organizations representing Canadian industry. For information on how to contact the ICG or other appropriate industry representatives, please contact the Chemicals Evaluation Division of Environment Canada. Member organizations are listed below.

Industry Coordinating Group (ICG)

1. Adhesives & Sealants Manufacturers' Association of Canada
2. Canadian Association of Chemical Distributors
3. Canadian Association of Petroleum Producers
4. Canadian Ceramics Society
5. Canadian Chemical Producers' Association
6. Canadian Electrical Association
7. Canadian Manufacturers Association
8. Canadian Manufacturers of Chemical Specialties Association
9. Canadian Paint & Coatings Association
10. Canadian Petroleum Products Institute
11. Canadian Portland Cement Association
12. Canadian Pulp & Paper Association
13. Canadian Steel Environmental Association
14. Canadian Textiles Institute
15. Crop Protection Institute of Canada
16. Ecological & Toxicological Association of Dyestuffs Manufacturing Industry
17. Electrical and Electronic Manufacturers Association
18. Industrial Biotechnology Association of Canada
19. Soaps and Detergents Association of Canada
20. Society of Plastics Industry
21. The Mining Association of Canada

The *Canadian Chemical Producers Association* has a *Chemical Referral Centre* that can be reached at (800) 267-6666 to obtain information on emissions of substances and the appropriate industry contacts. The NERM (National Emissions Reducing Masterplan) database has been operational since 1992. The centre has

information on over 350 substances of environmental or health concern. A report entitled *Reducing Emissions* is released in the fall of each year with the data from the previous year. The report can be obtained by contacting the *Chemical Referral Centre.*

2.7 Directories and Lists of Academic Expertise

Information available from academia includes knowledge of other scientists working in a related field, knowledge of current research activities and unpublished data. Listings of scientists and fields of expertise can be found using the resources which follow.

The Canadian Network of Toxicology Centres located in Saskatoon, SA has published the *CNTC/RCCT Directory of Toxicological Expertise in Canada* (CNTC/RCCT 1994).

The Natural Sciences and Engineering Council of Canada (NSERC) in Ottawa, Ontario maintains a database of all current research awards. Listings can be selected on a variety of parameters, including the use of title words and areas of application and discipline codes. Information provided in a listing may include among other things the name and institutional affiliation of the principal investigator, title and amount of the awards. The database is accessible on the Internet, and may be down loaded for searching (URL: gopher://gopher.nserc.ca/). Information obtained from the database can be useful in providing knowledge of current work and names of contacts working in an area of interest. The knowledge in turn can be used to obtain information on up-to-date unpublished work and potential researchers for data generation. The NSERC general information phone number is (613) 995-6295.

The National Science Foundation in Arlington, Virginia maintains abstracts for all research awards made since 1989. Each abstract contains a summary of the research to be conducted, and the name and address of the researcher. The abstracts are available in a fully indexed text database. This information is available on the Internet (URL: http://www.nsf.gov/nsf/awards.htm). The NSF general information number is (703) 306-1130.

2.8 Legislative Notices

Efforts should be made to gather as much information as possible on a voluntary basis. When data gaps exist however, section 16 and 18 notices are an effective means of obtaining additional information. Data gaps should be identified as early as possible in the problem formulation stage given that the process of preparing and executing the notices may take several months. The Use Patterns Section of the Chemicals Control Division of Environment Canada will work in conjunction with assessors to prepare Section 16 and 18 notices. All notices must go through legal

services and be signed by the director of the Commercial Chemicals Evaluation Branch of Environment Canada.

Before notices are sent out, assessors should identify the appropriate companies to which it should be sent and clearly define the types of information required. This ensures that notices are read and acted upon by people knowledgeable in the area and that replies will be useful to the assessment. Since few individuals and companies subscribe to the *Canada Gazette*, it is also helpful to send a copy of the notice to relevant trade associations. The associations should be encouraged to make their members aware of their reporting obligations.

2.8.1 Section 16 Notices

Section 16 of CEPA authorizes the gathering of existing information for the *purpose of assessing whether a substance is toxic or capable of becoming toxic* (in the absence of certain types of data, gaps critical to the assessment of a substance may be filled, or at least the knowledge of whether or not the required data exist can be determined). Section 16 notices must be signed by the Minister of the Environment and must be published in the *Canada Gazette*. Persons described in the notice (*e.g.*, any person engaged in any activity involving more than x kilograms of a specified substance, whether alone or in a mixture) in Canada must respond to the notice by the deadline given (usually 5-6 weeks from the date of the *Gazette* publication).

One may request information that the person may have in their possession or to which that person may reasonably be expected to have access. This includes unpublished toxicological studies or information that will contribute to the characterization of entry and exposure (*e.g.*, importation, uses, releases, presence in products, losses to the environment). It is also legitimate to request information on supplier and customer lists, to identify additional persons that may need to be canvassed.

Person(s) may make binding claims of confidentiality, so the use of the information may be severely restricted. If persons do not reply, there is a possibility they are not involved with the substance. If they were involved and failed to reply to the *Gazette* notice, an inspector may be sent to check for evidence of non-compliance.

For additional details consult the document entitled *Preparation and Execution of Subsection 16(1) Notices under the Canadian Environmental Protection Act* (Environment Canada 1991c) which is available from the Use Patterns Section of the Commercial Chemicals Evaluation Branch.

2.8.2 Section 18 Notices

Section 18 of CEPA can be used when the Ministers of Environment Canada and Health Canada have *reason to suspect that a substance is toxic or capable of becoming toxic.* Section 18 provides three methods to gather information about a specified substance. The information may be obtained from any person engaged in any activity involving the specified substance, within certain limitations. The three parts to Section 18 are described below, and each one has slightly different procedures to follow.

A Section 18 1(*a*) notice is published in the *Canada Gazette* and requires those described in the notice and engaged in an activity involving the substance to notify the Minister (Environment Canada) of their involvement. Section 18 1(*a*) is thus a means of identifying persons engaged in any activity involving the substance.

A Section 18 1(*b*) notice is in the form of a written letter sent directly to targeted persons, perhaps identified from a Section 18 1(*a*) notice. Any person engaged in an activity involving the substance, and who receives the notice, must provide any specified information in their possession or to which they can reasonably be expected to have access. The request does not need to be published in the *Canada Gazette*, nor does there seem to be any limitation on the types of questions that may be asked.

A section 18 1(*c*) notice is a written notice sent to those persons engaged in the importation and or manufacture only, of the substance in question. These persons may be required to perform toxicological and other tests specified by the Minister, and to submit the test results once completed. Section 18 1(*c*) therefore cannot be directed at persons who are only processing, using or re-selling the substance. The notice should clearly identify the protocol to be followed for the required test, or offer reasonable alternatives.

2.9 Generation of Data Through Research

This section discusses filling data gaps for ecological risk assessments under CEPA (*i.e.,* obtaining additional technical data by means of tests or original research). Research activities will be coordinated from a program perspective by the Chemicals Evaluation Division, to ensure a consistent approach and efficient and cost-effective use of resources.

In order to ensure that research is conducted in the most timely and cost-effective manner, appropriate partners should be involved in the conduct or sponsorship of the work. Partner involvement may include: industry sponsorship or conduct of the research (may involve Section 18 Notices); co-funding with other organizations (*e.g.*, with other government departments); conducting the research in

Environment Canada research laboratories; finding financial support through already-established programs or "piggybacking" on existing research activities.

After preliminary data collection and problem formulation, assessors will identify data gaps and recommend research activities that are required to complete the assessment. Recommendations for research that is not essential, but would provide useful additional information, may also be recommended. It is, however, unlikely to be sponsored except where it can be combined with other necessary research. An ecological risk assessment review group will review the proposed data generation needs and identify overall program research priorities and the most efficient means of fulfilling those needs (details of this process are explained in the policy document). The lead assessor will be responsible for overseeing the generation of data for their substance.

2.10 References

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Problem Formulation

Problem formulation is the planning phase in ecological risk assessment. This phase includes the development of an *initial scoping* and a *pathways analysis*, consideration of *receptor sensitivity*, analysis of the *ecological relevance* of potential receptors, selection of *assessment endpoints* and associated *measurement endpoints*, and the development of a *conceptual model*.

The following sections give background information about assessment endpoints and measurement endpoints, and present an example of a problem formulation.

3.1 Assessment Endpoints

According to Suter and Barnthouse (1993), defining an assessment endpoint involves identifying the valued attributes of the environment that are at risk and defining these attributes in operational terms. Suter (1993) notes that an operational definition of an assessment endpoint includes a *subject*, the ecological value to be protected, a *characteristic* of the subject, for example, reduction in population size, and a *numerical expression* of the effect, for example, the probability of >10% reduction in harvestable yield. There are five attributes that an assessment endpoint should satisfy:

- ecological relevance,
- unambiguous operational definition,
- accessibility to prediction or measurement,
- susceptibility to the priority substance, and
- societal relevance.

Under CEPA, the societal relevance of assessment endpoints is considered at the risk management stage, which follows risk assessment for substances determined to be CEPA "toxic".

3.2 Measurement Endpoints

Appropriate measurement endpoints must be selected for each assessment endpoint identified. Selection of measurement endpoints involves consideration of several criteria (U.S. EPA 1992a,b):

- relevance to an assessment endpoint (*i.e.*, when an assessment endpoint cannot

be directly measured, measurement endpoints should be chosen that are correlated with or can be used to predict changes in the assessment endpoint),

- consideration of indirect effects (*e.g.*, if population viability of trout is the assessment endpoint, measurement endpoints may include possible effects on trout prey species),
- sensitivity and rapidity of measurement endpoint response (*i.e.*, for early-warning of ecological effects),
- signal-to-noise ratio (because the possibility of detecting stressor-related effects may be greatly reduced if a measurement endpoint is highly variable),
- frequency of false-positive and false-negative indications of an ecological effect (which affects the degree of uncertainty about the extrapolation from a measurement endpoint effect to an assessment endpoint),
- statistical power (*i.e.*, how much data would be required to demonstrate an effect),
- consistency with assessment endpoint exposure scenarios (*i.e.*, the measurement endpoint should be exposed by similar routes and to similar concentrations or doses and forms of a substance as the assessment endpoint),
- degree of substance specificity (*e.g.*, measurement of acetylcholinesterase inhibition could be used to demonstrate responses to certain types of pesticides), and
- practicality issues (*e.g.*, ease or economy of measurement, availability of historical data bases).

Table 3.1. Examples of potential assessment endpoints and associated measurement endpoints.

Assessment Endpoint	***Measurement Endpoint***
Decrease in numbers of aquatic algae	8-d LOEL, *Scenedesmus quadricauda*
Decrease in numbers of aquatic invertebrates	48-h LC_{50}, *Daphnia magna* 16-d reproduction EC_{10}, *Daphnia magna*

Assessment Endpoint	***Measurement Endpoint***
Decrease in numbers of fish	96-h LC_{50}, fathead minnow 120-d growth EC_{10}, rainbow trout
Decrease in numbers of amphibians	7-d LC_{50}, narrow-mouthed toad embryo-larvae 9-d LC_{50}, leopard frog 9-d larval survival, *Ambystoma gracile*
Decrease in numbers of benthic organisms	Changes in benthic invertebrate community structure (field studies) 72-h mortality in *Rhepoxynius abronius*
Decrease in rate of nutrient cycling through adverse effects on soil microorganisms	Effects on nitrogen fixation, CO_2 evolution
Damage to terrestrial plants	Damage to needles of *Pinus taeda* (atmos. exposure) Red. growth of green beans (soil exposure)
Decrease in numbers of mammalian wildlife	Effects on deer & cattle (field studies) Inhalation LOEL, rats 90-d oral NOEL, rats Oral LD_{50}, rats
Reduction in reproductive capacity of mink	EC_{10} for reproductive impairment in mink
Reduction in number of wild birds	Field studies of fish-eating birds LD_{50} ring-necked pheasants LOEL, mallard ducks (food exposure)

3.3 Case Study: Example of a Problem Formulation

Problem formulation is an iterative process. In many cases, little information about a substance may be initially available, and the problem formulation will be very general and qualitative. As more information is obtained and analyzed, the problem formulation will take on a sharper focus, will be more explicit in its identification of assessment and measurement endpoints, and will present more quantitative details.

The following is an example of a more advanced problem formulation, where a considerable amount of information about the entry, exposure and effects of the substance has been obtained and analyzed.

Problem Formulation for the Ecological Assessment of Dibutyl Phthalate

Initial Scoping

Synonyms for dibutyl phthalate include:

DBP
1,2-Benzenedicarboxylic acid, dibutyl ester
Phthalic acid, dibutyl ester.

The substance has the molecular formula $C_{16}H_{22}O_4$ and a molecular weight of 278.4.

Physical/chemical properties relevant for the determination of the environmental fate of dibutyl phthalate include:

Physical state: Colourless, oily liquid at room temperature
Vapour pressure: 0.01 Pa @25°C
Henry's Law constant: 6.4 $Pa \cdot m^3 \cdot mol^{-1}$
Water solubility: 10 $mg \cdot L^{-1}$
Log K_{ow}: 4.31 - 4.79

Pathways Analysis

Dibutyl phthalate is not currently produced in Canada. Approximately 540 tonnes per year are imported, mainly as a plasticizer in polyvinyl emulsions. Additional dibutyl phthalate is imported in plastic products. Most environmental releases are believed to be directly to the atmosphere, but dibutyl phthalate has also been detected in liquid effluents from chemical plants, municipal sewage treatment plants and textile mills. Dibutyl phthalate is not persistent in air or surface water (half-life of a few days), but may be more persistent in soils and sediments under anaerobic conditions (half-life sometimes exceeding 26 weeks).

The environmental distribution of dibutyl phthalate predicted by a Level III Fugacity Model is:

Air: 57.7%
Soil: 33.5%
Water: 8.8%
Sediment: 0%.

The environmental compartments of concern therefore appear to be air, soil and possibly surface water. Dibutyl phthalate has been detected in various media in Canada. For example:

Air: 4.5 $ng \cdot m^{-3}$ (average, along Niagara River)
Water: <1 $\mu g \cdot L^{-1}$ (ave.); 4 $\mu g \cdot L^{-1}$ (max.)
Sediment: 0.65 $mg \cdot kg^{-1}$ (max.)
Soil: <0.1 - 1.4 $mg \cdot kg^{-1}$
Biota: 8.1 $mg \cdot kg^{-1}$ (max.)(skinless fillet from long-nose suckers)

Receptor Sensitivity

Among terrestrial plants, cabbage appears to be sensitive to dibutyl phthalate in air. Soybeans and corn appear to be sensitive to dibutyl phthalate in soil. Among aquatic organisms, fish appear to be slightly more sensitive than algae and invertebrates.

Ecological Relevance

Cabbage, soybeans and corn are not themselves of ecological importance in the natural environment, but serve as surrogates for terrestrial plants that are primary producers, provide food and cover for wildlife and provide soil cover to reduce erosion and moisture loss. Fish are an important component of the communities of many water bodies in Canada and are vital to the well-being of piscivorous fish, birds and mammals.

Assessment Endpoint Selection

Damage (induction of chlorosis and reduction in rates of germination and growth) to terrestrial plants was selected as an assessment endpoint for both air and soil exposure. Reduction in fish production was chosen as the assessment endpoint for exposure in surface water. Impairment in the reproduction of mink was selected as an assessment endpoint to address concerns for wildlife exposed to dibutyl phthalate in air, water and food.

Measurement Endpoint Selection

Effects on growth of cabbage through exposure in greenhouse air was selected as the measurement endpoint associated with potential harm to terrestrial plants via aerial exposure. Effects on germination and growth of soybeans and corn through exposure in soil were chosen as the measurement endpoints associated with potential harm to terrestrial plants through soil exposure. Effects on growth and survival of rainbow trout following long term exposure (*i.e.*, ~100 days) were selected as the measurement endpoints associated with potential harm to aquatic organisms.

Embryotoxic and teratogenic effects in mice were chosen as the measurement endpoints associated with potential harm to mink.

Conceptual Model

Dibutyl phthalate enters the Canadian environment from its use as a plasticizer in polyvinyl emulsions. Most releases are believed to be directly to the atmosphere, but the substance has also been detected in a number of liquid effluents from a variety of sources. Dibutyl phthalate is predicted to partition to air, soil and water, and this has been confirmed by a number of monitoring studies in Canada. Terrestrial plants, fish and mink are the assessment endpoints. Effects on cabbage, soybeans, corn, rainbow trout and mice were chosen as appropriate measurement endpoints. The initial ecological risk assessment will be carried out using the worst-case quotient method to estimate risk. For air, the highest average gas-phase concentration reported for air in Canada will be selected as the worst-case estimated exposure concentration (EEC), and this figure will be divided by the estimated no effect concentration[1] (ENEC) of dibutyl phthalate causing a reduction in growth of cabbage plants. For water, the highest concentration of dibutyl phthalate reported for Canadian surface waters will be divided by the ENEC for growth or survival of rainbow trout. To estimate the risk to wildlife from exposure to dibutyl phthalate, the highest estimated daily intake for mink will be divided by the ENEC for adverse effects on embryonic survival and development in mice. For any assessment endpoint with a quotient value ≤ 1, more refined analysis (*e.g.*, Monte Carlo simulation) will be used to estimate the probability of effects of differing magnitudes at locations of concern in Canada.

3.4 References

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[1]The estimated no effect concentration is calculated, in this example, by dividing the lowest reported LOEL from an appropriate measurement endpoint by an application factor to account for differences in species sensitivity and for the extrapolation from laboratory to field conditions. Chapter 8 discusses the use and selection of application factors in more detail.

U.S. EPA. 1992b. Peer review workshop report on a framework for ecological risk assessment. Risk Assessment Forum. United States Environmental Protection Agency. Washington, DC. EPA/625/3-91/022. 100 p.

Entry Characterization

The entry characterization phase identifies a substance's anthropogenic and natural sources in Canada and estimates the amounts and frequencies of its releases into the Canadian environment.

4.1 Identification of Sources

Table 4.1 presents matrices to summarize and organize entry information and assist in the analysis of source data These matrices should be tailored to the specific needs of each assessment. For substances with well defined production and use patterns, the matrices may be simplified. For complex assessments such as mixtures or effluents, the matrices may have to be expanded.

Natural Sources

The matrix presented in Table 4.1A may be used for the analysis and organize information related to natural sources.

The earth's crust and upper mantle are the primary sources of metals and other elements. These substances are released slowly by the processes of weathering and erosion of crustal rock (Kabata-Pendias and Pendias 1992), or by more catastrophic processes such as volcanic eruptions. Metals and other elements cycle among and within the atmospheric, aquatic and terrestrial compartments of the environment. Their ultimate resting place (or "sink") is marine sediment, which is gradually incorporated back into the earth's interior by the subduction of oceanic plates and a new cycle begins (Speidel and Agnew 1982).

Anthropogenic Sources

Many industrial and commercial activities result in the release of potentially harmful substances into the environment. An information matrix based on a life-cycle approach is presented in Table 4.1B.

Table 4.1. Generic information matrix for source identification.

(A) Natural Sources

Activity	***Volcanoes***	***Sea Spray***	***Fires***	***Weathering of Rock***	***Others***
Evaluation of Relative Importance					
Accountability Centres in Governments					
Available Information					

(B) Anthropogenic Sources

Activity	***Life-cycle Framework***					
	Raw Material Extraction	***Chemicals Synthesis***	***Manufacturing & Processing***	***Sales Distribution***	***Use***	***Disposal***
Evaluation of Relative Importance						
Accountability Centres in Governments						
Interested Parties						
Available Information						

(C) Foreign Sources

Activity	***Long Range***	***Short Range***
Evaluation of Relative Importance		
Accountability Centres in Governments		
Interested Parties		
Available Information		

Foreign Sources

Persistent substances may enter the Canadian environment by long range transport from distant sources. Less persistent substances may also enter the Canadian environment if a source is located near the Canadian border. The matrix presented in table 4.1C can be used to summarize information about these sources.

4.2 Characterization of Releases

Table 4.2 presents a generic matrix for characterizing releases. This matrix should be adapted to the specific needs of each assessment.

Table 4.2. Generic information matrix for release characterization.

Type of Information	***Significant Sources***			
	Source #1	***Source #2***	***Source #3***	***Etc.***
Number of sources in Canada				
Quantities of substances released: • Concentrations • Loadings				
Forms of releases: • Physical properties • Chemical properties				
Environmental media of concern				

There are several ways of estimating releases.

1) Releases may be estimated by multiplying a substance's concentration in an effluent by the effluent's flow rate. Variations in concentration and flow rate must be considered.

2) Releases may be also be estimated by applying emission factors to production volume throughputs. This method expresses estimated releases to the environment as a percentage of production or process volume. Emission factors may be developed from monitoring data, models, or professional judgment. Such factors should only be used for processes for which they were developed.

3) Total environmental releases may be roughly estimated by subtracting the amount of outputs of a substance (*e.g.*, exports, domestic consumption) from the amounts of inputs (*e.g.*, imports, production). The major difficulty with this technique is finding sufficient data to account for all inputs and outputs.

Examples of estimating releases are presented in Case Studies 4.1, 4.2 and 4.3.

4.3 References

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Woltering and Bishop. 1989. Evaluating the environmental safety of detergent chemicals: A case study of cationic surfactants. *In* D.J. Paustenbach (ed.) The risk assessment of environmental and human health hazards. John Wiley and Sons, New York. pp. 345-389.

Case Study 4.1. Estimating releases of detergent chemicals to the environment from municipal wastewater treatment plants.

Monoalkyl quaternary ammonium compounds (MAQs) are cationic surfactants that work in combination with other laundry detergent ingredients for removal of grease and oil stains and to improve dissolution of granular detergents in the wash. In 1987, U.S. industry produced approximately five million kg of MAQs and the bulk had the potential for disposal into the environment. To estimate MAQ concentrations in sewage effluent and sludge from wastewater treatment plants in the U.S. in 1987, Woltering and Bishop (1989) conducted the following calculations.

Concentration of MAQs in wastewater influent (C_{iw})

= total daily usage / total daily wastewater (WW) flow
= 13,698 kg MAQ per day / (230 million people)(507 L WW per person day)
= 1.3698×10^{10} mg per day / 1.1661×10^{11} L per day
= 0.117 mg MAQ·L^{-1} of influent

Concentration of MAQs in wastewater effluent (C_{ew})

= [(% total sewage flow receiving primary treatment) x (1 - estimated removal efficiency)] + [(% total sewage flow receiving secondary treatment) x (1 - estimated removal efficiency)]
= $0.25[C_{iw}(1 - 0.30)] + 0.75[C_{iw}(1 - 0.90)]$
= 0.020 + 0.008 mg MAQ·L^{-1} of effluent
= 0.028 mg MAQ·L^{-1} of effluent

Concentration of MAQs in municipal digested wastewater sludge (C_{ds})

= (C_{iw}) x (municipal wastewater flow rate / digested sludge flow rate) x (treatment removal efficiency)
= 0.110 mg·L^{-1} x 260 x 0.3
= 8.58 mg·L^{-1}, or on a dry sludge-suspended solids (SS) basis where SS = 0.04 kg·L^{-1}
= 214.5 mg MAQ·kg^{-1} dry solids

The above estimates can be used as input to fate and pathways analyses to estimate MAQ concentrations in surface waters or in sludge-amended soils.

Case Study 4.2. Estimating annual natural releases of mercury (Hg) into the global atmosphere using a mass balance approach.

If it is assumed that fluxes of mercury into and out of the global atmosphere are approximately in a steady state, the total amount of mercury released to the atmosphere annually from natural sources can be calculated as the difference between the total amount that is deposited onto the earth's surface annually and the estimated total annual anthropogenic emissions.

Amount of mercury deposited from the atmosphere annually (calculated using data on mercury concentrations in rainwater and total annual precipitation, and estimated dry deposition velocities):

= total wet deposition + total dry deposition.
= 4×10^9 g Hg·year^{-1} + 4×10^9 g Hg·year^{-1}.
= 8×10^9 g Hg·year^{-1}.

Amount of mercury releases from anthropogenic sources annually (estimated as the sum of releases from known industrial sources):

= 2.5×10^9 g Hg·year^{-1}.

Therefore, amount of mercury released from natural sources to the global atmosphere annually:

= (total wet + dry deposition) - anthropogenic releases
= 8×10^9 g Hg·year^{-1} - 2.5×10^9 g Hg·year^{-1}.
= 5.5×10^9 g Hg·year^{-1}.

The above was adapted from Lindquist and Rodhe (1985). See Rasmussen (1994) for a discussion of the uncertainties associated with these estimates.

Case Study 4.3. Estimating acetone releases to air, water and soil.

Acetone is used both as an industrial solvent and as an intermediate in the production of other products. To estimate releases of acetone to air, water and soil, OECD (1989) used the RLTEC (ReLease from the TEChnosphere) model. This model calculates the relative flows (P_i/P) of a substance into the air (i = 1), water (i = 2) and soil (i = 3) compartments relative to the marketing volume P. The model calculates P_i/P in $(kg \cdot d^{-1})/(kg \cdot d^{-1})$ using the following formula:

$P_i/P = \{\Sigma j\ [(R_j/100) \times (D_j/100) \times (F_{(j,i)}/100)]\} \times W_i$, where
P_i = Mass flow in kg/d into the compartment
P = Marketing volume in $kg \cdot d^{-1}$ in the geographic area of interest
j = Use-pattern class to which the substance belongs (*e.g.*, solvents)
R_j = Percentage contribution of a substance to use-pattern class j
D_j = Substance dispersivity expressed as % released to the environment
$F_{(j,i)}$ = % of emission of the use-pattern class j to the the compartment
W_i = Factor that describes effect of wastewater treatment

Acetone belongs to two use-pattern classes, solvents (sol) and intermediates (int) with approximately 50% use for each ($R_{int} = R_{sol} = 50\%$). Solvents are considered highly dispersive ($D_{sol} = 100\%$) to the environment while intermediates are not ($D_{int} = 2\%$). Approximately 50% of both solvent and intermediate use emissions are to air, with the remaining 50% use emissions to water for each use pattern class ($F_{int,air} = F_{int,water} = F_{sol,air} = F_{sol,water} = 50\%$; $F_{int,soil} = F_{sol,soil} = 0\%$). Wastewater treatment is assumed to have no effect on acetone removal for emissions to air and soil ($W_{air} = W_{soil} = 1$) while emissions to water will be reduced by 64% ($W_{water} = 0.36$).

Therefore for acetone,

$P_{air}/P = [(50/100) \times (2/100) \times (50/100)] + [(50/100) \times (100/100) \times (50/100)]$
$= 0.255$

$P_{wat}/P = \{[(50/100) \times (2/100) \times (50/100)] + [(50/100) \times (100/100) \times (50/100)]\} \times 0.36$
$= 0.092$

$P_{soil}/P = 0$ (*i.e.*, no emissions to soil)

If marketing volumes data are available on a regional basis, then the above information could be input into fate and pathways analyses to estimate environmental exposures for each region in Canada.

5

Exposure Characterization

The purpose of this phase of the assessment is to verify and refine the exposure portion of the pathways analysis developed during problem formulation, with the objective of accurately quantifying contact between a substance[1] that has been released from identified anthropogenic sources, and appropriate risk receptors. To this end, it is necessary to review and refine the preliminary characterization of:

- physical and chemical properties of the substance released (Section 5.1),
- key properties of the receiving media, and the media to which the substance partitions (Section 5.2),
- dominant environmental processes that affect the fate of the substance (Section 5.3), and
- harmful transformation products that should be included in the assessment (Section 5.4).

This information, along with data from detailed entry characterization (described in Chapter 4), should be used to refine, and to the extent possible quantify, the original pathways analysis. This involves verification of decisions originally made concerning:

- the degree of partitioning of the substance among various environmental compartments (Section 5.5.1),
- the locations and sizes of the areas selected for assessment (Section 5.5.2),
- the identity and main routes of exposure of risk receptors (Section 5.5.3).

Exposure should be determined as *Estimated Exposure Values (EEVs)* for identified risk receptors (Section 5.6). Exposure values are expressed as concentrations or doses, and should ideally be based on empirical (monitoring) data, but outputs from fate and exposure models may be acceptable in some cases (Sections 5.6.1 to 5.6.3). EEVs, should generally be based on data for bioavailable forms of the substance (Section 5.6.4), and summarized as frequency distributions that reflect both real spatial and/or temporal variability, as well as errors and uncertainties associated

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[1] Discussion in this Chapter focuses on single substances or chemically related groups of substances. Exposure characterization for complex mixtures and effluents is described in Chapter 7.

with key exposure parameters (Section 5.6.5).

Maximum measured EEVs are used as numerators in risk quotients for tier 1 risk analysis, while entire EEV distributions are used for tier 2 (Chapter 8). When results of tier 2 risk analysis indicate that actions to reduce exposure may be required (*i.e.*, when tier 2 EEVs ≥ ENEVs), and releases from natural sources may have contributed significantly to measured EEVs, an attempt should be made to apportion tier 2 EEVs among identified anthropogenic and natural sources (Section 5.7). Results of this exposure apportionment exercise are used for tier 3 risk analysis (Chapter 8).

Box 5.1. *Some Physical and Chemical Properties of Potential Importance for Organic Substances*

Molecular Formula
Molecular Weight ($g \cdot mol^{-1}$)
Melting Point (°C)
Boiling Point (°C)
Density ($g \cdot cm^{-3}$ at 20°C)
Molar Volume ($cm^3 \cdot mol$)
Molecular Volume (nm^3)
Total Surface Area (nm^2)
Heat of Fusion ($kcal \cdot mol^{-1}$)
Fugacity Ratio at 25°C
Water Solubility ($mg \cdot L^{-1}$ at 25°C)
Vapour Pressure (Pa at 25°C)
pH, pKa
Light Absorption
Henry's Law Constant ($Pa \cdot m^{-3} \cdot mol^{-1}$)
Octanol-Water Partition Coefficient (K_{ow})
Bioconcentration Factor
Organic Carbon Partition Coefficient (K_{oc})
Rate Constants for Key Fate Processes

The above was adapted from Mackay *et al.* (1992).

5.1 Nature and Properties of the Substance

Information on the physical and chemical properties of the substance determined during problem formulation should be refined as required. For example, values chosen for a few key parameters used in fate or exposure models may significantly affect model outcomes. Values for such parameters, and their associated uncertainties, should be determined as accurately as possible. Experimental methods of quantification using accepted protocols (*e.g.*, OECD 1993a) are preferred, particularly for tier 2 risk analysis. However, values calculated as described, for example, by Lyman et al., 1990 or OECD (1993b), may be acceptable for less critical parameters, especially for tier 1 risk analysis.

As indicated in Box 5.1, relevant parameters for organic substances include molecular weight, molecular volume, solubility, vapour pressure, partition coefficients, dissociation constants, and environmental fate rate constants (see Section 5.3.4). For

Box 5.2. *Some Physical and Chemical Properties of Potential Importance for Inorganic Substances*

Chemical Elements
- Physical State at 25°C
- Atomic Number
- Atomic Radius (nm)
- Atomic Weight
- Isotopes (and relative abundances)
- Density ($g \cdot cm^{-3}$ at 20°C)
- Boiling Point (°C)
- Melting Point (°C)
- Vapour Pressure (Pa at 25°C)
- Water Solubility ($mg \cdot L^{-1}$ at 25°C)
- Common Valences
- Ionic Radii (nm)

Common solid compounds
- Molecular Formula
- Molecular Weight
- Density ($g \cdot cm^{-3}$ at 20°C)
- Vapour Pressure (Pa at 25°C)
- Melting Point (°C)
- Boiling Point (°C)
- Solubility under environmentally relevant conditions ($mg \cdot L^{-1}$ at 25°C)
- Rate of dissolution under environmentally relevant conditions

Common dissolved complexes
- Molecular Formula
- Molecular Weight ($g \cdot mol^{-1}$)
- Equilibrium Constant

inorganic substances relevant properties vary depending upon the chemical forms (*e.g.*, atoms, compounds or complexes) being characterized. Some important physical and chemical parameters for inorganic substances are listed in Box 5.2.

QSARs

QSARs relate the molecular characteristics of selected classes of organic substances to their properties or behaviour. They may be used, for example, to calculate such properties as solubility, vapour pressure, partition coefficients, and Henry's law constant (Lyman *et al.* 1990; OECD 1993b). They are typically generated using either graphical or statistical regression techniques, and as such may be regarded as a type of statistical model. Solubility data, for example, may be regressed against K_{ow} and melting point, for a range of chemicals within a particular class (*e.g.*, alcohols, alkanes, PAHs) for which solubilities have been measured. The resulting regression equations (or QSARs) can then be used to estimate the solubility of other chemicals in the same class for which empirical data are unavailable, or for which experimental methods are subject to appreciable error (*e.g.*, when determining solubility of extremely hydrophobic compounds).

To illustrate, the solubility of rigid PAHs can be estimated from the following equation,

$$\log S = -0.88 \log K_{ow} - 0.01 T_M - 0.012$$

where S is solubility ($mol \cdot L^{-1}$), K_{ow} is the octanol-water partition coefficient, and T_M is melting point (Lyman 1990a). This equation was developed using data for 32 different PAHs, and the correlation coefficient was 0.979 (Yalkowsky and Valvani 1979). Using this equation, the solubility of the PAH naphthacene, which has a log K_{ow} of 5.91 and T_M of 357°C, is calculated to be 1.65×10^{-9} $mol \cdot L^{-1}$ (Lyman 1990a). As Mackay *et al.* (1992) noted, predictions based on QSARs should eventually be confirmed (if possible) by experimental methods.

5.2 Nature and Properties of the Receiving Environment

Information on the physical and chemical properties of the receiving media (including the media to which the substance partitions), that influence the behavior, chemical form, and/or environmental concentrations of the substance, should also be refined, as needed. The information required varies, depending upon the application (*e.g.*, single or multimedia fate model, calculation of a process-specific half-life etc.), and the nature of the media and key fate processes. Parameters of possible importance include light intensity, pH, oxidation potential, temperature, concentrations of other chemical substances (*e.g.*, organic carbon), nature and abundance of solid phases (Table 5.1).

For fate and exposure modeling, data such as intermedia partition coefficients, physical dimensions and average bulk densities of environmental compartments, advective residence times, advective and diffusive flow rates etc., may also be needed (Mackay et al. 1992). Values for key environmental properties (and their associated uncertainties) used in fate or exposure models for tier 2 risk analyses should, if possible, be based on field data from the area of concern. For tier 1 risk estimates, or for less critical environmental properties, empirical data for similar areas or estimates based on professional judgement may be used.

5.3 Fate Processes

Information on the nature and rates of key transport and transformation processes, which affect the environmental persistence and/or bioavailability of the substance, should be refined as required. Although rates of fate processes may be calculated (*e.g.*, OECD 1993b) for tier 1 risk estimates, key rate values (and their associated uncertainties) should if possible be determined empirically - using acceptable laboratory and/or field test methods (*e.g.*, Kox et al. 1993; OECD 1993a) - when used in tier 2 risk analyses.

Table 5.1. Some key environmental properties determining the effectiveness of various environmental fate processes.

Fate Process	***Principal Compartments Affected***[a]				***Key Properties of Compartments***[b]
	Air	***Water***	***Soil***	***Sedi-ment***	
Photolysis	✔	✔	✔	(✓)	light intensity
Hydrolysis	✔	✔	✔	✔	pH, temperature
Oxidation-Reduction	✔	✔	✔	✔	oxidant/reductant concentrations (*i.e.*, pE)
Adsorption-Desorption	(✓)	(✓)	✔	✔	grain size of solids, organic content, mineral types and abundances, pH, pE
Loss by Volatilization		✔	✔	(✓)	temperature, grain size, organic content, mineral types and abundances
Precipitation-Solubilization	(✓)	✔	✔	✔	temperature, pH, pE, ionic strength

[a] Blanks signify compartments that are essentially unaffected by a process; (✓) indicates that fate process occurs; ✔ indicates compartments where fate process is likely to be strongest.

[b] Sources include Manahan (1991), Lyman *et al.* (1990) , Sposito (1989), Hebert and Miller (1990) and Ankley *et al.* (1994).

Individual transport and transformation processes of environmental importance are discussed in Sections 5.3.1 and 5.3.2, respectively. Methods of estimating the extent to which a substance is likely to accumulate in exposed biota are considered in Section 5.3.3 (Bioaccumulation). Methods of determining rates of individual fate processes are discussed in Section 5.3.4.

5.3.1 Transport

Information on the transport of substances released into the environment is used to determine (using, for example, data on intermedia transport rates) the extent to which substances accumulate in individual environmental compartments (Section 5.5.1) and to locate the geographic limits of areas likely to be affected (Section 5.5.2)(Mackay

and Paterson 1993). Movement of a substance released to the environment can occur as a consequence of advection (*i.e.*, physical entrainment in mobile media such as air or water), molecular diffusion (*i.e.*, the movement of pure substances - not mixtures - in response to chemical disequilibrium), or eddy diffusion (*i.e.*, movement attributable to turbulent mixing of mobile media). Volatilization is usually considered to be a type of diffusive transport.

Advection

In air and surface waters, advective processes are relatively rapid and are capable of carrying substances over long distances. The potential for long range atmospheric transport is greatest for substances that persist in air as gases or in fine suspended particles. In the aquatic compartment, substances that are soluble, or components of very fine suspended matter, can likewise be transported over long distances. Removal of substances from air and water compartments by gravitational settling of solid phases (*e.g.*, water droplets, dusts, suspended sediments) is a type of advective intermedia transport. Water soluble gaseous substances, for example, can be effectively removed from air by wet deposition (rainfall), while substances present in coarse atmospheric particles are also removed by dry deposition (*e.g.*, dustfall). In sediments and soils, examples of advective transport include entrainment of dissolved substances in slowly moving interstitial water (*e.g.*, groundwater moving down a hydraulic gradient), and burial of sediment (*i.e.*, downward "movement" of solid phases relative to the sediment/water interface) beneath settling particulate matter. Rates of advective processes are readily quantified by multiplying the concentration of a substance in the migrating medium by the flow or transport rate of the medium (Mill 1993; Mackay 1991).

***Box 5.3.** Intermedia Diffusive Transport*

The rate of diffusive intermedia transport, N (moles·hr^{-1} or kg·yr^{-1}), can be calculated as follows:

$$N = kA(C_1 - C_2K_{12})$$

where k is the transport rate coefficient (m·hr^{-1}), A is the area between the media (m^2), C_1 and C_2 are the concentrations in the two media, and K_{12} is the intermedia partition coefficient, which is equal to (C_1 x C_2^{-1}) at equilibrium. Note that at equilibrium, when there is no transport, the term ($C_1 - C_2K_{12}$) becomes zero.

The above was adapted from Mackay and Paterson (1993).

Diffusion

Diffusive processes are normally slower than advective ones. Eddy diffusion occurs when mixing associated with turbulent flow in air or water transports a

substance from regions of high concentration to regions of low concentration (Drever 1988). In the case of molecular diffusion, pure substances diffuse toward areas with lower concentrations at rates that are proportional to concentration differences (Box 5.3). Molecular diffusion is most effective at smaller scales (*e.g.*, exchanges at the interface between media, such as air and water), and in media where mobility is limited (*i.e.*, soil and sediment).

Within a given medium, substances diffuse down a concentration gradient following Fick's Law[2] (Drever 1988; Sposito 1989; Mackay 1991). For example, if the concentration of a dissolved substance is higher in sediment pore water than in the overlying water column, some of the substance would be expected to diffuse upwards from the sediment back into the overlying water. Depending upon the rate of diffusion, this could be an important remobilization process. In this example, the rate of diffusion would be slower than in a pure solution, because diffusion paths are more tortuous, and for some substances adsorption onto surfaces of solid particles could retard transport rates.

For movement between media, key quantities are the transport rate coefficient (k), an intermedia partition coefficient (K), and the intermedia area (A)(Box 5.3). As Mackay and Paterson (1993) noted, methods of calculating or experimentally determining intermedia transport coefficients are described by Thibodeaux (1979), Mackay (1991) and Lyman *et al.* (1990). Diffusion stops when chemical equilibrium has been achieved (*i.e.*, when concentrations have been equalized throughout the system). Diffusive exchange between air and water by volatilization and absorption can, for example, be modelled in this way (Mackay, 1991).

Volatilization

Henry's Law constant (H)[3] values provide an indication of the potential for loss of substances from water by volatilization (Howard *et al.* 1990). When H values are less that 10^{-7} atm-m^3·mol^{-1} a dissolved substance is essentially nonvolatile, whereas if H

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[2] Fick's Law may be represented as $J = D(c-c')\cdot x^{-1}$, where J is the rate of diffusion of a substance across a unit area in a unit time, D is the diffusion coefficient, c and c' are concentrations of the substance in mass per unit volume at two points in an unmixed solution, and x is the diffusion distance between the points.

[3] A substance's Henry's Law constant (H, in atm-m^3·mol^{-1}) can normally be calculated as,

$$H = P_{vp} \cdot S^{-1}$$

where P_{vp} is its vapour pressure in atmospheres, and S its water solubility in mol·m^{-3}. If this relationship cannot be applied (see Mackay (1991), p. 75) H can be measured directly as the air-water partition coefficient.

values exceed 10^{-3} atm-m^3·mol^{-1} volatilization will be rapid (Thomas 1990a). Other factors affecting rates of volatilization from water include the presence of other substances (*e.g.*, adsorbents, electrolytes) and the physical properties of the water body (*e.g.*, depth, flow velocity and turbulence). As Thomas (1990a) and Mill (1993) have noted, volatilization rate constants can be calculated for dissolved species using the Liss-Slater two-film model (Liss and Slater 1974; Smith *et al.* 1981; Smith *et al.* 1983).

Volatilization processes from soil are more complex and difficult to model (Howard *et al.* 1990). Complications include adsorption of the substance by solid phases, evaporation of the water at the soil surface, and the wick effect that brings more water and dissolved chemical to the surface (Thomas 1990b). Existing methods for estimating volatilization rates from soil are, as a result, generally not very accurate (Thomas 1990b).

5.3.2 Transformation

Transformation processes can involve a physical change (*e.g.*, direct transfer from a liquid or solid to a vapour phase), a chemical change (*e.g.*, hydrolysis reactions involving the cleavage of an organic molecule), or both (*e.g.*, precipitation of a dissolved metal ion by reaction with other ions in water). Purely physical changes are normally abiotic, while chemical changes can be biologically mediated. Several important transformation processes controlling the fate of organic and inorganic substances are described below.

Complexation/Chelation

A complex may be defined as a dissolved species formed from two or more simpler species, each of which can exist in aqueous solution (Drever 1988).

Inorganic Substances. Dissolved aluminum ions (Al^{3+}), for example, complex with hydroxyl ions ($Al(OH)_2^+$,$Al(OH)_4^-$), while cadmium (Cd^{2+}) forms a series of complexes with cyanide ions (*e.g.*, $Cd(CN)^+$, $Cd(CN)_2$, $Cd(CN)_3^-$) (see Box 5.4). These metal ions are referred to as

***Box 5.4.** Formation of Metal Complexes*

By reaction with hydroxide ion:

$$Al^{3+} + 4OH^- \leftrightarrows + Al(OH)_4^-$$

By reaction with cyanide ion:

$$Cd^{2+} + CN^- \leftrightarrows CdCN^+$$

By reaction with water molecule:

- solvation

$$Fe^{3+} + 6H_2O \leftrightarrows Fe(H_2O)_6^{3+}$$

- hydrolysis

$$Zn^{2+} + H_2O \leftrightarrows ZnOH^- + H^+$$

The above was adapted from Drever (1988), Manahan (1991), and Sposito (1989).

the central group, and the associated anions (OH^-, CN^-) are called ligands (Sposito 1989). In aqueous solution "free" cations (*e.g.*, Fe^{3+}) actually exist as weak "aquo ion" complexes with neutral water molecules (*e.g.*, $Fe(H_2O)_6^{3+}$). Although some ligands can bind to metals at only one site (*e.g.*, OH^-,Cl^-, H_2O) others, called chelates, can form multiple bonds. Since the strength of complexes tends to increase with the number of bonding sites, chelates are more stable than complexes with single bonds (Manahan 1991). A variety of natural and synthetic organic substances (*e.g.*, citric acid, EDTA (ethylenediaminetetraacetic acid), humic and fulvic acids) can form chelates with metal ions.

Because of their potential to form soluble complexes with a variety of ligands, dissolved concentrations of a metal cannot always be assumed to represent concentrations of the free (and typically most bioavailable) aquo-ion species. The formation of soluble complexes tends to decrease availability of free ions for participation in other reactions (*e.g.*, adsorption or precipitation), and hence increases the apparent solubility of solids containing the metal (Drever 1988; Manahan 1991).

Methods of estimating the rates of formation of chemical complexes are described by Sposito (1989). Rate controlling parameters are solution composition, temperature, and pressure. According to Sposito (1989), rates of formation of most inorganic complexes in soil pore waters are relatively rapid, with reactions reaching the half-way point (*i.e.*, time at which half of the total amount of a metal ion in solution has been complexed) in less than one hour.

Table 5.2 taken from Sposito (1989), lists some of the principal trace element complexes expected to be found in well aerated soil pore waters.

Organic Substances. Hydrophobic organic chemicals form complexes with naturally occurring dissolved (and colloidal-sized) organic carbon (DOC) in water. As noted in section 5.6.4, chemical aggregates so formed are typically too large to pass through biological membranes, and therefore substances held in such complexes are generally not bioavailable (Di Toro *et al.* 1991). They are similarly less available to participate in other fate processes such as volatilization and hydrolysis.

The extent to which complexation occurs depends on the degree of hydrophobicity of the organic compound (as measures, for example by its solubility or log K_{ow}), and the nature and amount of DOC present. As indicated in Appendix II, the degree of partitioning to DOC can be predicted using the equilibrium partitioning method, when the total dissolved concentration of the compound, DOC levels, and the K_{oc} of the substance are known. In practice however, because of the difficulty of predicting K_{oc} values for DOC in surface waters (Suffet *et al.* 1994) , this method is normally only applied to sediment or soil porewaters (*e.g.*, Di Toro *et al.* 1991).

Table 5.2. Representative trace element species in oxygenated soil pore waters.

Cation	*Principal Species in Typical Order of Relative Abundance*[a]	
	Acid Soils	***Basic Soils***
Al^{3+}	org, AlF^{2+}, $AlOH^{2+}$	$Al(OH)_4^-$, org
Ni^{2+}	Ni^{2+}, $NiSO_4$, $NiHCO_3^+$, org	$NiCO_3$, $NiHCO_3^+$, Ni^{2+}, $NiB(OH)_4^+$
Cu^{2+}	org, Cu^{2+}	$CuCO_3$, org, $CuB(OH)_4^+$, $Cu[B(OH)_4]_4$
Zn^{2+}	Zn^{2+}, $ZnSO_4$, org	$ZnHCO_3^+$, $ZnCO_3$, org, Zn^{2+}, $ZnSO_4$, $ZnB(OH)_4^+$
Mo^{5+}	H_2MoO_4, $HMoO_4^-$	$HMoO_4^-$, MoO_4^{2-}
Cd^{2+}	Cd^{2+}, $CdSO_4$, $CdCl^+$	Cd^{2+}, $CdCl^+$, $CdSO_4$, $CdHCO_3^+$

[a] org = organic complexes with, for example, fulvic or humic acids.

When DOC levels are in the normal range for natural freshwaters (*i.e.*, 3-10 $mg \cdot L^{-1}$) (Larson and Weber 1994), the fraction of organic compounds associated with DOC is typically relatively small (likely <10% of the total present), even for very hydrophobic substances (*e.g.*, Eadie *et al.* 1990). Complexation is more important, however, in bog waters and soil and sediment porewaters when DOC levels are elevated (*i.e.*, in the 20-50 $mg \cdot L^{-1}$ range and higher). For example, Di Toro *et al.* (1991) calculated that more than 90% of a hydrophobic chemical (log K_{OC} = log K_{OW} = 6.0) dissolved in the porewater (DOC content up to 50 $mg \cdot L^{-1}$) of a sediment containing 2% organic carbon may be complexed with DOC.

Dissolution/Precipitation

Inorganic Substances. The fate and bioavailability of metals (and other elements) released into the environment in solid form (*e.g.*, fly ash in stack gases, suspended solids in liquid effluents) will depend heavily on their solubility under the conditions prevailing in the receiving environment. Dissolution may occur as a result of a variety of chemical processes including hydrolysis, acid/base reactions, oxidation and reduction (Box 5.5). While some substances may have a high theoretical (equilibrium) solubility, if they are chemically inert their rates of dissolution may be very slow. Dissolution rates vary depending upon the nature of the substance, the total surface area exposed, as well as on parameters such as pH (acidity) pE ("oxidizability"), and concentration of solute in the receiving water (Sposito 1989).

Box 5.5. *Examples of Dissolution Reactions for Some Inorganic Compounds*

Hydrolysis of magnesium silicate (foresterite)

$$Mg_2SiO_4(s) + 4H_2O \rightarrow 2Mg^{2+} + 4OH^- + H_4SiO_4$$

Acid dissolution of aluminum hydroxide

$$Al(OH)_3(s) + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$$

Oxidation of sulphur (in zinc sulphide) by oxygen

$$ZnS(s) + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-}$$

Reduction of ferric hydroxide in acidic conditions

$$Fe(OH)_3(s) + 3H^+ + e^- \rightleftharpoons Fe^{2+} + 3H_2O$$

The above was adapted from Drever (1988), Krauskopf (1979), and Sposito (1989); "(s)" indicates that a substance is in the solid phase.

Box 5.6. *Examples of Precipitation Reactions for Metal Ions*

Oxidation of Fe(II) to Fe(III) by oxygen

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H_2O \rightarrow Fe_3O_3(s) + 4H^+$$

Precipitation of iron sulphide

$$Fe^{2+} + S^{2-} \rightarrow FeS(s)$$

Hydrolysis of trivalent chromium

$$Cr^{3+} + 3H_2O \rightarrow Cr(OH)_3(s) + 3H^+$$

The above was adapted from Krauskopf (1979), Di Toro *et al.* (1990) and Dhanpat *et al.* (1987); "(s)" indicates that a substance is in the solid phase.

Elements released in dissolved form may be removed from solution (and transformed into less bioavailable forms) by precipitation either directly, or indirectly (*i.e.*, "coprecipitated" as a minor component within another precipitating phase). Precipitation may occur in response to changes in temperature, pH, oxidation potential (oxidation/reduction reactions), or to increases in concentration of one (or more) components of the precipitating compound (Box 5.6). Dilution of a concentrated solution of a metal salt (*e.g.*, in an industrial effluent) by neutral or basic surface waters may increase the extent of hydrolysis of the metal ion and cause its precipitation as an hydroxide. Examples of some trace elements commonly found associated with iron, aluminum and manganese oxide (including hydroxide) precipitates in soils are shown in Table 5.3. Similar associations would be expected in oxidized aquatic sediments (Levinson 1980).

Table 5.3. Trace elements associated with oxide phases in soils[a].

Precipitated Phases	***Associated Trace Elements***
Iron and aluminum oxides	Cu, Zn, Mo, As, Ni, Mn, Se, V, B, P
Manganese oxides	Zn, Co, Mo, As, Ni, Fe, Se, Pb, P

[a] adapted from Sposito (1989).

Organic Substances. Substances released in gaseous, liquid and solid forms can dissolve to varying degrees in water. For most organic chemicals, solubility is measured in distilled water at a defined temperature (Mackay *et al.* 1992). Methods of calculating solubility based, for example, on K_{ow}, K_{oc} or BCF (bioconcentration factor) values are described by Lyman (1990a). Solubility in the field may vary from laboratory or calculated values depending upon ambient temperature, salinity and the presence of dissolved organic matter such as natural humic and fulvic acids (Lyman 1990a). Solubilities of ionizable compounds such as organic acids and bases are also influenced by pH (Mackay *et al.* 1992).

As is the case with inorganic substances, the solubility of organic chemicals is an important determinant of environmental fate. For example, the solubility of gas phase organic chemicals in cloud water droplets may control the extent of their removal from the atmosphere by wet deposition. Normally, only soluble polar low molecular weight chemicals partition significantly to cloud droplets, but for chemicals that are rapidly transformed in such droplets (*e.g.*, by photooxidation; see discussion of photolysis below), droplets can become "sinks" even for low solubility substances (Mill 1993). Similarly, the solubility and rate of dissolution of organic non-aqueous phase liquids (NAPLs) spilled onto soil are important determinants of the extent of contamination of local groundwater (*e.g.*, Lesage and Brown 1994).

Sorption/Desorption

Sorption is a general term that encompasses both adsorption and absorption processes. Adsorption is the accumulation of matter at the interface between a solid phase and an aqueous solution. It is distinct from absorption, which is slower and occurs when an adsorbed substance diffuses into the interior of a solid.

Inorganic Substances. The concentration of trace elements in natural waters (including porewaters) is often much lower than would be expected on the basis of equilibrium solubility calculations. The most common reason for these low concentrations is adsorption to (or coprecipitation with) solid phases such as hydrous metal oxides and organic matter (Table 5.3)(Drever 1988; Sposito 1989).

Adsorption may involve formation of strong inner-sphere, or weaker outer-sphere[4] *complexes* between functional groups (*e.g.*, carboxyl or hydroxyl groups) on the solid surface, and dissolved ions (Sposito 1989). Ions can also be weakly adsorbed as *diffuse ions* that neutralize surface charge, but are not associated with specific functional groups. Adsorption of cations can be understood in terms of exchange reactions involving the displacement of hydrogen ions; for some anions, adsorption may be represented as displacement of hydroxyl ions (Box 5.7).

Box 5.7. *Representation of (Inner-sphere) Adsorption Reactions Involving Hydroxyl Functional Groups*

Exchange of a metal cation (M^+) with H^+

$$]\text{-O-H} + M^+ \rightleftarrows]\text{-O-M} + H^+ \quad (1)$$

Exchange of phosphate anion with hydroxyl ions

$$]\text{-}(OH)_2 + HPO_4^{2-} \rightleftarrows]\text{-}HPO_4 + 2OH^- \quad (2)$$

"]" represents a solid surface. As pH decreases H^+ concentrations increase, and the equilibrium in equation (1) is shifted to the left, bringing adsorbed metal ions into solution.

The above was adapted from Drever (1988).

Adsorption reactions are particularly important in soils and sediments because of their potential to cause the accumulation of substances in these media. However, such reactions may also reduce a substance's bioavailability, especially if it is subsequently absorbed. Adsorption capacities vary, depending upon solid type, and the nature (*e.g.*, charge and radius) of the adsorbed ions (Sposito 1989). Soil humus, and hydrous iron and manganese oxides are effective adsorbents because of the abundance (and for humus, the variety) of their functional groups, while the permanent negative charge of clay minerals contributes significantly to their effectiveness as adsorbents for cations (Sposito 1989). Adsorption increases in proportion to the exposed surface area (which is inversely related to grain size) of the adsorbing solid. pH is also a key determinant of the effectiveness of adsorption processes. For cations,

[4] An inner-sphere complex is one in which no water molecule is interposed between the surface functional group and the adsorbed ion or molecule. In an outer-sphere complex, at least one water molecule is interposed between the functional group and the bound species (Sposito 1989).

adsorption processes are generally least effective at low pHs, and strongest at high pHs (Box 5.7). The relationships between anion adsorption and pH are more complex (Sposito 1989).

Adsorption of both cations and anions is typically rapid, with reactions approaching completion on time scales of minutes or hours, although days or even weeks may be required for equilibrium to be entirely achieved (Sposito 1989). In general, desorption reactions are slower than adsorption reactions (Benson *et al.* 1994), but desorption of weakly bound (diffuse-ion and outer-sphere complex) ions may be relatively fast (Sposito 1989).

Cation exchange capacity (CEC) measurements provide a general indication of the potential of different substrates (*e.g.*, a clay mineral, a bulk soil or sediment) to adsorb cations. CECs are measured as the amount (in moles, or "equivalents") of an "index" ion (*e.g.*, ammonium, NH_4^+) adsorbed per unit weight of adsorbent at a pH of 7 (Drever 1988). Capacities so measured can range from lows of <1 $mol \cdot kg^{-1}$ for clay minerals up to 9 $mol \cdot kg^{-1}$ for some humic substances. Although a high CEC indicates a high potential for adsorbing cations, the amount of a particular ion adsorbed will vary depending upon its ability to displace other cations (*e.g.*, Ca^{+2}, Mg^{+2}, Al^{+3}) that already occupy the adsorption sites.

Adsorption can be quantified experimentally by adding a known amount of a substance to a slurry of solids (*e.g.*, soil particles) in water, and measuring the solid:water partition coefficient (K_p) after chemical equilibrium has been established. Because of the variety of factors that influence adsorption of inorganic substances, however, K_p values determined empirically on one set of samples are of limited use in predicting the extent of adsorption in other samples. Models that have been developed to predict metal adsorption have been reviewed by Diamond and Mudroch (1990). However, as these authors noted, most such models have not been tested under natural conditions.

Organic Substances. Organic chemicals partition between water and solids in sediment, soil or biological tissue by various nonspecific sorption processes (Mill 1993). For non-ionic, nonpolar compounds the partitioning process is normally controlled by organic phases (*e.g.*, solid humic material, lipids), into which such chemicals mix (or "dissolve") as they would in an organic solvent (Mill 1993). Thus, when empirically determined solid:water partition coefficients are normalized to the fraction of organic carbon (f_{oc}) present in the solid phase, the resulting carbon-normalized partition coefficient (K_{oc}) can be used to estimate the extent of sorption to other similar solids, if their organic carbon content is known (Box 5.8). When K_{oc} cannot be estimated from empirical data, Di Toro *et al.* (1991) have proposed that within the limits of experimental error, K_{oc} can be assumed to be approximately equal to

K_{ow} (see Appendix II for a more complete discussion of partitioning of hydrophobic compounds).

For ionizable compounds (*e.g.*, organic acids and bases) sorption processes are more complex, involving simultaneous partitioning of neutral forms to organic carbon, as well as ion exchange-type reactions with inorganic phases in sediment and soils (Suffet *et al.* 1994). For organic acid compounds, significant sorption of the anion form generally does not occur unless the aqueous pH is at least 2 units above the pK_a (Suffet *et al.* 1994)[5]. The cationic forms of organic bases, on the other hand, normally partition to sediment to a greater extent than the corresponding neutral form. As for metals, organic cation exchange reactions are site specific, and limited by available sites and by competition among all cations including hydrogen ions (Mill 1993). While the sorption of organic acids can be modelled, no methodology currently exists for predicting sorption of organic bases (Suffet *et al.* 1994).

Box 5.8. *Adsorption of Organic Substances*

The extent of partitioning between solid and liquid phases is expressed by a partition coefficient K_p, where

$$K_p = [C]_S \bullet [C]_W^{-1}.$$

and $[C]_S$ and $[C]_W$ are the concentrations in the solid and water phase, respectively. Since for non-ionic nonpolar organic compounds K_p generally depends mainly on the organic (or lipid) content of the solid, the adsorption coefficient for such chemicals is often normalized to the fraction of organic carbon (f_{oc}) in the solid phase as follows

$$K_p \bullet f_{oc}^{-1}.$$

This carbon-normalized coefficient is called a K_{oc}.

For non-ionic nonpolar organic compounds in soils and sediment, if K_{oc} and f_{oc} are known, and $f_{oc} > 0.2\%$ (Di Toro *et al.* 1991), K_p can be estimated as

$$K_p = K_{oc} \bullet f_{oc}.$$

Although it is often assumed that adsorption is a relatively rapid phenomenon, and that equilibrium it is essentially achieved in 24 h, several weeks or more may be required to achieve complete equilibrium for some hyrophobic chemicals (*e.g.*, Ball and Roberts 1991). Typically sorption occurs rapidly at first, then continues at a slower rate. The rapid phase is has been interpreted to reflect adsorption involving sites near the particle-water interface, and the slow phase to reflect diffusion of the chemical to

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[5] pK_a is defined as the negative log (base 10) of the equilibrium constant (K) for the dissociation reaction $RH \rightleftharpoons R^- + H^+$, where $K = [R^-] \cdot [H^+] \cdot [RH]^{-1}$.

internal more remote sites within the particle (Gas Research Institute 1995). Desorption processes may be much slower than sorption (*e.g.*, Kan *et al.* 1994). Furthermore, although it is frequently assumed that adsorption is completely reversible, a portion of a sorbed chemical may be resistant to desorption (*e.g.*, Kan *et al.* 1994). The greater the period of "aging" (*i.e.*, contact between the chemical and the sorbing solid phase), the greater is the amount of chemical that becomes resistant to desorption and therefore less bioavailable (Gas Research Institute 1995).

K_p (*i.e.*, solid:water partition coefficient) values for strongly sorbed chemicals can exceed 10^5, whereas K_p values for weakly sorbed chemicals are less than 10 (Karickhoff *et al.* 1979). K_p values are normally high for organic chemicals with low water solubilities (Mill 1993). Besides the organic matter content of solids, parameters that influence K_p include grain size, solid to solution ratios, and for ionizable compounds, salinity, cation exchange capacities and pH (Lyman 1990b).

The net effect of sorption is to slow the overall rate of loss of organic chemicals from the water column through processes such as hydrolysis, photooxidation or volatilization (Mill 1993). However, substances adsorbed to suspended solids in surface waters are not as available as dissolved species for uptake by organisms, and may eventually be removed from the water column by gravitational settling and burial in sediments.

Oxidation/Reduction

An oxidation/reduction (redox) reaction involves the transfer of electrons from one chemical species to another. Oxidation occurs when electrons are lost, reduction when they are gained.

Inorganic Substances. Redox reactions are important because changes in an element's oxidation state can have significant effects on its behaviour in the environment (*e.g.*, oxidation of soluble Fe(II) to insoluble Fe(III) species). Whether a substance participates in redox reactions is determined by the availability of free electrons (measured as pE)[6], which is in turn a function of the concentration of oxidizing and reducing agents to which it is exposed. Oxidizing agents of importance in terrestrial and aquatic systems include free oxygen, and manganese and iron oxides (Drever 1988). Photochemical reactions in surface waters and the atmosphere can produce even stronger oxidants, such as hydrogen peroxide and hydroxyl radicals (Zafiriou 1983; Manahan 1991). Examples of the oxidation of the cuprous ion (Cu^+) ion

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[6] Just as pH (a measure of acidity) is the negative logarithm (base 10) of hydrogen ion activity, pE (a measure of "oxidizability") is the negative logarithm of the free electron activity (*i.e.*, $pE = -\log(e^-)$). For more information on the concept of pE, see Drever (1988), Manahan (1991) or Pankow (1991).

by such oxidants are presented in Boxes 5.9 and 5.12. Principal reducing agent in natural systems is decomposing organic matter (Box 5.9).

Redox reactions involving iron and manganese can, in addition to their direct effects on the oxidation states of other elements, have important indirect effects on their mobility. For example, reduction and consequent dissolution of iron and manganese oxides in soils that have been flooded could bring a variety of adsorbed metal species (*e.g.*, see Table 5.3) into the soil solution. Similarly, oxidation and the resulting dissolution of amorphous iron sulphide (a form of "acid-volatile" sulphide) in organic surface sediments could cause the remobilization of other metals (*e.g.*, copper and cadmium) tied up in the pyrite phase (Di Toro *et al.* 1990).

Box 5.9. *Examples of Redox Reactions*

Reduction Half-Reactions[a] for Two Oxidants (O_2 and MnO_2) and Copper

$$1/4\ O_2(g) + H^+ + e^- \rightleftarrows 1/2\ H_2O$$

$$1/2\ MnO_2 + 2H^+ + e^- \rightleftarrows 1/2\ Mn^{2+} + H_2O$$

$$Cu^{2+} + e^- \rightleftarrows Cu^+$$

Oxidation Half-Reaction[a] for a Reducing Organic Species (Formate) and Copper

$$1/2\ CHO_2^- \rightleftarrows 1/2\ CO_2 + 1/2\ H^+ + e^-$$

$$Cu^+ \rightleftarrows Cu^{2+} + e^-$$

Combined Redox Reactions Involving Copper

- *Oxidation of Cu(I) to Cu(II) by manganese oxide*

$$1/2\ MnO_2 + Cu^+ + 2H^+ \rightleftarrows 1/2\ Mn^{2+} + Cu^{2+} + H_2O$$

- *Reduction of Cu(II) to Cu(I) by organic matter*

$$1/2\ CHO_2^- + Cu^{2+} \rightleftarrows 1/2\ CO_2 + Cu^+ + 1/2\ H^+$$

The above was adapted from Sposito (1989).

[a] a complete redox reaction requires the combination of oxidation and reduction half-reactions such that the number of electrons (e^-) on the two sides of the equation are equal and therefore cancel out.

Organic Substances. Reductive and oxidative transformations are distinguished from other processes (*e.g.*, hydrolysis) by determining if a change in the oxidation state of the atoms involved in a reaction process has occurred (Larson and Weber 1994)[7]. Reductive transformations of organic substances are categorized according to the type of functional group affected. Such transformations

[7] See Larson and Weber (1994) for a description of how this is done.

include, for example, reductive dehalogenation and reductive dealkylation (Larson and Weber 1994).

For many chemicals containing susceptible functional groups, reduction is the dominant transformation pathway in reducing environments such as subsurface soils and aquatic sediments, organic-rich sewage sludge, hypolimnia of stratified lakes and anaerobic segments of eutrophic rivers. Naturally occurring reductants include organic matter, sulphide minerals and reduced metals. Reduction rates in the natural environment are difficult to predict accurately because of the complexities of the environment, and the variety of possible reductants (Larson and Weber 1994). Nevertheless QASRs have been developed for predicting reductive transformation rate constants for certain classes of chemicals in specific environments (*e.g.*, Peijnenburg *et al.* 1992).

Molecular oxygen is the most abundant oxidizing agent in the atmosphere and water column (Larson and Weber 1994). Reactions between molecular oxygen and organic compounds are typically microbially mediated. For example, the oxidation of benzene by molecular oxygen may represented as follows:

$$C_6H_6 + O_2 \xrightarrow{\textit{microbes}} C_6H_4(OH)_2 \qquad \text{(Scow 1990).}$$

Such reactions can eventually result in complete "mineralization" (*i.e.*, conversion of organic substances to their inorganic constituents such as CO_2, H_2O etc.). Photochemical reactions in surface waters and the atmosphere can produce very strong oxidants, such as hydrogen peroxide and hydroxyl radicals (see following section on *Photolysis*). An example of a photooxidation reaction involving an aldehyde and an hydroxide radical is presented in Box 5.12. As Mill (1993) has noted oxidation of organic chemicals typically gives products that are more water soluble, less volatile and less subject to bio-uptake than the parent compounds.

Further information on redox reactions involving organic compounds can be found in Larson and Weber (1994).

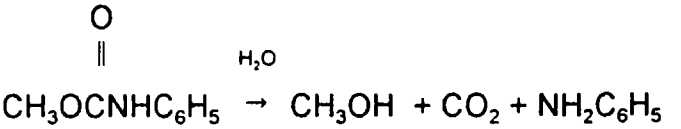
Hydrolysis

Inorganic Substances. Hydrolysis reactions between water and inorganic substances are defined as those involving cleavage of the water molecule (*i.e.*, H^+ and OH^- ions are formed from H_2O), but not necessarily of the inorganic substance, and the formation of either alkaline or acidic solutions (Krauskopf 1979; Pankow 1991). This definition is different than that for reactions with organic chemicals (see below). Hydrolysis reactions are important in the natural weathering of silicate minerals (Box 5.5), as well as dissolution (Box 5.5), complexation (Box 5.4) and precipitation (Box 5.6) processes for metals.

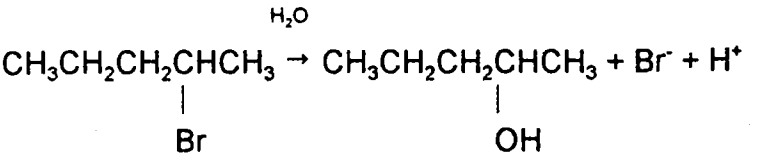
Organic Substances.
Hydrolysis reactions involving organic substances are reactions with water wherein a covalent bond in the original substance is cleaved, and a new bond with the hydroxide (OH^-) ion is formed. Several types of reaction mechanisms (defined by the type of reaction centre where hydrolysis occurs) may be involved (Larson and Weber 1994).

Box 5.10. *Hydrolysis of Organic Substances*

- *Hydrolysis of a carbamate producing an alcohol and an amine*



- *Hydrolysis of an alkyl halide producing an alcohol*



The above was adapted from Harris (1990a).

Many organic compounds are unaffected by hydrolysis. Examples of classes of compounds which are relatively or completely inert with respect to hydrolysis are alkanes, alkenes, alkynes, benzenes, biphenyls, PAHs, PCBs, halogenated aromatic compounds, aromatic nitro compounds, aromatic amines, alcohols, phenols, glycols, ethers, aldehydes, ketones and carboxylic acids. Types of organic functional groups that are susceptible to hydrolysis include carbamates, amines, amides, carboxylic, phosphoric and sulphuric acid esters (Box 5.10)(Harris 1990a).

Hydrolysis reactions are important because their products (*e.g.*, alcohols, acids and carbonyls), are often more water soluble and less subject to bio-uptake or volatilization than their parent compounds (Mill 1993). Hydrolysis reactions are sensitive to pH, and may be promoted by acidic and/or basic conditions; rates of hydrolysis increase as temperatures rise (Mill 1993). Sorption to sediment can reduce hydrolysis rates (Macalady and Wolfe 1985).

Further details on hydrolysis of organic chemicals, including methods used to experimentally measure and to calculate (using QSARs) reaction rates, can be found, for example Mill (1993) and Larson and Weber (1994).

Volatilization

Volatilization involves the transfer of a substance from a liquid or solid, to a vapour phase. If the substance is initially in a pure state (*e.g.*, crystals of a native element) it can be considered a transformation process. However, if it is initially

present within another substance (*e.g.*, dissolved in water), it is more accurately described as a diffusive transport process (see section 5.3.1). Vapour pressure is a measure of a pure substance's tendency to volatilize.

Vapour pressures range from over 10,000 Pascals (Pa) for highly volatile organic compounds, to about 10^{-7} Pa for non-volatile ones (Box 5.11). As indicated by their very low vapour pressures, most stable forms of metals and metalloids do not volatilize to a significant degree at ambient temperatures in the natural environment[8]. Exceptions of note include elemental mercury, and methylated metal species (see following section on *Biotransformation*), which have vapour pressures similar to those of volatile and semi-volatile organic compounds.

Box 5.11. *Vapour Pressures (P)[a] of Some Organic and Inorganic Substances*

Substance	*P(Pa)*
acetone	35990
tetramethyl tin	14700
benzene	12700
tetramethyl lead	4300
1,2-dichlorobenzene$_{(L)}$	196
elemental mercury (Hg^0)$_{(L)}$	0.3
hexachlorobenzene$_{(S)}$	0.23×10^{-2}
decachloro-PCBs$_{(S)}$	0.5×10^{-7}
elemental zinc$_{(L)}$	2.0×10^{-12}
copper chloride$_{(L)}$	1.1×10^{-14}
aluminum oxide$_{(L)}$	6.5×10^{-77}

The above was adapted from Mackay *et al.* (1992), Grain (1990), and extrapolated from data in Weast (1969) using equation 14-3 of Grain (1990).

[a] pressure excerpted by a vapour in equilibrium with its own solid (S) or liquid (L) phase at 25°C. 1 mmHg = 133.3 Pa (Pascals).

Photolysis

Sunlight photolysis (or photoreaction) of chemicals occurs in surface waters, on soil and in the atmosphere. Photoreactions can be divided into two types: direct and indirect. A direct photoreaction occurs when solar radiation (at wavelengths above 300 nm) is absorbed by a chemical and the energy is used to form excited or radical species, which react further to form stable products (Mill 1993). Indirect photolysis (or photooxidation) involves reaction of a substance with intermediate oxidants formed during photolysis of dissolved organic matter (*e.g.*, humic acid) in water or soil, or photolysis of ozone or NO_2 in the atmosphere (Mill 1993).

[8] However, many metals species may be released in gaseous form in atmospheric emissions from pyrometallurgical (high temperature) industrial processes, as well as from volcanoes.

Box 5.12. *Photolysis Reactions Involving Dissolved Metal Species*

Direct Reaction:
reduction of Fe(III) to Fe(II) and cleavage of an iron hydroxide complex

$$(Fe(OH^{\cdot})(H_2O)_5)^{2+} \xrightarrow{h\nu} (Fe(OH)(H_2O)_5)^{2+}$$

$$(Fe(OH)(H_2O)_5)^{2+} \xrightarrow{h\nu} (Fe(H_2O)_6)^{2+} + (OH\cdot)$$

Indirect (Photooxidation) Reactions:
oxidation of Cu(I) to Cu(II) by an intermediate oxidant (H_2O_2)

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + OH\cdot + OH^{-}$$

$$Cu^{+} + OH\cdot \rightarrow Cu^{2+} + OH^{-}$$

The above was adapted from Weschler *et al.* (1986).

Inorganic Substances. Absorption of visible and ultraviolet light by dissolved metal complexes can cause a charge transfer (redox reaction) between the ligand and the metal, and if sufficient light energy is absorbed, the complex may be cleaved. An example of such a direct photolysis redox reaction involving the cleavage of a ferric hydroxide/aquo complex and the production of an hydroxyl radical is shown in Box 5.12. Various indirect photooxidation reactions involving photochemically produced oxidants (*e.g.*, hydroxyl radicals and ozone) and dissolved metal species are also possible (see Box 5.12). Further information on photolysis reactions involving dissolved metal species in the atmosphere (cloud droplets) and surface waters can be found in Weschler *et al.* (1986) and Zafiriou (1983), respectively.

Organic Substances. Photoreactions control the fate of many organic chemicals in air and water, and often create oxidation products that are more water soluble, less volatile and less subject to bio-uptake than the parent compounds (Mill 1993). Key parameters are the rate at which a substance absorbs light and the efficiency of the absorption process (quantum yield) at wavelengths above 300 nm in the solar spectrum (Harris 1990b; Mill 1993). As Mill (1993) has noted, detailed descriptions of photolytic processes can be found, for example, in Mill and Mabey (1985) and Atkinson (1986).

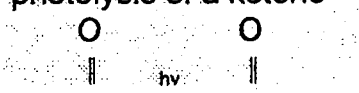
An example of a direct photolysis reaction causing the photodissociation of a ketone is shown in Box 5.13. Relatively few organic compounds photolyze directly at significant rates. Compounds for which direct photolysis in the atmosphere is a significant removal process include conjugated alkenes, carbonyl compounds (including aldehydes and ketones), some halides and nitrogen compounds (Manahan 1991).

Most indirect photoreactions in water involve oxidants such as singlet oxygen or free oxyradical reactions (Mill 1993). Only phenols, furans, aromatic amines, sulphides

Box 5.13. *Examples of Photolysis Reactions Involving Organic Chemicals*

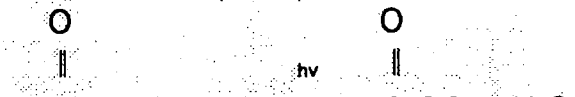
Direct Reaction

photolysis of a ketone



Indirect (Photooxidation) Reaction

of an aldehyde by an hydroxide radical (in air)



The above was adapted from Manahan (1991).

and nitro aromatics undergo indirect photolysis in water (Mill and Mabey 1985). In the atmosphere, photooxidation normally results from reaction with OH radicals. Compounds affected include alkanes, olefins, alcohols and simple aromatics (Atkinson 1986, 1987). As indicated in Box 5.13, oxygen is incorporated into the structure of such compounds as carbonyl or peroxide products (Mill 1993).

Methods of estimating rates of both direct and indirect photolysis using QSARs are reviewed by Mill (1993).

Biotransformation

Inorganic Substances. Microorganisms influence the mobility and distribution of metals (and other chemical elements) in the environment more than any other life form. As Trudinger *et al.* (1979) noted, this is because microorganisms comprise most of the earth's biomass, have rapid generation times, and occupy a wide variety of habitats (including surface and groundwaters, sediments and soils). The principal microorganisms involved are bacteria, blue-green algae, fungi and protozoa (Olsen 1983). They influence the fate of the elements primarily by inducing oxidation/reduction (see Box 5.9), methylation, or surface adsorption (binding) reactions.

Methylation has received the most attention of all of the biologically mediated reactions of metals, because of the increased bioavailability (and in some cases toxicity) of methylated species (Campbell *et al.* 1988). Chemical elements that are methylated by microorganisms in the natural environment include mercury, tin, arsenic and selenium. Although lead was originally thought to be methylated biologically, the evidence for this has been challenged (Campbell *et al.* 1988).

Negatively charged ligands (*e.g.*, phosphoryl, carboxyl, sulphydryl and hydroxyl groups of proteins and lipids) are responsible for surface adsorption of metals at cell surfaces (Olsen 1983). The ability of microorganisms to accumulate dissolved forms of many metals (bioconcentration factors up to 10^5; Newman and Jagoe 1994) is evidence of the efficiency of these binding processes. Metals accumulated by microorganisms may then contribute to the dietary intake of organisms at higher trophic levels.

Organic Substances. Biotransformation can be defined as any biologically induced change that alters the molecular integrity of an organic substance. Effects of biotransformation can range from a minor change in the parent compound to complete mineralization. Organic compounds can be used by microorganisms (immediately or following acclimation) as an energy or nutrient source, or they may be co-metabolized.

Mineralization (*i.e.*, conversion to carbon dioxide, water, nitrate and phosphate) of organic compounds is usually due almost entirely to biotransformation. Reactions involved in biotransformation can be oxidative, reductive, hydrolytic or conjugative (Scow 1990).

Factors affecting the rate of biotransformation are physical/chemical properties and concentration of the substrate, species composition, population densities, previous history, inter- and intra-species interactions, temperature, pH, moisture, oxygen availability, salinity, sunlight intensity, and presence of other substances (Lee *et al.* 1989; Scow 1990). Generally, aerobic processes are faster than anaerobic ones.

Further information on biotransformation, including methods of determining process rates by both experimental and theoretical means can be found in, for example, Scow (1990), OECD (1993a) and Mill (1993).

5.3.3 Bioaccumulation

Bioaccumulation (*i.e.*, the net accumulation of a substance by an organism as a result of uptake from all routes of exposure) is an important fate process. Substances that bioaccumulate strongly may be present in significant amounts in food sources of predator organisms. The potential to bioaccumulate is a necessity for biomagnification (the accumulation and transfer of a substance via the food chain due to ingestion, resulting in an increase of the internal concentration in organisms at succeeding trophic levels), although biomagnification does not occur with most substances (Cowan *et al.* 1995a; CEU 1994; U.S. EPA 1994).

The extent to which a substance bioaccumulates is the combined result of the competing processes of uptake, distribution, transformation and excretion. If the substance is available for uptake by the organism over a period of time, these four processes reach a dynamic equilibrium (apparent plateau or steady-state) which is characterized by a constant ratio of the concentration of the substance in the organism and in the exposure medium (*e.g.*, water or food). This ratio is referred to as the bioconcentration factor (BCF)(OECD 1993a). BCFs are usually calculated in controlled laboratory tests in which biota (usually fish) are exposed to dissolved substances in an appropriate medium (usually water). When the ratio is derived from accumulation through both dermal contact and ingestion of food, it is called the bioaccumulation factor (BAF). BAFs calculated from field data are the preferred measurement of

accumulation potential, although both BAFs or BCFs can be used depending upon the availability and quality of data. BAFs and BCFs are technically difficult to measure for substances with high K_{ow}s, due to the problem of achieving a steady state using test protocols of short duration. BCFs and BAFs can be calculated using QSARs (*e.g.*, OECD 1993b), if the uncertainties associated with such values are acceptable.

The lipid content of organisms is an important determinant of their capacity to accumulate organic chemicals. This is indicated, for example, by the fact that when wet weight based BCFs for organisms of different types are normalized for lipid content, the variations among organisms are greatly reduced (Gobas and Mackay 1989). For a given type of aquatic organism, the main factors that affect its lipid content are season and diet. Seasonal variation in lipid content is related to the sexual cycle and water temperature. Scarcity of food results in depletion of the organisms lipid stores while an abundance of food may lead to higher lipid levels (Gobas and Mackay 1989).

For nonpolar, nonionizable substances such as pesticides, herbicides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs), the potential to bioaccumulate is predominantly due to substance hydrophobicity (Veith *et al.* 1980). An understanding of how hydrophobicity affects bioaccumulation for the nonpolar, nonionizable substances is well developed (see for example, Cowan *et al.* 1995a).

A substance's BCF can be estimated from its K_{ow} using a QSAR of the form,

$$\log BCF = a + b \cdot \log K_{ow}$$

where a and b are empirical constants. Depending upon the organisms and chemicals studied, values for b have been reported to range between about 0.3 and 1.5 (mean = 0.57), and those for a between -3.0 and 2.6 (mean = 0.42)(Gobas and Mackay 1989). As indicated by the variability of these "constants", there may be considerable uncertainty associated with BCFs calculated from K_{ow}s.

It is generally accepted that a log K_{ow} value of 5 corresponds to a BCF for fish of approximately 5000 (*e.g.*, Environment Canada 1994). A log K_{ow} value of 4.3 typically corresponds to a BCF value of approximately 1000 (ECETOC 1995), while a log K_{ow} value of 3 corresponds to a BCF for lipophilic and non-metabolizable substances of approximately 100 (CEU 1994). The direct linear relationship between log K_{ow} and log BCF does not apply for substances with a log K_{ow} above 6 (Environment Canada 1994; CEU 1994). It should be noted, however, that such substances still have the potential to bioconcentrate and high BCFs have been measured for some substances with large K_{ow}s tested within their water solubility range (CEU 1994).

For substances having a log K_{ow} ranging from 4.5 to 8, dietary exposure is most critical (ECETOC 1995). For large molecular weight (MW) substances such as polymers (*i.e.*, MW > 1100) and for extremely hydrophobic substances (*i.e.*, log K_{ow} > 10), bioaccumulation may not occur due to steric hindrance or solubility restrictions on uptake (Opperhuizen *et al.* 1985).

5.3.4 Characterizing the Nature and Rates of Key Fate Processes

This section examines, in a general way, the use of experimental testing and QSARs to evaluate the nature and rates of fate processes. Information relating to specific fate processes is presented in the preceding sections.

The rate at which a substance is affected by a given transformation or physical removal process, can usually be related to the substance's concentration (C), by a pseudo first-order rate constant k' (Box 5.14). If this rate constant is known (*e.g.*, based on results of experimental testing), the time required to transform or remove half of the original amount in the compartment by that process (*i.e.*, the process specific half-life) can be calculated as $0.693 \cdot (k')^{-1}$ (Box 5.14). Rate constants (*i.e.*, k or k' values) for a variety of fate processes affecting organic substances can be estimated using QSARs (see previous discussion of individual fate processes) if uncertainties associated with such estimates are within

Box 5.14. *Rate Quantification of Loss Processes*

It is often assumed that loss processes can be expressed by a simple relation such as,

$$\text{Rate} = k \cdot [C] \cdot [E]$$

where,

k = rate constant for the removal process,
C = concentration of the chemical, and
E = environmental property responsible for loss.

Although values of E usually vary with time, they can frequently be represented by temporally or spatially averaged values, based on field measurements. If E is set at a constant average value, then the rate equation simplifies to a pseudo first order relation,

$$\text{Rate} = k' \cdot [C]$$

where $k' = k \cdot [E]$. If k' has been determined under controlled laboratory conditions, or can be estimated from empirically derived structure activity relations (SARs), the time required for loss of half of the original amount of the substance can be calculated as follows:

$$t_{1/2} = \ln 2 \cdot (k')^{-1} = 0.693 \cdot (k')^{-1}.$$

For example, if the degradation rate constant for a radioisotope were 0.0693 h^{-1}, its half-life would be 10 hours.

The above was adapted from Mill (1993) and Mackay (1991).

acceptable limits. Ultimately, however, predictions based on QSARs should be confirmed by experimental methods (Mackay *et al.* 1992).

Experiments using simplified systems in controlled laboratory conditions are usually the preferred approach to determining the nature and rate of key fate processes. The OECD (1993a), for example, provides guidelines for experimental testing of adsorption/desorption, biodegradation and bioaccumulation. Microcosm and mesocosm tests, which incorporate more of the complexities of the natural environment, can also be used to predict a substance's environmental fate (*e.g.*, Lay *et al.* 1985). Test systems need not be full-scale re-creations, however, to be useful (Covello and Merkhoffer 1993). Scale models (*i.e.*, physical replicas of a part of the environment that have been "scaled down" for study in the laboratory) are sometimes adequate when studying fate processes, such as physical transport in groundwater (Knox *et al.* 1993). Full-scale field testing (*e.g.*, tracer studies) of groundwater flow patterns (Knox *et al.* 1993) may also be appropriate in some cases.

As Covello and Merkhofer (1993) have noted, experimental tests may be limited because:

- test conditions do not adequately replicate natural conditions,
- comparing results of different tests is difficult due to the wide diversity of testing methods (*e.g.*, of microcosm designs) currently in use, and
- distinguishing a significant effect from natural fluctuations can be problematic, especially in more complex test systems.

5.4 Transformation Products

To date, assessments of priority substances under CEPA have focussed only on the parent substance. However, if a transformation product, or break-down product, is known to exhibit toxic effects, consideration should be given to determining the ecological effects of the substance.

5.4.1 Current Approaches

Several organizations were contacted with regard to whether they had guidelines or regulations for dealing with transformation products for existing substances. These included Health Canada, the United States Environmental Protection Agency, the Commission of European Union (CEU) and the Organization of Economic Cooperation and Development (OECD). Currently, no policy or guidelines exist for estimating effects of transformation products in hazard or risk assessments of existing substances. In the organizations contacted, expert judgement is applied on a

case-by-case basis to determine the need for further investigation of the effects of transformation products.

Guidance for identifying transformation products that require further investigation is provided in a document for registration of pesticides in Canada, prepared under the Pest Control Products (PCP) Act by Agriculture Canada, Environment Canada and the Department of Fisheries and Oceans (1987). In this document, transformation products are defined as those present at a level of greater than 10% of the parent pesticide at any time during laboratory studies on the physicochemical properties of the substance, or present at an accumulated level of greater than 8% of the parent pesticide after termination of laboratory fate tests. When a transformation product is observed, information on the fate and toxicity of this product is obtained and an evaluation is pursued.

5.4.2 Assessing Transformation Products under CEPA

During data collection an effort should be made to include information on transformation products. Products of transformation reactions should be evaluated for their potential to cause significant adverse effects to the environment on a case-by-case basis. Professional judgment should be used, taking into account a substance's inherent toxicity, environmental persistence and bioaccumulation potential. Substances that are (or are suspected to be) more toxic than the parent priority substance should be examined with particular care. Those that meet the criteria for either persistence of bioaccumulation for Track 1 substances (Table 5.4) under the federal Toxic Substances Management Policy (Government of Canada 1995), likewise merit careful scrutiny.

Table 5.4. Recommended criteria for the selection of substances for management under Track 1 of the federal Toxic Substances Management Policy.

Persistence[a]	***Bioaccumulation***[b]
Medium *Half-life* air ≥ 2 days water ≥ 6 months soil ≥ 6 months sediment ≥ 1 year	BCF or BAF ≥ 5000 and/or Log K_{ow} ≥ 5

If a transformation product is considered to have the potential to cause significant adverse effects to the environment, an assessment of the ecological effects of the product should be conducted. In cases when the environmental distribution of the transformation product is clearly linked to its parent substance, the assessment of the transformation product should be incorporated into that of the parent substance.

5.5 Pathways Analysis

Pathways analysis involves integrating available data on releases of substances from identified sources (see Chapter 4), with information on their properties and those of the receiving environment, and the nature and rates of key transport and transformation processes. The objective is to refine and verify the account of the fate of the substance that was developed for problem formulation.

Generally, detailed pathways analysis should, to the extent possible, be quantitative. Thus a pathways analysis could take the form of a complex computer-based fate model that describes (in space and time) the movement of substances from sources to risk receptors. For example, a Gaussian plume model could be used to describe the movement in air of coarse particulate substances released in stack gases, and their eventual accumulation in local surface soils that support sensitive plant populations. In practice, however, many pathways analyses are only partially quantifiable, and must be expressed in a less precise, conceptual fashion. Thus, if the atmospheric emissions mentioned above could not be mathematically modelled, the pathways analysis might be expressed in the form of a statement that, because the substances are released as coarse, dense solids (as determined by direct monitoring), they are likely (given results of modelling and other studies conducted elsewhere, for example) to be deposited on soils close to the stack, mostly in a down-wind direction.

A key aspect of detailed pathways analysis is verification, based in part on direct observations made in the area of concern. Prior to empirical verification, a pathways analysis is an untested hypothesis. In the example cited, for example, available information on the amount of the substances of concern in soils collected at varying distances from the source stack could be examined. The observed distribution of these substances could then be compared to that expected based on the pathways analysis[9]. When observed and expected results are substantially different, a pathways analysis should be re-evaluated.

During detailed pathways analysis, the following aspects of the initial analysis developed during problem formulation should be verified:

- identity of the principal receiving media, and media where the substance accumulates,
- locations and geographic boundaries of contaminated areas selected for evaluation, and

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[9] Methods of relating measured concentrations in the field, to identified natural and anthropogenic sources are described in Appendix III.

- identity and main routes of exposure of risk receptors.

5.5.1 Identification of Principal Contaminated Media

Predicted partitioning of substances among environmental media (based, for example, on knowledge of physical and chemical properties, or fugacity calculations), should normally be confirmed by chemical analyses of samples collected within the area of concern. For example, an insoluble substance released directly to water would be expected to accumulate in sediment near the point of release. This could be confirmed by collection and analyses of water and sediment samples near the identified source, and in an appropriate reference area. Guidance on determining the quality of such chemical data is offered in Section 5.6.2 and in Appendix III.

5.5.2 Identification of Geographic Area(s) of Concern

The size and locations of the geographic areas selected for evaluation will vary depending upon the nature and distribution of the principal sources (see Chapter 4), and the nature and rates of key fate processes affecting the substance. Although fate models and expert judgement may be used to initially identify areas of concern, during detailed exposure characterization monitoring information should be used to define, as precisely as possible, areas where exposures are likely to be high.

In general, when releases are from a limited number of point sources *(e.g.*, manufacturing plants), evaluations should initially be undertaken at a local scale, in areas centred on known sources (CEU 1994). For some large point sources, however, information on the substance's fate and transport (*e.g.*, results of monitoring or modelling studies) may indicate that a larger scale, regional assessment is most appropriate. When substances enter the environment from diffuse sources (*e.g.*, combustion of gasoline), regional scale evaluations are normally required (CEU 1994). For natural substances (*e.g.*, metals), information on the distribution of natural sources (*e.g.*, bedrock, mineral deposits) should also be considered when defining regional boundaries.

5.5.3 Refining Selection of Risk Receptors

In addition to being sensitive and ecologically relevant (see Chapter 3), organisms that have been selected for evaluation as risk receptors should be amoung those most likely to be exposed to the substance. For a substance that partitions to sediment (*e.g.*, an insoluble substance released to water), benthic invertebrates, aquatic macrophytes, and bottom-feeding fish would be among the most exposed. Classes of organisms that could be affected by substances that partition to other media are presented in Table 5.5. Within such general groupings, organisms of concern should be further specified based on expected major routes of exposure, sensitivity and

ecological relevance (see Chapter 3 and Section 5.5.4). For example, if mammals are identified as being potentially at risk from exposure to a substance that has a high potential to bioaccumulate, sensitive predator species should be preferentially selected as risk receptors.

Information on the distribution of potentially exposed organisms in Canada and their preferred habitat should be consulted to ensure that organisms selected for evaluation are likely to be have been present in the area chosen prior to contamination. Other factors that could increase exposure of candidate organisms such as diet, mobility, and body size, as well as stage in the reproductive cycle, and seasonal changes in physiology (Suter 1993b) should also be considered.

Table 5.5. Organisms most exposed to substances in different types of media.

Media	***Most Exposed Organisms***
Sediment	microorganisms, benthic invertebrates, aquatic macrophytes, and bottom-feeding fish.
Surface Water	zoo- and phyto-plankton, fish, aquatic macrophytes, amphibians, reptiles
Air	plants, mammals, birds, amphibians, reptiles
Biota	mammals, birds, amphibians, reptiles
Soil	microorganisms, plants, soil invertebrates
Groundwater	microorganisms, zooplankton

5.5.4 Verification of Routes of Exposure

In most exposure scenarios it is necessary to identify the main routes by which organisms selected for evaluation are exposed. An organism may be exposed to a substance because of dermal contact with contaminated media (*i.e.,* water, air, soil or sediment), ingestion of contaminated food, water, soil or sediment, or respiration of contaminated air or water. A summary of some potentially important routes of exposure for different types of organisms is presented in Table 5.6.

In many exposure scenarios, it can be assumed that one route of exposure is dominant and that other routes can in practice be ignored (Suter 1993b). For microorganisms, exposure is normally attributed to contact with the host medium (*e.g.,*

Table 5.6 Potentially important routes of exposure for different types of organisms[a].

Organisms	***Some Important Routes of Exposure***								
	Contact				***Ingestion***			***Respir-ation***[b]	
	surface water	air	soil[c]	sedi-ment[c]	food	soil, sedi-ment[c]	water	air	water
phyto-plankton	✔								
zooplankton	✔								✔
micro-organisms	✔		✔	✔					
aquatic macrophytes	✔			✔					
vascular terrestrial plants		✔	✔						
benthic invertebrates				✔	✔	✔			✔
soil invertebrates			✔		✔	✔		✔	✔
fish	✔				✔				✔
amphibians and reptiles	✔				✔	✔	✔	✔	
birds					✔	✔	✔	✔	
mammals					✔	✔	✔	✔	

[a] blanks signify that exposure routes are usually unimportant; ✔ indicates most important routes of exposure

[b] respiration is considered to be a special case of exposure by contact, with either the lung or gill

[c] including porewater

water, soil, sediment). Because of their small size and large area/volume ratio, uptake of chemicals by zooplankton is usually a result of contact with water (Newman and Jagoe 1994; Gobas 1993). Uptake by phytoplankton and submerged aquatic macrophytes is also likely due to direct exchange between organisms and water (Geyer *et al.* 1984; Gobas *et al.* 1991), although highly contaminated sediments may also contribute significantly to the exposure of some aquatic macrophytes (Campbell *et al.* 1988). For fish, respiration of water through the gill and contact with skin are often the main routes of exposure to both organic and inorganic substances (McKim 1994; Clements 1994). However, consumption of food may be important for fish exposed to persistent bioaccumulative chemicals with log K_{ow}s in the range 4.3 or higher (Oliver and Niimi 1983; Bruggeman *et al.* 1981). Contact with contaminated soil is normally the principal route of exposure for vascular plants, although for some volatile substances, direct contact with air may be equally or more important (Trapp *et al.* 1990).

In the case of benthic and soil invertebrates, mammals, amphibians, reptiles and birds, several different routes of exposure may be important. However, for benthic and soil invertebrates it can often be assumed that exposure to nonionic, nonpolar organic chemicals is determined primarily by contact with sediment or soil pore waters (Di Toro *et al.* 1991; van Gestel and Ma 1988)[10]. For wildlife, exposure is most likely to result from ingestion of food or water, or respiration of air, although dermal contact and preening may be important in some cases.

5.6 Quantifying Exposure

This stage of exposure characterization involves quantifying exposure for identified risk receptors. Although biomarkers have been proposed for this purpose, their utility is usually limited by the ambiguity of their relationship to specific chemical agents (Section 5.6.1).

Exposure should be quantified as Estimated Exposure Values (EEVs) for each risk receptor in each area of concern. EEVs based on empirical (monitoring) data are preferred (Section 5.6.2), particularly for tier 2 and 3 risk analyses, but outputs from mathematical models may be used in some cases (Section 5.6.3). EEVs should be based on data for bioavailable forms of a substance, except possibly for tier 1 risk analysis (Section 5.6.4). Higher tier EEVs should be expressed as distributions of values that reflect the real spatial and/or temporal variability of exposure, as well as uncertainties associated with exposure measurements, and ignorance of true values for parameters used in calculations (Section 5.6.5). EEVs should be apportioned among identified anthropogenic and natural sources for tier 3 risk analysis (Section 5.6.6).

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[10] Ingestion may also be an important route of exposure however, if a substance has a log K_{ow} above about 4.5 (Landrum and Robbins 1990).

5.6.1 Approaches to Quantification

Use of Biomarkers

Biomarkers are "measurements of body fluids, cells, or tissues that indicate in biochemical or cellular terms the presence and magnitude of toxicants or of host response" (Committee on Biological Markers 1987 *in* Suter 1993c). Biomarkers represent an organism's attempt to compensate for, or tolerate, stressors in the environment (Cormier and Daniel 1994). Depending upon how they are interpreted, biomarkers can be used as indicators of either exposure or effects. However, some biomarkers are more useful in one role than the other, because they have clearer relationships to one process (either exposure or induction of effects)(Suter 1993c).

Biomarkers of exposure are biochemical or physiological changes that indicate that an organism has received an internal dose of a chemical. One example of a biomarker for animals is the induction of hepatic mixed function oxidases by a variety of xenobiotic chemicals (Rattner *et al.* 1989). Other examples are DNA or protein adducts of electrophilic chemicals or chemicals metabolically activated to an electrophilic state that have become bound to a macromolecule (Shugart *et al.* 1987). Potential examples of biomarkers for plants include nitrate reductase as a marker for exposure to nitrogen oxides (Norby 1989), and free radical scavengers as indicators of exposure to photochemical oxidants or other pollutants that induce the production of free radicals (Richardson *et al.* 1989; Suter 1993c).

Biomarkers of effects can also be used as indicators of exposure. Potentially useful biomarkers of effects include the frequency of DNA breaks (Shugart 1988), delta-ALAD inhibition (a mechanism of lead toxicity; Dieter and Finley 1979), and acetyl cholinesterase inhibition (the mechanism of organophosphate and carbamate pesticide toxicity; Coopage *et al.* 1975). Biomarkers of effects are not nearly as well documented for plants as for animals (Suter 1993c).

To be useful for exposure assessment, it must be shown that biomarkers increase in a regular and predictable manner with increasing exposure to a specific substance. In the PSL assessment of PAHs (polycyclic aromatic hydrocarbons), for example, adducts found in mammals known to originate from PAHs were used to establish PAH exposure (Environment Canada and Health Canada 1994a). Such exclusivity is often difficult to demonstrate however, and biomarker data must be used with particular caution when assessing exposure. Research focussed at establishing the connection between biomarkers, sources (*i.e.*, chemical agents) and effects is essential if these "early warning" systems are to be used to their fullest potential. However, since unambiguous evidence of such cause-effect relationships is rarely available (Suter 1990), biomarker data may be considered as part of the weight of evidence for exposure, but exposure characterization should normally be based on

more conventional dose or concentration data.

Use of Concentration and Dose Data

Exposure may be estimated based on quantities of a substance with which an organism comes in contact (*i.e.*, conditions external to the organism), or the quantities that are absorbed internally (*i.e.*, that cross cell membranes)(Suter 1993b). For situations in which direct contact with one contaminated medium is the dominant route of uptake, EEVs may be quantified as a *simple concentration* (*e.g.*, $\mu g \cdot L^{-1}$). However, when exposure results from intake by ingestion and/or inhalation, exposure should be determined based on *rates of intake* (*i.e.*, external doses), calculated as the product of the concentrations in air, food and drinking water, and rates of inhalation (*e.g.*, m^3 air · kg^{-1} body weight · day^{-1}) or ingestion (*e.g.*, g food · kg^{-1} body weight · day^{-1}). Changing concentrations to intakes by multiplying by rates of inhalation or ingestion is an example of what Suter (1993b) calls a simple "exposure conversion model". When more than one route can contribute significantly to uptake, net exposure from ingestion and inhalation can be calculated as a combined external dose. An example of such a calculation applied to a mammalian species is presented in Table 5.7.

Table 5.7. Example of a maximum daily intake (*i.e.*, external dose) calculation for an adult mink exposed to hexachlorobenzene along a contaminated stretch of the St. Clair River, Ontario.

Medium	***Maximum Concentration[b]***	***Intake of Medium***	***Maximum Daily Intake ($ng \cdot kg\text{-}bw^{-1} \cdot day^{-1}$)***
Air	0.29 $ng \cdot m^{-3}$	0.55 $m^3 \cdot day^{-1}$	0.16
Water	87 $ng \cdot L^{-1}$	0.1 $L \cdot day^{-1}$	8.7
Diet 1: 100% fish	283 $ng \cdot g^{-1}$	215 $g \cdot day^{-1}$	60,845
Diet 2: 100% birds or mammals	30 $ng \cdot g^{-1}$	158 $g \cdot day^{-1}$	4740
Total Daily Intake - for Air, Water and Diet 1			60,854
Total Daily Intake - for Air, Water and Diet 2			4749

[a] Bioavailability factor for air, water and food assumed to be 1 (see below).
[b] Concentration data obtained from Health Canada and Environment Canada (1993), assuming that concentrations in birds and mammals are approximately equal.
[c] Methods of estimating intake are described in Moore *et al.* (1996)

Table 5.7 is based on output from a computerized multi-media exposure model

developed by the Canadian Wildlife Service (Brownlee *et al.* 1995). This model should be used to make exposure estimates for birds, mammals, amphibians and reptiles.

Net exposures resulting from dermal contact with more than one medium, or a combination of dermal contact and ingestion and/or inhalation are more difficult to determine. In such cases internal exposures may be estimated using empirical data on the concentration of a substance in the body of organisms (see Section 5.6.4), or by assuming that the concentration within organisms is in equilibrium with that in the surrounding medium (see description of the equilibrium partitioning method of determining effects in Chapter 6). Alternatively, QSARs may be used to estimate body burdens or toxicokinetic models used to derive estimates of internal dose (Suter 1993b). Because of the potentially large uncertainties associated with the assumption that organisms are in chemical equilibrium with their surroundings, and with the outputs of QSARs and toxicokinetic models, use of empirical body burden data is preferred. Unfortunately, however, because concentrations in bioassay test organisms are rarely reported, body burdens often cannot be used to assess risk of harmful effects (Suter 1993b).

As Suter (1993b) stressed, since assessment of risk typically involves comparison of exposures in field situations with those causing effects in toxicological tests, methods of quantifying exposures of field and test organisms should be consistent. In practice this means that the routes of exposure, and the forms and bioavailabilities of substances administered and/or measured should be similar in both situations. Consistency of form and bioavailability is least problematic when exposure is primarily to soluble substances in water, or gaseous substances in air; it is most problematic when exposure results from contact with solid phases (*e.g.*, soil, sediment, food)(Suter 1993b). Because of lack of data on uptake efficiency from food sources, it is sometimes assumed that the bioavailability of all forms of substances that are orally administered are equal (Suter 1993b). The preferred approach to ensuring consistency, however, is to base exposure estimates on measured concentrations of bioavailable forms of the substance of interest (Section 5.6.4). In such cases bioavailable concentrations must be determined in a similar fashion in field situations and in toxicological tests. For example, given an effects study that indicates harm to terrestrial plants grown in solutions containing high concentrations of a substance in dissolved form, field exposure should ideally be estimated based on dissolved concentrations in soil pore waters.

5.6.2 Use of Field Data

When assessing exposure to priority substances, available data on concentrations at regional scales, and near major points of release in Canada,

should be identified and used to estimate exposure to risk receptors. The reliability of key data should be evaluated based on the adequacy of sampling, analytical and data reporting methods, and its consistency with other relevant information (*e.g.*, data from similar areas elsewhere, or results of modelling studies).

> ***Box 5.15.*** *Quantification of Precision (P) at the 95% Confidence (2S) Level*
>
> Using data from the repeated analysis of a representative sample:
>
> $$P(\%) = 2S \cdot C^{-1} \cdot 100$$
>
> where C is the mean measured concentration in the sample, and S the standard deviation of the measured values. Multiplication by 100 converts the quotient to a percent. To achieve 95% confidence, the analysis should ideally have been repeated 30 or more times.
>
> The above was adapted from Fletcher (1981).

To permit evaluation of data quality, methods of sample collection, handling, storage and analysis should be described in adequate detail, either in the primary source or in an accessible cited reference. Methods used should follow accepted protocols (*e.g.*, CCME, 1993), and be adequate to avoid changes in chemical form (if chemical species are to be determined), contamination, or loss of analyte prior to or during analysis. For example, it is generally believed that to accurately determine background levels of most metals in surface waters it is preferable to use "ultra-clean" sampling and laboratory techniques (Nriagu 1994). Since such procedures were not applied in many studies undertaken prior to the early 1980s, much of the older data on background metal levels in waters must be interpreted with caution. Furthermore, recent studies of the effects of variations in sample filtration procedures suggest that worldwide averages for certain metals may be in substantial error due to filtration artifacts (Horowitz *et al.* 1992). Air drying of soil and sediment samples prior to analysis should be avoided, particularly when determining levels of volatile organic substances (which could be lost from the sample) and the chemical form of metals (because of changes caused by drying and oxidation)(Mudroch and Bourbonniere 1991).

Information on the accuracy (correctness), precision (reproducibility), and sensitivity (particularly limits of detection) of analyses should be available. Accuracy of measurements for a particular sample type (*e.g.*, water, sediment) can be evaluated by comparing results of analysis of certified reference materials (usually expressed as a mean of several determinations) to the certified values. Although less reliable, samples can be spiked with analyte (preferably immediately after collection) and the percent recovery determined. Precision (P) can be estimated by, for example, repeated analysis of one or more representative samples, or duplicate analyses of a subset of samples selected at random from those being analysed (Fletcher 1981). Precision data

may be represented graphically (Fletcher 1981), but are more frequently presented numerically (Box 5.15). Since analytical precision varies with sample matrix and the amount of analyte present, samples selected for precision estimation should be representative of the range of samples being analysed. Although the acceptability of results depends on the purpose of the study, in general when replicate analysis of a single sample are within 20% of the mean at approximately the 95% confidence level, precision is considered adequate. Less precise data may be acceptable in some circumstances, however.

Because analytical precision decreases as measured concentrations approach detection limits, reported values that are at or only slightly above detection limits are normally very imprecise (see data quality section of Appendix III). Generally, the sensitivity of an analytical method is adequate only if concentrations in most of the samples tested exceed detection limits. However, if analytical methods are very sensitive such that detection limits are lower than the Estimated No Effects Value (ENEV) for a particular risk receptor, a "not detected" result may be useful[11].

Selected locations and numbers of sampling stations, and times of sample collection, should permit characterization of the spatial (*i.e.*, geographic) extent, and temporal (*e.g.*, diurnal, seasonal) variations of exposure in areas expected (based on results of the pathways analysis) to be most severely impacted. Samples should also be obtained from appropriate control or "background" areas, for comparison. Fixed site monitors (*i.e.*, stationary devices capable of collecting samples periodically or continuously) may be established at locations where temporal variations in concentrations are expected to be significant (*e.g.*, near point sources of variable strength). The problem of spatial variation may be addressed by using either a random or systematic strategy for locating sampling stations. Ideally exposure estimates should be based on recent data (*i.e.*, no more than a few years old), but older data may be acceptable if they are believed to be: (i) accurate, (ii) amounts released have been stable over time, and (iii) substances are persistent and occur in media that are normally compositionally stable (*i.e.*, buried soils and sediments). Older data may also be used when estimating historic (*e.g.*, background) concentrations of a substance, or for a tier 1 risk analysis.

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[11] For example, if an ENEV is 1 $\mu g \cdot L^{-1}$, the detection limit is 0.1 $\mu g \cdot L^{-1}$, and none of the samples collected in an area of concern contain detectable concentrations of the substance, exposure information would be sufficient to indicate that harm to exposed organisms is unlikely.

As Covello and Merkhofer (1993) noted, limitations of the monitoring approach include:

- difficulty of collecting statistically meaningful samples of concentration values that capture the temporal and spacial variability of the natural environment,
- random variation make it difficult to distinguish trends, and
- technological limitations (*e.g.*, detection limits of analytical methods may be high).

Despite these limitations, uncertainties associated with monitoring data are generally less than those based on output from mathematical models. Furthermore, in situations where data quality is poor, additional monitoring can often be undertaken (time and resources permitting) to reduce uncertainties to acceptable levels. Thus, monitoring data are preferred when attempting to quantify exposure.

5.6.3 Use of Calculated Values

Models used to calculate exposure values can range from simple "exposure conversion" types, to large computer-based multi-media fate models. They can vary greatly, therefore, in their data requirements, costs, difficulty of use, types of output and accuracy. Care should be taken when choosing a model, to ensure that it is appropriate for the needs of the assessment.

EEVs may be calculated by applying simple exposure conversion models to empirical exposure data. For example,

- equilibrium models (see Appendix II) may be used to calculate concentrations of bioavailable forms of a substance,
- body burden values may be calculated as the product of measured concentrations in an exposure medium and a bioaccumulation factor (BAF), or
- total rate of intake may be calculated as the sum of measured concentrations in food, water and air, multiplied by consumption rates (*e.g.*, Table 5.7).

Monte Carlo or other simulation methods (see Chapter 8) may likewise be used when calculating EEVs by multiplying or dividing distributions of exposure parameters.

Fate and exposure models use information on the physical and chemical properties of a substance and parameters such as biodegradation, hydrolysis, and oxidation rate constants, combined with data on the amounts and mode of its release,

to calculate the amounts and concentrations of the substance in various environmental media. According to Fiksel and Scow (1983)(as cited in Covello and Merkhoffer 1993), factors that differentiate various fate models include, types of substances considered, environmental transport media, geographic scale, source characteristics, and time frame. Reviews of such models have been published by, for example, ECETOC (1992), Mackay and Paterson (1993) and Cowan *et al.* (1995b). Guidance on the selection of models for application to surface water, groundwater and air compartments has been prepared by the U.S. EPA (1987, 1988, and 1991).

Outputs of models may be very uncertain, and verification of model outputs is therefore normally required. Model outputs are only as good as the quality of input data, and the expressions used for describing the various partitioning, transport and transformation processes. Often there is overconfidence in the accuracy of the computed results and a lack of appreciation of the sensitivity of the results to errors or variation in the parameters used to build the model (Mackay and Paterson 1993).

Verification of model outputs may be difficult, especially for complex multi-media steady-state models. Problems that are encountered when verifying models against conditions in the natural environment include:

- natural temporal and spatial variability of concentrations in the environment,
- environmental monitoring data are usually available mainly for sites close to pollution sources, and averages calculated from such data tend to be higher than concentrations predicted by models,
- rates and amounts of substances released to the environment are rarely known accurately, and
- transportation and reaction rate constants represented by single values in models vary in the natural environment, and there may be significant uncertainties associated with their measurement.

When the quality or quantity of empirical data are limited, outputs from appropriate fate and exposure models may be used as part of a weight-of-evidence approach to quantifying EEVs. However, if there is insufficient empirical data of acceptable quality, outputs from exposure models should usually not be used as the sole source of EEVs. Exceptions may occur, however, particularly for tier 1 risk analysis, when exposure models are simple and uncertainties associated with calculated exposure values are small. An example would be a dilution model where a measured concentration in an effluent is divided by a dilution factor.

5.6.4 Determining Bioavailability

In this section the concept of bioavailability is first considered in general terms, after which specific recommendations are made for estimating exposure to bioavailable forms of substances.

Background

A substance is bioavailable if, under the conditions of exposure, it can be taken up by organisms. Bioavailability is usually quantified as the net concentration of bioavailable forms of the substance (the "effective" exposure) with which an organism is in contact. The bioavailability of a substance is determined by its chemical form, the physical and chemical characteristics of the media (*e.g.*, water, soil, food) in which it occurs, the receptor species, and the route of exposure (*e.g.*, dermal contact, ingestion, inhalation). Methods currently used to determine the bioavailability of both organic and inorganic substances have recently been reviewed by Hamelink *et al.* (1994).

In general it is the "free", dissolved, un-ionized forms of organic chemicals that are transported across biological membranes, and it is primarily these forms that are considered to be bioavailable (Mayer *et al.* 1994; Suffet *et al.* 1994). The bioavailability of hydrophobic (*i.e.*, nonionic and nonpolar) organic substances in natural waters (including porewaters in sediments and soils), is largely determined by their interaction with organic matter (often measured as total organic carbon or "TOC")(Gobas and Zhang 1994). Although a variety of physical and chemical factors can influence the bioavailability of ionizable organic compounds, pH is of particular importance because of its influence on the equilibrium between ionized and un-ionized species (Mayer *et al.* 1994).

For metals, it is the "free" or hydrated dissolved ions (*e.g.*, $Cu(H_2O)_x^{2+}$) that are normally considered to be the principal bioavailable forms (Newman and Jagoe 1994)[12]. However, oxyanions (*e.g.*, chromate or CrO_4^{2-}, and arsenate or AsO_4^{3-}) are also taken up by organisms (Benson *et al.* 1994), and there is evidence that some dissolved organic and inorganic metal complexes (*e.g.*, $AgCl^0$, CuOH-citrate^{2-}) are bioavailable (Campbell 1995). The concentration of "free" dissolved inorganic ions can be influenced by a variety of relatively complex chemical and biochemical processes. Key variables include ambient pH and pE conditions, as well as the nature of other dissolved and solid phases present. Once in the "free" dissolved state, bioavailability (*i.e.*, uptake by organisms) can be further influenced by factors such as concentrations of hydrogen and hardness (*i.e.*, calcium and magnesium) ions , as well as temperature

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[12] Some metals (*e.g.*, mercury and tin) can also form lipophilic organometallic compounds (*e.g.*, $(CH_3)_2Hg$) that readily cross biological membranes (Benson *et al.* 1994).

and salinity (Campbell and Stokes 1985; Mayer *et al.* 1994; Knezovich 1994; Campbell 1995).

Substances that occur in solid form (either in the pure state, or as an "impurity" in other substances) may become bioavailable if they are soluble under the conditions of exposure. In this context "solubility" is understood to be a function of both a substance's theoretical equilibrium solubility, and its rate of dissolution. Thus, a pure substance can have a high equilibrium solubility, but if it is inert and exposure is of limited duration, it may contribute little to the "effective" exposure. If the substance is present in small amounts in another material (*e.g.*, in food, or in a particular soil phase), "effective" exposure will vary with the stability of the matrix. Solubility is determined differently, depending upon the conditions of exposure. Thus, a substance that is not soluble in water but dissolves in acids, could be soluble in an acidic soil or in the gut after ingestion.

Estimating Concentrations of Bioavailable Forms of Substances

Exposure to chemical substances in the field is often estimated based on measured "total" concentrations, representing the sum of the concentrations of both highly bioavailable (*e.g.*, dissolved) and essentially non-available (*e.g.*, solid, relatively insoluble) forms. True "effective" (*i.e.*, bioavailable or bioactive) concentrations are in such cases unknown, although total concentrations do establish upper limits on "effective" exposure estimates. The difference between "total" and bioavailable concentrations may be negligible when, for example, the exposure medium is lake water containing little dissolved organic carbon or solid suspended matter, but it can be quite large (one to three orders of magnitude) when characterizing exposure in soils or sediments (*e.g.*, Freedman and Hutchinson 1980). Furthermore, results of studies with both organic chemicals and metals indicate that relationships between concentrations in soils and sediment, and biological uptake and effects are typically stronger when bioavailable as opposed to total concentrations are measured (Di Toro *et al.* 1991; Luoma 1983; Sillanpaa 1982).

Body burdens are the most accurate measure of "effective" exposure. This is because it is the accumulation of a substance at a sensitive target site within an organism which is responsible for harmful effects (McCarty 1987). Furthermore, as Landrum *et al.* (1992) noted, use of body burdens to quantify exposure avoids complications arising from uncertainties regarding bioavailability and accumulation processes. Therefore, it is recommended that body burden data be used where possible to characterize exposure. Unfortunately, toxicity data based on body residues are scarce, particularly for sub-chronic and chronic studies, and the toxicological significance of body burden data is therefore often unknown.

Since it is usually not possible to determine the dose at the target site(s) of

action, the concentration of a substance within the whole body of an organism may be used as a surrogate. Care must be taken, however, when estimating whole body burdens of metals, to ensure that measured exposures reflect internal and not surface accumulations. Plants, for example, should be carefully cleaned prior to measuring body burdens to ensure that all surface dust is removed (Morrison *et al.* 1974). Surface accumulations are of particular concern in the case of small organisms which have large surface areas relative to masses. Hare (1992) reported, for example, that from 2% to nearly 100% of the metal burden of whole aquatic insects was surface-bound, depending upon the metal and insect type. When possible, such surface accumulations should be removed prior to analysis by rinsing organisms in acid (Hare 1992). Even data on the internal metal content of organisms may not be indicative of potential to cause biological effects, however (Cain *et al.* 1995). Consequently, metal levels in cytosol are the preferred measure of internal exposure.

When tissue concentration data are lacking, values may be predicted using empirically derived regression equations (*e.g.,* Martens 1968; Tessier *et al.* 1984). These relate concentrations of the substance in organisms to levels in exposure media, and physical and chemical properties of the media such as pH, clay or organic matter content. However, caution should be used when applying such equations to organisms or environmental conditions that differ significantly from those for which the regressions were developed.

When body burden data cannot be used, it is recommended that exposure be estimated based on contact with dissolved and/or "soluble" forms of the substance (an exception may be made when evaluating "worst-case" exposure conditions for tier 1 risk analysis). Methods that can be used to measure or calculate concentrations of dissolved bioavailable forms of both organic and inorganic substances in different environmental media are described in Appendix II. Generally, estimates based on empirical data are preferred, but calculated values may be used if uncertainties are within acceptable limits. If concentrations of individual bioavailable species (*e.g.*, free aquo ions) cannot be estimated, the total concentration of all dissolved forms (based, for example, on analysis of filtered or centrifuged water samples) may be acceptable. "Corrections" for the presence of other dissolved substances that can influence uptake (*e.g.*, H^+, Ca^{2+} and Mg^{2+} ions) should be applied if appropriate (see Appendix II).

Exposure to "soluble" solid forms of metals and metalloids in sediment, soil, food and inhaled particulates can be measured using a variety of partial extractants (*e.g.*, water or cold dilute acids; see Appendix II) in the laboratory (Campbell *et al.* 1988; Pickering 1981). Extractants can be selected to approximate the conditions of exposure (*e.g.*, in soil porewater, or in the gut after ingestion), or to obtain information on concentrations of specific forms of the substance (*e.g.*, those adsorbed to the surface of solid particles). Because of the complexity of factors that can influence bioavailability of solid phases, the appropriateness of a given extractant must be

evaluated carefully. If concentrations of substances that alter bioavailability in these media (*e.g.*, acid volatile sulphides in sediment) are known, exposure data should be "corrected" (or normalized) for their presence.

When exposure is estimated as a net rate of intake, a bioavailability factor ranging from 0 to 1 may be applied to total intake values for each exposure medium (see footnote a, Table 5.7). Unless information indicates otherwise, the bioavailability factor for ingested and inhaled substances is usually assumed to be 1 (U.S. EPA 1992).

When available data do not permit quantitative characterization of bioavailable concentrations, an indication of relative bioavailability can sometimes be obtained from the physical and chemical properties of the exposure medium. For example, in water, soil or sediment, elements that exist in solution as cations (such as copper and zinc) will tend to be adsorbed less effectively and hence be more bioavailable in acidic than in basic conditions (see Section 5.3.2). Similarly in soils and sediments, the bioavailability of both organic and inorganic substances tends to decrease as organic matter (which is an effective adsorbing agent) increases. For ingested or inhaled solids (*e.g.*, dry soil or food) bioavailability is inversely related to the grain-size of the particles ingested or inhaled, because finer particles are more easily dissolved.

5.6.5 Treatment of Temporal and Spatial Variability [13]

EEV distributions may reflect both real spatial and/or temporal variability of exposure, as well as uncertainties associated with exposure measurements, and ignorance of true values for key parameters used in calculations (Hoffman and Hammonds 1994). General guidance on treatment of variability in EEVs arising from heterogeneity is presented here. A description of estimation methods for quantitative uncertainty analysis is presented in Chapter 8.

The measured maximum EEV, or the 98th percentile of EEV distributions based on a large number (*e.g.*, $\geq$1000) of values determined by Monte Carlo simulation methods, should be used as numerators in risk quotients for tier 1 risk estimates. For tier 2 risk analyses, the entire distribution of EEVs should be used. Whenever possible, for higher tier EEVs, spatial and temporal variations should be separated. In such instances, EEVs may take the form of frequency distributions that reflect the variability of exposures at the same time but at a different location, or at different times at a particular monitoring station. If sample locations were selected at random, and organisms are assumed to be uniformly distributed within the sampled area, EEV distributions representing spatial variability can be used to estimate the proportion of the population of risk receptors that are exposed at levels above the ENEV. If sampling

[13] This section is essentially identical to that in the Guidance Manual.

times were selected appropriately, temporal EEV distributions may likewise be used to estimate the proportion of time that exposure values exceed the ENEV at a particular monitoring station.

For discontinuous exposures, the timing, duration and frequency of exposure are important. Timing may be a key determinant of exposure for mobile organisms with seasonal migration patterns. In such cases, EEVs should be based on data for times when risk receptors are likely to be exposed to the substance.

Generally, exposure is characterized by estimating typical exposure values for specified time intervals such as a day or month. The length of time used to determine average exposure depends upon whether exposure is episodic or continuous, and upon the acute or chronic nature of the assessment endpoint. Short exposure integration periods are used when exposure is episodic or assessment endpoints are acute. Longer periods -- those of a month or more -- should be used with chronic endpoints.

If exposure values are based on infrequent sampling of mobile media such as air and river water, variations in intensity of sources, and flow and dilution characteristics must be considered when determining if such data are representative. EEVs for persistent substances that are based on one-time or short-duration sampling of relatively immobile media, such as soils and sediments, may often be assumed to represent longer exposure periods.

If samples were collected frequently relative to the preferred exposure integration period, typical exposure concentrations that are representative of the preferred time interval should be determined. This would apply, for example, if samples were collected monthly, and an integration period of a one year was considered optimal. Because of uncertainties about the shape of data distributions, medians should generally be used to estimate typical exposure values (Garrett 1991)[14]. If required for tier 2 uncertainty analysis, confidence limits may be estimated for medians (*e.g.,* Dixon and Massey 1969).

Tier 2 EEVs are often expressed as frequency distributions intended to reflect the variability of exposure of individuals within an exposed population at a specified time (U.S. EPA 1992). To determine the exposure of individuals when assessment endpoints are chronic, spatial variations in exposure values should be integrated (or at least averaged) over areas that correspond to the "home range" of individual organisms. Areas involved could be as small as a few m^2 for small immobile

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[14] In situations where the parent distributions are approximately normal, an arithmetic mean may be used. A geometric mean may be used for distributions that approximate lognormality.

organisms, or as large as 100s of km^2 for large mammals. In practice, however, such integration is usually not possible because of limited knowledge of the home-range of exposed individuals, and the limited sample densities of most field surveys. Consequently, tier 2 EEV distributions are typically based on "raw" or unaveraged exposure data. When interpreting EEVs based on such "raw" data it should be recognized that there will be a tendency to overestimate the proportion of a population that is exposed at concentrations above a selected effect threshold (Hattis and Burmaster 1994).

5.7 Apportioning Measured EEVs Among Identified Sources

When releases from sources other than those of concern may have contributed significantly to measured EEVs, it is desireable to apportion EEVs among identified sources. This step is required for tier 3 risk analysis, when contributions of natural and anthropogenic sources to exposure must be distinguished (Chapter 8).

Methods that may be used for source apportionment are described in Appendix III. They can be simple, such as comparing concentrations of a substance in an exposure medium to distance from a point source (*e.g.*, Freedman and Hutchinson 1980). In other cases, more complex mass balance models (*e.g.*, Gordon 1988), or specialized statistical or chemical methods (*e.g.*, Forestner 1983; Maenhaut *et al.* 1989) may be required.

Since there are large uncertainties associated with results of most source apportionment methods, several independent methods should be applied whenever possible, using a weight-of-evidence approach.

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6

Effects Characterization

6.1 Introduction

In the effects characterization phase, a *Critical Toxicity Value* (CTV) is determined for each assessment endpoint identified in problem formulation. The CTV is the quantitative expression of low toxic effect (*e.g.*, EC_{10}) on the measurement endpoint which is used to estimate toxicity to the selected assessment endpoint. All available toxicity information such as single species and multispecies toxicity tests is critically evaluated for their acceptability in terms of data quality (Appendix IV). Other possible supporting lines of evidence (*e.g.*, Equilibrium Partitioning Approach, QSARs) are also critically evaluated as part of the weight-of-evidence approach to determining CTVs. Only studies of acceptable quality are given further consideration. If at least one acceptable study for a measurement endpoint is not available for each assessment endpoint, additional data must be generated. Information from the dose-response curves from these studies are extracted to yield refined measurement endpoints (*e.g.*, EC_{10}). The measurement endpoint(s) indicating the lowest toxic effect that pertains to the selected assessment endpoint is then usually taken as the CTV. A CTV may be a point estimate for tiers 1 and 2, or take the form of a distribution (*e.g.*, $EC_{10} \pm 95\%$ confidence limits) if it is to be used in an uncertainty analysis (Section 8.2). During effects characterization, it may become apparent that the assessment and/or measurement endpoints originally identified are not appropriate. For example, if a more extensive literature search indicates that different organisms are more sensitive than previously believed. In such cases, the problem formulation would have to be revised and different endpoints identified.

In this chapter, the types of effects information that may be available for use in conducting risk assessments are discussed, including the advantages and limitations of single and multispecies tests, and the estimation of toxicity values using Quantitative Structure Activity Relationships (QSARs)(Section 6.2.5). Considerations for determining the acceptability of toxicity studies are outlined in Appendix IV. The aim of section 6.3 is to describe briefly how information is extracted from the dose-response curve and to recommend preferred methodologies for determining CTVs. The aquatic and terrestrial effects characterization sections (Sections 6.4 and 6.5, respectively) integrate information presented in previous sections and provide guidance on determining CTVs for assessment endpoints residing in these environmental compartments. Abiotic effects, such as tropospheric ozone formation and stratospheric ozone depletion, are discussed in section 6.6.

6.2 Types of Effects Information

Studies on single species, multispecies, ecoepidemiology, body burdens, quantitative structure activated relationships (QSARs), and the equilibrium partitioning method can all be used to characterize effects on the measurement endpoint(s) of concern. Evaluating data quality issues for these studies and investigating other supporting lines of evidence further reduce the uncertainty in determining the CTV (Appendix IV).

6.2.1 Single Species Toxicity Tests

Single species toxicity tests are designed to determine the effects of substances on organisms of a single species under specified test conditions. Such tests are required for obtaining information about the concentrations of substances and durations of exposure that cause changes in survival, reproduction, growth, physiology, biochemistry or behaviour of individuals within particular species (Cairns 1983). Biochemical or physiological perturbations may also have implications for population effects (Section 1.2). Such lower organization level effects include endocrine disruption (Colburn et. al. 1993), genotoxicity (Anderson et al. 1994) and immune suppression. Standard measurement endpoints are available for some of these examples (OECD 1993a; Kramer and Giesy 1995).

The usefulness of single species tests for predicting effects depends on the degree to which predictions can be extrapolated to natural systems with confidence, and the tests' replicability and reproducibility. These conditions affect the degree of statistical uncertainty surrounding the predictions (Cairns 1992).

Advantages of Single Species Toxicity Tests

Single species toxicity tests make it easier to determine the direct effects of varying individual test conditions. In the case of microcosm or mesocosm tests interactions among species or environmental components may mask the effects. For the greatest degree of confidence in the results, data should be generated using standardized test methods such as those referred to above. If other test methods are used, the procedures must be described in sufficient detail so that the reliability of the results can be evaluated.

Single species toxicity tests have generated an enormous toxicological data base for aquatic organisms (Cairns 1983). The standardized test methods developed by agencies such as Environment Canada, the United States Environmental Protection Agency and the Organisation for Economic Co-operation and Development enhance the likelihood of achieving reproducible results when single species tests are carried out by researchers in different laboratories. Examples of some of these test protocols

are listed in Section 6.4.1

Disadvantages of Single Species Toxicity Tests

Single species tests are unable to predict effects at higher levels of ecological organization under the complex conditions found in the environment. Complexities of population dynamics, such as age structure, density dependence and time delays can alter impacts at the individual level so that they become more or less pronounced at the population level. Characteristics of ecosystems such as changes in competition, predation, community function, ecosystem energy flow, and nutrient cycling cannot be predicted from single species tests (Cairns 1983). Unlike many microcosm and mesocosm tests, single species toxicity tests are not designed to integrate the simultaneous study of toxicity and various chemical transformation and partitioning processes.

Points to Consider

When using single species laboratory tests for assessing risk in the environment, the following points should be kept in mind. Variation may exist among species in physiological or biochemical factors such as uptake and metabolism that can alter the potential toxicity of a substance to a particular species. Inbred laboratory strains may have an unusual sensitivity or resistance to the tested substance that is difficult to predict. Behavioral and ecological parameters (*e.g.*, stress factors such as competition, seasonal changes in temperature or food bioavailability, disease, or exposure to other chemicals) can affect species sensitivity to a substance. These factors make it difficult to extrapolate the results of single species laboratory tests to field situations.

Many of these uncertainties associated with single species toxicity testing can be accounted for in the risk assessment by the use of application factors or by means of a quantitative uncertainty analysis (Chapter 8). Ideally, the results of a number of single species *and* multispecies toxicity tests would be available to the ecological risk assessor, because the two types of tests complement each other to present a more accurate characterization of effects of a substance on the environment than either type used alone.

The following lists some of the criteria for assessing the quality of single species toxicity tests (modified from Emans et al. 1993 and CCME 1995):

- Tests should employ currently acceptable laboratory practices (Appendix IV).
- A distinct dose-response relationship should be evident.

- In each experiment, several (*e.g.*, five) concentrations should be tested, including a control.
- Responses and survival of controls must be measured and should be appropriate for the life stage of the test species used.
- Each test concentration should have at least two replicates.
- Concentrations of the test substance should be measured several times during the experiment including at the beginning and end of the test to show that the desired concentration was maintained.
- Physical-chemical parameters such as pH, temperature, total organic carbon (TOC), and hardness should be measured.

6.2.2 Multispecies Toxicity Tests

Introduction

This section introduces some of the attributes of multispecies tests including microcosm, mesocosm and field tests. They can be defined as physical models that include in their design, ecological components such as species, functional groups, or habitat types, that simulate processes as they occur in nature (SETAC 1992). Some examples of the types of systems in use, the kinds of endpoints measured, and their usefulness are discussed. Finally, general guidance for the use of multispecies tests is provided for assessors intending to use published data or to generate new data.

A *microcosm* can range from a small laboratory-scale simulation of a portion of an ecosystem to a large outdoor tank. Typically, they are represented by bench top containers set up to model a soil profile, a sediment compartment or an aquatic environment (SETAC 1992). Microcosm-based tests are appearing in the literature in increasing numbers and a few examples of protocols for standardized multispecies test methods have been developed (see below). These include both aquatic and terrestrial systems.

Microcosms derived from littoral or shallow-water ecosystems are especially useful for experiments with substances. Littoral ecosystems are both ecologically important as major feeding areas for many fish and birds and vulnerable because they occupy a zone of high human activity (Giddings 1986).

Terrestrial microcosms can be made from mixed cultures of organisms and artificial substrates (Asumus *et al.* 1980). They may also be made from intact portions

of the ecosystem by extracting this material using a soil-coring device. Intact soil microcosms are believed to be an improvement over other test systems because they preserve ecosystem level interactions such as nutrient cycling processes and plant/microbial interactions. They also maintain soil microsite chemistry (Gilfillan 1965). The most common type of soil microcosm is described as the soil core method (Van Voris *et al.* 1985). The soil core method uses a small diameter (8-10 cm) intact plug of the soil column as a test system.

A *mesocosm* is a simulated part of the environment used as a test system for predicting the fate and effects of substances at a scale ranging between laboratory microcosms and large, complex, natural ecosystems (Grice and Reeve 1982; Odum 1984). In general, mesocosm tests are performed outdoors, and may consist of an elaborately controlled environment or nothing more than an enclosed area in a field or pond. Overall, mesocosms are better than microcosms at approximating natural ecosystems (Taub 1985).

Several aquatic mesocosm test protocols have been described in the literature for various test purposes. For example, one was developed for pesticide product registration in the United States (Touart 1988). Mesocosms are large enough to support several trophic levels including populations of predators and prey. Using the same example, a finfish is included that feeds on algae at its juvenile life stage, and on invertebrates or insects at its adult stage. Mesocosms, such as Touart's (1988), can occupy an area of 0.1 acres (405 m^2) and a maximum depth of 2 metres. The sides should be sloped to provide a littoral area for macrophyte growth and fish reproduction. Aquatic field tests in general follow the same conditions as aquatic mesocosms, but usually on a larger scale.

Terrestrial mesocosms have been used for several decades. In 1966, an experiment in an acre-sized field at the University of Georgia was conducted. It involved a community-level study of the effect of an acute insecticide on a cultivated field of millet. Special attention was made to arthropod guilds and small mammals (Barrett 1968). Terrestrial enclosures up to an acre in size are the most common dimension and description for this scale of modelled ecosystem.

Field tests and mesocosms may be similar in definition and purpose, and will be discussed together below. Originally, larger mesocosms were referred to as field tests. Field tests normally involve the isolation of terrain or part of a body of water. They contain the normal flora and fauna that would be found under unperturbed conditions. Variables, such as nutrients or substances, are added in a controlled manner to examine the impact on the populations found within the test areas.

Advantages of Multispecies Tests

Ecologists and toxicologists have recognized the weakness of using single-species tests alone for assessing potential ecosystem impacts (Cairns 1981). Multispecies test designs have incorporated various features to provide a system that integrates both fate and effects processes (Harrass and Sayre 1989). Field studies can be used to confirm whether predicted fate, chronic effects, or bioaccumulation actually occur under reasonably realistic field conditions, and may also be used to reveal secondary effects that can result from species interactions (OECD 1995a). Multispecies tests are useful for demonstrating ecosystem recovery processes following a spill or stress, and as a method to rank substances based on ecosystem impacts (Harrass and Sayre 1989). They may be particularly useful tools in the ecological assessment of complex mixtures and effluents (Chapter 7).

Multispecies test systems offer an isolated area of the ecosystem that can be experimentally perturbed to measure the extent of the effect of a disturbance. Multispecies test systems allow testing of hypotheses, describe the role of key species, and reveal the basic properties of the whole ecosystem (Odum 1984). Multispecies tests therefore have an advantage over single species laboratory studies because they can simultaneously provide a better insight into direct and indirect effects, routes of exposure, and various chemical transformation and partitioning processes under natural or near-natural conditions (Cairns and Mount 1990; U.S. EPA 1992a).

Disadvantages of Multispecies Tests

Microcosm experiments, like single species tests, are not globally sensitive to all stresses. When microcosms lack appropriate target species for substances with specific modes of action, little effect will be detected (Pratt *et al.* 1993). Toxicity to individuals (as measured by single-species tests) is not always reflected in toxicity to populations, and population interactions tend to dampen responses at the community level (Koojiman 1985).

Kersting (1984) notes that there are difficulties in reproducing results because complex interactions can vary randomly from one system to another. This means that results may be highly variable, so that meaningful differences are often obscured.

Microcosms require a period of stabilization for component species, especially if they have been assembled artificially (Kersting 1984; Mothes-Wagner *et al.* 1992). Problems of scale, created by lack of habitat variability, high surface area to volume ratio (edge effects) and container size (wall effects) can also be significant (Giesy and Alred 1985). Artificial communities tend to be less complex and variable than natural ones (Giesy and Alred 1985). Natural communities are often difficult to sustain in an

artificial arrangement and there may be extinctions, and changes in community structure, irrespective of substance exposure (Buikema and Voshell 1993).

Multispecies tests can be costly to set up and run. A full-scale field study may cost three to four times as much as a single species toxicity test or a soil core microcosm test (Van Voris *et al.* 1985).

Field tests may be hampered in their execution because of uncontrolled situations such as meterological conditions or disruptions due to interference from unwanted pests or other natural events (U.S. EPA 1992a). Although they may add realism to the modelled or enclosed environment, they can be disruptive to the experimental results.

Points to Consider

Multispecies tests are still models, and accordingly, projections to natural ecosystems must be made with great caution (Odum 1984). Most of the same precautions and considerations that apply to terrestrial mesocosms apply to field tests as well.

Emans *et al.* (1993) presents the following general criteria for assessing the quality of multispecies toxicity tests using freshwater systems, although they are also applicable to terrestrial systems:

- A distinct dose-response relationship should be evident.
- Several taxonomic groups in natural or nearly natural ecosystems should be exposed to at least one test concentration for a longer period.
- In each experiment, several (*e.g.*, five) concentrations should be tested, including a control and at least two test concentrations.
- Each test concentration should have at least two replicates.
- Concentrations of the test substance should be measured several times, including at the beginning and end of test.
- Physical-chemical parameters such as pH, temperature and hardness should be measured.
- Measurement endpoints at higher levels of organization such as diversity and species richness should be measured as well as endpoints at lower levels such as population density and biomass.

Harrass and Sayre (1989) suggest that acceptable multispecies test data include three key features: *credibility, applicability* and *endpoint interpretability*. Assessors should ensure that these features are found in any multispecies test protocol used to generate data for an assessment.

- *Credibility.* The protocol should have developed past the research stage to where a recognizably consistent procedure is used. Endorsement of the protocol by members of a standards-setting organization such as the American Society for Testing of Materials (ASTM) also contributes to the credibility of a protocol.

- *Applicability.* When the potential impacts of concern can be expressed only when ecological interactions are present, microcosm test methods may prove a more efficient approach to data collection than other available test methods. Secondly, when available information suggests that a wide variety of ecotoxicity information will be needed, microcosm tests could prove efficient at providing data on a large number of species, tested under similar exposure conditions (Harrass and Sayre 1989). The usefulness of these test systems in an assessment context depends on the extent that the test system simulates environmental intricacies and interactions on a small scale (U.S. EPA 1992a).

- *Endpoint Interpretability.* A protocol should produce results that relate to meaningful and reasonably measurable endpoints. Two types of endpoints have been identified for ecosystems: structural and functional. Structural elements of an ecosystem are those based on populations such as species presence, organism densities, biomass, or relative abundance patterns (Sheehan 1984). Functional elements are those based on material and energy movement throughout an ecosystem such as primary productivity, decomposition and nutrient cycling (Sheehan 1984).

6.2.3 Ecoepidemiology

Introduction

Ecoepidemiology attempts to determine the causes of observed effects in the field by examining spatial and temporal relationship between these effects and suspected causal agents (*i.e.*, PSL substances). Effects of concern include diseases in individuals and populations, disturbances in communities, and disruptions of ecological systems. In most risk assessments, laboratory toxicity data are used to predict adverse effects on the environment, whereas ecoepidemiology starts with observed field effects and attempts to identify causes.

Ecoepidemiology was used in the assessment of several substances on the first Priority Substances List. For example, biological surveys upstream and downstream from Canadian municipal waste treatment plants showed that chlorinated wastewater effluents caused changes in benthic community structure (*e.g.*, reduction in diversity, shifts in species composition)(Environment Canada and Health and Welfare Canada 1993). Reproductive failure and anomalies in fish-eating birds on the Great Lakes and on the west coast of Canada correlated strongly with levels of polychlorinated dibenzodioxins and polychlorinated dibenzofurans in eggs and adult tissues (Environment Canada and Health and Welfare Canada 1990). Damage to trees in Germany and Finland was cited as evidence of risk to the environment posed by tetrachloroethylene (Environment Canada and Health Canada 1993).

Advantages

Ecoepidemiology provides a method for tracking down likely causes of observed environmental effects. Evidence assessed using epidemiological criteria may be used in conjunction with other laboratory-derived information to determine the potential of priority substances to cause harmful effects. According to Suter (1993a), causality is established by demonstrating concordance between the findings of real but uncontrolled observational studies and controlled but somewhat unreal toxicity tests. This linkage is provided by indicators of exposure and diagnostic effects. Evidence that the same mechanisms are at work in laboratory tests and field observations provides further support of common causation. The desirability of multiple lines of evidence must be recognised. Suter states that the goal of assessments is not to establish scientific truth, but to establish a sufficient body of evidence to allow a decision, or to establish the conclusion most supported by the preponderance of evidence.

Ecoepidemiology may prove especially useful in assessments of complex mixtures since direct cause and effect relationships are difficult to determine in the laboratory (Chapter 7). Confidence in causal relationships can be increased by careful selection of reference sites and evaluation of changes along a concentration gradient where differences in other environmental factors are minimized (U.S. EPA 1992b).

Statistical associations derived from well-controlled experimental studies can aid in establishing causal relationships even when the causative agent has not been demonstrated conclusively. Decisions may also be made on the basis of observational evidence alone. For instance, cigarette smoke has been identified as the contaminated vehicle that is associated with increased rates of lung and other cancers, and heart and respiratory disease. It was not necessary to identify precisely which component in the smoke is the prime offender before instituting preventative measures.

Disadvantages

It must be kept in mind when using ecoepidemiology that there are a number of confounding factors that can obscure the effects of the substance under investigation, including differences in habitat quality between areas, natural variations in environmental parameters within areas, the possible occurrence of other, perhaps undetected, stressors, and the possibility of movement of organisms into or out of the study area (U.S. EPA 1992b).

The results of ecoepidemiology will often be inconclusive, and the best that can be expected is to reach the most reasonable explanation based on the evidence at hand. In ecoepidemiology, most studies are observational, and experiments to confirm cause-effect relationships may be difficult or impossible to carry out.

Points to Consider

Ecoepidemiology has the same basic principles as epidemiology. The following criteria are adapted from Fox (1991) and can guide assessors in objectively assessing the relationship between a suspect substance and an adverse environmental effect.

- *Time Order.* Does exposure to the substance precede the effect in time? This may be difficult to establish in systems with little historic data. The timing and nature of initial events are often obscure, and long latency periods may exist between exposure and effect.

- *Strength of the Association.* Do cause and effect coincide in their distribution? Is the prevalence or severity of the effect in exposed populations large relative to unexposed populations when matched for age, gender, calendar period, etc.?

- *Specificity of the Association.* Is there an association between specific populations or particular areas and the effect? The uniqueness of the effect strengthens one's confidence in causality. Could the effect be due to a different cause? Could the proposed cause produce other effects? In locations where multiple perturbations are present, for instance in the Great Lakes, specificity may be complicated by interactions, commonality of modes of action and interspecific differences in sensitivity.

- *Consistency of the Association.* Has the association been repeatedly observed in different places, circumstances, times and species, or by other investigators with different research designs and objectives? Exact replication is not generally available to the ecoepidemiologist, and in many cases a variety of repeated studies may also be impossible (*e.g.*, repeating the undefined exposures that occurred at Love Canal). In ecoepidemiology, the occurrence of an association

in more than one species or population is very strong evidence for causation.

- *Coherence of the Association.* Is the cause-effect interpretation consistent with our current understanding of the biological mechanism(s) underlying the effect? Is an exposure-response relationship evident? Do remedial actions lead to altered frequency or severity of the effects? Do controlled studies of animal models using the methods of different bioscience disciplines or studies of free-living wildlife support the proposed relationship?

- *Probability.* Statistical significance may help decide how much attention to give a particular result. However, "lack of statistical significance gives quantitative but not logical grounds for rejecting an epidemiological hypothesis. Before rejecting an hypothesis, statistical power must always be considered" (Susser 1986). Statistical power is the probability of statistically detecting an effect that is present in nature. By trying to minimize the chance of making acceptance errors, scientists inadvertently increase the chances of failing to detect real effects (rejection errors), some of which may be harmful or costly (see glossary for definitions of Type I and Type II errors, and power of the test). The design of the test and sample size determine statistical power and the probability of negative results.

- *Predictive Performance.* An hypothesis drawn from an observed association is able to predict a previously unknown fact or consequence. Is there concordance between well-conducted field observations and controlled laboratory toxicity tests? Predictive performance is a strongly affirmative criterion, particularly when it produces new knowledge.

These criteria do not provide proof of an environmental cause and effect relationship, but they do provide a process and framework on which to build a balanced judgement. Of these criteria, only four: strength, consistency, predictive performance, and statistical coherence (monotonic dose-response relationship) strongly affirm causality. Similarly, only incompatibility on the basis of time order, factual implausibility, and lack of consistency upon replication, detract from causality sufficiently to reject a causal hypothesis with confidence.

6.2.4 Critical Body Burden (CBB)

Introduction

Body burden is the total amount of a substance an organism has taken up from all sources over time and retained in the body. Critical body burden (CBB) is the minimum tissue concentration of a substance that causes an adverse effect on the measurement endpoint, the reproductive potential of *Daphnia*, for example (adapted

from ECETOC 1995).

Traditionally, results from acute and chronic toxicity tests are typically expressed in terms of the concentration in the external medium associated with the biological response of interest (ECETOC 1995; Environmental Management Associates 1994). There are limitations to this approach, however. These include difficulties in determining the bioavailable fraction of the environmental concentration (Section 5.2.3), and determining total exposure when there are multiple uptake routes, pulsed exposures, non-steady-state exposure or substance transformations (Landrum *et al.* 1992).

From a physiological perspective, it is the concentration of a substance at the site of toxic action within the organism that determines whether a response is observed, regardless of the external concentration (McCarty 1991). The exact concentration of a substance at the site of toxic action within individual cells or tissues is difficult to measure or the site may not be known. By measuring whole-body residues (CBB) in organisms showing an adverse effect, such as death in lethality tests, it may enable concentration-response relationships to be replaced with dose-response relationships. This latter relationship more accurately describes the dynamics of toxic action (McCarty 1991). Therefore, CBB provides a reasonable surrogate for residue concentrations at the site of toxic action.

Advantages

For hydrophilic compounds with a log $K_{ow} < 1.5$, the bulk of the substance resides in the water phase, so CBBs are expected to be similar to the LC_{50} concentrations (McCarty *et al.* 1992). There is a high correlation between CBBs and results of traditional toxicity tests based on water concentrations.

The CBB method can be used for a number of different types of organisms for narcotic substances. Research on narcotics, mostly using fish, suggests that adverse effects occur when the CBB is reached in the organism (McCarty 1991; McCarty *et al.* 1992; McCarty and Mackay 1993). CBBs of less than 0.5 $mmol \cdot kg^{-1}$ at death indicate a specific mechanism of action, whereas a body burden between 0.5 and 2 $mmol \cdot kg^{-1}$ is indeterminate with respect to mechanism of action (McCarty and Mackay 1993). For non-lethal endpoints, lower values can be expected. For example, using growth in mussels as the endpoint gave a measured CBB value of 4 $\mu mol \cdot kg^{-1}$ (Donkin *et al.* 1989). Measured data for acute exposures indicate that CBBs between 2 to 6 $mmol \cdot kg^{-1}$ resulted in 50 per cent mortality for small fish and invertebrates (McCarty 1991). Estimated body burdens vary by a factor of 3-4 compared to acute LC_{50}s that range over five orders of magnitude for the same compounds (McCarty 1991; McCarty *et al.* 1992). Some recent data on terrestrial earthworms exposed to two chlorobenzenes agree with measured data (*i.e.*, LC_{50}) for fish (Belfroid *et al.* 1993).

CBBs can be used to assess the toxicity of mixtures that have the same mode of toxic action and are well characterized (Chapter 7). McCarty (1986), McCarty *et al* (1992) and Abernethy *et al* (1988) suggest that narcotics are essentially of equal strength on a molar residue basis and, therefore, the toxicity of mixtures of these substances is additive. Based on this additivity theory, Gobas (1992) suggests that acute lethality occurs if the sum of the substance concentrations in the organism reaches the threshold level. Since many of the major high-volume organic chemicals are largely narcotic in nature, toxicity from this mode of action has the potential to be assessed and managed as the sum of the contributing substances (McCarty and Mackay 1993).

The CBB concept can also be applied to metals. For example, concentrations of metals in tissues of terrestrial plants are often used to assess potential for toxic effects (Kabata-Pendias and Pendias 1992). In the assessment report for Cadmium and its compounds (Environment Canada and Health Canada 1994), critical cadmium concentrations in ungulate kidneys were identified above which adverse effects were expected.

Disadvantages

The lipid content of an organism is a major modifying factor affecting the body burden of many substances in an organism. For organisms with high lipid content, lipophilic substances may be disproportionately higher in the lipids than at the target site. Under these circumstances, using CBB as a surrogate for the target site(s) of action may overestimate the concentration at the target site(s) of action. Assessors should carefully consider the lipid content of organisms being monitored and give preference to results with organisms of low lipid content[1] unless residue concentrations at the site of toxic action can be determined (McCarty and Mackay 1993).

Strong evidence for CBBs of organic substances has been shown for acute toxicity of narcotics. CBBs may be very different for substances acting by different mechanisms, but are probably for substances with the same mode of action. McCarty and Mackay (1993) estimated CBBs for organic substances in fish for several modes of toxic action. These include narcosis, polar narcosis, respiratory uncoupler, acetylcholinesterase (AchE) inhibitor, membrane inhibitor, central nervous system convulsant, and respiratory blockers. Different classes of toxic action appear to be associated with different CBBs, but the ranges within several classes span two or three orders of magnitude.

There are many confounding factors to be considered when applying the CBB

[1]Less than 10% lipid content.

method to metals. Care must be taken when interpreting whole-body data on metals to ensure that surface contamination of the organism has not significantly contributed to measured body burdens (see Section 6.4). This is particularly important for small organisms in which the body surface area is large compared to the body volume. Preliminary data compiled by McCarty and Mackay (1993) suggests that CBBs might vary widely from metal to metal, and are likely to be very different for metals that are micronutrients (*e.g.*, copper) than for those that are not (*e.g.*, lead). For example, in a study of chronic lethality in the benthic crustacean *Hyalella azteca* exposed to cadmium, addition of chelating compounds increased the EC_{50} by as much as 35 times, while CBBs changed only 16% (38-44 $\mu g \cdot g^{-1}$). Alteration of the EC_{50} due to changes in water hardness (10x) or addition of sediments (1000x) changed the CBB by a factor of about two (Borgmann *et al.* 1991). On the other hand, CBBs in rainbow trout exposed to arsenic were temperature-dependent, possibly because the dominant form of the metal changed as temperature increased (McGeachy and Dixon 1990).

Point to Consider

- The dose (or CBB) at the target site(s) of action can provide a more direct measure of a predicted adverse effect than an external exposure concentration since problems associated with estimating bioavailability and accumulation, are essentially eliminated (Landrum *et al.* 1992).

- Since it is usually difficult to determine the dose at the target site(s), the total body burden (CBB) of a substance within an organism may be used as a surrogate for the dose at the target site(s) of action assuming equilibrium between compartments within the organism.

- Research on narcotics, mostly using fish, suggests that acute toxic effects occur when a CBB of ≈2-6 $mmol \cdot kg^{-1}$ is reached in the organism.

- The CBB concept can also be applied to metals.

- CBBs may be used to assess the toxicity of mixtures, if the substances in the mixture act by the same mode of action and are well characterized.

- To date, sufficient evidence for CBBs of organic substances has been found only for acute toxicity of narcotics in aquatic organisms, and much more research is required before the general applicability of the concept can be determined. However, if body burden information is available, assessors should use the information along with more traditional toxicity information in conducting the effects characterization.

- When possible and appropriate, body burden data should be summarized and

compared to tissue residues (body burden) data collected in the field. This information may be used as the basis for the risk assessment or as part of the overall weight-of-evidence.

6.2.5 Quantitative Structure Activity Relationships (QSARs)

Introduction

Quantitative structure activity relationships (QSARs) are estimation methods used to predict the effects of chemical substances and are based primarily on the structure of the substance (CEU 1995). QSARs were originally developed as statistical models relating biological activity to chemical structure. QSAR models are now available for a number of endpoints required for ecological risk assessment, including aquatic and terrestrial toxicity endpoints. QSARs have been used to evaluate data, determine the need for additional research, rank chemicals, and estimate biodegradation, bioaccumulation, exposure, and toxicity.

QSARs are based on comparisons of the toxicity of a chemical with the chemical structure or physical and chemical properties using a number of analytical models (Hermens 1989). Toxicological QSARs have three components (Turner *et al.* 1987). These are chemical structure descriptors--hydrophobicity, electronic and steric effects and structural and topological indices-- biological activity, and the technique used to derive the relationship between these parameters such as simple graphical plots, regression analysis.

A number of national and international programs have carried out evaluations of QSAR models including the Commission of the European Union (CEU 1995), the U.S. EPA (U.S. EPA 1994a), and jointly by the U.S. EPA and CEU (OECD 1995b). The QSAR models generated by the CEU have undergone critical evaluation and the accuracy quantified. Results of the U.S. EPA/CEU joint project concluded that the QSAR models used for predicting ecotoxicity to fish and *Daphnia* performed well in estimating toxic effects. Table 6.1 lists five QSARs recommended by the CEU (1995) to predict a range of effects on aquatic organisms. These QSARs are based on the octanol-water partition coefficient (Kow) as the descriptor variable and they can be applied to substances that act by a non-specific mode of action known as narcosis. In principle, any substance can act as a narcotic, therefore, the QSARs presented in Table 6.1 are considered to predict a minimal toxic effect (OECD 1992a). The general group of substances that act by narcosis include the aliphatic and aromatic hydrocarbons (CEU 1995). A scheme has been developed by Vehaar *et al.* 1992) that enables an assessor to assign substances to the class of narcotics based on their structural characteristics. The assessor is encouraged to refer to Verhaar *et al.* (1992) for specific, detailed guidance on how to classify a certain compound (*i.e.*, has a log K_{ow} between 0 and 6; a molecular mass (MW) of not more that 600 Daltons; includes only

Table 6.1 Selected QSARs for aquatic toxicity[a].

Endpoint	*QSAR*
96 hour LC_{50} fish (fathead minnow)	-1.41 - 0.85($\log K_{ow}$)
48 hour EC_{50} *Daphnia magna* immobilization	-1.19 - 0.95($\log K_{ow}$)
72 hour EC_{50} algae growth	-1.23 - 1.00 ($\log K_{ow}$)
28 day NOEC (zebra fish and fathead minnow)	-2.35 - 0.87($\log K_{ow}$)
21 day NOEC *Daphnia magna* growth and reproduction	-1.70 - 1.04($\log K_{ow}$)

[a] From CEU (1995)

organic compounds that consist of carbon, hydrogen, nitrogen, oxygen, sulphur and/or halogens (excluding iodine), etc.).

The QSARs listed in Table 6.1 are externally validated and, when applied correctly, can help the assessor to estimate and determine the most sensitive species for the selected substance (CEU 1995). Guidance is provided for this select group of substances because it is the only group of substances for which reliable QSARs are currently developed.

The U.S. EPA has developed a program known as ECOSAR that uses QSARs to estimate the toxicity of industrial substances (U.S. EPA 1994a). ECOSAR contains over 100 QSARs for 40 chemical classes to predict acute and chronic toxicity to fish (both fresh and saltwater), water fleas (daphnids), green algae, and a 14 day LC_{50} for earthworms in artificial soil. Approximately 50% of QSARs are for neutral organic chemicals; the remainder are for discrete organic chemicals such as esters, amines, phenols, anilines, or aldehydes. QSARs available from the U.S. EPA ECOSAR program are listed in U.S. EPA (1994a).

TOPKAT, developed by Health Designs, Inc. (HDI 1990), uses structure-activity relationships and statistical techniques to estimate various effects of substances, including *Daphnia magna* EC_{50}, fathead minnow LC_{50}, and aerobic biodegradability.

Advantages

QSARs can be used in the ecological risk assessment process in a number of ways, including: (i) providing justification for additional testing, (ii) making preliminary estimates of toxicity of a substance, and (iii) validating existing empirical data.

Disadvantages

QSARs are developed on the assumption that for all substances that interact by the same mechanism with target sites, the effects depend on the same principal properties of the chemicals. Different mechanisms of interaction will depend on different chemical properties, therefore, different QSARs must be developed for each mode of action. As a result, QSARs can only be applied successfully for substances that interact according to the presumed underlying mode of action.

Points to Consider

For QSARs that are to be used in the risk assessment process, the endpoint estimated from the QSAR must be compatible with the assessment endpoint identified in the problem formulation. Validation of a QSAR model involves comparing experimental data for various chemicals to QSAR predictions with the result being a validated QSAR if there is agreement between measured and calculated values (OECD 1993b; OECD 1995b). QSARs selected for use in the assessment should be critically evaluated by experts or by the assessor, if the assessor has considerable expertise in the field of using QSARs. The principles advocated by the CEU (1995) for the selection and use of QSARs should be followed.

Assessors dealing with QSARs that have not been critically validated must be aware of the uncertainties associated with the selection of parameters and the appropriate models. Errors in model selection may result in errors in toxicity estimates (OECD 1992a). QSARs always have limitations and it is important to know and respect them for each model. Assessors should use the following criteria when selecting ecotoxicity QSARs that have not been critically evaluated (OECD 1992a):

- The substances of interest and those used in the model should be similar in terms of structure and mode of action.

- The model should be validated in terms of range of application and predictive capability. This can be done by comparing experimental and predicted biological data for substances not included in the model development.

- Relevant statistical methods should be used to evaluate the data and the statistical significance of the model. For example, the correlation coefficient (r) indicates the validity and accuracy of the model. The statistics will also include the estimated standard deviation of the prediction errors and the standard error of the estimate(s). The F-test is suitable for testing the significance of individual descriptors and the significance of improving the correlation by adding more chemical descriptors to the equation (Hermens 1989).

- The data used to develop the QSAR should be described or referenced (*e.g.*, information about the test species, soil type, etc.).

- A detailed description of the domain of the model should be stated. This includes the structural rules defining the group of substances and the ranges of the model parameters for which the model is valid.

- The descriptors used in the QSAR model should be defined, and should not be correlated with other descriptors. The model should reflect the process being described by the QSAR, *(i.e.*, the physical/chemical and/or biological interactions) and the technique used to generate the model should be reported.

6.2.6 Equilibrium Partitioning (EqP) Method

Introduction

The equilibrium partitioning method of effects estimation calculates effect levels for organisms dwelling in sediments and soils, using empirical data for effects of dissolved substances on water-column organisms. To do so, it assumes that water-column organisms and those in other compartments are equally sensitive to substances, and that chemical equilibrium has been established among all phases of contaminated media.

This method has been used, most often, to calculate effects levels for sediment-dwelling (*i.e.*, benthic) invertebrates (Di Toro *et al.* 1991). The method has been proposed for use to estimate sensitivities of soil-dwelling organisms (CEU 1995), and could in principle be applied to groundwater organisms. At present, this method is routinely used only for hydrophobic, nonpolar, nonionic organic substances, although its applicability to other types of substances (*e.g.*, metals) has been investigated (Di Toro *et al.* 1990; Suter 1993a).

Advantages

Because of the assumption of equal sensitivity, effects concentrations for sediment- or soil-dwelling biota (for which data are often not available) can be determined using toxicity data for water-column organisms (for which data often are available). For example, a CTV based on effects of a dissolved substance on *Daphnia* (CTV_d), may be assumed to be applicable to dissolved concentrations in sediment porewaters to which benthic invertebrates are exposed. Justification for this assumption is greatest when test organisms and those selected as assessment endpoints belong to related taxonomic groupings (*e.g.*, invertebrates).

Because of the assumption of chemical equilibrium, if the concentration in any

one phase (porewater, solids, or biota) is known, concentrations in the other phases can be calculated. Therefore a CTV_d applied to porewater, for example, can be converted to a solid phase CTV_s value for bulk soil or sediment if the mass fraction of organic carbon in the solid phase (f_{oc}), and the substance's organic carbon partition coefficients (K_{oc}), are known (Di Toro *et al.* 1991). That is,

$$CTV_s = f_{oc} \cdot K_{oc} \cdot CTV_d$$

For example, if a CTV_d is 10 $\mu g \cdot L^{-1}$, the K_{oc} is 1000 $L \cdot kg^{-1}$, and the f_{oc} of the solid phase is 0.1 (*i.e.*, the solid phase is composed of 10% organic carbon), the estimated CTV for the bulk phase, CTV_S, is 1000 $\mu g \cdot kg^{-1}$. If the K_{oc} for a substance is unknown, it can be estimated from measured octanol-water partition coefficient (K_{ow}) values by assuming that $K_{oc} \approx K_{ow}$ (Di Toro *et al.* 1991).

Disadvantages

The main disadvantage of the EqP method of effects estimation is the large uncertainty associated with its assumptions (Chapman 1989). The method assumes that chemical equilibrium between porewater and the organic carbon fraction of solid phases has been established. As Suter (1993a) noted, the validity of this assumption can be questioned, particularly for surface soils subject to wetting and drying and freeze-thaw cycles. As described by Di Toro *et al.* (1991), the EqP method of effects estimation makes two additional assumptions:

- The concentration of the substance in biota resident in the medium (*i.e.*, a contaminated sediment, soil, etc.) is in equilibrium with concentrations in the aqueous and solid phases.

- Water-column organisms, and organisms in the contaminated medium are equally sensitive to the substance.

The method has also been criticized because of the assumption that dermal contact is the primary route of exposure and, therefore, that exposure via ingestion of solid phases is not adequately addressed (Chapman 1989). Calculations by Landrum and Robbins (1990) suggest that ingestion is the primary route of exposure for benthic invertebrates, when substances have log K_{ow}s above about 4.5. According to Di Toro *et al.* (1991), however, route of exposure is irrelevant when applying this method since, at equilibrium, a substance's fugacity (or escaping potential) is identical in both porewater and solid phases, and therefore its availability for uptake by organisms should be the same regardless of whether exposure occurs from contact with porewater or ingestion of solids. Because of concern about underestimating the importance of the ingestion pathway, CEU (1995) has recommended that calculated effect values should be interpreted with particular caution for substances that have a log $K_{ow} > 3$ (*i.e.*, $K_{ow} >$

1,000).

The EqP method should only be applied to solid phases in which f_{oc} is larger than 0.002 (*i.e.*, those containing over 0.2% organic carbon), since when f_{oc} is less than 0.002 factors other than organic carbon begin to significantly influence the partitioning of hydrophobic substances (Di Toro *et al.* 1991).

Points to Consider

Given the numerous assumptions made when applying the EqP method of effects estimation, and the fact that field validation of effects predictions based on EqP is still in progress (Adams *et al.* 1992), effects values calculated using this method should be considered as provisional, screening values only. Such data may be used as part of a "weight-of-evidence" argument for selecting a particular CTV, but they should normally not be used as the primary source of evidence for such a value.

6.3 Deriving Critical Toxicity Values (CTVs)

The dose-response curve is the graph describing the response of individuals, populations or other biological systems to a range of doses of a substance. For simplicity, the definition of dose in this section is broadly defined to include concentrations of a substance in the exposure medium. Generally, the percentage of organisms responding or the magnitude of effects at each dose is plotted. The distribution that typically results is the sigmoid-shaped curve (Figure 6.1A). This section briefly describes how information is extracted from the dose-response curve.

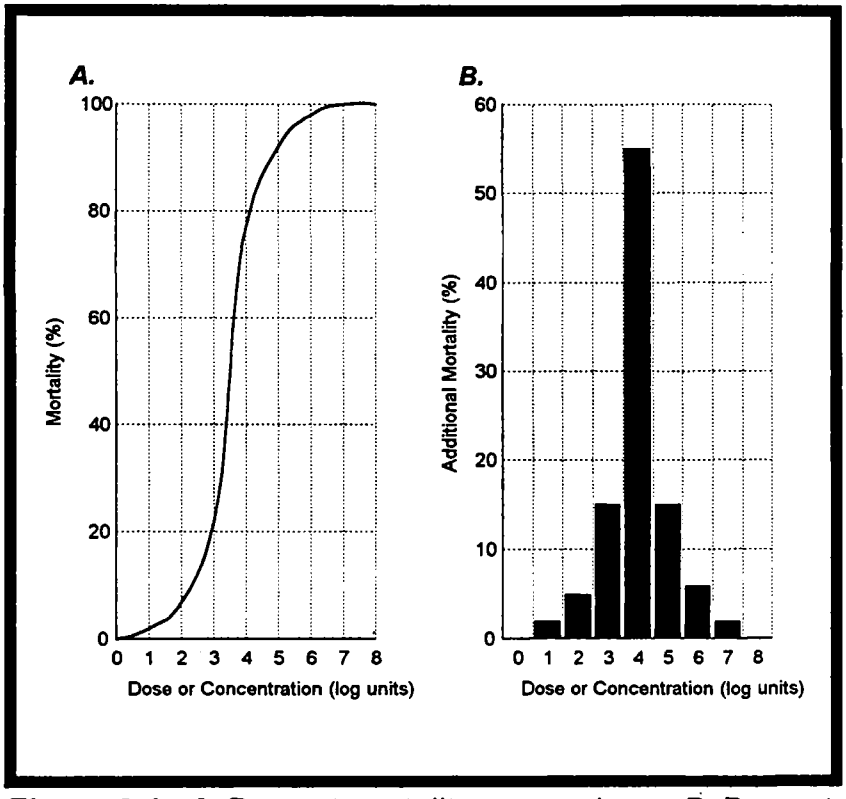

Figure 6.1. ***A.*** Percent mortality versus dose. ***B.*** Percent additional mortality at dose$_x$ compared to dose$_{x-1}$.

The origin of the sigmoid dose-response curve is straightforward. If additional mortalities only are plotted at each

concentration, the resulting distribution will be a normal distribution (Figure 6.1B). This distribution is expected since responses or traits that are controlled by numerous sets of genes (*e.g.*, growth, fecundity, mortality) tend to follow a normal distribution.

Three parameters of the sigmoid curve are often used to summarize the dose-response curve: (I) the dose that results in 50% of the measured effect (*e.g.*, LC_{50}, EC_{50}, LD_{50}), (ii) the slope of the linear part of the curve that passes through the midpoint, and (iii) the dose that defines the effects threshold or no effects level (*e.g.*, NOEL, LOEL, EC_1). All three parameters are important, if information from the dose-response curve is to be used in an ecological risk assessment. Consider the following hypothetical example. Test organisms are exposed to substances X, Y and Z in separate experiments at concentrations ranging from 0 (the control) to 10 units. At the end of the experiments, the number of dead organisms in each treatment is counted and plots of mortality versus concentration are prepared for each substance (Figure 6.2). The results indicate that the concentrations of substances X and Y causing 50% mortality are the same while the 50% effect for substance Z occurs at a much higher concentration. Using this information as the basis for a risk analysis, one would conclude that the relative risk ranking for the substances is X = Y > Z assuming equal exposure concentrations in the environment. This answer would be correct if concentrations in the environment were similar to the LC_{50} concentrations for substances X and Y (*i.e.*, 4). If concentrations of X, Y and Z in the environment were lower (*i.e.*, 1 or 2), the relative risk ranking would be Z > Y > X. At an intermediate concentration in the environment (*i.e.*, 3), the relative risk ranking would be Y > Z > X. Therefore, using information from the entire dose-response curve rather than single measures will produce more accurate risk estimates of the effects of substances on biota.

A variety of statistical techniques exist to estimate median lethal or effective doses, slopes and effects thresholds. These are briefly reviewed below. For more detailed reviews, see Stephan (1977), Snedecor and Cochran (1980), Gelber *et al.* (1985), Pack (1993) and van der Hoeven (1994).

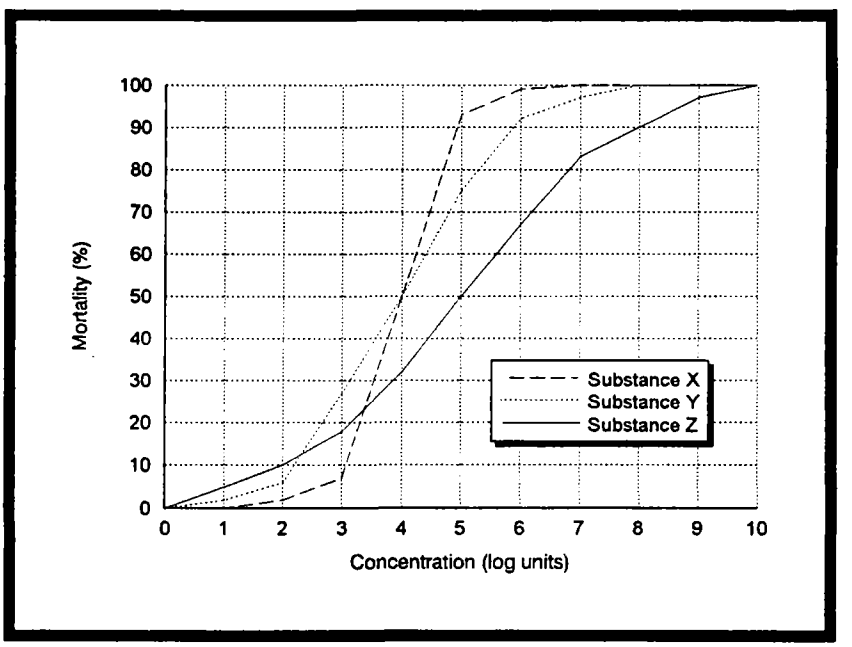

Figure 6.2. Comparison of three hypothetical dose-response curves.

6.3.1 Estimating Median Toxic Effects

Perhaps the most common technique for estimating median lethal (*e.g.*, LC_{50}) or effective concentrations (*e.g.*, EC_{50}) is graphical interpolation. This technique essentially involves plotting the results (*e.g.*, percent mortality) for each exposure treatment, estimating the best-fitting function by human judgment and reading the dose that corresponds to the effect of interest (*e.g.*, LC_{50}). Often the data are transformed (*e.g.*, logarithmic transformation of dose and probit transformation of response) in order to produce a more linear plot (Rand and Petrocelli 1985). The major advantages of this method are its simplicity and lack of assumptions. Unusual dose-response relationships (*e.g.*, those involving hormesis or stimulation at low doses) can therefore be observed. The disadvantages are that confidence limits cannot be calculated, interpolation is subject to human bias, and estimates of effects outside the middle portion of the curve are tenuous (*e.g.*, LC_1). The LD_{50}, LC_{50} or EC_{50} estimated by graphical interpolation is generally accurate and usually similar to estimates derived from formal statistical analyses (Rand and Petrocelli 1985; Pack 1993). Graphical interpolation should not be used to estimate effects outside the middle portion of the curve (*i.e.*, <16% or >84%) and cannot be utilized in an uncertainty analysis because of the inability to calculate confidence limits.

Parametric methods, moving average interpolation and non-parametric methods are the most common statistical methods for estimating median lethal and effective doses. If there are biological reasons to support the assumption that the underlying distribution of the dose-response curve is normal (with or without a log transformation of dose), then the most efficient method is to transform the response data with a probit or logit transformation and estimate with the maximum likelihood method, parameters a and b in the equation:

$$Y = a + b \cdot D$$

where Y is the proportion responding (in probit or logit units), D is the dose or concentration, and a and b are fitted constants (Gelber *et al.* 1985; Suter 1993b). Once parameters a and b have been estimated, the dose or concentration corresponding to Y = 0.5 (*i.e.*, the LD_{50}, LC_{50} or EC_{50}) can be calculated. One should be aware that maximum likelihood methods may not converge on the median lethal or effective dose if the data do not conform to the assumed model (*e.g.*, log-probit function). Generally, parametric methods also require at least two observations of partial kills (0% < mortality < 100%) or other partial effects (see van der Hoeven 1991 for an alternative method when only one treatment cause partial effects).

The moving average interpolation method can only be used to calculate the median lethal or effective dose if treatment doses are in a geometric series (Gelber *et al.* 1985). By transforming doses to a logarithmic scale, uniform spacing is achieved

between doses. Essentially, the method involves calculating a moving mortality rate for each dose and then interpolating linearly between consecutive values of the moving mortality rate on either side of 0.5 (Gelber *et al.* 1985). This method cannot be used to calculate quartiles other than the median lethal or effective dose, and it is difficult to calculate variance if doses are not geometrically spaced. Despite these limitations, this method is frequently employed and does produce accurate estimates of median lethal and effective doses (Stephan 1977).

The Spearman-Karber and trimmed Spearman-Karber methods are non-parametric methods for estimating median lethal and effective doses and are therefore model free (Gelber *et al.* 1985). The latter method simply ignores extreme values in the two tails of the dose-response curve (*e.g.*, if $\alpha = 10$, only the middle 80% of the curve is used to estimate the median dose). Both methods require at least two observations of partial kills or other effects. The calculations can be performed easily and are considered quite reliable, often producing the same results as the parametric probit method (Gelber *et al.* 1985).

From a practical point of view, rigid rules are not required for selecting among the available graphical and statistical procedures; for most types of data the estimates of the median lethal or effective dose and their confidence limits will not vary significantly (Stephan 1977). The crucial point for assessors is to ensure that for any given method, the assumptions have been met (*e.g.*, normality for parametric methods) and the limitations understood (*e.g.*, confidence limits cannot be calculated with graphical interpolation, quartiles other than 50% lethal or effective dose cannot be calculated with moving average interpolation).

6.3.2 Estimating Low Toxic Effects

Analysis of variance (ANOVA) is the most common method for estimating low toxic effects (*i.e.*, LOELs and NOELs). Generally, the first step is to transform the data to produce a normal distribution (see figure 6.1B), because normality is a critical assumption of the parametric ANOVA procedure. The transformation depends on the type of data but may include, for example, a logarithmic transformation of the doses if the plot of incremental additional effects versus dose is positively skewed, or an arc-sine square root transformation for response data expressed as a proportion (*e.g.*, % normal larvae at hatch)(Snedecor and Cochran 1980; Gelber *et al.* 1985). The next step is to test for equivalence of the carrier and non-carrier control treatments. The ANOVA is then performed on the treatment groups and, if the null hypothesis that all treatments have the same effect is rejected (*i.e.*, a significant *F*-score, usually at $P < 0.05$), multiple comparison tests (*i.e.*, Dunnett's procedure or preferably William's test) are performed between treatment groups to determine which treatments are different from the control treatment. Gelber *et al.* (1985) have suggested that the preliminary ANOVA *F*-test is unnecessary and statistically inefficient. The LOEL (or LOEC) is the

lowest dose producing a significant effect in the multiple comparisons tests; the NOEL (or NOEC) is the highest dose not producing a significant effect. The MATC is generally reported as the range between the NOEL and LOEL or as the geometric mean of the two doses.

The use of NOELs, LOELs and MATCs as the basis for estimating "safe" doses (or "true" no effects levels in the environment) has been severely criticized (*e.g.*, Skalski 1981; Stephan and Rogers 1985; Bruce and Versteeg 1992; Hoekstra and Van Ewijk 1993; Pack 1993; van der Hoeven 1994; Landis and Yu 1995; Chapman *et al.* 1996; Suter 1996) for the following reasons:

- When two or more treatments are compared and the hypothesis is tested that they do not differ (*i.e.*, the null hypothesis or H_0), H_0 can be rejected but *never* accepted. Therefore, the NOEL (*i.e.*, acceptance of H_0) is an invalid conclusion to draw from a scientific experiment.

- Hypothesis testing procedures clearly state the α value but generally leave the β value unconstrained. This means that the typical test will be conservative on the side of saying that there is no toxicity present even when toxicity is present (a Type II error)(Masters *et al.* 1991). Thus, the use of the NOEL is in direct contradiction to the precautionary principle when used to set "safe" levels (Peterman and M'Gonigle 1992; Power *et al.* 1995).

- The choice of the α value can influence the ANOVA determination of the NOEL and LOEL values. Put another way, a concentration in a test with a $P = 0.056$ is generally considered to have caused no effect (if $\alpha = 0.05$), while a concentration resulting in $P = 0.044$ is considered to have caused an adverse effect (Stephan and Rogers 1985). The dependence on α is unfortunate, because there is no adequate rationale for selecting α.

- The NOEL and LOEL are always test concentrations and do not innately correspond to biologically relevant thresholds (Stephan and Rogers 1985; Bruce and Versteeg 1992; Pack 1993).

- Poor experimental design (*e.g.*, small sample size, improper spacing of treatment doses, large intra-treatment errors) can mistakenly indicate that the substance is less toxic than it really is (Stephan and Rogers 1985; Bruce and Versteeg 1992; Pack 1993). Commonly, the experimental NOEL corresponds to 10% to 20% effect and may range as high as 50% effect (Stephan and Rogers 1985; Suter *et al.* 1987; Moore and Caux 1996). LOELs are often much higher. Again, this is in direct contradiction to the precautionary principle.

- Most of the information in the dose-response curve (*e.g.*, the slope, confidence

limits) is lost (Bruce and Versteeg 1992; Pack 1993) and thus the investigator has no means of evaluating the reasonableness of the test results, and cannot, for example, use the results to estimate risks of differing severity.

An alternative approach for estimating (almost) no effects is to use the probit, logistic or other appropriate model to estimate the dose-response function from the observed data. This approach generally requires a minimum of four treatments and a control and involves specifying a model, and estimating the parameters in the model by means of a curve-fitting analysis. The curve-fitting may be done with nonlinear regression methods or weighted linear regression on linearly transformed data (Nyholm *et al.* 1992). The advantage of nonlinear regression is that treatment responses that exceed one relative to the control need not be discarded, and control responses may be easily included as a parameter in the regression. The disadvantage is that the calculation of confidence limits is complex and often cannot be performed by standard software packages. The alternative is to first transform the response data to produce a linear dose-response relationship and then conduct a weighted linear regression. The appropriate transformation for simple monotone sigmoid curves is the probit transformation if the data are quantal (*i.e.*, categorical) or a logistic transformation if the data are continuous. If the objective is to estimate threshold doses or doses that cause very small effects (<1%), or if the dose-response curve is unusual (*e.g.*, curve is asymmetric, hormesis is occurring, little or no effect at highest test dose), other models often with more parameters are required (*e.g.*, hockey-stick model, Tukey-lamda family of models, Weibull model, extensions of logistic model)(Cox 1987; Sebaugh *et al.* 1991; Nyholm *et al.* 1992; Van Ewijk and Hoekstra 1993). Such models likely require more than five test concentrations for parameter estimation (Pack 1993; van der Hoeven 1994).

Most dose-response models assume symmetry of response (*i.e.*, the upper and lower tails are mirror images). These models are generally robust except at the extremes of the dose-response curve where the confidence intervals can be quite large (*e.g.*, $<EC_1$)(Sebaugh *et al.* 1991; Pack 1993). A comparison of two-, three- and four-parameter logistic models for estimating low dose effective concentrations of chemicals to *Daphnia magna* by Sebaugh *et al.* (1991) indicated that the two-parameter probit model produced accurate estimates at the 10 and 50% effects levels, and acceptable estimates at the 5% effect level. Similarly, Moore and Caux (1996) found that the two parameter logistic, probit and Weibull models produced similar EC_x point estimates when x was between 10 and 90%. These studies suggest that the x in the EC_x estimation should not be less than 10% because otherwise the estimate becomes model dependent. Stephen and Rogers (1985) and Moore and Caux (1996) further note that the importance of model selection is reduced by requiring that the x in the EC_x estimation be obtained only by interpolation. These results suggest that an EC_{10} estimated by interpolation from a dose-response model with adequate goodness of fit when compared to the observed data (*i.e.*, $P > 0.05$) will be accurate enough to serve

as the CTV (Sebaugh *et al.* 1991; van der Hoeven 1994; Moore and Caux 1996). If a CTV calculated in this way is used in place of a NOEL, LOEL or MATC, a more robust and scientifically valid CTV will result (Pack 1993). Further, development of a dose-response function with confidence limits makes it possible to estimate the probability of effects of differing severity.

A recent study by Moore and Caux (1996) found that the EC_x approach failed to provide adequate model fits for >80% of the 181 toxicity data sets examined (when choice of model was restricted to sigmoid-shaped models). Generally, lack of fit was due to inappropriate experimental design for regression analysis (*i.e.*, treatments were few in number and widely spaced), or because the toxicity test results had a poor dose-response relationship. Note that with poor dose-response data, the conventional hypothesis testing approach would likely determine a NOEL and LOEL that underestimate chemical toxicity. Thus, the ECx approach precludes the use of poor quality information, whereas the hypothesis testing approach will not only use such information, but will do so in a direction opposite the precautionary principle.

7.4.3 A Simple Case Study

To illustrate the EC_x approach, a hypothetical dataset has been created on the effects of chemical X on survival of a fish species. Examination of the data indicated that the dose-response relationship is a simple sigmoid-shaped curve, although the upper tail appears to taper much more slowly than does the lower tail. To make the curve symmetrical, the first step of the analysis was to apply a logarithmic transformation to the concentrations data. An EC_x statistical package developed as a Microsoft EXCEL spreadsheet was then used to take advantage of a built-in macro (Solver) that functions as a general purpose optimization engine for regressions analysis (see Caux and Moore 1996 for a description of the package). Solver uses the method of maximum likelihood and a quasi-Newton search algorithm is used to estimate the parameters in the logistic, probit and Weibull equations shown below.

Logistic Model

Model 1 is the standard linear logistic model widely used for modeling the dependance of quantal or continuous data on explanatory variables. The model assumes a symmetric response and has the classic sigmoid shape typical of many dose-response curves. The equation used in the statistical package is:

$$Y = \left(\frac{e^{\beta_0 + \beta_1 x}}{1 + e^{\beta_0 + \beta_1 x}} \right) \cdot 100$$

where Y is the estimated percent response of the exposed population, *x* is the exposure concentration (in log units), and β_0 and β_1 are the fitted parameters.

Probit Model

Model 2 is the probit model, also widely used for modeling quantal dose-response data. The probit model assumes a symmetric response and has the shape of the normal distribution in its cumulative form:

$$Y = \int_{-\infty}^{\infty} f(x) \cdot d(x) = 1$$

where

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

and where *x* is the exposure concentration, μ is the center of the distribution and σ^2 its variance. In the package, Y is converted from a fractional response to percent units.

Weibull Model

The equation for the Weibull model used is:

$$Y = \left(1 - e^{-\kappa x^{\tau}}\right) \cdot 100$$

where *x* is the exposure concentration, and κ and τ are the fitted parameters.

Results

Figure 6.3 indicates that the three models produce similar EC_{10} and EC_{50} point estimates for this hypothetical example. The adequacy of the models fits was determined by the *G*-test, and the results indicated excellent goodness of fit ($P > 0.95$ for all three models). In this example, the Weibull model produced the best goodness of fit ($P = 0.996$) and, as such, the EC_{10} point estimate from this model would be chosen as the CTV in an assessment of a priority substance.

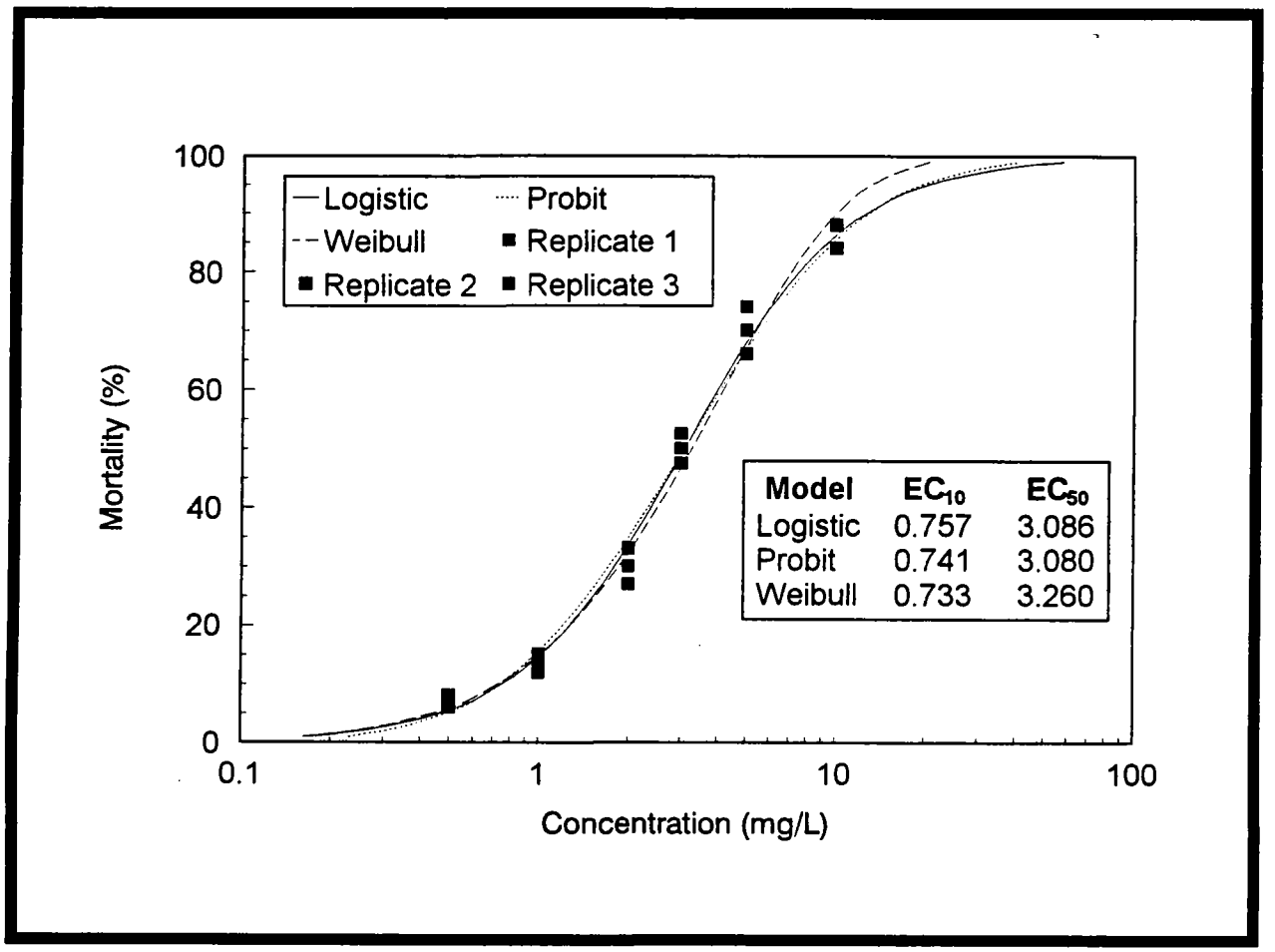

Figure 6.3. Percent mortality of fish versus concentration of a hypothetical chemical. Nonlinear regression curves for logistic, probit and Weibull model equations are shown. The EC_{10} and EC_{50} point estimates (mg/L) estimated by the models are quite similar.

6.4 Aquatic Effects Characterization

6.4.1 Pelagic Biota

Background

Pelagic biota are free-swimming or free-floating aquatic organisms that inhabit the water column. Examples include phytoplankton, zooplankton and most fish.

Table 6.2 lists a large number of pelagic biota have been used successfully in toxicity tests. Data should be generated using recognized protocols such as those from Environment Canada, Organization for Economic Cooperation and Development (OECD), United States Environmental Protection Agency (U.S. EPA), the American

Society for Testing and Materials (ASTM), etc. If other test methods are used, the procedures must be described in sufficient detail so that the reliability of the results can be evaluated.

Table 6.2 Organisms for use in bioassays and/or toxicity tests.

Test Organism	*Test*	*References*
BACTERIA		
Photobacterium phosphoreum	5, 15, 30m In	Environment Canada 1992a
Activated sludge microorganisms	30m, 3h	OECD 1993c
ALGAE		
Selenastrum capricornutum	72, 96h G	Boutin *et al.* 1993; Environment Canada 1992b; OECD 1993c;
Scenedesmus subspicatus	72, 96h G	U.S. EPA 1985a
Scenedesmus quadricauda	96h G	OECD 1993c
Chlorella vulgaris	72, 96h G	U.S. EPA 1985a
Skeletonema costatum	96h G	OECD 1993c; U.S. EPA 1985a
Thlassiosira pseudonana	96h G	U.S. EPA 1985a
Isochrysis galbana	96h G	U.S. EPA 1985a
		U.S. EPA 1985a
AQUATIC PLANTS		
Lemna gibba	7d S/G	Boutin *et al.* 1993; U.S. EPA 1985a
ECHINOIDS		
Strongylocentrotus droebachiensis	20m F	Environment Canada 1992c
Strongylocentrotus purpuratus	20m F	Environment Canada 1992c
Dendraster excentricus	20m F	Environment Canada 1992c
Abracia punctulata	20m F	Environment Canada 1992c
Lytechinus pictus	20m F	Environment Canada 1992c
MOLLUSCS		
Crassostrea virginica	96h G	U.S. EPA 1985a
CRUSTACEANS		
Daphnia sp.	24h I, 48h S, 14d S/R, 21d S/R	Environment Canada 1990a, b; OECD 1993c; U.S. EPA 1985a
Ceriodaphnia dubia	48h S, 7d R	Environment Canada 1992d
Mysidopsis bahia	96h S, 28d S/G/R	U.S. EPA 1985a
Penaeus aztecus	96h S	U.S. EPA 1985a
Penaeus duorarum	96h S	U.S. EPA 1985a
Penaeus setiferus	96h S	U.S. EPA 1985a

Test Organism	*Test*	*References*
FISH		
Brachydanio rerio	96h S, 14d S/G	OECD 1993c; U.S. EPA 1985a
Pimephales promelas	96h S, 7d S/G, 14, 28d S/G/R	Environment Canada 1992e; OECD 1993c; U.S. EPA 1985a
Cyprinodon variegatus	28d S/G/R	U.S. EPA 1985a
Menidia menidia	28d S/G/R	U.S. EPA 1985a
Menidia peninsulae	28d S/G/R	U.S. EPA 1985a
Cyprinus carpio	96h S, 14d S/G	OECD 1993c; U.S. EPA 1985a
Oryzias latipes	96h S, 14d S/G	OECD 1993c; U.S. EPA 1985a
Poecilia reticulata	96h S, 14d S/G	OECD 1993c; U.S. EPA 1985a
Lepomis macrochirus	96h S, 14d S/G	OECD 1993c; U.S. EPA 1985a
Oncorhynchus mykiss	96h S, 14, 60d S/G/R, 90-120d S/G/R	Environment Canada 1990c,d, 1992f; OECD 1993c; U.S. EPA 1985a
Oncorhynchus kisutch	90-120d S/G/R	Environment Canada 1992f
Salmo salar	90-120d S/G/R	Environment Canada 1992f
Salvelinus fontinalis	60d S/G/R	U.S. EPA 1985a
Gasterosteus aculeatus	96h S	Environment Canada 1990e

Legend: In = inhibition of light production, G = growth, S = survival, F = fertilization, I = immobilization, R = Reproduction

Toxicity test results are often used to estimate potential adverse effects of the substance in the Canadian environment. Canadian species or closely related species should be used to minimize the uncertainty associated with extrapolating results from one species to another. Only reliable, reproducible studies (Appendix IV) can be used for determining a CTV. From the set of acceptable studies, the test result indicating the lowest toxic effect, such as the lowest derived $EC_{10,}$ should be used as the CTV.

Assessment Approach

Single Species Tests. The results of single species toxicity tests have often been used for deriving water quality objectives or guidelines for substances, or for estimating no effects concentrations. Toxicity tests may be short-term acute tests or longer-term chronic tests. Full lifecycle tests that determine effects on embryonic development, hatching or germination success, survival of juvenile stages, growth, reproduction and survival of adults are preferred for the determination of the CTV. In the absence of full lifecycle tests, results from partial lifecycle tests using the most sensitive stages of the lifecycle may be employed. When possible, EC_{10} values should be calculated for each test. Otherwise, a valid LOEL© value may be used. In the absence of any long-term toxicity data, results from short-term toxicity tests (LC_{50}s or EC_{50}s) may be used. Results from tests using organisms from different trophic levels (*e.g.*, phytoplankton, zooplankton, fish) should be used to determine which populations, communities and ecosystem processes are most sensitive.

Multispecies Tests. For most substances, results from single species toxicity

tests are the most abundant source of effects data on pelagic biota. However, results from multispecies tests and from ecoepidemiology studies can be extremely useful to characterize direct and indirect effects under natural or near-natural conditions. Multispecies toxicity tests are discussed in Section 6.2.2, while ecoepidemiology is discussed in Section 6.2.3. Field test results are particularly valuable for characterizing the effects of complex mixtures and effluents on pelagic biota (Chapter 7).

CBBs. Body burden data should be evaluated whenever they are available to derive or support the CTV. CBB determines the minimum tissue concentration of a substance in the organism that causes an adverse effect (Section 6.2.4). This approach is particularly relevant for substances such as metals, where it may be difficult to determine the concentration of biovailable forms in the environment. It also integrates all routes of intake by the test organisms, including uptake from food and water. Toxicity tests which also measure the CBB are not common, but when available they could be used in conjunction with tissue monitoring data (body burdens) to estimate risk.

Determining the CTV for Pelagic Biota

- From the set of available toxicity studies, only those of an acceptable quality can be used for determining a CTV.
- Results from full lifecycle tests are preferred for determining a CTV, but when they are not available, results from partial lifecycle tests using the most sensitive stages of the life cycle may be employed.
- When possible, EC_{10} values should be calculated for each test; otherwise,.a valid LOEL© value may be used.
- In the absence of any long-term toxicity data, results from short-term toxicity tests may be used.
- When available, body burden data should be evaluated and, if appropriate, used to derive or support the CTV.
- Toxicity test results for organisms from different trophic levels should be considered in order to determine the types of organisms that are most sensitive to the substance.
- Because toxicity test results are used to estimate the potential harmful effects of the substance in the Canadian environment, Canadian species or closely related species should be used in order to minimize the uncertainty associated with the estimation.

- From the set of acceptable studies, the test result indicating the highest degree of toxicity (*e.g.*, the lowest derived EC_{10}) is used as the CTV for pelagic organisms.

6.4.2 Benthic Biota

This section will outline the importance of sediments to benthic biota, discuss the types of sediment information available, and provide guidance on how to determine CTVs for benthic organisms from the types of information typically available. Given that there are fewer standardized toxicity testing protocols available for benthic organisms than for pelagic organisms, several approaches to assessing toxicity to benthic organisms are discussed.

Background

Sediments are an important component of aquatic ecosystems. They provide habitat to organisms such as aquatic plants, worms, insects, amphipods, and molluscs that spend a major portion of their lifecycle living on or in aquatic sediments. Sediments act as sinks, and subsequently, as sources of substances that have entered the aquatic environment. Substances found in sediments may adversely affect benthic species and/or bioaccumulate in benthos and to higher trophic levels. Concern has increased over the number of tumours being observed in many species of fish, especially those that have direct contact with sediments (Black and Bauman 1991). Recently, protecting sediment quality has been viewed as a logical and necessary extension of water quality protection (Bahnick *et al.* 1981; Beller and Barrick 1988; CCME 1995; Chapman and Long 1983; Ingersoll 1991, 1995; U.S. EPA 1990; Washington Department of Ecology 1991).

Assessment Approaches

The Water Quality Institute (Denmark) and RIVM (1995) provide a compendium of available standardized test methods. Environment Canada has also produced a number of sediment toxicity methods (Environment Canada 1994a,b). These toxicity tests, however, don't pertain to the toxicity testing component of the procedure but rather to sediment handling[2]. In addition to toxicity tests, Lee *et al.* (1989) and U.S. EPA (1994b) have developed methods for estimating bioaccumulation in sediment organisms (Section 5.6). Fewer standardized toxicity tests are available for benthic organisms than for pelagic organisms, and for many substances, spiked sediment toxicity test results are not available. Some benthic organisms have been routinely used in water column tests. However, only a limited number of these spiked sediment toxicity tests have been standardized to examine an organism's exposure to sediment-associated substances such as whole sediment, pore waters or elutriates. Overall,

[2]How sediments are spiked or how long the substances is allowed to equilibrate.

assessors must be flexible and will need to evaluate any potentially relevant benthic toxicity information by applying sound scientific principles and QA/QC considerations (Appendix IV). Due to the complexities of interpreting data in the sediment compartment, assessors are advised to consult with sediment specialists when applying the following approaches.

MacDonald *et al.* (1992) provide a brief description of the methodology for each of the many approaches available for assessing the toxicity of substances in sediment, their major advantages and limitations and current uses. Of the available approaches the most relevant for assessments of priority substances are:

- spiked sediment toxicity tests,
- co-occurrence of substance and biological data in field sediments,
- benthic community structure assessments, and
- equilibrium partitioning approach.

Assessors should locate all acceptable sediment toxicological data on Canadian marine and freshwater species. These data should cover a range of feeding behaviours, substrate preferences, locomotion, and degree of association with bottom sediments. Sediment toxicity tests must use the appropriate sediment phase since benthic organisms may be exposed to some or all of these phases during their lifecycle. Qualitative and quantitative sources of uncertainty with the toxicological data should be documented. These uncertainties will be taken into account in selecting application factors or in conducting uncertainty analysis during risk characterization.

A description and the application of each of these approaches is provided below.

Spiked Sediment Toxicity Tests. To establish cause and effect relationships, organisms are exposed to sediments that contain known (spiked) concentrations of a substance or mixture (Water Quality Institute (Denmark) and RIVM 1995). Spiked sediment toxicity tests are suitable for all classes of substances, whether alone or in mixtures, and most types of sediments. In addition, precise data on the biological effects of various substances can be generated. A spiked sediment toxicity test is directly analogous to a water column test except the substance and test species are added to solid-phase sediments, not water. Researchers can use a standard clean sediment to provide inter-laboratory comparability. Artificially prepared sediments may also be used over field sediments thereby avoiding concerns that the sediments may have been contaminated with other substances. Assessors should be aware about concerns regarding the viability of organisms in artificial sediments. Data interpretation still relies on expert judgment. For example, sediment

spiking may be strongly influenced by the methodology and this may affect the comparability of results.

As with pelagic biota, the results of single species toxicity tests may be used to determine the CTV. Toxicity tests may be short-term acute or longer-term chronic tests. Full lifecycle tests that include a determination of effects on embryonic development, hatching or germination success, survival of juvenile stages, growth, reproduction, and survival of adults are preferred. In the absence of full lifecycle tests, results from partial lifecycle tests using the most sensitive stages of the lifecycle may be employed. In the absence of any long-term toxicity data, results from short-term toxicity tests (LC_{50}s or EC_{50}s) may be used.

The assessor should be aware that in conducting spiked sediment toxicity tests, field verification may be required. This is to assess the effects of possible substance interactions and the effects of physical sediment variables on the responses of benthic organisms.

Co-occurrence Associations of Chemical and Biological Data in Field Sediment. Often no suitable spiked sediment toxicity tests will be available from the literature. When this is the case, a weight-of-evidence approach should be used to establish associations between a substance's concentrations in sediments and observed adverse biological effects. These associations can be based on data from laboratory tests conducted on field-collected sediments that contain mixtures of substances. These are referred to as co-occurrence data. Field data in the literature, should be evaluated on a case-by-case basis to determine their usefulness.

CCME (1995) provides a further discussion of the co-occurrence approach based on work by Long (1992), Long and Morgan (1990), and Long and MacDonald (1992). Other types of co-occurrence approaches include the apparent effects threshold (AET), sediment quality triad and informal evaluations of chemistry and biological responses (U.S. EPA 1992c). Sediment specialists should be consulted when applying a co-occurrence approach.

This approach involves the reviewing of individual studies using field sediment as well as databases (*e.g.*, National Status and Trends Program as described in CCME 1995) that have a compilation of data generated from field studies that consist of matching field sediment chemistry and biological effects. A possible advantage of this approach is that no additional fieldwork or laboratory investigations may be required. Data may come from many sites in the United States and Canada. Assessors should be aware, however, that the information that is compiled from databases comes from a wide variety of sediment types--with different particle sizes and different background concentrations of trace and major elements--and have been combined resulting in possible unknown biases. Furthermore, the compilation and evaluation of the required

data are labour intensive and require sound knowledge of sediment chemistry and biology.

Benthic Community Structure Assessment Approach. This is another line of evidence in the weight-of-evidence approach used to compare test and reference stations to determine the existence and magnitude of effects on infaunal species. It also identifies spatial and temporal trends in sediment quality (Diaz 1992; La Point and Fairchild 1992; Persaud *et al.* 1992; Reynoldson and Zarull 1993; Reynoldson *et al.* 1995; Warren 1971). Measurements include species diversity and abundance, measures of species colonization or emigration rates and the rate or re-establishment of populations following perturbation (Cairns *et al.* 1979). A variety of statistical methods are available to determine the community assemblages including average linkage clustering, K-means, divisive clustering techniques and ordination (Reynoldson and Zarull 1993).

This assessment technique is recognized as an *in situ* method for determining sediment quality that can be applied to a wide variety of aquatic ecosystems and a wide variety of chemical groups.

The disadvantage of this technique is that while the above information is useful, cause and effect relationships cannot be easily inferred from community structure data alone (see Section 6.2.3). Spiked sediment toxicity tests can provide this information, since they are specific, and are usually capable of discerning the cause of structural changes as well as quantifying dose-response relationships. While many tests can be conducted *in situ*, the need for strict control over exposure conditions means that most toxicity tests are conducted in the laboratory. Used in combination with spiked sediment data, community structure information can provide useful site-specific information on the effects of priority substances to benthic organisms.

Equilibrium Partitioning. The equilibrium partitioning approach (see Section 6.2.6) is a method of estimating effects for sediment-dwelling invertebrates using appropriate toxicity data for pelagic species, partition coefficients, and bulk sediment chemistry data. It is routinely used for hydrophobic, nonpolar, nonionic organic substances, and its applicability to metals is under development. It is recommended for use when the sediment solid phase contains more than 0.2% organic carbon.

The approach is attractive in that it relies on information that is generally available and is therefore applicable to a wide variety of aquatic ecosystems. The theory is well developed and is undergoing field verification. However, there are large uncertainties associated with the assumptions underlying the theory (Section 6.2.6).

Assessors should be aware that data normalization to acid volatile sulphide (AVS) for metals and total organic carbon (TOC) for non-polar organics may be required, and that the method assumes equilibrium between sediment and interstitial

water, which may not be true in many situations. It is recommended that, in general, effects values calculated using this method be considered as screening values only. The data may be used as part of the weight-of-evidence approach for selecting a CTV, but should not normally be used as the primary source of evidence for such a value.

Important Considerations

A number of factors should be considered when evaluating the usefulness of sediment toxicity information. These include: phase of sediment tested, organism used, sediment collection and handling procedures, and sediment characterization.

Sediment assessment is complicated by the fact that sediment toxicity tests have been designed for different sediment phases, namely whole sediments (solid phase), suspended sediments, elutriates, sediment extracts, or pore (interstitial) water. Results from one phase may not be directly applicable to all phases. Therefore, the selection of the phase and organisms to test depend on the objectives of the study defined during problem formulation. For example, if the toxicity of a sediment to benthic animals must be determined, then the whole sediment should be used. On the other hand, if the pore water or elutriate approaches can be used, it may be possible to use pelagic or epibenthic species. Existing data suggest that pore water is the appropriate fraction for predicting bulk sediment toxicity, while elutriate is not (Ankley *et al.* 1991). However, elutriates may be an appropriate test fraction if sediment suspension is of concern.

Sediment collection, handling and other methodological issues can affect the relevance of test results. Factors include: type of sediment sampling, degree of sediment disturbance during sampling, storage duration and conditions, mixing, sieving, sterilizing, dilutions and settling times. Guidance on these issues is available in ASTM (1991), Burton and McPherson (1994), CanTox 1993, Environment Canada and MENVIQ (1993), Environment Canada (1995a,b,c), Loring and Rantala (1992), and Schropp and Windom (1988).

A wide range of parameters are relevant in characterizing the sediment associated with solid phase tests. Information on the following key parameters is helpful to interpret the toxicity test results (OECD 1992b):

- *Particle size distribution* may influence the partitioning of chemicals, particularly ionizable organics, between sediment and water. In solid phase tests, the tolerance range of the chosen organisms to particle size must also be considered.

- *Dissolved oxygen* is a critical factor to monitor in overlying water, particularly in sediments with high biological or chemical oxygen demand. Test protocols

specify the percent oxygen at which overlying water should be renewed.

- *Total organic carbon (TOC) content* is the dominant normalizing factor in equilibrium partitioning equations for bioavailability of nonpolar chemicals.

- *Total ammonium concentration* resulting from the natural degradation of organic matter is frequently a source of toxicity in sediments from eutrophic water systems and should be measured in overlying water or in some instances pore water.

- *Acid volatile sulphide (AVS)* is a dominant factor controlling the bioavailability of some cationic metals, and should be reported in tests on these substances.

- *pH* is a key factor influencing the bioavailability and toxicity of some substances (*e.g.*, ammonia). pH is also an important determinant in evaluating the tolerance range of some organisms. It should be measured in overlying water and the solid phase sample.

These factors are important in determining the bioavailability of a substance to sediment biota. Some relationships between sediment factors and observed adverse effects have been demonstrated, to a limited extent, in controlled laboratory studies. However, these relationships are not predictable in field situations--in helping to predict adverse effects.

Determining the CTV for Benthic Organisms

- In general, assessors should attempt to locate all acceptable data on Canadian marine or freshwater species that cover a range of benthic trophic levels.

- To be useful as measurement endpoints, toxicity tests must use the appropriate sediment phase (*e.g.*, whole sediment, pore water, elutriate), because benthic organisms may be exposed to some or all of these phases during their lifecycle.

- Assessors should document qualitative and quantitative sources of uncertainty associated with the toxicological data used since this will be taken into account in selecting application factors or conducting uncertainty analysis during risk characterization.

- Spiked sediment toxicity tests are preferred for determining the CTV. If only one type of data exists, assessors will have to decide on a case-by-case basis whether the type of information reported in the study is sufficient to establish adverse effects at the levels determined in the environment. Equilibrium partitioning information should not be used as the sole source of evidence for

the CTV.

- When there is no spiked sediment data, it is recommended that the lowest acceptable EC_{10} from a chronic study relevant to the assessment endpoint be used for the CTV. When chronic effects data are not available or when an acute study is most sensitive, the LC_{50} or EC_{50} or other significant EC_x should be used for the CTV.

- In the absence of spiked sediment data, a weight-of-evidence approach, as described in CCME (1995), be used to establish associations between concentrations of substances in field sediments and adverse biological effects. The approach involves reviewing individual field sediment toxicity studies as well as databases that compile data from field sediment toxicity tests--co-occurrence data consists of matching sediment chemistry and biological effect data.

- CTVs should also be evaluated in conjunction with other information such as the natural background concentrations of substances and site-specific biological assessments. Information on background concentrations of natural substances can be used to estimate the extent to which anthropogenic activities have contributed to the concentrations of sediment-associated chemicals measured at a site. Such information is particularly important for metals and certain organic substances that may be enriched through natural processes. Assessors should note if effect thresholds are below background concentrations of natural substances. Site-specific biological assessments along with chemical analyses of sediments also provide important information for confirming the toxicological predictions made using the CTV.

6.4.3 Groundwater Biota

Groundwater has been traditionally viewed as a resource for drinking water, agriculture, and industry. However, the groundwater ecosystem also provides habitat, food and nutrient cycling for microbes (bacteria and protozoa) and micro- and macroinvertebrates (copepods and amphipods) (Botosaneanu 1986; Danielopol 1992; Notenboom and Boessenkool 1994; Marmonier *et al.* 1993). Until recently, little research has been undertaken on the effects of substances on the biota residing in groundwater ecosystems. Under CEPA, the groundwater ecosystem, like air, surface water, soils and sediment, is an environment to be protected. The fate and effects of selected substances on this ecosystem are to be assessed.

Background

Groundwater is defined as water that occupies pores and crevices in rock and soil in the phreatic (saturated) zone. Excluding glaciers and ice caps, groundwater

accounts for over 95% of all freshwater available on earth. As a result of its large volume and the fact that all water moves continually through the hydrologic cycle, groundwater has a substantial influence on all freshwater systems (Simons and Ainsworth 1993). Groundwater systems have significant benefits in that they improve the water quality of groundwater but also support surface water food chain ecosystems and may improve the water quality of rivers, streams, wetlands and estuaries (Simons pers. comm. 1994, 1995; Gibert *et al.* 1990).

Historically, protection of groundwater in Canada focussed on preserving groundwater as a resource for present and future generations (Environment Canada 1987). Prior emphasis centered solely on human health, although this is changing to include both human health and the environment. This new emphasis is reflected in various government documents, including the draft Federal Freshwater Strategy, which advocates the sustainable use of groundwater ecosystems and protection of groundwater ecosystems through prevention of pollution, reduction/elimination of contaminants, and conservation/restoration of habitat (Environment Canada 1995d). The conservation of biological diversity, which also includes protection of species diversity within groundwater ecosystems, and the ecosystem approach, have been incorporated into a revised CEPA (House of Commons 1995) and is one of the objectives of the Canadian Biodiversity Strategy (Environment Canada 1995e).

The groundwater ecosystem is characterized by a mix of biotic and abiotic conditions. The ecosystem is devoid of light and there are few primary producers, with the exception of the chemolithotrophic bacteria (Danielopol *et al.* 1994.) It has relatively stable physical and chemical conditions, detrivorous food chains, is oligotrophic with hypoxic or anoxic conditions, and is generally carbon limited (Notenboom *et al.* 1994). Groundwater can be categorized on the basis of aquifer type and groundwater flow system. The three main types of aquifer may be defined as: karstic aquifers (limestone areas), porous or interstitial aquifers (*e.g.*, floodplain or ocean shore) and subsurface aquifers (Gibert *et al.* 1990). The saturated subsurface includes an "upper zone" of active flow strongly affected by local precipitation events, a "medium zone" of deeper flow only moderately influenced by local precipitation events, and a "lower zone" of relatively stagnant water unaffected by local precipitation (Chapelle 1993). The physical composition of the aquifer will influence the organisms residing in the subsurface environment and the availability of chemicals to groundwater organisms. Important physical factors include whether it is fractured or fissured rock, sand, clay or silt, the organic carbon content of the aquifer material, and the porosity and permeability of the aquifer.

Historically, groundwaters have been considered to be sparsely inhabited by living organisms and were treated solely as a source of exposure for surface-dwelling organisms from groundwater discharges to springs and other surface water bodies. However, it is now known that within the groundwater ecosystem diversified forms of

life occur, including both microbes (*e.g.*, bacteria, protozoa) and invertebrates (*e.g.*, copepods, amphipods)(Botosaneanu 1986; Danielopol 1992; Marmonier *et al.* 1993).

Groundwater organisms are grouped as stygoxens or epigean surface-dwelling biota that appear rarely in ground water (*e.g.*, the amphipod *Gammarus fossarum*); stygophiles, epigean organisms that occur in both surface water and groundwater but have not adapted to subterranean life; and stygobites, true groundwater organisms that have adapted or specialized to the subterranean environment (*e.g.*, *Salentinella delamarei*)(Mormonier *et al.* 1993). The hyporheos region (an intermediate zone below the water/substratum interface in streams) includes fauna that are both occasional and permanent. The occasional hyporheos refers to larvae of the surface benthos that spend part of their life cycle in this habitat. The permanent hyporheos refers to species such as copepods and mites which complete their life cycle in this environment (Williams and Hynes 1974). Stygobites have specialized to the groundwater environment with respect to morphology (loss of body pigment, reduction or loss of eyes, hypertrophy of non-optic sensory organs, relative lengthening of appendages), physiology (reduction of metabolic rates, less frequent reproduction) and ethology (photophobic, high thigmotactism).

The subsurface environment differs from surface environments in that there are few trophic levels. Food resources usually originate from the surface in the form of biomass and detritus. Food webs are simple, with few trophic links (Gibert *et al.* 1994). The primary consumers are groundwater microbes, including bacteria, fungi and protozoans. The secondary trophic layer is a consumer or grazer level consisting of micro- and macroinvertebrates (Gibert *et al.* 1994). Higher trophic levels include predators; examples in groundwater include crustaceans and annelids (Chapelle 1993).

Groundwaters contain a wide range of habitats and diversity of species (Gibert *et al.* 1994). In the case of aquifer microflora, the diversity is lower than the surface microflora but the diversity does not appear to decrease with depth (Gounot 1994). The taxonomy of groundwater microorganisms is still poorly developed. Gounot (1994) reviewed reports on distributions and taxa of microorganisms in groundwater and sediment, which included: *Pseudomonas*, *Achromobacter*, *Acinetobacter*, *Aeromonas*, *Alcaligenes*, *Chromobacterium*, *Flavobacterium*, *Moaxella*, *Caulobacter* and *Bacillus*, to name a few. Protozoa, including yeasts and low numbers of fungi eukaryotic microorganisms, were detected in groundwater samples at various depths. In most interstitial or porous groundwater habitats, a diversified crustacean population and a rich worm fauna exists (Danielopol *et al.* 1994; Culver 1994).

Investigation into the ecology of alluvial aquifers in a large river-lake catchment area in western United States and Canada has demonstrated the presence of diatoms, protozoa, free living bacteria and over 80 taxa of groundwater invertebrates. These included both stygophiles and stygobites in the alluvial aquifers, ranging from

Trichoptera, Plecoptera, Diptera, Copepoda, Ostracoda and Oligochaeta (Stanford *et al.* 1994).

Distributions of groundwater biota, both microbes and invertebrates, have been detected in karst regions in caves and wells more than 100 m below the surface. The majority of invertebrates are present 1-10 m down in nonkarstic (*i.e.*, interstitial) environments, whereas bacteria are frequently found in nonkarstic aquifers hundreds of meters below the surface (Strayer 1994). Ghiorse and Wilson (1988) speculated that bacteria may live thousands of meters below the earth's surface. The major limitation for decline in species distribution and densities seems to be a function of local environmental conditions rather than depth.

Microbial growth in groundwaters is reported to be limited by the low concentration of organic carbon and oxygen typically observed in pristine aquifer environments, although Gounot (1994) reported that sufficient oxygen is available in pristine aquifers to support a minimum level of microbial respiratory activity. In shallow aquifers, organic carbon filters down from the surface, resulting in increased heterotrophic populations. Soluble nitrogen and phosphorus appear also to be low whereas carbon dioxide is usually abundant in shallow groundwaters (Gounot 1994). Studies carried out in Borden, Ontario, indicated that microbial occurrence and activities were inhibited by the low dissolved oxygen and organic carbon content in the aerobic aquifer (Barbaro *et al.* 1994).

The groundwater environment receives its organic matter from the surface and then transforms, stores and exports groundwater and organic matter, in some areas in large quantities, to rivers, lakes and wetlands (Gibert *et al.* 1990; Vanek 1987; Bornette and Large 1995; Hynes 1983). Gibert *et al.* (1990) categorize groundwater-surface ecotones into five types based on hydrologic dynamics, on the direction of material fluxes and relationships between underground and surface water flow. These are: 1) soil/porous aquifer; soil/karstic aquifer interface (epikarstic); 2) sinkstream or spring; 3) stream underflow; 4) sinkstream of lake bottom; and 5) infiltrating lentic water.

The presence of a groundwater/surface water interaction zone or ecotone populated by both groundwater and surface water organisms is becoming widely recognized (Pugsley and Hynes 1986; Hynes 1983; Williams 1989). The population of organisms that dwell in the zone bordered by the stream above and the groundwater below is known as the hyporheos (Williams and Hynes 1974). The hyporheic zone is the region where water is sent to the stream in areas of groundwater discharge (upwelling zones) and, conversely, downwelling zones are the interstitial regions where the hyporheic zone receives water from the surface (Henry *et al.* 1994). Studies of this habitat indicated that both stream and groundwater invertebrates can exist (Gibert *et al.* 1990; Williams 1989; Williams and Hynes 1974). Groundwater inflow and outflow have

also been shown to be a major factor in the chemical composition and biological dynamics of many lakes and rivers (Vanek 1987; Hynes 1983). Studies have shown that this ecotone between the two systems is characterized by a zone of species richness in some regions (Godbout and Hynes 1982; Bornette and Large 1995) to a zone of intermediate biodiversity between the two adjacent environments (Gibert *et al.* 1990). For example, Gibert reported that the species diversity in a karstic spring was greater in the surface environment (*e.g.*, 13 species) and low in the groundwater environment (*e.g.*, 2 to 3 stygobiont species). In the ecotone between the two environments, diversity was intermediate (*e.g.*, 5 to 9 species). Godbout and Hynes (1982) confirmed that the densities of invertebrates in the hyporheos was at least three times greater than in the surface zone in a Canadian river. Bornette and Large (1995) reported higher species richness in the hyporheos zone in the Rhone River in France.

Table 6.3. Classification of soil mobility potential of chemicals based upon HPLC retention times (McCall *et al.* 1981).

K_{oc}	***Mobility Class***
0 - 50	Very high
50 - 150	High
150 - 500	Medium
500 - 2000	Low
2000 - 5000	Slight
> 5000	Immobile

Populations of hyporheos fauna have been shown to exist in a number of Canadian rivers, and similar fauna were found in the hyporheos environment in both Europe and North America (Williams 1989). Vanek (1987) and Hynes (1983) reported on numerous studies where inflowing groundwater and the related temperature and oxygen are important to the spawning success of some salmonids and brown trout.

Substances with the lowest K_{ow} and K_{oc} values are of most concern to groundwater endpoints because they travel the furthest and create the largest plumes (Lesage pers. comm. 1995). Once groundwaters are contaminated, they are difficult, if not impossible to restore. A classification of soil mobility potential based on the K_{oc} of a chemical is presented in Table 6.3 (McCall *et al.* 1981). K_{oc} values ranging from zero to 500 indicate that the substance is mobile in soil and will move easily through soil to the groundwater environment.

Substances with high K_{ow} and K_{oc} values are also of concern as they tend to adsorb to organic matter in the saturated zone and may be a source of contamination in the future. Knowledge of the physical-chemical properties of the substance and the composition of the groundwater habitat through which the substance is transported is essential.

Contamination of groundwater ecosystems by substances may result in very slow recovery of biota and extinctions of groundwater biota may be irreversible (Strayer 1994).

Assessment Approaches

Although a number of approaches exist to evaluate the effect of priority substances in surface water, little research has taken place to determine the effects of substances on natural populations of groundwater ecosystems.

No standard toxicity test protocols exist for groundwater organisms and only effects on bacteria mineralization and acute toxicity tests with groundwater invertebrates are described in the literature. Although no standardized toxicity test protocols exist for groundwater, assessors should use all available data as long as good general QA/QC practices and sound scientific principles are followed. In addition, all available data from the approaches described below should be included in a weight-of-evidence approach.

Single Species Tests. A limited number of single species toxicity tests have been performed on the effects of chemicals on bacteria and groundwater-dwelling crustaceans and annelids (van Beelen *et al.* 1991; Notenboom and Boessenkool 1992, 1994; Barr 1976; Bosnak and Morgan 1981; Meinel and Krause 1988; Meinel *et al.* 1989). Toxicological endpoints included decrease in mineralization, acute lethality and immobility. Testing methods for other endpoints, such as growth and reproduction, have not been developed due to difficulties in reproduction of groundwater biota under laboratory conditions and the long generation times of the organisms (Notenboom and Boessenkool 1992).

Comparison of the relative sensitivities of groundwater invertebrates to surface water organisms is difficult due to the lack of information on physiology, life history and sublethal effects. Preliminary data from acute studies with mortality or immobility as endpoints indicate that groundwater organisms may be more or less sensitive than their surface water relatives. For the metals cadmium and zinc, the surface water isopod *Lirceus alabamae* was 14 and two times more sensitive than the groundwater stygobite *Caecidotea bicrenata* (Bosnak and Morgan 1981). In contrast, the groundwater isopod *Caecidotea stygia* was more sensitive to nickel, cadmium, and chromium than the surface-dwelling isopod *Lirceus fontinalis* (Barr 1976). Comparison of limited data sets for the groundwater-dwelling micro-crustacean *Parastenocaris germanica* and available information from tests with *Daphnia magna* indicate that there is little difference in sensitivity between the two species (Notenboom and van Gestel 1992).

In the absence of direct toxicity testing on groundwater-dwelling biota, ecotoxicological testing using groundwater fauna surrogates such as surface water

biota and soil organisms may be used (van den Berg and Roels 1991; Notenboom and Boessenkool 1994; Notenboom and van Gestel 1992).

Effects Data Using Surface Water Organisms. Given that certain ground- and surface water crustaceans appear to have similar sensitivities based on limited acute toxicity studies, it is recommended that toxicity test information on surface water crustaceans that are functionally similar to groundwater species should be used as surrogates for groundwater crustaceans (Notenboom and van Gestel 1992; Notenboom and Boessenkool 1994; Keddy *et al.* 1994). To determine a CTV for other important functional groundwater organisms such as bacteria, groundwater toxicity data are necessary.

Effect Data Using Soil Organisms. Toxicity to soil organisms is thought to be controlled by the soil pore water concentration (van Gestel and van Straalen 1994; van Gestel and Ma 1990). Studies suggest that the sensitivity of earthworms is similar to some aquatic organisms. Therefore, it is possible that effects threshold data for groundwater organisms could be estimated from toxicity results with soil-dwelling organisms such as earthworms (van den Berg and Roels 1991). However, given the uncertainties involved in the use of such surrogates, CTVs should not be based solely upon effects data from soil-dwelling organisms.

Due to the lack of data on chronic toxicity of substances and the uncertainty involving extrapolating from surface water and soil organisms to groundwater biota, considerable application factors may be incorporated to compensate for this lack of knowledge. Notenboom and Boessenkool (1994) suggest an application factor of 1000.

Groundwater-Surface Water Interaction Zone. An additional approach to estimating the effects of substances on groundwater biota is consideration of the groundwater-surface water interaction zone or ecotone. This approach involves estimating the concentration of substances in the water at the groundwater-surface water ecotone and on the groundwater organisms that have adapted to this environment. A limitation of this approach is that due to dilution and volatilization, the "true" concentrations of the substances will not be detected in the groundwater.

Important Considerations

The ability of groundwater biota to exist is a function of the environmental conditions in which they find themselves. The range of conditions in groundwater that biota are able to tolerate is too extensive to list here, however, the important factors necessary for growth and survival are presented below. Knowledge of these conditions will enable assessors to evaluate a study and determine if the effects on groundwater biota are due to the substance or to inhospitable conditions.

- *Temperature.* The temperature is an important factor in the growth of groundwater biota. In the case of bacteria, life is supported by a series of enzymatically catalyzed chemical reactions. These reactions are limited by minimum temperatures between 0 to 20°C. The average temperature in Canada is approximately 8C (Lesage pers. comm. 1995).

- *Oxygen.* Oxygen either in the gaseous or dissolved form, is essential for some groundwater organisms such as bacteria, other obligate aerobes and invertebrates (Gounot 1994; Danielopol *et al.* 1994). Other biota, such as the facultative anaerobes, prefer to use oxygen if it is available, while for the obligate anaerobes, the presence of molecular oxygen either inhibits growth or will kill the organism (Chapelle 1993). In the majority of pristine aquifers there is sufficient O_2 or other electron acceptors to support a minimum level of microbial respiratory activity (Gounot 1994). Due to the low amounts of nutrients and slow growth rates, oxygen demand is low, except in aquifers that have been contaminated by high levels of utilizable organic carbon.

  Exposure of the groundwater copepod (*Parastenocaris germanica*) to cadmium, zinc, pentachlorophenol and 3,4-dichlorophenol under normoxic (10 $mg \cdot L^{-1}$ O_2) and hypoxic (0.1 $mg \cdot L^{-1}$ O_2) conditions indicated that oxygen concentrations within the 0.1 to 10 $mg \cdot L^{-1}$ O_2 range have negligible influence on the groundwater copepod and probably other similarly adapted groundwater species (Notenboom *et. al.* 1994).

- *pH.* pH in natural groundwater systems commonly ranges from about 4 to 9. These values are usually a reflection of the effects of the carbonate or silicate minerals that make up the aquifers (Chapelle 1993). In groundwater contaminated by municipal waste, pH levels may vary from as low as 3 to as high as 11. Although biota such as bacteria are generally capable of withstanding wide extremes in pH, some bacteria and microcrustaceans may undergo adverse effects in an environment where pH conditions are significantly different from those to which they are accustomed.

  Studies on the sensitivities of invertebrates in groundwater indicated pH-dependent toxicity when exposed to cadmium and zinc at pHs ranging from 5-8 (Meinel and Krause 1988; Meinel *et al.* (1989).

- *Sediment texture.* Sediment texture has been shown to affect the distribution of both microbes and invertebrates (Ghiorse and Wilson 1988; Strayer 1994). The importance of sediment texture is related to a number of factors, such as hydraulic conductivity (a measure of the speed water flows through an aquifer) which in turn affects the supply rates of dissolved substances such as oxygen, organic carbon and nitrate. Other factors include size of the particle areas and

pore spaces for biological colonization and the suitability of the sediment for burrowing (Strayer 1994).

Determining the CTV for Groundwater Biota

Use of simple exposure screening strategies and laboratory toxicity tests are recommended for evaluating effects of priority substances on groundwater organisms. Due to the lack of toxicity data for groundwater organisms, use of surrogate species may in some instances be warranted in deriving the CTV.

- Assessors should review appropriate databases (with emphasis on the groundwater environment) for physical-chemical properties and toxicological information on groundwater biota.

- When selecting toxicity studies, the test organisms should be representative of Canadian groundwater biota in terms of function, trophic level and route of exposure. An ideal data set would include a microorganism function, a grazer such as a protozoan, and a predator such as a crustacean. When reviewing toxicity studies, the assessor should be aware of the influence of pH, oxygen content, temperature and sediment texture on the bioavailability of the substance and hence toxicity of organic and inorganic substances.

- If no groundwater toxicity data are available and groundwater biota have been identified as being exposed to elevated levels of a substance(s), surrogate species such as surface water crustaceans or soil organisms may be used to determine the CTV for functionally similar species in groundwater. The CTV should be based on surrogate species that are functionally similar to the groundwater endpoints of interest.

- Assessors should also use any available data from the groundwater-surface water interaction zone and be aware of the advantages and limitations of using data from this zone.

- Assessors should identify areas of uncertainty (both qualitative and quantitative) in the effects characterization. These may include uncertainties regarding relationships between the substance and the groundwater ecosystem, uncertainties associated with study parameters, and natural variations in groundwater systems.

- The CTV should be based on a weight-of-evidence approach. Data from chronic, full life cycle studies measuring nonlethal effects such as growth and reproduction are preferred. The preferred quantitative expression of this information is an EC_{10}. Alternatively, LOELs or NOELs may be used if

calculation of an EC_{10} is not possible. If only acute toxicity data are available or are more sensitive than the chronic information, the CTV may be calculated from an LC_{50}, EC_{50}, or other significant EC_x.

6.5 Terrestrial Effects Characterization

6.5.1 Soil Biota

The soil ecosystem is a vital environment with many roles including providing food, habitat and nutrient cycling for microorganisms, invertebrates, plants, and mammals. Soil is a complex medium. Substances found in soils may exist as distinct particles in soil, dissolved in soil water, vaporized in soil air, or adsorbed or absorbed to mineral/organic particles. Depending on soil properties (*e.g.*, surface texture, pH, organic carbon content, temperature, moisture content, and redox potential), soils may act both as chemical and biological filters and may lessen the impact of substances entering groundwater and the atmosphere. Soil properties also affect the bioavailability of a substance. Important functions carried out by soil organisms include decomposition of organic matter, mineralization of nutrients and synthesis of humic substances (van Leeuwen and Hermens 1995).

Background

Soil biota are defined as organisms that spend at least part of their life cycle in soil. Soil organisms may live in the litter layer of the soil, in the mineral soil, in soil pore water, or above ground. For the purposes of priority substance assessments soil organisms include microorganisms, invertebrates, and plants (mammals, reptiles and amphibians are considered under Section 6.5.3 on wildlife). There is an immense variety and abundance of multicellular animals in the soil environment. The most common are protozoans and nematodes, with populations of up to 10^9 individuals per square meter (van Gestel and van Straalen 1994). The larger fauna include snails and slugs (Mollusca), earthworms (Lumbricidae), and arthropods such as mites (Acarina), springtails (Collembola), woodlice (Isopoda), and millipedes (Diplopoda).

Plants are essential components of the ecosystem as they are the primary producers of oxygen and primary food source for all heterotrophic organisms. While most toxicological research has been conducted to examine the effects of substances on agricultural plant species, assessors should also examine the literature for effects on non-target plants. Plants may be exposed to substances at various life stages and, depending on the physical-chemical properties of the substance, through various exposure routes (*e.g.*, direct contact of seeds and roots in soil, uptake of soil solution by roots, aerial deposition on leaves, translocation within the plant). The problem formulation stage should alert assessors as to which exposure routes are most likely to be of concern for various soil biota.

Assessment Approaches

As described generally in section 6.2, a variety of approaches exist to examine the effects of priority substances on soil-dwelling biota including:

- single species toxicity tests in the laboratory or field,
- multi-species tests,
- equilibrium partitioning approach, and
- QSARs.

All available data from these types of approaches should be considered in a weight-of-evidence approach. Several special considerations for assessing effects of substances to soil-dwelling biota are outlined below.

Single Species and Multispecies Toxicity Tests. In terrestrial ecotoxicology, a variety of protocols exist to assess effects on microorganisms, invertebrates and plants. There is currently only one internationally harmonized soil toxicity test using invertebrates. This is the acute earthworm toxicity test. The OECD toxicity guidelines for acute toxicity use the earthworm species *Eisenia fetida* and *Eisenia andrei* in the filter paper contact test and the artificial soil test (OECD 1984). Although both earthworm species are not soil-dwelling species and are usually found in compost or dung, they are easy to culture in the laboratory. The contact filter paper test is a toxicity screening test and effects in soil cannot be predicted (van Leeuwen and Hermens 1995). Effects data from the artificial soil test can be applied to natural soils using the sorption data equation:

$$LC_{50n} = (f_{oc} \cdot K_{oc}) \cdot LC_{50a}$$

where,

LC_{50n} = concentration in natural soil to which soil organisms are exposed which is estimated to be lethal to 50 percent of the organisms

f_{oc} = mass fraction of organic carbon in the solid phase

K_{oc} = organic carbon partitioning coefficient

LC_{50a} = concentration in artificial soil to which soil organisms are exposed which is estimated to be lethal to 50 percent of the organisms

An inventory of toxicological data prepared by Denneman and van Gestel (1990) indicates that well characterized soil toxicity information is limited, largely as a result of

only a few standardized testing procedures. Detailed reviews of effects testing of earthworms (Christensen and Mather 1994), and terrestrial arthropods (van Straalen and van Gestel 1992) have been prepared. In addition, considerable research is presently underway to standardize lethal and sublethal toxicity test procedures for a broader range of soil-dwelling organisms (van Straalen and van Gestel 1992; Leon and van Gestel 1994; Christensen and Mather 1994; NISRP 1991; SECOFASE 1993; VKI 1994). For plants, the U.S. EPA and OECD have developed protocols for terrestrial plant effects testing (OECD 1993d; U.S. EPA 1985b,c,d). While current standardized toxicity tests use artificial soils for reproducibility among laboratories and substances, assessors should also consider tests using field soils when available. Toxicity test data using the OECD artificial soil test have been shown to correlate well with field data (Christensen and Mather 1994). In Canada, a proposed guideline for nontarget plant testing and evaluation is available which recommends U.S. EPA and ASTM protocols for terrestrial and aquatic plant effects testing (Boutin *et al.* 1993). Since these protocols are at various stages of development and standardization, data should be evaluated with good general QA/QC practices and sound scientific principles in mind. Common endpoints that are useful for the assessment of priority substances for soil-dwelling biota are described below.

- *Microorganisms.* Tests exist for assessing functional and structural effects of substances on individuals, populations, and communities. Decomposition, respiration and organic nutrient (N, S, P) cycles are examples of soil processes whose rates may be adversely affected by priority substances. While it is acknowledged that these cycles should be examined, it is recognized that it may be difficult to integrate currently available literature into an assessment because of: (I) uncertainties in interpretation of results, including variability seen in dose-response relationships (Denneman and van Gestel 1990), (ii) frequent lack of reference chemicals, and (iii) uncertainty over appropriate controls. However, soil process data have the desirable property of ecological relevance - the use of these measures as indicators of ecosystem performance is well established (Paul and Clark 1989). Further, data on effects of common substances on some soil microbial processes is abundant (for example, see Bååth 1989). Examples of testing of soil microbial function involves studying the toxic effects on the carbon cycle, and the nitrogen cycle.

  A discussion on microbial ecology in organic nutrient cycling as indicators of soil quality (CCME 1995) identified N-fixation, nitrification, decomposition and respiration as potentially useful endpoints. Of these, N-fixation and nitrification data are preferred, but the carbon cycling measures may be used when the former are unavailable.

- *Invertebrates.* Studies on these organisms may measure biochemical, physiological, individual, population, or community level effects. The majority of

laboratory studies evaluate survival, growth and reproduction in individual species. Some terrestrial mesocosm studies have examined the interactions of substances on plants and invertebrates representing several trophic levels (Eijsackers 1994).

Another group of invertebrates which must be mentioned when dealing with terrestrial toxicity are the "beneficial arthropods". This group includes invertebrates that spend part of their life in or on soil and that are believed to improve agriculture (van Leeuwen and Hermens 1995). Examples of these species include pollinators such as the honey bee, *Apis mellifera*, and predatory and parasitic species that attack pest organisms. These include organisms in the Order Coleoptera: the Family Carabidae--ground beetles, Staphylinidae--rove beetles, and Coccinellidae--ladybirds, and other predators such as spiders (van Leeuwen and Hermens 1995). Ecotoxicological effects to these terrestrial invertebrates are not included in the Guidance and Resource documents as they are assessed separately by the Pest Management Regulatory Agency of Health Canada.

- *Plants.* Studies of effects of chemicals on plants are concerned with survival, growth rate and reproduction of individual species. In addition, studies on the uptake and translocation of substances within plants may be useful in assessing exposure to herbivores. Effects of substances in the field are often mitigated due to environmental factors (*e.g.*, wind, temperature, rainfall conditions), plant anatomy (*e.g.*, cuticle thickness), and physiological states of the plant (*e.g.*, reduced growth rate in the field compared to the greenhouse)(Garrod 1989). It is therefore recommended that both greenhouse and field studies be considered in deriving the CTV.

Equilibrium Partitioning (EqP) Approach. When faced with limited soil toxicity data, aquatic toxicity data using organisms relevant to the terrestrial environment may be used in EqP calculations for screening purposes (see section 6.2.6 for a general discussion of the EqP approach). The reasoning behind using aquatic toxicity data to predict effects values in soil is that the sensitivities of aquatic species and terrestrial species are expected to be similar, taking exposure conditions into account (VKI 1994). Aquatic species considered to be possible surrogates for related terrestrial organisms include crustaceans, insect larvae, annelids, plants and algae (VKI 1994). Use of surrogate aquatic toxicity data for soil organisms should only be used for species primarily exposed to substances in the pore water and not for species that ingest soil or accumulate substances from food. Direct single species or mesocosm toxicity tests should be used for the latter species. The assumption that the sensitivity of terrestrial species is comparable to the sensitivity of aquatic organisms has not yet been confirmed. The assessor should attempt to compare the effects data for aquatic species to effects data for comparable terrestrial organisms.

When converting effects concentrations in water (CTV_d) from aquatic effects data to effects concentrations in soil (CTV_s), two modifying factors must be considered, namely soil organic carbon content (f_{oc}) and soil water content (f_w) such that (modified from VKI 1994):

$$CTV_s = ((f_{oc} \cdot K_{oc}) + f_w) \cdot CTV_d$$

where,

CTV_s = critical toxicity value for soil biota
f_{oc} = mass fraction of organic carbon in the solid phase
K_{oc} = organic carbon partitioning coefficient (where $K_{oc} \approx K_{ow}$, the octanol-water partition coefficient)
K_d = adsorption coefficient in soil where $K_d = K_{oc} \times f_{oc}$ (see section 6.2.6)
f_w = mass fraction of water content in soil
CTV_d = critical toxicity value of a dissolved substance on an aquatic organism.

Assessors should evaluate whether the EqP approach assumptions as described in Section 6.2.6 are met.

QSARs. QSARs can also provide supporting information in the weight-of-evidence approach. While QSARs may be used to support the selection of the CTV, QSARs alone may not be used to derive the CTV. QSARs have been developed using the results of acute toxicity tests on earthworms for chlorophenols, chlorobenzenes and dichloroaniline (van Gestel and Ma 1990; van Gestel *et al.* 1991). In addition, the U.S. EPA ECOSAR program has derived a QSAR to predict the ecotoxicity of industrial substances using a 14 day LC_{50} test for earthworms in artificial soil (U.S. EPA 1994a). Assessors should refer to Section 7.2.5 for general information on QSARs.

Important Considerations

Soil properties play a key role in determining the sorption, speciation in the case of metals, and consequently the bioavailability of substances to soil organisms. These properties include pH, total organic carbon content (TOC), redox potential and related moisture content, and particle size distribution (% of sand, silt, clay), and clay type. While these factors influence bioavailability and toxicity, it is impossible to state typical ranges for each property appropriate to all Canadian soils throughout the year. These factors are important in determining the bioavailability of a substance to soil biota and therefore the levels of these factors in soil used in laboratory toxicity tests should mimic the actual soil of concern in the environment. In the case of pH, corresponding test conditions will enable assessors to ascertain that toxicity is due to the level of the substance and not for uncontrolled pH conditions. A draft report on the behaviour of groups of substances in general categories of Canadian soils is available (Environment

Canada, unpublished). Some examples illustrating the importance of these factors are described below; note that pH, TOC, and particle size distribution are also important properties in sediments and are discussed in section 6.4.2 on benthic biota.

- *pH.* pH is probably the most important soil property affecting the speciation of elements in soil solutions, the possible precipitates that may form, and the extent of adsorption of elements onto both mineral and organic surfaces (Evans and Spiers 1993). At certain pHs, elements may either be strongly held or very mobile which in turn will strongly influence the resulting toxicological behaviour of the substance. Heavy metal solubility is enhanced at lower pHs resulting in increased bioavailability. The cation exchange capacity (CEC) of the soils is also reduced at lower pHs, resulting in changes in the microbial population which may also affect the biodegradability and bioavailability of substances (van Leeuwen and Hermens 1995).

- *Organic Carbon Content.* The total organic carbon content in soils is important as metals react with functional groups contained within humic material to form complexes and because non-ionic hydrophobic organic compounds partition into soil organic matter (Evans and Spiers 1993). However, there are difficulties in defining appropriate ranges of organic carbon content because: (I) there are few thermodynamic data available with which to make predictions, and (ii) retention of hydrophobic compounds depends to a greater degree on their K_{oc} values than on the content of organic carbon in soil (Evans and Spiers 1993). The effects of high organic matter on both metals and organic substances results in a reduced bioavailability and toxicity. Low organic matter reduces the CEC, soil buffering capacity, the sorption of toxic substances, and the soil water-holding capacity. In addition, it alters the physical structure of the soil and decreases microbial activity (van Leeuwen and Hermens 1995).

- *Redox Potential.* The decrease of the redox potential may result in the mobilization of oxide-sorbed toxic substances as it dissolves iron and manganese oxides. By increasing the redox potential, heavy metals will be mobilized by dissolving metal sulphides (van Leeuwen and Hermens 1995).

- *Surface Texture.* The surface texture is the relative proportions of sand, silt and clay in the surface horizon and affects both the hydraulic and attenuation properties of soil (Evans and Spiers 1993). The cation or anion exchange capacity (CEC or AEC) of a soil is an important soil property as it affects the sorption of cations (*e.g.*, metals) or anions (*e.g.*, organic anions). The CEC or AEC depends on the inorganic clay content, and type of clay, the organic matter content and pH. Soils with low CEC or AEC will have a low capacity to sorb cations or anions (van Leeuwen and Hermens 1994). The clay fraction is composed of both phyllosilicate clays and secondary minerals, such as hydrous

ferric oxides. The clay minerals are important in that many elements form either inner- or outer-sphere complexes with the clay surfaces and are retained to differing extents depending on their intrinsic complexation constants and the pH of the soil. The proportion of clays is important for estimating the attenuating properties of soils. High clay content may reduce the bioavailability of many organic substances and heavy metals and in so doing, reduce the toxicity (van Leeuwen and Hermens 1995).

- *Oxygen Concentration.* The majority of terrestrial ecotoxicological research has been carried out under aerobic conditions. However, diffusion of oxygen in soil becomes limited in deep soil layers where anaerobic conditions may prevail. In anaerobic conditions, denitrifying, sulfate-reducing, and methanogenic metabolic pathways become critical and it is important to examine these processes for both chlorinated compounds and metals (Doelman and Vonk 1994). Lower oxygen conditions may result in reducing conditions, speciation of heavy metals and may effect the breakdown of organic substances (van Leeuwen and Hermens 1995).

- *Moisture Content.* A complex interaction exists between the type of substance and its expected partitioning among soil mineral particles, soil organic matter and soil water. Partitioning behaviour is determined by the dissociation coefficient of the substance and the degree of lipophilicity (van Gestel and Ma 1990), soil moisture content, and exposure route (*e.g.*, dermal ingestion, ingestion, inhalation). For instance, plant roots are primarily exposed to the soluble fraction of a substance and thus are more exposed during moist conditions, than during dry soil conditions.

- *Temperature.* As in other media, temperature affects a chemical's vapour pressure and solubility in water, thereby affecting the rate of uptake by organisms such as earthworms. Assessors should determine whether the temperature regime in the test is relevant to natural environmental conditions.

- *Salinity.* The salinity of soils can be an important factor whereby higher salinity increases the solubility of toxic substances by altering the ion exchange equilibrium, increasing the soluble complexation, and decreasing chemical thermodynamics, in addition to reducing microbial activity (van Leeuwen and Hermens 1995).

- *Exposure of Soil Biota.* Soil organisms can be exposed via three routes: (I) oral uptake (food or water), (ii) dermal uptake from the soil solution, and (iii) inhalation from soil air. For soft-bodied organisms living in close contact with the soil and soil water, toxicity is considered to be controlled by soil pore water concentration (van Gestel and van Straalen 1994). For organisms with firm or

hard cuticles, such as many arthropods, oral uptake may be a more important route. Therefore, assessors should examine substance partitioning within soil compartments, and the life habits of soil biota to determine the relevance of available toxicity test data.

- *Relevance of Test Conditions to Actual Field Conditions.* Some soil toxicity tests on earthworms examine effects after exposure to substances in a solution applied to filter paper; such results are not relevant to the natural environment. This test is useful in comparing the relative toxicity of various substances, or for assessing the effects of worst-case exposure (full body exposure to free product). Its use in estimating CTVs in the natural environment is limited.

Determining the CTV for Soil Biota

- Assessors should review appropriate databases for information on physical and chemical properties and effects information related to soil biota. Due to the complexity of the soil environment and the present state of knowledge of the interaction between soils and biota, use of laboratory tests, micro- and mesocosm tests with appropriate QA/QC practices are recommended for evaluating effects on soil-dwelling biota. Predictive approaches (*e.g.*, EqP and QSARs) are also recommended as screening mechanisms or as part of the weight-of-evidence to determine the CTV.

- Test organisms should ideally be representative of Canadian species and soils. Due to the heterogeneity of soils, assessors should be aware of the influence of organic matter, pH, particle size distribution and other soil properties on bioavailability and hence toxicity of organic and inorganic chemicals.

- Toxicity information should ideally include data from a wide range of trophic levels and from both above ground and soil dwelling biota. An ideal data set would include soil organisms (microorganism function, soil arthropod, earthworm), above ground invertebrates (predatory mite, parasitic wasp, honeybee and herbivore)(OECD 1995b), and three plant species (a monocot, a dicot, and a conifer).

  If no toxicity information on soil biota is available, surrogate data in the form of aquatic acute and chronic toxicity data for terrestrial species primarily exposed to a substance via the soil pore water phase can be used. Crustaceans, insect larvae, annelids, plants and algae may be relevant aquatic organisms groups.

  There is considerable uncertainty involved in the EqP approach as it applies to lipophilic substances, and it is therefore recommended that for such substances, direct toxicity testing results should be used.

- Sources of uncertainty (both qualitative and quantitative) should be identified at all stages of the soil effects assessment. This will assist in selecting an application factor (see section 8.1) and for defining appropriate research needs, as required.

- The CTV is obtained from a weight-of-evidence approach that examines all appropriate available data. Ideally data from chronic, full life cycle studies measuring nonlethal effects (such as growth, and reproduction) are preferred. The preferred quantitative expression is an EC10, followed by a LOEL or NOEL (see section 6.3). When only acute toxicity data are available or are more sensitive than chronic effects data, the CTV may be calculated from an LC_{50}, EC_{50} or other significant EC_x.

- For plants the difficulty in extrapolating results from one species to another (*i.e.*, surrogate species) has been well demonstrated, unless they belong to the same genus (Reynolds 1984). Extrapolation across families, therefore, is not justified.

6.5.2 Wildlife

This section discusses the types of toxicity information available for wildlife, available protocols for wildlife toxicity studies, and provides guidance on how to approach a wildlife risk assessment.

Background

Traditionally, the definition of wildlife has been limited to birds and mammals. In 1990, the definition of wildlife was expanded by a Federal/Provincial committee to include wild mammals, birds, reptiles, amphibians, fish, invertebrates, plants, fungi, algae, bacteria, and other wild organisms in order to give governments a clear mandate to take conservation actions on any wild species or ecosystem (Canadian Wildlife Service 1990). For assessment purposes, wildlife refers to wild mammals, birds, amphibians, and reptiles.

Depending on the physical and chemical properties of the substance and the route of entry into the environment, wildlife may be exposed to substances:

- through dermal contact with soil, sediment, water or air,

- by inhalation of contaminated air,

- through oral intake of aquatic or terrestrial prey,

- by accidental ingestion of soil or sediment (*e.g.*, diving ducks), or

- from cleaning feathers or fur (Appendix III).

Wildlife toxicity testing began in the 1950s as a consequence of wildlife losses due to use of DDT and other pesticides. The available wildlife testing protocols have recently been reviewed by Hoffman *et al.* (1995). The bulk of the wildlife toxicity literature pertains to pesticides and effects on non-target avian populations. Available avian protocols include acute oral (LD_{50}), short-term dietary (LC_{50}), chronic reproduction, embryotoxicity/teratogenicity, behavioral and field toxicity tests. Mammalian wildlife assessments rely heavily on the use of laboratory data (see Hodgson and Levi 1987 for overview of tests) generated for human assessments, although U.S. EPA protocols are available for the mink and European ferret. The range of sensitivity to substances depends on taxonomic class (birds are generally considered more sensitive than mammals, amphibians or reptiles), age, size (smaller species consume more substance per body weight) and life-history characteristics. Generalizations should be applied with caution as there are always exceptions (Tucker and Leitzke 1979).

A summary of the amphibian literature (Harfenist *et al.* 1989) indicated that neither test species or protocols are standardized. Although the available information is limited, the aquatic life stages appear to be the most sensitive for amphibians. This work is currently being updated by the Canadian Wildlife Service and will also include a review of the literature for reptiles. A compendium of available amphibian tests has been recently completed by The Water Quality Institute (Denmark) and RIVM (1995).

Assessment Approaches

The majority of wildlife toxicity data available in the literature have been generated for pesticidal substances and bioaccumulative non-pesticidal organics and metals. For the majority of priority substances, data will be sparse. All wildlife toxicity data available for the substance of interest will be considered provided the causal relationship is proven and good experimental practices are followed (Appendix III). Due to differences in wildlife physiology and sensitivity between classes, interclass extrapolations of quantitative data are not recommended for ecological risk assessments of priority substances. Only data on mammals are used to derive a CTV for mammalian wildlife species and avian data to derive a CTV for avian wildlife species. However, when physiological similarities exist between classes and the mechanism of action is known, data may be discussed qualitatively in relation to another class to provide supporting evidence for the assessment.

For wildlife, endpoints such as mutagenesis, reproductive and developmental toxicity (including effects on spermatogenesis, fertility, pregnancy rate, number of live embryos, neonatal mortality, egg-shell thinning, egg production, hatchability, and chick

survival), reduction in growth and reduced survival are preferred as they may be directly related to gene pool biodiversity and potential population level effects. Chronic studies on organ-specific effects may be used if the effect can be shown to reduce survival in wildlife. Particular attention should be paid to substances that are either endocrine disrupters or genotoxins. Endocrine disrupters interfere with the production, release, transport, metabolism, binding, action or elimination of natural ligands in the body responsible for the maintenance of homeostasis and the regulation of developmental processes (Colborn *et. al.* 1993). Genotoxins alter genetic structure or function in individuals that ultimately result in decreased population abundance or irreversible changes in the variability within gene pools. This occurs via the induction of malignant tumors, decreases in reproductive success, or altered genotypic diversity (Andersen *et. al.* 1994).

Field Studies. Data from peer-reviewed field studies are preferred over all other types of studies for development of a CTV. The study must be of sub-chronic or chronic exposure, provide a substance-specific dose-response relationship and include reproductive or survival endpoints. Field studies can integrate many environmental factors that cannot be replicated in a laboratory study. Possible measurement endpoints include: reduced survival; impaired reproduction; altered behaviour that can cause changes in breeding or ultimate survival, care of young, inter-species interactions, and food consumption; changes in physiological condition; increased vulnerability to predation; decreased resistance to disease and weather; decreased nesting growth or shortened breeding season due to decreased food supply; and loss of habitat.

Laboratory Toxicity Tests. When field studies are not available, peer-reviewed laboratory studies may be used to develop a CTV, with preference given to wildlife species over traditional laboratory animals. Laboratory studies can control for external interferences, or isolate responses in a manner not possible in field studies in order to obtain a better understanding of individual parameters and to determine cause and effect relationships. When using single species laboratory tests for estimating risk to wildlife, the following points should be kept in mind. Variation may exist among species in physiological or biochemical factors such as uptake and metabolism that can alter the potential toxicity of a substance to a particular species. Inbred laboratory strains may have an unusual sensitivity or resistance to the tested substance that is difficult to predict. Behavioral and ecological parameters (*e.g.*, stress factors such as competition, seasonal changes in temperature or food bioavailability, disease, or exposure to other substances) may change species sensitivity to a substance. Many of these uncertainties can be accounted for in the risk assessment with the use of application factors or by means of a quantitative uncertainty analysis (Chapter 8).

Body Burdens. In field studies, the body burden of a substance (usually a metal or bioaccumulative organic) in wildlife is often measured to establish exposure to the

substance. This information can be compared to critical body burdens of the substance (see section 6.2.4) measured during toxicity testing for risk characterization. For naturally occurring substances (*e.g.* metals), knowledge of background levels is also necessary. This technique is particularly relevant for metals, where it is difficult to predict the quantity of bioavailable substance in the environment. Unfortunately, as critical body burdens are not routinely measured, this information is not available for most substances.

Determining the CTV for Wildlife

- In general, assessors should attempt to locate all acceptable field and laboratory data on wildlife species as well as studies with exposure during critical life stages (*e.g.*, reproduction and development) of laboratory rodent species and birds.

- Wildlife data are expected to be sparse for most priority substances. Therefore all wildlife data for a substance will be considered, regardless of the methodology used, provided a causal relationship is proven and good experimental practices are followed.

- Attention should be paid to substances which are either endocrine disrupters or genotoxins.

- Assessment and measurement endpoints should have similar exposure routes. For a volatile substance that partitions into the air, an inhalation study is preferred and for a hydrophobic substance that partitions into biota, an oral ingestion study is preferred.

- Assessors should document qualitative and quantitative sources of uncertainty associated with the toxicological data used, since this will need to be taken into account during risk analysis.

- It is recommended that where available, the lowest acceptable EC_{10}, LOEL or the highest acceptable NOEL in that order of preference from a reproductive effects study, for example, be used for deriving the CTV. If a reproductive effect study is not available, reduced survival endpoints may be used.

6.6 Effects Mediated Through the Atmosphere

6.6.1 Introduction

This section describes atmospheric effects and provides guidance to assessors in identifying the measurement endpoints and effects thresholds that may be used in assessing atmospheric effects under CEPA. Atmospheric effects include direct effects such as air quality reduction as represented by ground level ozone formation, and climate change due to enhanced warming of the atmosphere. An example of indirect effects is stratospheric ozone depletion that results in enhanced human health risks on Earth. In order to arrive at a "toxic" determination in the PSL process, a legal foundation is required. CEPA uses two different sub-sections of section 11, to draw the distinction between the two types of atmospheric effects, and thereby meet the statutory requirement.

For a substance to be "toxic" under section 11(b) of CEPA, it must enter the environment in a quantity or concentration or under conditions constituting or that may constitute a danger to the environment on which human life depends. Section 11(b) attempts to address the effects or issues not covered under section 11(a)--direct toxic effects on the environment or under 11(c)--direct toxic effects on human health. In this section, 11(b) effects have been labelled as "indirect effects".

For assessment purposes under CEPA, both ground level ozone formation, and global warming will be considered as direct effects and therefore assessed under section 11(a). Stratospheric ozone depletion will be considered as an indirect effect and assessed under section 11(b).

The characteristics of substances known to be associated with each atmospheric effect are outlined in section 6.6.2. The methods that are available to quantify such effects are described with examples in section 6.6.3. Section 6.6.4 discusses the thresholds that lead to an assessment decision.

6.6.2 Substance Characteristics

Stratospheric Ozone Depletion

When screening substances to determine if they could cause stratospheric ozone depletion, the following physical characteristics or behaviour of the substance should be taken into consideration during the problem formulation stage.

- In general, substances with tropospheric sinks or removal mechanisms will be unlikely to act as ozone depleters (Molina and Rowland 1974).

- Most ozone depleting substances are halocarbon gases. Upon reaching the upper atmosphere, the halogen bearing substance is cleaved by high energy, short-wavelength (190-230 nm) radiation to release free halogen (Rowland 1988):

- From a substance standpoint, ozone depleting substances are transparent--do not absorb radiation between ≈230 and ≈700 nm and do not photolyze--in the troposphere. They are inert towards the hydroxyl radical (OH·) and other oxidants (Molina and Rowland 1974). They have atmospheric lifetimes measured in years.

- Ozone depleting molecules are insoluble in water, thereby reducing the potential for dissolving in rain drops and subsequent removal from the atmosphere by rainout (Rowland 1988).

Ground level Ozone Formation

The formation of ozone (O_3) and other photochemical smog components over urban and rural areas is the result of a complex non-linear interaction of atmospheric substances, sunlight and meteorology. Of most significance among the precursors of smog are nitrogen oxides (NO_x) and hydrocarbons (HC). However, because O_3 production is separated in time and space from precursor emissions, there is a need for an *a priori* method for characterizing the O_3 forming potential or reactivity of ambient substance mixtures. In general:

- The substance must be volatile at ambient temperature and pressure conditions.

- The substance is a reactive hydrocarbon in the troposphere.

- Meterological conditions are important for the promotion of ozone forming reactions, such that the highest ozone concentrations are found at high temperatures, high levels of solar radiation and low wind speeds.

- The concentration of other airborne substances is important since the formation reaction depends on reactions with several other substances, especially nitrogen oxides, whose concentration in air should exceed several $\mu g/m^3$.

Ozone is formed in the lower atmosphere by the photolysis of nitrogen dioxide (NO_2) to nitrogen monoxide (NO) and atomic oxygen, which reacts with O_2 to produce O_3 . However, some of this ozone subsequently reacts with nitrogen monoxide (NO) to produce NO_2 and O_2 so the concentration of ozone stabilizes. When volatile organic compounds (VOCs) are present in the atmosphere, they react to form radicals that either consume NO or convert NO to NO_2. The concentration of ozone can then

increase because it is no longer being used to oxidize NO to NO_2. The concentration of nitrogen oxides becomes the limiting factor in ozone formation when it is low compared to the concentration of VOCs (modified from Spedding 1974).

It has been shown that high ozone days in areas downwind of urban centres may be caused by climatic conditions that transport ozone and ozone precursors over hundreds of miles (Kelly *et al.* 1986; Clarke and Ching 1983).

Global Warming

A substance has certain characteristics if it is likely to contribute to global warming. Such substances are gases at ambient temperatures and pressures, absorb energy in the infra-red portion of the spectrum, show absorption bands in the "atmospheric window" (800-1200 cm^{-1}), and have significant atmospheric lifetimes (*i.e.*, a year and longer)(de Leeuw 1993).

6.6.3 Quantification of Atmospheric Effects

Stratospheric Ozone Depletion

Ozone Depleting Potential (ODP) is defined as the ratio of calculated ozone column change for each unit mass of a gas emitted into the atmosphere relative to the depletion calculated for an equal mass of reference gas CFC-11 (ODP=1). In a first approximation, the ODP-value can be calculated using the formula:

$$ODP = (\tau_S / \tau_{CFC\text{-}11})(M_{CFC\text{-}11} / M_S)((n_{Cl} + \alpha n_{Br}) / 3)$$

where,

$T_{CFC\text{-}11}$	=	atmospheric lifetime ($\tau_{CFC\text{-}11}$ = 60 y)
T_S	=	atmospheric lifetime of substance S
$M_{CFC\text{-}11}$	=	molecular mass ($M_{CFC\text{-}11}$ = 137.5 $g \cdot mol^{-1}$)
M_S	=	molecular mass of substance S
n_{Cl} and n_{Br}	=	the number of Cl and Br atoms per molecule
α	=	a measure of the effectiveness of Br in ozone depletion with respect to Cl; a reasonable value is α = 30.

A sample calculation is provided to understand how the formula is applied. For example, using the ODP for Methyl chloroform (CH_3CCl_3) and substituting the numerical values into the formula yields:

$$\begin{aligned} ODP &= 6.3\ y/60y \times 137.5\ g \cdot mole^{-1}/132.4\ g \cdot mole^{-1} \times 3/3 \\ &= 0.105 \times 1.038 \times 1 \\ &= 0.11 \end{aligned}$$

In general, ODP values approach zero for species with atmospheric lifetimes less than one year (CEU 1995).

Ground Level Ozone Formation

To estimate Ozone Forming Potential (OFP), a method known as the Photochemical Ozone Creation Potential (POCP) index is defined in a report for the Commission of the European Union (CEU 1995). It is a measure of the relative effect on ozone of a unit mass of organic substance compared to that caused by an equivalent mass of ethene. By definition, ethene has a POCP value of 100. A first indication of episodic ozone formation can be obtained from a reactivity scale based on the rate constant for the (OH-hydrocarbon)-reaction and the molecular weight of a substance, "S".

$$\text{OH-scale} = (k_s / M_s)(M_{ethene} / k_{ethene}) \times 100$$

where k_s = reaction rate constant at T = 298 K for the reaction with the OH-radical
($K_{ethene} = 8.5 \times 10^{-12}$ cm^3 mole^{-1} sec^{-1})
M = molecular mass (M_{ethene} = 28 g/mole)

A sample calculation using toluene:

$$\text{OH-scale} = \frac{5.4 \times 10^{-12}}{92.13} \times \frac{28}{8.5 \times 10^{-12}} \times 100$$

$$= \frac{151.2}{783.1}$$

$$= 19.3\ (\%)$$

In addition to using the above reactivity scale calculation to determine the relative Ozone Forming Potential, there are additional methods available for estimating the potential of a single substance to contribute to tropospheric formation. These methods can be employed in a second round of estimations for substances that are shown to exceed the threshold in the first round.

One method uses reactivity scales that take into account the kinetic reactivity--how quickly the VOC reacts to form a free radical--and the mechanistic reactivity--how much ozone is formed by its reaction. In general, a reactivity scale is a numerical ranking system where each VOC is assigned a number giving a measure of how its emissions affect ozone formation.

Two sets of reactivity scales have been calculated: the Maximum Incremental Reactivity (MIR) scale and the Maximum Ozone Incremental Reactivity (MOIR) scale (Russell *et al.* 1995). Substance for which the reactivity factors are not available, will need to consult with experts in the field to arrange for their generation using complex computer simulations.

Global Warming

Global Warming Potential (GWP) is defined as the ratio of calculated warming for each unit mass of a gas emitted into the atmosphere relative to the calculated warming for a mass unit of the reference gas CFC-11. Assessors will be able to estimate the GWP of a substance "S", using the following formula (de Leeuw 1993).

$$GWP = (T_s / T_{CFC\text{-}11})(M_{CFC\text{-}11} / M_s)(S_s / S_{CFC\text{-}11})$$

where

T_s = atmospheric lifetime ($T_{CFC\ 11}$ = 60 y)
M_s = molecular mass ($M_{CFC\ 11}$ = 137.5 g·mol^{-1})
S_s = IR absorption strength in the interval 800-1200 cm^{-1}
$S_{CFC\text{-}11}$ = IR absorption strength derived from references below.

Methods for deriving infrared absorption strengths (S_s and $S_{CFC\text{-}11}$) are described by Rogers and Stephens (1988) and Kagann *et al.* (1983)(CEU 1995).

A sample calculation of GWP is provided using CFC-12 as an example.

GWP = (120y/60y) X (137.38 g·mole^{-1}/120.92 g·mole^{-1}) X (3240/2389 cm^{-2} atm^{-1})

= 2.0 X 1.14 X 1.4
= 3.09

6.6.4 *Thresholds for Determination of "Toxic" for Atmospheric Effects.*

Stratospheric Ozone Depletion

Ozone depleting substances with a calculated ODP greater than zero may be subject to some level of control in their use. Therefore, any substance with an ODP will be sufficient justification for a "toxic" 11(b) determination, and therefore regulation, under CEPA.

Tropospheric Ozone Formation

There is much uncertainty associated with the methodology and the physical and chemical processes to confidently ascribe a threshold above which a VOC could be

considered "toxic" due to its ozone forming potential. However, using the formula described above, any substance with an ozone forming potential of 5 or greater should be considered a concern. To take advantage of the science as it exists today, ozone forming potentials should be taken into consideration in a weight-of-evidence approach that will be followed in PSL assessments. In addition, this data will be useful to risk mangers in determining the extent and appropriateness of regulatory control for those VOCs found to be toxic.

Global Warming

The initial calculation of de Leeuw (1993) does not account for the impact posed by the quantity of the substance released to the atmosphere, but indicates that the substance will behave as a global warmer under atmospheric conditions. Therefore substances that are shown to have an estimated GWP of 0.05 or greater should be "flagged" and noted as a concern.

The flagged substance will be subject to an expert study using a General Circulation Model or equivalent to determine if the quantity released, combined with its global warming potential results in a significant effect on climate change. It may be determined to be "toxic" under Section 11(a) of CEPA if a significant effect can be seen in the overall climate change equation.

These GWP estimates will be useful for developing a weight-of-evidence approach for the assessment of trace gases that could play a role in the radiative balance of the Earth and for providing risk managers with a quantitative benchmark when considering regulatory control measures for substances found to be "toxic" under CEPA.

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Chapter 7

Complex Substances

7.1 Introduction

Most of the work in environmental toxicology and ecological risk assessment has focused on individual substances. However, in nature, biota are often exposed to complex substances such as mixtures or effluents[1].

There are three types of complex substances:

- 1) those composed of related substances having similar physical and chemical properties (*e.g.*, PAHs, PCBs, dioxins);
- 2) those that are generated or released at a given time and place (*e.g.*, emissions from smelters, effluents), that have a relatively defined and constant composition, but that are not necessarily composed of related substances (*i.e.*, constituents); and
- 3) those, that are often commercially or chemically unrelated (*i.e.*, having different physical and chemical properties), and that occur by coincidence at a given time and place (*e.g.*, landfill leachate)(adapted from U.S. EPA 1986, 1988; Vouk *et al.*, 1987).

For the purposes of this document, complex substance refers to either type 2 or 3 as described above. This chapter focuses on complex substances composed mainly of classes of unrelated substances. However, information in this chapter can be used to conduct an ecological risk assessment of related substances--often released from diffuse sources. An example would be discharges of effluents or emissions from a facility where related constituents are believed to be the cause of potential environment effects. These assessments would be source specific such as those involved with type 2 and 3 substances.

The ecological risk assessment of complex substances have several complications including: I) partitioning and persistence of constituents of complex substances after their release in the environment, ii) additive versus interactive effects among constituents, iii) abiotic aspects of ecosystems, and iv) interactions between populations, and between populations and the environment. Because often these data are unavailable, different methods are required to conduct an ecological risk assessment of a complex substance.

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[1] See definition in glossary

. The focus of this chapter is to emphasize the differences between assessments of complex and individual substances. Several preferred methods are presented outlining uncertainties and ways of reducing them, factors to consider when evaluating the validity of a particular study and examples of approaches. Other methods are also presented. A weight-of-evidence approach should be used to determine risk (see section 7.6 for additional information).

Some of the information and considerations addressed in other chapters of the document may also apply to the assessment of complex substances. To avoid repetition, assessors should refer to appropriate chapters when clarification or additional information is needed on a particular issue. Additional reading materials pertaining to complex substances are referred to when needed.

Studies needed to conduct an ecological risk assessment of complex substances are not always available. In such cases, research should generate the appropriate data. Research needs can be identified using computer-based models. However, such models are less useful in the assessment of complex substances because they often have to be site specific. If site-specific models are available, model outputs can be used as long as the outputs are supported by empirical data (*e.g.*, ambient monitoring data). When computer-based models are used, model experts should be consulted with regard to advantages, limitations and assumptions.

The United States, The Netherlands and Denmark and have recommended methods to assess the environmental effects of effluents (U.S. EPA 1991; Petersen *et al.* 1995; Adriaanse *et al.* 1995; De Zwart 1995; Groot and Villars 1995; Petersen *et al.* 1994; Tonkes *et al.* 1995; van Loon and Hermens 1995). A brief overview of the United States Environmental Protection Agency method is presented in Dorn and Compernolle (1995). A summary of methods used in other countries can be found in De Zwart (1995), Groot and Villars (1995) and Tonkes *et al.* (1995). These methods should be consulted when conducting assessments of complex substances. It is recognized that some of the methods/recommendations/procedures recommended by other countries may not apply to the Priority Substances List (PSL) Program. However, they do provide an overview, advantages, limitations etc. of similar methods proposed in this document and useful complimentary information can be found. Although the methods outlined by other countries focus on effluents, some aspects may also be useful for the assessment of mixtures (*e.g.*, characterization, limitations and capabilities of assessment methods).

7.2 Data Collection and Generation

Most of the guidance and information sources presented in chapter 2 apply to complex substances.

Complex substances are not usually assigned a Chemical Abstracts Service Registry Number. They are often referred to under various technical names. In stage 1 of data collection, assessors should be aware of the various technical names that represent a particular complex substance. For example, while searching for data on waste crankcase oils, technical names used as keywords include: waste crankcase oil, used crankcase oil, waste oil, used oil, waste lubricating oil, used lubricating oil, waste motor oil, used motor oil, spent oil, etc.

Group parameters[2] of a complex substance are also useful when searching for data. For example, technical names and group parameters (see underlined keywords below) for chlorinated wastewater effluents include: chlorinated wastewater effluent, chlorinated effluent, chlorinated sewage, residual chlorine, chlorine residual, chlorination, etc. Key constituents of complex substances could be used as keywords during data collection. For example, if sulphur dioxide is a key constituent of a mixture released from a stack, sulphur dioxide should be used as a keyword during data collection. These strategies increase the probability of obtaining all available data. However, by using such an array of keywords, particularly during electronic database searching, many irrelevant data may be retrieved. To reduce their number, Boolean Logic (*e.g.*, operators such as OR, AND, NOT used to group, connect or eliminate specified terms) could be used during the search. In addition, assessors can use, as a second type of key word, the source of release of a complex substance to the environment.

Most complex substances listed on the PSL are already assigned predetermined source(s) of release. In such cases, the source of release of a complex substance can be used as a keyword as part of the search strategy. Source(s) of release can also be expressed by a variety of technical names. For example, the pulp mill "theme" can be cited in information sources as pulp mill, bleached pulp, paper mill, kraft mill, bleaching effluent, kraft bleaching, etc. For complex substances listed on the PSL with no predetermined source(s) of release (*e.g.*, waste crankcase oils), the characterization of entry using a lifecycle approach is essential and must be completed in order to use the sources of release in the search strategy (*e.g.*, road oiling for waste crankcase oils).

Once stage 1 of data collection is completed, assessors must determine whether data essential to the assessment are available. Assessors must identify data gaps in order to request such data during stage 2 and stage 3 of data collection. When such data are unavailable, data gaps must be identified as early as possible since some approaches may require long lead times to generate data (Stage 4).

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[2] See definition in glossary or in section 7.7.1

7.3 Problem Formulation

In problem formulation the goals, breadth and focus of the assessment are established; data gaps are identified; and a strategy for proceeding with the assessment is devised. This phase includes *initial scoping*, *pathways analysis*, consideration of *receptor sensitivity*, an analysis of the *ecological relevance* of potential receptors, selection of *assessment endpoints* and associated *measurement endpoints*, and the development of a *conceptual model* .

A complex substance must be thoroughly characterized in the problem formulation stage. The characterization should be representative of the entire complex substance since complex substances can be variable temporally (*e.g.*, quantity and composition) and spatially (once released). Such variability is likely to influence ecotoxicological characteristics of complex substances. Sampling methods are, therefore, an essential determinant in characterization of complex substances (see section 7.7.3 on sampling methods).

The characterization is carried out in initial scoping and pathways analysis where entry and exposure are identified. Continuous refinement of this characterization is necessary throughout the assessment process. Since initial scoping and pathways analysis are considered essential "building blocs" for subsequent phases of problem formulation, this section will focus on these two phases only. For information on other phases, refer to chapter 3.

7.3.1 Initial Scoping

The first step involves reviewing the rationale presented by the Minister's Expert Advisory Panel outlining the reasons for selecting the complex substance for the Priority Substances List and its expected major focus of the assessment.

The characterization of a complex substance involves identifying various technical names of the substance and, on a qualitative basis, identifying potential constituents of concern, group parameters and sources of release (see section 7.2 for additional information).

Physical and chemical properties of constituents and group parameters indicate possible fate, transport and composition of the complex substance following release. Assessors should be aware that the toxicity properties of constituents and group parameters, and many transport and transformation processes may be influenced by interactions between constituents in the complex substance and by the characteristics of the site(s) of release.

7.3.2 Pathways Analysis

Pathways analysis considers entry of the substance into the environment and the probable environmental fate and routes of exposure of the substance in order to estimate the geographic distribution of the substance in the Canadian environment, ecosystems at risk and potential risk receptors.

To characterize the environmental releases of a priority complex substance into the Canadian environment, data required include:

- amounts generated or produced, imports, exports and consumption data,
- significant sites of release in Canada (*e.g.*, type of organization, type of industry, etc),
- volumes or flow rates (*e.g.*, $L \cdot day^{-1}$, $kg \cdot day^{-1}$) discharged or quantities emitted (*e.g.*, $mg \cdot kg^{-1}$ waste, $g \cdot day^{-1}$) of the complex substance to the environment,
- type of environmental compartment receiving the release (*e.g.*, streams, rivers, lakes, soil, atmosphere, etc.);
- patterns of releases (*e.g.*, continuous, intermittent, seasonal), and
- a brief description of the life cycle of the complex substance for predicting environmental releases, including:
  - storage, distribution and transportation, and
  - use and disposal.

The objectives of characterizing the environmental fate and routes of exposure of complex substances are to:

- identify the probable environmental partitioning (*e.g.*, to air, soil, surface or ground water, sediment, biota) and fate of the substance,
- estimate the geographic distribution and concentration ranges of the substance in the Canadian environment,
- identify the ecosystems at risk, and
- identify the living or non-living components of the ecosystems that may be exposed to the substance.

Once the substance and its release are sufficiently characterized, its environmental partitioning, fate and geographic distribution can be determined and involves analyzing the following data:

- physical and chemical properties of constituents and group parameters of complex substances,
- persistence of constituents and group parameters in various environmental compartments,
- bioavailability and tendency of constituents and group parameters to bioaccumulate in living tissue, and
- volumes or flow rates discharged or quantities emitted to various compartments of the environment.

This data can be obtained, for example, from chemical monitoring of constituents and group parameters obtained from field and laboratory studies involving chemical analysis (Sections 7.5 and 7.6).

Computer-based models can also predict the environmental fate of complex substances. However, practical applications of model outputs are less useful than those for individual substances. The behavior of complex substances cannot necessarily be predicted based on behavior of individual constituents (*i.e.*, the whole is not necessarily the sum of its parts)(Parkhurst, 1986). Data on physical and chemical properties, interactions between constituents, and between constituents and the receiving environment are often unavailable. Such approaches may, therefore, only be used for a qualitative fate assessment.

Understanding how constituents and group parameters in complex substances behave is essential in considering receptor sensitivity, identifying assessment and measurement endpoints, and assembling a conceptual model.

7.4 Entry Characterization

Entry characterization identifies sources of release and quantifies the amounts released to the Canadian environment using a lifecycle approach.

7.4.1 Identification of Sources

The objectives are mainly qualitative and include:

- updating lifecycle events of the complex substance,
- identifying domestic and transboundary sources of entry of complex substances into the Canadian environment.

A lifecycle approach may not be necessary for substances with predetermined sources of release (*e.g.*, air emission from a specific smelter). For substances with no predetermined source of release, an evaluation of the lifecycle is essential for characterizing entry. Additional keywords identified during the characterization of entry should be used in the search strategy (Section 7.2).

7.4.2 Characterization of Releases

Once the sources of release have been identified, entry characterization should focus on a quantitative analysis of the release characteristics with the following objectives:

- refining the classes of constituents, potential constituents of concern and group parameters identified in problem formulation;
- identifying the frequency and pattern of release (*e.g.*, continuous, intermittent);
- refining amounts and forms (*e.g.*, composition of the complex substance, chemical and physical state of constituents) generated or produced;
- using monitoring data to 1) update volumes or flow rates or quantities from all sources emitted to the environment, and 2) identify concentrations of major constituents, constituents of concern and group parameters in the releases using chemical monitoring data;
- using the above to quantify amounts in the release.

Outputs from site-specific computer-based models can estimate releases. The model outputs must be supported by empirical data and used as part of a weight-of-evidence approach. In general, site-specific monitoring data provide the most accurate means of estimating substance concentrations and rates of release in stack gases, effluents, spills, etc. However, monitoring data are often unavailable. In such cases, mass-balance type models or emission factors can be used to estimate releases or data might have to be generated.

7.5 Exposure Characterization

Exposure characterization quantifies the relationship between a complex substance's source inputs and its resulting geographic distribution in space and time (spatial and temporal scale), and identifies populations at risk.

The distribution of complex substances between different media is determined by transport of water, air and particulate matter, by chemical and biological transformation processes and by distribution processes, such as absorption and desorption on sediment and suspended material, evaporation from the water and soil phase and bioaccumulation in organisms. Distribution processes can be regarded as equilibrium processes. The equilibrium distribution depends to a great extent on the physical and chemical properties of a substance and the media concerned (*e.g.*, fat content of organisms, organic hydrocarbon content of sediment and suspended material) (Adriaanse *et al.* 1995).

The media of concern should be used to define the spatial and temporal scale of the assessment. This media is not always the immediate media in which a complex substance was released. For instance, for hydrophobic substances discharged to an water system, the distribution processes may result in an accumulation of such substances in sediments. Therefore, sediment monitoring data should be used to define the spatial and temporal scale of the assessment.

7.5.1 Fate and Spatial and Temporal Scales

Because of the complexity involved in assessing mixtures and effluents, the physical and chemical properties of constituents and the receiving environment can only be used on a qualitative basis to predict the fate of complex substances. Fate and exposure models can predict the fate of complex substances and the spatial and temporal scales of the assessment. However, model outputs are less practical than those for individual substances because models are site specific. For this reason, the model outputs must be supported by empirical data and used as part of a weight-of-evidence approach.

Chemical field monitoring of key constituents and group parameters are the preferred approaches that quantitatively determine the fate and spatial and temporal scales of the assessment. Monitoring variables (measures of exposure and effects) include constituents and/or group parameters identified to be the cause of environmental harm. When chemical field monitoring studies are unavailable, monitoring data may be obtained from field and laboratory-ambient toxicity tests. In the latter type of study, samples of complex substances taken from the receiving water at various distances from the release point of release undergo chemical analysis and toxicity bioassays in a laboratory. Results from field and laboratory-ambient toxicity

tests can determine the potential for exposure at a given distance from the release point and used directly in the effects and risk characterizations.

Potentially harmful constituents and group parameters can be excluded in a particular field or laboratory chemical analysis test--budget constraints, not part of objectives, difficulty in detecting, etc. When the data is available, these should be used to determine the persistence and bioavailability of constituents and define the spatial and temporal scale of the assessment. Research should generate the data if its unavailable.

7.5.2 Identification of Organisms Exposed to Complex Substances

Organisms selected for evaluation should be among those most at risk because of high exposure to the substance. Potential for exposure should be based on knowledge about how a substance is distributed in the environment and major routes of exposure for different types of organisms. Data should be collected on the spatial and temporal distributions of potentially exposed organisms in Canada and their preferred habitat. This will ensure that organisms selected for evaluation are likely to have been present in the areas of concern prior to the onset of contamination. Other factors that could affect exposure such as diet, mobility, and body size should also be considered when selecting organisms for evaluation (see Appendix III).

7.6 Effects and Risk Characterizations

Effects characterization determines whether complex substances are causing adverse effects to exposed organisms. By using field and laboratory-ambient toxicity tests that compare exposure and effects data, assessors can directly conduct a risk characterization.

The occurrence of constituents in complex substances can influence toxicity in two ways. First, the interactions of constituents can cause a toxic effect that is qualitatively or quantitatively different from that of any of the constituents acting alone, as is the case with additive, antagonistic or synergistic effects. Second, the effects of one constituent may influence the kinetics of uptake, metabolism, and excretion of other constituents (Suter 1993). Because of these factors, complex substances require different methods for assessing ecological risks.

The preferred methods for this phase of the assessment are, in order of preference:

- field toxicity tests (*e.g.*, *in situ* biological testing, community surveys)
- laboratory-ambient toxicity tests, and

- laboratory toxicity tests using whole effluent or whole mixture samples.

Constituents of complex substances often partition into different environmental compartments, such as soil, water, biota, etc., and single species tests are customarily conducted in only one of these compartments. Field studies at the community and ecosystem levels could provide a more realistic assessment of effects (Vouk *et al.* 1987). However, such studies are often unavailable and other types of field toxicity tests, including population level studies and *in situ* bioassays, can be useful.

Bioassays provide toxicological data only, unless they are performed in combination with chemical analysis--extraction and fractionation techniques (Section 7.7.1). By chemically characterizing a complex substance in field and laboratory-ambient toxicity testing, exposure and effects data can be used directly in a risk characterization.

Field toxicity tests, laboratory-ambient toxicity tests and whole effluent and mixture tests have a number of advantages:

- Field toxicity tests can provide direct evidence of effects to organisms in the environment.

- Field and laboratory-ambient toxicity tests involving chemical analysis can provide data on the fate of complex substances, exposure concentrations of constituents and group parameters, effects and risk to organisms. They do so by taking into account the characteristics of the constituents and the receiving environment that are difficult to characterize by other means (Porcella *et al.*, 1986).

- Field and laboratory-ambient toxicity tests reflects effects in which the bioavailability of constituents are incorporated in addition to their concentrations and intrinsic toxicities.

- Laboratory-ambient toxicity tests can evaluate the persistence of the complex substance.

- Whole effluent and mixture tests can provide worst-case estimates of adverse effects.

In order to use such methods, assessors must demonstrate that the observed effects are due to the complex substance and not to substances released from other sources.

Assessors should always try to determined the constituents and group

parameters responsible of the environmental harm. However, such data may not always be available using these methods. In this case, research may have to be carried out to generate the data.

Other laboratory methods can identify and assess the potential adverse effects of constituents. These include i) artificial testing systems (microcosm and mesocosm tests), ii) effluent and mixture fractionation methods (also known as Toxicity Identification and Evaluation), iii) the representative substance class method, and iv) the individual substance method. These methods are presented in section 7.6.3.

While field toxicity tests, laboratory-ambient toxicity tests and whole effluent and mixture toxicity tests are the preferred methods to assess complex substances, assessors should use a combination of these tests to build a weight-of-evidence approach. Other laboratory methods can also be used in a weight-of-evidence approach. The use of integrating or combining approaches to assess adverse effects of complex substances have been recommended by other organizations including the United States Environmental Protection Agency and The Netherlands Monitoring Water Quality in the Future Project (U.S. EPA, 1991; Adriaanse *et al.*, 1995; van Loon and Hermens, 1995; De Zwart, 1995: Tonkes *et al.*, 1995; Groot and Villars, 1995). These organizations focussed on the assessment/control of water quality impacts caused by discharges of effluents. For a discussion on the capabilities and limitations of biological surveys, whole effluent toxicity test and the individual substance methods, refer to U.S. EPA (1991). The Sediment Quality Triad approach is an example of a structured integrative method of determining sediment contamination and assessing complex substances in sediments (Chapman 1989).

Ecological effects models are not available for the assessment of complex substances (Vouk *et al.*, 1987).

7.6.1 Preferred Methods for Effluents

There are no standard protocols or approaches for directly determining the effects of effluents on the structure and function of natural populations, communities and ecosystems. However, there are approaches, including some that have been used for effluents previously listed on the Priority Substances List, that have proven to be successful for assessing the ecological risk of effluents. These approaches are discussed below.

Information on methods for measuring the acute or chronic toxicity of effluents and receiving waters to freshwater or marine organisms are available (Environment Canada 1990a,b; De Zwart 1995; Klemm *et al.* 1991; Lewis *et al.* 1991; Weber *et al.* 1991). This information can be used when evaluating the QA/QC and validity of a study.

7.6.1.1 Field Toxicity Tests

One approach is to use caged test organism exposed to the conditions in the receiving water system. The toxicity response can be either evaluated at regular intervals in time, or by (semi) continuous monitoring. In general, the first option is associated with effects such as lethality, growth and reproduction, while the second option is design to evaluate physiological or behavioural responses. The second approach involves conducting biological surveys. Two types of controls can be used:

- Spatial Controls
  - *in situ* toxicity studies using caged organisms located upstream and downstream of the discharge, and
  - surveys of community structure, population survival, or other biological endpoints upstream and downstream of the discharge.
- Temporal Controls
  - *in situ* toxicity studies using caged organisms located upstream and downstream of the discharge and conducted before and after a process change (*e.g.*, switching to discharges of non-chlorinated effluents), and
  - surveys of community structure, population survival, or other biological endpoints conducted before and after a process change upstream and downstream of the discharge.

These approaches compare the results of upstream (*i.e*, control site) and downstream surveys and/or toxicity tests and determine if adverse effects have occurred (*e.g.*, lethality, growth impairment, reproduction, changes in community structure and function).

The uncertainties associated with this method in determining risk to the environment are variability in effluent composition and quantity, and in the flow and quality of the receiving water. A proper sampling scheme is, therefore, essential for such tests. Refer to section 7.7.3 for information on sampling methods. Factors to consider when evaluating the validity of a field study involving releases to a water system are presented in section 7.7.2.

Samples for biological surveys have to be representative of the area of concern and a variety of appropriate habitats should be collected--usually benthic invertebrates.

Ecological Effects

Ecological integrity is achieved when the combination of physical, chemical and biological status are favourable.

The physical and chemical status of a water system are part of the habitat for biological communities and form the boundary conditions for biological status (De Zwart 1995). Therefore, a change in the physical and chemical status can influence the biological and ecological status of the water system. Spatial and temporal controls can be used to monitor these status and determine if adverse effects have occurred. Such data can be used as part of a weight-of-evidence approach. This approach can also be used for laboratory-ambient toxicity tests. Examples of measurements of these status are presented in Table 7.1.

Table 7.1. Examples of measurements of physical, chemical and biological status (De Zwart 1995).

Physical Status	***Chemical Status***	***Biological Status***
- depth of water system - shore development - substrate composition - flow - turbidity - temperature - canalization - mechanical disturbances	- concentrations of nutrients and salts - oxygen levels - pH - degradable organic	- eco-epidemiology - community structure and function - species composition

Functional aspects of ecosystem such as energy flow and mineral cycling are two important driving forces behind ecosystem performance. Examples of quantifiable processes include primary productivity in plant, soil respiration, production over respiration, nitrogen mineralization, organic decomposition, etc. (De Zwart 1995).

7.6.1.2 Laboratory-ambient Toxicity Testing

Samples of receiving water and/or sediments are taken upstream (controls) and at various distances downstream of the point of discharge and laboratory toxicity testing and chemical analysis (extraction, fractionation; see section 7.7.1) are conducted on the samples. In doing so, this approach can provide data on the fate, exposure concentrations and effects (incorporating bioavailability and persistence) of the complex substance, and therefore of the risk that the substance poses to exposed organisms. When a decline in toxicity is abrupt, rather than gradual, it may imply that constituents are degraded or have been transported to other media.

The uncertainties associated in determining risk to the environment using this method are variability in effluent composition and quantity, and in the flow and quality of the receiving water. A proper sampling scheme is, therefore, essential for such tests. Refer to section 7.7.3 for information on sampling methods. Another uncertainty is the behaviour (*e.g.*, degradation, evaporation, etc) of constituents in the effluent. Using appropriate testing schemes such as flow-through, renewal and static tests can reduce some of the uncertainty. Factors to consider when evaluating the validity of such studies are presented in section 7.7.2.

A change in the physical and chemical status of a water system can influence the biological status and therefore, the ecological integrity of a water system. The physical and chemical status can be used as part of a weight-of-evidence approach (see Section 7.6.1.1 for additional information).

7.6.1.3 Laboratory Toxicity Testing Using Whole Effluent

Whole effluent toxicity tests are usually conducted in the laboratory and involve either short-term (acute) or long-term (chronic) exposures (if effluent sample remains stable). Toxicity can be measured by using effluent samples obtained at the point of discharge (*i.e.*, at the pipe) and by conducting toxicity tests on the samples. This approach can be used as a worst-case scenario to screen effluent for potential toxicity (*i.e.*, effects at 100% effluent concentration). If no toxicity is observed, no adverse effects are expected to occur downstream of the discharge.

When effects are observed, dilutions of the 100% effluent can be used to estimate, for example, a LC_{50}. Uncertainties of this approach, other than those presented in section 7.6.1.2, include extrapolation to the assessment endpoint and to chronic exposure effects (if applicable)(De Zwart 1995). In other words, characterizing risk involves linking the inherent toxicity of the effluent, as measured in the laboratory, to concentrations in the environment and demonstrating that biota are exposed or have the potential to be exposed to the effluent or its constituents (*e.g.*, using field studies). To do this, assessors must demonstrate that concentrations of harmful constituents and group parameters measured in the dilution samples also exist in the field. Extrapolation to chronic exposure effects may be difficult unless the effluent monitoring variables (*e.g.*, constituent, group parameter) has a short half-life (*e.g.*, TRC for chlorinated waters).

7.6.2 Preferred Methods for Mixtures

As with effluents, there are no standard protocols or approaches to determine the effects of mixtures on the structure and function of natural populations, communities and ecosystems.

The main difference in designing approaches to assess the ecological risk of mixtures, as compared to effluents, is that effluents are usually discharged to water systems whereas mixtures can be discharged to various environmental compartments including air, land and water. Therefore, the experimental design of the preferred testing methods will not only depend on the use, physical and chemical properties and ultimate fate of the mixture, but also on the type of environmental compartment that is receiving it. Based on these considerations, approaches to assess the ecological risk of mixtures are determined on a case-by-case basis.

Results from field and laboratory-ambient toxicity tests provide direct evidence of environmental effects. Simple toxicity endpoints include, for example, lethality, and growth and reproduction. Ecological integrity is another type of endpoint and requires the analysis of the physical, chemical and biological status of a particular ecosystem. For a discussion on *ecological effects* relating to discharges/transportation of mixtures into aquatic systems, refer to section 7.6.1.1. For mixtures released to terrestrial ecosystems, ecological effects (*e.g.*, decomposition of organic material, cycling of mineral nutrients) can be determined using spatial and temporal control approaches to monitor these status and determine if adverse effects have occurred. Professional judgement is required.

7.6.2.1 Field Toxicity Tests

Aquatic Ecosystems

Approaches used to conduct an assessment of mixtures discharged to water bodies are similar to those of effluents, particularly for continuous water flow systems (*e.g.*, rivers). For instance, mixtures discharged to aquatic systems having a continuous water flow (*e.g.*, rivers), spatial and temporal upstream control sites can be used.

Spatial and temporal controls can also be used for mixtures discharged to aquatic systems having little or no water flow (*e.g.*, lake, harbor) . However, the difference between this approach and that used for continuous water flow systems is choosing a proper control site (since there are no upstream sites) for both the *in situ* toxicity tests and the community and population surveys. The control sites must have similar characteristics (*e.g.*, naturally occurring biota, physical and chemical properties of the sediments, water, etc.) to those of the affected study sites.

Uncertainties associated in determining risk for mixtures discharged and/or transported (*e.g.*, deposition, leaching) to aquatic systems are similar to those of effluents (Section 7.6.1.1). Sampling methods are presented in Section 7.7.3.

Terrestrial Ecosystems

Since approaches used to determine the ecological risks of mixtures are designed on a case-by-case basis, examples using waste crankcase oils (WCOs) are presented below (Environment Canada and Health Canada 1994). During the WCOs assessment, an attempt was made to follow its lifecycle from the point of collection to ultimate disposal. Three scenarios outlined ways in which WCOs enter the Canadian environment--road oiling, burning and land disposal (Table 7.2). The examples are not meant to be an exhaustive list of approaches. Professional judgment must always be used when designing an approach to assess a particular mixture.

Table 7.2. Approaches and type of controls to conduct field toxicity studies of WCOs.

Use and Disposal Scenario	***Approach***	***Control***
burning as fuel	*in-situ* tests using caged organisms in fields	spatial and/or temporal controls
road-oiling used for dust suppression	*in-situ* tests using caged organisms in nearby streams and fields	spatial and/or temporal controls
disposal to land	*in-situ* tests using vegetation and/or microorganisms	spatial and/or temporal controls

In the first scenario, emission particulates are deposited on nearby soil and vegetation. Effects can be determined on a qualitative or quantitative basis using spatial and temporal controls. Observations on the color and size of affected vegetation can be compared to those of background (control site) vegetation. A quantitative analysis could involve a biological survey (*e.g.*, species compositions) of vegetation or invertebrates living in soil and comparing results to those of background findings; in doing so, effects can be determined when, for example, tolerant species have replaced sensitive species. Another option would be to conduct an *in-situ* toxicity tests using caged organisms downwind of the emission and comparing responses to those of a control site. Examples of temporal controls include I) comparing *in-situ* toxicity results before and after a process change, and ii) comparing toxicity testing results using current levels of constituents in the vicinity of the emission and background levels acquired before the facility was constructed. If the constituents of concern in the emission can be identified and field chemical monitoring and toxicity data exist for each constituent, the individual substance method could be used (Section 7.6.3.2).

Air dispersion models can be used to predict the transport and diffusion in the atmosphere of emissions from stack releases. These numerical models predict the concentration of emissions that occur in air (at ground level) in the vicinity. The results of the model should reflect local conditions such as lake effects and stack plume fumigation conditions. All models provide more realistic predictions when using actual local meteorological data (Report of an Expert Panel 1994a). Predictions must be supported by empirical data and used as part of a weight-of-evidence approach.

Uncertainties associated in this scenario are the variability of emission rates and composition, and wind currents (if applicable). Wind currents play an important role in distributing emissions and can influence the selection of a proper control site. The analysis of wind current data should be based on historical data. When there is no consistent wind current direction, a background or control site must have similar physical, chemical and biological characteristics than the affected site. Emission rates may vary depending upon the waste feedstock composition, facility size, operating conditions, and the flue gas treatment and emissions control technology used. The composition of emissions vary depending on, for example, temperature distributions and mixing conditions. For additional information on factors that influence emissions and their composition, see Report of an Expert Panel (1994a). Factors to consider when evaluating the validity of a field study involving air emissions are presented in section 7.7.2.

In the second scenario, leachates of WCOs enter roadside streams where spatial (upstream) and temporal (before the application of WCOs) controls can be used. A proper sampling scheme (Section 7.7.3) will determine the composition and quantity of the mixture entering the stream. Some constituents of WCOs applied to roads are likely to volatilize or be transported via particulate matter to neighbouring fields. Spatial and temporal controls can also be used in this instance, but choosing a proper control site is likely to be more difficult than that involving discharges or transportation of complex substances to water systems. One reason for this is that water flow as a vehicle provides a more uniform distribution of constituents of a complex substance (Vouk *et al.*, 1987). Choosing a control site for constituents transported via air can involve analysis of wind currents. A control site should have similar physical, chemical and biological characteristics to the site of interest. Uncertainties associated with this approach are similar to those described for laboratory-ambient toxicity tests for effluents (Section 7.6.1.2). Factors to consider when evaluating the validity of a field study involving emissions to air are presented in section 7.7.2.

In the disposal to land scenario, temporal controls can be used by conducting a biological survey of microorganisms or by monitoring functional aspects of the ecosystem before and after application of WCOs. Spatial controls can be used for volatile constituents and constituents transported by particulate matter to nearby

vegetation; in this case a proper control site is essential. Comparing species composition of the affected populations to that of the controls can determine if adverse effects have occurred. Examples of adverse effects could involve difference in growth or in enzymes activities of the populations of concern and the controls.

7.6.2.2 Laboratory-ambient Toxicity Testing

Adverse effects can be determined by collecting air, soil or water samples containing constituents of the mixture from various sites near the release and conducting toxicity tests on the samples using the assessment or measurement endpoint(s). Uncertainties associated with this approach are similar to those described for the same scenario in the previous section (Section 7.6.2.1). Factors to consider when evaluating the validity of such studies are presented in section 7.7.2.

Using the scenarios presented in Table 1, laboratory-ambient toxicity tests could involve, for example, the collection of particulates, settling from the atmosphere, and estimating particulate deposition rates. These particulates could then be applied to laboratory organisms at the calculates rates. Deposition rates could be collected over a specified time period or per volume of WCOs burned. The test organisms could be vegetation living near the emission.

Another example could involve the collection of contaminated sediments from nearby streams where road runoff of WCOs has accumulated. Laboratory toxicity tests and chemical analysis could be conducted on these samples. The toxicity tests could involve, for example, local benthic invertebrates. Results can provide the mixture's fate, exposure and effects that can then be used to determine risk.

7.6.2.3 Laboratory Toxicity Testing Using Whole Mixture

Whole mixture toxicity tests are usually conducted in the laboratory and involve either short-term or long-term exposures. Whole mixture samples are used directly in laboratory toxicity testing.

Examples include applying WCOs or landfill leachates directly to the organisms likely to be exposed (*e.g.*, bird eggs), feeding organisms diets containing the complex substance, or applying the complex substance to laboratory soil plots to observe the response of organisms living in the soil.

This approach can be used as a worst-case scenario to determine potential adverse effects. If no toxicity is observed for whole mixtures, no adverse effects are expected to occur to the assessment endpoint. If adverse effects are observed, assessors must demonstrate that the assessment endpoint(s) has the potential to be exposed to the whole mixture. Such data can then be used in risk characterization.

7.6.3 Other Laboratory Methods to Assess Complex Substances

7.6.3.1 Fractionation Method

Fractionation reduces the complexity of effluents and mixtures. Aqueous or organic solutions of organic constituents are divided into more defined groups, each containing related constituents. These fractions can then undergo toxicological testing. Fractions determined to cause adverse effects can either be chemically analyzed to identify the harmful constituents, or further fractionated and tested to more precisely identify harmful constituents. This method is often referred to as Toxicity Identification and Evaluation (TIE). The method, therefore, provides a mean of identifying groups of harmful constituents (Parkhurst 1986; Vouk *et al.* 1987). For information on fractionation techniques, see section 7.7.1.

7.6.3.2 Individual Substance Method

This method identifies and quantifies all constituents of a complex substance, determines the effects and calculates the contribution of each constituent to the total effect of the complex substance. A disadvantage of this method is encountered for complex substances having many constituents such that it becomes exceedingly time consuming and costly to identify, quantify and conduct toxicological tests on each constituent (Parkhurst 1986). However, when a complex substance is composed of a few constituents only, and an *estimated exposure value* (EEV) and *an estimated no effect value* (ENEV) are known for each constituent, then a deterministic risk analysis can be conducted. Refer to chapter 5 and 6 for information on how to determine these values.

Organisms exposed to several substances simultaneously requires consideration of the possible interactions between its constituents and between their effects on the organisms. A joint action is defined as similar or independent (see below), and as interactive depending on whether one constituent does or does not influence the biological action of the other. Most of the toxicological research on the joint action of constituents have been performed on complex substances composed of only a few constituents that are noninteracting. It has been demonstrated that joint action of such constituents in the aquatic environment are likely to be additive (Konemann 1981; Lloyd 1986; Calabrese 1991; Enserik *et al.* 1991 ; Spehar and Fiandt 1986). An aquatic toxicological study involving many constituents also demonstrated additivity (Konemann 1981).

There are two types of noninteracting joint action: I) similar joint action or concentration addition where constituents act independently to produce similar biological effects so that the concentration of one constituent of a mixture can be expressed in terms of another, and ii) independent joint action, no addition or response

addition where constituents act on different biological systems or affect the same biological system differently owing to different modes or sites of action (Mumtaz *et al.*, 1994).

Similar Joint Action or Concentration Addition

The toxicity of a complex substance is determined by identifying constituents with similar mode of action and by calculating their joint toxicity. To do this, the ratio of each constituent's concentration(EEV) and toxicity (ENEV) is calculated. Each ratio is termed the toxic unit (TU) and can be summed since they are all in the same units. In a complex substance of 5 constituents, the same effect will be observed when each constituent is present at a concentration of 0.2 TU. The similar joint action model can be expressed as:

$$CST_{sja} = \sum EEV_i / ENEV_i = 1 \qquad (i = 1 \text{ to } n)$$

where CST_{sja} is the complex substance toxicity based on similar joint action, EEV_i and $ENEV_i$ are the estimated exposure value and the estimated no effect value, respectively, for each constituent i, and n is the total number of constituents. Results of the CST_{sja} analysis can be interpreted in the same way as a tier 1 quotient for an individual substance. Briefly, if the CST_{sja} is less than one, there is a low probability of an adverse effect to the assessment endpoint. As the CST_{sja} approaches unity, the level of concern increases. When the CST_{sja} is equal to or exceeds unity, a more detailed analysis is required; consult chapter 8 for additional information.

Limitations of the model are the same as those of the quotient method for individual substances. In general, the model does account for the number of organisms who might be affected by exposure or the magnitude potential adverse effects (*i.e.*, $CST_{sja} \geq 1$) (Mumtaz *et al.*, 1994). The use of concentration addition is also limited by the possibility of the biological assumptions on which this concept is based.

It is recommended that the CST_{sja} approach be used when a complex substance is composed of only a few constituents that are characterized both chemically and toxicologically. A concern regarding the model is that it may be overly conservative (*i.e.*, it may overestimate risk) if constituents act by different modes of action. In such cases, independent joint action may be a more appropriate approach.

Independent Joint Action

Independent joint action is another common approach to the assessment of complex substances. The model assumptions are: I) independent modes of action are meet, and ii) the susceptibilities of organisms to different constituents are the same. For a complex substance of n constituents, the model can be expressed as:

$$CST_{ija} = \sum EEV_i / ENEV_i = n \qquad (i = 1 \text{ to } n)$$

where CST_{ija} is the complex substance toxicity based on independent joint action, EEV_i and $ENEV_i$ are the estimated exposure value and the estimated no effect value, respectively, for each constituent *i*, and *n* is the total number of constituents. By assuming there is no combined effect, the CST_{ija} is, therefore, the highest TU associated with the complex substance; the highest TU alone can be used to characterized the risk associated with exposure to the complex substance.

The result of using this model may underestimate risk when the assumptions are not valid. For instance, when many or all constituent toxicity thresholds are exceeded:

$$5/1 + 10/3 + 4/2 + 8/2 = 5$$

Another example includes different susceptibilities of organisms to constituents. Populations that are most sensitive to constituent A are least sensitive to constituent B and populations that are most sensitive to constituent B are least sensitive to constituent A. Based of this scenario, the calculated risk would be additive. van Leeuwen and Hermens (1995) concluded based on a reviewing other studies that substances with independent modes of action almost behave like concentration addition.

Approaches to Assessing Interactions

Much data in the biomedical literature indicates that substances may interfere with one another, altering the magnitude and sometimes the nature of the toxicologic response. When interactions occur between constituents, other types of complex substance toxicity occurs: I) partial addition (toxicity between no addition and concentration addition), ii) antagonistic (toxicity less than no addition), and iii) synergism (toxicity greater than concentration addition).

Attemps to take into account the uses of interaction data in component-based risk assessments of complex substances have been proposed as part of a weight-of-evidence scheme. The method entails a review of relevant data on all possible binary combinations of constituents of a complex substance, data about the toxicity and pharmacokinetics of the constituents, and interactions data on related constituents. For additional details about this approach, consult Mumtaz and Dunkin (1992) and Mumtaz *et al.* (1994).

7.6.3.3 Representative Substance Class Method

A complex substance is qualitatively analyzed and a representative constituent is identified as being of biological significance from each class of constituents.

Toxicological testing is conducted with each representative constituent and its effects are assumed to represent the constituent class as a whole. Based on this extrapolation, a determination is made of the contribution of each class of constituents to the total effect of the complex substance (Parkhurst, 1986). Such a determination can be performed using the models presented in the individual substance method (Section 7.6.3.2). A limitation of this method is that accurate extrapolations can only be made if all constituents of each class have similar effects. Frequently, constituents have been selected to represent a class simply because some data existed or they were easy to analyze. In fact, they were not really representative of a class (Vouk *et al.*, 1987).

7.6.3.4 Artificial Test Systems

Artificial test systems are also referred to as mesocosms and microcosms systems. These systems may be used for both functional (various rate processes) or structural (trophic balance) measurements or simply toxicity test measurements (*e.g.*, lethality).

Some artificial streams have been used to simulate natural environments (Crossland 1985; Fairchild *et al.* 1987; Dorn *et al.* 1991; Crossland *et al.* 1992). Many studies on complex substances have been conducted using sediment and soil microbial communities. Microbial communities control critical pathways in energy fixation, organic decomposition, cycling of essential nutrients, and the degradation of complex substances. These processes can provide important evidence of disruption in "normal" system function (Vouk *et al.* 1987).

Artificial Test Systems can contribute to the understanding of the effects of complex substances and constituent interactions if chemical transformation and partition kinetics are measured simultaneously with structural and functional responses of the system (Vouk *et al.* 1987). Applications of these systems in ecological risk assessment is still at the experimental stage. An uncertainty of this approach is the extrapolation of results to the environment. However, results generated from these studies can be used in a weight-of-evidence approach. Professional judgement is required. Refer to section 6.2 of the guidance manual and 6.2.2 of the resource document for additional data on mesocosms and microcosms tests.

7.7 Issues and General Information

7.7.1 Characterization of Group Parameters

Group parameters are based on analytical-chemical techniques and determine elements or chemically defined group of constituents in complex substances. It is essential for a group parameter that the constituents that are quantified are in principle

known. A group parameter does not necessarily quantify anthropogenic sources, but also co-determines natural substances.

Two techniques used to separate chemical groups of a complex substance include extraction and fractionation. These techniques are also called Toxicity Identification and Evaluation(TIE).

Organic constituents of a complex substance can be extracted from water into a liquid phase or onto a solid phase. Examples of procedures include liquid-liquid extractions and adsorption onto resins and C_{18} solid phase. Water samples of a complex substance can be fractionated prior to or after quantitative extraction. Other media samples such as soil, sediment and particulate matter should be extracted for organic constituents prior to fractionation. Examples of procedures include ultrafiltration (molecular weight fractionation) and reversed phase high performance liquid chromatography (hydrophobicity fractionation). An overview of these procedures and case examples are presented in Parkhurst (1986), Dorn and van Compernolle (1995) and van Loon and Hermens (1995). Detailed procedures are outlined in several United States Environmental Protection Agency guidance documents (Mount and Anderson-Carnahan 1989; Mount 1989: Klemm *et al.* 1991; Norberg-King *et al.* 1991; Norberg-King 1991). Examples of group parameters and their derivations using such procedures is outlined in Figure 7.1.

The extraction of organic constituents of a complex substance can be conducted in a quantitative or biomimetric manner. The quantitative approach is more traditional. It determines the total amount of related constituents (*e.g.*, having similar physical and chemical properties) in a particular complex substance. The biomimetric extraction is a relatively new approach (van Loon and Hermens, 1995). The objective is to simulate the uptake of organic constituents by aquatic organisms. Group parameters can be characterized by using an extraction and/or fractionation procedure that selectively separate groups of constituents of a complex substance having similar physical and chemical properties.

Group parameters can be used as monitoring variables to determine fate, exposure and effects--measures of exposure and effects. However, they are not necessarily causal agents or the agents causing the most harm. For example, AOX has been used as a group parameter to characterize the organochlorine constituents in pulp mill effluents. However, the acute toxicity of the effluents have been correlated with the concentration of substances in the low molecular size fraction of the effluent (Report of an Expert Panel 1994b). van Loon and Hermens (1995) stated that, in general, elemental analysis on organic extractions of water samples (*e.g.*, EOX) are recommended over total elemental determinations (*e.g.*, AOX) since extracted substance fractions are largely composed of bioavailable (hydrophobic, low molecular weight) organic substances. Total elemental determinations co-determine high

molecular weight substances that are biologically unavailable.

Data on group parameters might be available simply because they were easy to characterize, detect and/or quantify. Specific constituents or group parameters identified to be the cause of harm should be used to determine fate, exposure and effects.

Example of group parameters used for the assessment of waste crankcase oils and chlorinated wastewater effluents listed on the first Priority Substances List include hexane extractable materials (HEM) and total residual chlorine (TRC), respectively.

7.7.2 Factors of Consideration for Field and Laboratory-ambient Tests

Factors to consider when evaluating the validity of field and laboratory-ambient toxicity studies involving releases of complex substances to a water system or air are:

- Releases to water systems: Are there any other point sources located upstream or in the vicinity that could be influencing results? Examples of other point sources could be other effluent discharges, landfills leachates seeping in the water systems or underground storage tanks leaking nearby.

  Releases to air: Are there any other point sources located upwind or in the vicinity that could be influencing results? An example of another point source could be a stack emission. When particulates are deposited in a water system, other point sources in the water system should be identified. Other point sources might not have been documented and should be considered when analysing the validity of results of a study.

  If other point sources are identified, high "background" concentrations (*i.e.*, control sites) might arise. Effects might be occurring to tested organisms that are not indicative of your complex substance, especially when you are assessing the effects of a substance released from a particular source.

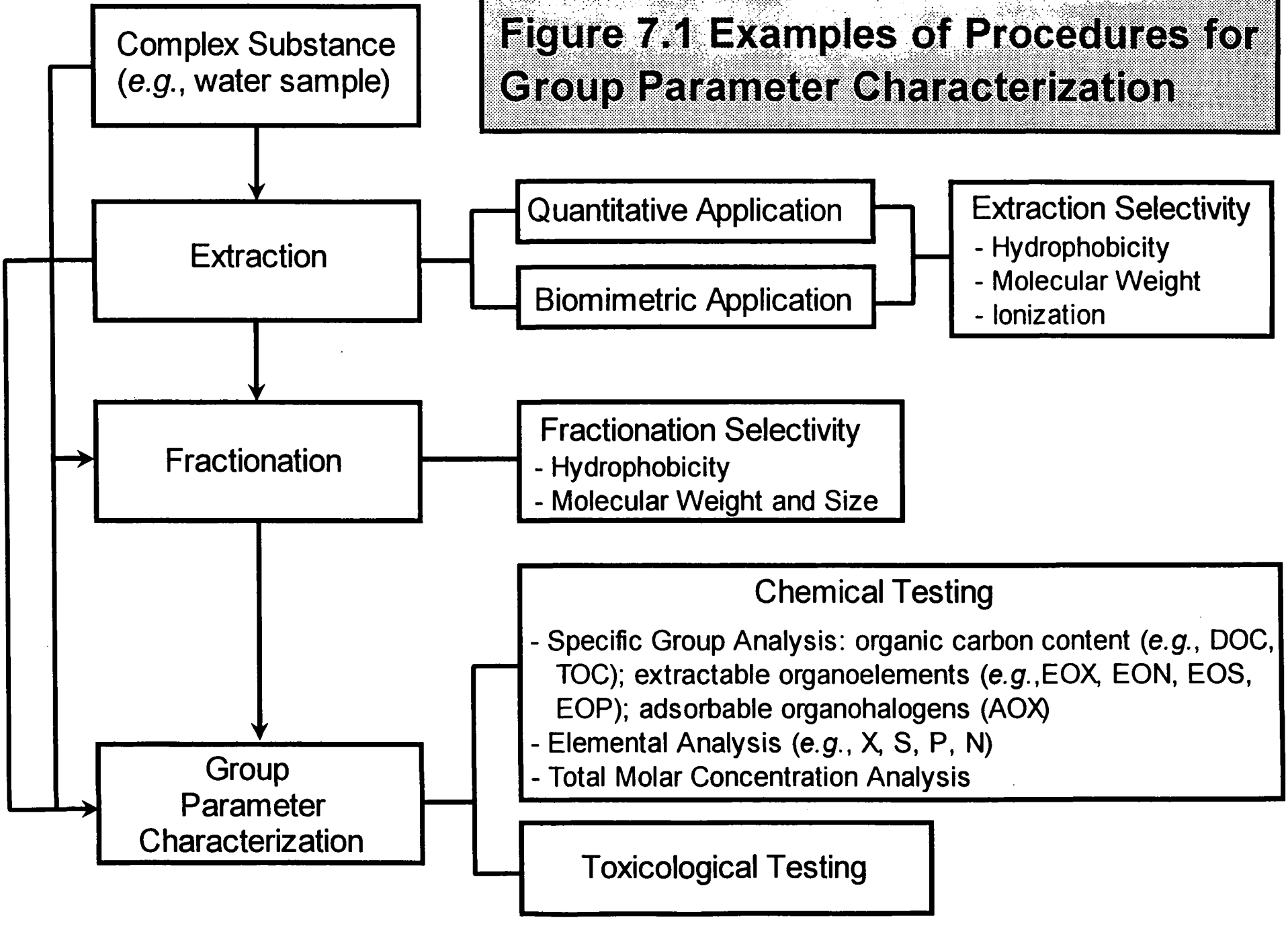
- Are non-point or diffuse sources influencing results? (*e.g.*, agricultural runoff from surrounding land).

- Are there any disturbances in the area? (*e.g.*, dredging activities could resuspend and redistribute substances in bottom sediments).

7.7.3 Sampling Methods

Effluent sampling is an integral and fundamental part of any effluent monitoring project. The effluent sample provides the basis for testing and evaluating the

Figure 7.1 Examples of Procedures for Group Parameter Characterization



properties and potential effects of the effluent. Therefore, it is important that the test effluent samples are representative of the characteristics (*e.g.*, composition) of entire effluent stream (Bender, 1986). Since an effluent may vary significantly in quantity and toxicity either randomly or with regular intervals, an evaluation of the sampling design is important.

There are three basic types of sampling methods: grab, composite and continuous.

Grab samples involve collecting effluent or ambient waters for only a brief time interval. Grab samples are recommended for short-term (acute) and long-term (chronic) toxicity tests of effluents that have a relatively constant composition. If an effluent quality varies considerably with time, grab samples may also be preferable because of the ease of collection and the potential of observing toxicity spikes in effects. However, because the sampling in conducted on a relatively infrequent basis, the chances of detecting spikes depend on the frequency of sampling. To detect toxicity spikes, grab samples should be taken regularly and randomly over a period of time that is dictated by a study of plant operations.

Composite sampling involves the collection and pooling of a series of samples over a specified period of time (*e.g.*, 24 hours). The end sample contains all toxicity spikes. Such a technique provides average concentrations of constituents or group parameters over the specified period of time and, therefore, cannot describe changes in effluent quality. As a result, it cannot identify concentrations of constituents or group parameters that may have adverse environmental effects unless the average concentrations of the end sample exist in the field. Composite samples are usually used for chronic tests.

Continuous sampling and exposure to test organisms are ideal to determine effluent variability and spikes.

The choice of sampling method affects the magnitude of the variations in effluent quality. The sampling frequency affects our ability to detect problems and to determine how long they might have and may exist. (Bender, 1986). Both the duration and magnitude of variations in effluent quality have significant impacts on the interpretation of chemical monitoring and biological testing. Selection of sampling methods, locations and measurement frequencies should, therefore, preferably depend on the variability in effluent composition and quantity, and the purpose of the monitoring. For laboratory-ambient toxicity testing, the choice of sampling methods and frequency can be more difficult than in whole effluent sampling since multiple effluent sources may be involved (see Section 7.7.2). The interpretation of results from laboratory studies requires some understanding of these relationships.

Temporal and spatial variability in water quality are caused by natural processes and human activities. Hydrological and meteorological factors (*e.g.*, storms, rainfall, river flow), and also the physical, biological and chemical processes (*e.g.*, seasonal growth and decay of vegetation, temperature dependency of purification and nutrition) cause natural variations. Human activities that can affect variability include polluted runoff, leaching, operation of sewer overflows, accidental spillages and leakages. These should be taken into account when interpreting monitoring data (Adriaanse *et al.* 1995).

For additional data on effluent sampling methods, sources of effluent variations, statistical methods and sampling strategies, refer to Bender (1986), Adriaanse *et al.* (1995) and De Zwart (1995).

Although this section focussed on water (effluent) sampling, the importance of sampling methods for other media are equally important when characterizing a complex substance. The types of sampling methods are similar for other media. An effort should be made, for all types of media sampling, to understand the relationship between a sampling method and its influence on the characterization and toxicological testing of a complex substance. A guidance document on the collection and preparation of sediments for the physical and chemical characterization and biological testing of substances is available from Environment Canada (Environment Canada 1994).

7.8 References

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8

Risk Analysis

The first step of risk characterization is to conduct an *ecological risk analysis* to determine the likelihood and magnitude of adverse effects to assessment endpoints as a result of exposure to the priority substance (definition adapted from Suter 1993). In this chapter, the approaches and methods used to conduct a risk analysis will be described. The second step of risk characterization, summarizing and describing the results of the risk analysis for the risk manager and other stakeholders, is discussed in chapter 9 (Risk Communication).

Risk analysis combines the results of the characterization of entry, exposure and effects. The available quantitative methods for risk analysis may be subdivided into quotient and probabilistic methods. A *quotient* is calculated by dividing the *estimated exposure value* (EEV) by the *estimated no effect value* (ENEV). The ENEV is calculated by dividing the *critical toxicity value* by an appropriate *application factor.* The first part of this chapter (section 8.1) describes the quotient method in more detail.

Probabilistic risk characterization methods integrate entry, exposure and effects by comparing distributions of input values rather than point estimates. Such an approach facilitates a more explicit consideration of the sources of uncertainty in the risk analysis. Also, rather than focussing on the risk of exceeding the ENEV, these methods consider the entire relationship between dose and response. Thus, the probability of adverse effects of a broad range of magnitudes may be considered. The second part of this chapter (section 8.2) describes the available methods.

For many naturally occurring substances, there are naturally enriched areas in Canada. In these areas, resident organisms will have developed tolerance to the substance of interest. However, there is a potential for harmful effects to these resident organisms if exposure is further increased as a result of anthropogenic contamination. A Tier 3 analysis attempts to account for these issues by adjusting ENEVs to account for expected tolerances in naturally enriched areas, and by partitioning exposure into its natural and anthropogenic components. The third part of this chapter (section 8.3) addresses this issue. Appendix III describes methods for partitioning net exposure among different sources.

Probabilistic or uncertainty analyses may be applied at the individual, population or community levels of organization. Methods applied at the individual level do not consider effects beyond those considered in most toxicity tests (*e.g.*, reductions in survival, growth or reproduction of individuals, usually of a single species)(Gaudet *et al.* 1994). To estimate effects at higher levels of organization generally requires linking toxicity test results with population or community level simulation models. Less often,

field tests may be carried out. The final part of this chapter (section 8.4) considers some of the available simulation models and discusses how they may be used to estimate the ecological consequences of exposure to priority substances at higher levels of organization.

8.1 Quotient Method

The first step of an ecological risk assessment of a priority substance is to calculate a quotient by dividing the estimated exposure value (EEV) by the estimated no-effect value (ENEV) for each assessment endpoint:

$$\text{Quotient} = \text{EEV/ENEV}$$

If the quotient is less than one, the implication is that there is a low probability of an adverse effect to the assessment endpoint. If the quotient is one or greater, the potential for an adverse effect exists (CEU 1994; Rodier and Mauriello 1993; Calow 1993).

The quotient method does not explicitly consider uncertainty. Rather, it is a single point estimate of the potential for an adverse effect. Examples of possible sources of uncertainty include poor knowledge of the system, extreme system variation, incorrect scales, wrong model, incomplete data, unforeseen interactions, and extrapolation errors (Cothern 1988; Smith and Shugart 1994; Ahlers *et al.* 1994). Rough qualitative estimates of uncertainty are valuable and provide an approximation of the relative risk of alternative decisions and allow identification and ranking of key factors in the assessment process (Covello and Merkhofer 1993).

8.1.1 Advantages and Limitations of Quotient Method

The quotient method is accepted worldwide and is simple to use (Rodier and Mauriello 1993; Finley and Paustenbach 1994). Generally, the entry, exposure and effects data required (*e.g.*, locations of major releases, release pathways, monitoring data, median effects doses, etc.) are readily available or can be estimated. Therefore, implementation is easy and costs are low.

The method, however, has several limitations. The quotient method is only semi-quantitative since a value of one or greater gives little indication of the probability and magnitude of a particular effect to an assessment endpoint. There are also assumptions implicit in using the quotient method: (i) the exposure conditions in nature (*i.e.*, duration, pattern) are similar to the conditions in the toxicological test, and (ii) the data from laboratory tests can be extrapolated (*i.e.*, by use of application factors) to estimate the no effects value for the assessment endpoint in the environment.

Worst-case quotients are usually hyperconservative. For example, if chronic effects to fish are the endpoint of concern, they are unlikely to be exposed to the maximum reported water concentration of a substance over their entire lifetime. Thus, there is a very low probability of effects for cases in which the worst-case quotient is less than one. Worst-case quotients greater than one, however, give little indication of whether effects are probable.

If the worst-case quotient is close to one and there is still much uncertainty regarding the outcome of the risk characterization even after refinements, then further toxicity testing is required. Figure 8.1 suggests that as more tests are conducted, the uncertainty about the response threshold is reduced and eventually it becomes clear that the estimated no-effect value is clearly above or below the estimated exposure value (Cairns *et al.* 1978; Cairns 1980). The confidence intervals are represented in the assessment by the magnitude of application factors.

8.1.2 Rationale for Proceeding to Probabilistic Risk Assessment

Quotients do not adequately estimate the magnitude of the problem for substances that have the potential to cause adverse effects (*i.e.*, quotients ≥ 1). In addition, there may still be significant uncertainty and overconservatism in using deterministic point estimates to estimate risk. The preferred approach is to use probabilistic methods to estimate risk. Therefore, if a refined quotient is close to or exceeds one, probabilistic or quantitative uncertainty analyses are recommended to determine the probability of adverse effects. These techniques are further discussed in section 8.2.

8.1.3 Application Factors

Ideally, the ENEV would be based on chronic endpoints (*e.g.*, EC_{10}) measured in controlled field tests for a wide array of appropriate measurement endpoints. Such datasets are rarely, if ever, available. Generally, only laboratory toxicity data are available on a few surrogate species. The likelihood that a laboratory test conducted on a typical bioassay species (*e.g.*,

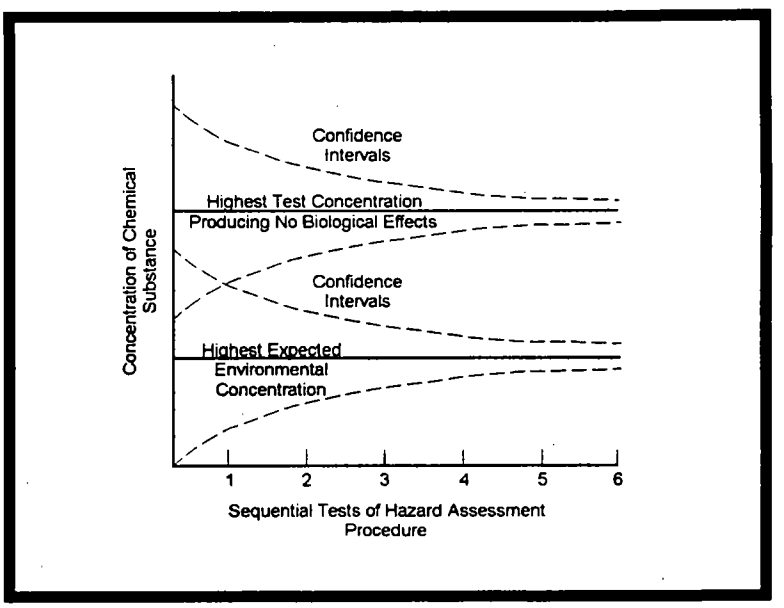

Figure 8.1. Iterative procedure demonstrating increasingly narrow confidence limits for estimates of the EEV and ENEV (modified from Cairns *et al.* 1978).

rainbow trout) will be entirely representative of an assessment endpoint (*e.g.*, no effect to pelagic fish species) is low. As a result, application factors (sometimes referred to as extrapolation, safety or uncertainty factors) are applied to the test results to account for shortcomings in the available data.

Safety or application factors were first used in the 1950s when the U.S. Food and Drug Administration proposed that a 100-fold factor be used as an "adequate margin of safety" and applied to exposure standards for food additives and contaminants. At that time, the proponents, Barnes and Denz (1954), stated that:

> *"The margin of safety concept is a reasonable approach to the matter, but its acceptance should not fool researchers and/or the public into believing that there is any experimental or theoretical basis for its existence".*

Since that time, many of the sources of uncertainty for which safety factors were intended have been identified. Empirical data have also been assembled that provide limited support for some of the application factors currently in use (*e.g.*, Suter *et al.* 1983; Romijn *et al.* 1991a,b; OECD 1992; Calabrese and Baldwin 1993; Pack 1993).

Several extrapolations (*e.g.*, laboratory to field conditions, between phyla, between levels of organization) are required to convert the critical toxicity value observed for a measurement endpoint to an ENEV for the corresponding assessment endpoint. Application factors are used to account for the uncertainties inherent in such extrapolations.

Intraspecies Variability. Results of toxicity testing vary within a species due to differences in age and sex, the influence of circadian and seasonal biological rhythms, conditions under which the animals are kept, and other factors. Kenaga (1978) in tabulating the range of acute toxicity values for 75 pesticides for eight species found that the average range of toxicity values for one species using one chemical was about 0.5 orders of magnitude, while the maximum was 2.5 orders of magnitude.

Interspecies Variability. Large variations in sensitivity can occur even within phyla, a crucial point when extrapolating from a measurement to an assessment endpoint. Kenaga (1978) found the maximum range of toxicity values for one chemical between four species of birds was often <1 and rarely >2 orders of magnitude. Tucker and Haegele (1971) showed that the range of toxicity values for six species of birds for any one chemical fell within one order of magnitude for 11 chemicals, and within two orders of magnitude for the other five chemicals studied. There was no correlation between phylogenetic relationship and toxicological susceptibility. Tucker and Crabtree (1970), in comparing the oral LD_{50} of 51 pesticides using the mallard and at least one other species of bird, found that the ranges of LD_{50}s between species for a given chemical were within one order of magnitude 69% of the time and all were within

two orders of magnitude. Mineau and Peakall (1986), analyzing avian toxicity data for groups of structurally similar chemicals, found little similarity in response for closely related species.

Laboratory to Field Extrapolation. Toxicity data derived from laboratory studies generally have limited relevance to field situations. Laboratory conditions do not permit the integration of the numerous environmental influences on a substance's behaviour, nor the influences on the various organisms exposed to the substance. Laboratory studies do not include the multiple stresses usually present in the field. In addition, bioassay endpoints commonly used in toxicity testing may not be the most important endpoints for species in the natural environment.

The interaction among components of an ecosystem creates situations where minor effects on a particular population are magnified to large effects on other populations. Conversely, other effects are "dampened" by ecosystem processes. Exposure to a chemical may compromise an organism's ability to escape predators or locate prey. These are sublethal effects in a laboratory study, but can have profound effects on species survival in the wild.

The limited ecological relevance of laboratory studies, as well as inter- and intra-species differences in responses to substances preclude generalizations among species concerning toxicological responses and support the use of application factors as an alternative.

8.2 Uncertainty Analyses

> *"A decision made without taking uncertainty into account is barely worth calling a decision".*
>
> Richard Wilson and colleagues (taken from Finkel 1990)

All scientific activities are concerned with identifying and reducing uncertainty. In ecological risk assessment, the concept of risk and uncertainty are closely related since without uncertainty there is no risk. Risk is the probability that an event will occur and if it is certain that the adverse effect will or will not occur, there is no risk (Finkel 1990; Suter 1990). Uncertainty is an inherent part of ecological risk assessment because: (i) risk assessments are based on model calculations, (ii) models are mimics of reality, and (iii) data bases are almost always incomplete (Suter 1993).

O'Neill and Gardner (1979) identified three types of uncertainty in ecological risk assessment: model structure, parameterization, and stochasticity. Other ways of dissecting uncertainty are described by Finkel (1990), ASTM (1994), Rowe (1994), Smith and Shugart (1994) and others. Model structure uncertainty includes the selection of assessment and measurement endpoints, the determination of the

relationship between a substance and the endpoints, and the relationship between the substance, endpoints and the ecosystem. Parameter uncertainty is associated with the inputs to a model. For example, inputs to the estimates of exposure and effects in a calculated quotient are often estimated from laboratory studies, exposure models or quantitative structure activity relationships (QSARs). Therefore, uncertainty arises in assuming that these parameters correctly estimate parameters in the natural environment. Uncertainty is also introduced by assuming that model parameters can be represented by single values when it is known that they vary both spatially and temporally in natural systems. Stochasticity refers to variation in natural systems or endpoint responses that can be attributed to uncontrolled natural processes (*e.g.*, storms, droughts).

Uncertainty has important consequences in communicating the results of a risk assessment to a risk manager charged with making an environmental decision. For example, if a quotient of 1.3 was calculated, then there is the expectation that the risk manager should initiate risk reduction measures. However, if the risk assessor had instead stated that the best quotient estimate was 1.3, but that the quotient could lie between 0.0013 and 13 depending on the application factors chosen, the risk manager may select a different course of action (*e.g.*, ask for more research to reduce uncertainty). Thus, estimating and communicating uncertainty is a crucial aspect of the ecological risk assessment process.

Uncertainty analysis may be qualitative or quantitative. Qualitative uncertainty analysis involves identifying the sources and causes of uncertainty and the consequences of these uncertainties to the risk assessment conclusions. Rough qualitative estimates of uncertainties are valuable and may provide, for example, an approximation of the relative risk of alternative decisions or a ranking of the key assumptions in the risk analysis (Covello and Merkhofer 1993).

Uncertainty may be quantitatively estimated using Monte Carlo simulation techniques, interval analysis, fuzzy arithmetic or by some other technique. Such techniques often have rigorous statistical assumptions and may have large data requirements. Nevertheless, these techniques are useful, particularly when the objective of the assessment is to determine the likelihood of a specified effect occurring (*e.g.*, the probability of a population experiencing a 25% decline in reproductive fecundity), rather than determining if it is possible for an estimated no effects value to be exceeded.

8.2.1 Qualitative Uncertainty Analysis

Smith and Shugart (1994) examined uncertainty in relation to the three phases of ecological risk assessment, problem formulation, analysis (entry, exposure and effects), and risk characterization (risk analysis and risk communication). The first

stage, problem formulation, involves uncertainties in the choice of appropriate endpoints, choice of model and modelling approach, choice of scale, and availability of information.

In the analysis phase, potential sources of uncertainty include:

- variation in the composition, magnitude, frequency and duration of releases and discharges,
- knowledge of the physical and chemical properties of the substance (*e.g.*, solubility, persistence, log K_{ow}),
- the temporal and spatial scales of exposure, and the matching of those scales with the ecological scales of the risk assessment,
- knowledge of substance transformation due to chemical, physical, and biological actions,
- the heterogeneity of the populations (abundance, life stages, etc) at risk,
- interactions among multiple stressors,
- reproducibility of laboratory and field studies,
- extrapolation of laboratory toxicity test results to field conditions, and
- extrapolation of toxicity test results for measurement endpoints to assessment endpoints.

Table 8.1 lists some of the sources of uncertainty inherent in most ecological risk assessments of substances. In general, two approaches are used in dealing with these sources of uncertainty. The first and most common approach is to use application factors to calculate an estimated no effects value (the quotient denominator) in the hope that by applying such factors, unknown and sensitive biota in the environment will be protected (see section 8.1). However, as indicated in table 8.1, there are other sources of uncertainty that may not be accounted for by application factors. These include lack of knowledge about the system, stochastic events in natural ecosystems, and consequences of multiple stressors. These sources of uncertainty do not negate the results of ecological risk assessments that use application factors to calculate a quotient. Since sources of uncertainty do exist, however, it is critical that assessors acknowledge their existence and that expert judgement be used to ensure that the

Table 8.2. Sources of uncertainty in ecological risk assessments of priority substances (adapted from Cothern 1988; Smith and Shugart 1994).

Source of Uncertainty	*Importance*	*Magnitude of Effect*	*Accounted for by Application Factors*
Poor knowledge of system	Without such knowledge, impossible to use expert judgement or build useful models	Many orders of magnitude	No
Extreme system variation, incorrect scales, surprises	Extreme events such as hurricanes or droughts may change consequences of exposure to a substance	"	No
Wrong model, endpoints or exposure routes	May lead to missed effects or an underestimation of predicted effects	"	No
Data collection and entry practices	Errors during data collection and entry may lead to mistakes in estimating risk	Less than two orders of magnitude	No
Design of laboratory experiments and QA/QC	Adherence to standard protocols is necessary to avoid errors induced by lack of care	"	No
Mistakes in experimental design and analysis	Can affect estimation of critical toxicity value	"	No
Interactions	Uncertainty introduced by not accounting for interactions among stressors or species	"	Possibly
Extrapolation from acute to chronic effects levels	Can affect estimation of critical toxicity value	"	Yes
Extrapolation from test species to other species	Rank order of species sensitivity changes between chemicals	"	Probably - limited data support factors in use
Extrapolation from laboratory to field conditions	Conditions in the field, particularly those affecting bioavailability, can change substance toxicity	"	Yes
Extrapolation from low to high levels of organization	Few data exist to verify that NOELS derived from studies of individuals are protective of higher levels of organization	"	Possibly

quotient calculated is defensible. The same logic applies to any deterministic or fixed model used in developing an ecological risk assessment. The second approach for dealing with sources of uncertainty is to conduct probabilistic or quantitative uncertainty analyses.

8.2.2 Quantitative Uncertainty Analysis

The quantitative consideration of uncertainties in risk analysis, and the expression of the estimated effect as a probability or possibility is what distinguishes risk assessment from hazard assessment. Stating the effect in probabilistic or possibilistic terms forces the identification of sources of uncertainty and quantification of their impact on risk estimation (Suter 1993). This section is intended to provide background information on quantitative uncertainty analysis and on some of the techniques available to estimate uncertainty.

Quantitative estimates of uncertainty are obtained through the use of statistical and computer models. With statistical models, uncertainty is expressed by measures of variance (*e.g.*, 95% confidence limits) and power (*e.g.*, 1 - β)(Snedecor and Cochran 1980; Kaiser 1989; Peterman 1990). Quantitative uncertainty associated with computer models can be estimated by Taylor series expansion, Monte Carlo simulation, Baye's theorem, fuzzy numbers or a variety of other techniques to produce a single number that estimates uncertainty or a distribution of output that provides information on the range and magnitude of uncertainty (Covello and Merkhofer 1993; ASTM 1994; Smith and Shugart 1994). The type of method selected by the assessor will depend on the nature of the problem and the available information.

8.2.3 Estimation Methods for Quantitative Uncertainty Analysis

In simple cases, input variable distributions (or probability density functions, PDFs) can be combined using simple mathematical relationships (Finkel 1990). For example, exposure to a substance may be calculated by multiplying the substance concentration in a medium by the ingestion rate and dividing the product by body weight. If these input PDFs are lognormally distributed (which is often the case), the uncertainty analysis can be completed with a few simple calculations on a calculator (Slob 1994).

More often, complex quantitative uncertainty analyses will be required. The classical approach to estimating uncertainty requires that input parameter estimates be derived from available data, where probabilities are numbers associated with events and risk is a measurable property of the physical world. Monte Carlo simulation is one method of estimating probability using the classical approach. In most analyses of priority substances, Monte Carlo simulation (see below) is the preferred method. Appendix V shows the results of a Monte Carlo simulation that estimated the probability

of adverse effects on mink exposed to hexachlorobenzene in the St. Clair River, Ontario area. In cases where Monte Carlo simulation is not necessary, appropriate or feasible, other methods such as Taylor series expansion, Baye's theorum and fuzzy numbers may be used to estimate uncertainty. Some of these methods are described below.

Taylor Series Expansion

Taylor series expansion can be used in some cases although the algebra is somewhat tedious, particularly with non-linear models (Covello and Merkhofer 1993). Essentially this method involves calculating uncertainty in the output variable by breaking down each input PDF into moments (*i.e.*, mean, variance, skewness, kurtosis) and combining this information using a linear, cubic or quadratic equation that can be solved analytically. Once the moments of the output distribution have been calculated, a PDF can be selected to fit the moments. Taylor series expansion now seems obsolete as the main objection against Monte Carlo simulation - time and effort to perform extensive calculations - has been virtually eliminated by recent improvements in computing capabilities (Slob 1994).

Monte Carlo Simulation

Monte Carlo simulation is a technique for integrating and propagating probability density functions (PDFs) through mathematical simulation models (Covello and Merkhofer 1993). The technique involves computing the output of the risk equation for many sets of combinations of inputs. The combinations of input values are obtained by random sampling from the PDFs assigned to the input variables. The resulting distribution of outputs is then interpreted as an approximation of the "true" output probability distribution. The more sets of combinations of inputs (*i.e.*, simulations) used in the analysis, the better will be the convergence of the Monte Carlo generated output distribution to the "true" distribution. Typically, 1,000 to 100,000 simulations are performed, requiring a few minutes to half an hour of computing time (on a 486/66 MHz desktop computer) depending on the number of simulations, model complexity, the sampling strategy employed by the Monte Carlo method, and several other factors (Finkel 1990). Inexpensive software packages such as Crystal Ball, @Risk and Prism have recently become available to perform Monte Carlo simulations. Monte Carlo simulations have, for example, been used to evaluate human health risks associated with contaminated drinking water and soil, and incinerator emissions (Finley and Paustenbach 1994; Smith 1994), and ecological risks associated with toxic chemicals (Webb *et al.* 1993; MacIntosh *et al.* 1994) and fish harvesting practices (McAllister and Peterman 1992).

Several variations of the Monte Carlo method for sampling from the input PDFs are available. One variation is importance sampling, where values of particular

importance (*e.g.*, values in the extreme tails of the input PDFs) are sampled more often and then given reduced weight in order to obtain improved resolution in the tails of the ouput distributions (Covello and Merkhofer 1993). In stratified sampling, the distributions for input PDFs are divided into intervals and input values are obtained by sampling from within each interval, rather than from the distribution as a whole. The most popular version of stratified sampling is latin hypercube sampling. This method divides each input PDF into equiprobable intervals and then randomly samples from within each interval. Latin hypercube sampling is more precise than conventional Monte Carlo sampling because the entire range of the input PDFs is sampled in a more even, consistent manner (Iman and Helton 1988; Decisioneering 1993). The stability of the output probability distribution is thus increased, particularly in cases where the uncertainty is dominated by a few input PDFs (Covello and Merkhofer 1993). The increased accuracy of this method comes at the expense of additional memory requirements to hold the full latin hypercube sample for each input PDF.

Difficulties may arise when using the Monte Carlo method if the relationship between input variables (PDFs) is not known. Covariance between input variables can have an important effect by either exaggerating or reducing estimated uncertainty in the output compared to the uncorrelated case, particularly in the tails (Smith *et al.* 1992; Ferson and Long 1994). If such covariance relationships are linear and the raw data exist to calculate the Spearman rank-order correlation coefficient, @Risk and Crystal Ball have the capability to induce the dependencies between input variables in the analyses (Decisioneering 1993; Smith *et al.* 1992). If the covariance relationship between input variables cannot be measured, a strong relationship is suspected, and the variables have an important influence on the output, then the analysis becomes problematic. Dependency bounds analysis (Ferson and Long 1994) and fuzzy arithmetic (Kosko and Isaka 1993; Ferson and Kuhn 1993, 1994) have been suggested as alternative approaches in these cases, because the results of such analyses do not depend on knowledge about the covariance relationships among input variables.

Sensitivity analysis may be used to quantify the relative importance of input variables in a model. The results of such an analysis provide information that can be used to rank the importance of the input variables, and also to prioritize the areas where additional research may be required (Smith and Shugart 1994). Sensitivity analysis may also help identify ways to improve the predictive abilities of a simulation model (Kirchner 1994). Evaluators should be aware, however, that sensitivity analysis is of limited use if the model is highly nonlinear or if there are strong relationships between input variables.

Bayesian Methods for Quantifying Uncertainty

The Bayesian approach is more general than classical probability in that probability is a function not only of the event, but of the the state of knowledge of the

event. The state of knowledge depends on the information, experience, and theories of the individual performing the assessment (Covello and Merkhofer, 1993).

Statistical methods can be used to estimate measures of central tendency and variance around the central measure. Since data are usually limited, there is some uncertainty (in the form of ignorance) about the estimated central measure and the associated variance. The main limitation of the classical approach is the lack of adequate data to confidently characterize input PDFs. The Bayesian view permits probability distributions to be assigned to variables whose true values are unknown. The Bayesian or subjective method for risk estimation relies heavily on probabilities estimated by experts.

Generally, the first step in applying the Bayesian approach to quantify uncertainty is to assemble a panel of experts. Methods used to assemble the panel and to query panel members have been developed (see references in Covello and Merkhofer 1993). The literature on the subject recommends that trained interviewers follow a systematic process to elicit probability judgments from each panel member independently. The probability distributions obtained from each panel member may then be aggregated through sharing and discussion of information amongst panel members (*i.e.*, behavioural aggregation) or by some mechanical averaging procedure. The derived distribution from this or related exercises is known as the prior probability distribution (Covello and Merkhofer 1993).

If new information becomes available, the prior probability distribution may be updated using Baye's theorem to produce a posterior probability distribution. Baye's theorum states that the posterior probability that a hypothesis H is true is proportional to the prior probability of H being true (*i.e.*, p(H)) and the conditional probability that datum D will be observed given that H is true. Thus, the posterior probability that H is true given that D has been observed (p(H | D)) is:

$$p(H \mid D) = [p(D \mid H) / p(D)] \times p(H)$$

The quantity p(D) is a normalizing factor because the posterior probabilities of the alternative hypotheses must sum to unity.

Commonly with the Bayesian approach, probability trees rather than simulation methods are used to convert uncertainties in the input variables into the corresponding estimates for the output variables (*e.g.*, Chao *et al.* 1994). Each node in the tree represents an uncertainty in the risk model. Consequence estimates are determined by running the model for sets of inputs corresponding to the values specified by branches along each path. Controlling the size of probability trees is crucial, since if there are more than a few uncertain variables the resulting terminal nodes may result in severe computational problems. Sensitivity analysis is valuable to identify the variables that

contribute to the bulk of the uncertainties (Covello and Merkhofer 1993).

Fuzzy Numbers

Conventional risk analysis reports measured variables in terms of means and errors around the mean, which can be expressed as a plus or minus value or as intervals. Interval analysis is an alternate and simple method that can be used to propagate uncertainty through calculations (Ferson and Kuhn 1994).

Fuzzy numbers are a general type of interval where the bounds or range on the measurement vary depending on the confidence one has in the estimate. The notion of possibility theory was introduced to quantify non-statistical forms of uncertainty such as vaguely defined variables and ill-defined instructions (Ferson and Kuhn 1994).

Fuzzy numbers can be thought of as representing a range of values or intervals ranging from zero to one. The range of values are narrowest at possibility-level one which corresponds to the greatest optimism about the degree of uncertainty. At possibility-level zero is the range of values that are "just possible". In between are intermediate levels of possibility. Fuzzy numbers can be derived from empirical data and a limited amount of data. Given as little as a highest and lowest value and an estimate of the best value, these three numbers describe a triangular fuzzy number. Input fuzzy numbers are combined as specified by the risk equation by means of simple algebraic equations.

An advantage of fuzzy numbers is that this method requires no assumption of independence of input variables, as is required with probability theory. As with probabilistic risk analysis, possibility analysis produces quantitative, conservative estimates of uncertainty that can be expressed as a best estimate with conservative bounds on the prediction (Ferson and Kuhn 1994). The fuzzy numbers method, however, is relatively new to ecological risk assessment and has not yet gained widespread acceptance.

8.3 Estimating Risks Due to Anthropogenic Sources for Naturally Occurring Substances

Organisms occupying naturally enriched areas are generally more tolerant to substance exposure then organisms occupying other areas. In such cases exposure should, if possible, be separated into its two components: the natural component (EEV_n) and the anthropogenic component (EEV_a). Chapter 5 and Appendix III of this document describe methods that may be used to accomplish this separation.

If the EEV_n for bioavailable forms of the substance (see Appendix II) exceed the estimated no effects values (ENEVs) for sensitive endpoints, the ENEV should be

refined. This involves:

- defining a lower bound for the ENEV,
- evaluating the choice of assessment and measurement endpoints, and
- evaluating the relative tolerance of assessment and measurement endpoints.

These steps arose from a workshop on effects to organisms in naturally metal-enriched areas, held at Trent University in August, 1995 (Hutchinson 1996).

Bounding the ENEV

When natural exposure (EEV_n) has been elevated for an extended period, resident organisms evolve to tolerate such exposure. In such areas, the ENEV should not be below the EEV_n. Unfortunately, estimating the EEV_n can be difficult. When the EEV_n can only be estimated as a single mean value, the lower boundary of the ENEV should be the mean EEV_n. In cases where the EEV_n can be characterized as a distribution, the lower boundary of the ENEV should be the 90th percentile EEV for the area of concern[1].

Evaluating the Choice of Endpoints

Assessment and measurement endpoints should be representative of classes of organisms that are the least likely to develop high tolerance, but are still relevant to the site of exposure. Potential for tolerance in different strains of a species or in related types of species may be evaluated by reviewing the literature to determine whether high effect thresholds have been reported, particularly when test organisms were pre-exposed to a substance. When assessment endpoints are found to belong to a class of organisms that is highly tolerant, different endpoints may be chosen. For example, aquatic invertebrate species might be substituted for algae, if review of the literature indicates that invertebrate species are much less likely to develop high tolerance than algal species.

Evaluating the Relative Tolerance of Assessment and Measurement Endpoints

Assessment endpoints should exhibit tolerances that are similar to those of corresponding measurement endpoints. When assessment endpoints are likely to be

[1] Depending upon the shape of the EEV distribution, setting the minimum tier 3 ENEV at the maximum EEV could result in a tier 3 ENEV that is much higher than typical exposure values. Thus, using the maximum EEV would seem inappropriate. Alternatively, setting the minimum ENEV equal to the median EEV would imply that assessment endpoints are adversely impacted by natural levels of the substance in up to half of the area of concern - an unlikely occurrence.

more tolerant than measurement endpoints, consideration should be given to reducing or even eliminating the application factors employed to derive the ENEV. If this approach is inappropriate because of large uncertainties, new toxicity studies may be required. Ideally area-specific organisms would be chosen for testing. A bioassay protocol for obtaining toxicity data relevant to plants inhabiting naturally enriched areas has been proposed by Hutchinson (1996).

8.4 Estimating Ecological Consequences

If the only problem facing ecological risk assessors was to determine the probability of exceeding a toxicity threshold or other specified effects level, then modeling at the population and community levels of organization would not be necessary (Barnthouse 1993). Generally, however, it is necessary to estimate the 'ecological costs' of exposure to a priority substance in order that these 'costs' can be compared to the social and economic costs of different risk management alternatives.

Population models have a long history of use in resource management and impact assessments, and several publications have extended their use to toxicological assessments (*e.g.*, Tipton *et al.* 1980; Barnthouse *et al.* 1990). Barnthouse (1993) gives an excellent overview of the state-of-the-art with regards to assessing the effects of stressors on populations.

In general, three approaches to modeling population dynamics have been used to assess ecological effects: individual-based models (DeAngelis *et al.* 1991), demographic models and bioenergetics models (Bartell *et al.* 1992). Each of these approaches has a general level of acceptance in the scientific community. As well, software packages that are user friendly, easy to use and capable of propagating uncertainty are available (*e.g.*, RAMAS/age, RAMAS/stage).

For each approach, however, the data requirements are usually extensive (*e.g.*, life table data and stressor exposure/response relationships for demographic models), and complete data sets are rarely available for the types of toxicological assessments carried out by regulatory agencies. Further, considerable expertise is required to use population models and to correctly interpret the results.

Community and ecosystem level models can be used to explore how substances could affect higher order endpoints such as food web structure, system stability and resilience, and ecosystem production and nutrient cycling. Bartell (unpubl.) and Suter and Bartell (1993) concluded that 15-20 aquatic and 5-10 terrestrial community and ecosystem level models exist that could be used or slightly modified to estimate higher order effects due to substances. Examples include SWACOM for estimating effects to pelagic food webs in northern dimictic lakes (Bartell *et al.* 1992) and AQUATOX for estimating effects to aquatic food webs in streams, rivers and reservoirs (Park *et al.*

1987). Few of these models, however, would meet the following minimum criteria for routine use in regulatory programs: (i) ease of use, (ii) flexibility with regards to choice of stressor, system and selection of endpoints, (iii) ease of obtaining input data, and (iv) ability to propagate uncertainty through the analyses. Further, considerable expertise is required to use the models, and with many models there has not been adequate field testing to verify model structure and predictions. A lack of clear goals in the regulatory community in defining assessment endpoints, spatial and temporal scales, and acceptable levels of uncertainty for decision-making is likely the reason why community and ecosystem models for routine use in regulatory programs have not been developed.

Notwithstanding the difficulties with verifying and validating models, population and community models are useful in a number of ways: (i) they can be used to strengthen the weight-of-evidence for conclusions established by other means, and (ii) they can be used to identify key functional and structural aspects of the system under consideration (Oreskes *et al.* 1994).

Field and mesocosm studies can also be used to estimate ecological consequences. Given their costs, however, they are not likely to be feasible with the majority of priority substances.

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9

Risk Communication

9.1 Introduction

Risk assessments are becoming increasingly influential in shaping risk management decisions and for communicating risks to stakeholders, the media and the public (Hoerger 1990). This chapter outlines some of the general types of risk communication and identifies benefits and limitations of effective risk communication.

Effective risk communication involves a number of components including: understanding the public's perception of specific hazards and risks; making messages clear; gaining trust and credibility; transmitting scientific information; and transmitting information on uncertainty (Freudenberg and Rursch 1994).

Management of risk involves integration of societal, economic and political concerns along with the scientific information about risks. Good risk management decisions are based on a clear understanding of risks.

9.2 General Types of Risk Communication

Effective communication of risk to the public is more than the transmission of messages from experts to non-experts. The objective should be to provide a communication process that meets the needs of the recipients, not just to provide more convincing messages or to advance particular viewpoints. As stated by Johnson and Slovic (1994), we should not "expect the authority of science to awe laypeople into silence".

There are four major types of risk communication (Federal Inter-departmental Committee on Biotechnology 1993):

- communication to inform and educate people about risks,
- communication to change behaviour and result in protective action,
- communication as part of policy setting, problem solving and conflict resolution, and
- communication to provide disaster warning and emergency information.

The first three types of risk communication pertain to the Priority Substances Assessment Program. Communication materials may be need to be meet any or all of these objectives.

9.3 Benefits and Limitations of Effective Risk Communication

Improving communications is likely to have certain benefits, even though there are limitations to what good, and even excellent, risk communication can accomplish.

Effective risk communication:

- improves or increases the amount of accurate information that recipients use for decision-making, and satisfies them that they are adequately informed,
- provides opportunities for communication and feedback between interested parties,
- helps achieve a better understanding of public perceptions, needs and concerns,
- addresses the magnitude and acceptability of specific risks in light of the values and concerns of the affected parties (Rao 1995; Shrader-Frechette 1995),
- helps focus societal attention and resources on major problems and issues (Rao 1995),
- helps set policies involving levels of acceptable risk,
- helps reduce the tensions between communities, agencies, and industrial groups,
- provides information about the choices at hand and their implications, and helps recipients to make informed decisions, and
- contributes to effective risk assessment and management.

There are also limitations to what effective risk communication can accomplish. For example:

- Effective communication and better understanding of risks and options will not always eliminate conflict, lead to consensus, facilitate risk management decisions, or result in support for government decisions (Federal Inter-departmental Committee on Biotechnology 1993; Johnson and Slovic 1994).
- Provision of risk information can help people comprehend the magnitudes associated with risks, but will not always result in agreement on levels of acceptable risk, or ensure systematic minimization of risk. Risk management

decisions that benefit some groups or individuals may harm others. Moreover, individuals and groups do not always share interests, values and concerns.

- Good risk communication cannot always improve a situation, but bad risk communication almost always makes things worse.

- Good risk communication can fuel conflict by emphasizing who stands to win and lose in different scenarios.

- Successful risk communication does not always lead to better decisions because risk communication is only one aspect of risk management.

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Appendix I

Glossary

Absorption: The diffusion of a substance adsorbed onto the surface of a solid, into the interior of the solid.

Acute/chronic ratio: A species mean acute value divided by the chronic value for the same species. Such ratios can be used to convert the median lethal results of a short-term study to an estimated long-term no-effect concentration.

Acute toxicity test: A toxicity test of short duration in relation to the life span of the test organism (*e.g.*, usually ≤4 days for fish).

Adsorption: The accumulation of matter at the interface between a solid phase and an aqueous solution.

Advection: A transport process involving the physical entrainment of a substance in mobile media such as air or water.

Alpha (α): A symbol for a Type I error in hypothesis testing that is expressed as a probability or proportion (*e.g.*, 0.05 or 5%). A Type I error is the probability of rejecting the null hypothesis when in fact the null hypothesis is true. In hypothesis testing, α is specified by the user prior to carrying out the analysis.

Atmospheric window: A portion of the spectrum (700 to 1400 cm^{-1}) of the atmosphere that transmits most of the thermal radiation from the Earth's surface and lower atmosphere.

Beta (β): A symbol for a Type II error in hypothesis testing that is expressed as a probability or proportion. A Type II error is the probability of accepting the null hypothesis when in fact the null hypothesis is false. The magnitude of Type II error β is generally inversely related to the magnitude of the Type I error α that will be tolerated.

Bioaccumulation: The net accumulation of a substance by an organism as a result of uptake from all routes of exposure.

Bioaccumulation factor (BAF): The ratio of the steady state concentration of a substance in an organism due to uptake from all routes of exposure, to the concentration of the substance in the medium to which the organism was exposed.

Bioavailable substance: A substance that is present in a form that can be readily taken up by exposed organisms.

Bioconcentration: The net accumulation of a substance directly from aqueous solution by an aquatic organism.

Bioconcentration factor (BCF): The ratio of the steady state concentration of a substance in an organism due to uptake via contact with water, to the concentration of the substance in the test water; and/or the ratio of the uptake rate constant to the depuration constant, assuming first order kinetics.

Body burden: The amount of a substance that has accumulated in the tissue of an exposed organism, usually expressed as the concentration of the substance in a particular organ, or in the whole organism.

Carrier and non-carrier controls: Toxicity tests for certain substances may use a carrier to aid in dispersing the test substance evenly in the test medium. Carrier and non-carrier controls are conducted with and without the carrier, respectively, in order to determine the effects of the carrier on the test organisms.

Complex: Dissolved species formed from two or more simpler species each of which can exist in aqueous solution.

Complex Substance: Consists of an heterogeneous association of many substances (*i.e.*, constituents) that are not necessarily related and are either released at a given time and place or occur at a given time and place; see definition of mixture and effluent; they do not include classes of related compounds (see Introduction of Chapter 7 for exceptions).

Chronic toxicity test: A toxicity test that spans a significant portion of the life span of the test organism (*e.g.*, 10% or more) and examines effects on such parameters as metabolism, growth, reproduction and survival.

Contact Group: A group of representatives of federal government departments who are interested in PSL2 ecological risk assessments and who will provide a link to others in their departments and to their clients who may be able to contribute to the assessment process.

Critical body burden (CBB): The minimum concentration of a substance that causes an adverse effect on the measurement endpoint (*e.g.*, reproductive potential of *Daphnia*) of interest.

Critical toxicity value (CTV): The quantitative expression (*e.g.*, EC_{10}) of the measurement endpoint that indicates the greatest degree of toxicity for each selected assessment endpoint. Critical Toxicity Values are used in risk characterization for the calculation of an Estimated No Effects Value (ENEV).

Cumulative probability distribution: A curve or mathematical expression that quantifies uncertainty over a variable. It associates a probability with all values in the set of possible values. The probability associated with each value of the variable is that of the occurrence of a value less than or equal to the specified value.

EC_x: The concentration of a substance that is estimated to have a specified effect (*e.g.*, immobilization, reduced growth) on x% of the test organisms. The duration of the test must be specified.

Ecological Risk Assessment Review Group: A group of risk assessors, risk managers and other interested parties who will review the problem formulation stage and data gaps and recommend research priorities for PSL2 substances.

EEV: Estimated exposure value.

Effluent: A liquid complex substance composed of many substances *(i.e.*, constituents) that are not necessarily related and emerging from a pipe or similar outlet and discharged primarily into aquatic systems (*e.g.*, industrial discharge, sewage effluent).

Elutriate: An aqueous solution obtained by adding water to a solid substance (*e.g.*, sediment, tailings, drilling mud, dredge spoil), shaking the mixture, then centrifuging or filtering it or decanting the supernatant.

Endrocrine disrupter: A substance that interferes with the production, release, transport, metabolism, binding, action or elimination of natural ligands in the body responsible for the maintenance of homeostasis and the regulation of developmental processes.

ENEV: Estimated no effects value.

Enhanced radiative forcing: This effect, known as global warming, results from re-radiation of infra-red energy released from trace gases in the atmosphere.

Environmental Resource Group: A group of people drawn from government, the private sector and academia who will assist the Environmental Substance Leader in the conduct and review of the ecological risk assessment for a substance.

Environmental Substance Leader: An Environment Canada employee who is charged with conducting the ecological risk assessment for a substance.

Equilibrium: A condition in which the ratio of the concentrations of a substance in two or more phases (*e.g.*, pore water and particulate phases of bottom sediments) is constant.

Flow-through toxicity test: A toxicity test in which solutions in test vessels are renewed continuously by the constant inflow of a fresh solution or by a frequent intermittent inflow.

Food web structure: Consists of many interlinked food chains (*i.e.*, organisms forming a series through which energy is passed). A typical food chain structure consists of: producer (*e.g.*, green plant) → primary consumer (*e.g.*, herbivore) → secondary consumers (consisting of smaller then, at subsequent trophic levels, larger carnivores).

Genotoxicity: The ability of a substance to damage the genetic material of an organism which is then passed onto the next generation and, consequently, has population effects.

Group parameter: Group parameters are based on analytical-chemical techniques and determine specific elements or chemically defined group of harmful constituents in complex substances. It is essential for a group parameter that the constituents which are quantified are in principle known. Examples of specific determinations are Dissolved Organic Carbon (DOC) and Adsorbable OrganoHalogen (AOX). A group parameter does not necessarily quantify anthropogenic sources, but also co-determines natural constituents of complex substances.

Halocarbon gas: Hydrocarbon gas containing at least one atom of halogen, *e.g.*, bromine, chlorine, fluorine.

Hydrolysis reaction: For organic substances, a reaction involving the introduction of a water molecule or a hydroxide ion into an organic molecule, resulting in the cleavage of a chemical bond in the organic molecule. For inorganic substances, a reaction involving a water molecule and an inorganic substance, resulting in the cleavage of the water molecule.

Immune suppression: The suppression of the immune reaction of the immune system by a substance which leaves the organism vulnerable to infection, disease, etc.

Interpolation: The process of estimating a value between two or more known values.

LC_{50}: The concentration of a substance that is estimated to be lethal to 50% of the test organisms. The duration of the test must be specified.

LD_{50}: The dose that causes mortality in 50% of the organisms tested.

Life table data: A description of the age-specific survival of cohorts of individuals in relation to their age or stage of development.

LOEC: Lowest observed effect concentration. The lowest concentration in a toxicity test that caused a statistically significant effect in comparison to the controls.

LOEL: Lowest observed effect level. The lowest dose in a toxicity test that caused a statistically significant effect in comparison to the controls.

MATC: The maximum allowable toxicant concentration, generally presented as the range between the NOEC(L) and LOEC(L) or as the geometric mean of the two measures.

Mean: The arithmetic average of a set of numerical observations calculated as the sum of the observations divided by the number of observations.

Mineralization: Breakdown of an organic substance to form carbon dioxide, water, nitrate and phosphate ions.

Mixing zone: A defined area both in space and time of effluent mixing in the receiving water. Points within this zone are affected by short-term exposure to the greatest concentrations of the effluent.

Mixture: A liquid, solid or gaseous complex substance composed of many substances (*i.e.*, constituents) that are not necessarily related and released into various environmental compartments including water, air and land (*e.g.*, waste crankcase oils, creosote-impregnated waste materials, landfill leachate, smelter emissions).

Mode of action: The manner in which a substance causes an adverse effect in an organism, *e.g.*, narcosis, acetylcholinesterase inhibition, central nervous system seizure.

Monotonic Dose-Response Curve: A dose-response curve in which the dependent variable (response) either increases or decreases, but not both, as the independent variable (dose) increases.

Narcotic substance: Any substance that induces narcosis, *i.e.*, a reversible state of stupor, insensibility or unconsciousness in an organism. The mechanism of narcosis is non-specific and, consequently, a narcotic substance's toxicity is entirely dependent on its tendency to partition to the tissue of the organism.

NOEC: No observed effect concentration. The highest concentration in a toxicity test not causing a statistically significant effect in comparison to the controls.

NOEL: No observed effect level. The highest dose in a toxicity test not causing a statistically significant effect in comparison to the controls.

Nutrient cycling: The dissipation of energy in ecosystems through the transport, decomposition, and recycling of materials bound up in the biomass, living or dead, of system components. Nutrient cycling can often be constrained by the availability to primary producers of essential raw materials, including macronutrients (*e.g.*, phosphorus, nitrogen, calcium) and trace nutrients (*e.g.*, iron, manganese, molybdenum).

Pelagic biota: Aquatic organisms living in the water column of a body of water, rather than along the shore or in the bottom sediments.

Photolysis - Direct: The decomposition or reaction of a substance on exposure to light. Occurs when sunlight is absorbed by a substance and the energy is used to form excited or radical species, which react further to form stable products.

Photolysis - Indirect (or photooxidation): The reaction of a substance with intermediate oxidants formed during photolysis of dissolved organic matter in water or soil, or photolysis of ozone or NO_2 in the atmosphere.

Photosynthesis: The elaboration of organic matter (carbohydrate) from carbon dioxide and water with the aid of light energy.

Phytoplankton: The plant component of plankton.

Plankton: Minute plant and animal life passively floating or weakly swimming in a body of water.

Pore water: Water occupying the space between sediment particles. The amount of pore water is expressed as a percentage of the wet sediment, by weight.

Probability density function: A probability distribution describing a continuous random variable. It associates a relative likelihood to the continuum of possibilities.

Regression analysis: An analysis based on empirical data of the relationship between a variable and one or more other variables that takes into account the degree of correlation among the variables.

Releases: In the context of this guidance manual, releases refers to the actual material being released into the environment. Releases are generally considered to be specific to each source since the natural or anthropogenic processes responsible for the generation and release of the substance of interest are specific to each source. Releases are characterized both in terms of the quantities released into the environment as well as in terms of the physical and chemical properties of the substance.

Sediment: Natural particulate matter that has been transported to, and deposited at the bottom of a body of water. The term can also describe a substrate that has been experimentally prepared, and into which the test organisms can burrow.

Sensitivity analysis: The computation of an output distribution's sensitivity with respect to the input probability distributions.

Solid phase sediment: The whole, intact sediment. It is not a form or derivative of the sediment such as an elutriate or a resuspended sediment.

Sorption: A general term that encompasses both absorption and adsorption processes.

Sources: In the context of this guidancemanual, the term source refers to the physical location or process from which a substance of interest is released into the environment.

Spiked sediment: A control, reference, or other clean sediment to which a test substance (such as a chemical, or mixture of chemicals) has been added then mixed thoroughly through the sediment.

Spiked sediment toxicity test: An assay using a test organism that is exposed to specified concentrations of a substance-spiked sediment over a specified time period to determine any effects.

Standard deviation: A measurement of the variability of a distribution. Standard deviation is the square root of the variance.

Steady state concentration: A condition in which the concentration of a substance in a particular medium is constant.

Vapour pressure: The pressure exerted by the vapour phase of a substance when it is in equilibrium with the liquid or solid form from which it is derived. Vapour pressure may be considered a measure of a pure substance's tendency to volatilize.

Variance: A measure of the dispersion, or spread, of a set of values about a mean. When values are close to the mean, the variance is small. When values are widely scattered about the mean, the variance is larger. Variance is the mean of the squares of the standard deviations from the mean of the distribution.

Volatilization: The transfer of a substance from a liquid or solid to a vapour phase.

Zooplankton: The animal component of plankton.

Appendix II

Estimating Concentrations of Bioavailable Forms of Priority Substances

II.1 Introduction

When body burden data cannot be used to quantify exposure to bioavailable forms of a substance, concentrations of appropriate dissolved and/or "soluble" forms of the substance in key exposure media (*e.g.*, surface waters, or porewaters of sediment or soils) should be used.

The forms of a substance that are bioavailable should be determined on a case-by-case basis, taking into account the nature of the substance and the assessment endpoint(s) selected. In the case of organic and metallo-organic (*e.g.*, methyl mercury) compounds, it is primarily neutral (*i.e.*, un-ionized) freely dissolved forms which are available for uptake (Suffet *et al.* 1994). Concentrations of such forms may be reduced by binding to dissolved and solid forms of organic matter in soils, sediments, and waters (Di Toro *et al.* 1991).

For metals, free dissolved "aquo ions" (*e.g.*, $Zn(H_2O)_6^{2+}$) are often considered to be the most bioavailable species (Benson *et al.* 1994). However, oxyanions (*e.g.*, chromate (CrO_4^{2-}), and arsenate (AsO_4^{3-})) are also taken up by organisms (Benson *et al.* 1994), and there is evidence that some dissolved organic and inorganic metal complexes (*e.g.*, $AgCl^0$, CuOH-citrate^{2-}) are bioavailable (Campbell 1995). Concentrations of particular dissolved inorganic species are influenced by a variety of factors including pH and pE conditions, and the abundance and nature of other dissolved and solid phases.

Concentrations of dissolved bioavailable forms of substances may be measured directly, or calculated from data on "total" concentrations in water, soil or sediment, using equilibrium models.

Various partial chemical extractants that dissolve "weakly bound" solid-phase materials (such as those adsorbed to the surface of clay minerals, or co-precipitated with iron or manganese oxides) may be used to quantify concentrations of "soluble" inorganic substances in soils and sediments, as well as food and inhaled solids. These "soluble" concentrations reflect reserves of potentially bioavailable forms of elements that could be solubilized (over time) after, for example, ingestion or changes in soil or sediment pH or pE conditions.

II.2 Methods of Quantification for Organic Substances

II.2.1 Measured Concentrations

When routine analytical methods (*e.g.*, gas chromatography) are applied to samples from which suspended solids have been removed by filtration or centrifugation, measured concentrations include both bioavailable free dissolved molecules, and unavailable forms sorbed to dissolved organic matter (DOC). However, if dissolved organic matter levels are low (*e.g.*, DOC $\leq$ 5 mg·L^{-1}; Eadie *et al.*, 1990), or the chemical is not particularly hydrophobic (*e.g.*, log $K_{ow} \leq 3$), filtration or centrifugation followed by routine analysis may be adequate to estimate concentrations of free bioavailable forms. Otherwise, more specialized analytical procedures that are sensitive only to free dissolved forms, such as "headspace" (based on analysis of air in equilibrium with water) or dialysis methods should be used (Suffet *et al.* 1994).

II.2.2 Calculated Concentrations

In the absence of empirical data on concentrations of free dissolved forms of hydrophobic organic chemicals in water, levels can be calculated using fate or exposure models (see for example, ECETOC (1992) and Cowan *et al.* (1995)).

Examples of the use of the *equilibrium partitioning (EqP) method* to calculate concentrations of free dissolved forms of non-ionic non-polar organic contaminants are described below. These methods assume that equilibrium has been established between free dissolved concentrations of a substance, and concentrations in organic carbon phases.

Sediment and Soil

Starting with the measured total concentration of a non-ionic, non-polar organic contaminant in soil or sediment (C_s), an estimate of the organic carbon content of the solid phase (f_{oc}), and an estimate of the K_{ow} for the substance, the truly dissolved concentration ($C_{d\text{-}free}$) in porewater can be calculated (Di Toro *et al.* 1991) as follows:

$$C_{d\text{-}free} = C_{s,oc} \cdot K_{oc}^{-1} \quad (1)$$

where,

$$C_{s,oc} = C_s \cdot f_{oc}^{-1} \quad (2)$$

and assuming that

$$K_{oc} \approx K_{ow} \quad (3)\,.$$

For sediments or soils with an organic carbon fraction (f_{oc}) of greater than 0.002 (or 0.2%) by weight, organic carbon is generally the predominant phase controlling chemical sorption. However, if $f_{oc} < 0.002$, other factors influence partitioning (*e.g.*,

particle size and sorption to inorganic mineral fractions) as much or more than organic carbon. Thus, the above model should only be used if $f_{oc} > 0.002$ (Di Toro *et. al.* 1991).

Free dissolved concentrations can also be calculated from measurements of "total" dissolved concentrations in porewater ($C_{d\text{-}total}$), if the dissolved organic carbon content of the porewater (C_{DOC}) is known. Measured concentrations of organic chemicals in sediment and soil porewaters normally represent the sum of both free ($C_{d\text{-}free}$) and DOC-bound ($C_{d\text{-}OC\text{-}bound}$) forms. So that,

$$C_{d\text{-}total} = C_{d\text{-}free} + C_{d\text{-}OC\text{-}bound} = C_{d\text{-}free}\,(1 + C_{DOC} \cdot K_{DOC}) \quad (4)$$

where K_{DOC} is the equilibrium partition coefficient for the DOC and water phases. $C_{d\text{-}free}$, the free dissolved concentration, is calculated as follows:

$$C_{d\text{-}free} = C_{d\text{-}total} \cdot (1 + C_{DOC} \cdot K_{DOC})^{-1}. \quad (5)$$

This calculation can be applied to both sediment and soil porewaters, assuming that K_{DOC} is approximately equal to K_{ow} (Di Toro *et al.* 1991).

Surface Water

In water samples from which suspended solids have not been removed, the measured total concentration (C_{total}) of an organic chemical is the sum of concentrations of free dissolved ($C_{d\text{-}free}$) and dissolved organic carbon-bound ($C_{d\text{-}OC\text{-}bound}$) forms, as well as particulate organic carbon-bound ($C_{p\text{-}OC\text{-}bound}$) forms. That is

$$C_{total} = C_{d\text{-}free} + C_{d\text{-}OC\text{-}bound} + C_{p\text{-}OC\text{-}bound}, \quad (6)$$

and therefore,

$$C_{total} = C_{d\text{-}free}\,(1 + C_{DOC} \cdot K_{DOC} + C_{POC} \cdot K_{POC}), \quad (7)$$

where K_{POC} is the equilibrium partition coefficient for the suspended particulate organic carbon and water phases, and C_{POC} is the concentration of suspended particulate organic carbon in the sample. $C_{d\text{-}free}$, the free dissolved concentration, is thus calculated as:

$$C_{d\text{-}free} = C_{total} \cdot (1 + C_{DOC} \cdot K_{DOC} + C_{POC} \cdot K_{POC})^{-1} \quad (8)$$

where $K_{POC} \approx K_{ow}$ (Gobas and Zhang 1994). K_{ow} is however generally a poor predictor of K_{DOC} for naturally occurring dissolved organic matter in surface waters (Gobas and Zhang 1994). Consequently K_{DOC} should usually be determined empirically, on a site-specific case-by-case basis.

If reliable empirical values for K_{DOC} are not available, equation 8 should

generally not be used. However, when levels of dissolved organic matter are low (*e.g.*, DOC $\leq$ 5 mg·L^{-1}), the fraction of the total concentration associated with DOC is likely to be small (< 10%) even for very hydrophobic compounds (Eadie *et al.* 1990). Under such circumstances equation 8 can be simplified to

$$C_{d\text{-}free} = C_{total} \cdot (1 + C_{POC} \cdot K_{POC})^{-1}, \quad (9)$$

and K_{POC} may be assumed to be approximately equal to K_{ow} (Gobas and Zhang 1994).

II.3 Methods of Quantification for Inorganic Substances

II.3.1 Measured Concentrations

Dissolved Forms

The net concentration of dissolved forms of a metal in a water sample can be determined when suspended solids have been removed (*e.g.*, by filtration or centrifugation) and samples are analyzed by conventional means (*e.g.*, inductively coupled plasma atomic emission spectrometry). Specialized separation and/or detection procedures are required, however, to determine concentrations of individual dissolved species, such an aquo ion or a particular metal complex. Methods that can be used for this purpose are reviewed by Pickering (1995). Chromatographic separation methods could be used, for example, to isolate a metal species from a sample matrix prior to analysis by routine atomic absorption spectrometry. Alternatively, samples could be analyzed directly using more specialized analytical methods such as nuclear magnetic resonance spectrometry, or potentiometry (using ion-selective electrodes).

"Soluble" Solid Forms

Concentrations of weakly bound forms of metal in solids, such as sediment, soil, food and inhaled particulates, may be determined using a variety of partial chemical extractants, applied either singly or in sequence. Partial extraction methods for application to sediment have been reviewed by Campbell *et al.* (1988); those for soil were reviewed by Pickering (1981). Some extractants are intended to solubilize only particular components of the solid phase (*e.g.*, organic matter). Others are designed to estimate the proportion of the total metal content of a solid phase that could dissolve under particular conditions, such as in the gut of an organism, or in the micro-environment near the roots of plants. The suitability of a particular extractant must be assessed on a case-by-case basis, taking into account the route of exposure and chemical forms of the element that are expected to be bioavailable. Care must be exercised applying data for an extractant that correlate well with element uptake in one area, to another area where the bioavailable forms of the element may be different.

II.3.2 Calculated Concentrations

When empirical data on specific bioavailable forms are lacking, equilibrium models may be used to directly estimate concentrations of dissolved or weakly bound metal species.

A variety of equilibrium models have been developed that can predict concentrations and forms of metal species in solution at a given time under specified conditions (Drever 1988). REDEQL (Morel and Morgan 1972), GEOCHEM (Sposito 1983) and MINEQL (and modifications thereof, including MINTEQA1(Brown and Allison 1987), and MINEQL+ (Schecher and McAvoy 1991)) are among the most comprehensive and widely applied (Sposito 1983). Input parameters required are total concentrations of the metals and ligands to be considered, temperature, and solution properties such as pH and pE. Outputs include the identity and concentrations of individual dissolved species, as well as the proportion of total concentrations that have been precipitated or adsorbed onto solid phases (Sposito 1983; Mattigod and Page 1983). GEOCHEM was developed primarily for application to soil solutions, while REDEQL and MINEQL were designed more for use with surface waters (Sposito, 1983). As Drever (1988) noted, results of studies by Nordstrom *et al.* (1979) indicated that output data for trace metals from different models can vary depending upon the sources of thermodynamic data used in the programs, and on the way pE conditions are determined.

In the absence of empirical data, equilibrium models can be used to estimate concentrations of various potentially bioavailable metal species in water and porewater. However, because of the uncertainties associated with many of the assumptions made in such calculations (including the assumption of equilibrium), the results must be interpreted with caution.

II.3.3. "Corrections" for Substances that Reduce Bioavailability

Uptake of metals as aquo ions may be reduced by competition for adsorption sites on the surface of exposed organisms between the aquo ions and hydrogen, calcium or magnesium ions (Campbell 1995). For example, a decrease in pH may decrease uptake of zinc or cadmium, when concentrations of bioavailable forms of these metals remain constant (Campbell and Stokes 1985). Furthermore, as water hardness increases the toxicity (an effect of uptake) of many metals decreases (Erickson *et al.* 1994). These effects may be addressed by normalizing metal concentrations to concentrations of the competing ions. For example, normalized EEVs could be generated by dividing concentrations of an aquo ion by the total concentration of calcium and magnesium (*i.e.*, hardness) ions in a solution. Alternatively, exposure may be determined as body burdens if, for example, regression equations relating metal uptake, pH, hardness and metal concentrations in solution can be generated.

In anoxic sediment, secondary sulphide minerals can bind metals and render them unavailable to biota (see for example Ankley *et al.* 1991). Digestion in cold HCl will dissolve these sulphides (called "acid volatile sulphides" or AVS) and liberate metals associated with these phases, as well as some other weakly bound forms. Di Toro *et al.* (1990) have recommended that, in anoxic sediments, exposure to bioavailable metal species could be quantified based on HCl-extractable molar concentrations ($C_{HCl\text{-}XT}$) "normalized" (*i.e.*, divided by) to measured molar "acid volatile sulphide" (C_{AVS}) concentrations. In the case of copper (Cu), which forms a relatively insoluble sulphide phase, acute toxicity (*i.e.*, exceedence of the LC_{50} value) would not be expected as long as $C_{HCl\text{-}XT\text{-}Cu} \cdot (C_{AVS})^{-1} < 1$ (Di Toro *et al.* 1992). Some assumptions and limitations of this approach have been reviewed recently by Mayer *et al.* (1994).

In oxic sediment or soil, secondary iron oxides can bind metals limiting their bioavailability. Concentrations of such oxides can be estimated by treating samples with selective partial extractants. Results of studies by Tessier *et al.* (1984) and Campbell and Tessier (1991) suggest that exposure to bioavailable forms of metals could be quantified on the basis of concentrations of weakly bound metals, "normalized" to the concentration of iron present in the iron oxide phase. Preliminary data suggest that such normalized exposure estimates correlate well with element uptake by aquatic macrophytes in limited geographic areas (Campbell and Tessier 1991).

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Appendix III

Partitioning Net Exposure Among Different Sources

III.1 Overview

When there is evidence that releases from sources other than those of concern have contributed significantly to measured EEVs, it may be desirable to apportion EEVs among identified sources. This step is useful for substances found to be CEPA "toxic" for which actions to reduce exposure are required. However, from a risk assessment perspective it is only necessary for tier 3 risk analysis, when EEVs must be apportioned between natural and anthropogenic sources (Chapter 8).

This Appendix focuses on methods of distinguishing natural and anthropogenic sources of metals. Since many potentially harmful organic compounds occur in the environment naturally (Gribble 1994), source apportionment may also be required for organic substances. Most of the methods described for metals (see summary - Table III.1) are also applicable to organic substances. For example,

- enrichment in modern surface sediment compared to deeper older horizons (*cf*, Section III.2.4) has been used to infer a recent anthropogenic increase in atmospheric loadings of dioxins and furans (*e.g.*, Kjeler and Rappe 1995), and

- elevated concentrations of dioxins and furans near urban or industrial areas relative to rural ones (*cf*, Section III.2.4) have been used as evidence of anthropogenic origins (*e.g.*, Czuczwa and Hites 1984).

Although statistical methods are not covered in this Appendix, assessors should be aware one potentially powerful tool – factor analysis. Examples of the application this method to source apportionment can be found in Gordon (1988).

Since there are significant uncertainties associated with the results of most source apportionment methods, several independent methods should be applied whenever possible, and results interpreted using a weight-of-evidence approach.

III.2 Distinguishing Natural and Anthropogenic Sources of Metals

This section of Appendix III examines current methods of estimating the relative contribution of anthropogenic and natural sources of trace metals and metalloid elements in the environment. It is generally agreed that an understanding of natural background concentrations and cycling processes is necessary in order to assess the extent and impact of anthropogenic releases of metals to the environment. However,

because of the limited amount and quality of information available there are often large uncertainties associated with attempts to quantify the relative contribution of natural and anthropogenic sources to global, regional, and local scale geochemical cycles. There are, for example, large uncertainties associated with estimating total metal emissions to the atmosphere globally, and with distinguishing the importance of sources of metals observed in environmental samples collected in remote ecosystems. As a result, in the scientific literature of the past 25 years it has at times been imposible to achieve consensus about the relative significance of anthropogenic and natural sources of metals in the environment, particularly in remote areas such as the Canadian Arctic.

Existing techniques to estimate the relative contribution of natural and anthropogenic sources, and the uncertainties associated with these techniques, are summarized in Table III.1. Each of these techniques is discussed in later sections of this Appendix.

III.2.1 Data Quality Considerations

This section describes several data quality criteria that should be considered by risk assessors when critically evaluating results of published studies. The criteria considered include (i) the quality of the analytical data (*i.e.*, precision and accuracy), and (ii) the representativeness of the data. In this section, "representativeness" refers to both the adequacy of the study design and the statistical treatment of the data.

Analytical Quality

To enable the reader to assess the validity of a study's conclusions, authors must provide an assessment of the quality of the analytical data. Ideally, such an assessment includes a measure of the precision of the analytical method using appropriate replicate analysis, and a measure of the accuracy through the use of closely matched standard reference materials (Hall 1993; 1995). Accuracy cannot be easily assessed where standard reference materials are not available. This is a particular problem in the analysis of natural waters for trace metals. In such cases, interlaboratory comparisons can serve to identify a systematic bias in results (Hall 1993).

The ratio of the metal concentration in the sample relative to the method detection limit is often used as a guide to the uncertainty associated with reported data. This ratio tends to be low in biological samples, such as body fluids, which have a complex matrix containing high concentrations of interfering substances. The ratio also tends to be low in aqueous samples which contain metals in ultratrace concentrations (ppt or ng L^{-1} range and lower). Extreme care is required to carry such samples through all stages of the analysis - collection, storage, preconcentration and determination - without introducing contamination or losses.

Table III.1. Current tools used to quantify the relative contribution of natural and anthropogenic sources of trace metals in rural and remote areas.

Section	*Methods*	*Sample Media*	*Sources of Uncertainty*
III.2.2	Global inventories of industrial and natural emissions to the atmosphere	n/a	•scarcity of temporally and spatially representative data to calculate emission factors •lack of gaseous flux data •statistical treatment of data •the role of non-atmospheric pathways (e.g., seafloor interactions)
III.2.3	Enrichment in sample relative to average crustal abundance (often normalized to Si or Al) used to identify industrial source	•rain, snow, ice cores •dry deposition (aerosols) •mosses and lichens •sediments and soils	•natural organic & inorganic partitioning and enrichment processes cause natural trace metal levels (and elemental ratios) to vary - by orders of magnitude for some media
III.2.3	Trace element signatures used to identify industrial sources	•rain, snow, ice cores •dry deposition (aerosols)	•possibility of same trace element signatures arising from natural processes
III.2.3	Element isotope signatures used to distinguish different anthropogenic sources	•rain, snow, ice cores •dry deposition (aerosols) •mosses and lichens •sediments and soils	• possibility of same isotope signatures arising from natural sources.
III.2.3	Particle size to indicate source: •metals on < 2 µm fraction assumed industrial source; •2-10 µm fraction (and larger) assumed locally derived	•atmospheric aerosols	•particle size is not necessarily diagnostic, as soil dust also contains fine fraction which may become airborne. This fraction is also often naturally enriched in metals.
III.2.4	Enrichment in modern surface samples compared to samples from deeper older horizons; used to infer an increase in atmospheric loading of trace metals	•soil •lake sediments •peat bogs	• possibility that enrichments may result from influence of natural diagenetic processes in sediments, or natural accumulation due to plant uptake & decay in soils.
III.2.4	Regional scale spatial variations in metal concentrations used to infer anthropogenic influences	•soil •mosses •sediments	•possibility that variations are due to changes in rock and till lithologies or climate and vegetation
III.2.5	Mass balances (input-output budgets) used to quantify anthropogenic loadings to parts of the environment (*e.g.*, watersheds).	n/a	•limited data on inputs, particularly from natural sources.

A number of handbooks and review articles (e.g., Keith 1988; Baeyens 1992) indicate that there has been an overall decrease in "average background concentrations" of trace metals in marine and fresh waters reported in the 1980s literature compared to the 1960s literature. This downward trend over the past decades is not attributed to pollution abatement measures, but rather to the elimination of errors caused by contamination during sampling (Barcelona 1988) and to lower detection limits resulting from the development of more sensitive instruments (Baeyens 1992). For example, Fitzgerald and Watras (1988) showed that, as investigators recognized and controlled their sampling errors, background Hg concentrations reported for surface waters of Vandercook Lake (Wisconsin, USA) decreased from about 241 ng L^{-1} in 1983 to 0.5 ng L^{-1} in 1986. Similarly,

earlier studies of methods of environmental sampling and analysis (*e.g.*, Patterson and Settle 1976; Bruland and Franks 1979) concluded that the apparent decrease in average levels of Pb and other trace metals in the oceans was due to improvements in sample collection and handling techniques.

A frequently quoted "rule of thumb" is that trace metal studies completed prior to the 1980s should be disregarded, on the assumption that older data cannot be considered reliable. While it is true that there have been significant improvements in sampling and analytical methods, as indicated by the above-quoted reviews, publication date is not necessarily a valid measure of scientific merit. First, the use of a new instrumental method of detection is not an automatic guarantee of high quality data. The sample collection, preparation, decomposition, and preconcentration steps are just as critical to precision and accuracy as the detection step (Hall 1995). Second, many researchers who published trace metal work before 1980 carefully monitored and reported their analytical precision and accuracy. On the other hand, there are many post-1980 publications which contain no assessment of data quality whatsoever. It is the ratio of the metal concentration in the sample to the method detection limit that should be used as a general guide to the reliability of the analytical data, rather than the publication date.

Quality of Study Design

Apart from the analytical quality of the data (precision and accuracy), another important concern is the representativeness of the data. To determine the degree to which a study area is influenced by anthropogenic sources of metals, it is critical that the field survey be designed to adequately characterize the natural background variation in that area. Many studies which attribute regional spatial variations of metals in rural and remote areas to human perturbation of the environment were designed on the assumption that "background" may be taken as a constant value over large geographic regions (discussed further in Section 4.1). The assumption of a "constant average background" is not supported by world-wide geochemical survey data, which indicate that the natural abundance of trace elements in sample media such as sediments, soil and bedrock can vary by 2 to 3 orders of magnitude over short distances, and up to 5 or 6 orders if samples from rare types of high-grade mineral deposits are included (Darnley 1995).

The importance of obtaining representative data has been emphasized in the estimation of Pb emissions to the atmosphere from natural sources. For example, Nriagu's (1989) estimate of the global Pb flux from volcanoes ranges over four orders of magnitude from 540 kg yr^{-1} to 6,000 t yr^{-1}. This 10,000-fold uncertainty was attributed to the difficulty in obtaining temporally representative data due to the episodic nature of volcanoes (Nriagu 1989). Jaworowski *et al*

(1981, 1983) observed that orders of magnitude variation in natural atmospheric Pb concentrations also occur *spatially*, depending on proximity to volcanoes and other geological anomalies. Their study design was based on the premise that to obtain globally representative emissions data using glacier ice and snow cores, one must sample from various parts of the Earth, and not only from Greenland and Antarctica as had been the practice of other workers. Although Jaworowski *et al.* (1981, 1983)'s work has been criticized (Patterson 1983), the point to be made is that if data are not spatially and temporally representative (usually because there are too few sampling sites and/or too short a sampling period), then a global inventory based on that data will be erroneous.

Although the above refers to the atmospheric compartment, it is equally important to characterize variations in natural background concentrations in terrestrial systems. A recent humus and till survey in Manitoba, Canada (Henderson and McMartin 1995) is an example of a mapping study designed to account for atmospheric fallout in the context of the natural geological background variation. A lack of attention to background variation can lead to erroneous conclusions. For example, a US-EPA study (Crockett and Kinnison 1979) investigated the concentration gradient of Hg in soil around a major coal-fired power plant. Previous studies using the same sample type (soil) in the same location had concluded that Hg concentrations were significantly higher in the vicinity of the power plant due to local atmospheric fallout. The US-EPA study, on the other hand, concluded that Hg concentrations around the plant were not significantly elevated above background. It was explained by the authors (Crockett and Kinnison 1979) that the earlier investigations had limited usefulness due to the small number of samples involved, inadequate statistical treatment of the data, and lack of attention to confounding factors such as terrain and natural background levels of Hg.

Statistical Treatment of Data

Talbot and Simpson (1983) observed that the mineral exploration industry assumes *a priori* that environmental data are positively skewed and often display polymodal characteristics, whereas in the past some ecologists and biologists have based their interpretation of environmental data on the *a priori* assumption that the samples are taken from a normally distributed population[1]. These authors warned against the serious errors that may arise out of the latter assumption. In particular, the unwarranted use of an arithmetic mean may attach undue importance to a few extreme values. Talbot and Simpson (1983) join many exploration geochemists (Miesch 1976; Rose *et al.* 1979; Garrett and Goss 1979;

[1] Deviation of environmental data from normality is now widely recognized by environmental scientists.

Brooks 1995) in recommending that a sound statistical approach is to carefully examine the spread of the data before assuming a normal population, and to report median and modal values, or geometric means.

The importance of evaluating the statistical methodology can be illustrated by examining existing inventories of anthropogenic metal emissions to the atmosphere. First, the statistical reduction of data must properly account for the regional variability of the metal content of raw material in each source category. This was considered by Voldner and Smith (1989) to be the overriding priority in calculating emission inventories. Their survey of coal burned in North America, for example, indicated that Hg concentrations in coal range from 0.10 to 0.24 ppm ($g\ t^{-1}$), depending on the type of coal being burned and the geological origin of the coal (Voldner and Smith 1989). Second, if emission estimates are calculated by averaging high and low values for each source category, then estimates will be inordinately sensitive to the choice of the high value due to the fact that metal contents of raw material tend to be positively skewed and to vary by orders of magnitude. Such a practice may cause significant errors in global estimates, because of the importance attached to a few extreme values.

III.2.2 "Mobilization Factors"

A common approach to evaluating the relative contribution of anthropogenic and natural sources of metals involves the use of "mobilization factors" (Galloway *et al.* 1982; Lantzy and Mackenzie 1979). Mobilization factors are based on global atmospheric emission inventories, and are generally calculated as the ratio of anthropogenic to natural emissions expressed on an annual basis.

Caution is advised in the use of "mobilization factors", however. First, anthropogenic emission inventories are often constructed using production and consumption statistics, and emission factors, based on literature surveys and professional judgment (Voldner and Smith 1989). Without actual measurements of anthropogenic emissions (*i.e.*, source tests), firm conclusions cannot be made regarding the magnitude of atmospheric metal emissions. Second, natural emission estimates frequently vary by orders of magnitude. Consequently, ratios of estimated anthropogenic to natural emissions ("mobilization factors") may be very uncertain.

In addition, it should be noted that mobilization factors based on atmospheric emission inventories do not take into account direct industrial releases to water, or disposal of solid wastes. Similarly, natural release of metals to the environment by chemical and physical weathering processes, mobilization along aqueous pathways, the role of biogeochemical cycling, and chemical interactions between seawater and the seafloor are not considered. A

comparison of natural and anthropogenic sources solely on the basis of emissions to the atmosphere may therefore be misleading.

Natural Emissions Inventories

Natural emission estimates are extrapolated from very sparse data sets, and most are calculated using literature data originally collected for other purposes. As a result, there are large discrepancies among estimates of the global metal flux from natural sources. For example, differences in natural Hg emission estimates are illustrated in Figure III.1. A similarly wide range of estimates, up to 125,000 t/yr, was cited by the OECD (1994).

The degree of uncertainty in natural emission estimates is such that completely different conclusions may be drawn regarding the significance of anthropogenic inputs. For example, in the case of Hg, the global anthropogenic to natural ratios ("mobilization factors") vary from <0.2% to 59%, using the natural emission estimates in Figure III.1 and holding the anthropogenic emission estimate constant[2] at 3,600 t yr^{-1} (from Nriagu and Pacyna 1988).

Although there have been significant improvements in environmental sampling and analysis over the past 25 years (Section III.2.1), there is no evidence that the discrepancies among existing global inventories are caused by differences in analytical quality. For example, the background value of 1 ng m^{-3} used in the estimate by Weiss *et al.* (1971) is in agreement with measurements of background concentrations of Hg in air (1-4 ng m^{-3}) cited by Lindqvist *et al.* (1991). Thus, it is differences in the methods of estimation rather than differences in analytical quality that have created the discrepancy between the more recent Hg flux estimate by Lindqvist *et al.* (1991, Figure III.1) and the earlier estimate by Weiss *et al.* (1971, Figure III.1). Similarly, the natural emissions inventory published by Nriagu in 1989 (Figure III.1) was based on a survey of previously published literature.

The primary cause for discrepancies among emission estimates is the lack of representative data. A critical issue is the lack of data on natural gaseous emissions of metals from volcanic activity, passive crustal degassing, and methylation. As illustrated in Figure III.2, estimates based on the particulate flux alone are generally much lower than estimates based on the total flux (gaseous flux plus particulate flux). Lantzy and Mackenzie (1979) included both estimation

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[2] Uncertainties associated with anthropogenic emisson estimates are discussed in the following section.

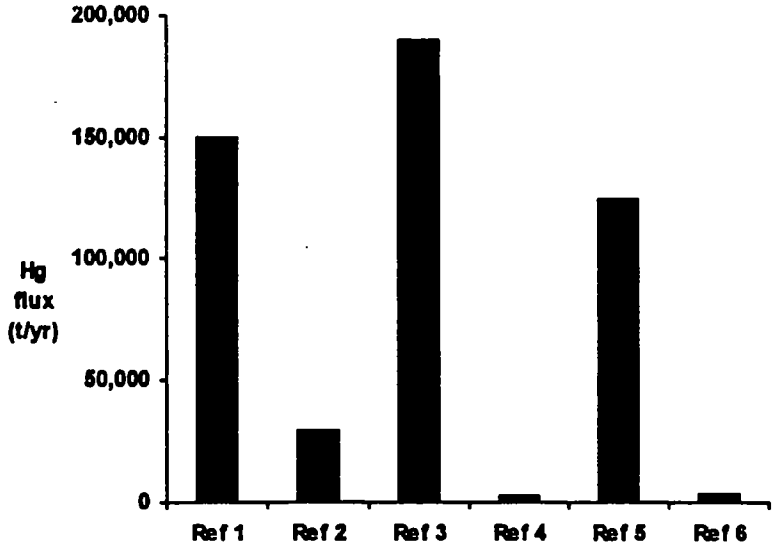

Figure III.1. Variation in estimates of the natural global Hg flux arising from different methods of calculation. (1) Weiss *et al.* 1971; (2) Lantzy and Mackenzie 1979; (3) Jaworowski *et al.* 1981; (4) Nriagu 1989; (5) IPCS 1989; (6) Lindqvist *et al.* 1991. The 1989 estimate by IPCS (Ref 5) ranges from 25,000 to 125,000 t/yr, and refers to "crustal degassing" only.

methods to calculate the global Hg flux (Figure III.2). When crustal degassing was included along with the particulate flux, the total flux estimate was three orders of magnitude higher than the estimate based on particulate flux alone (displayed on a logarithmic scale in Figure III.2). Similarly, global Pb flux estimates based on particulate emissions alone by Kownacka *et al.* (1990) are about two orders of magnitude lower than those that also take into account emissions of gases (Figure III.2). Globally representative data describing the gaseous metal flux from natural sources are needed, therefore, to reduce the uncertainty of atmospheric emission estimates of volatile metals.

Anthropogenic Emissions Inventories

When determining the reliability of "mobilization factors", the representativeness of the values used to calculate existing anthropogenic inventories must also be evaluated. As was noted previously (in Section III.2.1), the statistical reduction of data used in making estimations must properly account for the regional variability of the metal content of raw material in each source category (Voldner and Smith 1989). In addition, global estimates calculated by averaging high and low values for each source category are inordinately sensitive

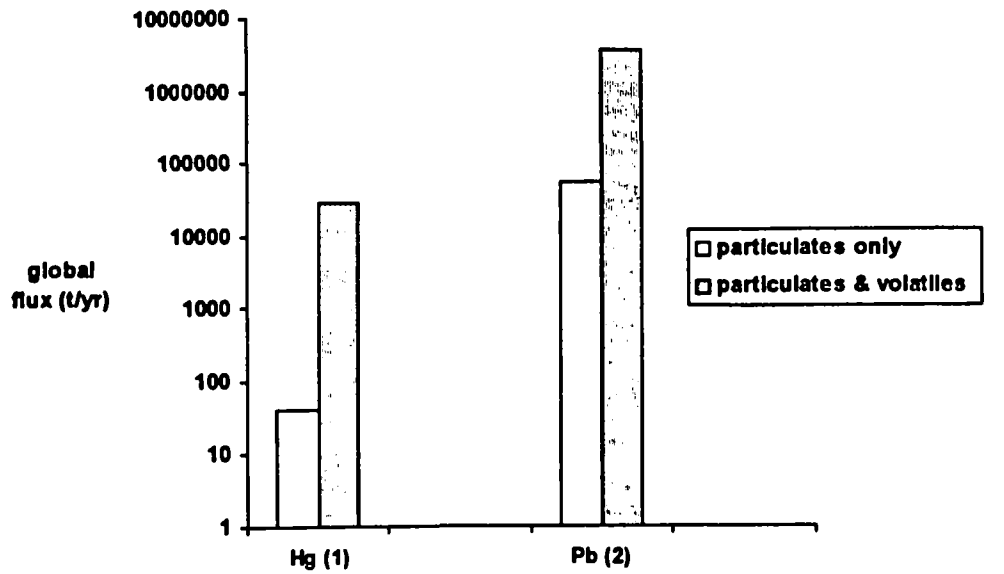

Figure III.2. Different estimates of natural global emissions based on different methods of calculation by the same authors. (1) Hg estimate by Lantzy and Mackenzie 1979, and (2) Pb estimate by Kownacka *et al.* 1990. Note the logarithmic scale.

to the choice of the high value. Thus, the magnitude of emissions may be either overestimated or underestimated depending on the choice of the high value.

Uncertainties associated with anthropogenic emission estimates are reflected by wide discrepancies among emission inventories. An example is provided in Table III.2, which compares local, regional and global inventories of selenium (Se) emissions from the non-ferrous metal smelting sector. A regional inventory (EPS 1977) estimated total Se emissions from all Canadian Cu-Ni mining and processing sources at 138 t yr^{-1}. Except to say that the estimates were based on source testing and literature reviews, this inventory did not detail the method of calculation. For a single Canadian location (at Sudbury, Ontario), Nriagu and Wong (1983) estimated that the total release of Se to the environment was 630 t yr^{-1}, of which 50 t yr-1was dispersed through the atmosphere and the remainder was released as liquid or solid waste. This estimate was based on 1977 production and recovery figures and an estimated average Se concentration of 40 g t^{-1} in the ore. In a later global inventoryof atmospheric releases, however,

Table III.2. Emission of Se from Cu-Ni production: among local, regional, and global estimates.

Estimated Se Emission	*Method of Calculation*	*Emission Factor (g t^{-1})*	*Reference*
LOCAL: Sudbury, Ont. 630 t yr^{-1} to environment as a whole 50 t yr^{-1} to the atmosphere ;	Average Se content of Cu-Ni ore (*i.e.*, 40 g t^{-1}) multiplied by total Cu-Ni ore produced in 1977 (*i.e.*, 17 x 10^6 t yr^{-1}) = 680 t yr^{-1}; minus amount of Se recovered (*i.e.*, 50 t yr^{-1}) = 630 t yr^{-1}. Method for determining atmospheric proportion (50 t/yr) not given.	Total release: 630/680 = 90% Atmospheric release: 50/680 = 7.4%	Nriagu and Wong (1983)
REGIONAL: Canada 138 t yr^{-1} to environment as a whole from all operations in Canada	not given, except to say that the figure refers to all Cu-Ni mining and processing sources across Canada, based on literature reviews/source testing	not given	EPS (1977)
GLOBAL 713 - 2137 t yr^{-1} to atmosphere (for 1983) plus a component of the following: 18 - 176 t yr^{-1} 3.8 - 19 t yr^{-1}	emission factor multiplied by total Cu-Ni produced, increased by a factor of 1.67 to account for volatile forms additional emission factors used to account for: mining non-ferrous metal ore secondary non-ferrous metal production	50 - 150 (x 1.67) plus additional 1 - 2.5 1 - 5	Nriagu and Pacyna (1988)

emission factors used for this source category were significantly higher, ranging from 50 to 150 g t^{-1} (Nriagu and Pacyna 1988). These were further increased by a factor of 1.67 to account for "volatile Se", as well as additional factors to account for "mining and secondary production" (Table III.2). Such discrepancies among inventories indicate the need for refinement and standardization of methods of estimating anthropogenic metal emissions.

III.2.3 Source Apportionment Using Receptor Models

In the context of this Appendix, "source apportionment" means determining the relative contribution of natural and anthropogenic sources to the metal content of an environmental sample collected at a given sampling site. While there have been major advances in the measurement of ultratrace concentrations of metals in environmental samples (Boutron *et al.* 1994), the literature indicates a need for further development of methods to distinguish metals that are of anthropogenic rather than natural origin. For example, the problem of non-uniqueness[3] can occur in air parcel back trajectory models where chemical evidence for an anthropogenic source could equally be used as evidence for a natural source. Problems can also arise when attempting to identify sources of metals in environmental media such as rain, snow and ice cores, soils and sediments.

This section explains some of the uncertainties associated with current source apportionment techniques and suggests possible methods to address these uncertainties.

Elemental Tracers

Certain trace elements in aerosol samples have been used as characteristic indicators of anthropogenic sources in air parcel back trajectory models. For example, selenium and arsenic have been used as characteristic tracers of coal combustion, and their presence in aerosols collected at eastern USA sampling sites has been interpreted as evidence of air contamination by stack emissions in the Ohio Valley (Keeler and Samson 1989). Similarly, Zn has been used as a characteristic anthropogenic tracer in Canada, indicating contamination from either coal combustion or iron and steel manufacturing (Environment Canada 1994).

The use of elemental associations as anthropogenic indicators is complicated by the fact that elemental associations typical of coal and ore are also found in common rock types, and may be reflected in the organic soil, sediment and vegetation overlying these rocks (Levinson 1974). If natural elemental associations at the receptor site can be well-constrained and are known to be distinct from those of the anthropogenic source, such a technique

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[3] The term "non-uniqueness" is used in numerical modeling to describe a model which has two different solutions (Oreskes *et al.* 1994). For example, the extent to which the chemical signature of a given air mass is attributable to stack emissions or natural sources such as windblown dust and biogenic debris, is often unknown.

has potential usefulness in distinguishing overlapping anthropogenic and natural influences at the local scale. Particular care must be taken, however, when such findings are extrapolated to a broader regional scale, because of uncertainties arising from the fact that elements used as anthropogenic tracers (such as Se, As, and Zn) also occur naturally in unconsolidated earth materials in significant and often highly variable concentrations (Darnley 1995). For example, soil geochemical maps (Shacklette and Boerngen 1984) indicate that large areas of central USA are naturally enriched in selenium and arsenic. It is likely that windblown dust originating in these areas would also be naturally enriched in selenium and arsenic, raising questions about the validity of using these elements as characteristic tracers of coal combustion in central USA.

In total, about 19% of the world's land surface has some multi-element data available in the form of geochemical maps (Darnley 1995). Where available, these spatial data could help evaluate uncertainties associated with elemental tracer methods.

Enrichment Factors

The enrichment of metals in inorganic solids (*e.g.*, atmospheric particles or aquatic sediments) relative to the average crustal abundance (normalized against a reference element such as Si or Al) is a commonly used tool to identify anthropogenic sources (Chester 1986; Rahn 1976). The enrichment factor technique was used by Murozumi *et al.* (1969) to calculate the natural component of Pb in ice cores, and by Loring (1990) to assess the extent of metal contamination of aquatic sediments.

Care must be taken, however, when using the enrichment factor method. For example, when applying this method to the atmosphere it is often assumed that chronological changes in element ratios (*e.g.*, Pb/Si ratios) in polar snows reflect parallel chronological changes in the atmosphere, and that enrichment in ratios above average crustal abundance reflect inputs of metal from industrial sources. The validity of the latter assumption may be questioned, however, since natural enrichment of a metal relative to Al and Si can occur, for example, in gaseous emissions of metals from natural sources (*e.g.*, volcanic activity, crustal degassing). Elevated enrichment factors also occur in airborne dust derived from rock types that are naturally enriched in the metal (e.g., sulphides), weathering products of rock of "average" composition (e.g., metal oxides and hydroxides), organic matter, and biogenic particles such as pollen.

Uncertainties associated with the source of enrichments may be addressed through the development of improved methods of fingerprinting natural sources, such as those Hinkley (1992) used to investigate the variation of rock-forming metals in sub-annual increments of modern Greenland snow. Merefield *et al.*

(1994) used a combination of fingerprinting methods in the vicinity of an opencast coal mine, in South Wales, UK. The methods involved analyzing the mineral content by XRD, and the particle size, shape and geochemistry by scanning electron microscopy with energy dispersive x-ray analysis (EDAX). Using these methods the authors were able to distinguish dust arising on-site from the coal workings, from that attributable to local and more remote off-site sources.

Isotopic Signatures

Isotopes of certain elements may be present in unique combinations in emissions from different sources. Data on the relative abundance of lead isotopes have been used, for example, to distinguish between natural and anthropogenic pathways of Pb in mining areas, where the signatures of the various contributing sources can be well-constrained (Gulson *et al.* 1994; Church 1994). Ratios of strontium isotopes have also been used to determine the influence of marine and calcareous soil sources in wet deposition from Sweden (Wickman and Jacks 1991). Measurements of both strontium and neodymium isotopic ratios of dusts in the Antarctic have likewise served to define sources and place constraints on southern hemispheric circulation models (Grousset *et al.* 1992). Chlorine isotopes also have potential as an additional tool to aid in atmospheric source apportionment (Tanaka and Rye 1991). Since the early 1980s it has been possible to determine Cl isotopic ratios with a precision smaller than the natural variations (Eggenkamp 1994).

When identifying sources using isotopic methods, contributions from both anthropogenic as well as natural sources should be considered. Useful data on natural sources may be obtained for example, from recent studies of lead isotope ratios in bedrock (*e.g.*, DeWolf and Mezger 1994), as well as of physical and chemical weathering and transport processes affecting Pb isotopic signatures in glacial till and soil (*e.g.*, Bell and Franklin 1993; Erel *et al.* 1994). Although results of such studies are typically published in the geological literature, they have direct relevance to atmospheric models, due to the presence of soil and sediment particles in windblown dust.

Assessors should be aware of the uncertainty that arises when natural sources have not been characterized[4]. If such uncertainties are considered to be unacceptably large, new data to characterize natural sources may be required.

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[4]For example, the range of Pb isotope ratios in natural earth materials (i.e., not exposed to anthropogenic Pb) varies at least as widely as the Pb isotope ratios of lead additives, fossil fuel and smelter products.

Particle Size

Atmospheric modeling often relies on the particle size spectrum of an element in an aerosol sample to evaluate the source. In a number of studies (*e.g.*, see Schichtel and Husar 1991) elements in the fine particle fraction (<2.5 μm) have been apportioned to various industrial sources, while elements found in the coarser fraction (generally 8-15 μm) have been apportioned to either natural or industrial sources.

This technique is based on the observation that

- low temperature, mechanically-generated, crustal (and sea-salt) particles tend to be coarser than particles generated from high-temperature processes, such as smelting and fossil fuel burning, and
- metals released from high temperature processes, tend to be associated with the sub-micron particle size range (Chester 1986).

However, the assumption that fine particle size is a unique identifier of anthropogenic sources may result in an overestimation of the anthropogenic component of aerosols. This is because particles smaller than 2 μm are abundant in natural soil and sediment, and metals become concentrated in these fine materials whether the source is anthropogenic or natural. A major reason for the association of metals with fine-grained particles is the relatively large surface area of the fine particles available for adsorption and other metal bonding mechanisms. Furthermore, the fine fraction (<2 μm) of soil and sediment tends to be enriched in substances active in metal bonding, including hydrous oxides and hydroxides, organic substances and other weathering products (Forstner and Wittman 1983). Thus, although particle size may provide useful information on potential sources, whenever possible other lines of evidence should also be considered.

Chemical Extractions

The use of partial chemical extractions to estimate the biological availability of trace metals in soil and sediment is discussed in Appendix II. Partial chemical extractions applied in a prescribed sequence (called "sequential extractions") are also used widely to determine mechanisms of metal accumulation in sediments and soils and to compare mechanisms of metal transport in natural as well as polluted environments. A limited number of studies have used sequential extractions for the purpose of distinguishing natural and anthropogenic sources. Most use extraction techniques in combination with other techniques (*e.g.*, physical separation techniques and electron microprobe studies) to establish identities of individual particles on the basis of characteristic

morphologies and chemical composition (Kersten and Forstner 1989). For a description of extraction techniques and their limitations in the context of source assessment, the reader is referred to the review by Kersten and Forstner (1989).

Sequential extraction studies of natural environments have shown that trace metals are partitioned among several substrates in soils and sediments, and that partitioning behaviour is strongly influenced by the concentrations of the different substrates in the sediment (Kersten and Forstner 1989). It is important to understand the complexity of natural partitioning behaviour before attempting to distinguish natural and anthropogenic inputs on the basis of chemical extractions. Interpretation errors may arise from the misconception that metals from geological sources are confined to the mineral fraction of soil and sediments, and are thus immobile and unavailable to organisms. For example, it is sometimes erroneously assumed that

- metals found in the weakly-bound or water-soluble phases must have an anthropogenic origin, or
- metals associated with the organic fraction must be derived solely from atmospheric deposition.

These issues are discussed further in the following section.

III.2.4 Distribution In Remote and Rural Ecosystems

Interpretation of Regional Spatial Variations

In remote areas surveyed at a regional or continent-wide scale, spatial variations in metal concentrations in environmental media such as soils, sediments and vegetation have been used to infer historic increases in atmospheric metal loading (Nater and Grigal 1992; Steinnes 1990; Ouellet and Jones 1983). However, when interpreting such regional chemical data it should not be assumed, as is sometimes done, that metals derived from geological sources are negligible compared to anthropogenic sources. Moreover, it should not be assumed that metals from geological sources are confined to the mineral fraction of soil and sediments, while metals associated with vegetation and humic matter are derived solely from atmospheric deposition or other anthropogenic sources.

These assumptions are inconsistent with data derived from the application of established mineral exploration techniques which use vegetation and humic matter as indicators of metal concentrations in underlying bedrock and glacial drift (Brooks 1995; Dunn 1995). These techniques were developed on the basis of the natural biogeochemical metal cycle (Rose *et al.* 1979; Levinson 1974). The term "biogeochemical cycle" indicates the interaction of biology, geology and

chemistry, and is defined by O'Neill (1985) as "the breakdown of rock to form soils, the uptake of the mobilized chemicals by plants, and the return of the dead plant material to the soil ready for further uptake".

The next two sections explain the importance of understanding natural accumulation processes in a wide geographic and latitudinal range of environments when quantifying the anthropogenic component of metals in environmental media.

The assumption of a "constant background". The assumption of a constant background is common in models which attribute regional spatial variations of metals in rural and remote areas to human perturbation of the environment. The assumption that "background" may be taken as a constant value is not supported by geochemical survey data, which indicate that the natural abundance of trace elements in many surface media such as glacial sediment, soil, and bedrock can vary by 2 to 3 orders of magnitude over short distances, and up to 5 or 6 orders of magnitude if samples from rare types of high-grade mineral deposits are included (Kettles and Shilts 1994; Darnley 1995).

Ledin *et al.* (1989) stated that the use of a single average background value in the interpretation of environmental media can be entirely misleading. This comment is supported by their study of metals in pristine groundwater, monitored at 126 stations across Sweden during 1985-87, which indicates that natural metal concentrations in groundwater vary by at least an order of magnitude (10-fold) in relation to local geology *(e.g.*, Pb varied from 0.02 to 0.30 $\mu g\ l^{-1}$. In Canada, large geographic areas are characterised by naturally elevated trace metal concentrations (e.g., As, Cd, Cu, Hg, Ni, Pb, Zn) in aquatic sediment that exceed guidelines and clean-up criteria designed to protect the environment (Painter *et al.* 1994).

As noted in a recent US-EPA study by Gubala et al (1995), the highly variable background concentrations of metals found in bedrock and soils often make it very difficult, if not impossible, to isolate and describe the phenomenon of long range atmospheric transport in remote ecosystems such as the Arctic.

Factors affecting the natural distribution of metals. Interpretation of the natural background variation of metal concentrations must consider both geological variation and climatic/topographic influences. First, the degree to which bedrock and drift geochemistry influences spatial variation in metal contents should be assessed. For example, a till survey in south-eastern Sweden by Andersson and Nilsson (1992) indicated that elevated Cu, Cr, Co, Ni and V concentrations are characteristic of till derived from one Precambrian sequence while elevated Pb concentrations are characteristic of till derived from another Precambrian sequence. Such information should be considered when determining the relative strengths of anthropogenic and natural sources of metals

in the terrestrial environment.

Second, the degree to which organic carbon influences spatial variations in metal contents needs to be assessed. Metals have an affinity for organic matter in soils (Levinson 1974; Rose *et al.* 1979; Jeffrey 1987), in lake sediments (Coker *et al.* 1979), and in marine sediments (Rashid 1985). The variation in organic matter with variation in climate and geographical setting is thus a governing influence on the regional distribution of metals in the environment (Garrett *et al.* 1990; Garrett and Hornbrook 1976). Lindqvist *et al.* (1991) illustrated the importance of considering organic matter in the interpretation of latitudinal variations of Hg in Swedish forest soils. The interpretation that anthropogenic sources account for the north-south variation in Hg contents of Swedish humus was based on the assumption that a single average background value per unit area was valid for the entire country (Lindqvist *et al.* 1991). However, if the increased bulk density and thicker humus layer in southern Sweden were considered, the "background" Hg value would be three times higher in the south than in the north (Lindqvist *et al.* 1991).

Interpretation of vertical enrichment in soils and sediments

A large number of studies use changes in the metal content of samples of organic lake sediments or forest soils of varying age to infer changes in atmospheric input to the ecosystems where these samples are collected. Unless such studies address the accumulation processes which cause metals to become naturally enriched in these media, it is difficult to verify their conclusions.

Uncertainty in the interpretation of metal enrichment in organic forest soil arises from the fact that naturally occurring metals such as Pb typically become concentrated in the upper few centimeters of undisturbed soils, due to their incorporation in living plants and accumulation in the decomposing litter of the humus layer. Once in the surface layer, Pb and other metals tend to be held strongly by organic matter (Nuorteva 1990; O'Neill 1985; Rose *et al.* 1979). A number of studies have misinterpreted these natural biogeochemical concentrating effects as surface contamination by atmospheric fallout as noted by O'Neill (1985) and Ter Haar (1986).

Organic lake sediments are commonly used as a historic record of atmospheric loading in lakes remote from industrial point sources (*e.g.,* Ouellet and Jones 1983; Lindqvist *et al.* 1991). In this technique, the sediment layers are dated, and metal concentrations in each layer are assumed to reflect atmospheric deposition at the time of sedimentation. However, it has been established that under some conditions natural processes (diagenesis and remobilization) can also lead to the enrichment of metals at the top of the sediment column (Cline and Upchurch 1973; Carlson *et al.* 1978; Cornwell 1987; Farmer 1991; Rasmussen

1994; Coker 1995). Thus, it should not be assumed that surface enrichment in remote lake sediments reflects atmospheric loading. Processes which can lead to the remobilization of trace metals in sediments have been reviewed by Kersten and Forstner (1989).

III.2.5 Mass Balance Models

Mass balances (input-output budgets) are commonly used to evaluate the relative significance of anthropogenic loadings of substances to an environmental compartment such as a waterbody. The mathematical treatment of geochemical mass balances in watershed systems is conceptually identical to that of an individual reservoir in global geochemical cycles (Velber 1986). That is, the mass balance input and output terms are generally treated as functions of the flux of water and the concentration of the substance of interest (Velber 1986). It is a major undertaking to obtain a realistic estimate of total loadings to a water body, as all the sources and pathways in the geosphere and biosphere, as well as the atmosphere, need to be included (Forstner and Wittman 1983).

An important example of a regional scale mass balance is that of the Great Lakes watershed system, located in eastern North America on the border between Canada and the USA. Both the US-EPA (1994) and the International Joint Commission (IJC 1988) have concluded that the atmosphere is the dominant pathway for Pb and Hg in the Great Lakes region. The IJC (1988) estimated that, on average, 83% of the total Pb loading to the Great Lakes is derived from the atmosphere, based on individual estimates for each lake shown in Table III.3. The US-EPA (1994) estimated similar proportions for Lakes Superior, Michigan and Huron (Table III.3). Although it is reported that the best trace metal information available is for Pb (IJC 1988), an examination of the calculations in Table III.3 indicates that there are significant discrepancies between the input and output data.

One area of uncertainty is the quantification of metal inputs from local anthropogenic sources compared to long-range atmospheric influences. Major source categories in the Great Lakes region include the production of electricity and heat, combustion of fuels in industrial, commercial, and residential units, including wood combustion, manufacturing and use of various industrial goods, mobile source emissions, incineration of municipal and industrial wastes, and incineration of sewage sludge (Keeler *et al.* 1993). A recent evaluation of available data on anthropogenic sources of airborne metals in the Great Lakes region (Keeler *et al.* 1993) indicates that there are significant uncertainties in the existing estimates of inputs from these sources, and emphasizes the difficulty in obtaining quantitative information.

With respect to the natural component of the Great Lakes mass balance,

the US EPA (1994) commented that, at present, there is a limited understanding about the natural sources of trace metals. In particular data are lacking on inputs of products of natural weathering of geologic materials in lake catchment basins via surface and groundwater flow. Until such data are obtained conclusions about the relative importance of atmospheric deposition should, following the US EPA (1994) example, acknowledge this limitation.

Table III.3. Annual lead inputs and outputs for the Great Lakes and the fractions attributed to atmospheric pathways (from IJC 1988; US EPA 1994).

Lake	***Total Input*** $kg\ yr^{-1}$	***Total Output*** $kg\ yr^{-1}$	***Net Flux*** $kg\ yr^{-1}$	***% of total input attributed to atmospheric loading (direct + indirect)***	
				IJC (1988)	***USEPA (1994)***
Superior	241	828	-587	97	95
Michigan	543	472	71	99.5	95
Huron	430	496	-66	98	95
Erie	567	2010	-1440	46	
Ontario	428	490	-64	73	

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Appendix IV

Evaluating Data Quality Issues

Sound scientific judgment is required on the part of assessors when evaluating the test procedures and results of toxicity studies. Studies need to be critiqued for good laboratory practices. Data quality is also important for exposure assessment and fate parameters, physical and chemical characterization of substances, and other baseline information. If there is missing information, the author should be contacted. When a well-conducted study is used in determining the critical toxicity value or an estimated exposure concentration, it is possible to reduce the uncertainty surrounding this value. Unacceptable studies are not used.

IV.1 Quality Assurance/Quality Control (QA/QC)

There are issues of data quality to be aware of when evaluating any toxicological study. Assessors must consider the importance of missing information, inappropriate protocols or other weaknesses in the studies to decide if the data are scientifically acceptable. This section discusses issues to be aware of in relation to toxicological data quality, and identifies common problems encountered in the scientific literature. For discussions of specific protocols, see the references cited in this section.

General Considerations

Assessors need to be familiar with the test procedures that are used in environmental toxicology. Such procedures outline standard test conditions and design, test concentrations, temperature, characteristics of the medium, water hardness, pH, statistical techniques, detection limits, controls, results for standard reference samples, etc. With regard to toxicity test data, assessors should consider, in particular, light and dark cycles, condition, age and sex of test species, daily survival and responses of controls. For brief reviews of toxicity methods and the QA/QC issues associated with them, see Environmental Management Associates (1994) and Landis and Yu (1995).

Laboratory researchers do not necessarily have the risk assessor in mind when a study is being conducted and reported. Occasionally information on detection limits, sample size and details of sample collection, how means were calculated, etc., are not clearly reported. These details are crucial to the assessor. In such cases, the authors of the study should be contacted for the missing information.

Information on the limitations of test results is not easy to obtain if not presented in the published paper. Ideally, authors should state the limitations of their results, to give the assessor a feel for the strengths and weaknesses of the study.

Examples of Common Problems

In analyzing scientific papers, it is crucial that basic chemical and biological principles with good laboratory practices be adhered to. During the course of evaluating the data collected for substances on the first Priority Substances List, there were problems that were repeatedly noted. For example:

- Henry's Law constant is the relationship between solubility in water and vapour pressure. It can be determined experimentally using rate constants, or calculated by dividing vapour pressure by solubility. It is crucial that these parameters apply to the same phase (*i.e.*, either solid or subcooled liquid). It was found, however, that Henry's Law constant was occasionally calculated without caution as to the phase of the substance. The resulting values were therefore meaningless.

- Bioconcentration data are credible only if: (i) the concentration of the substance in water remained constant during the test, and (ii) equilibrium was attained. Equilibrium occurs when the ratio of the concentration in the organism (wet weight) and the mean concentration of the chemical in water becomes constant. The bioconcentration factor (BCF) cannot be properly estimated unless a sufficient period of time has elapsed so that equilibrium conditions can be established. It should be remembered that substances with high BCFs move across membranes slowly, and thus such substances may display artificially low BCFs in tests of short duration. Also, highly soluble compounds give artificially high BCFs in tests of short duration, but in the longer term give much lower BCFs.

- For volatile chemicals a steady state concentration of the substance in water must be attained and demonstrated during toxicity tests. There are many examples of toxicological studies on volatile substances that were conducted in an aquarium under static (open) conditions without renewal. Under open-static conditions, volatile substances leave the water phase and transfer into the air phase, so after 48 or 96 hours the actual concentration of the substance in water is unknown but definitely lower than the nominal concentration. Such studies should not be used in assessments. Acceptable protocols for volatile substances are available and include flow-through, static with renewal and closed-static systems with measured concentrations. Under these conditions the nominal and levels of substance in the water should be similar.

- Steady state concentration is not only applicable to volatile substances. It is also important for hydrophobic substances to measure concentrations during the course of the experiment, as they may adsorb to the walls of the containers.

Recommendations

The following questions are useful reminders when evaluating toxicity studies:

- Was the test medium collected, handled and stored according to standardized protocols?
- Did the test employ currently acceptable laboratory practices of exposure and environmental controls?
- Are there solvent controls and appropriate analytical controls?
- Are the responses and survival of controls measured and appropriate for the life stage of the test species used?
- Are the appropriate abiotic variables for each medium (*e.g.*, temperature, pH, dissolved O_2, water hardness, acid volatile sulphide, total organic carbon) recorded and in the relevant range?
- Are the statistics appropriate?
- Were the biota acclimatized to the experimental conditions before the experiment was begun? What were the selection criteria for their use in the test (age, sex, weight, size, variety)?
- What was the mortality rate of test organisms the week before the test?
- Was the concentration in the test medium measured at the beginning and completion of the test and at regular intervals during the test?
- How frequently were observations made on the test organism? Do these give adequate information on general appearance, health or behaviour?
- Were the endpoints appropriate (embryonic development, early life-stage, survival, growth, reproduction, adult survival)?
- Were deviations from the test method reported?
- If the substance is inorganic, is the bioavailable species the one being tested?
- For inorganics, did the oxidation state of the ion remain constant during the course of the experiment?

- Were the extrapolations done correctly?

The following illustrates some QA/QC issues in evaluating a single species toxicity test:

- A sufficient number of concentrations should be tested so that a dose-response relationship can be determined.
- Responses and survival of controls must be measured and should be appropriate for the life stage of the test species used.
- Concentrations of the test substance should be measured at least at the beginning and end of the test to show that the desired concentration was maintained.
- Physical-chemical parameters such as pH, temperature, total organic carbon (TOC), and hardness should be measured.

Other Data Quality Issues

Original references should be obtained so that data can be properly evaluated. There are examples in the scientific literature where a value for a certain physical/chemical parameter has been quoted repeatedly. The original reference may indicate a high degree of uncertainty associated with the value that is not recognized in subsequent publications. For bis(chloromethyl)ether, which was listed on the first Priority Substances List, a log K_{ow} was quoted for more than ten years of literature. What was not mentioned was that the value was calculated from water solubility, and that the original value for water solubility was itself a calculated value. Water solubility could not be measured because the hydrolysis half-life for this substance is less than a second. As a result, the reported log K_{ow} for this substance is meaningless.

A great deal of variability exists in the quality of published toxicity data. A rigid format for evaluating toxicity data is not the answer, but a scientific evaluation for each test should be conducted. Assessors should become familiar with issues of data quality so a thorough review and accurate assessment of the substance can be completed.

IV.2 Supporting Lines of Evidence

All key data used in ecological risk assessments have their own assumptions and associated uncertainties (Suter 1993a). All possible lines of evidence leading to a critical toxicity value should therefore be evaluated. Supporting lines of evidence such as QSARs and EqP (for soil and sediment toxicity) provide additional insight into the

data from acceptable scientific studies (CCME 1995). Such supporting evidence may reduce the uncertainty about the data obtained, and could reduce the size of the application factor necessary for calculating the estimated no-effect concentration in the risk characterization phase of the assessment.

Evaluating Effects Information

- Sound scientific judgement is required on the part of assessors when evaluating the test procedures and results of toxicity studies. Studies need to be critiqued for good laboratory practices. If there is missing information, the author should be contacted. Examples of common problems and reminders when performing a critique of a study are given in section 6.3.1. Once a study is deemed acceptable, the results can be used in the assessment of toxicity. Unacceptable studies are not used. When a well-conducted toxicity study allows for the determination of a critical toxicity value, it may be possible to reduce the uncertainty surrounding this value by exploring other lines of evidence (section 6.3.2).

IV.3 References

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Monte Carlo Simulation of Effects of HCB to Mink

Hexachlorobenzene (HCB) is a persistent substance that accumulates in tissues and biomagnifies up the food chain suggesting that biota at higher trophic levels (*e.g.*, predatory birds and piscivorous mammals) are at the greatest risk of exposure. Although widespread, the highest levels of HCB in Canada are found in the Great Lakes and connecting channels. Since mink (*Mustela vison*) is a piscivorous mammal known to be particularly sensitive to the effects of organochlorine substances, we assessed whether mink populations in the Great Lakes area are experiencing adverse effects as a result of exposure to HCB[1]. We conducted a Monte Carlo simulation to estimate the probability that the total daily intake of HCB for mink living near the St. Clair River exceeds specified effects doses for reproductive impairment.

V.1 Equations

Effects Endpoint. Percent decline in reproductive success of adult female mink from a laboratory feeding study (Bleavins *et al.* 1984) was calculated with the formula:

$$RS_i = (KB_i / KB_c) \times 100$$

where RS_i is the the reproductive success of mink dams measured as total kit biomass per mink dam in treatment i six weeks after birth (KB_i) standardized to the total kit biomass per mink dam six weeks after birth in the control treatment (KB_c). A linear regression of RS_i on log-transformed HCB dietary concentrations ($ng \cdot g^{-1}$) was then performed. Estimated effects doses were calculated as follows:

$$ED_x = RS_i \times IR_{fc}$$

where ED_x is the dose estimated to cause x percent declines (*i.e.*, 5%, 10%, 15%, 20%, 25%, 30%, 35%) in reproductive success of exposed female mink, and IR_{fc} is the measured food intake rate for one kg captive female mink ($g \cdot kg^{-1}$ b.w.$\cdot day^{-1}$).

Exposure. Total daily intake for female mink in the St. Clair River area near Sarnia, Ontario was calculated as follows:

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[1]This appendix is a shortened version of a paper entitled "The Effects of Hexachlorobenzene to Mink in the Canadian Environment: An Ecological Risk Assessment" by D.R.J. Moore, R.L. Breton and K. Lloyd. The paper has been submitted to *Environmental Toxicology and Chemistry* and is currently under review.

$$E = (C_a \times IR_a) + (C_w \times IR_w) + ((C_f \times P_f)/(AE_f \times GE_f) \times MR_{fw}) + ((C_c \times (1-P_f))/(AE_c \times GE_c) \times MR_{fw})$$

where E is exposure ($ng \cdot kg^{-1}$ b.w.$\cdot day^{-1}$); C_a, C_w, C_f, and C_c are the concentrations of HCB in air ($ng \cdot m^{-3}$), water ($ng \cdot L^{-1}$), fish ($ng \cdot g^{-1}$) and crustaceans ($ng \cdot g^{-1}$); IR_a, and IR_w are the intake rates of air ($m^3 \cdot day^{-1}$) and water ($L \cdot day^{-1}$) for one kg wild female mink; P_f is the proportion of fish in the diet of wild female mink; AE_f (unitless) is the assimilation efficiency for mammals eating fish; GE_f (kcal/g) is the gross energy of fish; AE_i (unitless) is the assimilation efficiency for small mammals eating crustaceans; GE_c (kcal/g) is the gross energy of crustaceans; and MR_{fw} (kcal/day) is the metabolic rate for wild female mink. The above equation assumes that the mink diet near the St. Clair River consists of fish and crustaceans; available field data for riverine systems indicates that this may reasonably represent reality during certain periods of the year (Alexander 1977). Mink, however, are opportunistic carnivores and often consume small mammals, amphibians, birds and plants when these prey are available.

Risk. The probability (P) of HCB causing effects of differing severity (x) to mink reproductive success was calculated using the simple formula:

$$P_x = E/ED_x$$

The proportion of Monte Carlo simulations with $P_x \geq 1$ was determined in separate runs for each of 5, 10, 15, 20, 25, 30 and 35% declines in reproductive success.

V.2 Probability Density Functions for Input Variables

Concentration in Air (C_a). Several studies have found that HCB concentrations in air average approximately 0.15 $ng \cdot m^{-3}$ over much of south and central Ontario (Environment Canada 1990, 1991; Lane *et al.* 1992) The probability density function (PDF) for this variable assumed a lognormal distribution with a mean of 0.15 $ng \cdot m^{-3}$ and a standard deviation of 0.07 based upon a 1988-1989 monitoring study of HCB levels in downtown Windsor and at a rural site on Walpole Island (Environment Canada 1990). A lognormal distribution was selected for the input PDF (Figure 1) because substance concentrations in environmental media are typically right skewed as a result of undergoing a series of independent random dilutions following release (see description of the *Theory of Successive Random Dilutions* by Ott 1995).

Concentration in Water (C_w). The PDF for this variable was based on a 1985 monitoring study that determined HCB concentrations on the Canadian side of the St. Clair River from Sarnia to approximately 35 km downstream (Oliver and Kaiser 1986). The mean concentration of HCB in this portion of the river was calculated to be 15.7 $ng \cdot L^{-1}$ with a standard deviation of 25.5. As with air, a lognormal distribution was

assumed for this PDF on theoretical grounds (Ott 1995) and because only four of 16 samples were above the calculated mean (Figure 2).

Concentration in Fish (C_f). In a 1983 monitoring study of organochlorine tissue residue levels in young-of-the-year spottail shiners (*Notropis hudsonius*) collected from the St. Clair River near Sarnia, Suns *et al.* (1983) found a mean HCB concentration of 231 $ng \cdot g^{-1}$ (wet weight) with a standard deviation of 26. There were insufficient samples taken in this study to construct a frequency distribution; in the absence of such information, the PDF for this variable was assumed on theoretical grounds to be lognormally distributed (Ott 1995)(Figure 3). Further, it was assumed that the levels of HCB in shiners were representative of the levels likely to occur in other nearshore fish that are part of the mink diet.

Concentration in Crustaceans (C_c). The PDF for this variable was based on the results of a 1982 biomonitoring study in which clams (*Elliptio complanatus*) were exposed for three weeks at 13 stations in cages anchored in the nearshore of the Canadian side of the St. Clair River (Kauss and Hamdy 1985). Near Sarnia, the mean HCB concentration in clam tissues was 24 $ng \cdot g^{-1}$ (wet weight) with a standard deviation of 3. There were insufficient samples taken in this study to construct a frequency distribution; in the absence of such information, the PDF for this variable was assumed on theoretical grounds to be lognormally distributed (Ott 1995)(Figure 4). As above, it was also assumed that the levels of HCB in clams were representative of the levels likely to occur in other nearshore invertebrates that are part of the mink diet.

Proportion of Fish in Diet (P_f). The PDF for this variable assumed that the proportion of fish in the mink diet ranged from 61% to 85%, as was found in a study of the stomach contents of mink living near the Sable River and Hunt Creek in upper Michigan (Alexander 1977). For this analysis, we assumed a triangular distribution with a best estimate of 75% (Figure 5).

Air and Water Intake Rates (IR_a and IR_w). Point estimate intake rates of 0.48 $m^3 \cdot day^{-1}$ and 0.093 $L \cdot day^{-1}$ were used in this analysis for air and water, respectively. Point estimates were used for the air and water intake rates because: (i) these parameters are likely correlated with food intake rate, but without a measured correlation coefficient, it would be difficult to account for this covariance in the Monte Carlo simulation, and (ii) air and water are minor routes of exposure for mink. These point estimates were based upon the following allometric equations for mammals:

$$IR_a = (0.5458\ Wt^{0.8}) \cdot Wt^{-1}$$
$$= (0.5458 \times 0.578\ kg^{0.8}) \cdot 0.578\ kg^{-1}$$
$$= 0.48\ m^3 \cdot day^{-1} \text{ (normalized to a 1 kg mink)}$$

$$IR_w = (0.099\ Wt^{0.9}) \cdot Wt^{-1}$$

$= (0.099 \times 0.578\ kg^{0.9}) \cdot 0.578\ kg^{-1}$
$= 0.093\ L \cdot day^{-1}$ (normalized to a 1 kg mink)

Food Intake Rate for Captive Mink (IR_c). The food intake rates for wild and captive mink differ because the former are at times under greater environmental stress and must expend more energy foraging. The food intake rate for captive female mink has been measured and was found to have a mean of 160 $g \cdot day^{-1}$ (normalized to a 1 kg female mink) with a standard deviation of 10 (Bleavins and Aulerich 1981). There was insufficient data to fit a distribution to the data; a lognormal distribution was selected based on input rate data sets in the human health literature and theoretical considerations (Ott 1995)(Figure 6).

Assimilation Efficiency and Gross Energy of Fish and Crustaceans. Metabolizable energy of fish is calculated by multiplying the assimilation efficiency for mammals eating fish (AE_f) times the gross energy of fish (GE_f). Similarly, the metabolizable energy of crustaceans is the assimilation efficiency for small mammals eating crustaceans (AE_c) times the gross energy of crustaceans (GE_c).

$$ME_f = AE_f \times GE_f$$

$$ME_c = AE_c \times GE_c$$

The food intake rate for each prey item can be estimated by dividing the metabolic rate of wild female mink (MR_{fw}) by metabolizable energy.

The assimilation efficiency of fish consumed by mink was estimated to be 0.91 with minimum and maximum values of approximately 0.8 and 0.96, respectively (values based on best professional judgement after examination of measured AEs for other animals consumed by mammals (see U.S. EPA 1993). A triangular distribution was used to represent AE_f (Figure 7). Available datasets and theoretical considerations suggest that assimilation efficiencies should be lognormally distributed (Hattis and Burmaster 1994); in this case, however, no standard deviation was available and thus a triangular distribution was used as the next best alternative.

The assimilation efficiency of crustaceans by mink was estimated to be 0.87 with a standard deviation of 0.049 (estimates based upon measured AEs for small mammals consuming insects)(U.S. EPA 1993). A lognormal distribution was used to represent AE_c with the upper extreme truncated at 1.0 (Figure 8).

The gross energy of fish has been measured in numerous studies and has a mean of 1.2 kcal/g wet wt and a standard deviation of 0.24 (U.S. EPA 1993). A normal distribution was used to represent GE_f (Figure 9).

The gross energy of crustaceans was measured to be 0.8 kcal/g wet wt in one study. No standard deviation was measured, but based upon variation measured in other invertebrates, the minimum and maximum values were estimated to be approximately 0.44 and 1.16. A triangular distribution was used to represent GE_c (Figure 10).

Metabolic Rate of Wild Female Mink (MR_{fw}). The mean metabolic rate of wild female mink standardized to one kg body weight can be estimated using the allometric equation:

$$MR_{fw} = 0.6167\ (g\ wt)^{0.862} \cdot wt^{-1}\ (kg)$$

Using this formula with the mean measured body wt of wild female mink during summer and fall (578 g) produces an estimated metabolic rate of 256.4 kcal·day^{-1}. The 95% confidence limits are 110 kcal·day^{-1} and 507 kcal·day^{-1}, respectively, based upon the observed body weights in a field study (Mitchell 1961) and the following equation outlined in the U.S. EPA wildlife exposure factors handbook (U.S. EPA 1993):

$$95\%\ CI_{\log y} = \log y \pm c[d + e(\log Wt - (\text{mean } \log Wt))^2)^{0.5}$$

The values for each of the parameters above are listed in table 3-4 of the handbook for non-herbivorous mammals. On the basis of theoretical considerations, metabolic rate is assumed to be lognormally distributed (Ott 1995)(Figure 11).

Reproductive Success (RS). Bleavins *et al.* (1984) fed mink dams *ad libitum* a basal diet with either 0 (control), 1, 5, 25, 125, or 625 mg·kg^{-1} added HCB for 331 days. The total biomass of kits/female (average kit body weight at six weeks of age x average number of kits per lactating female) was calculated for each treatment. The dose-response function was then estimated by linear regression following a logarithmic transformation of the dose and biomass values. The doses estimated to cause 5, 10, 15, 20, 25, 30 and 35% declines in reproductive success (ED_x) were determined from the dose-response function (Figure 12).

V.3 Monte Carlo Simulation

Separate Monte Carlo analyses were run on Crystal Ball to calculate the probability that wild female mink in the St. Clair River area near Sarnia, Ontario are experiencing 5, 10, 15, 20, 25, 30 and 35% declines in reproductive success. Each simulation had 10,000 runs and latin hypercube sampling was used to ensure adequate sampling from all portions of the input PDFs.

V.4 Output

Figure 13 shows the output PDF for wild female mink exposed to HCB in the St. Clair River area near Sarnia. The analysis indicates that the total daily intake for mink in this area could range from 4,925 to 403,159 ng·kg^{-1} b.w.·day^{-1} with a median of 39,275 ng·kg^{-1} b.w.·day^{-1}. Superimposed on the exposure PDF are the PDFs for 5, 20 and 35% declines in reproductive success. Since, the PDF for a 35% decline in reproductive success is to the right of the exposure PDF, it is highly unlikely that declines in reproductive success could be >35% for wild mink living in this area. Figure 14 compares probabilities to severity of effects. The results indicate high probabilities of relatively minor effects (*i.e.*, <15% decline in reproductive success) and low probabilities of more serious effects (*i.e*, >30% decline in reproductive success).

V.5 Limitations of Monte Carlo Simulation

The sensitivity analysis from the Monte Carlo simulation indicated that the key input PDFs in the analysis were the metabolic rate for wild female mink (Spearman rank correlation coefficient, r = 0.88), gross energy of fish (r = -0.34), and concentration of HCB in fish (r = 0.19). The metabolic rate for wild female mink used in the analysis was an estimate, and no corresponding measurements of this variable are available for wild mink. The potential magnitude and direction of this source of uncertainty are unknown.

Other key sources of uncertainty include the assumptions that HCB levels in spottail shiners were representative of other nearshore fish species, and that the levels measured in the 1980s are representative of recent and current conditions. With regard to the latter assumption, it has been shown in a number of monitoring studies that levels of HCB and other organochlorines in tissues of birds and mammals in Canada have been declining at a slow rate since the late 1970s (*e.g.*, Canadian Wildlife Service, unpubl.; Noble and Elliott 1986). Therefore, current risks of HCB to mink in the St. Clair River area near Sarnia may be somewhat lower than the risks presented in Figure 14.

V.6 Conclusions

Based on the results of this analysis, HCB seems to pose little risk to piscivorous mammals in the Great Lakes region of Canada. Despite choosing an assessment endpoint known to be highly sensitive to organochlorines, we found that the only location of concern for mink in the Great Lakes region was a short stretch of the St. Clair River shoreline (<35 kms). At this location, however, there is a moderate to high probability of mink experiencing 5 to 25% declines in reproductive success due to HCB exposure.

V.7 Figures

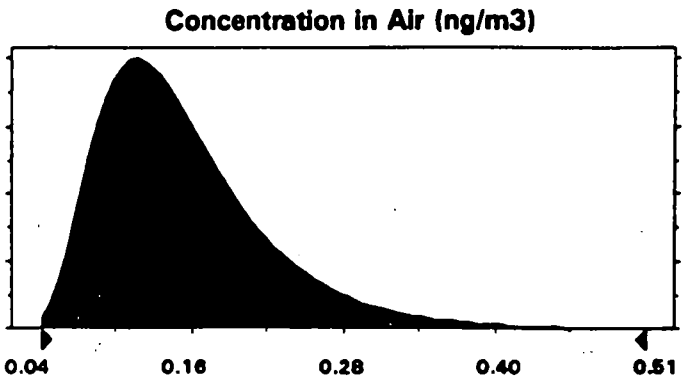

Fig. 1. Concentration of hexachlorobenzene in air in south and central Ontario.

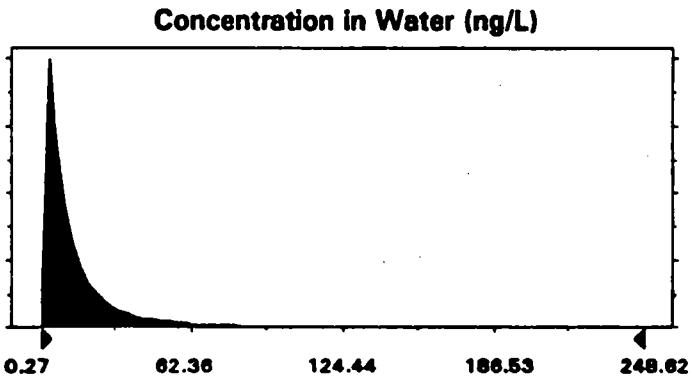

Fig. 2. Concentration of hexachlorobenzene in the St. Clair River from Sarnia, Ontario to approximately 35 km downstream.

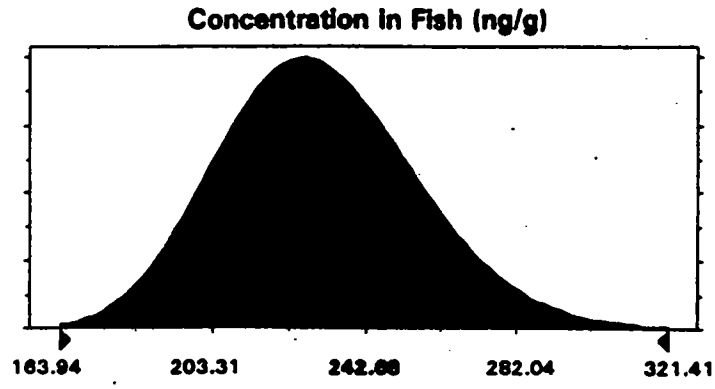

Fig. 3. Concentration of hexachlorobenzene in tissues of young-of-the-year spottail shiners (*Notropis hudsonius*) collected from the St. Clair River near Sarnia, Ontario.

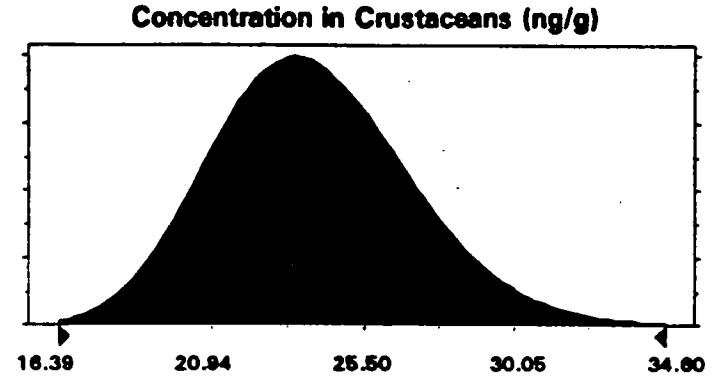

Fig. 4. Concentration of hexachlorobenzene in tissues of clams (*Elliptio complanatus*) collected from the St. Clair River near Sarnia, Ontario.

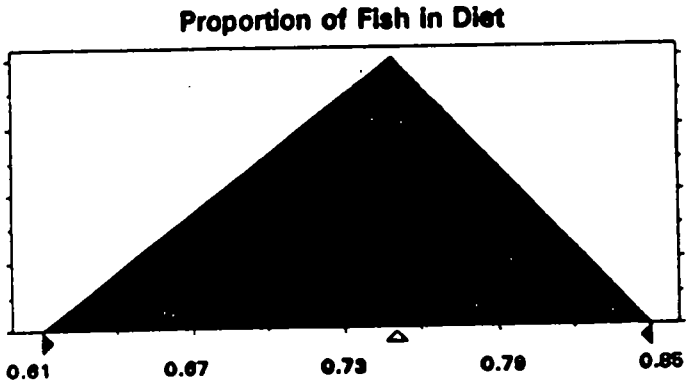

Fig. 5. Proportion of fish in the stomach contents of mink (*Mustela vison*) living near the Sable River and Hunt Creek in upper Michigan.

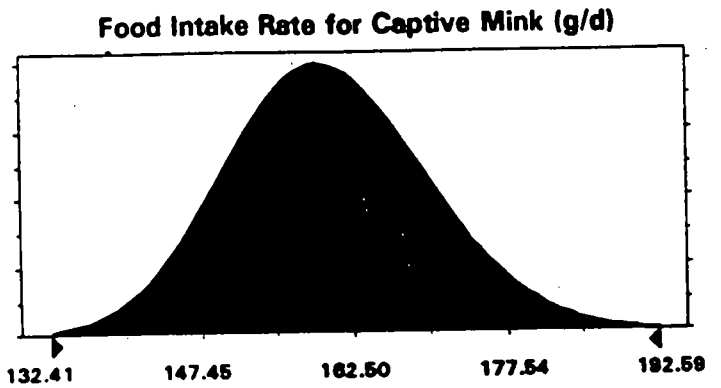

Fig. 6. Food intake rate for captive female mink (*M. vison*) normalized to a 1 kg mink.

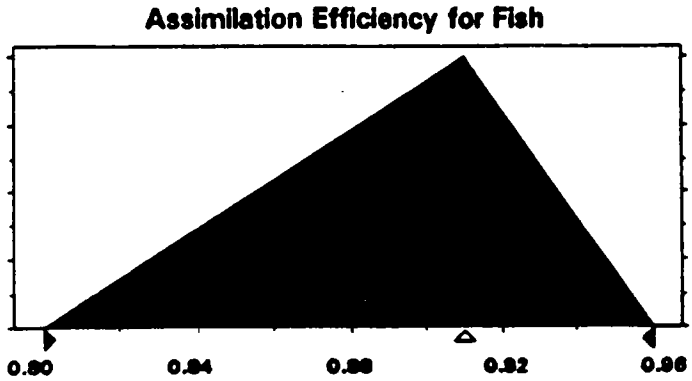

Fig. 7. Assimilation efficiency of fish consumed by mink (*M. vison*).

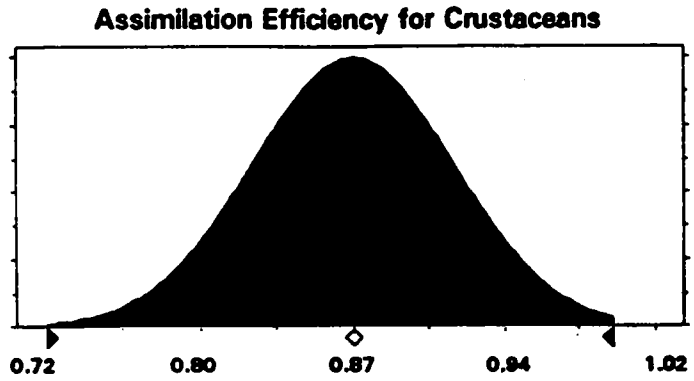

Fig. 8. Assimilation efficiency of crustaceans consumed by mink (*M. vison*).

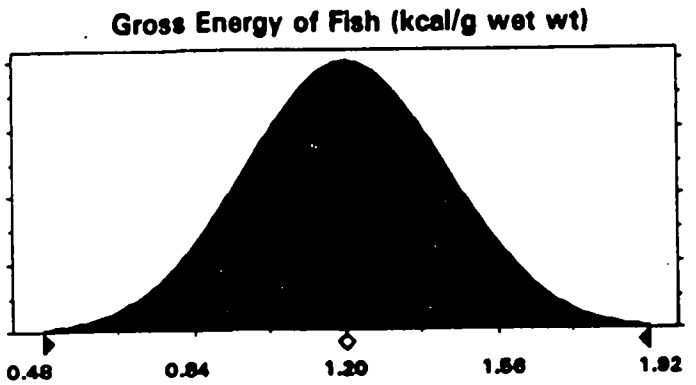

Fig. 9. Gross energy of fish.

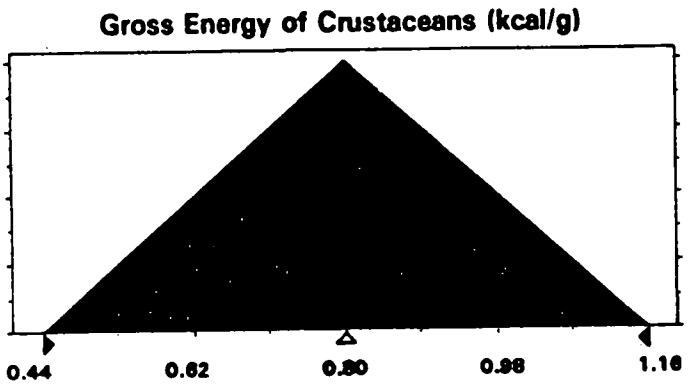

Fig. 10. Gross energy of crustaceans.

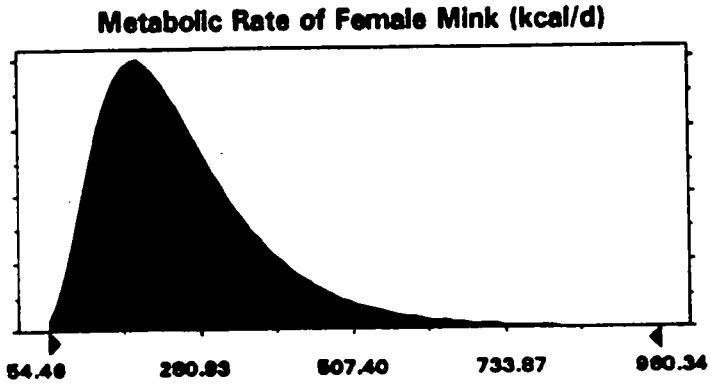

Fig. 11. Metabolic rate of wild female mink (*M. vison*).

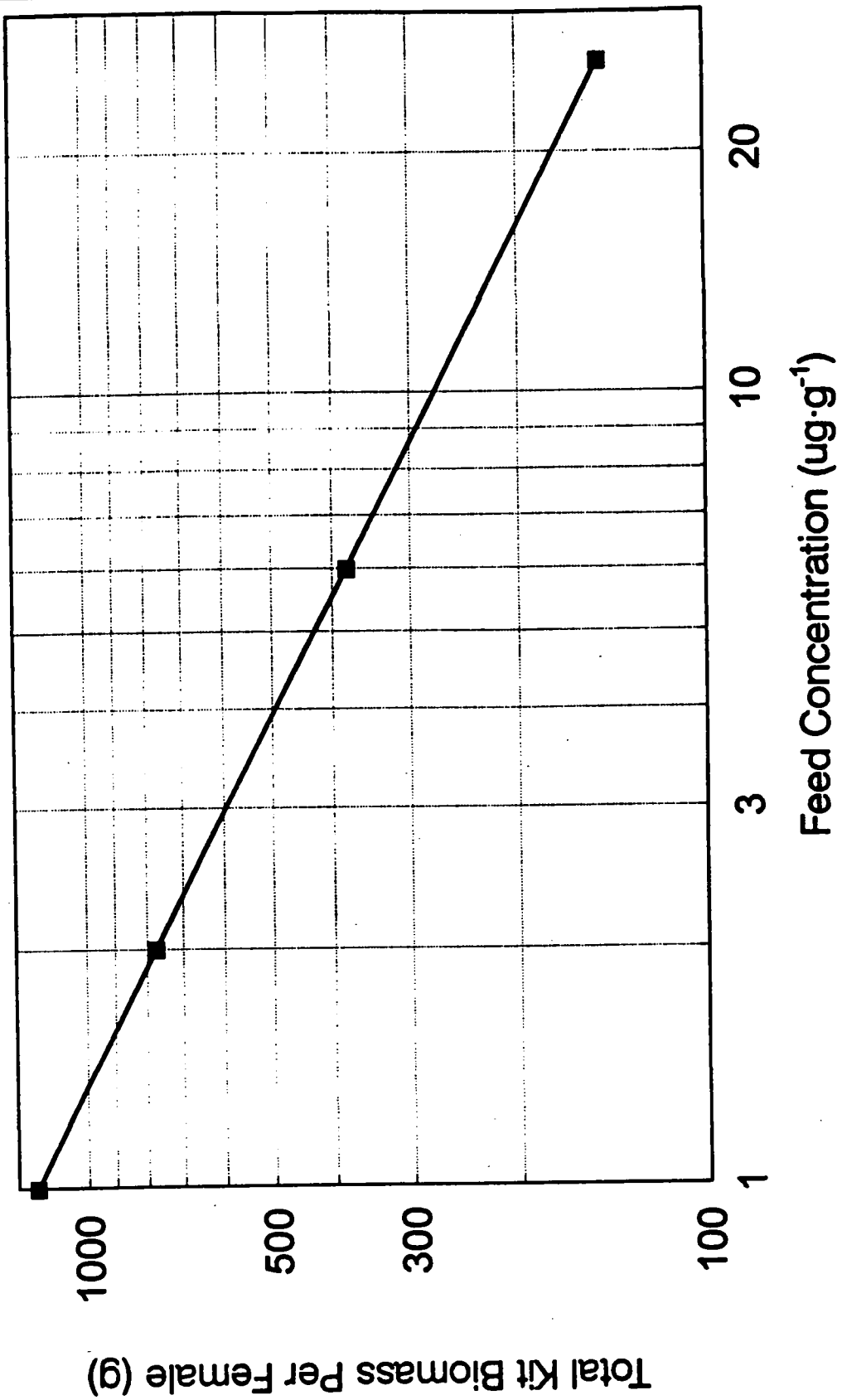

Fig. 12. Total kit biomass per female mink (*M. vison*) exposed to HCB for 331 days in the diet. The dose-response function was estimated by linear regression following a logarithmic transformation of the dose and biomass values.

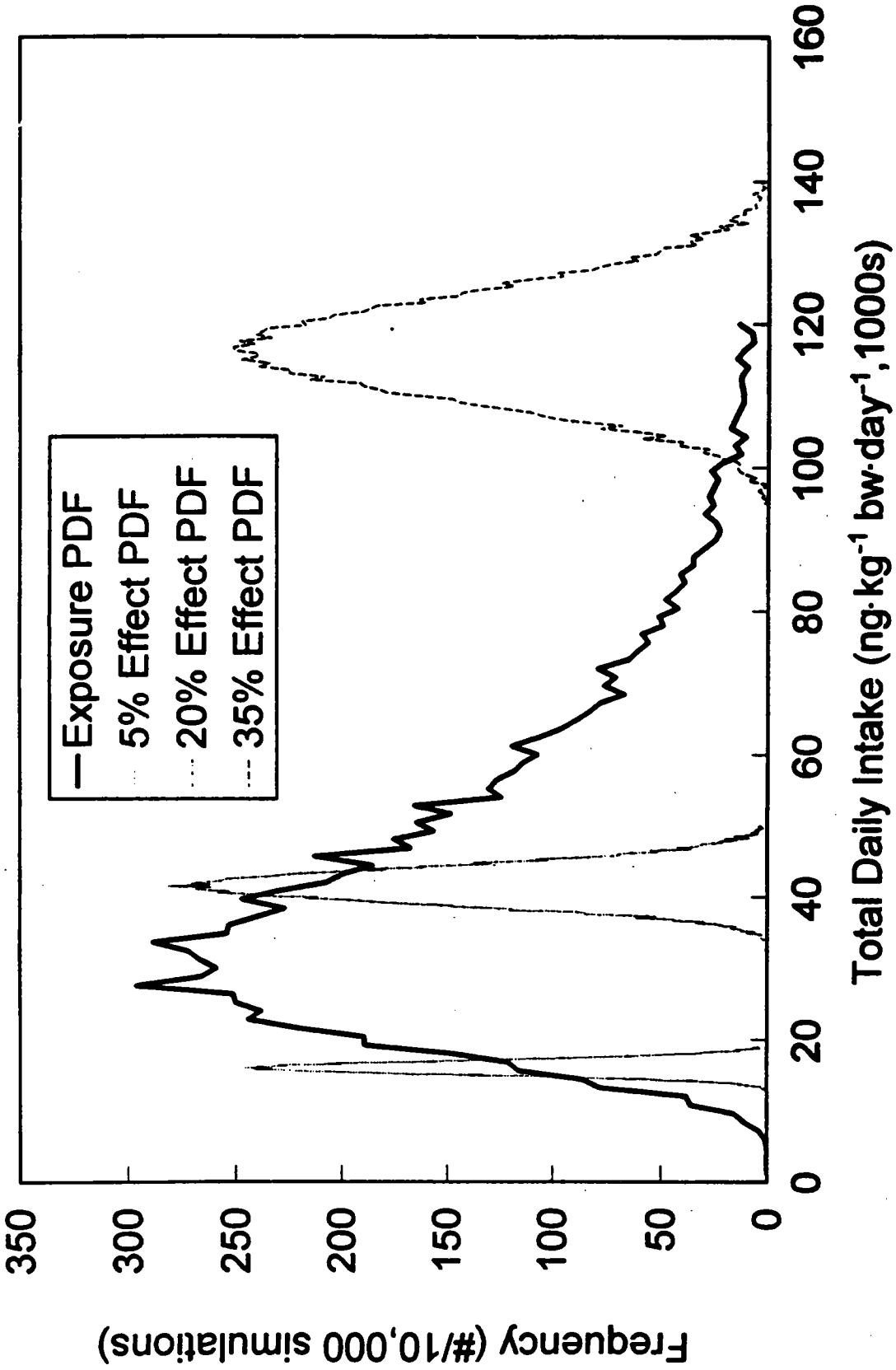

Fig. 13. Exposure probability density function (PDF) for female mink (*M. vison*) exposed to hexachlorobenzene along the St. Clair River near Sarnia, Ontario. The PDFs for 5%, 20% and 35% declines in reproductive success of female mink are also shown.

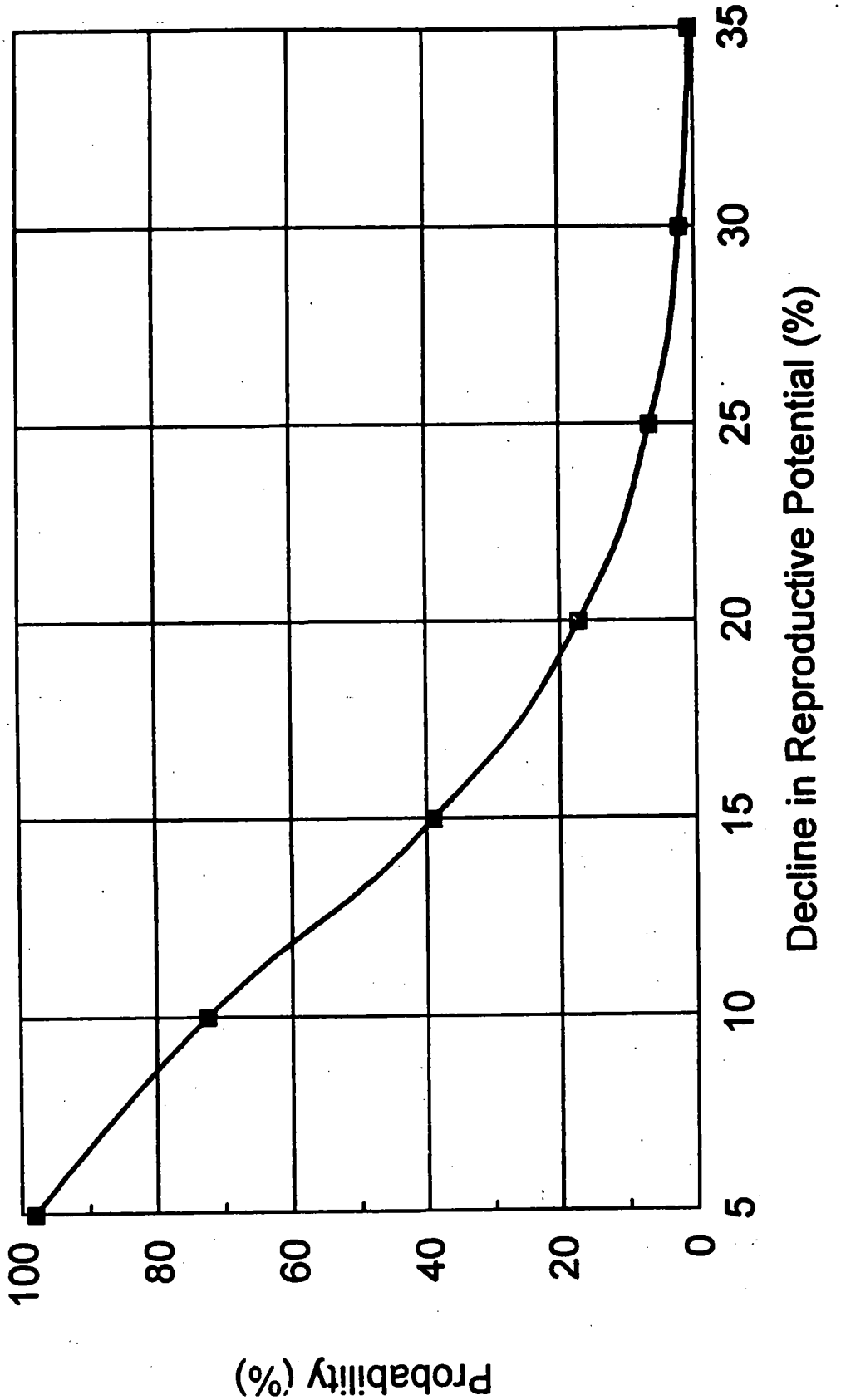

Fig. 14. Function relating probability to magnitude of effects for mink (*M. vison*) exposed to hexachlorobenzene along the St. Clair River near Sarnia, Ontario.

V.8 References

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