

Canadian Environmental Protection Act, 1999

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## **PRIORITY SUBSTANCES LIST ASSESSMENT REPORT**

## **Releases from Primary and Secondary Copper Smelters and Copper Refineries**

**Releases from Primary and Secondary Zinc Smelters and Zinc Refineries** 

Environment Canada Health Canada

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## LIST OF ACRONYMS AND ABBREVIATIONS

а	annum (year)
Ag	silver
As	arsenic
CCR	Canadian Copper Refinery (Noranda)
Cd	cadmium
CEPA	Canadian Environmental Protection Act
CEPA 1999	Canadian Environmental Protection Act, 1999
CEZinc	Canadian Electrolytic Zinc (Noranda)
CH <sub>4</sub>	methane
CL	critical load
CL $CL_{25}$	25th percentile critical load
$CL_{25}$ $CL_{50}$	median critical load
$CO_2$	carbon dioxide
COPD	chronic obstructive pulmonary disease
Cr	chromium
СТО	Cominco Trail Operations
CTV	Critical Toxicity Value
Cu	copper
d/s	downstream
$EC_{50}$	median effective concentration
EEM	environmental effects monitoring
EEV	Estimated Exposure Value
ENEV	Estimated No-Effects Value
EPA	Environmental Protection Agency
EPI	Exposure Potency Index
ERG	Environmental Resource Group
FIAM	free-ion activity model
GSC	Geological Survey of Canada
GSD	geometric standard deviation
HBM&S	Hudson Bay Mining and Smelting
Hg	mercury
IADN	Integrated Atmospheric Deposition Network
IAM	Integrated Assessment Model
K <sub>d</sub>	distribution coefficient (ratio of bound:dissolved metal)
$LC_{50}$	median lethal concentration
$LD_{50}$	median lethal dose
LEL	Lowest-Effect Level
LOAEL	Lowest-Observed-Adverse-Effect Level
MEF	Ministère de l'Environnement et de la Faune du Québec
MMER	Metal Mining Effluent Regulations
MMLER	Metal Mining Liquid Effluent Regulations
MOE	Ministry of Environment
MUC	Montreal Urban Community
MWTP	municipal wastewater treatment plant
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N <sub>2</sub> O	nitrous oxide
NAPS	National Air Pollution Surveillance network
Ni	nickel
NPRI	National Pollutant Release Inventory
OME	Ontario Ministry of the Environment
Pb	lead
PEL	Probable Effect Level
PLE	pressure-leach-electrowin process
PM	particulate matter
$\mathbf{PM}_{10}$	particulate matter less than or equal to 10 $\mu$ m
PM <sub>2.5</sub>	particulate matter less than or equal to 2.5 $\mu$ m
PSL	Priority Substances List
RDIS	Residual Discharge Information System
RLE	roast-leach-electrowin process
RQ	risk quotient
Se	selenium
SEL	Severe-Effect Level
SMAV	Species Mean Acute Value
SO <sub>2</sub>	sulphur dioxide
SO <sub>4</sub> <sup>2-</sup>	sulphate
$TC_{05}$	tumorigenic concentration associated with a 5% increase in incidence of
	or mortality due to cancer
TD <sub>05</sub>	tumorigenic dose associated with a 5% increase in incidence of or mortality
	due to cancer
TEL	Threshold Effect Level
Tl	thallium
TP	total particulate
TSP	total suspended particulate
TU	toxic unit
VOC	volatile organic compound
WHO	World Health Organization
WWTP	wastewater treatment plant
Zn	zinc

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Assessments of the two substances "Releases from primary and secondary copper smelters and copper refineries" and "Releases from primary and secondary zinc smelters and zinc refineries" have been conducted and reported together due to the similar nature of the two types of facilities and the common approach used in assessing their releases. For the purposes of these assessments, a smelter is defined as a facility that uses hightemperature chemical processes to recover base metals, while a refinery is a plant in which impurities are separated from metals using thermal or electrolytic processes. Zinc operations use integrated processes that are a combination of smelting and refining and are conventionally referred to as "zinc plants." The six copper smelters, four copper refineries and four zinc plants currently operating in Canada were considered in the assessments.

Releases from copper smelters/refineries and zinc plants are complex mixtures, containing varying amounts of numerous substances. Since most releases (on a mass basis) are discharged to air, and releases to air have the greatest potential for causing widespread effects, these assessments have focused on environmental and human health risks of air emissions. The components of releases to air that were examined most closely are sulphur dioxide (SO<sub>2</sub>), the metals (largely in the form of particulate matter) copper, zinc, nickel, lead, cadmium, chromium and arsenic, and particulate matter less than or equal to 10 microns (PM<sub>10</sub>). For facilities having multiple operations, source emission attribution was evaluated to estimate the fraction of ambient and deposited contaminants attributable to those operations that are the subject of these assessments.

Risk due to  $SO_2$  released from copper smelters/refineries and zinc plants was assessed based on both direct exposure to  $SO_2$  and associated acidic deposition. Effects thresholds for direct exposure to SO<sub>2</sub> were based on vegetation exposed for periods of 1 hour (acute) and one growing season (chronic). Results for direct exposure indicate that there is a risk to vegetation over varying areas near both copper smelters/ refineries and zinc plants, to a maximum distance of about 10 km. For acidic deposition, it was determined that copper smelters contributed up to 8% (relative to all anthropogenic and natural sources) of the SO<sub>2</sub> resulting in acidic deposition at the four eastern Canadian receptor areas considered. Copper refineries and zinc plants were responsible for significantly lower fractions (up to 0.1% and 0.2%, respectively). U.S. sources were the largest contributors at all four receptor sites.

Endpoint organisms were identified for exposure to each metal examined in both aquatic and terrestrial environments (relating to deposition to surface waters and land, respectively). The 95th percentiles of natural background metal concentrations were used as lower limits for the effects thresholds. The transport and fate of metals deposited on surface waters and soils were modelled to permit estimation of critical metal deposition values ("critical loads") - defined as the amount of annual deposition required for steady-state metal concentrations to reach these low effect concentrations in receiving surface waters and soils. Probabilistic modelling was based on the range of receptor conditions (soil types, pH, lake size, etc.) encountered on the Canadian Shield. Estimated free metal ion concentrations were assumed to be representative of the concentration of biologically available metal.

Estimated annual metal deposition rates were compared with 25th percentile critical loads representative of effects on sensitive organisms under 25% of conditions in sandy soils or acidic lake water of the Canadian Shield. It was concluded that there is potential for effects on aquatic and/or soil-dwelling organisms from exposure to steady-state concentrations of metals in the vicinity of copper smelters/refineries and zinc plants resulting from emissions (especially of copper and zinc, respectively) from these facilities. Impacted areas were estimated to extend up to about 13-14 km from the facilities. In all cases, it is recognized that the range of impact is dependent on the emissions of the individual facilities as well as on local meteorology and geography. Range of impact is also dependent on the percentile of the critical load on which the comparisons are based. A lower percentile critical load, representing risk under a smaller fraction of Canadian Shield conditions, would result in estimation of impacts to greater distances. It is also recognized that emissions from zinc plants using exclusively pressure-leach technology will be significantly less than those from plants using roasting processes.

Screening-level evaluations of the environmental effects of aquatic releases from the three facilities (namely Cominco-Trail, Noranda-CCR and Noranda-CEZinc) that are not currently required to report their aquatic releases under the Metal Mining Liquid Effluent Regulations of the Fisheries Act were conducted. Constituents of releases to water considered in these assessments include all metal contaminants reported to be present, as well as ammonia, fluoride and pH. The results of the assessments of these three facilities indicated the potential for detrimental effects on the environment. However, the indicators of risk were fairly low, especially given the slightly conservative nature of the assessment.

The assessed facilities are also sources of carbon dioxide, nitrous oxide, methane and volatile organic compound (VOC) emissions. The former three contribute to global climate change, while VOCs contribute to tropospheric photochemical ozone creation, and some VOCs contribute to stratospheric ozone depletion. Emissions of all of these substances from copper smelters and refineries and zinc plants are, however, minor in comparison to those from other emission sources.

The health assessment addressed potential risks to nearby populations from current releases from copper smelters/refineries and zinc plants in Canada. Based on recent data, concentrations of arsenic, cadmium, chromium, nickel, lead,  $SO_2$  and particulate matter in air are generally increased in the vicinity of most Canadian copper smelters/refineries and zinc plants in relation both to proximity to the facilities and background concentrations at remote sites.

The results of available epidemiological studies of human populations resident near copper smelters/refineries and zinc plants are inadequate to characterize the potential for both cancer and non-cancer effects from releases from such facilities. Based on assessments conducted previously on the Priority Substances List under the Canadian Environmental Protection Act (CEPA), carcinogenicity is considered to be the critical effect for arsenic, cadmium, chromium and nickel, in light of the sufficient weight of evidence for lung tumours in occupational populations or experimental animals following inhalation of compounds of each of these metals. The range of annual mean concentrations of PM<sub>10</sub> near Canadian copper smelters/refineries and zinc plants overlaps those associated with increased cardiorespiratory morbidity and mortality in recent extensive epidemiological studies of the general population exposed to ambient air pollution in various countries, including Canada. The concentrations of SO<sub>2</sub> in ambient air in the vicinity of all Canadian copper smelters/ refineries and zinc plants occasionally exceed health-based guidelines intended to protect against cardiorespiratory effects. Although not directly considered in this assessment, it is also recognized that SO<sub>2</sub> is an important precursor in the secondary formation of respirable particulate matter, especially the fine fraction  $(PM_{25})$ . Levels of airborne lead also exceed health-based guidelines near certain of the Canadian facilities involved in smelting copper, indicating potential for lead-induced health effects.

Based on available data, it has been concluded that emissions from copper smelters and refineries and from zinc plants of metals (largely in the form of particulates) and of sulphur dioxide are entering the environment in quantities or concentrations or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. Based on available data, it has been concluded that emissions from copper smelters and refineries and emissions from zinc plants are not entering the environment in quantities or concentrations or under conditions that constitute or may constitute a danger to the environment on which life depends. Based on available data concerning the effects of PM<sub>10</sub>, sulphur dioxide and compounds of arsenic, cadmium, chromium, lead and nickel, it has been concluded that emissions from copper smelters and refineries and from zinc plants of PM<sub>10</sub>, of metals (largely in the form of particulates) and of sulphur dioxide are entering the environment in quantities or concentrations or under conditions that constitute or may constitute a danger in Canada to human life or health. Therefore, metals (largely in the form of particulates) contained in emissions from copper smelters and refineries, metals (largely in the form of particulates) contained in emissions from zinc plants, PM<sub>10</sub> and sulphur dioxide are considered "toxic" as defined in Section 64 of the Canadian Environmental Protection Act, 1999 (CEPA 1999).

There are a number of ongoing initiatives that address different release components of copper smelters/refineries and zinc plants. These include activities resulting from the Base Metals Smelting Sector Strategic Options Process, the Canada-wide Standards initiative for  $PM_{10}$  and  $PM_{2.5}$ , and the Canada-wide Acid Rain Strategy for Post-2000. There are also activities resulting from the addition of  $PM_{10}$  to Schedule 1 of CEPA 1999. Any investigations of options to reduce exposure as a result of these assessments should be integrated with these initiatives. Comparison of estimated exposure to arsenic, cadmium, chromium and nickel in the vicinity of Canadian copper smelters/refineries and zinc plants with the tumorigenic potency indicates that the priority for investigation of options to reduce human exposure to releases from these facilities is considered to be in the high range for copper smelters, to range from low to high for copper refineries, and to range from low to high for zinc plants. Comparison of levels of lead, SO<sub>2</sub> and PM<sub>10</sub> in ambient air with healthbased guidelines or with concentrations at which health effects have been observed also suggests that the priority for options analysis is high, especially for facilities where copper is smelted.

Given existing controls on effluents put in place by the companies or imposed by Provincial governments or other authorities, Federal prevention or control actions under the Canadian Environmental Protection Act, 1999 (CEPA, 1999) are not recommended at this time. It is believed, however, that an increase in contaminant concentrations or loadings or changes in conditions affecting bioavailability (such as pH) have the potential to significantly increase risk to the environment. It is important that facility operators recognize that if information, such as monitoring data, shows a significant increase in contaminant concentrations or loadings or changes in conditions affecting bioavailability, such information may be subject to reporting under Section 70 of CEPA, 1999.

Assessment of releases from copper smelters/refineries and zinc plants necessitated evaluation of a limited number of components from the complex mixture of substances released. The constituents of emissions to air examined generally represent the substances released in the greatest quantity. This selection does not imply that other release constituents do not pose a risk. Investigations of options for risk management should also take into consideration other substances of potential concern, some examples of which include mercury, selenium, dioxins and furans.



# **1.0 INTRODUCTION**

The Canadian Environmental Protection Act, 1999 (CEPA 1999) requires the federal Ministers of the Environment and of Health to prepare and publish a Priority Substances List (PSL) that identifies substances, including chemicals, groups of chemicals, effluents and wastes, that may be harmful to the environment or constitute a danger to human health. The Act also requires both Ministers to assess these substances and determine whether they are "toxic" or capable of becoming "toxic" as defined in Section 64 of the Act, which states:

- ...a substance is toxic if it is entering or may enter the environment in a quantity or concentration or under conditions that
- have or may have an immediate or long-term harmful effect on the environment or its biological diversity;
- (b) constitute or may constitute a danger to the environment on which life depends; or
- (c) constitute or may constitute a danger in Canada to human life or health.

Substances that are assessed as "toxic" as defined in Section 64 may be placed on Schedule 1 of the Act and considered for possible risk management measures, such as regulations, guidelines, pollution prevention plans or codes of practice to control any aspect of their life cycle, from the research and development stage through manufacture, use, storage, transport and ultimate disposal.

Based on initial screening of readily accessible information, the rationale for assessing "Releases from primary and secondary copper smelters and copper refineries" provided by the Ministers' Expert Advisory Panel on the Second Priority Substances List (Ministers' Expert Advisory Panel, 1995) was as follows: A wide variety of substances is released into the Canadian environment from primary and secondary copper smelters and refineries. The individual chemical components of releases from these facilities include particulate matter, copper, lead, arsenic and sulphuric acid. The Panel recognizes that assessing the effects of these releases will be difficult from a human health perspective. Releases are often very complex, containing variable mixtures of individual compounds. Often there are no epidemiological studies on populations living near such point sources. For populations at some distance, it may be difficult to attribute effects to the source under examination since other sources can contribute to exposure. Nonetheless, given the large volumes released and the persistent and hazardous nature of some of those substances, an assessment is required to determine the nature and extent of local and long-range ecological and health effects.

The rationale provided by the Panel for assessing "Releases from primary and secondary zinc smelters and zinc refineries" was the same, except that the individual components identified were particulate matter, zinc and sulphuric acid.

Because of their similarities, assessments of whether these two PSL substances are "toxic" under Section 64 of CEPA 1999 were conducted in parallel, and the findings are reported together in this Assessment Report. Since most releases (on a mass basis) are discharged to air and releases to air have the greatest potential for causing widespread effects, these assessments have focused on environmental and human health risks of air emissions. Levels in air were also expected to better reflect current releases than is the case for other environmental media, which can be strongly influenced by high historical emissions. Releases to water from several Canadian copper smelters and refineries and zinc smelters and refineries (more conventionally "zinc plants") will be included in the effluents



regulated under the revised Metal Mining Liquid Effluent Regulations (MMLER) and Guidelines of the *Fisheries Act.*<sup>1</sup> Releases subject to the *Fisheries Act*<sup>2</sup> were not examined in these assessments.

Although potential impacts on both the environment and human health are considered in these assessments, the focus of the assessment is on environmental effects. This is due primarily to limitations of available epidemiological studies of human populations near copper smelters and refineries and zinc plants, which are exposed directly to releases from these facilities, and difficulties in assessing the effects of mixtures based on data from mammalian toxicity studies on individual compounds. These limitations were recognized in the rationale for these assessments provided by the Ministers' Expert Advisory Panel.

Since the entries included on the second Priority Substances List relate to "releases" from copper smelters and refineries and zinc plants, the human health assessment was focused on populations in the vicinity of these facilities. which are expected to be most exposed to substances emitted from them, and on evaluating the potential impacts of current releases. Consequently, the health-related sections of this report contain a summary of recent environmental levels of a number of substances near these facilities in Canada, obtained in response to a questionnaire sent to the companies. A review of available epidemiological studies of populations in the vicinity of copper smelters and refineries and zinc plants is also included. Given the number and variety of substances released from copper smelters and refineries and zinc plants, the health assessment builds on previous work for information on health effects and exposureresponse for individual substances, relying on

other assessments conducted under the PSL assessment program and other programs.

Descriptions of the approaches to assessment of the effects of Priority Substances on the environment and human health are available in published companion documents. The document entitled "Environmental Assessments of Priority Substances under the *Canadian Environmental Protection Act*. Guidance Manual Version 1.0 — March 1997" (Environment Canada, 1997a) provides guidance for conducting environmental assessments of Priority Substances in Canada. This document may be purchased from:

> Environmental Protection Publications Environmental Technology Advancement Directorate Environment Canada Ottawa, Ontario K1A 0H3

It is also available on the Commercial Chemicals Evaluation Branch web site at www.ec.gc.ca/ substances/ese/eng/esehome.cfm under the heading "Guidance Manual." It should be noted that the approach outlined therein has evolved to incorporate recent developments in risk assessment methodology, which will be addressed in future releases of the guidance manual for environmental assessments of Priority Substances.

The approach to assessment of effects on human health is outlined in the following publication of the Environmental Health Directorate of Health Canada: "*Canadian Environmental Protection Act* — Human Health Risk Assessment for Priority Substances" (Health Canada, 1994), copies of which are available from:

<sup>&</sup>lt;sup>1</sup> The Metal Mining Liquid Effluent Regulations (MMLER) and Guidelines, which are currently in force, will be replaced by the Metal Mining Effluent Regulations (MMER), which are anticipated to come into force in 2002.

<sup>&</sup>lt;sup>2</sup> Only smelter or refinery effluents that are combined with those from mining operations fall under the *Fisheries Act* regulations.

HECS Publishing Healthy Environments and Consumer Safety Branch Health Canada Tunney's Pasture Address Locator: 3100A Ottawa, Ontario K1A 0L2

or on the Environmental Health Program publications web site (www.hc-sc.gc.ca/ehp/ehd/ catalogue/bch.htm). The approach is also described in an article published in the Journal of Environmental Science and Health — Environmental Carcinogenesis & Ecotoxicology Reviews (Meek et al., 1994). It should be noted that the approach outlined therein has evolved to incorporate recent developments in risk assessment methodology, which are described on the Existing Substances Division web site (www.hc-sc.gc.ca/ exsd-dse) and which will be addressed in future releases of the approach paper for the assessment of effects on human health.

Informal questionnaires were used to obtain the most recent information available from Canadian industry on releases, environmental concentrations and the ecological effects of their releases. The search strategies employed in the identification of additional data relevant to assessment of potential effects on the environment (prior to fall 1999) and on human health (prior to March 2000 for monitoring and epidemiological data on nearby populations only) are presented in Appendix A. Review articles were consulted where appropriate. However, all original studies that form the basis for determining whether releases from copper and zinc smelters and refineries are "toxic" under CEPA 1999 have been critically evaluated by staff of Environment Canada (entry and environmental exposure and effects) and Health Canada (human exposure and effects on human health). In addition, a number of reports were prepared under contract in support of the environmental component of these assessments; these are also listed in Appendix A.

The environmental components of these assessments were led by P. Doyle and D. Gutzman, with support from D. Caldbick, A. El-Shaarawi, C. Fortin, A. Green, M. Lapointe, D. Morin and J. Sanderson on behalf of Environment Canada. Sections of the Assessment Report and the supporting documentation related to the environmental assessment of copper and zinc smelters and refineries were prepared or reviewed by the members of the Environmental Resource Group (ERG), established by Environment Canada in August 1997 to support the environmental assessment. ERG members were selected based on their expertise in fields of particular significance to these assessments, including releases from the base metal smelting sector, aquatic and terrestrial effects, atmospheric dispersion modelling, metal transport and fate, metal speciation, critical loads, ambient sulphur dioxide (SO<sub>2</sub>) and acid deposition. Members include:

- J. Ayres, Environment Canada
- G. Bird, Canadian Nuclear Safety Commission
- U. Borgmann, Environment Canada
- S. Daggupaty, Environment Canada-
- W. de Vries, DLO Winand Staring Centre, The Netherlands
- M. Diamond, University of Toronto
- G. Dixon, University of Waterloo
- R. Garrett, Natural Resources Canada
- B. Hale, University of Guelph
- D. Hart, Beak International Inc.
- K. Hedley, Environment Canada
- W. Hendershot, McGill University
- R. Hoff, University of Maryland Baltimore County
- D. Hrebenyk, SENES Consultants Ltd.
- T. Jackson, Environment Canada
- P.K. Leung, Environment Canada
- S. Linzon, Phytotoxicology Consultant Services Ltd.
- K. Lloyd, Environment Canada
- M. Sheppard, ECOMatters Inc.
- S. Sheppard, ECOMatters Inc.
- J. Skeaff, Natural Resources Canada
- A. Tessier, University of Quebec
- P. Thompson, Canadian Nuclear Safety Commission

Industry representatives on the ERG who monitored the assessment process include:

Cominco Ltd. — M. Edwards and G. Kenyon Falconbridge Ltd. — R. Telewiak Hudson Bay Mining and Smelting (HBM&S) Ltd. — W. Fraser Inco Ltd. — T. Burnett, C. Ferguson and W. Szumylo Noranda Ltd. — J. Moulin and H. Veldhuizen

In addition to members of the ERG, the following individuals reviewed and provided comments on environmental sections of the supporting documentation:

- H. Allen, University of Delaware
- B. Antcliffe, Department of Fisheries and Oceans
- N. Belzile, Laurentian University
- G. Bonham-Carter, Natural Resources Canada
- T. Burnett, Inco Ltd.
- D. Chambers, SENES Consultants Ltd.
- P. Chapman, EVS Environmental Consultants
- B. Duncan, Cominco Ltd.
- L. Evans, University of Guelph
- D. Gamble, Agriculture and Agri-Food Canada
- A. Germain, Environment Canada
- M. McLaughlin, CSIRO, Australia
- M. Moran, Environment Canada
- M. Power, University of Waterloo
- R. Prairie, Noranda Ltd.
- M. Sadiq, University of Guelph
- R. Stager, SENES Consultants Ltd.
- H. Veldhuizen, Noranda Ltd.

Individuals who reviewed and provided substantive comments on the draft environmental assessment report and who have not been recognized above include:

> D. Bezak, Manitoba Conservation Department

P. Campbell, Institut National de la Recherche Scientifique – Eau
V. Chapados, Noranda Ltd.
D. Daoust, Noranda Ltd.
M. Edwards, Cominco Ltd.
W. Fraser, HBM&S Ltd.
B. Keller, Laurentian University
J. Leclerc, Noranda Ltd.
K. Taylor, Environment Canada

Supporting documentation and sections of this Assessment Report related to human health were prepared by the following staff of Health Canada:

> K. Byrne H. Hirtle M.E. Meek R. Newhook

The health-related supporting documentation was circulated for comment to the following representatives of the smelting and refining companies who are members of the ERG for this assessment, primarily to ensure the accuracy of the information contained therein concerning the copper smelters and refineries and zinc plants that their companies operate:

M. Edwards, Cominco Ltd.W. Fraser, HBM&S Ltd.R. Prairie, Noranda Ltd.W. Szumylo, Inco Ltd.R. Telewiak, Falconbridge Ltd.

Due to reliance on measures of exposureresponse derived from peer-reviewed sources for comparison with ambient levels of components of releases, external review of the health-related sections of the assessment was less extensive than for other assessments on Priority Substances. The health-related sections in the Assessment Report were reviewed externally by M. Younes, World Health Organization (WHO) International Programme on Chemical Safety and M. Dourson, Toxicology Excellence for Risk Assessment. The health-related sections of the Assessment Report were reviewed and approved by the Health Protection Branch Risk Management meeting of Health Canada.

The entire Assessment Report was reviewed and approved by the Environment Canada/Health Canada CEPA Management Committee.

A draft of the Assessment Report was made available for a 60-day public comment period (July 1 to August 30, 2000) (EC/HC, 2000b). Following consideration of comments received, the Assessment Report was revised as appropriate. A summary of the comments and responses is available on the Internet at:

#### www.ec.gc.ca/substances/ese/eng/psap/ public/main.cfm

The text of the Assessment Report has been structured to address environmental effects initially (relevant to determination of "toxic" under Paragraphs 64(a) and (b)), followed by effects on human health (relevant to determination of "toxic" under Paragraph 64(c)).

Copies of this Assessment Report are available upon request from:

Inquiry Centre Environment Canada Main Floor, Place Vincent Massey 351 St. Joseph Blvd. Hull, Quebec K1A 0H3 or on the Internet at:

www.ec.gc.ca/substances/ese/eng/psap/ final/main.cfm

Unpublished supporting documentation, which presents additional information, is available upon request from:

Existing Substances Branch Environment Canada 14th Floor, Place Vincent Massey 351 St. Joseph Blvd. Hull, Quebec K1A 0H3

or

Existing Substances Division Health Canada Environmental Health Centre Tunney's Pasture Address Locator: 0801C2 Ottawa, Ontario K1A 0L2





### 2.0 SUMMARY OF INFORMATION CRITICAL TO ASSESSMENT OF "TOXIC" UNDER CEPA 1999

### 2.1 Identity

#### 2.1.1 Definitions and scope

#### 2.1.1.1 Smelters and refineries

For the purposes of these assessments, a smelter is defined as a facility that uses high-temperature chemical processes to recover base metals (MAC, 1995). A refinery is understood to be a facility in which impurities are separated from metals using thermal or electrolytic processes (MAC, 1995). In these assessments, both electrorefineries and electrowinning facilities are considered to be refineries.

Since several metals are recovered from individual smelters and refineries, for the purposes of these assessments a "copper" smelter or refinery is understood to be a facility in which one of its primary commercial products is more or less pure copper metal. Similarly, a "zinc" smelter or refinery has more or less pure zinc metal as one of its primary products.

Primary smelting and refining produce metal directly from ores and concentrates, while secondary smelting and refining produce metal from scrap and/or process waste (Environment Canada, 1997b). The distinction between primary and secondary smelting is not always clear in practice, however, since some predominantly primary smelters use recycled metals to supplement their primary feed.

In a typical copper smelter, a sulphide concentrate or calcine is heated with fluxing agents to about 1200°C, to effect a phase separation into a molten sulphide matte containing copper and iron and an overlying molten slag containing iron oxide, silica and lime. The matte is then subjected to converting and fire refining to produce an impure copper metal known as anode copper, which contains about 99% copper, and minor and trace elements (Skeaff, 1997). Casting of the impure metal into anodes, the configuration suitable for electrorefining, may take place in either the smelter or refinery. A copper refinery then electrolytically refines the anode copper to produce pure copper.

Zinc may be produced using either a roast-leach-electrowin (RLE) process or a pressure-leach-electrowin (PLE) process. Roasting refers to the heating of concentrate to oxidize and drive off sulphur oxide gases. In roasters, zinc and iron sulphides in the concentrate are converted to oxides, and the resulting solid product (calcine) is sent to leaching. Leaching can be under acidic conditions, neutral conditions or a combination. Zinc and non-ferrous metals are extracted, producing a zinc sulphate leach liquor. In the pressure-leach process, zinc concentrate is reground and agitated in an autoclave with oxygen and sulphuric acid. Iron and zinc sulphides are thereby converted to iron and zinc sulphate and dissolved in the leachate. Leach liquor from either the roast-leach or pressureleach process is purified and directed to electrowinning. In electrowinning, an electric current is passed through the purified liquor, causing the zinc sulphate to chemically decompose and zinc metal to deposit on the cathode. Cathodes are stripped mechanically, and the zinc is melted and cast.

Since the RLE process is a hightemperature chemical process, facilities using it to recover zinc may be considered to be, at least in part, "smelters" as defined previously. However, zinc production facilities may also be considered "refineries" as defined previously, in that they



include an electrowinning step. Because of the ambiguity concerning their classification, these facilities are commonly referred to as "zinc plants". The term "zinc plants" is used in this report to describe facilities involved in recovering zinc using RLE or PLE or a combination of the two.

#### 2.1.1.2 Releases

For the purposes of these assessments, a release is considered to be any current discharge to the ambient environment. Past releases, which were often larger and less well controlled than at present, are not included.

Releases considered in these assessments include all current on-site discharges to air and water from Canadian copper smelters and refineries and zinc plants. Releases to air include emissions from "point" (e.g., tall stack) and "area" sources (e.g., low stacks or fugitive emissions from concentrates stored on-site). Effluents considered include both process and cooling waters that are entering surface waters either directly or indirectly (e.g., after passage through a municipal water treatment plant).

As noted in Section 1.0, releases to water from copper smelters and refineries and zinc plants that will be included in effluents regulated under the revised Metal Mining Effluent Regulations (MMER) of the *Fisheries Act* are not examined in these assessments. Releases from off-site activities related to copper and zinc smelting and refining (e.g., releases from the shipment of feed materials or wastes and landfilling of wastes) were also not considered in these assessments.

Direct impacts of the storage of smelter or refinery wastes (e.g., slags) on lands within the boundaries of facilities were also not examined, since land owned by the facilities is not considered part of the ambient environment. However, leachate or runoff from such wastes that enters ambient off-site waters and wind-blown fugitive emissions from such wastes that are transported off-site were in principle included.

#### 2.1.2 Facilities included in assessments

All copper smelters and refineries and zinc plants currently operating in Canada were included in these assessments.3 Using the definitions presented in Section 2.1.1, six copper smelters, four copper refineries and four zinc plants were identified (Tables 1 and 2). Those with effluents that will be regulated under the revised MMER of the Fisheries Act are identified in these tables. As noted in Section 1.0, risks associated with direct releases to water from these facilities were not assessed. Screening-level assessments of the risk to the environment of aquatic releases were conducted for the Noranda-Canadian Copper Refinery (CCR), Noranda-Canadian Electrolytic Zinc (CEZinc) and Cominco-Trail Operations (CTO).

The Falconbridge-Kidd Creek and HBM&S copper smelters are primary smelters. No currently active stand-alone secondary copper smelters were identified. However, a relatively small portion of the feed entering the Noranda-Horne facility, and to a lesser extent the Noranda-Gaspé facility, is recycled copper-bearing material (Hatch Associates, 1997). These smelters could be considered to be predominantly primary copper smelters that engage in some secondary smelting.

Two primary nickel/copper smelters were also assessed. They are the Falconbridge-Sudbury and Inco-Copper Cliff plants. The Inco plant produces impure copper as well as nickel products. The Falconbridge operation produces only a nickel/copper matte, which is shipped to Norway for further processing (Environment Canada, 1997b). The Falconbridge smelter has been included in these assessments because the operations carried out at Sudbury are the first step of a smelting process that ultimately leads to the production of copper metal.

<sup>&</sup>lt;sup>3</sup> The electrowinning facility associated with the Boliden-Westmin Gibraltar Mines facility located at McLeese Lake, B.C., was not considered in detail. The operation was very small (annual copper production of about 2000 tonnes) and did not report any releases to air or water to the National Pollutant Release Inventory (NPRI). The plant ceased operation in 1999.

Facility	Туре	Location	Copper production (tonnes/year)	Year	Effluent subject to MMER	Source of production data
Noranda-Horne	Copper smelter	Rouyn-Noranda, Que.	213 000	1995	yes	А
Falconbridge- Kidd Creek	Copper smelter	Kidd Creek (Timmins), Ont.	99 000	1996	yes	А
HBM&S	Copper smelter	Flin Flon, Man.	74 000	1995	yes	В
Noranda-Gaspé	Copper smelter	Murdochville, Que.	103 000	1995	yes	А
Inco-Copper Cliff	Nickel/copper smelter	Copper Cliff (Sudbury), Ont.	120 000 plus 75 000 Ni sulphide matte	(C)	yes	С
Falconbridge- Sudbury	Nickel/copper matte smelter	Falconbridge (Sudbury), Ont.	60 000 matte (~55% Cu)	1995	yes	A B
Noranda-CCR	Copper electrorefinery	Montreal East, Que.	347 000	1995	no	А
Falconbridge- Kidd Creek	Copper electrorefinery	Kidd Creek (Timmins), Ont.	104 000	1995	yes	В
Inco-Copper Cliff	Copper electrorefinery	Copper Cliff (Sudbury), Ont.	88 000	1993	yes	В
Inco-Copper Cliff	Copper electrowinning plant	Copper Cliff (Sudbury), Ont.	15 000	(C)	yes	C

 TABLE 1
 Copper production facilities whose releases were assessed

A - Environment Canada, 1997b.

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B – Hatch Associates, 1997.

C - Approximate recent figures, Skeaff, 1997.

Of the four copper refineries identified, three are electrorefineries (Noranda-CCR, Falconbridge-Kidd Creek and Inco-Copper Cliff) and one is an electrowinning plant (Inco-Copper Cliff). Throughout the balance of this report, the Inco-Copper Cliff copper refineries will be referred to as a single operation.

Of the four zinc plants identified, one uses a RLE process (Noranda-CEZinc), one uses a PLE process (HBM&S), and two use both processes (Cominco-Trail and Falconbridge-Kidd Creek). All process only concentrates from zinc ores and hence are "primary" plants. No secondary zinc production plants were identified in Canada.

#### 2.1.3 Release constituents examined

Constituents of releases to water considered in these assessments include all metal contaminants reported to be present, as well as selenium (Se), fluoride, ammonia and pH (hydrogen ion activity).

The components of releases to air that were examined most closely are SO<sub>2</sub>, particulate



Facility	Туре	Location	Zinc production (tonnes/year)	Year	Effluent subject to MMER	Source of production data
Cominco	RLE/PLE	Trail, B.C.	264 000	1995	no	A
Noranda-CEZinc	RLE	Valleyfield, Que.	223 000	1995	no	А
Falconbridge-Kidd Creek	RLE/PLE	Kidd Creek (Timmins), Ont.	131 000	1996	yes	А
HBM&S	PLE	Flin Flon, Man.	93 000	1995	yes	В

 TABLE 2
 Zinc production facilities whose releases were assessed

A - Environment Canada, 1997b.

B-Hatch Associates, 1997.

matter (PM) and seven metals (copper-Cu, zinc-Zn, nickel-Ni, lead-Pb, cadmium-Cd, chromium-Cr and arsenic-As<sup>4</sup>). These include the vast majority (on a mass basis) of substances released to air from Canadian copper smelters and refineries and zinc plants (e.g., NPRI, 1995, 1996; RDIS, 1995). Past emissions of both SO<sub>2</sub> and several of these metals from Canadian copper smelters and refineries and zinc plants have been reported to cause environmental harm (e.g., Sanderson, 1998). Hexavalent Cr compounds, inorganic As compounds, inorganic Cd compounds, and oxidic, sulphidic and soluble inorganic Ni compounds were assessed under PSL1 and were found to be CEPA toxic. It should be pointed out, however, that these assessments were not specific to copper smelters and refineries and zinc plants - they considered all sources of entry of the compounds into the environment and therefore do not on their own satisfy the mandate of the current assessments. Other components of releases to air that were examined in the environmental assessment are carbon dioxide ( $CO_2$ ), nitrous oxide ( $N_2O$ ) and volatile organic compounds (VOCs).

Among the substances reported in releases to the atmosphere from Canadian copper smelters and refineries and zinc plants that were not examined in these assessments are mercury (Hg) and, in the case of at least one copper smelter, dioxins and furans (Environment Canada, 1997b). While it is recognized that releases of such substances have the potential to harm the environment and human health, their fate in the environment (including accumulation pathways in organisms) is complex and uncertain. The decision not to consider such substances in these assessments was in part a practical one, taking into consideration the anticipated uncertainties associated with estimating their fate (including long-range transport, bioaccumulation and biomagnification) in the environment.<sup>5</sup> As noted in Section 3.1.1.1.3, this decision contributes to the uncertainty of the overall risk characterization. Polychlorinated dibenzodioxins and polychlorinated dibenzofurans were on the first PSL and were found to be CEPA toxic. Mercury is also on the list of CEPA toxic substances (Schedule I). As pointed out above, however, these conclusions were not based specifically on copper smelters

<sup>&</sup>lt;sup>4</sup> It should be noted that As is a metalloid rather than a metal. For simplicity, it will be referred to throughout this report as a metal. As will be noted in Section 2.4.1.1.3, however, there were circumstances under which As was necessarily handled differently than metals.

<sup>&</sup>lt;sup>5</sup> Some of the difficulties associated with assessing Hg using the critical load approach used in these assessments are discussed in de Vries and Bakker (1998).

and refineries and zinc plants as the sources of entry to the environment.

### 2.2 Entry characterization

Voluntary questionnaires were sent to industry in 1998 to verify and update existing information on the chemical constituents of releases, the amounts (expressed as rates) of substances released, the conditions of release (e.g., stack heights and temperatures), the physical and chemical forms of substances released, and concentrations in waste streams (e.g., effluents) and in environmental media near Canadian copper smelters and refineries and zinc plants. Other information collected included the configuration of effluent waste streams and source apportionment of emissions for facilities having multiple operations.

The most recent empirical data available for a complete calendar year were generally used for estimating exposure to metals and ambient  $SO_2$ . Data for 1995 were used for atmospheric metal dispersion modelling and for  $SO_2$ source–receptor modelling. All empirical data used in these assessments are for 1995 or a more recent year.

#### 2.2.1 Releases to air

#### 2.2.1.1 Sulphur dioxide

Information on emissions of gaseous  $SO_2$  from copper and zinc facilities is summarized below. Data described are for 1995, since these were the most recent available at the time of information collection. Further detail is provided in SENES Consultants (1999a).

Approximately 99% of the SO<sub>2</sub> emissions from copper and zinc facilities in 1995 were derived from copper smelters, as compared to 1% from copper refineries and zinc plants (see Table 3). Approximately 85% of the SO<sub>2</sub> emissions from these facilities were generated by three copper smelters: Inco's nickel/copper smelter complex in Sudbury, Ontario; Noranda's Horne copper

1995 <sup>1</sup>					
Facility	SO <sub>2</sub> releases in 1995 (tonnes/year)				
Copper smelters					
Noranda-Horne	169 532				
Noranda-Gaspé	43 200				
HBM&S-Flin Flon	162 107				
Falconbridge-Sudbury	45 000				
Inco-Copper Cliff	236 000				
Falconbridge-Kidd Creek	5 230				
Copper refineries					
Noranda-CCR	No data				
Falconbridge-Kidd Creek	1 300				
Inco-Copper Cliff	<10				
Zinc plants					
Noranda-CEZinc	3 300				
HBM&S-Flin Flon	0				
Falconbridge-Kidd Creek	960				
Cominco-Trail	1 752				

**TABLE 3**Releases of SO2 to the atmosphere in1995 1

<sup>1</sup> Data presented are based on unpublished emissions data from the Residual Discharge Information System (RDIS, 1995), the 1995 annual report for the Eastern Canada Acid Rain Program (Environment Canada, 1995) and additional information provided by facility operators.

smelter in Rouyn-Noranda, Quebec; and the HBM&S copper smelter in Flin Flon, Manitoba. By 1995, total SO<sub>2</sub> emissions from the copper smelters listed in Table 3 had been reduced by over 61% from 1980 emission levels, and by a total of 63% from copper smelters and refineries and zinc plants as an industry group. Emissions from zinc plants had been reduced by 94%, mainly due to the elimination of SO<sub>2</sub> emissions from the HBM&S zinc plant after 1993. Trend analyses for SO<sub>2</sub> emissions from copper refineries over this period were unavailable because emissions from the Noranda-CCR refinery were incomplete, while emissions from the Inco refinery at Sudbury and the Falconbridge refinery at Kidd Creek were included in the total

 $SO_2$  emission inventories from their associated smelters over this period. Although some data on refinery emissions were obtained for the Inco and Falconbridge-Kidd Creek refineries (personal communication with facility operators), the inconsistent consideration of anode casting as either a smelter process or a refinery process complicates their interpretation.

In 1995, emissions from copper and zinc facilities accounted for approximately 37% of  $SO_2$  emissions from sources in eastern Canada. However, total  $SO_2$  emissions in eastern North America are dominated by emissions from the United States, with  $SO_2$  emissions in the eastern United States accounting for about 86% of total emissions in eastern North America (Environment Canada, 1997c). Consequently, as a source group, copper and zinc facility emissions represent a much smaller component of total  $SO_2$  emissions in eastern North America. For example, in 1995,  $SO_2$  emissions from Canadian copper smelters and refineries and zinc plants represented only about 5% of the total  $SO_2$  emissions in this region.

#### 2.2.1.2 Metals

The following discussion focuses on metal emissions in 1995, as the dispersion modelling used data from that year. The year 1995 was selected for use as it was the most recent year for which detailed data were available at the time the modelling was begun. No data were identified on the chemical or physical forms of the emitted metals. Most emissions of the metals considered below may, however, be assumed to be in particulate form.

The total annual releases of Cu, Zn, Ni, Pb, Cd and As from the copper and zinc facilities in 1995 are summarized in Table 4. Data in this table are based largely on 1995 data from the NPRI (1995), supplemented with information obtained directly from the facility operators. A more detailed discussion of these releases is provided in SENES Consultants (2000).

The total amount of trace metals released by a facility depends to some extent on the

concentration of that element in the raw material fed into the process, as well as on the type of process used, the facility production rate and the efficiency of control equipment at the point of release. If the smelter derives a large proportion of its raw materials from a variety of mining operations, the variability in the concentration of trace elements can result in large fluctuations in trace element release rates, depending on which concentrate is being processed at any given time. Further, for any given trace element, the quantity released in the process exhaust stream will also depend on the temperature of the smelting or the refining process in use. The more volatile elements, such as As, Cd, Pb and Zn, are more likely to be liberated during the process if the temperature is high than are less volatile elements, such as Cu and Ni. Finally, the quantity of each element released is also dependent on the efficiency of the emission control equipment in use at each facility (i.e., multi-cyclones, electrostatic precipitators or baghouses). For all of these reasons, it is not surprising that the data in Table 4 display a high degree of variability in the emission rates among the facilities. The differences range over two to three orders of magnitude for most of the trace metals within each of the three facility categories (i.e., copper smelters, copper refineries and zinc plants).

Among copper smelters, the Inco-Copper Cliff facility ranked highest in 1995 for emissions of trace Cu, Ni and As releases. The Noranda-Horne smelter was a close second for both Cu and As. Noranda-Horne also had the highest emission rates for both Zn and Pb. The highest emission rate for Cd was reported by the HBM&S copper smelter at Flin Flon, followed closely by both Noranda-Horne and Falconbridge-Sudbury.

As with the copper smelters, the trace metal emission rates from copper refineries also vary significantly among the various facilities. As was the case with  $SO_2$  (Section 2.2.1.1), a lack of consistency for inclusion of anode casting as a smelter or a refinery operation complicates interpretation of these data.

Facility			Met	tal (tonnes/ye	ear)		
	Cu	Zn	Ni	Pb	Cd	As	Cr
Copper smelters							
Noranda-Horne	123	100	1.4	355	4.7	39	1.6
Noranda-Gaspé	1.4	2.8	0.78	17	0.22	16	ND
HBM&S-Flin Flon	62	58	ND	31	6.0	4.5	ND
Falconbridge-Sudbury	9.0	1.9	10.2	13.8	4.5	1.0	0.47
Inco-Copper Cliff <sup>2</sup>	132	9.5	87	39	2.4	48	ND
Falconbridge-Kidd Creek	29	4.8	0.2	9.4	0.44	0.78	ND
Copper refineries							
Noranda-CCR	2.6	ND	0.027	1.27	ND	0.086	0.00
Falconbridge-Kidd Creek	neg.	neg.	neg.	neg.	neg.	neg.	ND
Inco-Copper Cliff	28	ND	0	0	ND	1.1	ND
Zinc plants							
Noranda-CEZinc	0.7	106	ND	0.9	0.9	0.2	ND
HBM&S-Flin Flon	0	0	ND	0.12	0.004	0	ND
Falconbridge-Kidd Creek	0.16	8.3	0.013	0.06	0.03	4.8	ND
Cominco-Trail 3	ND	18	ND	0.25	0.015	ND	ND

#### TABLE 4 Releases of metals to the atmosphere in 1995<sup>1</sup>

ND - Not determined; neg. - negligible

<sup>1</sup> Emission values for Cu, Zn, Ni, Pb, Cd and As were used for dispersion modelling. Chromium was considered only in the assessment of risk to human health. Trace metal emission data were based largely on NPRI data (NPRI, 1995) with additional information provided by facility operators. Values have been rounded for presentation.

<sup>2</sup> Values shown are based on the average of results from two samplings of the main Inco stack, one from 1994 and the other from 1996. It should be noted that these values differ significantly from those reported to the NPRI in 1995 for the smelter complex (Inco reports releases from the copper refinery separately). NPRI (1995) values for the smelter complex were: Cu-107.04; Zn-15.65; Ni-417.76; Pb-68.23; Cd-ND; As-7.32 tonnes.

<sup>3</sup> Cominco-Trail is a combined facility, including both a zinc plant and a lead plant. NPRI data are reported for the overall facility and do not distinguish between the plants. Therefore, the values shown in the table were based on 1995 source attribution data provided by facility operators in response to a questionnaire from Environment Canada. It is believed that the provided list of emission sources reportedly associated with the zinc plant was incomplete, resulting in underestimation of emissions from this operation. For comparison, more accurate metal emission estimates for the Cominco zinc plant in 1998 (personal communication with facility operators) were: Zn-125; Pb-0.36; Cd-0.124; As-0 tonnes. The facility operators point out that the 1998 estimates are based on releases for the point sources associated with each operation (zinc and lead). This is an oversimplification because of the numerous recycle streams between zinc and lead operations. Therefore, there is considerable uncertainty associated with these values.

Emission rates for trace metals from zinc plants also vary by two to three orders of magnitude. Among zinc plants, the Noranda-CEZinc facility had the highest emission rates for Cu, Zn, Pb and Cd. In fact, the Zn emission rate from this facility exceeded that from all other copper and zinc facilities, including the emissions from the Noranda-Horne copper smelter. However, as discussed in the footnote to Table 4, it is believed that the emissions attributed to the Cominco zinc plant in 1995 may have been significantly underestimated. For comparison, Zn emission values attributed to the Cominco zinc plant for 1998 were estimated at 125 tonnes (personal communication with facility operators), greater than those from any of the other copper or zinc facility operations for 1995. The Falconbridge-Kidd Creek plant had the highest emission rate for As among the zinc plants and was the only zinc plant to report Ni emissions, although the rate is very low. Releases of all metals from the HBM&S zinc plant were reported to be very low, since, in contrast to the others, this plant does not use a high-temperature roasting process.

#### 2.2.1.3 Particulate matter

Table 5 summarizes 1995 emissions of total particulate (TP) matter for the copper and zinc facilities as contained in the Residual Discharge Information System (RDIS, 1995). The table also includes emission data for the size fraction less than or equal to  $10 \ \mu m \ (PM_{10})$  and the fraction less than or equal to  $2.5 \ \mu m \ (PM_{2.5})$ .

These data indicate that the Inco copper smelter at Copper Cliff had the highest TP emission rate at 7052 tonnes per year in 1995. Note that this total includes TP emissions from the copper refinery and nickel refinery as well as from the smelter. The Noranda-Horne copper smelter ranks second at 1339 tonnes per year, followed by the Falconbridge copper smelter at Sudbury, with 1181 tonnes per year. The lowest reported TP emission rate for the copper smelters is 430 tonnes per year at the Noranda-Gaspé facility.

TP data for two of the three copper refineries are included in the TP emissions from the copper smelters (Inco at Copper Cliff and Falconbridge-Kidd Creek). Only the Noranda-CCR facility is listed as a separate copper refinery source, at 7.1 tonnes per year.

Among the zinc plants, the highest TP emission rates listed in the RDIS (1995) are for the Noranda-CEZinc and Cominco-Trail facilities, both of which emit about 150 tonnes per year. TP emissions from the FalconbridgeKidd Creek zinc plant are not listed separately and are included with emissions from the copper smelter and refinery located at this site.

TP emissions from RDIS (1995) may be subdivided into three categories (Table 5):

- fugitive sources consisting of dust from roads, wind erosion of exposed surfaces, and releases from material handling and storage on-site;
- low-elevation sources consisting of releases from short stacks (defined as less than 30 m high); and
- high-elevation sources consisting of all releases from stacks greater than 30 m high.

There are some anomalous features associated with these TP emissions. For example, three copper smelters list identical estimates of fugitive emissions of 500 tonnes per year. These appear to be notional numbers, and are unlikely to have been based on detailed emission calculations. In addition, fugitive emissions are not reported for any of the Noranda facilities, or for Cominco-Trail. Because of these anomalies. and the fact that trace metal to TP mass ratios at several sites appear to be unusually high, TP emission data in Table 5 must be interpreted with particular caution. It should be noted that there are some inconsistencies between facilities in the reporting of both TP and metals emissions. Among the sources irregularly reported are fugitive emissions from the production, storage and handling of concentrates, exhaust from baghouses and wind-blown dust from uncovered tailings. The emissions sources reported by four zinc and copper processing facilities have been evaluated and are detailed in SENES Consultants (1999b).

Although data on the size of the particles released were very limited, it is expected that fugitive releases are relatively coarse (>2  $\mu$ m). Results of preliminary work on particle size distributions of PM obtained from the stack of the Inco smelter indicate that the particles are extremely fine, with 80% less than 3  $\mu$ m (Burnett, 1998).

Facility		Total part	iculate (TP)		PM <sub>10</sub>		
	(tonnes/year)		Percent		(tonnes/year)	(tonnes/year)	
		Fugitive	Low stack	High stack <sup>4</sup>			
Copper smelters							
Noranda-Horne	1339	_	2	98	1091	866	
Noranda-Gaspé	430	-	-	100	301	117	
HBM&S-Flin Flon	717	48	-	52	427	180	
Falconbridge-Sudbury	1181	42	6	52	857	665	
Inco-Copper Cliff 5	7052	7	2	91	6654	5531	
Falconbridge-Kidd Creek	504	99	1	_	187	97	
Copper refineries							
Noranda-CCR	7.1	_	100	_	5.2	4.0	
Falconbridge-Kidd Creek		included with copper smelter emissions					
Inco-Copper Cliff		included with copper smelter emissions					
Zinc plants							
Noranda-CEZinc	153	_	100	-	119	107	
HBM&S-Flin Flon	78	100	-	-	67	23	
Falconbridge-Kidd Creek		in	cluded with copp	er smelter emissi	ons	· <del>-</del> - <b></b> -	
Cominco-Trail	156	-	100	-	134	115	

TABLE 5	Releases of total particulate (TP) matter, particulate matter less than or equal to $10 \mu m (PM_{10})$
	and particulate matter less than or equal to 2.5 $\mu$ m (PM <sub>2.5</sub> ) to the atmosphere in 1995 <sup>1.2</sup>

<sup>1</sup> Data obtained from RDIS (1995). Values have been rounded for presentation. As the reliability of some of these data has not been established, there is considerable uncertainty associated with some values.

<sup>2</sup> Some emission values include sources that are associated with and reported by the facilities, but which are not the subject of these assessments. Owing to questions on the reliability of the data, more rigorous evaluation of source attribution was not warranted and was in some cases precluded.

<sup>3</sup> It should also be noted that PM (mostly in the form of  $PM_{2.5}$ ) can form from condensation of smelter gases after release to the atmosphere. Therefore, attribution of ambient  $PM_{2.5}$  based on emissions could underestimate the proportion due to smelting processes.

<sup>4</sup> "High stacks" are defined in this assessment as being more than 30 m in height.

<sup>5</sup> TP values for Inco-Copper Cliff include emissions from the smelter complex, the copper refinery and the nickel refinery.

The values for TP emissions discussed above do not take into account the secondary formation of PM. Secondary processes involve the formation of PM (usually  $PM_{2.5}$ ) in the atmosphere as a result of physical and chemical transformation of gases. Sulphur dioxide, nitrogen oxides and VOCs are among the major contributors to the formation of  $PM_{2.5}$  (EC/HC, 2000a).

2.2.1.4 Carbon dioxide, nitrous oxide, methane and volatile organic compounds

Emissions of gaseous CO<sub>2</sub>, N<sub>2</sub>O, methane (CH<sub>4</sub>)<sup>6</sup> and VOCs from copper and zinc processing facilities are summarized in Table 6. These compounds are of significance due to their influence on abiotic atmospheric effects such as climate change and the formation of ground-level ozone.

As mentioned in the previous section, both VOCs and nitrogen oxides are significant precursors in the secondary formation of PM<sub>2.5</sub>. Total emissions of the oxides of nitrogen from the facilities being considered in these assessments were about 1800 tonnes in 1995 (RDIS, 1995).

#### 2.2.2 Releases to water

Information on releases to water from CCR. CEZinc and CTO is summarized below. Further details are provided in Beak International (1999).

Annual average loading rates from the three facilities into their receiving environments are shown in Table 7. Factors applied to annual averages to estimate maximum short-term (monthly and four-day mean) loading rates are summarized in Table 8. These factors are based on empirical loading information. Concentrations of release components in undiluted effluents are shown in Table 9.

#### 2.2.2.1 Canadian Copper Refinery

The waste metal loadings from CCR (Table 7) are released to the Montreal Urban Community (MUC) wastewater treatment plant (WWTP), which discharges in turn to the mid-channel St. Lawrence River east of l'Île aux Vaches. On a volume basis, approximately 7% of the wastewater leaving CCR is treated process water, and the remainder is untreated cooling water drawn from the St. Lawrence River. On a mass basis, Cu and Se are the two most significant loadings. In 1995, these metal loadings comprised 0.82 and 3.58 tonnes, respectively. Loadings of most metals increased significantly in 1996.

The MUC-WWTP removes much of the CCR loading prior to entry into the St. Lawrence River. Typical removal rates at the MUC-WWTP and the total annual loadings of pertinent metals to the St. Lawrence River in MUC-WWTP treated effluent were taken from Deschamps et al. (1998). There is considerable uncertainty in both removal rates and loadings for certain metals, such as As and Se, that are measured at the MUC-WWTP at concentrations close to the analytical detection limit.

The subsequent assessment of biological exposures to metal in the St. Lawrence River and associated effects on aquatic biota must be based upon the loadings from the MUC-WWTP (not CCR), since these are the loadings actually received by the St. Lawrence River. However, it is important for the purposes of this assessment to identify the proportional contribution that CCR makes to the release of metals in MUC-WWTP effluent. This proportion is calculated for each metal as follows:

$$P_{CCR} = L_{CCR} / [(C_{MUC} / [1 - R_{MUC}]) * Q_{MUC}]$$

where:

- $P_{CCR}$  = proportional contribution of CCR (fraction),
- $L_{CCR}$  = metal loading from CCR to MUC-WWTP (mg/s),
- $R_{MUC}$  = metal removal rate at MUC-WWTP (fraction),

<sup>&</sup>lt;sup>6</sup> While technically a VOC, CH<sub>4</sub> has been listed separately from other VOCs in Table 6. Unlike other VOCs, due to its negligible photochemical reactivity, CH4 is not of significance in the formation of ground-level ozone or as a precursor in the secondary formation of PM. Methane is included here, however, as it is of significance to climate change.

Facility		Releases in 19	95 (tonnes/year)	
	CO <sub>2</sub>	$\frac{N_2O}{(as CO_2 eq.)^2}$	CH <sub>4</sub> (as CO <sub>2</sub> eq.) <sup>2</sup>	VOCs
Copper smelters				
Noranda-Horne	105 210	490	36	2.08
Noranda-Gaspé	120 090	1 630	95	1.37
HBM&S-Flin Flon	NR	NR	NR	NR
Falconbridge-Sudbury	NR	NR	NR	1.81
Inco-Copper Cliff	NR	NR	NR	3.03
Falconbridge-Kidd Creek	NR	NR	NR	4.62
Copper refineries				
Noranda CCR	80 917	264	43	2.05
Falconbridge-Kidd Creek	NR	NR	NR	included in copper smelter value
Inco-Copper Cliff	NR	NR	NR	included in copper smelter value
Zinc plants				
Noranda-CEZinc	42 288	437	21	1.16
HBM&S-Flin Flon	NR	NR	NR	NR
Falconbridge-Kidd Creek	NR	NR	NR	included in copper smelter value
Cominco-Trail	NR	NR	NR	NR

TABLE 6	Releases of carbon dioxide ( $CO_2$ ), nitrous oxide ( $N_2O$ ), methane ( $CH_4$ ) and other volatile
	organic compounds (VOCs) to the atmosphere in 1995 <sup>1</sup>

NR - Releases not reported

<sup>1</sup> Data obtained from the Residual Discharge Information System (RDIS, 1995).

- <sup>2</sup> To facilitate their interpretation in terms of potential influence on climate change, values for N<sub>2</sub>O and CH<sub>4</sub> have been converted to equivalents of CO<sub>2</sub> using global warming potential multipliers of 310 and 21, respectively (Jaques *et al.*, 1997).
- C<sub>MUC</sub> = metal concentration in MUC-WWTP effluent (mg/L), and
- $Q_{MUC}$  = volume of MUC-WWTP effluent (L/s).

The proportional contribution that CCR makes to the metal loading from the MUC-WWTP to the St. Lawrence River (Table 7) ranges from approximately 0.1% for metals such as Cd and Cr to approximately 1% for Cu and Ni, 10% for As and approaching 100% for Se.

Most of the metals released at the MUC-WWTP outfall are presumed to be in dissolved or adsorbed form. The total metal release was assumed to be available to partition with suspended solids in receiving water, and to contribute accordingly to exposures of aquatic biota.

Temporal variability in the MUC-WWTP loadings is uncertain. Neither monthly mean nor daily loading data were available.

	Release	Year	Noranda-	Montreal	Montreal WWTP to	Noranda-CEZinc to		Cominco	Cominco-Trail to Columbia River	bia River	
WWTP1         Total         % CCR         combined         Total         Total           1995         0.820         23.9         1.39         0.241         32.4         2           1996         1.45         25.9         -         0.780         15.5         -           1996         1.45         25.9         -         -         0.666         0.26           1998         -         -         -         -         -         0.666         0.26           1998         -         -         -         -         -         -         -         -           1998         -         -         -         -         -         -         -         -         -           1998         -	component		CCK to Montreal	St. Lawrei	nce Kiver <sup>2</sup>	St. Lawrence River (Beauharnois Canal) <sup>3</sup>	All outfalls	C-II	outfall <sup>5</sup>	C-II	C-III outfall <sup>5</sup>
1995         0.820         23.9         1.39         0.241         32.4 $-$ 1996         1.45         25.9         -         -         0.780         15.5         -           1998         -         -         -         -         -         0.780         15.5         -           1998         -         -         -         -         -         0.66         0.26         -           1995         -         -         -         -         3.24         1837         -         -           1995         0.094         7.20         1.04         - <th></th> <th></th> <th>I dLMM</th> <th>Total</th> <th>% CCR</th> <th></th> <th>combined <sup>4</sup></th> <th>Total</th> <th>% zinc operations</th> <th>Total</th> <th>% zinc operations</th>			I dLMM	Total	% CCR		combined <sup>4</sup>	Total	% zinc operations	Total	% zinc operations
1996 $1.45$ $25.9$ $ 0.780$ $15.5$ $-$ 1998 $     0.66$ $0.26$ 1995 $     0.66$ $0.26$ 1996 $      -$ 1996 $0.044$ $7.20$ $1.044$ $   -$ 1996 $0.400$ $8.60$ $    -$ 1998 $      -$ 1998 $0.041$ $3.20$ $0.31$ $0.138$ $56.3$ $-$ 1998 $      -$ 1998 $      -$ 1998 $      -$ 1998 $      -$ 1998 $      -$ 1998 $      -$ 1998 $      -$ 1998 $      -$ 1998 $      -$ 1998 $      -$ 1998 $     -$	Си	1995	0.820	23.9	1.39	0.241	324		1		
1980.660.26 $1995$ 3.24 $1837$ - $1996$ 4.11 $137$ - $1996$ 0.0947.20 $104$ $1996$ 0.400 $8.60$ $1996$ 0.400 $8.60$ $1996$ 0.400 $8.60$ $1996$ 0.041 $3.20$ $0.31$ $0.138$ $56.3$ $1996$ 0.050 $3.50$ $1996$ 0.010 $0.50$ $1998$ $1996$ 0.010 $0.50$ $1998$ 0.03 $1.20$ $9.75$ $1998$ 0.150 $1.00$ 0.510.24 $1998$ 0.010 $0.50$ $1998$ 0.014 $5.40$ $0.15$ $1998$ 0.014 $5.40$ $0.12$ $1998$ 0.014 $5.40$ $0.12$ $1998$ 0.014 $5.40$ $0.12$ $1998$ <td></td> <td>1996</td> <td>1.45</td> <td>25.9</td> <td>I</td> <td>0.780</td> <td>15.5</td> <td>I</td> <td>I</td> <td>ı</td> <td>I</td>		1996	1.45	25.9	I	0.780	15.5	I	I	ı	I
19953.241837-19964.11137-199853.136.419960.0947.201.0453.136.419980.4008.6019980.4008.6019980.0413.200.310.13856.3-19960.0503.50199819980.0100.5019980.0100.5019980.0100.5019980.0100.5019980.0100.5019980.0100.5019980.0100.5019980.0131.0019980.0145.400.1219980.0145.4019980.0145.4019980.0108.1019980.0108.10		1998	I	I	I	I	0.66	0.26	71	0.40	82
1996 $   +$ $+$ $11$ $137$ $-$ 1998 $     53.1$ $36.4$ 1995 $0094$ $7.20$ $104$ $   -$ 1996 $0400$ $8.60$ $    -$ 1998 $      -$ 1996 $0040$ $3.50$ $    -$ 1998 $      -$ 1998 $      -$ 1998 $      -$ 1998 $      -$ 1996 $0010$ $0.50$ $    -$ 1996 $0.010$ $0.50$ $    -$ 1998 $      -$ 1996 $0.150$ $1.00$ $    -$ 1996 $0.010$ $     -$ 1996 $0.010$ $     -$ 1996 $0.010$ $     -$ 1996 $0.010$ $     -$ 1996 $0.010$ $ -$	Zn	1995	1	I	1	3.24	1837	1	1	1	1
198         -         -         -         -         53.1         36.4           1995         0.094         7.20         1.04         -		1996	I	I	ı	4.11	137	I	I	ł	I
1955 $0.094$ 7.20 $1.04$ $  -$ <		1998	I	I	I	F	53.1	36.4	16	14.1	66
1996 $0.400$ $8.60$ $   -$ </td <td>Ni</td> <td>1995</td> <td>0.094</td> <td>7.20</td> <td>1.04</td> <td>1</td> <td>1</td> <td>t t</td> <td>I</td> <td></td> <td>1</td>	Ni	1995	0.094	7.20	1.04	1	1	t t	I		1
1998         -		1996	0.400	8.60	ļ	I	I	I	I	I	I
195         0.041         3.20         0.31         0.138         56.3         -           1996         0.050         3.50         -         0.0         36.7         -           1998         -         -         -         0.0         36.7         -         -           1998         -         -         -         -         -         7.00         2.57         -           1995         0.006         0.40         0.07         0.013         2.36         -         -           1996         0.010         0.50         -         -         0.010         1.91         -           1998         -         -         -         -         -         0.236         -           1998         0.150         1.20         9.75         -         0.24         -         -           1996         0.150         1.00         -         -         0.01         0.93         -         -           1998         -         -         -         -         0         0.93         -         -           1996         0.014         5.40         0.12         -         0.93         -         -     <		1998	ł	I	ł	I	I	ł	I	I	ļ
1996       0.050       3.50       -       0.0       36.7       -         1998       -       -       -       -       -       7.00       2.57         1995       0.006       0.40       0.07       0.013       2.36       -         1996       0.010       0.50       -       0.010       1.91       -         1996       0.010       0.50       -       0.010       1.91       -         1998       -       -       -       0.010       1.91       -         1996       0.150       1.20       9.75       -       0.51       0.24         1996       0.150       1.00       -       -       0.51       0.24         1998       -       -       -       -       0.92       0.18         1996       0.014       5.40       0.12       -       -       0.92       0.18         1996       0.010       8.10       -       -       -       -       -       -	Pb	1995	0.041	3.20	0.31	0.138	56.3	i I	1	. 1	1
1998         -         -         -         -         7.00         2.57           1995         0.006         0.40         0.07         0.013         2.36         -           1996         0.010         0.50         -         0.010         1.91         -           1998         -         -         -         -         0.50         1.91         -           1998         -         -         -         -         0.010         1.91         -           1998         -         -         -         -         0.010         1.91         -           1995         0.093         1.20         9.75         -         0.51         0.24           1996         0.150         1.00         -         -         3.08         -           1998         -         -         -         -         -         0.92         0.18           1996         0.014         5.40         0.12         -         -         -         -         -           1996         0.014         8.10         -         -         -         -         -         -         -         -         -         -         - </td <td></td> <td>1996</td> <td>0.050</td> <td>3.50</td> <td>1</td> <td>0.0</td> <td>36.7</td> <td>Ĩ</td> <td>I</td> <td>I</td> <td>I</td>		1996	0.050	3.50	1	0.0	36.7	Ĩ	I	I	I
1995         0.006         0.40         0.013         2.36         -           1996         0.010         0.50         -         0.010         1.91         -           1998         -         -         -         0.010         1.91         -           1998         -         -         -         -         0.010         1.91         -           1998         -         -         -         -         0.051         0.24         -           1996         0.150         1.20         9.75         -         -         0.51         0.24           1996         0.150         1.00         -         -         -         0.92         0.18           1998         -         -         -         -         -         0.92         0.18           1996         0.014         5.40         0.12         -         -         -         -           1996         0.010         8.10         -         -         -         -         -		1998	1	I	I	1	7.00	2.57	37	4.43	98
1996       0.010       0.50       -       0.010       1.91       -         1998       -       -       -       -       0.51       0.24         1995       0.093       1.20       9.75       -       0.51       0.24         1996       0.150       1.00       -       -       11.6       -         1998       0.150       1.00       -       -       0.308       -         1998       -       -       -       0.92       0.18       -         1998       -       -       -       -       0.92       0.18       -         1996       0.014       5.40       0.12       -       -       0.92       0.18         1996       0.010       8.10       -       -       -       -       -       -       -         1996       0.010       8.10       - <t< td=""><td>Cd</td><td>1995</td><td>0.006</td><td>0.40</td><td>0.07</td><td>0.013</td><td>2.36</td><td>I</td><td></td><td>1</td><td>1</td></t<>	Cd	1995	0.006	0.40	0.07	0.013	2.36	I		1	1
1998     -     -     -     0.51     0.24       1995     0.093     1.20     9.75     -     11.6     -       1996     0.150     1.00     -     -     3.08     -       1998     -     -     -     -     0.92     0.18       1996     0.014     5.40     0.12     -     0.92     0.18       1996     0.010     8.10     -     -     -     -		1996	0.010	0.50	I	0.010	16.1	I	I	I	ł
1995     0.093     1.20     9.75     -     11.6     -       1996     0.150     1.00     -     -     3.08     -       1998     -     -     -     -     0.92     0.18       1995     0.014     5.40     0.12     -     -     0.92     0.18       1996     0.010     8.10     -     -     -     -     -		1998	Ι	I	I	I	0.51	0.24	25	0.27	95
1996     0.150     1.00     -     -     3.08     -       1998     -     -     -     -     0.92     0.18       1995     0.014     5.40     0.12     -     -     -       1996     0.010     8.10     -     -     -     -     -	As	1995	0.093	1.20	9.75		11.6	I		1	1
1998         -         -         -         0.92         0.18           1995         0.014         5.40         0.12         -         -         -         -         -         -           1996         0.010         8.10         -		1996	0.150	1.00	I	I	3.08	I	I	I	I
1995     0.014     5.40     0.12     -     -       1996     0.010     8.10     -     -     -       1000		1998	I	I	I	I	0.92	0.18	46	0.74	84
0.010 8.10	C	1995	0.014	5.40	0.12	1	I		1	J	
		1996	0.010	8.10	ł	1	I	I	I	I	I
ł		1998	I	1	ı	I	I	I	I	I	Ι

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**TABLE 7**Annual loading rates of effluent components (tonnes/year)(continued)

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component Hg 190 Se 190 Ag 190 Ag 190	1 1995 1996 1998 1996 1998 1998	CCR to Montreal WWTP 1 	St. Lawrence River <sup>2</sup> Total % CCR  2.30 100 1.70 -	ce River <sup>2</sup> % CCR 	St. Lawrence River (Beauharnois Canal) <sup>3</sup> 0.002 - 2.50	All outfalls combined <sup>4</sup>	C-II Total	C-II outfall <sup>5</sup> al % zinc	C-III Total	C-III outfall <sup>5</sup> al % zinc
		WWTP1	<b>Total</b> 2.30 1.70	% CCR	0.002 0.0 0.0 2.50	combined <sup>4</sup>	Total	% zinc	Total	% zinc
	95 96 96 95 95	3.58		· · · 0 ·	0.002 0.0 2.50		-	operations		operations
	96 98 96 95 95	а. 3.58 9.82	- - 2.30 1.70	100	0.0 - 2.50	0.06	I	1	I	1
	98 95 98 95	- 3.58 9.82	_ 2.30 1.70	100	2.50	0.05	I	I	I	I
	95 96 95	3.58 9.82	2.30 1.70	100	2.50	0.05	0.01	46	0.04	84
	96 98 95	9.82	1.70	ł		I	I	ł	I	I
	98 95				1.98	I	I	I	I	I
	95	i	I	I	I	1	1	1	1	I
161		0.023	2.00	0.26	I	i	I	I	I	I
	1996	0.030	1.10	I	I	I	I	I	I	I
19	1998	-	1	1	I	I	ſ	I	1	I
TI 19	1995	I	I	I	Ι	1	I	I	I	1
19	1996	l	I	I	1	I	ļ	ſ	I	I
19	1998	I	I	I	I	3.42	0.0	1	3.42	17
Ammonia 19	1995	1	1	1	24.0	500	I	I	1	I
19	1996	I	I	I	21.8	446	I	I	I	ł
19	1998	I	ł	I i	1	122	0.0	ł	35.8	74
Fluoride 19	1995	I	I	I	I	ļ	1	I	I	I
19	1996	I	I	I	1	i	I	ì	I	I
19	1998	1	1	I	I	I	0.0	1	88.7	85

<sup>1</sup> NPRI (1995, 1996) and Noranda-CCR data.
<sup>2</sup> Deschamps *et al.* (1998) and (1) above.

<sup>3</sup> NPRI (1995, 1996) and Noranda-CEZinc data. <sup>4</sup> NPRI (1995, 1996) and Cominco-Trail data.

<sup>5</sup> Cominco-Trail, loading and sewer flow data.

Parameter	Averaging period	Ratio o to	of maximum short-term annual mean loading ra	mean tes
		Noranda-	Comine	co-Trail <sup>2</sup>
		CEZinc <sup>1</sup>	C-II outfall	C-III outfall
Cu	1 month	3.9	2.03	1.79
	4 days	-	6.40	3.42
Zn	1 month	1.7	2.13	2.00
	4 days	4.76	3.92	5.54
Pb	1 month	_	2.57	1.39
	4 days	-	5.99	3.15
Cđ	1 month	2.4	1.87	1.43
	4 days	_	6.82	3.98
As	1 month	_	1.38	1.73
	4 days	_	2.85	5.41
Hg	1 month	6.2	2.95	2.08
	4 days	-	5.94	5.37
Se	1 month	2.8	_	
	4 days	_	_	-
Tl	1 month	_	<u> </u>	3.09
	4 days	-	_	19.30 <sup>3</sup>
Ammonia	1 month	_	_	1.28
	4 days	-	-	2.26
Fluoride	1 month	_	_	1.13
	4 days	_	_	1.67

Factors applied to annual effluent loadings to estimate maximum short-term loading rates **TABLE 8** (maximum monthly and four-day mean loadings)

<sup>1</sup> Noranda-CEZinc data (1995).

<sup>2</sup> Cominco-Trail data (1998).

<sup>3</sup> Driven by a Tl upset event in April 1998.

#### 2.2.2.2 Canadian Electrolytic Zinc

The waste metal and ammonia loadings from CEZinc (Table 7) are released to the Beauharnois Canal in the St. Lawrence River. On a volume basis, approximately 4% of the wastewater leaving CEZinc is treated process water, and the remainder is untreated cooling water drawn from

the Beauharnois Canal. On a mass basis, for the combined effluent, ammonia, Zn and Se are the three most significant loadings. In 1995, these loadings comprised 24.0, 3.24 and 2.5 tonnes, respectively. Process changes in 1999 have resulted in significant reductions in Se loadings from 1995 levels.



Release component	Noranda-CCR	Noranda-CEZinc	Cominco-T	rail – 1998 <sup>4</sup>
	1995 <sup>2</sup>	1995 combined <sup>3</sup>	C-II outfall	C-III outfall
Cu				
Annual mean	31	3.8	8.6	11.0
Maximum 1-month mean	_	14.9	19.0	20.0
Maximum 4-day mean	-	_	43	31.1
Mean % dissolved/adsorbed 1	-	-	65	62
Zn				
Annual mean	_	51.4	1194	390.3
Maximum 1-month mean	-	91.6	2600	767
Maximum 4-day mean	-	258	3615	1781
Mean % dissolved/adsorbed 1	-	91	38	59
Ni				
Annual mean	9	-	_	-
Mean % dissolved/adsorbed 1	-	-	_	_
Pb				
Annual mean	4	2.2	84.6	122.7
Maximum 1-month mean	_	_	225	166.9
Maximum 4-day mean	_	_	392	319 *
Mean % dissolved/adsorbed 1	-	-	23	34
Cd				
Annual mean	0.5	0.21	7.9	7.4
Maximum 1-month mean	_	0.54	15.1	10.4
Maximum 4-day mean	-	-	41.7	24.2
Mean % dissolved/adsorbed 1	-	-	80	81
As				
Annual mean	1		6.0	20.4
Maximum 1-month mean	-	-	8.8	36.0
Maximum 4-day mean	_	-	13.2	91.0
Mean % dissolved/adsorbed 1	-	·	89	79
Cr				
Annual mean	7	_		-
Mean % dissolved/adsorbed 1	_	-	-	

### TABLE 9Concentrations ( $\mu$ g/L) of metals and other constituents in undiluted effluents

n.

Release component	Noranda-CCR	Noranda-CEZinc	Cominco-T	'rail – 1998 <sup>4</sup>
	<b>1995</b> <sup>2</sup>	1995 combined <sup>3</sup>	C-II outfall	C-III outfall
Hg				
Annual mean	-	0.03	0.4	1.0
Maximum 1-month mean	-	0.24	1.2	2.1
Maximum 4-day mean	-	-	1.7	4.6
Mean % dissolved/adsorbed	-	-	-	_
Se				
Annual mean	3	39.7	_	_
Maximum 1-month mean	_	106	-	_
Mean % dissolved/adsorbed 1	_	-	_	_
Ag				
Annual mean	2.7	_		_
Mean % dissolved/adsorbed 1	_	_	-	_
TI				
Annual mean	-		0.0	94.8
Maximum 1-month mean	_	-	_	306
Maximum 4-day mean	-	-	-	1505
Mean % dissolved/adsorbed	_	-	-	94
Ammonia	···			
Annual mean	_	381	0.0	1175
Maximum 1-month mean	-	-	_	1232
Maximum 4-day mean	_	-	-	1843
Mean % dissolved/adsorbed	_	_	-	100
Fluoride				
Annual mean			0.0	2457
Maximum 1-month mean	-	-	-	2703
Maximum 4-day mean	-	_	_	3376
Mean % dissolved/adsorbed	_	-	_	100

#### Concentrations ( $\mu$ g/L) of metals and other constituents in undiluted effluents (continued) **TABLE 9**

<sup>1</sup> Percentage of total concentration that is dissolved, plus the adsorbed portion of that which is particulate, according to  $K_d$  and suspended solids in effluent.

<sup>2</sup> Annual means are based on weekly composite samples (Deschamps et al., 1998). Maximum monthly and 4-day average concentrations have been estimated from maximum monthly or 4-day mean loading and flow for the corresponding period.

<sup>3</sup> Concentrations calculated as annual loading (NPRI) ÷ annual discharge, based on weekly composite samples analysed in two effluent streams. Maximum monthly and 4-day average concentrations have been estimated from maximum monthly or 4-day mean loading and flow for the corresponding period.

<sup>4</sup> Concentrations calculated as mean daily loading (Cominco data) ÷ mean daily discharge.



\*

The treated process water (UNA) effluent and the cooling water (Principal) effluent have historically been discharged at separate points, about 1 km apart, on the Beauharnois Canal. However, they are now being (or will soon be) released together at the Principal effluent location. For the purpose of the assessment of biological exposures to effluent constituents in the Canal and associated effects on aquatic biota, the two effluents are considered here together as a combined effluent at a single point of release. As compared to a separate UNA discharge, this makes for a larger point source loading, lower end-of-pipe concentrations and less rapid nearfield dilution.

Virtually all of the ammonia released at CEZinc will be dissolved, and most of the metal released will be in dissolved or adsorbed form (labile). However, some 5–10% of the zinc may be in a fine particulate metal oxide or hydroxide form. This conclusion is based on CEZinc observations that approximately 60% of Zn in the UNA effluent is not dissolved. With an average 13 mg/L of suspended solids, we might expect 15% of Zn to be adsorbed based on distribution coefficients (Beak International, 1999), but the remaining 45% of Zn in UNA effluent must have a more integral association with PM. Metal oxide particles, formed in the roasting process, are unlikely to dissolve later if released. Metal hydroxide particles, formed in the water treatment process; may dissolve later, although slowly. Here it is assumed that  $20\% \times 45\% = 9\%$ of the total Zn loading is in such relatively inert forms. Only the portion of loading estimated to be in dissolved or adsorbed form (91%, Table 9) was considered to be available to partition with suspended solids in receiving water, and hence to contribute to exposures of aquatic biota.

Temporal variability in metal loading from CEZinc (Table 8) is based on 1995 monthly composite data for most metals and on daily data, which were available only for Zn. Maximum monthly average loadings range from 1.7 times the annual average to 6.2 times the annual average, depending on the metal. Factors for 4-day average loadings would be higher.

#### 2.2.2.3 Cominco Trail Operations

CTO includes zinc and lead refinery operations, as well as a fertilizer plant. There are three main combined effluent outfalls that contribute chemical loadings to the Columbia River, as well as some residual drainage from a historical landfill area via Stoney Creek. Most of the landfill drainage toward Stoney Creek is now collected and treated.

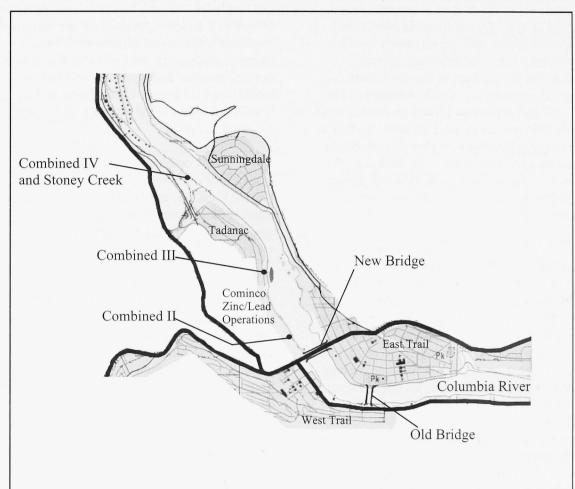
The Combined IV outfall (C-IV) and Stoney Creek are furthest upstream (Figure 1). The C-IV outfall, associated with the fertilizer plant, is the dominant source of ammonia, but a minor source of metal loadings. Stoney Creek is a significant source of metal loadings.

The Combined III outfall (C-III), approximately 1.3 km downstream from C-IV, is primarily associated with zinc operations. It is a source of ammonia and a significant source of metals and fluoride (Table 7). The C-II outfall, a further 0.8 km downstream, includes contributions from zinc sulphide leaching, as well as lead and other operations. It, too, is a significant source of metals.

A blast pond discharge (C-I) once existed further downstream, and was a very minor source of metal loadings, primarily associated with lead operations. This discharge no longer exists.

Recent (1998) loadings from CTO and specifically from the C-II and C-III outfalls are summarized in Table 7, along with 1995 and 1996 loadings for all CTO as reported in NPRI (1995, 1996). The average 1998 loadings from C-II and C-III were utilized in this assessment to represent the zinc smelting/refining operations at CTO.

The proportion of loading attributed to zinc operations (Table 7) was estimated for each metal in each outfall, based on an evaluation of toxic unit contributions from different sewers to each outfall (Duncan and Antcliffe, 1996). For C-II, only sewer #6 is associated with zinc operations (it drains the zinc sulphide leaching



**FIGURE 1** Map of Trail, B.C., showing the outfalls and sampling locations considered in the assessment of aquatic releases from the Cominco facility

plant and cadmium plant). For C-III, all contributing sewers are associated with zinc operations, except for the contributions from the effluent treatment plant, which were apportioned to lead and zinc operations based on inflow from these areas (60% from zinc operations). Table 7 shows that most of the C-III loadings (77–99% for metals) are related to zinc operations, while for C-II the proportion ranges from 25–91%, depending on the metal.

Virtually all of the ammonia and fluoride released from CTO will be in dissolved form. However, a significant portion of the metal loading, particularly for Zn and Pb, is evidently not in dissolved form, based on analysis of filtered and unfiltered effluent samples. With an average of 2–3 mg/L suspended solids in these samples, we might expect up to 5% of some metals to be adsorbed based on distribution coefficients (Beak International, 1999), but this cannot account for all of the undissolved fraction. Thus, the undissolved fraction may be substantially composed of metal oxides, hydroxides or other relatively inert forms. Only the portion of loading estimated to be in dissolved or adsorbed form (as shown in Table 9) was considered to be available to partition with suspended solids in receiving water, and hence to contribute to exposures of aquatic biota.

Temporal variability in chemical loadings from CTO (Table 8) is based on 1998 daily data for all chemicals. Maximum monthly loadings range from 1.2 times the annual average to 3 times the annual average, depending on the metal and outfall. Four-day average loadings may be as high as 2.2–6.8 times the annual average, depending on the metal and outfall.

### 2.3 Exposure characterization

#### 2.3.1 Releases to air

For releases to air, exposure is quantified both as concentrations in ambient air and as rates of deposition from air. Results for both empirical monitoring and model calculations are presented when available.

2.3.1.1 Sulphur dioxide

#### 2.3.1.1.1 Fate of sulphur dioxide in air

The fate of  $SO_2$  released to air, discussed briefly here, is considered in more detail in SENES Consultants (1999a).

The conversion of SO<sub>2</sub> to sulphate (SO<sub>4</sub><sup>2-</sup>) and its subsequent deposition are governed by a complex series of interactions that include transport and diffusion (i.e., dispersion), gasphase and aqueous-phase chemistry, meteorology, cloud physics, and dry and wet scavenging processes. Field studies of oxidation rates in clouds suggest that aqueous-phase oxidation mechanisms are considerably faster at converting SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> than gas-phase reactions. Aqueousphase oxidation of SO<sub>2</sub> in the atmosphere can occur in cloudwater, fogwater and rainwater, in deliquescent aerosol droplets at high relative humidity and in the liquid surface film condensed on aerosol particles (Radojevic, 1992).

Sulphate formed from oxidation of  $SO_2$  often takes the form of fine PM (PM<sub>2.5</sub>). For example, for samples collected at 14 urban sites in the National Air Pollution Surveillance (NAPS) network operating from 1986 to 1994, an average of 17% and up to 95% of PM<sub>2.5</sub> collected at each site was composed of  $SO_4^{2-}$  (Brook *et al.*, 1997, as summarized in EC/HC, 2000a).

According to Hidy (1994),  $SO_2$ concentration patterns tend to be consistent with the observed distribution of  $SO_4^{2-}$  concentrations (as a secondary pollutant) in air and rainwater, except that  $SO_4^{2-}$  is more widely and uniformly distributed than  $SO_2$  due to the time required for the transformation of  $SO_2$  to airborne  $SO_4^{2-}$ (about 1 day) and the efficient scavenging of  $SO_4^{2-}$  by precipitation.

Regional airborne SO<sub>4</sub><sup>2-</sup> concentrations exhibit episodic behaviour which is linked to stagnant high-pressure systems (Hidy, 1994). In general, high  $SO_4^2$  concentrations in eastern North America are associated with high temperatures, high absolute humidity, moderately low atmospheric pressures and wind speeds, and high ozone concentrations indicative of high oxidation potential. Thus, the year-to-year spatial variability of high SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> episodes is closely related to the path and frequency of migratory high-pressure systems. Regional high  $SO_4^{2-}$  episodes can occur in all seasons and are positively correlated with temperature, except in winter, when low temperatures associated with near-surface inversions and poor ventilation can also result in high  $SO_4^{2-}$  pollution episodes. In eastern North America, regional SO42- episodes typically last up to 5 days, but extended events may last up to 11 days. Monitoring studies in eastern Canada suggest that as much as 60-70% of the total annual wet SO4<sup>2-</sup> deposition may be deposited in a single deposition episode (Environment Canada, 1997c).

In contrast, the critical factors for dry deposition are the concentration of  $SO_2$  in the air very near the surface and the ability of the surface to "capture" pollutants that come into contact with it (Hicks, 1992). Dry deposition rates are characterized by a strong diurnal cycle and are intrinsically linked to ambient air concentrations. Very little deposition occurs at night, while high rates of daytime deposition are dominated by the frequency and intensity of high air pollution episodes. Recent research on dry deposition suggests that, on average, dry deposition accounts for about 25% of total (dry plus wet) sulphur deposition, although considerable



uncertainty remains in the estimates of dry deposition values (Environment Canada, 1997c). Furthermore, the relative magnitude of dry deposition contributions to total sulphur deposition varies seasonally, and the relative importance of wet versus dry deposition varies with location. Dry deposition is relatively more important than wet deposition in areas close to major source regions, while wet deposition dominates at greater distances, indicating the importance of long-range transport processes. Of the total sulphur emitted in eastern North America, it is estimated that about one-third of the annual average amount of anthropogenic sulphur emissions is wet-deposited in eastern North America, while two-thirds is either dry-deposited or transported out of this region.

#### 2.3.1.1.2 Concentrations of sulphur dioxide in air

This section includes a brief description of the analytical and statistical methods used to estimate SO<sub>2</sub> concentrations in air at monitoring stations located close to copper smelters and refineries and zinc plants. The approach used for source attribution is also described. Resulting data on SO<sub>2</sub> concentrations in air at these sites are summarized in Tables 10, 11 and 12.

Monitoring methods: Monitoring of ambient SO<sub>2</sub> levels is conducted using instrumental methods such as fluorescence detectors. These instruments work on a continuous basis or with a high sampling frequency, such as one reading per minute. The detector signals are averaged over some period of time (typically 5–15 minutes), and these values are recorded. The recorded levels are averaged over longer time periods (usually 1 hour and 24 hours) to determine whether permit levels and provincial regulations are being met.

Data sources and analysis: Data were generally obtained from the facility operators as 1-hour averages. These were then used in the

calculation of 24-hour and monthly average ambient SO<sub>2</sub> concentrations. Ambient concentrations averaged over the growing season were generally calculated from monthly averages. The growing season was defined to include the months April through October. One-hour and growing season averages were used in the assessment of risk to the environment. Twentyfour-hour averages were used in the assessment of risk to human health.

Environmental assessment: Handling of values below the detection limit ("non-detects") is a significant issue when dealing with ambient SO<sub>2</sub> data, for two reasons. First, up to 98% of the data may be non-detects. These values therefore exert a significant influence on temporal averages. Second, most monitoring is performed to ensure that relatively high, short-term thresholds are not exceeded. Therefore, monitoring is conducted or data are recorded to levels that are less sensitive than may be of significance when considering chronic exposure.

The normal method of correcting for non-detects is to set all values for non-detects to one-half the detection limit. This makes the assumption that non-detect values are equally distributed between zero and the detection limit. Detection limits for data used in this assessment ranged from 0.5 to 50 µg/m<sup>3</sup>. Setting non-detects to one-half the detection limit would have raised some estimates of seasonal average concentration by close to 25  $\mu$ g/m<sup>3</sup>. This would have caused the chronic effects threshold values for environmental organisms to be exceeded owing to non-detected concentrations. To preclude this, only non-detects having associated detection limits of less than 3 µg/m<sup>3</sup> were corrected to onehalf the detection limit. One exception to this was a facility having several monitors with detection limits of 13  $\mu$ g/m<sup>3</sup>. Non-detect values from these monitors were corrected to one-half the detection limit, as the percentage of non-detects was low, resulting in their having only a minor influence on seasonal averages.



Facility	Year	Emission-based source attribution (%)	Monitoring station I.D.	Distance (km) & direction relative to facility	Total number of measure- ments <sup>2</sup>	% detects	Concen- tration (µg/m <sup>3</sup> ) <sup>3,4</sup>
Copper smelters		· · · · · · · · · · · · · · · · · · ·	<u> </u>	<u> </u>	<u> </u>	L	
Noranda-Gaspé	1997	Copper smelter – 100%	Mines Gaspé	1.5 E	4902	12	27
			MEF site	1.7 SE	4790	12	<u>24</u>
Noranda-Horne	1997	Copper smelter – 100%	Rouyn Centre	1.5 S	4947	7	16
			Hotel de Ville	1.8 S	4929	24	<u>42</u>
			Parc Mouska	1.8 SW	4929	2.2	6
-			Noranda Nord	2.3 NW	4831	5	10
			Parc Tremblay	2.4 SE	4914	14	<u>26</u>
			Rouyn Sud-est	2.5 SE	4975	15	<u>29</u>
			Pneus Abitibi	3.2 SE	4963	25	<u>23</u>
HBM&S-Flin Flon	1998	Copper smelter – 100%	Staff house	0.7 SE	4848	60	37
		Zinc plant – 0%	Creighton	1.9 SW	4815	31	20
			Hapnot Collegiate	2.1 E	4193	18	13
			Aqua Centre	2.6 NE	4916	26	10
Copper refineries	-						
Noranda-CCR		Copper refinery – 100%		No SO <sub>2</sub> d	ata available		
Zinc plants							
Noranda-CEZinc	1998	Zinc plant - 100%	Boul. Cadieux	1.3 E	4925	41	27
	_		Louis IV Major	1.7 NW	5000	25	3
Combined sources							
Sudbury region (including Inco- Copper Cliff &	OME data 1997	Inco: - Copper smelter 84%	OME 77218 Copper Cliff	0.7 W Inco 23.4 SW Falc.	5070	57	14
Falconbridge- Sudbury)	Falc. data	- Copper refinery - 0% - Nickel refinery - 0%	Falconbridge (1995) (Falc. operated)	21.8 NE Inco 0.7 W Falc.	n/a	n/a	10– <u>23</u>
	1995	Falconbridge: - Copper smelter – 16%	OME 77225 A. Robinson School	3.0 SE Inco 20.3 SW Falc.	2085	56	14
			OME 77228 Dozzi Park	3.5 E Inco 20.2 SW Falc.	5020	42	9
			Sunderland (1995) (Falc. operated)	19.1 NE Inco 4.0 W Falc.	n/a	n/a	2–15
			OME 77203 Science North	4.2 E Inco 19.0 SW Falc.	4986	43	8
			OME 77065 Garson	17.5 NE Inco 4.9 SW Falc.	5127	62	10
			OME 77016 Ash Street	5.0 NE Inco 18.6 SW Falc.	5126	61	15
			OME 77201 Mikkola	7.8 SW Inco 29.8 SW Falc.	5090	62	9
			OME 77096 Long Lake	8.5 SE Inco 25.0 SW Falc.	5112	68	11

 TABLE 10
 Growing season average SO<sub>2</sub> concentrations at monitoring stations located near copper and zinc production facilities <sup>1</sup>

Facility	Year	Emission-based source attribution (%)	Monitoring station I.D.	Distance (km) & direction relative to facility	Total number of measure- ments <sup>2</sup>	% detects	Concen- tration (µg/m <sup>3</sup> ) <sup>3,4</sup>
			OME 77012 Skead	29.3 NE Inco 9.0 N Falc.	5102	71	16
			Wahnapitae (1995) (Falc. operated)	24.6 E Inco 9.7 SE Falc.	n/a	n/a	2–15
			OME 77075 New Sudbury	10.0 NE Inco 12.2 SW Falc.	5074	65	12
			OME 77028 Coniston	15.4 E Inco 10.8 S Falc.	5123	55	9
			OME 77206 Rayside	13.8 NW Inco 22.7 W Falc.	5130	51	4
			OME 77013 Hanmer	22.2 N Inco 14.9 NW Falc.	5117	46	7
Falconbridge-Kidd 1997 Creek	11	AMS #5	0.6 SE	4864	14	18	
Cleek		Copper refinery – 0% Zinc plant – 15%	AMS #6	0.6 S	4894	1.4	013
		Concentrator - 20%	AMS #1	1.4 NE	4918	14	<u>23</u>
			AMS #7	1.6 E	4909	1.7	0–13
Cominco-Trail	1998	Zinc plant - 85%	Downtown	0.8 SE	4885	78	25
		Lead plant – 15%	Trail Hospital	1.2 E	4889	96	<u>31</u>
			Butler Park	1.3 E	4726	99	<u>28</u>
			West Trail	1.4 SE	4889	99	<u>36</u>
			Warfield	2.4 W	4885	94	<u>24</u>
			Glenmerry	3.9 E	4890	84	<u>27</u>
			Oasis	4.3 NW	4888	98	15
			Columbia Gardens	10.5 SE	4860	99	<u>22</u>
			Genelle	12.7 NE	4887	97	9
			North Port, Wash.	19.0 S	4692	7	4
			Robson	27.1 N	4922	63	6

## TABLE 10 Growing season average SO<sub>2</sub> concentrations at monitoring stations located near copper and zinc production facilities <sup>1</sup> (continued)

<sup>1</sup> With the exception of the three monitoring stations indicated as being operated by Falconbridge-Sudbury, all data for the Sudbury region were provided by the OME (courtesy of D. Racette, Northern Region). All other data were provided by the individual companies. It should be noted, however, that some monitoring stations are not operated by the companies. These include the MEF-operated site at Gaspé and the Robson site near Cominco-Trail, which is operated by a local pulp mill.

<sup>2</sup> Total number of measurements refers to the number of 1-hour average values used to calculate the growing season average.

<sup>3</sup> Growing season average concentrations that exceed the Estimated No-Effects Value (ENEV) (10  $\mu$ g/m<sup>3</sup>) are shown in bold. Those that exceed the Critical Toxicity Value (CTV) (21  $\mu$ g/m<sup>3</sup>) are in bold and underlined. These effects thresholds are discussed in Section 2.4.1.1.

<sup>4</sup> For data obtained from HBM&S, Cominco and the OME (Sudbury region), values below the detection limit were corrected to one-half the detection limit. Data for Noranda-Gaspé, Noranda-Horne and Falconbridge-Kidd Creek were corrected for detection limit errors using the statistical method described in the text. Data for two of the monitoring stations at Kidd Creek could not be evaluated in this way due to a shortage of detected readings. Also, insufficient data were available for Falconbridge-Sudbury to allow any detection limit correction. Therefore, ranges within which these averages are expected to fall are shown. Data for Noranda-CEZinc were not corrected, as the detection limit was quite low (0.5 µg/m<sup>3</sup>).

Facility	Year	Emission-based source attribution	Monitoring station I.D.	Distance (km) & direction	Total num-	1	ber of val ntration r	
		(%)		relative to facility	ber of 1 hour values	<450 μg/m³	450- 900 μg/m <sup>3</sup>	>900 µg/m <sup>3</sup>
Copper smelters								
Noranda-Gaspé	1997	Copper smelter – 100%	Mines Gaspé	1.5 E	4902	4841	58	3
			MEF site	1.7 SE	4790	4753	29	<u>8</u>
Noranda-Horne	1997	Copper smelter - 100%	Rouyn Centre	1.5 S	4947	4919	25	3
			Hotel de Ville	1.8 S	4929	4883	42	<u>4</u>
			Parc Mouska	1.8 SW	4929	4922	6	1
			Noranda Nord	2.3 NW	4831	4825	6	0
			Parc Tremblay	2.4 SE	4914	4880	31	<u>3</u>
			Rouyn sud-est	2.5 SE	4975	4918	54	<u>3</u>
			Pneus Abitibi	3.2 SE	4963	4957	6	0
HBM&S-Flin Flon	1998	Copper smelter - 100%	Staff house	0.7 SE	4848	4747	66	<u>35</u>
		Zinc plant – 0%	Creighton	1.9 SW	4815	4753	51	<u>11</u>
			Hapnot Collegiate	2.1 E	4883	4862	17	<u>4</u>
			Aqua Centre	2.6 NE	4916	4894	17	<u>5</u>
Copper refineries								
Noranda-CCR		Copper refinery – 100%		No SO <sub>2</sub> o	lata availab	le		
Zinc plants								
Noranda-CEZinc	1998	Zinc plant – 100%	Boul. Cadieux	1.3 E	4925	4857	60	8
			Louis IV Major	1.7 NW	5000	5000	0	0
<b>Combined</b> sources								
Sudbury region (including Inco-	OME data	Inco: - Copper smelter - 84%	OME 77218 Copper Cliff	0.7 W Inco 23.4 SW Falc.	5070	5053	15	2
Copper Cliff & Falconbridge- Sudbury) <sup>3</sup>	1997 Falc.	- Copper refinery – 0% - Nickel refinery – 0%	Falconbridge (Falc. operated)	3.8 NE Inco 0.7 W Falc.	N/A		25 < 650 μ > 650 μg/i	
	data 1995	Falconbridge: - Copper smelter – 16%	OME 77225 A. Robinson School	3.0 SE Inco 20.3 SW Falc.	2085 (part year)	2072	11	2
			OME 77228 Dozzi Park	3.5 E Inco 20.2 SW Falc.	5020	5009	10	1
			Sunderland (Falc. operated)	3.1 NE Inco 4.0 W Falc.	N/A		36 < 650 µ > 650 µg/п	
			OME 77203 Science North	4.2 E Inco 19.0 SW Falc.	4986	4977	9	0
			OME 77065 Garson	17.5 NE Inco 4.9 SW Falc.	5127	5122	4	<u>1</u>
			OME 77016 Ash Street	5.0 NE Inco 18.6 SW Falc.	5126	5108	15	<u>3</u>
			OME 77201 Mikkola	7.8 SW Inco 29.8 SW Falc.	5090	5083	5	<u>2</u>

# TABLE 11 One-hour average SO<sub>2</sub> concentrations during the growing season at monitoring stations located near copper and zinc production facilities <sup>1</sup>

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### TABLE 11 One-hour average SO<sub>2</sub> concentrations during the growing season at monitoring stations located near copper and zinc production facilities <sup>1</sup> (continued)

Facility	Year	Emission-based source attribution	Monitoring station I.D.	Distance (km) & direction	Total num-		per of value	
		(%)		relative to facility	ber of 1 hour values	< <b>450</b> μg/m³	450– 900 μg/m <sup>3</sup>	>900 µg/m³
			OME 77096 Long Lake	8.5 SE Inco 25.0 SW Falc.	5112	5108	4	0
			OME 77012 Skead	29.3 NE Inco 9.0 N Falc.	5102	5091	11	0
			Wahnapitae (Falc. operated)	3.6 E Inco 9.7 SE Falc.	N/A		36 < 650 µ > 650 µg/r	
			OME 77075 New Sudbury	10.0 NE Inco 12.2 SW Falc.	5074	5061	13	0
			OME 77028 Coniston	15.4 E Inco 10.8 S Falc.	5123	5115	7	1
			OME 77206 Rayside	13.8 NW Inco 22.7 W Falc.	5130	5130	0	0
			OME 77013 Hanmer	22.2 N Іпсо 14.9 NW Falc.	5117	5114	3	0
Falconbridge-	1997	Copper smelter - 65%	AMS #5	0.6 SE	4864	4845	18	1
Kidd Creek		Copper refinery – 0% Zinc plant – 15%	AMS #6	0.6 S	4894	4894	0	0
		Concentrator – 20%	AMS #1	1.4 NE	4918	4888	30	0
			AMS #7	1.6 E	4909	4909	0	0
Cominco-Trail	1998	Zinc plant – 85%	Downtown	0.8 SE	4885	4872	13	0
		Lead plant - 15%	Trail Hospital	1.2 E	4889	4882	6	<u>1</u>
			Butler Park	1.3 E	4726	4697	28	<u>1</u>
			West Trail	1.4 SE	4889	4873	13	3
			Warfield	2.4 W	4885	4867	16	<u>2</u>
			Glenmerry	3.9 E	4890	4884	4	<u>2</u>
			Oasis	4.3 NW	4888	4884	2	<u>2</u>
			Columbia Gardens	10.5 SE	4860	4856	4	0
			Genelle	12.7 NE	4887	4887	0	0
			North Port, Wash.	19.0 S	4692	4692	0	0
			Robson	27.1 N	4922	4922	0	0

<sup>1</sup> With the exception of three monitoring stations operated by Falconbridge-Sudbury, all data for the Sudbury region were provided by the OME (courtesy of D. Racette, Northern Region). All other data were provided by the individual companies. It should be noted, however, that in some cases monitoring stations are operated by organizations other than the company. These include the MEF-operated site at Gaspé and the Robson site near Cominco-Trail, which is operated by a local pulp mill.

<sup>2</sup> The number of 1-hour averages that exceed the ENEV (450  $\mu$ g/m<sup>3</sup>) are shown in bold. Those that exceed the CTV (900  $\mu$ g/m<sup>3</sup>) are in bold and underlined. These effects thresholds are discussed in Section 2.4.1.1.1

<sup>3</sup> For Falconbridge-Sudbury, only summary data that indicated the number of exceedences of 650 µg/m<sup>3</sup> were available.

Facility	Year	Site	Distance (km) & direction, site type <sup>1</sup>	Num- ber of 24-	Arithmetic mean (µg/m <sup>3</sup> )	Maximum (µg/m <sup>3</sup> )	concen	iour tration ges <sup>3</sup>
				hour periods			0–125 μg/m <sup>3</sup>	>125 µg/m <sup>3</sup>
Copper smelters							_	
Noranda-Gaspé	1997	Gaspé	1.5 E, Rs	355	33.4 <sup>2</sup>	252	333	22
		MEF	1.7 SE, Rs	356	35.2	231	336	20
Noranda-Horne	1997	Pneus Abitibi	3.2 SE, Rs	365	22.6 <sup>2</sup>	128.3	364	1
		Rouyn Sud-est	2.5 SE, Rs	365	32.9 <sup>2</sup>	239	349	16
		Parc Mouska	1.8 SW, Rs	365	15.7 <sup>2</sup>	174	364	1
		Noranda Nord	2.3 NW, Rs	365	18.3 <sup>2</sup>	193	363	2
		Rouyn Centre	1.5 S, Rs	365	23.6 <sup>2</sup>	251	362	3
		Parc Tremblay	2.4 SE, Rs	365	29.5 <sup>2</sup>	256	358	7
		- Hotel de Ville	1.8 S, Rs	365	37.4	223	348	17
HBM&S <sup>4</sup>	1998	Staff house	0.7 SE, In/Co	365	31.7	548	335	30
		Creighton Fire Hall	1.9 SW, Co/Rs	365	16.3	305	353	12
		Hapnot Collegiate	2.1 E, Co/Rs	365	14.6	294	356	9
		Aqua Centre	2.6 NE, Rs	365	7.3	242	362	3
Zinc plants								
Noranda-CEZinc	1998	Boul. Cadieux	1.3 E, Ru	351	27.5	220	340	11
		Louis IV Major	1.7 NW, Rs	354	5.4	57	354	0
Combined sources								
Sudbury region 5,6	1997	Skead, Sudbury	F 9N, I 29.3 NE, Ru	365	15.6	208	364	1
		Hanmer, Sudbury	F 14.9 NW, I 22.2 N, Rs	365	8.2	109	365	0
•		Ash St., Sudbury	F 18.6 SW, I 5 NE, Rs	365	16.3	123	365	0
		Coniston	F 10.8 S, I 15.4 E, Rs	365	11.9	178	364	1
		Garson	F 4.9 SW, I 17.5 NE, Rs	358	11.0	101	358	0
		Sparks St., New Sudbury	F 12.2 SW, I 10.0 NE, Rs	365	12.8	130	364	1
		Long Lake, Sudbury	F 25 SW, I 8.5 SE, Ru	365	12.7	135	363	2
		Mikkola, Sudbury	F 29.8 SW, I 7.8 SW, Rs	365	10.0	179	364	1
		Science North	F 19.0 SW, I 4.2 E, Rs	363	9.8	161	362	1
		Rayside	F 22.7 W, I 13.8 NW, Ru/In	365	5.7	86	365	0
		Market St., Copper Cliff	F 23.4 SW, I 0.7 W, In/Rs	364	16.6	206	356	8

# TABLE 12Annual summary of 24-hour ambient air concentrations of SO2 near copper smelters and<br/>refineries and zinc plants in Canada

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Facility	Year	Site	Distance (km) & direction, site type 1	Num- ber of 24-	Arithmetic mean (µg/m³)	Maximum (µg/m <sup>3</sup> )	concen	iour tration ges <sup>3</sup>
				hour periods			0–125 μg/m <sup>3</sup>	>125 µg/m <sup>3</sup>
		Arthur Robinson School	F 20.3 SW, I 3 SW, Rs	178	12.6	166	176	2
		Dozzi Park, Sudbury	F 20.2 SW, I 3.5 E, Rs	363	10.6	104	363	0
Falconbridge-	1997	AMS # 1	1.4 NE, In/Ru	365	27.4 <sup>2</sup>	228	351	14
Kidd Creek		AMS # 5	0.6 SE, In/Ru	365	29.0 <sup>2</sup>	225	352	13
		AMS # 6	0.6 S, In/Ru	365	13.5 <sup>2</sup>	35	365	0
		AMS # 7	1.6 E, In/Ru	365	13.4 <sup>2</sup>	24	365	0
Cominco-Trail	1998	Oasis	4.3 NW, Ru/Rs	365	21.7	139	361	4
		Warfield	2.4 W, Rs	365	19.0	183	364	1
		Downtown	0.8 SE, Co	365	20.1	96	365	0
		Columbia Gardens	10.5 SE, Ru/In	365	18.3	151	363	2
		Butler Park	1.3 E, Rs	365	25.1	126	364	1
		Trail Regional Hospital	1.2 E, Rs	365	27.5	130	364	1
		Northport	19 S, Ru	365	3.2	44	365	0
		Robson	27.1 N, In	365	6.5	39	365	0
		West Trail	1.4 SE, Rs	365	31.5	148	363	2
		Glenmerry	3.9 E, Rs	365	21.8	111	365	0
		Genelle	12.7 NE, Rs	365	12.9	97	365	0

**TABLE 12** Annual summary of 24-hour ambient air concentrations of  $SO_2$  near copper smelters and<br/>refineries and zinc plants in Canada (continued)

<sup>1</sup> Site types: Rs=residential, Ru=rural, Co=commercial, In=industrial.

<sup>3</sup> The concentration ranges correspond to the WHO Air Quality Guideline for Europe 24-hour average concentration of SO<sub>2</sub> of 125  $\mu$ g/m<sup>3</sup> (WHO, 2000).

<sup>4</sup> Although it includes both a copper smelter and a zinc plant, HBM&S has been included with copper smelters, since it was reported that there were no releases to air from the zinc plant.

<sup>5</sup> Data from the OME (courtesy of D. Racette, Northern Region).

<sup>6</sup> For the Sudbury region, site locations are reported with respect to both the Falconbridge (F) and Inco (I) facilities.

 $<sup>^2</sup>$  The arithmetic mean value was calculated by substituting one-half of the detection limit for those samples that did not contain detectable levels of SO<sub>2</sub>. This assumption affects the calculated value markedly when detection limits are relatively greater and ambient concentrations relatively low. The effect of this assumption was minimal for most sites and affected the mean value by less than 30% for all sites except those marked with a "2" superscript.

Correction for non-detects when estimating chronic (i.e., growing season) exposures using data from monitors having higher detection limits was conducted as follows. This includes all monitors at the Falconbridge-Kidd Creek, Noranda-Horne and Noranda-Gaspé facilities, which had detection limits of 25-50 µg/m<sup>3</sup>. Seasonal averages for these sites were estimated using a statistical method (El-Shaarawi, 1989; El-Shaarawi and Esterby, 1992). This involved fitting detectable values to a suitable statistical distribution; using this distribution to estimate concentrations for sample values that were below the detection limit; and, finally, calculating the average using all detected and estimated values. The Weibull distribution was found to best describe the data (El-Shaarawi, 1999). It has the form:

 $F(x) = 1 - Exp\{-[(x - x_0)/k]^m\}$ 

where  $x_0$  is the regional background <sup>7</sup> concentration, which is taken to be 2.6 µg/m<sup>3</sup> (Linzon, 1999), and "m" and "k" are fitting parameters for shape and scale, respectively. Further information on the methods used is provided in CED (2000).

Growing season average concentrations are shown in Table 10. The percentages of values that were above the detection limit ("% detects") are also indicated. Values shown in bold are above the chronic Estimated No-Effects Value (ENEV) (10  $\mu$ g/m<sup>3</sup>), and those bolded and underlined are above the Critical Toxicity Value (CTV) (21  $\mu$ g/m<sup>3</sup>) for sensitive vegetation. These effects thresholds are discussed in Section 2.4.1.1.1. One-hour average concentrations are shown in Table 11. In this table, the number of 1-hour averages measured over the period of the growing season that fall into defined concentration ranges is indicated. The concentration intervals shown correspond to the acute (1-hour) ENEV (450  $\mu$ g/m<sup>3</sup>) and CTV (900  $\mu$ g/m<sup>3</sup>) for sensitive vegetation (discussed in Section 2.4.1.1.1). A more detailed description of these data and their processing is contained in CED (2000).

Human health assessment: The health assessment was based on data for the entire year, rather than being restricted to the growing season. Summary statistics for the 24-hour averages over the most recent year for which data were provided are summarized in Table 12 for all of the facilities except for Noranda-CCR, for which data were not obtained. For each site, the table includes the arithmetic mean and maximum concentration of SO<sub>2</sub> for the most recent year for which data were provided, as well as the identity, location and type of site (e.g., residential) and the number of samples. The frequency of samples with concentrations in various ranges, corresponding to the 24-hour WHO Air Quality Guideline for Europe for SO<sub>2</sub> of 125  $\mu$ g/m<sup>3</sup> (WHO, 1987, 2000), is also presented for each site.

The arithmetic mean values in Table 12 were calculated by assuming a value of one-half of the detection limit for those samples that did not contain detectable levels of  $SO_2$ . This assumption can affect the mean markedly when detection limits are relatively great (as for Falconbridge-Kidd Creek, Noranda-Gaspé and Noranda-Horne) and ambient concentrations relatively low. Those instances when the mean value is affected by more than 30% by this assumption are indicated in the table.

Near those facilities with multiple monitoring sites, the arithmetic mean 24-hour concentration of  $SO_2$  is generally increased in relation to the proximity to the facility. In addition, the mean level of  $SO_2$  at virtually all of the sites is elevated compared to background

<sup>&</sup>lt;sup>7</sup> Three "types" of background levels (ambient concentrations or deposition rates) must be considered in relation to atmospheric emissions in these assessments. "Natural background" refers to levels resulting only from natural sources. "Regional background" refers to levels that are considered typical of conditions over a large region such as the Canadian Shield. This may include some influence from distant anthropogenic sources as discussed in Section 2.3.1.2.2. "Local background" refers to levels in the immediate vicinity of the facilities that are due to all sources other than those being assessed. These values may be influenced by processes that are not the subject of these assessments, but which are being conducted at or near the copper or zinc processing facilities.



levels at remote or rural locations, which are reported to be 5  $\mu$ g/m<sup>3</sup> or less (FPACAQ, 1987; Linzon, 1999; WHO, 2000). As noted in the table, these increased levels are also reflected in exceedences of the 24-hour WHO Air Quality Guideline for Europe for SO<sub>2</sub> of 125  $\mu$ g/m<sup>3</sup>.

Source attribution: Both Table 10 and Table 11 include a column labelled "Emissionbased source attribution." These attributions are based on the percentage contribution of separate operations to total emissions from a facility. In relating these source attributions to monitored concentrations, it is assumed that the amount that each source is contributing to measured ambient SO<sub>2</sub> concentrations is proportional to its emissions. For facilities comprising only a copper smelter or copper refinery or zinc plant, 100% of SO<sub>2</sub> emissions from the facility may be attributed to those sources. However, for combined facilities, such as those at Sudbury, Kidd Creek or Trail, several different operations may be contributing to total SO<sub>2</sub> emissions. For these combined sources, the percentage contribution of each operation of concern to total SO<sub>2</sub> emissions from the facility has been estimated based on the following:

- The Sudbury region includes the Inco facility • as well as the Falconbridge facility. As they share an airshed, results for ambient SO<sub>2</sub> monitoring in this region are influenced by the presence of the two. The Inco facility includes a nickel/copper smelter, a copper refinery and a nickel refinery, while the Falconbridge-Sudbury facility includes only a nickel/copper smelter. Source attribution was determined using a combination of emission data for 1995 contained in MacLatchy (1996) and from personal communication with Inco facility operators. Due to a lack of data on emissions from the Inco nickel refinery, it was assumed that SO<sub>2</sub> emissions were --- like those from the Inco copper refinery negligible. No major process changes at either of these facilities are believed to have occurred since 1995.
- The Falconbridge-Kidd Creek facility includes a copper smelter, copper refinery,

zinc plant and concentrator. Source attribution was determined from 1995 emission data provided by Falconbridge. No major process changes are believed to have occurred at this facility since 1995.

- The Cominco-Trail facility includes a lead smelter and a zinc plant. The fraction of emissions attributable to the zinc plant was determined based on 1998 emission data provided by Cominco (personal communication with facility operators). These data reflect the significant process changes that took place at the facility in 1996.
- The HBM&S facility in Flin Flon includes a zinc plant and a copper smelter. Due to the process used, the zinc plant does not emit SO<sub>2</sub>. Therefore, all of the SO<sub>2</sub> detected is attributed to the copper smelter, and the facility is listed in Tables 10 and 11 as a copper smelter.

It should be noted that these attributions ignore background (natural, regional, local – defined in footnote 7 on page 37) contributions to measured concentrations. This omission may be significant at some facilities that include major  $SO_2$  emission sources that are not the subject of these assessments (e.g., the lead plant at Cominco-Trail). Details of the source attribution calculations are provided in CED (2000).

### 2.3.1.1.3 Deposition of sulphate from air

The deposition of sulphate in acid-sensitive regions of eastern Canada and its connection to release of  $SO_2$  from Canadian copper and zinc facilities is discussed briefly here, and in more detail in SENES Consultants (1999a).

Due to the relatively high  $SO_2$  emission rates associated with the Inco copper smelter in Sudbury, a number of studies have been directed at evaluating mesoscale impacts of these emissions. Chan *et al.* (1984) analysed concentrations of sulphur and selected trace metals in ambient air and precipitation within a radius of 40 km from the Sudbury area during the period mid-1978 to mid-1980. The downwind

concentrations of sulphate in precipitation and  $SO_2$  in ambient air were noted to be significantly higher than upwind concentrations, by as much as an order of magnitude in the case of SO<sub>2</sub>. However, the Inco smelter SO<sub>2</sub> emissions were estimated to contribute less than 20% of the total wet sulphur deposition during precipitation events within the 40-km distance from Sudbury. Furthermore, the ratio of wet-to-dry deposition was estimated to be 0.39, indicating that the magnitude of dry deposition was similar to that of wet deposition during precipitation events. Keller and Carbone (1997) examined changes in sulphate concentrations in lake waters over a 20year period from the mid-1970s to the mid-1990s in relation to reductions in sulphur emission rates from smelters in the Sudbury area. The study noted that, although overall sulphate concentrations in Sudbury area lakes have been greatly reduced as a result of reductions in sulphur emissions from levels in the 1970s to the present, a strong relationship remains between current sulphate concentrations and distance from the smelters. Keller and Carbone (1997) concluded that the current estimate of the "Sudbury" contribution, ranging from 54% at 10 km to less than 30% at 100 km from Sudbury, probably includes a substantial residual component from historically deposited sulphur stored in the catchment areas. This residual effect may represent an important factor in the rate of recovery in lake ecosystems from future reductions of SO<sub>2</sub> emissions. Although significant positive responses in lake water sulphate levels are evident from past  $SO_2$ emission reduction programs, the influence of residual sulphur levels from historical deposition may complicate the rate of recovery with respect to future reduction programs.

Since emitted  $SO_2$  can be transported over long distances from its sources, the assessment of regional-scale acidic deposition is largely based on computer modelling. The available long-range transport models can be subdivided into essentially two types of models: 1) comprehensive, dynamic models that incorporate physical and chemical processes, which are best suited for use in short-term, episodic studies; and 2) semi-empirical models that are computationally more efficient and less costly to run and which are better suited to evaluating long-term deposition effects.

Comprehensive modelling attempts to incorporate all the available knowledge about component processes into the model. Due to the extensive data and computational and human resources needed to develop and run such models, comprehensive models are often run on an episodic basis. This is appropriate because regional sulphate concentrations exhibit episodic behaviour that is linked to stagnant high-pressure systems. However, episodic deposition simulations do not necessarily satisfy all of the requirements for assessments of effects of emissions, because the latter are typically concerned with average annual deposition rates. Various aggregation schemes must then be used to determine the total annual deposition rate for the cumulative effect of acid deposition events during the year.

An alternative approach to the use of comprehensive models is to apply semi-empirical techniques to characterize oxidation, transport and deposition processes. Semi-empirical methods essentially assume that only the net effect of the individual processes needs to be considered in modelling the overall process. These models consist of simplified equations that describe the interactions between simplified processes.

An example of a semi-empirical technique for acid deposition in North America is the use of source-receptor relationships. Source-receptor modelling is a simplified method of relating changes in ambient concentrations or deposition of pollutants to changes in emissions. Such models rely on "transfer matrices," which assume that the total concentration or deposition of a pollutant at a receptor location is the sum of partial contributions, each of which is proportional to the emissions from a source or group of sources in a region. Thus, the transfer matrix is a mathematical expression of the atmospheric link

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between the long-range atmospheric transport and chemical transformation model, the observed ambient concentration or deposition rate, and the emissions from a specified group of sources or source regions. Although the transfer matrices may be developed using comprehensive modelling techniques to establish the source–receptor relationships, subsequent application of the transfer matrices assumes that the relationships remain stable, such that there is no need to use comprehensive models for every analysis.

Two such source-receptor models were considered in the evaluation of SO<sub>2</sub> emissions from copper and zinc facilities in Canada described in this report. The first was the Integrated Assessment Model (IAM), developed to support the assessment of ecological impacts at selected receptor sites in eastern North America due to changes in SO<sub>2</sub> emissions across the continent (Environment Canada, 1997c). The IAM is a framework of models that were designed to consider the entire acid deposition system as a whole - from emissions of acidifying pollutants through to aquatic, forest, agricultural, visibility, wildlife, materials and health effects. At present, the model can be used to perform quick calculations of the impact of regional SO<sub>2</sub> emission changes on wet sulphate deposition at a limited number of selected receptor sites. Specifically, SO<sub>2</sub> emissions have been grouped into a total of 40 source regions: 15 in Canada and 25 in the United States. The transfer matrix in the IAM source-receptor module is used to estimate the average annual total wet sulphate deposition at 15 receptor sites in eastern North America.

The second model considered involved the source-receptor matrices developed in 1996 by SENES Consultants Limited based on the MESOPUFF II model. The MESOPUFF II model was used to develop a source-receptor unit transfer matrix for 375 point sources of SO<sub>2</sub> emissions in eastern North America and 248 receptor points in Ontario, Quebec and the Maritime provinces (SENES Consultants, 1996a). The transfer matrix was developed in support of the Environment Canada project "SO<sub>2</sub> Emission Abatement Strategies and Economic Instruments."

The source-receptor relationships in the IAM are based on more detailed long-range transport modelling analyses using the Atmospheric Environment Service Long-Range Transport (AES-LRT) model (Olson et al., 1983). Consequently, for the purposes of this analysis, it is reasonable to assume that IAM is based on more reliable transformation and transport modelling, and that the IAM results provide a more accurate prediction of wet sulphate deposition rates for comparison with critical load values than the results derived from the MESOPUFF II model. For this reason, the remainder of the discussion will be based on the IAM results. A comparison of the results obtained using the IAM and MESOPUFF II models and discussion of their relative merits are contained in SENES Consultants (1999a).

The contribution of  $SO_2$  emissions from Canadian copper smelters and refineries and zinc plants to wet sulphate deposition in eastern Canada was calculated based on the SO<sub>2</sub> emission rates listed in Table 3. The analysis was conducted on selected lake cluster groups (Algoma, Ontario; Sudbury, Ontario; Montmorency, Quebec; and Kejimkujik, Nova Scotia), consistent with other recently completed evaluations of the impact of SO<sub>2</sub> controls on sulphate deposition (Environment Canada, 1997c,d; Lam et al., 1998; Jeffries et al., 1999). The incremental contributions of individual facility emissions<sup>8</sup> to wet sulphate deposition within the four lake cluster groups were estimated using the IAM source-receptor matrix. However, because IAM does not have a receptor at Sudbury, the nearest IAM receptor site to

<sup>&</sup>lt;sup>8</sup> Note that while the IAM source-receptor relationships are based on large source regions, the relationships used in this assessment account for the fractional or incremental contribution from the individual facilities being assessed.

Sudbury (i.e., at Muskoka, Ontario) was added to the analysis.

It is estimated that copper smelters contributed from 95-97.5% of the wet sulphate deposition originating from copper and zinc facilities in Canada at these receptor locations, in line with their dominant share of the total SO<sub>2</sub> emissions from copper and zinc facilities as a source group. From the perspective of individual facility contributions, this industry's wet sulphate deposition is largely dominated by SO<sub>2</sub> emissions from three copper smelters: Inco's Copper Cliff smelter in Sudbury, the HBM&S copper smelter at Flin Flon, and the Noranda-Horne copper smelter. Collectively, these three smelters are estimated to account for the following fractions of wet sulphate deposition (relative to SO<sub>2</sub> emissions from all Canadian copper and zinc facilities):

• 85% at Algoma, Ontario;

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- 87% at Montmorency, Quebec; and
- 76% at Kejimkujik, Nova Scotia.

Moving eastward, the significance of the emissions from the smelter at Flin Flon diminishes and is replaced by wet sulphate deposition from SO<sub>2</sub> emissions at the copper smelters operated by Falconbridge near Sudbury and Noranda-Gaspé. The latter contributes about 14% of the industry sector wet sulphate deposition at Kejimkujik, while the Falconbridge smelter contributes about 7–8% of the total wet sulphate deposition from copper and zinc facilities. Deposition rates at Sudbury were not calculated due to a lack of a suitable receptor point for IAM.

Relative to other sources of  $SO_2$ emissions in Canada, the analysis indicates that the  $SO_2$  emissions from the copper and zinc facilities (particularly the copper smelters) in 1995 represented a significant source of wet sulphate. Results are summarized in Table 13. At Algoma and Montmorency, the industry sector contributions of 0.572 kg/ha/a and 1.611 kg/ha/a, respectively, at 1995 emission rates, represented about 30% of the average wet sulphate deposition from all anthropogenic Canadian sources for the 1990-1993 period. At Kejimkujik, the industry sector's contribution was smaller, representing about 14% of anthropogenic Canadian source contributions between 1990 and 1993. However, with respect to all sources of SO<sub>2</sub> emissions in North America, the relative magnitude of the wet sulphate deposition from Canadian copper and zinc facilities is substantially lower. At 1995 emission levels, these facilities as a source group were estimated to contribute approximately 3% of the 1990-1993 average anthropogenically derived wet sulphate deposition at Algoma, 9% at Montmorency and 2% at Kejimkujik. Despite the fact that sources in eastern Canada account for only 14% of the total SO<sub>2</sub> emissions in eastern North America, eastern Canada receives approximately 41% of the total wet sulphate deposition (Environment Canada, 1997c). Longrange transport modelling and monitoring data suggest that U.S. sources contribute up to 90-95% of the sulphate deposition in the very southwestern parts of Ontario, with the proportion attributable to U.S. sources declining with distance from the border (Acidifying Emissions Task Group, 1997). Therefore, whereas the copper and zinc facilities represent a significant source group for sulphate deposition from Canadian sources, their contribution to acid deposition from all sources in North America is considerably smaller. Moreover, although the contribution of large copper smelters, such as those located at Sudbury, to total sulphate deposition may be significantly higher within a radius of about 100 km of the facility (Keller and Carbone, 1997), the relative percent contribution of these facilities, both individually and collectively as an industry group, is much smaller at the regional scale of eastern Canada.

It is worthwhile to compare deposition values estimated using IAM (Table 13) with empirical deposition results. Wet deposition rates based on sulphate measured in samples collected by the Ontario Ministry of the Environment (OME) are shown in Table 14. The wet sulphate deposition rate of 22.9 kg/ha/a modelled for Muskoka using IAM is in good agreement with empirical sulphate deposition data for the years



Source	(pr	Wet sulphate depo oportion of deposition att	osition – kg/ha/a ributed to specified so	ource)
	Algoma	Sudbury/Muskoka	Montmorency	Kejimkujik
North American SO <sub>2</sub> sources <sup>1</sup>				
Natural background	3.6 (21%)	4.0 (17%) Muskoka	4.8 (26%)	5.6 (40%)
Total of U.S. sources (1990–93 emissions)	12.0 (69%)	14.3 (62%) Muskoka	8.7 (46%)	6.3 (45%)
Total of Canadian sources (1990–93 emissions)	1.9 (11%)	4.6 (20%) Muskoka	5.3 (28%)	2.0 (15%)
Total of all North American sources (1990–93 emissions)	17.5 (100%)	22.9 (100%) Muskoka	18.8 (100%)	13.9 (100%)
Assessed Canadian SO <sub>2</sub> sources <sup>2</sup>				
Copper smelters (1995 emissions)	0.545 (3%)	1.561 (7%) Muskoka	1.570 (8%)	0.275 (2%)
Copper refineries (1995 emissions)	0.023 (0.1%)	0.002 (0.01%) Muskoka	0.011 (0.06%)	0.002 (0.01%)
Zinc plants (1995 emissions)	0.004 (0.02%)	0.003 (0.01%) Muskoka	0.030 (0.2%)	0.004 (0.03%)
Sector total (1995 emissions)	0.572 (3%)	1.566 (7%) Muskoka	1.611 (9%)	0.281 (2%)
Critical loads		······		
Surface waters (5% damage)	8.0	13.2 Sudbury	6.9	<6

### TABLE 13 Wet sulphate deposition rates in selected regions of eastern Canada for 1990–1993 estimated using the Integrated Assessment Model (IAM)

<sup>1</sup> Percentages in the section on North American SO<sub>2</sub> sources indicate the fractional contribution of source types to wet sulphate deposition from all North American sources. Due to rounding, values may not total 100%.

 $^2$  Percentages in the section on Assessed Canadian SO<sub>2</sub> sources indicate the fractional contribution of facility types to wet sulphate deposition from all North American sources.

1990–1993 at the three stations located near Muskoka (range of station averages — 16.4–19.5 kg/ha/a). The IAM rate of 17.5 kg/ha/a for Algoma is also in good agreement with the average value of 24.1 kg/ha/a measured at the Turkey Lake station, located in the Algoma region. It should be recognized that monitored results represent deposition at a single location, while IAM estimates average deposition over relatively large areas, within which there may be considerable local variability. Table 14 also shows sulphate deposition rates for 1995, the year on which the incremental sulphate deposition rates are based.



Monitoring station	Sulphate wet deposition rate <sup>1</sup> (kg/ha/a)									
	1990	1991	1992	1993	Average 1990–93	1995				
Sites located near Muskoka:				±						
Dorset	20.6	19.5	18.4	19.4	19.5	19.2				
Coldwater	20.8	14.9	15.3	14.6	16.4	16.3				
McKellar	19.5			14.5	17.0	10.0				
Site located near Algoma:										
Turkey Lake	22.2	17.7	29.6	27.0	24.1	20.2				

## **TABLE 14** Wet sulphate deposition rates at monitoring stations located near two of the receptor areas considered in deposition modelling

<sup>1</sup> Values are based on the unfiltered reactive sulphate content of wet-only deposition samples collected by the OME.

#### 2.3.1.2 Metals

### 2.3.1.2.1 Fate of metals in air

Metals released to air from copper smelters and refineries and zinc plants are typically in particulate form. Releases may be divided into those from fugitive and low-level sources, and those released from high-level stacks.

Relative to stack emissions, fugitive particles are relatively coarse and are generally deposited close to the point of release. Because of the short transport times, chemical forms of the deposited particles are expected to be very similar to those of the source materials.

The fate of substances in stack emissions depends upon the physical and chemical nature of the substance and on a variety of site-specific factors, including stack height, velocity of release, surface topography and local meteorological conditions, such as wind speed and direction and precipitation frequency. Metals associated with fine suspended particles may be transported relatively long distances before deposition.

Although recent stack testing data from the Inco operation (Burnett, 1998) showed that about 80% of its emissions (by mass) were fine

PM ( $<3 \mu m$ ), results of older in-plume studies for the Falconbridge and Inco-Copper Cliff plumes reported by Chan and Lusis (1986) and Chan et al. (1983) suggested that metals such as Cu and Ni may be primarily associated with coarse particle sizes (equal to or greater than 2.5 µm), with mass median diameters greater than 9 µm. On the other hand, these authors reported that other trace metals such as Pb, Zn and As occurred most frequently (but not always) with fine particles (less than 2.5 µm) and typically with particles with mass median diameters closer to 1 µm. Results for Cd (and Cr) tended to fluctuate from one sampling run to another, but Cd was more likely to be associated with the fine particle fraction. Cumulative plots for coarse particle distributions of Cu indicated that approximately 60-95% or more of the Cu was associated with particles greater than 2.5 µm. Cumulative plots for the other trace metals were not reported. The extent to which results of this older study are representative of current conditions is unknown.

No data were identified on the speciation or bioavailability of metals in Canadian air contaminated by smelter or refinery emissions. Limited data from both copper and zinc smelting and refining operations in other countries indicate that most metals are released as particulate oxides, sulphides and/or sulphates (Eatough et al., 1979; Harrison and Williams, 1983; Whyte et al., 1984). In the atmosphere, oxides may react with sulphuric acid to form more soluble sulphates (Franzin et al., 1979; Zwozdziak and Zwozdziak, 1986). Because of their solubility, sulphate forms are expected to be relatively bioavailable.

As discussed in more detail below, metals may be deposited from the atmosphere by both wet and dry deposition processes. As a result, they can accumulate in a variety of media, including surface soils, lakewaters and sediments. Concentrations of deposited metals in such media typically decrease exponentially with distance from a source. The radius of local enrichment resulting from past releases from Canadian smelters and refineries — relative to background values — has been reported to vary from several tens of kilometres up to over 100 km, depending upon the site, the media and metal of interest (John *et al.*, 1976; Glooschenko *et al.*, 1986; Zoltai, 1988; Dumontet *et al.*, 1990).

### 2.3.1.2.2 Deposition of metals from air — empirical

The following is a brief description of the types of monitoring data used to estimate annual soluble metal deposition. Also included are descriptions of the methods used for estimation of source attributions, water-soluble fractions of deposited metals and levels of regional background metal deposition. Notes providing greater detail on the handling of data have been compiled in CED (2000).

*Dustfall*: Dustfall monitoring involves exposing an open-topped canister containing a collection medium to the ambient air for some period of time. The collection medium is typically water but may include other liquids (e.g., alcohol/water mixtures) during winter months. Exposure time is typically 28–30 days. The collected material is then analysed for total metal content.

Dustfall samplers measure total deposition, as they collect both material

deposited during precipitation events (wet deposition) and particles settling under the force of gravity (dry deposition). Collection efficiency for micron- and submicron-sized particles is limited, however, and the results from dustfall monitoring may slightly underestimate total deposition. These monitors are generally used close to facilities, where the majority of deposition is due to gravitational settling of larger particulates.

All dustfall monitoring data were obtained in the form of total deposition rates (mass/area/time). As monitoring is usually continuous, results for individual dustfall samples from the same station can be summed for all samples collected over the period of a year. Total soluble annual deposition rates were then calculated using the appropriate fractions for metal solubility.

Results for dustfall monitoring are provided in Table 15. It is generally noted that annual deposition rates decrease with increasing distance from the facilities. In particular, elevated deposition rates of Cu, Zn, Pb and Cd may be seen. Monitoring of Ni in dustfall samples was not conducted near any of the facilities. Values shown in bold are above the 25th percentile critical loads (CLs), and those bolded and underlined are above the 50th percentile critical loads. These effects thresholds are discussed in Section 2.4.1.1.3.

Dry deposition from total suspended particulate (TSP): TSP monitoring involves collection of PM by passing ambient air through a filter. This is usually done using high-volume air samplers, where air is passed through the filters at rates of typically 1000–1500 L/min. Sampling usually takes place over a 24-hour period and is normally conducted one to two times per week. The collection filters are then analysed for total metal content, allowing determination of the concentration of metals in air. The OME uses continuous monitoring with low-volume air sampling. Air is continuously passed at a rate of about 2 L/min, and filters are changed every 28 days.



Facility	Year	Monitoring station I.D.	Distance (km) & direction relative				tion <sup>2</sup> (mg ution (%		
			to facility	Cu	Zn	Ni	Pb	Cd <sup>3</sup>	As
Copper smelters							J		L
Noranda-Gaspé	1997	1	0.6 S	1159	120		188	0.9	47
		13B	1.3 E	178	75		77	1.8	18
		12B	1.4 E	147	73		52	1.2	13
		10	1.5 E	<u>117</u>	37		39	0.4	7
		10B	1.5 E	<u>130</u>	<u>119</u>		40	0.3	8
		2	1.6 SE	<u>497</u>	84		<u>103</u>	0.7	21
~		11	1.8 E	<u>115</u>	38		<u>60</u>	0.3	7
		3	3.0 SE	<u>128</u>	38		47	0.2	9
		4	3.8 SE	<u>48</u>	38		18	0.1	5
		16	3.8 NW	<u>74</u>	28		38	0.3	6
		21	6.1 W	22	28		7	0.3	1
	-	17	6.8 NW	22	21		18	0.1	2
	· · ·	5	7.5 E	<u>47</u>	27		12	0.6	3
		6	12.5 E	23	26		8	0.1	1
Noranda-Horne	1997	O-2	3.2 W	29	28		25	0.5	
		N-2	3.2 N	<u>134</u>	70		<u>132</u>	1.2	<u>31</u>
		E-2	3.2 E	<u>54</u>	47		43	0.5	10
		S-2	3.2 S	<u>64</u>	59		<u>66</u>	0.6	11
		O-4	6.4 W	17	22		14	0.5	~4
		N-4	6.4 N	23	25		22	0.5	4
		E-4	6.4 E	<u>34</u>	26		27	0.5	5
		S-4	6.4 S	<u>21</u>	31		28	0.5	5
HBM&S				o dustfall	data availa	able			
Falconbridge-			N	o dustfall	data availa	able			
Sudbury									
Copper refineries									_
Noranda-CCR			N	o dustfall	data availa	uble			
Zinc plants									
Noranda-CEZinc	1997	В	0.6 E		2980			<u>16</u>	
		А	0.7 NE		<u>2564</u>			<u>15</u>	
		C (Cadieux)	1.3 E		<u>579</u>			3.1	
		F.	1.4 N		<u>490</u>			2.1	
		H (Louis IV M.)	1.7 NW		<u>184</u>			0.8	
		D	1.9 E		<u>345</u>			1.9	
		J	2.2 SW		<u>180</u>			1.8	
		I	3.4 W		264			1.9	
		G	3.6 NE		168			1.4	
		Е	3.8 E		<u>337</u>			1.9	

 TABLE 15
 Deposition of soluble metals in the vicinity of copper and zinc production facilities <sup>1</sup> – based on dustfall sampling

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Facility	Year	Monitoring station I.D.	Distance (km) & direction relative				tion <sup>2</sup> (mg ution (%		
			to facility	Cu	Zn	Ni	Pb	Cd <sup>3</sup>	As
Combined sources			<u> </u>			<b>.</b>	I	L	I
Inco-Copper Cliff (copper smelter, copper and nickel refineries)			N	o dustfal	l data avai	lable			
Falconbridge-	Source a	attribution:	- Copper smelter	66%	15%	87%	92%	79%	14%
Kidd Creek			- Copper refinery	0%	0%	0%	0%	0%	0%
			- Zinc plant	2%	24%	6%	1%	7%	86%
			- Concentrator	32%	61%	7%	7%	14%	0%
	1997	7	0.3 SE	<u>1281</u>	<u>2289</u>		<u>79</u>	22	14
		3	1.2 E	<u>469</u>	<u>964</u>		41	<u>7.2</u>	5
		8	2.0 NE	<u>314</u>	<u>449</u>		<u>81</u>	<u>5.5</u>	3
		9	2.0 E	<u>152</u>	<u>263</u>		<u>321</u>	2.7	1
		11	2.4 NE	<u>145</u>	<u>311</u>		35	1.9	1
		13	4.2 SW	<u>247</u>	<u>301</u>		36	<u>3.5</u>	9
Cominco-Trail	Source a	ttribution:	<ul> <li>Zinc plant</li> </ul>		90%		4%	36%	0%
			- Lead smelter		10%		96%	64%	100%
	1998	Downtown	0.8 SE		<u>1850</u>		<u>325</u>	<u>9.9</u>	5
		Tadanac	1.0 N		<u>1641</u>		<u>650</u>	<u>13</u>	11
		Trail Hospital	1.2 E		<u>892</u>		<u>235</u>	<u>4.8</u>	4
		Butler Park (1995 data)	1.3 E	63	<u>1945</u>		<u>407</u>	<u>40</u>	<140
		Stoney Creek	1.5 NW		<u>1802</u>		<u>339</u>	<u>9.3</u>	7
		Daniel St.	1.6 SE		<u>1216</u>		<u>224</u>	<u>5.6</u>	4
		Sunningdale	2.0 NE		<u>604</u>		<u>149</u>	3.2	4
		Duncan Flats	2.2 N		<u>1009</u>		<u>178</u>	<u>5.8</u>	4
		Warfield	2.4 W		<u>215</u>		<u>62</u>	2.4	3
		Glenmerry	3.9 E		<u>971</u>		<u>227</u>	<u>5.3</u>	4
		Oasis	4.3 NW		<u>382</u>		<u>114</u>	2.7	3
		Birchbank	7.0 N		<u>186</u>		<u>55</u>	2.7	2
		Columbia Gdn.	10.5 SE		<u>593</u>		<u>70</u>	3.2	3

### TABLE 15 Deposition of soluble metals in the vicinity of copper and zinc production facilities 1 – based on dustfall sampling (continued)

<sup>1</sup> Data for Butler Park (Cominco) were provided by the B.C. Ministry of Environment (MOE) (courtesy of E. Tradewell, Air Resources). All other data were provided by the individual companies. Both Butler Park and Tadanac (Cominco) are operated by the B.C. MOE. Monitoring sites are listed in order of distance from the facility, irrespective of direction.

<sup>2</sup> Values shown in bold meet or exceed 25th percentile critical loads. Those in bold and underlined exceed 50th percentile critical loads. This is based on comparison to soil pore water critical loads for Noranda-Gaspé, Noranda-CEZinc and Cominco-Trail, and to the more sensitive of soil pore water or surface water critical loads for Noranda-Horne and Falconbridge-Kidd Creek. These effects thresholds are discussed in Section 2.4.1.1.3.

<sup>3</sup> As typical detection limits for Cd are close to the critical loads used in these assessments, results for Cd that were below the detection limit were corrected to one-half of the detection limit prior to calculating annual deposition. This was found to have relatively minor effects on the final soluble deposition values (differences of 10-20%).



Particulate material that settles through gravity onto the ground or surface waters is referred to as "dry deposition." Calculation of dry deposition rates from measurements of TSP concentrations in air requires the application of a deposition velocity, which describes the rate of descent of a "typically" sized particle. A velocity of 0.2 cm/s was used in this work. This value has been used by the Integrated Atmospheric Deposition Network (IADN) in determination of rates of dry deposition to the Great Lakes and is discussed in Hoff et al. (1996). Hoff et al. (1996) point out that deposition velocity is a function of particle size, hygroscopic growth of the aerosol, wind speed and humidity. In particular, the effective deposition velocity of 0.2 cm/s is derived based on a small particle to large particle mass ratio of 1.5:1, for "small" and "large" particles having diameters of about 0.5 µm and 5 μm, respectively.

In-stack particle size data obtained for the main stack at Inco-Copper Cliff (Burnett, 1998) indicated that about 15% (by mass) of the PM was below 1  $\mu$ m, with another 65% falling in the range 1–3  $\mu$ m, and the remaining 20% larger than 3  $\mu$ m. This is in reasonable agreement with the mass ratios assumed in derivation of the deposition velocity used in this work. This does not, however, consider particulates from fugitive sources, which tend to be of larger size and settle more rapidly. It should be recognized that the value of 0.2 cm/s was derived for use over large areas (the Great Lakes) located some distance from emission sources, and its application could significantly underestimate the extent of dry deposition close to emission sources, particularly fugitive sources.

Once dry deposition rates have been estimated, they may be summed with independent measurements of wet deposition to obtain total deposition rates. Often, however, no data on wet deposition are available. In this circumstance, total deposition may be estimated by applying a factor to a dry deposition value that is representative of "typical" total:dry deposition ratios. Two approaches were considered in estimating what this factor should be.

The first approach used data from OME monitoring stations that had both wet-only deposition monitors (described later on) and TSP monitors. Based on these data, the percentages of total deposition (sum of wet plus dry) that are due to dry deposition have been calculated and are indicated in Table 16 for each metal. Results shown are based on annual average deposition<sup>\*</sup> values calculated from several years of data for seven stations located within 100 km of the zinc

Metal	Dry deposition as a percer	ntage of total deposition <sup>1</sup>
	Approach 1: OME sites (based on dry deposition & wet deposition) (<100 km from source)	Approach 2: Company sites (based on dry deposition & dustfall) (0.8–10.5 km from source)
Cu	19 ± 11 (38)	6(1)
Zn	18 ± 11 (38)	9 ± 7 (7)
Ni	$18 \pm 12$ (38)	
Pb	27 ± 12 (38)	$12 \pm 6$ (6)
Cd	26 ± 15 (38)	14 ± 9 (7)
As	24 ± 10 (15)	27 ± 9 (6)

 TABLE 16
 Percent contribution of dry metal deposition to total metal deposition

<sup>1</sup> Associated error values are sample standard deviations. Values in parenthesis are the number of values (monitoring stationyears) averaged. or copper processing facilities. It is seen from these results that dry deposition typically represents 20–25% of total deposition at sites located within 100 km of the sources. Most of these monitoring stations are located at least a few kilometres from facilities. Therefore, the proportion of coarse particles released from fugitive sources is likely to be small. These percentages are therefore expected to be reasonably accurate for deposition occurring some distance from the emission sources.

The second approach used data from company-operated stations that had both TSP and dustfall monitors. For these stations, the percentage of dry deposition was calculated by dividing the TSP-derived dry deposition by the dustfall-based total deposition. These results are also shown in Table 16 for the seven stations conducting both types of monitoring (five Cominco sites, one Noranda-CEZinc site, one Noranda-Gaspé site). These monitors are mostly located close to emission sources. Six of the seven stations considered are located between 0.8 and 4.3 km of the smelting facilities, with the seventh station located 10.5 km from the source. In general, the percentages obtained using this approach are somewhat less than those estimated from the OME data (see Table 16), the average dry deposition value (across the different metals) being 14%.

It is likely that both approaches underestimate the contribution of dry deposition to total deposition closer to emission sources. The first approach has been based on deposition further from sources, where larger particles represent only a small fraction of TSP. In the second approach, the deposition velocity of 0.2 cm/s is too low to account for larger particles, which represent a significant fraction of TSP close to sources.

Following consideration of this information, a factor (total:dry ratio) of 4 has been applied to estimate total deposition from dry deposition, corresponding to a dry deposition fraction of 25%. This is based on the first approach. Estimates of the proportion of dry deposition based on the second approach ranged from 6–27%, which would result in factors ranging from 4–17. These values were not used, as they are based on a limited number of samples and show significant variability. It must be recognized, therefore, that the total:dry ratio of 4 selected is the lowest factor that could be applied to dry deposition values in order to estimate total deposition, and that there is a high probability that this will underestimate total deposition especially closer to emission sources.

Deposition rates derived from TSP monitoring data are shown in Table 17. With the exception of the OME sites (Inco-Copper Cliff), all TSP monitoring was periodic. For each metal, the average of all values of metal concentration in air measured over one year was converted to a deposition rate using the deposition velocity of 0.2 cm/s. The dry soluble deposition rate was then calculated using the appropriate fraction for metal solubility. The factor of 4 was then applied to provide an estimate of total soluble deposition, shown as "est. of total" in Table 17.

As was seen in Table 15 for dustfall results, trends of decreasing deposition rates as a function of distance from the facility are also observed for the TSP-derived deposition rates (Table 17), and elevated deposition rates can be seen, especially for Cu, Zn, Pb and Cd. It should be noted, by comparing values in the two tables for monitoring at similar distances from the sources, that annual deposition rates estimated from TSP data are in nearly all cases somewhat lower than those measured in dustfall samples.

Wet plus dry deposition: In addition to monitoring TSP, from which dry deposition can be estimated, the OME and the IADN program monitor "wet-only" deposition. Wet-only monitors collect deposition in canisters that have covers. The apparatus have sensors that monitor moisture and activate a mechanism to open the lid when it is raining or snowing. The sensors are heated, which prevents the lid from remaining open after the precipitation event stops.

Facility	Year <sup>2</sup>	Monitoring station I.D.	Distance (km) & direction	Dry deposition or					g/m²/a) of tota	
			relative to facility	Estimate of total <sup>3</sup>	Cu	Zn	Ni	Pb	Cd 5	As
Copper smelters					·			L	<u> </u>	
Noranda-Gaspé	1997	Mines de Gaspé	1.5 E	Dry depn.:	6.9	2		7	0.1	1
		(10)		Est. of total:	<u>28</u>	10		30	0.2	5
Noranda-Horne	1996	MEF 8000	0.3 S	Dry depn.:				105	0.8	27
		(6 <sup>ieme</sup> rue)		Est. of total:				<u>420</u>	<u>3.0</u>	<u>108</u>
	1997	Arena Dave	0.7 S	Dry depn.:	<u>33</u>	31	0	57	0.9	12
		Keon		Est. of total:	<u>132</u>	<u>124</u>	1	<u>228</u>	<u>3.5</u>	<u>48</u>
	1996	MEF 8045	0.8 S	Dry depn.:			-	31	0.4	8
		(École ND.)		Est. of total:				<u>124</u>	1.5	34
	1997	Hotel de Ville	1.8 S	Dry depn.:	<u>19</u>	15	0	28	0.4	6
				Est. of total:	<u>76</u>	60	1	<u>112</u>	1.4	23
	1997	Laiterie Dallaire	2.9 SW	Dry depn.:	6.5	6	0	7	0.1	2
				Est. of total:	<u>26</u>	26	0	28	0.4	6
HBM&S	1997-	Prov. Bldg.	0.6 E	Dry depn.:	28	72		15	2.5	3
	1998	(Man-MOE)		Est. of total:	<u>112</u>	<u>286</u>		<u>59</u>	<u>9.8</u>	11
	1996-	Ruth Betts	1.1 SE	Dry depn.:	<u>16</u>	18		5	0.8	1
	1997	School.		Est. of total:	<u>65</u>	73		19	<u>3.0</u>	2
	1997-	Creighton Sch.	1.9 SW	Dry depn.:	8.4	11		3	0.5	1
	1998	(Man-MOE)		Est. of total:	<u>34</u>	42		13	2.1	3
	1996	Centoba Park	2.0 SE	Dry depn.:	<u>18</u>	10		3	0.5	0
	1997	Sewage Plant		Est. of total:	<u>74</u>	38		11	1.8	1
Falconbridge-	1995	Edison	0.8 W	Dry depn.:	2.3		3	1	0.8	< DL
Sudbury				Est. of total:	9.2		13	2	<u>3.4</u>	
	·	Pumphouse	1.0 SW	Dry depn.:	2.4		4	1	0.8	<dl< td=""></dl<>
				Est. of total:	9.6		15	2	<u>3.4</u>	
Copper refineries										
Noranda-CCR	1996-	Edward Rivet	0.5 NE	Dry depn.:	3.7	5	0	2	0.0	0
	1997	Civic Centre		Est. of total:	15	21	1	6	0.1	2
Zinc plants										
Noranda-CEZinc	1998	C	1.3 E	Dry depn.:		304			0.9	
	<u> </u>	(Cadieux)		Est. of total:		<u>1216</u>			3.6	

 TABLE 17 Deposition of soluble metals in the vicinity of copper and zinc production facilities <sup>1</sup> — based on total suspended particulate sampling



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Facility	Year <sup>2</sup>	Monitoring station I.D.	Distance (km) & direction	Dry deposition or	So S	luble d ource a	epositio attribut	on 4 (m tion ( <i>%</i>	g/m²/a) of tota	 or al)
			relative to facility	Estimate of total <sup>3</sup>	Cu	Zn	Ni	Pb	Cd <sup>5</sup>	As
Combined source	ces			·	- <b>I</b>	I	L	I	L	
Inco-Copper	Source	attribution:	- Copper smelter		72%	100%	69%	79%		86%
Cliff <sup>6</sup>			- Copper refinery		14%	0%	0%	0%		7%
			- Nickel refinery		14%	0%	31%	21%		7%
	1995–	OME 77070	0.7 W	Dry depn.:	<u>15</u>		15	<1		0
	1996	(Copper Cliff)		Est. of total:	<u>60</u>		58			1
		OME 77026	6.0 NE	Dry depn.:	7.4		11	1		
		(Federal Bldg.)		Est. of total:	<u>30</u>		44	3		
Falconbridge-	Source	attribution:	- Copper smelter		66%	15%	87%	92%	79%	149
Kidd Creek			- Copper refinery		0%	0%	0%	0%	0%	09
			- Zinc plant		2%	24%	6%	1%	7%	869
			- Concentrator		32%	61%	7%	7%	14%	09
	1997	AMS #6	0.6 S	Dry depn.:	77	<u>134</u>		20	1.7	5
				Est. of total:	<u>308</u>	<u>536</u>		<u>80</u>	<u>6.8</u>	18
		AMS #1	1.4 NE	Dry depn.:	23	50		6	0.7	2
				Est. of total:	<u>92</u>	<u>200</u>		24	2.7	7
		AMS #7	1.6 E	Dry depn.:	<u>14</u>	28		3	0.4	1
				Est. of total:	<u>56</u>	<u>112</u>		14	1.6	6
Cominco-Trail	Source a	attribution:	- Zinc plant			90%		4%	36%	
			- Lead smelter			10%		96%	64%	1009
	1998	Downtown Trail	0.8 SE	Dry depn.:		65		15	0.4	1
				Est. of total:		<u>259</u>		<u>62</u>	1.6	4
		West Trail	1.4 SE	Dry depn.:		43		12	0.4	1
				Est. of total:		<u>172</u>		47	1.6	4
		Warfield	2.4 W	Dry depn.:		24		8	0.3	1
				Est. of total:		96		31	1.2	3
		Glenmerry	3.9 E	Dry depn.:		47		14	0.4	1
				Est. of total:		<u>189</u>		<u>54</u>	1.6	6
		Oasis	4.3 NW	Dry depn.:		28		10	0.3	1
				Est. of total:		<u>112</u>		42	1.4	4
		Columbia	10.5 SE	Dry depn.:		49		13	0.5	1
		Gardens		Est. of total:		<u>197</u>		51	1.9	2

 TABLE 17
 Deposition of soluble metals in the vicinity of copper and zinc production facilities <sup>1</sup> — based on total suspended particulate sampling (continued)

-

Facility	Year <sup>2</sup>	Monitoring station I.D.	Distance (km) & direction	Dry deposition or	So S	luble d ource a	epositio attribut	on 4 (m tion (%	g/m²/a) of tota	or l) .
			relative to facility	Estimate of total <sup>3</sup>	Cu	Zn	Ni	Pb	Cd <sup>5</sup>	As
		Genelle	12.7 NE	Dry depn.:		20	·	7	0.3	1
		Northport, Wash.		Est. of total:		79		27	1.2	3
			19 S	Dry depn.:		6		3	0.2	0
				Est. of total:		24		10	1.0	2

# TABLE 17 Deposition of soluble metals in the vicinity of copper and zinc production facilities 1 — based on total suspended particulate sampling (continued)

- <sup>1</sup> With the following exceptions, all data were provided by the individual companies: Inco (all data provided by OME courtesy of D. Racette, Northern Region); HBM&S (data for Provincial Building and Creighton School provided by Manitoba- MOE courtesy of B. Krawchuk, Air Quality Management); CCR (data provided by Environment Canada courtesy of A. Germain, Quebec Region, and the Association des industries de l'est de Montréal [AIEM] courtesy of P. Frattolillo).
- <sup>2</sup> Due to data availability, in some cases 12-month periods other than calendar years were used. These include HBM&S (10/8/97 to 9/8/98 for Provincial Building and Creighton School; 17/8/96 to 16/8/97 for Ruth Betts School and Centoba Park) and CCR (26/7/96 to 25/7/97 for Edward Rivet Civic Centre). Due to limited sampling data available for 1996, deposition values for Inco-Copper Cliff are based on the average of values for the years 1995 and 1996.
- <sup>3</sup> Estimates of total deposition were determined by applying a factor of 4 to the calculated dry deposition. This was done prior to rounding the values for presentation.
- <sup>4</sup> Values shown in bold meet or exceed 25th percentile critical loads. Those in bold and underlined exceed 50th percentile critical loads. This is based on comparison to soil pore water critical loads for Noranda-Gaspé, Noranda-CCR, Noranda-CEZinc and Cominco-Trail and to the more sensitive of soil pore water or surface water critical loads for Noranda-Horne, HBM&S, Falconbridge-Sudbury, Inco-Copper Cliff and Falconbridge-Kidd Creek. These effects thresholds are discussed in Section 2.4.1.1.3.
- <sup>5</sup> As typical detection limits for Cd are close to the critical loads used in these assessments, where possible, results for Cd that were below the detection limit were corrected to one-half of the detection limit prior to calculating annual deposition.
- <sup>6</sup> For the OME data set, values below the detection limit for all metals were corrected to one-half of the detection limit.

As wet deposition monitoring is continuous, all results obtained over the period of one year were summed. The totals were normalized to a full year to account for any missing data. Values were converted to annual deposition rates ( $mg/m^2/a$ ), summed with the dry deposition values for the corresponding year, and converted to total soluble annual deposition rates using the appropriate solubility factor for each metal.

OME data for the Sudbury region determined as the sum of wet and dry deposition are shown in Table 18. IADN data were used only for calculation of regional background metal deposition (discussed later in this section).

Snowpack: Monitoring of metals in snowpack samples near the Noranda-Horne smelter was conducted by the Geological Survey of Canada (GSC) in the winter of 1997–98. Snow cores were collected over a three-day period at 82 locations, mostly at 3-km intervals along three transects, extending 50 km south, northeast and northwest from the smelter. Samples were thawed at low temperature (4°C) and filtered through 0.45-µm membranes, separating dissolved and particulate fractions. Each fraction was analysed for metal content, from which deposition rates were calculated. A detailed description of sample collection and analysis is provided in Kliza *et al.* (2000).

It should be noted that due to the method of handling the snowpack samples (filtration at 4°C a short time after thawing), the "dissolved" concentrations determined, and subsequent estimates of soluble deposition, are likely lower



TABLE 18	Deposition of soluble metals in the vicinity of copper and zinc production facilities — based
	on snowpack and combined ("wet plus dry") deposition sampling

Facility or region (data	Year	Monitoring station I.D.	Distance (km) & direction relative to facility	Facility				on <sup>3</sup> (mg ion ( <i>%</i>		
source and type)					Cu	Zn	Ni	Pb	Cd	As
Copper smelter	s		•	,						
Noranda-Horne	1997–	Selected radii	1-km radius		322	57	2	<u>195</u>	0.9	23
(GSC – snow-	1998		2-km radius		<u>205</u>	41	1	<u>140</u>	0.7	17
pack melt waters) <sup>1</sup>			3-km radius		<u>134</u>	30	1	<u>102</u>	0.5	13
waters)			4-km radius		<u>91</u>	23	0	<u>76</u>	0.4	10
			5-km radius		<u>63</u>	18	0	<u>58</u>	0.3	8
			10-km radius		<u>15</u>	7	0	18	0.2	3
			15-km radius		5	4	0	8	0.1	1
			20-km radius		3	2	0	4	0.1	1
Combined sour	ces									
Sudbury region	Source	attribution: - I	nco copper smelte	r	69%	65%	66%	69%		86%
(OME – sum of dry and wet deposition) <sup>2</sup>	- Inco copper refinery				13%	0%	0%	0%		7%
		- I	nco nickel refiner	ý	14%	0%	30%	19%		7%
		- H	Falconbridge copp	er smelter	4%	35%	4%	12%		0%
	1995	OME 5241 (Sud. Sci. Ctr.)	3.5 E 19.6 SW	Inco Falconbridge	6.9	3	2	3	0.1	0.4
	OME 5221 (Garson) OME 5201 (McFarlane L.) OME 5211 (Hanmer)		17.5 NE 4.9 SW	Inco Falconbridge	3.3	2	2	2	0.2	0.4
		8.8 SE 19.5 SW	Inco Falconbridge	3.6	2	1	1	0.1	0.3	
		22.2 N 14.9 NW	Inco Falconbridge	2.6	3	1	1	0.1	0.5	
		OME 5231 (Whitefish Falls)	22.6 SW 44.5 SW	Inco Falconbridge	1.5	2	1	0	0.0	0.2

<sup>1</sup> Snowpack data for the Horne facility were provided by Natural Resources Canada (courtesy of G. Bonham-Carter, D. Kliza and K. Telmer, GSC). Winter deposition is assumed to represent one-quarter of annual deposition.

<sup>2</sup> Dry deposition and wet deposition data for the Sudbury region were provided by the OME (courtesy of B. Kruschel and D. Orr, Environmental Monitoring and Reporting Branch). Deposition values represent the sum of monitored wet deposition, and dry deposition calculated from measurements of suspended particulates. For all metals, values below the detection limit were corrected to one-half of the detection limit.

<sup>3</sup> Values shown in bold meet or exceed 25th percentile critical loads. Those in bold and underlined exceed 50th percentile critical loads. This is based on comparison to the more sensitive of soil pore water or surface water critical loads for both Noranda-Horne and the Sudbury region. These effects thresholds are discussed in Section 2.4.1.1.3.

than those that would be determined after longer periods of time at higher temperatures.

The relation between dissolved deposition rate and distance from the facility for each

metal was characterized by the GSC (personal communication, G. Bonham-Carter) by fitting an exponential curve to the empirical data. Results for the "dissolved" fraction based on this study are shown in Table 18. All results shown are



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based on the fitted curves. Deposition rates have been calculated at each of several arbitrarily chosen radii. Dissolved deposition rates determined from the equations were converted from ng/cm<sup>2</sup>/winter (the units of deposition used in Kliza *et al.*, 2000) to mg/m<sup>2</sup>/a, assuming that the snowpack represents deposition over three months of the year.

Relative reliability of empirical deposition data: It is recognized that estimation of total deposition based in whole or in part on TSP data has significant uncertainty. There is uncertainty both in the deposition velocity assumed and in the fraction of total deposition due to dry deposition. It is further recognized that both of these can vary considerably as a function of distance from emission sources. Comparison of annual deposition estimated from TSP data with the more reliable annual deposition measured in dustfall samples indicates that TSP-based estimations are generally low by factors of 2–5.

There are also uncertainties associated with other methods. For example, dustfall monitors are known to slightly underestimate deposition due to their poor collection efficiency for very small particles. Estimation of annual deposition from snowpack monitoring assumes that deposition during the winter is representative of the entire year and that sampled cores contained onequarter of the annual deposition. Based on these factors, the relative reliability of total deposition estimates considered in this report is likely of the order dustfall  $\geq$  snowpack > dry + wet > TSP.

Source attribution: The "Combined sources" sections of Tables 15, 17 and 18 include information on source attribution. Source attribution is the percent contribution of separate operations to total emissions from the facility. It will be used as an estimation of how much each emission source may be contributing to monitored ambient or deposited metal concentrations. Source attributions of metal emissions for the combined facilities were determined as follows:

• The HBM&S facility in Flin Flon includes a zinc plant and a copper smelter. Due to the

pressure leach process used, metal emissions from the zinc plant are negligible. Therefore, all metal emissions are attributed to the copper smelter.

- The Cominco-Trail facility includes a lead smelter and a zinc plant. Attribution was determined based on 1998 emission data provided by Cominco (personal communication with facility operators). These data reflect the significant process changes that took place at the facility in 1997.
- The Inco-Copper Cliff facility includes a nickel/copper smelter, a copper refinery and a nickel refinery. Source attribution was determined using 1995 and 1996 NPRI (1995, 1996) emission data. No major process changes are believed to have occurred at this facility since 1995, and the differences in apportionment calculated for 1995 and 1996 were considered to reflect normal year-to-year variability. The average of these two years was used.
- The Sudbury region includes the Inco facility described above, as well as the Falconbridge facility. As these facilities share an airshed, results for monitoring in this region are influenced by the presence of the two. Attribution was estimated in the same way as for the Inco facility but with the inclusion of emissions from the nickel/copper smelter at Falconbridge.
- The Falconbridge-Kidd Creek facility includes a copper smelter, copper refinery, zinc plant and concentrator. Source attribution was determined based on 1995 emission data provided by Falconbridge facility operators. No major process changes are believed to have occurred at this facility since 1995. Emissions indicated as relating to storage and handling were equally distributed between the copper smelter and zinc plant. Emission of As as arsine from the zinc plant was included in the calculations.

It should be noted that these attributions ignore background (natural, regional, local) contributions to estimated deposition rates. This omission may be significant at some facilities that include major emission sources that are not

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subject to these assessments (e.g., wind-blown material from uncovered mill tailings). Details of the source attribution calculations are provided in CED (2000).

*Estimation of soluble fraction*: Environmental exposure in this assessment focuses on bioavailable metals that have been deposited to soils or surface waters in particulate or dissolved form. The assumption is made that the bioavailable portion of the metal is the free metal ion, which may be estimated from the fraction of deposited metal that is water-soluble.<sup>9</sup> As monitoring methods generally provide information on total deposition only, some means of estimating the soluble fraction is required. A limited number of data sources allowing calculation of the water-soluble fraction of deposited metals were identified. Each is described below, and results are summarized in Table 19.

Monthly monitoring of dustfall at Butler Park, located 1.3 km east of the Cominco-Trail facility, has been conducted by the B.C. Ministry of Environment (MOE) since 1971. The procedure includes filtration of the samples through 0.45- $\mu$ m membrane filters followed by analysis of both the dissolved and particulate fractions. The water-soluble fraction was calculated using data from the years 1989–1997.

When analysing TSP samples, the OME extracts the collection filters first with water, then with acid. Both fractions are analysed for metals. Data were obtained from the OME for 141 samples collected from 20 different monitoring stations in Ontario in 1995 and 1996. Samples collected at sites located within 100 km of Sudbury were treated as "near-field," while those collected further than 100 km were treated as regional background for the Canadian Shield.<sup>10</sup>

During the winter of 1997–98, the GSC collected snowpack samples from 82 sites within 50 km of the Noranda-Horne smelter. The samples

were melted and filtered through 0.45-µm filters, followed by total metals analysis of each fraction. Again, it is pointed out that the method used may underestimate the soluble fraction somewhat, as the samples were filtered before dissolution equilibrium had been established.

The values for Trail shown in Table 19 were used to calculate soluble deposition from total deposition related to the Cominco facility. Those shown for Sudbury were applied to Inco-Copper Cliff and Falconbridge-Sudbury. Those for Rouyn-Noranda were applied to the Horne facility. Owing to a lack of other smelter-specific data, the averages of the Trail, Sudbury and Rouyn-Noranda values were applied to all other facilities. The values for regional background were used only in deposition modelling (see Section 2.3.1.2.3). The consistency in the solubility values between the different facilities shown in Table 19 is worthy of note.

*Estimation of regional background deposition*: Data used to estimate regional background deposition of metals on the Canadian Shield are summarized in Table 20. "Regional background," as used in this report, means levels of deposition that might typically be expected to be found in areas not locally influenced by copper smelters and refineries, zinc plants or other associated operations. These values, however, may include deposition originating from other anthropogenic sources. Indeed, the data used in estimation of regional background deposition for these assessments are based on monitoring both in relatively remote areas and in areas influenced by other distant industrial sources.

All data used to estimate regional background deposition are based on the sum of dry deposition calculated from TSP monitoring and directly measured wet deposition. Handling of these data types was discussed earlier in this section. Data for six of the sites considered were obtained from the OME. Data collected for use in

<sup>\*</sup> Estimation of free metal ion concentrations from soluble metal concentrations is discussed in Section 2.4.1.1.3.

<sup>&</sup>lt;sup>10</sup> Choice of the Canadian Shield as a generic region in these assessments is explained in Section 2.4.1.

Metal		Sol	uble metal fraction (	%)	
		Near	-field		Regional background
	Trail (BC-MOE) <sup>1</sup>	Within 100 km of Sudbury (OME) <sup>2</sup>	Rouyn-Noranda (GSC) <sup>3</sup>	Average	>100 km from Sudbury (OME) <sup>2</sup>
Cu	55	59	66	60	42
Zn	73	74	69	72	69
Ni		68	36	52	59
Pb	71	38	71	60	26
Cđ	65	82	80	76	73
As	63	89	74	75	84

TABLE 19	Water-soluble metal fractions used in the estimation of bioavailable deposited metals
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<sup>1</sup> Data for Trail were provided by the B.C. MOE (courtesy of E. Tradewell, Air Resources). Soluble fractions are based on the analysis of 58, 70, 44, 35 and 6 dustfall samples for Cu, Zn, Pb, Cd and As, respectively.

<sup>2</sup> Data for the Sudbury region were provided by the OME (courtesy of R. McVicars and D. Toner, Laboratory Services Branch). Soluble fractions for Sudbury near-field represent the average of results for 54 TSP samples (51 for Cd), and those for regional background represent the average of results for 82 TSP samples (58 for Cd).

<sup>3</sup> Data for Rouyn-Noranda provided by Natural Resources Canada (courtesy of G. Bonham-Carter, D. Kliza and K. Telmer, GSC). Soluble fractions represent the average of results for 82 snowpack samples for Cu, Zn, Pb and As, 40 for Ni and 77 for Cd.

the IADN (1997) were also used in estimation of regional background. The IADN produces estimates of spatially averaged deposition over the entire area of each of the Great Lakes. This is based on monitoring at a number of stations around each of the lakes. The IADN site located on Burnt Island in Georgian Bay was also selected to use on its own, owing to its significant location --- upwind of Sudbury. Average regional background deposition rates were adjusted for solubility using the regional background soluble metal fractions shown in Table 19. The average values of regional background soluble metal deposition rates have been used in dispersion modelling (Section 2.3.1.2.3) and as benchmarks for empirical deposition data.

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To complement empirical data, dispersion modelling was also used to estimate metal deposition rates near "generic" facilities. The following is a summary of the approach used to estimate deposition rates. The method is described in detail in SENES Consultants (2000).

Existing copper smelters, copper refineries and zinc plants differ in the raw materials processed by each facility, the method used to process the raw materials, the types of control equipment used to limit atmospheric releases of air pollutants (and therefore total amounts of releases), the numbers and types of stacks from which the pollutants are released, and the geographic location in which each facility is located (which determines the dispersion meteorology). Consequently, in one sense, each facility may be considered to represent a relatively unique operation whose impact on the environment will be somewhat different from that of a similar facility in another location. On the other hand, these facilities also represent a limited set of industrial operations whose emissions of trace elements fall within a reasonably well-defined range of emission rates, and whose stack

TABLE 20 Estimation of annual regional background soluble metal deposition for the Canadian Shield

Metal					Average :	unnual total	Average annual total deposition (mg/m <sup>2</sup> /a)	mg/m²/a)					
			0N	OME <sup>1</sup>	- - - -			IADN – Great Lakes <sup>2</sup>	eat Lakes <sup>2</sup>		IADN <sup>3</sup>	Overall	Avg. soluble
	Gerald- ton	Quetico Centre	Moos- onee	Turkey Lakes	Grand Bend	Dorset	Lake Superior	Lake Huron	Lake Erie	Lake Ont.	Burnt Island	avg. (sample std. dev.)	depn. (mg/m²/a)
Cu	0.24	0.38	0.72	2.25	1.16	0.82					1.80	1.05 (0.74)	0.44
Zn	1.4	2.5	6.5	11.9	3.7	3.8					5.6	5.1 (3.5)	3.5
ï	0.08	0.22	0.32	0.61	0.26	0.43					0.84	0.39 (0.26)	0.23
Pb	0.39	0.68	0.79	1.57	0.93	1.08	0.70	1.48	2.40	1.84	1.59	1.22 (0.60)	0.32
Cd	0.03	0.07	0.70	0.30	0.09	0.06	0.21	0.08	0.19	0.09	0.07	0.17 (0.19)	0.13
As				0.10	0.09	0.13	0.18	0.17	0.28	0.19	0.21	0.17 (0.06)	0.14

<sup>1</sup> Data for the OME sites courtesy of B. Kruschel and D. Orr, Environmental Monitoring and Reporting Branch, OME. Due to variations in data availability, values of average annual total deposition for the OME sites have been averaged over between two and eight years, typically five to six years. Best estimates of dry and wet deposition were obtained independently of each other prior to summing. Almost all OME data used were from the period 1989-1995.

<sup>2</sup> Data for the IADN-Great Lakes courtesy of R. Hoff, Atmospheric Environment Service, Environment Canada. Values shown represent the averages from three years of monitoring (1992-1994).

<sup>3</sup> Data for IADN-Burnt Island site courtesy of R. Hoff, Atmospheric Environment Service, Environment Canada (TSP data) and W. Strachan, National Water Research Institute, Environment Canada (wet deposition data). Burnt Island data represent the years 1992-1996.

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characteristics also fall within a known range of heights, diameters, exhaust gas temperatures and velocities. Using these known ranges of emission rates and operating characteristics, it is possible to define both upper and lower bounds for airquality impacts due to these releases. Moreover, by assigning probability density functions to variables that differ between facilities, it is also possible to statistically determine the probability with which a given deposition rate is likely to occur for the given range of emission variables.

In this analysis, differences in emission rates and source release characteristics between facilities were addressed through statistical dispersion modelling for a set of "generic" facilities using a four-step process. First, a representative range of trace element emission rates, particle size distributions and release characteristics were developed to define source characteristics based on data provided by industry representatives for individual facilities. Second, probability distributions were assigned to the ranges of emission rates and release characteristics as suggested by the data provided by industry, and/or using professional judgement where data were unavailable. Third, a dispersion model (CALPUFF) was used to determine unit deposition rates for a discrete number of particle sizes and for a range of source characteristics. Finally, deposition rates were estimated at each receptor grid point downwind of the generic facility by multiplying the unit factors by the set of trace element emission rates and release characteristics. By repeating the last step many times for a randomly selected set of emission rates and source characteristics (referred to as trials), a range of possible deposition rates was calculated at each grid point, and a full set of trials was used to define a probability distribution for deposition rates (i.e., 25th percentile, 50th percentile, etc.).

The dispersion modelling analysis was conducted to a distance of 200 km from the generic facility, using a nested fine grid spacing of 1 km to a 10-km distance from the facility, and a 10-km grid resolution for distances 10-200 km from the facility. The analysis used meteorological data from North Bay, Ontario, averaged for the period 1989-1993. This period included one year (1990) with the highest total precipitation recorded over the Great Lakes region in the 50-year period 1948-1997. Therefore, potential wet deposition would be maximized using the 1990 meteorology. From a climatological perspective, the long-term trend in precipitation over the last 100 years in this region has been toward increasing precipitation levels. The probability of precipitation on any given day has increased for all categories of daily precipitation amounts. Therefore, it was considered appropriate that the extreme abovenormal precipitation for 1990 should be included in the analysis.

Three generic types of facilities were considered in this analysis, specifically:

- 1) a copper smelter,
- 2) a copper refinery, and
- 3) a zinc plant.

In addition to modelling the emissions from these three types of facilities individually, the analysis also considered the impact of combinations of facility types that may be located in close proximity, namely:

- 4) a copper smelter and zinc plant,
- 5) two copper smelters and a copper refinery, and
- 6) a copper smelter, a copper refinery and a zinc plant.

Therefore, the dispersion modelling analysis was conducted for a total of six facility scenarios, including three scenarios where only one type of facility is located at a site, and three scenarios where two or more facilities are located at the same site. The results are not intended to be representative of any existing single facility or combination of facilities. Instead, the results of the analysis represent a statistical merging of various ranges in operating conditions and emission rates to provide ensemble probability frequency distributions of trace metal deposition rates that would be expected to occur for the set



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Metal			Mass emission r	ates (tonnes/yea	ır)	
	Minimum	5th percentile	Median	Mean	95th percentile	Maximum
Copper smelte	ers (6)					
Cu	1.5	3.5	47.5	62.2	136.0	138.3
Zn	2.0	2.3	7.5	30.9	93.9	105.0
Ni	0.2	0.3	1.5	20.9	75.3	91.4
Pb	9.8	11.0	25.0	81.3	289.7	372.8
Cd	0.2	0.3	3.6	3.2	5.9	6.3
As	0.8	0.9	10.8	19.1	48.0	50.3
Copper refine	ries (3)					
Cu	0.001			13.88		27.75
Zn	0.001			0.001		0.001
Ni	0.001			0.014		0.027
Pb	0.001			0.64		1.27
Cd	0.001			0.001		0.001
As	0.001			0.56		1.12
inc plants (4)	)					
Cu	0.001			0.08		0.161
Zn	0.001			53.2		106.4
Ni	0.001			0.007		0.013
Pb	0.06			0.48		0.9
Cd	0.004			0.45		0.9
As	0.001			2.41		4.81

#### TABLE 21 Mass emission rates of trace metals used in dispersion modelling assessment of releases to air from generic facilities <sup>1</sup>

<sup>1</sup> Emission rates, as derived from Table 4, are based largely on NPRI data (NPRI, 1995) with additional information provided by facility operators. Further detail is provided in the text.

of operating conditions and release rates reported for these facilities.

Trace metal emission rates provided by copper smelter operators were generally reported separately for process stacks, low-level sources and total emissions. However, only total emissions were reported for some facilities. Lognormal probability distributions were fit to the total emissions data for those smelter facilities where the process stack and low-level emissions were also reported. Typically, there

was substantial variation in emission rates between the facilities.

The emission rates listed in Table 21 were derived from Table 4. Values listed as not determined (ND) or negligible (neg.) in Table 4 were assigned a nominal value of 0.001 tonnes per year. There were insufficient data on trace metal emissions from copper refineries and zinc plants to compute meaningful statistics for median, 5th percentile and 95th percentile values.



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Metal	High- elevation releases	Low- elevation releases	Fugitive releases
Copper smelters		<u> </u>	
Cu	35-95%	0–60%	5%
Zn	80–95%	0-15%	5%
Ni	45–90%	5–50%	5%
Pb	85-95%	0-10%	5%
Cd	80–95%	0-15%	5%
As	80-95%	0–15%	5%
Copper refineries			
Cu	0%	35-100%	0-65%
Zn	0%	50%	50%
Ni	0%	15-100%	0–15%
РЬ	0%	35–100%	0–65%
Cd	0%	100%	0%
As	0%	99–100%	0–1%
Zinc plants			
Cu	0%	100%	0%
Zn	0%	100%	0%
Ni	0%	100%	0%
Pb	0%	100%	0%
Cd	0%	100%	0%
As	0%	100%	0%

 TABLE 22
 Trace metal release partitioning among high- and low-elevation and fugitive releases to air

The total trace metal emissions were partitioned between high-elevation releases (i.e., stacks over 30 m high), low-elevation releases (stacks less than 30 m high) and fugitive releases, based on the information received from industry representatives. For copper smelters, the total trace metal emissions were increased by 5% to account for fugitive emissions that were not considered in the emission data reported by facility operators. The ranges of reported release rates are listed in Table 22.

Total deposition rates attributable to the facilities were determined at each location based on the simulated emission rates, partitioning between releases, particle size distribution and the modelled atmospheric dispersion. The total deposition rates were summarized across the probabilistic trials. The total soluble deposition rate for each metal was determined by multiplying the deposition from the facility by the average near-field soluble metal fraction (Table 19) and adding this value to the regional background soluble deposition rate (Table 20).

Table 23 shows the maximum distance from each facility type, or combination of facilities, where the 50th or 95th percentile estimates of total soluble deposition rates exceeded the benchmark deposition rate. The benchmark considered was the 25th percentile for critical load (deposition rate), discussed in Section 2.4.1.1.3. For some facilities, the benchmark levels for some trace metals were not exceeded at any distance considered. Note that the benchmark level is not exceeded at all locations closer than the maximum distance reported in the table, since the atmospheric dispersion has directional effects. The total area over which the critical load is exceeded will be less than the area calculated using the maximum distance. Isopleths for soluble Cu deposition in the region of a copper smelter, as estimated by dispersion modelling at the 50th and 95th percentiles, are shown in Figures 2 and 3 respectively.

#### 2.3.1.2.4 Concentrations of metals in ambient air

Data on the concentrations of As, Cd, Cr, Ni and Pb in ambient air were available for a small

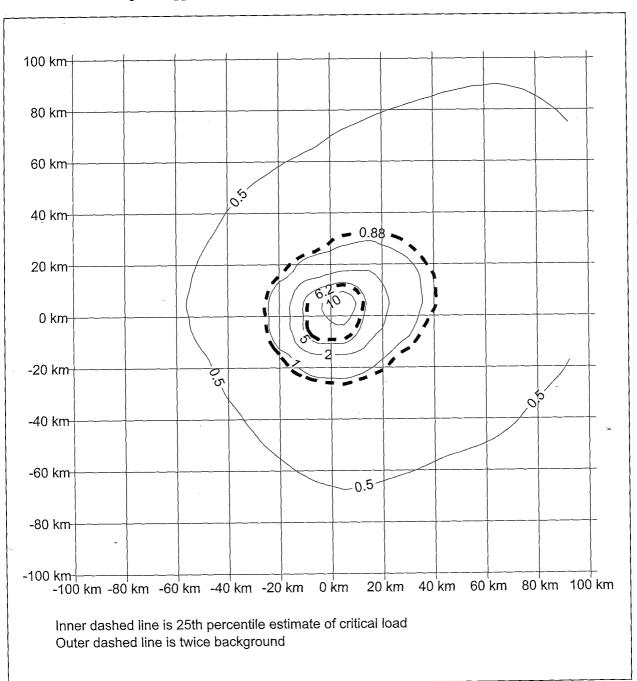
number of monitoring sites near Canadian copper smelters and refineries and zinc plants. In most cases, these were based on TSP collected using high-volume samplers, usually over a 24-hour period once or twice per week, and analysed for some or all of these metals (discussed in Section 2.3.1.2.2). A summary of the data, which were obtained from the companies or from provincial governments, is presented in Table 24. For each combination of site and metal for which data were available, the table includes the arithmetic mean concentration for the most recent representative year, as well as the identity, location and type of site (e.g., residential) and the number of samples. A relatively long averaging period was selected, because the critical effects for each of these metals are associated with longterm exposure. In those cases where there is more than one monitoring site, the mean concentration of the various metals is generally

Facility type	M	laximum dis	tance to whi	ch CL <sub>25</sub> is e	xceeded 1 (k	m)
	Cu	Zn	Ni	Pb	Cd	As
Based on comparison to 50th percentile modelle	d deposition					
Copper smelter	10	n.e.	2	2	4	n.e.
Copper refinery	7	n.e.	n.e.	n.e.	n.e.	n.e.
Zinc plant	n.e.	3	n.e.	n.e.	2	n.e.
Copper smelter and zinc plant	10	4	2	2	5	2
Two copper smelters and a copper refinery	16	2	4	5	7	2
Copper smelter, copper refinery and zinc plant	10	4	2	2	5	2
Based on comparison to 95th percentile modelle	d deposition					
Copper smelter	21	5	10	10	10	6
Copper refinery	10	n.e.	n.e.	n.e.	n.e.	n.e.
Zinc plant	n.e.	7	n.e.	n.e.	4	2
Copper smelter and zinc plant	21	7	10	10	10	6
Two copper smelters and a copper refinery	29	7	10	10	10	8
Copper smelter, copper refinery and zinc plant	21	7	10	10	10	6

TABLE 23	Maximum distance from facility where the modelled total soluble deposition rate exceeds the
	critical load

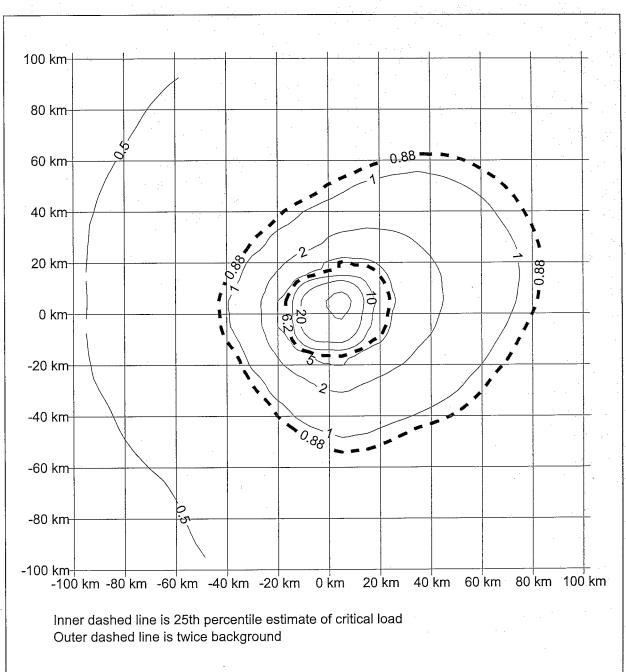
n.e. - Critical load is not exceeded.

<sup>1</sup> Maximum distance at which deposition exceeds the 25th percentile critical load (CL<sub>25</sub>) is based on comparison to the following CL<sub>25</sub>s (mg/m<sup>2</sup>/a): Cu=6.2, Zn=77, Ni=61, Pb=47, Cd=1.6 and As=27. These effects thresholds are discussed in Section 2.4.1.1.3.



# **FIGURE 2** Fiftieth percentile of total soluble deposition rates (mg/m<sup>2</sup>/a) estimated by dispersion modelling for copper emitted from a generic copper smelter

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**FIGURE 3** Ninety-fifth percentile of total soluble deposition rates (mg/m<sup>2</sup>/a) estimated by dispersion modelling for copper emitted from a generic copper smelter

Facility	Year	Site	Distance (km) & direction, site type <sup>1</sup>	Num- ber of sam- ples	Annual arithmetic mean concentration (µg/m <sup>3</sup> )				
					As	Cd	Cr	Ni	Pb
Copper smelters	s								
Noranda-Gaspé	1997	Mines de Gaspé	1.5 E, Rs	55	0.028	0.001	_	_	0.197
Noranda-Horne	1996– 1997	Arena Dave Keon	0.7 S, Rs	59	0.255	0.018	0.006	0.013	1.268
		Laiterie Dallaire	2.9 SW, Rs	58	0.033	0.002	0.005	0.005	0.155
		Hotel de Ville	1.8 S, Rs	46	0.124	0.007	0.006	0.008	0.629
		École Notre Dame	0.8 S, Rs	53	0.180	0.008	_		0.701
		250 6 <sup>ieme</sup> rue	0.3 S, Rs	55	0.589	0.015	_	-	2.339
HBM&S <sup>2</sup>	1996 <sup>3</sup>	Barrow Prov. Bldg.	0.6 E, In/Co	117	0.05	0.04			0.52
		Ruth Betts School	1.1 SE, Rs	115	0.01	0.01	-	_	0.15
		FF Sewage Plant	2.0 SE, Rs	115	0.01	0.01	-	_	0.08
Copper refinerie	25								
Noranda-CCR	1997	Centre Civic Edouard Rivet <sup>4</sup>	0.5 NE, In/Rs	21	0.008	0.000	0.003	0.011	0.034
Zinc plants					·				
Noranda- CEZinc	1998	Boul. Cadieux	1.3 E, Ru	45		0.019	-		_
Combined sourc	es								
Sudbury region <sup>5</sup>	1995– 1997	Edison	F 0.8 W, I 21.6 NE, Rs	120	0.007	0.016	0.011	0.077	0.025
		Pumphouse	F 1.0 SE, I 21.25 NE, In/Rs	121	0.007	0.016	0.011	0.089	0.026
		Federal Bldg. <sup>4</sup>	F 17.6 SW, I 6 NE, Rs/Co	9–57	~	0.00076	0.003	0.046	0.024
		Copper Cliff <sup>4</sup>	F 23.4 SW, I 0.7 W, In/Rs	10–60	0.006	0.0013	0.007	0.151	0.051
Falconbridge- Kidd Creek	1997 *	AMS #1	1.4 NE, In/Ru	61	0.036	0.014	~	~	0.16
		AMS #6	0.6 S, In/Ru	61	0.098	0.038	_	~	0.52
		AMS #7	1.6 E, In/Ru	61	0.029	0.008	_	-	0.09
Cominco-Trail	1998	West Trail	1.4 SE, Rs	59	0.0235	0.0094	_	~	0.261
		Oasis	4.3 NW, Ru/Rs	59	0.0252	0.0084	_		0.234
		Warfield	2.4 W, Rs	59	0.0162	0.0071	_		0.172
		Genelle	12.7 NE, Rs	58	0.0198	0.0070	_	-	0.152
		Glenmerry	3.9 E, Rs	58	0.0349	0.0096	_	_	0.304
		Downtown	0.8 SE, Co	58	0.0247	0.0101	_	_	0.344
		Columbia Gardens	10.5 SE, Ru/In	57	0.0140	0.0117	_	_	0.285
		Northport	19 S, Ru	27	0.0112	0.0061	_	-	0.058

# **TABLE 24**Annual average concentration of As, Cd, Cr, Ni and Pb in ambient air near copper smelters<br/>and refineries and zinc plants in Canada

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### **TABLE 24** Annual average concentration of As, Cd, Cr, Ni and Pb in ambient air near copper smelters and refineries and zinc plants in Canada (continued)

Facility	Year	Site	Distance (km) & direction, site type <sup>1</sup>	Num- ber of sam- ples	Annual arithmetic mean concentration (µg/m <sup>3</sup> )					
					As	Cd	Cr	Ni	Pb	
"Background"		Sites removed from point sources (both remote and anthropogenically influenced) in the Canadian Shield (OME sites) and Great Lakes (IADN sites) – these are the same sites used to estimate "background" soluble deposition (Table 20)		averaged over several years	0.00062 ± 0.00028 <sup>6</sup>	0.00026 ± 0.00023	-	0.00069 ± 0.00077	0.00402 ± 0.00419	

<sup>1</sup> Site types: Rs=residential, Ru=rural, Co=commercial, In=industrial.

- <sup>2</sup> Although it includes both a copper smelter and a zinc plant, HBM&S has been included with copper smelters, since, due to the process used, releases to air from the zinc plant are negligible.
- <sup>3</sup> After mid-1997, sampling was conducted only when the wind was blowing in the general direction of the monitoring stations; consequently, data collected after this point in time were not included, because they were not considered to be representative of potential exposure over the entire year.
- <sup>4</sup> The values presented for these sites were measured for the  $PM_{10}$  fraction, whereas the values at all other sites were determined on TSP.
- <sup>5</sup> For the Sudbury region, site locations are reported with respect to both the Falconbridge (F) and Inco (I) facilities.
- <sup>6</sup> Values presented are grand mean ± standard deviation across a number of sites (i.e., between 7 and 11) for each metal.
- Note: In calculating the summary statistics for each site, a value of one-half of the detection limit was assumed, wherever possible, for those samples that did not contain detectable levels. However, it was sometimes necessary to use the data as provided by the companies, and there was some inconsistency in the values that they assumed for samples that did not contain detectable levels of metals. Analyses in which the assumed values for such samples were varied systematically (as zero, half the detection limit, and the detection limit) indicated that the effect of this assumption was minimal except when the concentrations of the metals were relatively low.

increased, sometimes quite markedly (i.e., by two or three orders of magnitude), at those sites nearest the facility. Further, the mean airborne concentration of each of the metals near the copper smelters and refineries and zinc plants is consistently and substantially higher than regional background levels measured in areas of the Canadian Shield and the Great Lakes removed from point sources, although there is considerable variation among the facilities in the degree to which concentrations are increased.

### 2.3.1.3 Particulate matter

### 2.3.1.3.1 Fate of particulate matter in air

The diameter of PM released to the atmosphere from copper smelters and refineries and zinc plants can range from  $<1.0 \mu m$  up to about 20  $\mu m$ .

The following paragraphs, describing the fate of PM in the atmosphere, are largely summarized from EC/HC (2000a).

Particulate matter is generally subdivided into a fine fraction of particles 2.5  $\mu$ m or less (PM<sub>2.5</sub>) and a coarse fraction of particles larger than 2.5  $\mu$ m. PM may be "primary" (emitted directly into the atmosphere) or "secondary" (formed in the atmosphere through chemical and physical transformations). The principal gases involved in secondary particulate formation are generally SO<sub>2</sub>, nitrogen oxides, VOCs and ammonia. Primary particles are present in both the fine and coarse fractions, whereas secondary particles, such as sulphates and nitrates, are present predominantly in the fine fraction. Particulate matter may include a broad range of chemical species, including elemental carbon and



organic carbon compounds; oxides of silicon, aluminum and iron; trace metals; sulphates; nitrates; and ammonia.

Particle size is considered to be one of the most relevant parameters in characterizing the physical behaviour of PM in the atmosphere. Extremely small ("ultrafine") particles less than 0.1 µm in diameter (the nuclei mode) are formed primarily from the condensation of hot vapours during high-temperature combustion processes and from the nucleation of atmospheric species to form new particles. While the greatest concentration of airborne particles is found in the nuclei mode, these particles contribute little to overall particle mass loading due to their tiny size. They are subject to random motion and to coagulation processes in which particles collide to quickly yield larger particles. Consequently, these tiny particles have short atmospheric residence times.

Particles in the size range of  $0.1-2.0 \,\mu m$ (the accumulation mode) result from the coagulation of particles in the nuclei mode and from the condensation of vapours onto existing particles, which then grow into this size range. These particles typically account for most of the particle surface area and much of the particle mass in the atmosphere. The accumulation mode is so named since atmospheric removal processes are least efficient in this size range. These fine particles can remain in the atmosphere for days to weeks. Dry deposition and precipitation scavenging are the primary processes by which these fine particles are eventually removed from the atmosphere. It is calculated that precipitation scavenging accounts for about 80-90% of the mass of particles in the accumulation mode removed from the atmosphere (Wallace and Hobbs, 1977).

Particles larger than 2.0  $\mu$ m (the sedimentation or coarse mode) are typically associated with mechanical processes, such as wind erosion and grinding operations. Grinding operations result in the physical breakdown of larger particles into smaller ones to yield particles such as wind-blown soil and dust from

quarrying operations. These particles are efficiently removed by gravitational settling and therefore remain in the atmosphere for shorter periods of a few hours to a few days. They contribute little to particle number concentrations but significantly to total particle mass. While particles resulting from metal smelting are usually relatively small, recent studies have identified spherules larger than 2.0  $\mu$ m that are believed to be of pyrometallurgical origin (Kliza *et al.*, 2000).

### 2.3.1.3.2 Concentrations of particulate matter in ambient air

Data on the levels of PM in ambient air were available for a small number of monitoring sites near each of the Canadian copper smelters and refineries and zinc plants. A summary of the data, which were obtained from the companies and, in some instances, from the provinces, is presented in Table 25. For each site, the table includes summary statistics for concentrations of PM, including the arithmetic mean, standard deviation, minimum and maximum, and various percentiles, as well as the identity, location and type of site (e.g., residential).

In most cases, the data obtained were for TSP collected using high-volume samplers and measured gravimetrically (although respirable fractions [PM<sub>10</sub> and PM<sub>2.5</sub>] were determined near a few of the facilities). Because the health impacts of PM have been most extensively quantified based on the respirable fraction, the TSP concentrations were converted to estimated  $\mathrm{PM}_{\mathrm{10}}$  concentrations using the following regression:  $PM_{10} = 10^{(0.826 \times \log TSP)}$ . This equation was derived based on monitoring of TSP and PM<sub>10</sub> at 14 urban sites across Canada in the NAPS network between 1986 and 1994 (WGAQOG, 1999). The use of this approach to estimate PM<sub>10</sub> concentrations near the facilities is supported by the results of parallel surveys of TSP and PM<sub>10</sub> near the HBM&S copper smelter and zinc plant in Flin Flon and the Cominco lead-zinc smelter in Trail, supplied by the companies in response to requests for data on levels of PM in ambient air. In monitoring

Facility	Year	Site	Distance (km) & direction	Number	Annual Arith	Std. dev	Min.		Conce	Concentrations at the Nth percentile	is at the l	Nth perc	entile		Max.
			site type <sup>1</sup>	samples	mean			10	30	50	70	96	95	66	
<b>Copper smelters</b>															
Noranda-Gaspé	1997	Mines Gaspé	1.5 E, Rs	55	16.5	9.0	2.3	7.1	11.8	15.1	18.5	27.6	33.0	44.5	49.6
Noranda-Horne	1997	Arena Dave Keon	0.7 S, Rs	59	16.4	8.1	6.1	7.7	11.0	14.8	17.3	28.8	32.4	37.8	42.0
		Laiterie Dallaire	2.9 SW, Rs	58	17.90	9.7	7.1	8.7	11.6	15.2	20.3	31.7	40.1	44.7	48.0
		Hotel de Ville	1.8 S. Rs	46	19.1	12.0	1.5	7.9	10.8	15.5	24.0	35.3	42.7	49.8	51.3
		Ecole Notre Dame	0.8 S. Rs	54	16.1	9.9	4.4	6.7	10.3	13.1	18.4	31.1	34.8	45.1	50.4
		250 6 <sup>ieme</sup> rue	0.3 S. Rs	55	27.4	18.3	5.6	9.4	19.3	23.6	30.5	49.0	58.7	84.6	105.0
HBM&S <sup>2,3</sup>	1996-	Barrow Prov. Bldg.	0.6 E, In/Co	59	30.1	23.7	2	8.8	16	24	35	59.8	72.2	108.6	122
	- 844I	Ruth Betts School	1.1 SE, Rs	35	11.4	6.6	2.2	5.2	<i>T.T</i>	9.5	13.5	19.0	23.4	30.5	30.6
		FF Sewage Plant	2.0 SE, Rs	35	8.8	7.3	2.6	3.5	5.4	7.7	9.5	12.4	16.9	36.9	43.1
		Creighton School	1.9 SW, Co/Rs	16	16.3	8.9	3.6	7.6	11.0	14.3	19.5	26.7	30.2	40.0	65.2
<b>Copper refineries</b>	s														
Noranda-CCR	1996 4	Centre Civic Edouard Rivet	0.5 NE, In/Rs	28	6.0	2.8	2.7	3.5	3.9	5.0	7.3	9.9	11.4	12.8	13.3
Zinc plants															
Noranda-CEZinc	1998	Boul. Cadieux	1.3 E, Ru	45	21.5	12.9	3.3	7.8	13.3	18.4	26.0	39.2	48.7	51.6	53.7
<b>Combined sourcs</b>	s														
Sudbury region <sup>5</sup>	1995– 1997	Edison	F 0.8 W, I 21.6 NE, Rs	120	13.4	9.8	-	4.4	6.9	11.4	15.2	25.8	35.4	45.6	50.0
		Pumphouse	F 1.0 SE, I 21.25 NE, In/Rs	120	12.4	8.4	-	4.5	7.2	9.9	14.9	22	26.9	42.2	49.0
		Federal Bldg. <sup>4</sup>	I 6 NE, F 17.6 SW, Rs/Co	57	13.8	6.4	ŝ	7.6	6	13	16	22.4	24.4	33.3	35
		Nickel St., Sudbury <sup>4</sup>	F 23.4 SW, I 0.7 W, In/Rs	60	14.4	7.6	ç	6	9.7	13	17.3	24	27.2	34.6	37
Falconbridge-	1997	AMS # 1	1.4 NE, In/Ru	61	12.8	8.2	2.1	3.6	8.2	11.3	14.9	24.6	30.9	33.4	33.8
Kidd Creek		AMS # 6	0.6 S, In/Ru	61	23.6	18.1	2.3	6.9	14.8	20.3	25.6	43.2	48.1	80.6	123.9
		AMS # 7	1.6 E, In/Ru	61	13.7	6.6	0.7	7.9	9.1	12.2	16.6	21.9	26.0	32.0	37.5

**TABLE 25** Summary of estimated or measured concentrations of PM<sub>10</sub> (µg/m<sup>3</sup>) near copper smelters and refineries and zinc plants in Canada

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of estimated (continued)	d or measured concentrations of PM <sub>10</sub> (µg/m <sup>3</sup> ) near copper smelters and refineries and zinc plants in	
	of estimated (	(continued)
	<b>TABLE 25</b>	

Facility	Year	Site	Distance (km) & direction	Number of	Annual	Std.	Min.	1	Conce	Intration	is at the	Concentrations at the Nth percentile	entile		Max.
			site type <sup>1</sup>	samples	mean		L	10	30	50	70	96	95	66	
Cominco-Trail	1998	West Trail 4	1.4 SE, Rs	61	18.9	12.3	1.9	7.6	13.9	17.2	20.9	30.7	39.2	65.8	73.4
		Oasis <sup>4</sup>	4.3 NW, Ru/Rs	61	16.4	10.1	3.1	6.7	12.0	15.3	17.7	26.1	35.4	55.2	58.6
		Warfield	2.4 W, Rs	59	16.8	8.4	0.7	7.6	12.3	15.9	20.3	29.2	34.1	38	38.2
		Genelle <sup>4</sup>	12.7 NE, Rs	58	14.0	7.0	0	6.2	12.4	14.3	17.3	20.4	21.8	34.1	44.7
		Glenmerry	3.9 E, Rs	60	16.9	8.7	3.3	7.6	11.5	14.8	20.7	27.8	34.5	39.9	42.2
		Downtown	0.8 SE, Co	60	16.6	8.8	4.6	6.6	11.8	14.9	19.9	26.9	33.2	45.4	46.6
		Columbia Gardens	10.5 SE, Ru/In	59	16.7	7.8	2.1	6.6	11.7	16.1	20	26.8	30.6	36.4	37.9
		Northport <sup>4</sup>	19 S, Ru	29	16.4	14.1	0.6	4.1	LL	10.6	21.0	35.1	38.7	63.6	69.6

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<sup>1</sup> Site types: Rs=residential, Ru=rural, Co=commercial, In=industrial.

<sup>2</sup> Although it includes both a copper smelter and a zinc plant, HBM&S has been included with copper smelters, since, due to the process used, releases of particulate metals and SO<sub>2</sub> from the zinc plant are negligible. <sup>3</sup> After mid-1997, sampling was conducted only when the wind was blowing in the general directions of the monitoring stations and the town; consequently, data collected after this point in time were not included, because they were not considered to be representative of potential exposure over the entire year.

<sup>4</sup> Measured PM<sub>10</sub> values. For other sites, the PM<sub>10</sub> values were estimated from the concentrations of TSP, using the regression PM<sub>10</sub> = 10<sup>(0.326×10gTSP)</sup> (WGAQOG, 1999).

<sup>5</sup> For the Sudbury region, site locations are reported with respect to both the Falconbridge (F) and Inco (I) facilities.

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conducted at three locations over 10 months in 1998 in Flin Flon, the mean ratio of the measured  $PM_{10}$  to that estimated from TSP using the above regression was 1.04, 1.13 and 1.15, respectively, and was 1.11 overall. The corresponding ratios of the annual mean for 1998 at four sites in Trail were 1.38, 1.33, 0.81 and 1.18, with an overall mean ratio of 1.18.

Based on the data summarized in Table 25, in those cases where there was more than one monitoring site, the ambient concentrations of PM were generally increased the most at those sites nearest the facility. Further, the mean concentrations near most of the facilities were elevated above the background levels measured at remote sites in North America, which averaged between approximately 4 and 11  $\mu$ g/m<sup>3</sup> (WGAQOG, 1999). However, the impact of the copper smelters and refineries and zinc plants on ambient levels of PM was not as marked as for the metals (Section 2.3.1.2.4) or for SO<sub>2</sub> (Section 2.3.1.1.2), likely because of the wider variety of sources from which PM originates.

## 2.3.2 Releases to water

#### 2.3.2.1 Fate and concentrations

Information on the fate and environmental concentrations resulting from direct release to water from CCR, CEZinc and CTO is summarized below. Further details are provided in Beak International (1999).

The concentrations of chemicals released into a river environment may be as high as the concentrations in effluent at the end-of-pipe, but then decrease in a downstream direction along the centreline of the plume. This is associated with the widening or lateral dispersion of the plume. At any point downstream, concentrations decline with lateral distance away from the plume centreline. Eventually, a point may be reached where the effluent is fully mixed with river water (hence, there is no further dilution unless the river flow is augmented) or the chemical concentrations arising from the effluent are small in relation to natural background concentrations and hence of little biological significance.

Chemical concentrations in the effluent have been summarized in Table 9 for each of the three facilities. In addition, the proportion of chemical dissolved or adsorbed is indicated for each effluent.

The spatial pattern of chemical concentrations arising from the discharge must be considered, in conjunction with the movements of receptor species, to determine the chemical exposure concentrations experienced by these organisms. Since recent monitoring data were not available, plume models were developed in these assessments for releases from each of the operations. Based on these models, the expected patterns of relevant chemical concentrations in the receiving water and sediment were defined.

Estimated Exposure Values (EEVs) for fish are calculated in these assessments using a conservative spatial averaging approach, consistent with Environment Canada (1997a) guidance for Tier II exposure assessments. The fish is assumed to reside in the plume, with a home range immediately downstream of the outfall. Thus, a realistic worst-case spatially averaged EEV is determined. It is likely that only larger fish (200-300 mm in length) would be able to maintain position for prolonged periods in a 1 m/s current, and thus be resident in the plume. Thus, based on Minns (1995), a home range on the order of 10 000 m<sup>2</sup> is conservative for lake species. A smaller home range on the order of 1000 m<sup>2</sup> may be more appropriate for stream and creek species; however, fish in large rivers may be closer to the lake model. The smaller home range area was utilized for spatial averaging to calculate an upper-limit EEV.

EEVs for pelagic invertebrates are calculated in these assessments by assuming that the organisms drift along the plume centreline at the same velocity as the receiving water. As they travel, they experience declining concentrations until they reach the point downstream where the plume is no longer discernible from background. For the high-velocity receiving waters considered here, a 10-km trip takes only 3–4 hours. Most of the exposure above background occurs within the first few kilometres (i.e., within 1 hour). Thus, a reasonable maximum spatially averaged EEV is obtained by averaging exposure concentrations over a 1-km (20-minute) trip down the plume centreline.

EEVs for benthic invertebrates are calculated in these assessments as point concentrations at locations where habitat is generally suitable to support a benthic community. Spatial averaging is not appropriate, since movements of benthic invertebrates are extremely limited.

#### 2.3.2.1.1 Canadian Copper Refinery

A screening-level model (Sayre, 1973; NCRP, 1996) was used to define the spatial pattern of metal concentrations in the St. Lawrence River arising from the MUC-WWTP effluent. The CCR facility contributes to this effluent as outlined in Table 7. The model gives the concentration of any chemical constituent arising from the discharge, at any point in the river downstream, based on advection and symmetric lateral dispersion processes.

This model assumes vertical mixing, which is typically complete within a downstream distance of 7\*depth, or in this case about 50 m. It assumes that shoreline effects are negligible, as appropriate for the mid-river outfall of the MUC-WWTP. It also ignores any jetting or turbulent mixing that may occur in the immediate proximity of the outfall.

The lateral dispersion coefficient was 0.06\*depth\*velocity. A mid-river depth of 7 m and a velocity of 0.81 m/s were utilized in the model, based on cross-sectional area and flow information provided by Hudon and Sylvestre (1998). Using these input parameters and the chemical loadings for the MUC-WWTP for 1995 shown in Table 7, resulting chemical concentrations in water were estimated for the downstream St. Lawrence River. For each metal,

the maximum concentration in the plume is the concentration in the effluent that can be seen in the first few metres downstream of the outfall. The concentration declines with further distance down the plume centreline, rapidly at first and then more slowly.

The concentration of metal dissolved in water (i.e., not adsorbed on suspended solids) was computed at each point in the plume using a sorption model, as follows:

$$C_{diss} = C_{tot} / (1 + K_d * 10 * C_{ss} \times 10^{-6})$$

where:

- $C_{diss}$  = dissolved metal concentration (mg/L),
- $C_{tot}$  = total metal concentration (mg/L),
- $C_{ss}$  = suspended solids concentration (mg/L), and
- $K_d$  = distribution coefficient for soils (L/kg).

The  $K_d$  is increased by a factor of 10 to represent adsorption in aqueous systems, which is typically greater than that in consolidated soil (O'Conner and Connelly, 1980). Values of soil  $K_d$ were taken from Sheppard et al. (1992, 1999), except for Hg, where an aqueous value from Birge et al. (1987b) was used directly without adjustment. There is typically order of magnitude uncertainty in K<sub>d</sub> values. Suspended solids were considered to show the same pattern of spatial dispersion described above for metals, declining from an initial concentration in MUC-WWTP effluent (36 mg/L) to a Lac St. Louis background value of 4 mg/L (Rondeau, 1993). The dissolved metal concentrations computed in this manner are only slightly below the total metal concentrations, with the greatest differences near the outfall where suspended solids concentrations are highest.

The metal concentrations in newly formed sediments that might arise at each point in the plume were computed from the difference between dissolved and total metal concentrations, as follows:

$$C_{sed} = (C_{tot} - C_{diss}) * 10^6 / C_{ss}$$



where:

- C<sub>sed</sub> = metal concentration in sediment (mg/kg),
- C<sub>tot</sub> = total metal concentration in water (mg/L),
- C<sub>diss</sub> = dissolved metal concentration in water (mg/L), and
- C<sub>ss</sub> = suspended solids concentration in water (mg/L).

Whether sediments will actually settle out at a particular point depends upon the water velocity profile and particle size of solids. In this assessment, the location of areas likely to receive sedimentation is a matter of professional judgement, based on locations of embayments and backwaters in contact with the plume.

Similar calculations of concentrations of metals dissolved in water and deposited in newly formed sediments were performed using Lac St. Louis background concentrations in water (Rondeau, 1993) as a starting point. Regional background concentrations were then added to the incremental concentrations arising from the discharge (above) in order to estimate the overall concentrations experienced by aquatic biota at any point.

Based on these calculations and spatial averaging calculations for the mobile receptor species, as described above, the modelled annual average EEVs for different receptors exposed to available metals in the vicinity of the MUC-WWTP are listed in Table 26. The dissolved portion of metals in water ( $C_{diss}$ ) was considered to be available for fish, pelagic invertebrates and epibenthos, while the metal adsorbed to sediment ( $C_{sed}$ ) was considered potentially available to infaunal benthic organisms. The percentage of each exposure attributable to CCR, rather than regional background or various other municipal/ industrial users of the MUC-WWTP, is shown in parentheses.

TABLE 26	Modelled annual average exposure concentrations for 1995 effluent discharges from the
	MUC-WWTP, and the percentage of each concentration attributable to CCR

Release	Ann	ual average e	xposure conce	entration (pe	rcentage attri	butable to CC	R in parenthe	ses)
component	Fis (µg		Zooplar (µg			epifauna <sup>3</sup> g/L)	Benthic-i (mg	
Cu	<b>7.14</b> <sup>5</sup>	(1.18)	4.55	(1.05)	3.03	(0.89)	6.366	(0.89)
Ni	2.79	(0.64)	2.06	(0.36)	1.65	(0.36)	4.945	(0.36)
Pb	1.03	(0.22)	0.71	(0.18)	0.54	(0.14)	2.229	(0.14)
Cd	0.20	(0.04)	0.16	(0.03)	0.13	(0.02)	0.2092	(0.02)
As	0.79	(2.42)	0.71	(1.54)	0.66	(0.93)	1.32	(0.93)
Cr	2.45	(0.07)	1.83	(0.06)	1.44	(0.04)	0.4320	(0.04)
Se	0.73	(73.1)	0.50	(60.9)	0.38	(48.6)	1.909	(48.6)
Ag	<b>0.59</b> <sup>5</sup>	(0.23)	<b>0.36</b> <sup>5</sup>	(0.22)	0.22	(0.20)	0.2632	(0.20)

<sup>1</sup> Spatial average for fish resident in plume with  $30 \times 40$  m home range (average = 0.21\*maximum plume concentration).

<sup>2</sup> Time average for zooplankton drift down centre of plume for 1000 m (average = 0.12\*maximum plume concentration).

<sup>3</sup> Point concentration on plume centreline 1000 m from outfall.

<sup>4</sup> Point concentration in sediment on plume centreline 1000 m from outfall.

<sup>5</sup> Exceeds corresponding ENEV (Table 35).

## 2.3.2.1.2 Canadian Electrolytic Zinc

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Empirical data from a 1990 plume study were utilized to develop a near-field descriptive model of the effluent dilution pattern at the CEZinc UNA effluent discharge to the Beauharnois Canal. The data included Zn and Se measurements on a series of transects across the UNA plume. Selenium was the best tracer of the plume, since concentrations were well above background in the receiving water.

The data show concentrations that are highest near the outfall (about 10 m out from the bank) and declining in both downstream and lateral directions. The plume is not vertically mixed at the outfall (higher concentrations at depth) but is vertically mixed within 50 m. It was distinguishable above background at the time of the study to a maximum distance of a few hundred metres. The descriptive model reflects this pattern, with exponential decline from the outfall concentration in both lateral and downstream directions.

The Se loading at the time of this study was approximately 600 mg/s (52 kg/d). In order to generalize the model to accommodate different loadings for different chemicals and for the present-day combined effluent, the Se dilution model was multiplied by a loading ratio (new loading/600 mg/s). This has the effect of increasing or decreasing the plume concentrations and the extent of the plume above background as loadings are increased or decreased. However, the underlying plume shape (i.e., degree of change with distance) is assumed not to change with loading.

This purely descriptive near-field model does not conserve mass when extended in the downstream direction. Therefore, an alternate model is needed for the far-field region. A screening-level model for nearshore discharge (Sayre, 1973; NCRP, 1996) was used to define the far-field spatial pattern of chemical concentrations arising from the CEZinc combined effluent. A 10-km setback distance was used to achieve the observed lateral dispersion at the downstream edge of the near-field region. The model gives the concentration of any chemical arising from the discharge at any point in the Beauharnois Canal downstream, based on advection and one-sided lateral dispersion processes.

The lateral dispersion coefficient was 0.06\*depth\*velocity. An average depth of 5 m for the nearshore canal and a velocity of 0.5 m/s were utilized in the far-field model, based on cross-sectional areas from hydrographic charts and flow information provided by CEZinc (personal communication with facility operators). The depth and velocity are greater further out from shore (e.g., 7.5 m and 0.74 m/s). The flow data used were consistent with Hudon and Sylvestre (1998).

Using these models and input parameters and the maximum monthly or annual average loadings for 1995 from CEZinc (Tables 7 and 8), resulting chemical concentrations in water were estimated for the Beauharnois Canal downstream from CEZinc. For each chemical, the maximum concentration in the plume is the concentration in the effluent that can be seen in the first few metres downstream of the outfall. The concentration declines with further distance down the plume centreline (i.e., near the bank), rapidly at first and then more slowly.

At each point in the plume, the concentrations of metals dissolved in water (i.e., not adsorbed on suspended solids) and the concentrations in the solids that may contribute to newly formed sediments were computed as described in the preceding section. Ammonia was considered to be entirely dissolved (i.e., none adsorbed) and was not partitioned to sediments.

Similar calculations of concentrations of chemicals dissolved in water and deposited in newly formed sediments were performed using Lac St. Francis background concentrations in water (Rondeau, 1993) as a starting point. Regional background concentrations were then added to the incremental concentrations arising from the discharge (above) in order to estimate the overall concentrations experienced by aquatic biota at any point.

Based on these calculations and spatial averaging calculations for the mobile receptor species as described above, the modelled maximum short-term EEVs for different receptors exposed to metals in the vicinity of CEZinc are listed in Table 27. The percentage of each exposure attributable to CEZinc, rather than regional background, is shown in parentheses. Maximum short-term EEVs could not be estimated for Pb or ammonia, as data were not available to determine the factors for estimation of short-term loading rates from annual mean loading rates (see Tables 7-9). Exposure concentrations (µg/L) based on annual average loadings are, for Pb and ammonia respectively, 1.26 and 157 for fish, 0.46 and 16.8 for zooplankton, 0.41 and 7.99 for benthic-epifauna, and (in mg/kg) 1.70 and 0 for benthic-infauna.

## 2.3.2.1.3 Cominco-Trail Operations

Empirical data from a 1997 plume study (Frew, 1997) were utilized to develop a near-field descriptive model of the effluent dilution pattern at the C-III discharge from CTO to the Columbia River. The study was performed under low river flow conditions. The data included thallium (Tl) and other metal measurements across the plume at various points downstream, as well as photographs of dye dispersion. Thallium is a suitable tracer of the plume, since background river concentrations are low and Tl is mainly in dissolved form.

The Tl data show concentrations that are distinguishable above background for at least several kilometres downstream. The dye dispersion indicates initially rapid lateral mixing (in the channel behind an island where the discharge occurs) followed by slower lateral mixing. The descriptive model reflects this pattern, with exponential decline from the outfall concentration in both lateral and downstream directions.

TABLE 27	Modelled maximum short-term exposure concentrations for 1995 effluent discharges from
	CEZinc, and the percentage of each concentration attributable to CEZinc

Release	Maxim	um sho <mark>r</mark> t-ter	m exposure co	oncentration	(percent attril	butable to CE	Zinc in parent	heses)
component	Fis (µg		Zoopla (µg			epifauna <sup>3</sup> g/L)	Benthic-in (mg/	
Cu	7.73 5	(85.8)	1.61	(32.0)	1.21	(9.62)	2.545	(9.62)
Zn 7	41.10	(82.4)	14.56 *	(50.5)	7.82	(7.78)	101.7	(7.78)
Cd	0.32	(68.9)	0.12	(14.7)	0.10	(3.74)	0.1656	(3.74)
Hg	0.096	(89.7)	0.017	(40.3)	0.011	(13.4)	0.0796	(13.4)
Se	<b>49.06</b> <sup>5</sup>	(99.6)	3.99	(95.0)	1.06	(81.3)	5.308	(81.3)

Spatial average for fish resident in plume with  $40 \times 40$  m home range (average = 0.4\*maximum plume concentration) — maximum monthly average loading.

<sup>2</sup> Time average for zooplankton drift down centre of plume for 1000 m (average = 0.031\*maximum plume concentration) — maximum monthly average loading, except for Zn.

<sup>3</sup> Point concentration on plume centreline 1000 m from outfall — maximum monthly average loading.

<sup>4</sup> Point concentration in sediment on plume centreline 1000 m from outfall — maximum monthly average loading.

<sup>5</sup> Exceeds corresponding ENEV (Table 35).

<sup>6</sup> Based on maximum 4-day average loading.

<sup>7</sup> Zinc concentrations reflect the portion of loading dissolved or adsorbed at source.

The Tl loading at the time of this study was 172 mg/s (15 kg/d). To represent different loadings for different chemicals, the Tl dilution model was multiplied by a loading ratio (new loading/172 mg/s). This is the same approach that was used for the near-field portion of the CEZinc plume.

The same descriptive model was used to describe the near-field plume from the C-II outfall 0.8 km downstream. Concentrations rising from the two outfalls were added to estimate the combined concentrations at near-field locations further downstream.

For locations beyond several kilometres downstream from the C-III outfall, a far-field model was utilized, as previously described for CEZinc. A combined C-II + C-III loading was used, with a 90-km setback to achieve the observed lateral dispersion at the downstream edge of the near-field region. The lateral dispersion coefficient was 0.12\*depth\*velocity. A depth of 3 m and a velocity of 1 m/s were used, based on hydrological data from Aquametrix (1994) and MES (1997).

Using these models and input parameters and the maximum monthly or annual average chemical loadings from the zinc operations at Trail for 1998 (Tables 7 and 8), chemical concentrations in the downstream waters and newly formed sediments of the Columbia River were estimated, as previously described for CEZinc and CCR. The estimated maximum concentration in the plume (1 m from outfall) is approximately 1/25 of the effluent concentration. The concentration declines slowly with further distance down the plume centreline. The concentration increases again for some metals (particularly Zn) at the point where the C-II discharge joins the C-III plume, then continues to decline.

At each point in the plume, the concentrations of metals dissolved in water (i.e., not adsorbed on suspended solids) and the concentrations in solids that may contribute to newly formed sediments were computed as previously described for CEZinc and CCR. Ammonia was considered to be entirely dissolved (i.e., none adsorbed) and was not partitioned to sediments.

Similar calculations of concentrations of chemicals dissolved in water and deposited in newly formed sediments were performed using Birchbank background concentrations in water (MES, 1997), supplemented to account for the influence of the C-IV outfall and Stoney Creek just upstream of the C-III outfall, as a starting point. Birchbank is located about 3 km upstream of C-IV and Stoney Creek. These regional "background" concentrations were then added to the incremental concentrations arising from the CTO zinc operations (above) in order to estimate the overall concentrations experienced by aquatic biota at any point.

Based on these calculations and spatial averaging calculations for the mobile receptor species as described above, the modelled maximum short-term EEVs for different receptors exposed to metals, ammonia and fluoride in the vicinity of CTO are listed in Table 28. The proportion of each exposure attributable to CTO zinc operations, rather than regional background or lead operations or fertilizer operations, is shown in parentheses.

# 2.4 Effects characterization

## 2.4.1 Ecotoxicology

This section presents information on the effects of various release constituents on sensitive species of relevance to Canada. Effects information is summarized either as CTVs and ENEVs, expressed as concentrations in an exposure medium, or as critical loads. ENEVs and CTVs are, respectively, estimates of the upper limit of no effect and of low toxic effect concentrations. CTVs are derived from studies of toxic effects to relevant sensitive laboratory organisms (e.g., reduced reproduction in *Daphnia*). These laboratory effects data are the "measurement endpoints" for the assessment.  

 TABLE 28
 Modelled maximum short-term exposure concentrations for 1998 effluent discharges from Cominco-Trail, and the percentage of each concentration attributable to Cominco-Trail zinc operations

Release	Maxim	um short-te	rm exposure co	ncentration	(percentage att	ributable to	CTO in parent	heses)	
component	Fis (µg		Zoopla (µg		Benthic-ej (µg/		Benthic-i (mg/		
Cu <sup>6</sup>	1.66	(18.8)	1.65	(18.4)	1.65	(18.3)	3.47	(18.3)	
Zn <sup>6</sup>	44.44	(74.5)	44.3	(74.4)	36.5	(70.4)	<b>474</b> <sup>5</sup>	(70.4)	
Pb 6	2.30	(54.1)	2.57	(56.4)	2.72	(57.5)	11.15	(57.5)	
Cd 6	<b>3.08</b> <sup>5</sup>	(5.67)	3.20	(7.76)	<b>3.17</b> <sup>5</sup>	(7.40)	<b>5.08</b> <sup>5</sup>	(7.40)	
As 6	3.89	(18.3)	4.45	(25.6)	3.40	(10.1)	<b>6.81</b> <sup>5</sup>	(10.1)	
Hg	0.087	(57.7)	0.11	(61.1)	0.065	(52.0)	<b>0.46</b> <sup>5</sup>	(52.0)	
Tl 6	<b>67.9</b> <sup>5</sup>	(93.7)	21.2	(92.9)	2.27	(84.2)	33.6	(84.2)	
Ammonia	61.83	(50.7)	57.7	(49.0)	32.62	(29.8)	0	(0)	
Fluoride	172.7	(45.6)	150.0	(39.7)	108.7	(22.5)	0	(0)	

<sup>1</sup> Spatial average for fish resident in plume with 40 × 40 m home range (average = 0.88\*maximum plume concentration) — maximum monthly average loading.

- <sup>2</sup> Time average for zooplankton drift down centre of plume for 1000 m (average = 0.45\*maximum plume concentration) maximum 4-day average loading.
- <sup>3</sup> Point concentration on plume centreline 1000 m from outfall maximum monthly average loading.
- <sup>4</sup> Point concentration in sediment on plume centreline 1000 m from outfall maximum monthly average loading.

<sup>5</sup> Exceeds corresponding ENEV (Table 35).

<sup>6</sup> Metal concentrations reflect the portion of loading dissolved or adsorbed at source.

ENEVS are derived from CTVs — by dividing by an appropriate application factor (e.g., 10) and are intended to represent effect thresholds for receptors in the field. The critical effects of concern in the field (e.g., adverse reproductive effects on sensitive aquatic invertebrates) are the "assessment endpoints."

In these assessments, the critical effects of concern are harm to sensitive aquatic organisms (fish, invertebrates and plants) and soil-dwelling organisms (plants and decomposers). Although effects on wildlife were not examined, it was concluded in a recent review document (Welbourn, 1996) that there is very little evidence, based on the limited available data, that releases from copper smelters and refineries and zinc plants are causing adverse effects on wildlife under present conditions.

Critical loads may be defined as the amount of deposition required for contaminant levels to reach threshold effect values (e.g., ENEVs) in receiving media. These loads were calculated using transport and fate models as described below. For the assessment of the effects of metals released to the atmosphere, the conditions assumed in the modelled receiving media (i.e., sandy acidic soils and circumneutral to somewhat acidic lakes) were typical of those on the southern Canadian Shield. These assumptions were made because most of the metal production plants included in these assessments are located on the Shield. Furthermore, receiving media with properties similar to those assumed for fate modelling occur in many other regions of Canada.

To the extent possible, effect values derived in this section were estimated taking into

account bioavailability. CTVs for metals were estimated based on either free-ion or total dissolved concentrations in waters (either surface or soil pore waters). Critical loads for metals were estimated as deposition rates of total soluble metals.

The magnitude of the application factor used to derive ENEVs typically increases with the uncertainties associated with effect estimates, arising, for example, from limitations in the amount or quality of toxicity data, and extrapolation of laboratory effects data to field conditions (Environment Canada, 1997a). Since toxicity data were relatively abundant in these assessments, test organisms were typically closely related to organisms likely to be encountered in the field, and because all of the release constituents examined occur naturally, application factors used were very small typically 1, and never more than 2.

Because release constituents are present in the environment naturally, the upper bounds of natural bioavailable concentrations (typically 95th percentile values) were used to set lower bounds on ENEVs for these substances. This is justified based on the expectation that most natural organisms are unaffected by bioavailable concentrations typically found in nature. Of course, there may be exceptions. For example, near ore deposits, metal concentrations can be extremely high and harmful to some organisms. However, 95th percentiles of natural concentrations are usually not extreme, being within a factor of 2 or 3 of the geometric mean values (Bird et al., 1999). Harmful effects at such concentrations are therefore considered to be unlikely.

Several of the release constituents considered (e.g., Cu, Zn and Ni) are essential micronutrients for at least some organisms. Care must be taken to ensure that ENEVs for such substances are not within the deficiency range. This was accomplished by ensuring that the ENEVs selected are not below 95th percentile values of natural (bioavailable) concentrations, since concentrations equivalent to the 95th percentile natural values are expected to satisfy the nutritional needs of most organisms. Since the releases being assessed include a mixture of chemical substances (e.g., several metals and  $SO_2$  are released together to air), their combined effects can be different (greater or less) from those of their individual constituents. As explained below, data available for metals suggest that combined effects may be assumed to be additive. An alternative, less conservative approach is to assume that release constituents act independently (i.e., that there are no combined effects). In this section, only effects of individual release constituents are described. Combined effects are considered as appropriate in Section 3.0.

## 2.4.1.1 Releases to air

#### 2.4.1.1.1 Sulphur dioxide

Plants are among the most sensitive receptors affected by SO<sub>2</sub> in air (FPACAQ, 1987). Information on effects of SO<sub>2</sub> on vegetation has been reviewed by Linzon (1999). While in some cases the addition of low concentrations of SO<sub>2</sub> can be beneficial (Linzon, 1999), in general, accumulations of sulphur in leaf tissue beyond certain threshold levels have harmful effects (Linzon et al., 1979). Sulphur dioxide enters leaves mainly through the stomata and is toxic to the metabolic processes taking place in the mesophyll cells (Linzon, 1972). Acute injury is caused by a rapid metabolic accumulation of bisulphite and sulphite. When the oxidation product, sulphate, accumulates beyond a threshold value that the plant cells can tolerate, chronic injury occurs.

Acute injury can occur as the result of plant exposure to high concentrations of  $SO_2$  for short periods of time (one to several hours). The injury develops within several hours to a few days after exposure and manifests itself usually as necrosis of foliage accompanied by certain metabolic effects. Chronic injury can occur as the result of plant exposure to constant or intermittent low concentrations of  $SO_2$  over long periods of time (over one day to one or more growing seasons). The injury can include metabolic effects (physiological and biochemical), chlorosis of



foliage (becoming necrotic), reduction in plant growth and yield, and death of the plants. Results of acute and chronic studies with sensitive Canadian species are described briefly below.

Acute effects: Five studies reported acute injury to Canadian species at relatively low concentrations — between 524 and 1100  $\mu$ g/m<sup>3</sup>. Four were experimental studies where receptor species and exposure concentrations were controlled, and one by Dreisinger (1965) involved examination of effects of SO<sub>2</sub> in the field under natural (uncontrolled) conditions.

Metcalfe (1941) reported damaging begonia varieties in fumigations of 655 µg/m<sup>3</sup> (0.25 ppm) SO<sub>2</sub> for 1 hour under very humid conditions. Berry (1967) reported injuring foliage of potted eastern white pine at a concentration of 655 µg/m<sup>3</sup> (0.25 ppm) SO<sub>2</sub> for 1 hour. A high temperature (27°C) and a high relative humidity (70%) were maintained during the exposure of eastern white pine to SO<sub>2</sub> in a specially built greenhouse chamber. Murray et al. (1975) induced moderate to severe injury on several Kentucky bluegrass cultivars in artificial fumigations of 524  $\mu$ g/m<sup>3</sup> (0.20 ppm) SO<sub>2</sub> for 2 hours. Karnosky (1976) produced acute injury on foliage of trembling aspen in artificial fumigations with 910  $\mu$ g/m<sup>3</sup> (0.35 ppm) SO<sub>2</sub> for a period of 3 hours. Five aspen clones were tested, and three clones were injured slightly.

Dreisinger (1965) reported observations of acute injury to natural vegetation following SO<sub>2</sub> fumigations originating from copper and nickel smelters in the Sudbury area during a 10-year period (1954–1963). The lowest SO<sub>2</sub> concentrations for 1 hour found to be associated with a vegetative damaging fumigation were 1466  $\mu$ g/m<sup>3</sup> (0.56 ppm) for a crop species (buckwheat) and 1100  $\mu$ g/m<sup>3</sup> (0.42 ppm) for a forest tree species (trembling aspen).

Chronic effects: Six studies reported chronic injury to Canadian species at relatively low concentrations — between 21 and 74  $\mu$ g/m<sup>3</sup>.

Two studies with sensitive species were conducted in controlled experiments. Shaw et al. (1993) conducted long-term open-air fumigation experiments on Scots pine seedlings, using a predetermined pattern of hourly mean values of SO<sub>2</sub> based upon monitoring data from a site in central England. Although mean annual concentrations did not exceed 58 µg/m<sup>3</sup> (0.022 ppm) SO<sub>2</sub> over three years (1988, 1989 and 1990), up to 20% of the trees developed foliar necrosis during each growing season. Kropff et al. (1989) exposed broad bean plants under field conditions to a mean concentration of 74  $\mu$ g/m<sup>3</sup> (0.028 ppm) during the 1988 growing season. This resulted in a reduction of total drymatter production of 9%, and a seed yield reduction of 10%, compared to controls.

Four studies were conducted under natural uncontrolled conditions. The results of forest studies conducted over a 10-year period in the area near Sudbury affected by sulphur fumes were reported by Linzon (1971). It was found that chronic effects on forest growth were prominent where SO, air concentrations averaged  $44 \ \mu g/m^3$  (0.017 ppm), the arithmetic mean for the growing season for the 10-year measurement period. Chronic effects were slight where SO<sub>2</sub> annual concentrations averaged 21 µg/m<sup>3</sup> (0.008 ppm). In Celna, Czechoslovakia, Materna et al. (1969) reported moderate chronic injury to foliage of Norway spruce trees under the influence of an average growing season concentration of 50  $\mu$ g/m<sup>3</sup> (0.019 ppm) SO<sub>2</sub>, which occurred during 1966 and 1967. In studies conducted on the occurrence of lichens at Sudbury (Leblanc et al., 1972), the number of epiphytes found growing on balsam poplar trees was drastically reduced in zones where the annual growing season mean levels of SO<sub>2</sub> were over 52  $\mu$ g/m<sup>3</sup> (0.020 ppm), and slightly reduced in zones where the mean levels of SO<sub>2</sub> were over 26  $\mu$ g/m<sup>3</sup> (0.010 ppm). Similarly, in Sweden (Skye, 1964), it was found that the survival of lichens was poorer in areas with an annual SO<sub>2</sub> concentration of approximately 39 µg/m3 (0.015 ppm).

CTVs and ENEVs: CTVs and ENEVs estimated for chronic and acute conditions are

summarized in Table 29. Generally, effects of SO<sub>2</sub> observed in the field under natural conditions provide the best basis for estimation of effect thresholds (Linzon, 1999). Since the lowest chronic effect level identified  $(21 \,\mu g/m^3)$ was reported for a field study conducted in Canada under natural conditions (Linzon, 1971), this mean growing season value was chosen as the chronic CTV. Information on acute effects of SO<sub>2</sub> on sensitive species under natural field conditions is more limited. Only one study - in a natural Canadian forest --- was identified, with effects reported at 1-hour concentrations as low as 1100 µg/m3 (Dreisinger, 1965). Since two other 1-hour controlled experimental studies reported effects at a lower concentration (655  $\mu$ g/m<sup>3</sup>), a CTV of 900  $\mu$ g/m<sup>3</sup> was estimated. being the average of the experimental and the natural forest values.

Because of the uncertainties associated with these effects estimates (Linzon, 1999), a small application factor of approximately 2 was used to derive ENEVs —  $450 \ \mu g/m^3$  for acute (1 hour) and 10  $\mu g/m^3$  for chronic (annual or growing season) exposures. The chronic ENEV is several-fold above the estimated upper limit of natural annual mean SO<sub>2</sub> concentrations (approximately 2.6  $\mu g/m^3$ ) in Canada. Although an upper limit for 1 hour (acute) natural exposures was not identified, it is very unlikely given the low maximum natural annual average concentration that maximum 1-hour natural concentrations in Canada would exceed the acute ENEV.

## 2.4.1.1.2 Sulphate deposition

The following is a brief summary of information available on the likely impacts of sulphate deposition on aquatic organisms in the four acidsensitive regions of eastern Canada examined in these assessments. Potential for effects is evaluated in relation to critical loads for wet sulphate deposition. Further details on effect thresholds for aquatic systems and methods of critical load estimation are provided in Environment Canada (1997c,d).

Effects on aquatic organisms — CTV and ENEV: In Canada, the pH of aquatic ecosystems is used as a surrogate parameter to represent the complex relationships between water chemistry and biological effects (Jeffries et al., 1999). It has been determined that sensitive aquatic ecosystems require the maintenance of a pH level of 6.0 or higher. For example, it has been observed that Canadian lakes with pH values of less than 6.0 have fewer species of fish than similar lakes with higher pH values (Environment Canada, 1997d). In the language of these assessments, sensitive fish species may be considered to be assessment endpoints, and pH 6.0 represents a CTV. Since this is the threshold used for evaluation of effects of sulphate deposition, the application factor used to derive the ENEV was 1.0. This is justified because the critical effects data are based on extensive field observations in acid-sensitive parts of Canada.

*Effects on aquatic organisms* — *critical loads*: Using a pH of 6.0 as a criterion, aquatic fate and transport models have been used to

Parameter	Acute (1-hour) concentration (µg/m <sup>3</sup> )	Chronic (growing season) concentration (µg/m <sup>3</sup> )
CTVs	900	21
ENEVs	450	10
Upper limit of natural background <sup>1</sup>	_	2.6

TABLE 29 Acute and chronic CTVs and ENEVs for  $SO_2$  derived for terrestrial vegetation <sup>1</sup>

<sup>1</sup> Derivation of values is detailed in Linzon (1999).

estimate critical load values for wet sulphate deposition in selected lake cluster receptor areas in eastern Canada (Environment Canada 1997c,d). These critical loads may be described as  $CL_5s$ , since these loadings are considered to be suitable for the protection of 95% of the lakes in the cluster. There is some probability that the other 5% would be adversely impacted. Wet sulphate critical loads for the four acid-sensitive receptor regions selected for examination in these assessments were estimated by visual examination of acid sensitivity maps. Values range from less than 6 kg/ha/a for the Kejimkujik region of Nova Scotia to about 13 kg/ha/a for the Sudbury/Muskoka area (Table 13).

## 2.4.1.1.3 Metals (Cu, Zn, Ni, Pb, Cd, As)

*Bioavailability and the free-ion model*: The response of organisms to a toxic substance requires both contact and susceptibility. Contact in this case means more than physical contact; it almost always requires absorption of the dissolved metal into the organism. Absorption requires the metal to be free to move in the environment around the organism and requires that the metal be able to pass through the membranes into the organism. Both of these processes are highly dependent on the chemical form of the metal, and both control the net bioavailability of the metal.

The mobility of the metal in the environment around the organism is essentially determined by the proportion of the element in the solution phase. In surface water systems, this is assumed to be the concentration in filtered water, and in sediment or soil it is the concentration in the (filtered) pore water. Metals attached to particles suspended in water are mobile, but are not as bioavailable as the metals in solution and, as a first approximation, can be ignored. The metals in solution exchange to some extent with those on the solid phase, and a model of this relationship is needed to predict bioavailability. There are many possible models. In this assessment, a simple linear partitioning model is used. It defines the ratio of solid-phase metal to solution-phase as a partition coefficient,

 $K_d$ , which is assumed to depend upon many environmental factors.

The absorption of a metal into the organism requires the metal to pass through cell membranes. These can be as diverse as cells on the surface of fish gills or cells in plant roots. This typically requires diffusion of the metal to the membrane surface, movement through the membrane (this may be passive or, more rarely, metabolically facilitated), and, finally, movement of the metal away from the membrane inside the cell. The membrane is often envisioned as a cation exchanger, and metabolically facilitated passage through the membrane may involve carrier enzymes that are relatively specific to certain chemical forms of the metals. There are good evidence and support for the concept that the free-ion species of the metals are most able to pass through the membranes. This concept has been formalized in the free-ion activity model (FIAM) for metal absorption (Tessier et al., 1994). There is nothing exact or exclusive about this model, but it is the best at present for dealing with the issue of bioavailability. It should be noted that this approach does not account for the uptake of metals by ingestion and therefore underestimates exposure to metals for some organisms.

The application of FIAM requires a number of assumptions. For one, at environmental concentrations, it is assumed that activity and concentration are so similar that ion concentrations can be used rather than estimations of ion activities. It is also assumed that free-ion concentration can be estimated given the concentrations of the metal of concern and the important complexing ligands in the solution, as well as other geochemical characteristics such as pH and redox potential. Estimating chemical speciation is a rapidly evolving subject and has uncertainties associated with it, not only because of methodology but also because validation is very difficult. It is not easy to measure the free-ion concentration (or activity) of many metals. Despite the uncertainties, the estimation of free-ion concentrations is considered a more useful index of bioavailability than is reliance on total metal concentrations.

One of the major uncertainties in the estimation of free-ion concentrations is the variable effectiveness of dissolved organic matter as a ligand. Dissolved organic matter is typically the dominant ligand affecting the chemical speciation of metals, yet it is an amorphous substance that has proven very difficult to characterize quantitatively. In this assessment, two different geochemical speciation models were used. Each dealt with organic complexants differently. In one, the complexing characteristics of dissolved organic matter are modelled in terms of a diprotic acid, and parameters to reflect the interaction of a generic diprotic acid with the metals were used. In the other model, the behaviour of the natural dissolved organic materials was emulated with a specific mixture of six pure organic acids, for which the metal-ligand interaction parameters are well known. The results of the two models showed the same trends and were quantitatively very similar under some conditions of ligand concentration and pH and somewhat different under others. A geometric mean of the results was used. The two models were used to compute the fraction of dissolved metal present as free ion under what were considered low- and high-ligand concentrations, under low and high partial pressures of  $\text{CO}_2$  and over a range of pH. The pH range specified was relatively narrow, reflecting the acidic nature of the receiving aquatic and terrestrial environments on the Canadian Shield. The narrow, acidic pH range simplified the geochemical modelling and model interpretation, because at pH < 7, most of the dissolved metals are present as the free ions. The exceptions are Cu and to a lesser degree Pb, where the models indicated that complexes consume a substantial portion of the dissolved metal above about pH 6, depending as well on the other water chemistry attributes. Details of the modelling and interpretation are provided by Bird et al. (1999).

Arsenic, being a metalloid, differs in several ways from the metals being considered here. Arsenic may be present in the environment as a variety of species, normally as one of a number of oxyanions. FIAM is not applicable to such species. Further, the conversion between the chemical species is kinetically limited and at least partially mediated by microbes, and so is not suitably predicted with geochemical equilibrium models. It is also probable that more than one chemical species of As is responsible for toxic effects. It was therefore decided that the best conceptual model at this stage is to assume that all As in solution is bioavailable.

*Effects on soil-dwelling organisms* — *data handling*: There is a considerable amount of information in the literature on the uptake and effects of heavy metals on soil-dwelling organisms.

As a first-level analysis of information for the present assessment, only studies showing relatively sensitive effects were considered in detail. Documents supporting existing environmental guidelines and assessments (EC/HWC, 1993; EC/HC, 1994a,b; Environment Canada, 1996a-d, 1997e-i; CCME, 1997) were used to direct the literature search and to provide an expectation of sensitivity for each metal. There was further emphasis on recent literature, where possible, because it was more often complete and relevant with regard to free-ion effects and related geochemistry. Very few papers include free-ion measurements or estimates, and remarkably few provide enough ancillary information to allow users to estimate free-ion concentrations. By requiring information about or relevant to free-ion concentrations, some sensitive ecotoxicology studies that lacked such data were screened out. However, on the whole, this constraint did not seem to seriously affect the derivation of free-ion ENEVs.

Second-level analysis involved relevance, among other criteria. Relevant studies were those that used soils and organisms representative of those found on the Shield. Relevant ecotoxicology endpoints were also required. In the terrestrial environment, assessment endpoints were related to 1) the growth of native tree species and the efficacy of their root symbionts, and 2) the population of litter invertebrates and decomposers capable of maintaining steady-state levels of litter. A third assessment endpoint related to native plants in wetlands was proposed but in



practice was no different from 1) above, because there were no data specific to wetland species.

All ecotoxicology studies reported effects on some biological endpoint, but statistical significance and effect level were not always reported. In this assessment, emphasis was placed on sublethal chronic effects at effect levels less than 50%. For example, an effect level of 25% (EC<sub>25</sub>) for reproductive performance in the longterm study would be a preferred endpoint. In many cases, it was possible to interpolate effect levels to EC<sub>25</sub> even if only median effect levels such as EC<sub>50</sub> were formally reported. Results were not considered unless there was evidence of a statistically significant or otherwise unambiguous toxic effect.

Estimation of the fraction of the solutionphase metal present as free ion was done for every study with sensitive species where pH and solution-phase concentration were provided. In the ecotoxicology studies that used whole soils, it was common that solution-phase concentrations were not provided and only the concentration on the total soil (solid and liquid phases, on a dry weight basis) was reported. Since these studies were by far the most common, it was necessary to develop a means to estimate the solution-phase concentration from data on total soil concentrations. Because sorption in soils is very complex and very soil-dependent, it was considered inaccurate to extrapolate the solid/liquid partition coefficient,  $K_d$ , from other soils. Extrapolation was done only if the study reported corresponding tissue concentrations in higher plants. Tissue concentration is perhaps one of the best indices of bioavailability, because it is based on the actions of the organism. There is a negative correlation between K<sub>d</sub> and the plant:soil concentration ratio — high K<sub>d</sub> indicates strong sorption and corresponds to low plant uptake. This relationship has been parameterized in a first-order, log-log regression model and this model, was used (Bird et al., 1999) to estimate K<sub>d</sub> where solution-phase concentrations were not provided.

Once the ecotoxicology data were interpolated and adjusted as required, they were summarized and ranked from lowest to highest effect concentration. Numerous studies were listed. The 10 most sensitive were considered as possible sources of CTVs for soils. The methodology in CEPA/PSL assessments is to seek (as a starting point) relevant and reliable endpoints for the most sensitive species in the setting of concern. Thus, consideration was first given to the study showing relevant effects at the lowest effect concentration for each metal. This study was re-examined in detail to assure relevance and to compare it to the next few higher reported effects. Most confidence was placed in results from studies that were technically sound and unambiguously reported, and where the next higher effect concentrations were not markedly higher. Case-by-case arguments were developed and documented (Bird et al., 1999) to support the selection of the data that would become the CTV and ultimately the ENEV. All CTVs are reported as free-ion concentrations in soil pore water except for As, where CTVs are reported as concentrations of dissolved As in soil pore water.

The use of the 95th percentile background concentrations to set lower bounds for ENEVs required that these background data also be expressed as free-ion concentrations. In soils, statistical distributions of total soil background concentration were available, so the 95th percentile total concentration could be defined. The solid/liquid partition coefficient, K<sub>d</sub>, values applied in the critical load modelling for this assessment (see below) were not considered directly applicable to naturally occurring metal compounds to convert total concentration to solution-phase concentration, because the K<sub>d</sub>s were often estimated for metals recently added to soil. Therefore, the 95th percentile values from distributions of empirically determined K<sub>d</sub> values were used for the uncontaminated background soils to estimate the background solution-phase metal concentrations. An upper percentile K<sub>d</sub> was considered appropriate because naturally occurring metal compounds should be less mobile than recently added metals. By assuming



median pH and geochemical conditions, solution-phase background concentrations were converted to background free-ion concentrations.

*Effects on soil-dwelling organisms* — *CTV and ENEV values:* Chronic ENEVs for soil-dwelling organisms estimated for Cu, Zn, Ni, Pb, Cd and As are summarized in Table 30.

For Cu in soil, effect levels derived from the eight most sensitive studies (in order of decreasing sensitivity — Miles and Parker, 1979; van Gestel et al., 1991; Halsall, 1977; Chang and Broadbent, 1981; Schat and Ten Bookum, 1992; Korthals et al., 1996; Walsh et al., 1972, referenced and described in detail by Bird et al., 1999) spanned an order of magnitude in free-ion Cu concentrations in the solution phase, from 0.01 to 0.1 mg/L. This range encompassed both plants and decomposers. Upon detailed analysis, it was clear that the more sensitive studies were somewhat ambiguous. No one study was clearly the most appropriate to set the CTV, and a study in the midpoint of the range (Schat and Ten Bookum, 1992), with  $EC_{20}$  sublethal effects at 0.04 mg/L, was chosen. The effects were for root growth of a grass, and because there was no clear demarcation in effects between plants and decomposers among the sensitive studies, this concentration was used as the CTV for both plants and decomposers. It is an order of magnitude higher than the estimated 95th percentile background free-ion concentration, so the CTV was based solely on the effects data.

For Zn in soil, there was more demarcation of effect concentrations for plants and decomposers, so separate CTV values were set for each. The overall most sensitive study was for an Enchytraeid worm (Posthuma et al., 1997), and the study was superior among the others considered (referenced and described in detail by Bird et al., 1999) in providing the required data. The next most sensitive studies with invertebrates (Smit and van Gestel, 1996; Chang and Broadbent, 1981; Sheppard et al., 1993) had effect concentrations within about three-fold of the Posthuma et al. (1997) study, and so were supportive of the choice. The effect was an  $EC_{50}$ for decreased reproduction in a chronic exposure study, and the free-ion effect concentration used for the CTV was 0.28 mg/L. This is above the estimated 95th percentile background free-ion concentration, so the CTV for decomposers was based solely on the effects data. For plants, the most sensitive endpoint (Sheppard et al., 1993) was time to bloom initiation, and so was also a non-lethal effect in a chronic exposure study. The next most sensitive studies with plants (MacLean, 1974; Dixon and Buschena, 1988) had effect concentrations within about four-fold of the most sensitive, and so were supportive of the choice. The free-ion effect concentration used for the CTV was 0.46 mg/L, which is above the estimated 95th percentile background free-ion concentration, so that the CTV for plants was also based solely on the effects data.

 TABLE 30
 Background soil pore water metal concentrations and ENEVs derived for terrestrial endpoints 1

Parameter		Cu	Zn	Ni	Pb	Cd	As
95th percen	tile background (mg/L)	0.0041	0.14	0.024	0.006	0.00047	0.00062
ENEVs <sup>2</sup> (mg/L)	"Primary values" – for all organisms	0.04	0.28	0.2	0.12	0.008	0.07
	Trees & symbionts	0.04	0.46	0.2	0.12	0.008	0.07
	Decomposers	0.04	0.28		0.12	-	1.9

<sup>1</sup> Concentrations for As are expressed on a total dissolved basis. All others are on a free-ion basis.

<sup>2</sup> Due to the use of application factors of 1, ENEVs are equal to CTVs.

For Ni in soil, the most sensitive study reported free-ion effect concentrations an order of magnitude below all the others, and so was not considered sufficiently supported to use as the CTV. The second-most sensitive study (Dixon, 1988) was more consistent. It reported a non-lethal endpoint with an  $EC_{72}$  effect level at a free-ion concentration of 0.2 mg/L. The effect was the mycorrhizal infection of oak roots, a very relevant endpoint for boreal forests where symbiotic mycorrhizal relationships are often essential to tree survival. Because no invertebrate studies showed similar sensitivity, this value was chosen as the CTV. The five next most sensitive studies (Wilke, 1988; Dixon and Buschena, 1988; Dixon, 1988; Taylor, 1989; Taylor et al., 1992, referenced and described in detail by Bird et al., 1999) had effect concentrations within four-fold of 0.2 mg/L, providing strong support for the choice of CTV. This value is almost 10-fold above the estimated 95th percentile background free-ion concentration, so the CTV was based solely on the effects data.

For Pb in soil, the fifth most sensitive study (Seiler and Paganelli, 1987) was chosen for the CTV, even though it was about 10-fold less sensitive than the most sensitive study. The effect concentration was 0.12 mg/L for an EC<sub>40</sub> on shoot and root growth of spruce, a very relevant endpoint. The more sensitive studies (Balba et al., 1991; Miles and Parker, 1979) were for less relevant species (e.g., tomatoes) and had substantial uncertainties related to the K<sub>d</sub> values and fractions of soluble Pb present as free ion. The four next most sensitive studies (Chang and Broadbent, 1981; Seiler and Paganelli, 1987; Wilke, 1988; Dixon and Buschena, 1988) were within three-fold of the CTV, and thus supported the choice. Apart from two studies with microbial endpoints, only plant-related endpoints were among the 10 most sensitive, and so the CTV for decomposers was set the same as for plants. The CTV is almost 20-fold above the estimated 95th percentile background free-ion concentration, and so was based solely on the effects data.

For Cd in soil, the most sensitive study (Ibekwe et al., 1996) was also the only soilrelated study found that reported ecotoxicology data relative to free-ion concentrations. It used quite different techniques than all the other studies, in that free-ion concentrations were controlled in solution culture with specific chelating agents. Because the results were fivefold different from the next most sensitive and the technique was novel and not fully accepted in the literature, this study was not used for the CTV. The next most sensitive study (Wetzel and Werner, 1995) was used as the CTV, and it reported a non-lethal  $EC_{20}$  for a plant root symbiont with an effect concentration of 0.008 mg/L. No data for decomposers were among the 10 most sensitive studies. This CTV is 20-fold above the estimated 95th percentile background free-ion concentration, so the CTV was based solely on the effects data. This CTV is mid-way between, five-fold above and below, the studies ranked as less or more sensitive (Ibekwe et al., 1996; Wetzel and Werner, 1995; Bingham et al., 1975; Wilke, 1988; Taylor and Stadt, 1990, referenced and described in detail by Bird et al., 1999), and so is supported by the other studies.

For As in soil, the most sensitive study (Wetzel and Werner, 1995) was for plants and their symbionts grown on agar. It had an effect concentration five-fold lower than the next most sensitive studies. The seven next most sensitive studies (Steevens et al., 1972; Jacobs et al., 1970; Woolson, 1973; Jacobs and Keeney, 1970; Sheppard et al., 1982) had effect concentrations from 0.05 to 0.50 mg/L and were all for plants grown in soil. This is a more relevant growth medium, but the interpretation is complicated because in all seven cases, K<sub>d</sub> was estimated from plant:soil concentration ratios. The choice for CTV (Woolson, 1973) was made because the underlying K<sub>d</sub> was considered the most reliable of the seven studies. The effect level was an  $EC_{29}$ of 0.07 mg/L for a non-lethal effect on plant vield. This is more than 100-fold above the estimated 95th percentile background free-ion concentration, so the CTV for plants was based solely on the effects data. The only non-plant effect concentration among the 10 most sensitive

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studies was for phosphatase activity (Wilke, 1988), and this was used for a CTV for decomposer organisms. The effect level was an  $EC_{50}$  of 1.9 mg/L, well above background.

In all cases for CTVs in soil, the application factor was set to unity, in part because the measurement endpoints were quite applicable to the assessment endpoints related to tree and tree-symbiont growth and litter decomposition, but also because for some elements (particularly Zn) CTVs were not much above the 95th percentile natural background values. Thus, the CTVs become the ENEVs.11 When, for a given metal, ENEVs for plantrelated and decomposer-related effects differed (i.e., for Zn and As), the lower value was selected as the "primary" ENEV, used in calculation of "primary" critical loads (below) and risk quotients (Section 3.0). The choices for ENEVs (Table 30), when compared on a similar totalmetal bulk soil concentration basis, agreed well with existing summaries (CCME, 1991; Klepper and van de Meent, 1997).

Effects on soil-dwelling organisms critical loads: The ENEVs represent the concentration in the soil that, if exceeded, could cause non-lethal (e.g., 40%) reductions in performance of key organisms. There are many processes that link the concentration in soil to the deposition flux of metal to the soil and vegetation surface. These processes were dealt with using a model to simulate transport of water and contaminant in soil. Several assumptions were required.

The first assumption for the model development was that only the soluble metal in the flux to the soil surface would be considered. The insoluble fraction was assumed to be very slowly released and of no consequence. Also, flux of metal through the soil was assumed to be by diffusion and convective mass flux with water. Downward flux of water resulted from excess precipitation and upward flux from evapotranspiration and capillary rise. Finally, the metals were assumed to be sorbed onto the immobile soil solids following a  $K_d$  relationship. The model was formulated as an analytical solution to the convection/dispersion equation and was validated by Elrick *et al.* (1994, 1997).

The input parameters were selected to reflect boreal forest and Canadian Shield conditions (Sheppard et al., 1999). Parameters were assigned best-estimate values (medians of the distribution of possible values) for use in a deterministic manner and probability distributions of values for use in a probabilistic manner. For the probabilistic simulations (1000 repeated runs of the model), parameter values were chosen for each run from their statistical distributions, with care to consider appropriate correlations among parameters. The parameters set specifically for this assessment were net water flux (median 0.47, range 0.25–0.68 m/a), effective water velocity (median 3.6, range 3.5-10.7 m/a), moisture content (median 0.13, range 0.05-0.20 m<sup>3</sup>/m<sup>3</sup>), pH (median 5.1, range 3.5–7.0), dispersion coefficient (median 0.0067, range 0.005–0.01  $m^2/a$ ) and  $K_d$ . The geometric means specified for  $K_d$ -(L/kg) were Cu: 314, Zn: 63, Ni: 116, Pb: 534, Cd: 40 and As: 417. For each element, the geometric standard deviation (GSD) for K<sub>d</sub> was set at 5, and truncations were set at two GSDs above and below the geometric mean.

Another key assumption was to use the model results at steady-state soil concentrations, which is desirable because concentrations are constant in time after steady state is reached. Steady state was defined at the 5-cm soil depth. The model results showed that steady state may not be reached until several centuries of constant flux have passed (Sheppard *et al.*, 1999). Fluxes are unlikely to be constant for that long, although metalliferous areas in Europe have been successively exploited over such time periods. In the absence of some criterion to define time lapse, and recognizing that surface horizons will

<sup>&</sup>lt;sup>11</sup> As indicated, because application factors have been set to unity, ENEVs are equal to CTVs. It should be clearly recognized, however, that unlike typical ENEVs, these thresholds are levels that are known to cause low effects on sensitive organisms.

reach steady state much earlier than deeper horizons, only results at steady state were used. It should be recognized that because historic emissions from some facilities (and concomitant local deposition) were significantly greater than current emissions, metal concentrations in soils near some facilities must decrease to reach steady-state levels.

The model was run with an input of a unit flux density of soluble metal to the surface. Concentrations of free ion in solution at 5-cm depth were output. Because the model is linear with respect to concentration, the results could then be scaled with flux or concentration. The outcome was a ratio of steady-state soil concentration to input flux density. Because of linearity in the model, this ratio could be applied to any ENEV to predict the flux density that would result in that concentration.

It is assumed that natural background free-ion metal and contaminant free-ion metal have the same biological effect and the concentrations are additive. As a result, critical loads were defined as the flux density to the surface that will increment the expected median background free-ion concentration up to the concentration of the ENEV.

Deterministic runs with median values of all the parameters were used to define the "median" critical loads ( $CL_{50}$ ), and probabilistic runs were used to define the deviations from the median case. Deviations from median critical loads result from variations in background freeion concentrations and in model parameters. The ENEVs were in all cases assumed to be invariant. Variations in background and model parameters were intended primarily to represent spatial variability across the Shield.

A median critical load (50th percentile) is the flux density that will result in steady-state concentrations that are higher than the ENEV in 50% of Shield soils. Similarly, when deposition equals the 10th percentile critical load ( $CL_{10}$ ), 10% of soils on the Shield are predicted to have steady-state concentrations higher than the

ENEV. Effects equivalent to at least a 20% reduction in performance may be experienced by terrestrial organisms in this 10% of soils. Geometric mean, 25th and 10th percentile critical loads for soils are shown in Table 31.

Effects on aquatic organisms — data handling: In general, the handling of data and selection of CTVs for aquatic organisms were the same as for soil-dwelling organisms (Bird *et al.*, 1999). In surface water, the assessment endpoints were related to 1) the survival of populations of pelagic and/or benthic invertebrates, 2) survival of populations of fish, and 3) the productivity of populations of aquatic plants.

The objective of this portion of the work was to establish levels causing low chronic effects on organisms. However, in the ecotoxicology data for aquatic organisms, there is greater emphasis on acute than on chronic studies. To deal with this, a database was developed with data from studies where both acute and chronic effects were reported. In general, chronic effect concentrations were lower than acute effect concentrations, as expected, but there were no consistent changes in the ratio with organism or element. As a result, a median chronic:acute effect concentration ratio of 0.35 was calculated and used to convert pertinent acute effect concentrations to chronic effect concentrations. In deriving CTVs, preference was given to results of chronic studies, but results from acute studies were used when they had effect concentrations more than 2.8-fold (2.8 is the inverse of 0.35) lower than the similar chronic studies.

Case-by-case arguments were developed and documented to support the selection of the data that would become the CTV (Bird *et al.*, 1999). Often, pH and water hardness were used as criteria to select data. Data from studies using low pH (5.5–7.0) and water hardness (nominally below 10 mg/L) were preferred, since these match those typically encountered on the Canadian Shield. Because aquatic ecotoxicology has more routine bioassays with specific species, the decision was made to average the effect concentrations of studies using similar species

Metal	Assessment endpoint	Free-ion ENEV	Crit	ical load (mg/	m²/a)
		(mg/L pore water)	Geometric mean	25th percentile <sup>1</sup>	10th percentile <sup>1</sup>
Cu	Overall (primary)	0.04	25	19	15
	Trees & symbionts	0.04	25	19	15
	Decomposers	0.04	25	19	15
Zn	Overall (primary)	0.28	97	77	63
	Trees & symbionts	0.46	180	140	120
	Decomposers	0.28	97	77	63
Ni	Overall (primary)	0.2	86	76	68
-	Trees & symbionts	0.2	86	76	68
,	Decomposers	-	-	~	~
Pb	Overall (primary)	0.12	53	47	42
	Trees & symbionts	0.12	53	47	42
	Decomposers	0.12	53	47	42
Cd	Overall (primary)	0.008	3.9	3.1	2.5
۰ ب	Trees & symbionts	0.008	3.9	3.1	2.5
	Decomposers	_	-	_	-
As	Overall (primary)	0.07	30	27	24
	Trees & symbionts	0.07	30	27	24
	Decomposers	1.9	830	730	660

TABLE 31	Critical loads of soluble metal	for different terrestrial	assessment endpoints
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<sup>1</sup> Different percentile critical loads are based on probabilistic evaluation of metal transport and fate and assume that the ENEV is invariant.

and conditions, where the effect concentrations were comparable. In almost all cases, there were sufficient data to define CTVs for each of the three assessment endpoints. All CTVs and ENEVs are reported as free-ion concentrations except for As, where CTVs are reported as concentrations of dissolved As.

Effects on aquatic organisms — CTV and ENEV values: Chronic ENEVs for aquatic organisms estimated for Cu, Zn, Ni, Pb, Cd and As are summarized in Table 32.

For Cu and aquatic invertebrates, the study by Giesey *et al.* (1983) used appropriate low-hardness water and reported sensitive effects. They reported both computed and measured freeion concentrations, but for consistency the geochemical models applied throughout this report were used to generate the free-ion effect concentrations. The resulting CTV, when adjusted with the chronic:acute ratio, was 0.98  $\mu$ g/L. This is below the 95th percentile background free-ion concentration of 1.0  $\mu$ g/L, so the background free-ion value is used for the CTV.

For Cu and fish, several acute exposure studies were equally relevant (Cusimano *et al.*, 1986; Anadu *et al.*, 1989; Welsh *et al.*, 1996), and the average acute effect concentration was 1.9  $\mu$ g/L. Converted to chronic with the ratio 0.35, this becomes 0.67  $\mu$ g/L, which is below the



Parameter		Cu	Zn	Ni	Pb	Cd	As
95th percent	tile background (µg/L)	1.0	12	1.8	0.64	0.084	0.93
ENEVs <sup>2</sup>	"Primary values" for all organisms	1.0	39	18	6	0.18	21
(µg/L)	Invertebrates	1.0 3	48	35	6	0.18	300
	Fish	1.0 <sup>3</sup>	39	53	18	0.25	375
	Plants	2.6	45	18	39	5.5	21

 TABLE 32 Background surface water metal concentrations and ENEVs derived for aquatic endpoints<sup>1</sup>

<sup>1</sup> Values for As are expressed on a total dissolved basis. All others are on a free-ion basis.

<sup>2</sup> Due to the use of application factors of 1, ENEVs are equal to CTVs.

<sup>3</sup> CTVs are below the 95th percentile background concentration. Therefore, ENEVs were set equal to the 95th percentile background value.

95th percentile background free-ion concentration. Thus, as for the invertebrates, the CTV for Cu is set to the background free-ion value of  $1.0 \mu g/L$ .

For Cu and aquatic plants, only data for algae were found (Gachter *et al.*, 1973; Stokes, 1981; Vavilin *et al.*, 1995). They were equally relevant, and the average effect concentration was 2.6  $\mu$ g/L. This is above the 95th percentile background free-ion concentration, so the free-ion CTV was set at 2.6  $\mu$ g/L.

For Zn and aquatic invertebrates, the only study among those considered that used low-hardness water was that of Belanger and Cherry (1990), and so it was chosen for the CTV. An effect level of  $EC_{20}$  for reproduction after seven days was interpolated from their data, and this was at a free-ion concentration of 48 µg/L. This is four-fold above the 95th percentile background free-ion concentration of 12 µg/L, and so the CTV was based solely on the effects data.

For Zn and fish, several acute exposure studies were relevant. The most sensitive chronic study had higher effect concentrations than the acute studies, and so was not used. The three most sensitive acute studies (Cusimano *et al.*, 1986; Bradley and Sprague, 1985; Anadu *et al.*, 1989) used the same species, *Oncorhynchus mykiss* (rainbow trout), and were comparable, so the effect concentrations were averaged. Because they were acute studies, the factor of 0.35 was used, resulting in a CTV of 39  $\mu$ g/L. This is three-fold above the 95th percentile free-ion background concentration, so the CTV was based solely on effects data.

For Zn and aquatic plants, only data for algae were found, and the effect concentrations of the two most sensitive studies (Stokes, 1981; Bartlett *et al.*, 1974) were averaged to give a CTV of 45  $\mu$ g/L. This is well above background, so the CTV was based solely on effects data.

For Ni and aquatic invertebrates, the most sensitive study using appropriate water hardness was that of van Frankenhuyzen and Geen (1987). They reported growth and survival of caddisfly (*Clistoronia magnifica*), and from their data an EC<sub>25</sub> could be interpolated. The free-ion effect concentration, chosen as the CTV, was 35  $\mu$ g/L. This is 20-fold above the 95th percentile free-ion background concentration of 1.8  $\mu$ g/L, and so was used as the CTV.

For Ni and fish, sensitive data by Nebeker *et al.* (1985) for *Oncorhynchus mykiss* were chosen in preference to another species because data for this species were available for most of the elements considered in this assessment, allowing consideration of additive toxicity. Effect levels of  $EC_{25}$  for growth at



 $53 \mu g/L$  were used for the CTV, and this concentration is almost 30-fold above the 95th percentile free-ion background concentration.

For Ni and aquatic plants, only data for algae were found, and those of Stokes (1981) were used for the CTV. The  $EC_{25}$  was 18 µg/L, and because this is well above the background, it was taken as the CTV.

For Pb and aquatic invertebrates, only the study of Mackie (1989) both was sensitive and used low-hardness water. Several species were studied; the most sensitive was *Hyalella azteca*, where an acute effect level (LC<sub>50</sub>) was reported at 20  $\mu$ g/L. With adjustment using the chronic:acute ratio of 0.35, the CTV becomes 6  $\mu$ g/L. This is 10-fold above the 95th percentile free-ion background concentration of 0.64  $\mu$ g/L, and so was used as the CTV.

For Pb and fish, the study of Davies *et al.* (1976) was most appropriate and used *Oncorhynchus mykiss*. A chronic EC<sub>25</sub> for deformities in fry occurred at 18  $\mu$ g/L, and because this is well above the 95th percentile free-ion background concentration, it was used as the CTV.

For Pb and aquatic plants, only data for algae were found, and those of Stokes (1981) were used. A chronic effect level ( $EC_{25}$ ) was observed at 39 µg/L, and this was used as the CTV.

For Cd and aquatic invertebrates, three studies (two species in Lawrence and Holoka, 1991; one species in Suedel *et al.*, 1997) were comparable in methods and sensitivity, and so the effect concentrations were averaged. The exposures were chronic, and effect levels were no more than EC<sub>39</sub>. The average effect concentration, used as the CTV, was 0.18  $\mu$ g/L. This is about two-fold above the 95th percentile free-ion background concentration of 0.084  $\mu$ g/L, and so the CTV was based solely on effects data.

For Cd and fish, two studies using Oncorhynchus mykiss (Cusimano et al., 1986; Anadu et al., 1989) were comparable, so the average was used to derive the CTV. Both studies were of acute exposures, so the ratio 0.35 was used to estimate a chronic effect concentration of 0.25  $\mu$ g/L. This is above the 95th percentile free-ion background concentration, and so was used as the CTV.

For Cd and aquatic plants, only data for algae were found, and two studies (Vocke *et al.*, 1980; Stokes, 1981) used the same organisms and similar conditions. Thus, the effect concentrations were averaged to yield a free-ion CTV of 5.5  $\mu$ g/L, which is well above background.

For As and aquatic invertebrates, the acute exposure study of Passino and Novak (1984), when adjusted using the chronic:acute ratio of 0.35, was more sensitive than the chronic studies found. The study used As(V) and *Bosmina longirostris*. After adjustment, the effect concentration was 300  $\mu$ g/L (expressed as total dissolved As). This is well above the 95th percentile background concentration of -0.93  $\mu$ g/L, and so the CTV was based solely on effects data.

For As and fish, the study of Birge *et al.* (1983a) is suitable. They used *Oncorhynchus mykiss* with chronic exposure to As(III), and an  $EC_{25}$  was interpolated. The CTV, based on total dissolved As, is 375 µg/L, well above background.

For As and aquatic plants, the effect concentrations in two studies (Vocke *et al.*, 1980; Planas and Healey, 1978) were averaged, in part because of uncertainties in interpretation of the more sensitive study. The effect levels were  $EC_{42}$ and  $EC_{25}$ , and the average total dissolved effect concentration, used as the CTV, was 21 µg/L. Both studies used As(V). This CTV is well above background.

In all cases for CTVs in aquatic systems, the application factor was set to unity because the

measurement endpoints were considered to be quite applicable to the assessment endpoints and because, in some cases (e.g., for Cd and Zn), CTVs were not much above 95th percentile natural background values. Thus, in all cases, the CTVs become the ENEVs. The 95th percentile free-ion background concentration was used as the CTV (and ENEV) for Cu, for both aquatic invertebrates and fish. In all other cases, the CTVs (and ENEVs) were based on effects data. For each metal, the "primary" ENEV that was used in calculation of "primary" critical loads (below) and risk quotients (Section 3.0) was the lowest of the ENEVs estimated for invertebrates, fish and aquatic plants (Table 32). The choices for ENEVs, when compared on a similar dissolved-element basis, agreed very well with previous summaries (CCME, 1991; de Vries and Bakker, 1996). The agreement is not unexpected, since many of the same data were used in these summaries.

Effects on aquatic organisms — critical loads: As with the derivation of critical loads for soils, the first assumption in the aquatic environment is that only the soluble metal in the flux to the water surface need be considered. The water body is modelled as a mixing tank, with dilution water entering from the terrestrial catchment area. Loss of contaminant is by flushing downstream and burial in sediment. Transfer to sediment is modelled as a first-order process dependent on dissolved metal concentration and correlated to pH. The production of sediment by processes in the water column is independent of the rate of transfer of metal to sediment. It is assumed that once contaminants are buried by more than 10 cm of fresh sediment, they are effectively removed from the biotic environment. The transfer of contaminants to sediments is positively correlated to pH, so that in probabilistic analysis there is more transfer to the sediment if the water pH is higher.

The model parameters set for this assessment (Sheppard *et al.*, 1999) were water body/lake area (median  $1 \times 10^{5}$ , range  $1 \times 10^{4}$ - $7 \times 10^{7}$  m<sup>2</sup>), terrestrial catchment area

(median  $1 \times 10^6$ , range  $6 \times 10^4$ – $7 \times 10^7$  m<sup>2</sup>), water body/lake depth (median 4.7, range 0.7–27 m), sediment accumulation rate (median 0.17, range 0.012–2.6 kg/m<sup>2</sup>/a), thickness of new (biologically active) sediment (median 0.056, range 0.01–0.1 m), net precipitation (median 0.31, range 0.08–0.57 m/a), and water pH (median 6.2, range 5.5–7.0). The geometric mean, GSD and lower and upper bounds for the first-order rate constant for transfer to sediment, alpha (a<sup>-1</sup>), were specific for each element, but were all correlated to pH, with r=0.8. The geometric means (and GSDs) were Cu: 0.48 (4.0), Zn: 1.3 (3.7), Ni: 0.24 (7.5), Pb: 1.9 (3.7), Cd: 2.0 (3.7) and As: 1.5 (6.9).

The surface water model reaches steady state within a few years, so that considering results at steady state is not a difficult assumption. The model was run with an input of a unit flux density of soluble metal to the water surface, and concentrations of free ion in the water column were output. As with the soil model, the surface water model is linear with respect to concentration and can be scaled with flux or concentration. Critical loads were defined as the flux density to the water surface that will increase the existing, background free-ion concentration to the concentration of the ENEV.

The transfer of contaminants from the terrestrial catchment to the water body is difficult to model. In large part, this is related to the issue of time to steady state. With a constant flux of metal only to the surface of the water, steady state occurs in less than five years. But as discussed earlier, times to steady state for the top few centimetres of soil were up to several centuries. Thus, steady state for a watershed will be much longer, perhaps of the order of  $10^4$  years. Furthermore, high historic emissions have resulted in the accumulation of metals in the catchment areas of lakes located near some metal-processing facilities. Therefore, metal concentrations in these lakes would have to decrease to steady-state levels such as those estimated here.

It would not be reasonable to use the steady-state assumption for a watershed, and a decision to pick a specific time would affect how soil contamination is modelled. The delivery of contaminant from the terrestrial watershed to the water body is often parameterized as a delivery ratio. In theory, when atmospheric contamination is just beginning, the delivery ratio is near zero. Much of the contamination that deposited in the terrestrial environment is initially retained there. When the watershed is at true steady state, the delivery ratio is 1 by definition — the efflux from the terrestrial catchment area equals the influx. Thus, modelling the transfer of contaminant from the terrestrial catchment to the water body is very time-dependent. In addition, it is very site-specific and difficult to deal with generically. Here, it is assumed that there is no transfer from the terrestrial watershed, and in a separate calculation (Sheppard et al., 1999, Appendix) it is found that the potential underestimation of lake water concentration, assuming a delivery ratio of 0.25, is about fivefold.

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As with the soil critical loads, deterministic runs using median values of all the parameters define "median" critical loads, and the probabilistic runs were used to define the deviations from the median case. Deviations from median critical loads result from variations in background free-ion concentrations and in the selected model parameter values. The ENEVs were assumed to be invariant. Variations in background and model parameters primarily represent spatial variability, because it was assumed that receiving environments could be anywhere on the Shield.

The 25th and 10th percentile critical loads were computed in addition to the median (50th percentile) critical loads. The interpretation of a 10th percentile critical load, for example, is that at that flux density, 10% of lakes on the Shield would have steady-state concentrations higher than the ENEV. Non-lethal effects (of the order of 20% reduction in performance) may be experienced by aquatic organisms in this 10% of lakes. The calculated critical loads are shown in Table 33.

### 2.4.1.2 Releases to water

Information on the effects of direct release to water from CCR, CEZinc and CTO is summarized below. Further details are provided in Beak International (1999).

## 2.4.1.2.1 Whole-effluent toxicity

Whole-effluent toxicity test data indicate the percent concentration of effluent needed to kill half the test organisms (LC<sub>50</sub>), or the percent concentration needed to cut growth or reproduction in half (IC<sub>50</sub>), after a specified duration of test organism exposure to the effluent. Short-term (acute) tests are relevant for organisms, such as pelagic invertebrates, that will be exposed for short periods to the portion of the plume having elevated concentrations. Long-term (chronic) tests are more relevant for organisms, such as fish, that may hold position and reside at least partly in the plume for extended periods. Acute and chronic toxicity test data for the copper and zinc processing effluents consideredin this assessment are summarized in Table 34.

The CCR facility contributes to the metal content of MUC-WWTP effluent. Toxicity tests were performed on grab samples of the MUC-WWTP treated effluent, collected over a five-day period in 1996 (MEF/EC, 1998). These tests indicated that the effluent was not acutely toxic to either Daphnia magna (a pelagic invertebrate) or rainbow trout (Oncorhynchus mykiss). However, chronic tests indicated effects on growth of fathead minnows (Pimephales promelas). Chemicals implicated as potentially contributing to chronic toxicity of MUC-WWTP effluent included surfactants (non-ionic and anionic), heavy metals (Cu, Cr) and ammonia. There are some questions about the representativeness of the grab samples tested and the quality of the chronic test results, and plans have been made to repeat these tests.



Metal	Assessment	Free-ion ENEV	Critical load (mg/m²/a)			
	endpoint	(mg/L)	Geometric mean	25th percentile <sup>1</sup>	10th percentile	
Cu	Overall (primary)	1.0	13	6.2	3.2	
	Invertebrates	1.0	13	6.2	3.2	
	Fish	1.0	13	6.2	3.2	
	Plants	2.6	44	21	11	
Zn	Overall (primary)	39	490	270	160	
	Invertebrates	48	610	340	200	
	Fish	39	490	270	160	
	Plants	45	570	310	190	
Ni	Overall (primary)	18	120	61	34	
	Invertebrates	35	240	120	67	
	Fish	53	370	190	100	
	Plants	18	120	61	34	
Pb	Overall (primary)	6.0	110	62	38	
	Invertebrates	6.0	110	62	38	
	Fish	18	330	190	110	
	Plants	39	720	410	250	
Cd	Overall (primary)	0.18	3.0	1.6	0.98	
	Invertebrates	0.18	3.0	1.6	0.98	
	Fish	0.25	4.3	2.4	1.4	
	Plants	5.5	100	55	33	
As	Overall (primary)	21	300	150	80	
	Invertebrates	300	4300	2100	1200	
	Fish	375	5400	2700	1400	
	Plants	21	300	150	80	

## TABLE 33 Critical loads of soluble metal for different aquatic assessment endpoints

Different percentile critical loads are based on probabilistic evaluation of metal transport and fate, and assume that the ENEV is invariant.

Toxicity tests performed on treated CEZinc effluent in 1997 indicated both acute and chronic toxicity prior to pH adjustment of the test waters (pH 9.5-12). Acute tests with Daphnia magna, fathead minnows and rainbow trout exposed to pH-adjusted effluent in 1997 and 1998 indicated that effluent was non-toxic at pH 7.2-8.6. A 1998 effluent sample at pH 8.6 (unadjusted) was non-toxic to fathead minnows

and to algae Selenastrum capricornutum in chronic tests. Thus, pH would appear to be a critical factor in determination of effluent toxicity. The pH is now better controlled in the wastewater treatment process.

Acute toxicity tests performed on treated Cominco-Trail effluents in 1994-95 indicated rainbow trout LC<sub>50</sub>s at 8-77% of effluent



TABLE 34 Results of whole-effluent toxicity tests

Test species	Common name			TC <sup>50</sup> OF 10	-50 (% whole	LC <sub>50</sub> or IC <sub>50</sub> (% whole-effluent concentration)	ntration)		
		Montreal WWTP	Dro Dro	Noranda-CEZinc process water (UNA) <sup>2</sup>	c . A) <sup>2</sup>		Cominco-Trail (1994–95, 1998)	Cominco-Trail (1994–95, 1998) <sup>3</sup>	-
		(winter 1996) <sup>1</sup>	1997 pH 12	1997 pH ≤ 8.1 ⁴	1998 pH 8.6	C-II 1994–95	C-III 1994-95	C-II 1998	C-III 1998
D. dubia (7-d IC)	Water flea	1	I	1	>100	i I I	; ; 1	J	I
P. promelas (7-d IC)	Fathead minnow	21	>13	i	>100	1	I	J	1
Selenastrum (3-d IC)	Algae	>100	11.1	l	>100	l	1	I	I
D. magna (48-h LC)	Water flea	>100	16.4	>100	>100	1	I	]	I
P. promelas (96-h LC)	Fathead minnow	ſ	31.9	ł	>100	1	I	I	1
O. mykiss (96-h LC)	Rainbow trout	>100	5.3	>100	>100	8-77	11–26	71-100	76-100

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<sup>1</sup> MEF/EC (1998).

<sup>2</sup> Noranda-CEZinc data.

<sup>3</sup> Duncan and Antcliffe (1996) and recent Cominco data (personal communication with facility operators).

 $^4$  pH adjusted to 7.2–8.1 using CO<sub>2</sub> gas.

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concentration for C-II and 11–26% of effluent concentration for C-III (Duncan and Antcliffe, 1996). The main contributions to toxicity were from Cd and Zn for C-II and from Cd, Zn, Tl, fluoride and ammonia for C-III. More recent (1998) toxicity test data (personal communication with facility operators) indicate substantially reduced toxicity, with  $LC_{50}$ s of 71–100% for C-II and 76–100% for C-III following a cadmium reduction program. The C-IV outfall and Stoney Creek are not associated with current zinc operations, but, since they load upstream of C-II and C-III, they may contribute to effects observed in the river.

The implications of whole-effluent toxicity for aquatic organisms that reside in receiving waters can be judged by considering the spatial pattern of effluent dilution in receiving waters, as well as the effluent concentrations experienced by aquatic biota based on their likely locations and movements. Receiving water changes in pH and hardness, as compared to fullstrength effluent, may also be important factors.

#### 2.4.1.2.2 Derivation of CTVs and ENEVs

The potential effects of a chemical discharge to receiving water may also be estimated by comparing expected concentrations of individual chemicals in the plume to chemical concentration benchmarks (effect levels). These benchmarks, which represent estimates of low toxic effects to sensitive aquatic organisms, were used to define CTVs for aquatic organisms exposed to effluents. The application factor used to derive ENEVs was set to unity, to avoid having ENEVs within natural concentration ranges, and because the toxicity database is adequate for the chemicals considered. The ENEVs derived for application to lake waters of the Canadian Shield (Section 2.4.1.1.3) are in some instances not immediately suited for application to the harder, higher-pH waters of the St. Lawrence and Columbia rivers, the receiving bodies being considered in these site-specific assessments of aquatic releases. Further, values derived for generic application to the Canadian Shield considered only the metals Cu, Zn, Ni, Pb, Cd and As, while the aquatic

releases assessment must consider a number of other components as well. As such, separate effect levels, tailored to the receiving environments, were derived for use in the assessment of aquatic releases. Relevant ENEVs for a variety of different aquatic biota, for heavy metals, Se, ammonia and fluoride, are listed in Table 35. Their derivation is briefly discussed below.

Chronic values for fish and epibenthic invertebrates were obtained as the lowest relevant chronic values from the U.S. Environmental Protection Agency (EPA) aquatic toxicity database (U.S. EPA, 1984, 1985a,b, 1986, 1987; Suter and Tsao, 1996) or from other literature in some cases. These values were utilized as ENEVs in this assessment for fish and epibenthic invertebrates. The values for Cd, Cu, Ni, Pb and Zn were adjusted to hardness levels of 50 and 100 mg/L, based on U.S. EPA (1995) equations, to obtain ENEVs suitable for application to the Columbia and St. Lawrence rivers, respectively. Ammonia values for fish were adjusted to pH levels of 7.8 and 8.3, respectively, based on equations from Broderius et al. (1985) and assuming a 20°C water temperature.

For short-term exposure situations, acute rather than chronic toxicity test data should be considered. Acute values for pelagic invertebrates (zooplankton) were obtained as the lowest relevant Species Mean Acute Values (SMAVs) in the EPA database (U.S. EPA, 1980a,b, 1984, 1985a,b, 1986, 1987; NJDEP, 1996) or from other literature in some cases. These values were used as ENEVs in this assessment for pelagic invertebrates that may receive short-term water column exposures. The values for Cd, Cu, Ni, Pb and Zn were adjusted to hardness levels of 50 and 100 mg/L, based on U.S. EPA (1995) equations, to obtain ENEVs suitable for application to the Columbia and St. Lawrence rivers, respectively.

Sediment quality benchmarks were considered for the assessment of potential effects on benthic invertebrates from metal-contaminated sediments. Both federal and provincial agencies

Chemical		Chronic values		
	Fish (µg/L)	Benthos-epifauna (µg/L)	Benthos-infauna (mg/kg)	Zooplankton (µg/L)
Cu <sup>1</sup>	2.8-5.0 4	6.6–12.0 <sup>4</sup>	16 7	9.3–17.8 <sup>5</sup>
Zn <sup>1</sup>	52–94 <sup>2</sup>	82-150 4	120 7	244-440 5
Ni <sup>1</sup>	28–50 <sup>2</sup>	128–230 4	16 7	1478–2657 5
Pb <sup>1</sup>	50-121 <sup>2</sup>	6.9–16.7 4	31 7	447.8-1082 5
Cd <sup>1</sup>	0.84-1.44 2	0.92-1.59 4	0.6 7	12.2–26.6 5
As	375 <sup>2</sup>	450 <sup>3</sup>	67	812 6
Cr	30 <sup>2</sup>	6.13 <sup>3</sup>	26 7	23 6
Hg	0.23 <sup>3</sup>	0.96 <sup>3</sup>	0.2 7	2.9 6
Se	10 <sup>2</sup>	10 <sup>2</sup>	-	603 <sup>6</sup>
Ag	0.12 <sup>3</sup>	2.6 <sup>3</sup>	~	0.25 5
TI	20 <sup>2</sup>	130 <sup>3</sup>	~	905 <sup>6</sup>
Ammonia <sup>1</sup>	270–770 <sup>2</sup>	630 <sup>3</sup>	~	1000 6
Fluoride	3700 8	2800 8	~	5000 6

## TABLE 35 Estimated No-Effects Values (ENEVs) for aquatic organisms exposed to effluents

<sup>1</sup> Chronic and acute values for Cd, Cu, Ni, Pb and Zn are given for hardness = 50 and 100 mg/L, using U.S. EPA (1995) equations for hardness adjustment; chronic values for ammonia are given for pH 8.3 and 7.8, 20°C.

<sup>2</sup> Chronic values based on original literature: Cd – Rombough and Garside (1982), Ni – Birge et al. (1983b), Pb – Davies et al. (1976), As – Birge et al. (1983b), Cr – Grande and Anderson (1983), Se – Hermanutz et al. (1992), Crane et al. (1992), Tl – Zitko et al. (1975), ammonia – Broderius et al. (1985).

<sup>3</sup> Chronic values from Suter and Tsao (1996) based on U.S. EPA database.

<sup>4</sup> Chronic values based on Species Mean Chronic Values from U.S. EPA (1984, 1985a,b, 1986, 1987).

<sup>5</sup> Acute values based on SMAVs from U.S. EPA (1980a,b, 1984, 1985, 1986, 1987).

<sup>6</sup> Acute values from NJDEP (1996) based on U.S. EPA database.

<sup>7</sup> OMEE (1993), Lowest-Effect Level (LEL) represents 10th percentile of species screening-level distribution.

<sup>8</sup> Data from CEPA PSL Assessment Report for Inorganic Fluorides (EC/HC, 1993).

have defined sediment quality guidelines. These are chemical concentrations in whole sediments below which adverse effects on benthic biota are considered to be unlikely.

The federal interim sediment quality guidelines (CCME, 1999) list both Threshold Effect Levels (TEL) and Probable Effect Levels (PEL). The incidence of adverse effects at metal concentrations below the TEL is estimated at 2–11%, depending on the metal. The incidence of adverse effects at concentrations above the PEL is estimated at 12–49%. The Ontario sediment quality guidelines (OMEE, 1993) are more precisely defined as percentiles of the distribution of benthic species impairment levels (species screening-level concentrations). The Lowest-Effect Level (LEL) represents the 10th percentile (10% of species impaired at this level), and the Severe-Effect Level (SEL) represents the 90th percentile. The LEL was used here as the ENEV for assessment of benthic invertebrates that may receive chronic sediment exposures. The Quebec sediment quality guidelines (MEQ/EC, 1992) were defined in similar fashion, but using a 15th percentile to represent the minimal effect level. These values are slightly higher than the LEL for most metals.

There has been an interest in development of water quality benchmarks for metals that specifically refer to biologically available forms. However, there is not a clear consensus as to which metal species are available. The free metal ion concentration is the best predictor of the metal's bioavailability (Campbell, 1995). In soft acidic waters, free ions comprise most of the dissolved metal, while in hard alkaline waters, other dissolved forms predominate and are less available.

For assessment of releases to water, it is assumed that the empirical metal toxicity versus hardness relationships, as represented by the U.S. EPA (1995) equations for hardness adjustment, adequately reflect the differences in availability of dissolved metals between the Columbia and St. Lawrence rivers. As a conservative measure, lower-bound hardness values have been used for both rivers.

The ENEVs are somewhat above regional background in most cases. Exceptions were the fish and epibenthic ENEVs for Cd in the Columbia River, which were slightly below background and were therefore overridden by the background concentration in river water.

Further work is needed on the subject of metal bioavailability. In the interim, it is assumed for the screening-level aquatic releases portion of these assessments that all dissolved metal is bioavailable, and the water ENEVs in Table 35 reflect this. It is recognized that somewhat higher benchmarks, particularly for Cu, Ni and Pb, may provide adequate protection for aquatic life due to reduced availability of some dissolved species.

# 2.4.1.2.3 Environmental effects monitoring

There has been no recent environmental effects monitoring (EEM) at the MUC-WWTP or CEZinc. Thus, there is no field survey contribution to the weight of evidence regarding ecological effects at these facilities.

There have been recent (1995) EEM studies in the Columbia River downstream of the Cominco facilities (Figure 1). However, chemical contributions to the effects observed in this region of the Columbia River arose from multiple sources, including the zinc plant, the lead plant, the fertilizer plant and historical landfill operations. Still more recent (1999) monitoring studies (not yet available) are suggesting environmental improvement related to substantially reduced Cominco loadings.

Columbia River water was not acutely toxic in April 1995 to either *Daphnia magna* (48 hours) or rainbow trout (96 hours) at locations downstream (d/s) of the major CTO outfalls (i.e., d/s Stoney Creek, d/s Island (C-III), New Bridge d/s C-II) (Duncan, 1997). Nor was there chronic toxicity in the Microtox bioassay. Water quality conditions have improved since this time, although more recent river toxicity data are not yet available.

Periphyton communities colonizing artificial substrates in 1995 were somewhat reduced in abundance at d/s Island and Old Bridge stations, as compared to reference stations at Birchbank and Waneta (Duncan, 1997). These communities also showed reduced diversity at d/s Stoney Creek, d/s Island and Old Bridge as compared to Birchbank and Waneta. Periphyton productivity, indicated by chlorophyll *a* and dryweight biomass on sampling plates, was reduced at d/s Island and Old Bridge as compared to Birchbank and/or Waneta.

Microtox pore water bioassays in April 1995 indicated non-toxicity in sediments at New Bridge (as at Birchbank and Waneta). The New Bridge sediments consisted largely of historical slag deposits. The 14-day *Chironomus tentans* bioassay showed increased mortality and reduced growth at New Bridge as compared to Birchbank and Waneta, and also somewhat reduced growth at Waneta as compared to Birchbank (Duncan, 1997). These effects may have been related to the



shard-like texture of the slag and/or reduced food supply in these deposits.

Sediments collected in a back-eddy pool near Beaver Creek (about 10 km downstream from the C-III outfall) were found by Godin and Hagen (1992) to be toxic to *Daphnia magna* in solid-phase tests. NECL (1993) could not duplicate these results for *D. magna*, but found similar results for *Hyalella azteca*. Sediments from reference stations further upstream at Ryan Creek and downstream at Waneta were not toxic to amphipods.

Macroinvertebrate communities colonizing artificial substrates in 1995 were somewhat reduced in abundance and diversity at the d/s Island and New Bridge stations as compared to Birchbank and Waneta (Duncan, 1997). The d/s Stoney Creek and Old Bridge stations were not so affected. The community effects at New Bridge were consistent with the *Chironomus* bioassay results.

Colonization of artificial substrates is usually considered to reflect current water quality, although habitat features in the vicinity, such as water velocity, availability of natural substrate and food availability, can all influence the status of the natural community and hence the colonization success. Both periphyton and macroinvertebrate results suggest a depressed community from the Island downstream to New Bridge or Old Bridge (i.e., in the area most influenced by releases from C-III and C-II outfalls). The community status here may have been influenced by historical slag deposits in these areas and/or water quality at the time of study.

# 2.4.2 Abiotic atmospheric effects

Substances are also assessed to determine whether they have the potential to cause harm to the environment on which life depends as defined in Section 64(b) of CEPA 1999. A substance may be found toxic under Section 64(b) if it is contributing significantly to atmospheric effects such as the formation of photochemical ozone, the depletion of stratospheric ozone or climate change. The discussion that follows begins by examining the typical profile of substances that are capable of causing adverse atmospheric effects. Next, the extent to which these types of substances are released from Canadian copper smelters and refineries and zinc plants is discussed in relation to releases from other Canadian sources. This is followed by an evaluation of whether releases from Canadian copper smelters and refineries and zinc plants are likely to be harming the atmosphere. In the case of emissions from copper smelters and refineries and zinc plants, the release constituents of relevance are SO<sub>2</sub>, PM, CO<sub>2</sub> and VOCs.

# 2.4.2.1 Photochemical ozone creation

The formation of photochemical ozone is determined by several conditional parameters, but the relative importance of a typical precursor substance is dominated primarily by the reaction rate of the substance with tropospheric hydroxyl radicals (Bunce, 1996; Dann and Summers, 1997). In general, a substance capable of forming ozone must be a reactive compound and must also be volatile at ambient temperature and pressure (i.e., it is a VOC). Emission rates of VOCs, meteorological considerations such as temperature, and the degree of solar radiation present to drive the ozone-forming reactions are all important parameters (Bunce, 1996; Dann and Summers, 1997).

Based on the limited data available for 1995, only 16 tonnes (0.016 kilotonnes) of VOCs in total were reported released to the atmosphere from seven of the nine facilities of concern in these assessments (RDIS, 1995). The total reported VOC release for all of Canada in 1995 was 3575 kilotonnes (RDIS, 1995). The contribution from these smelters and refineries represents a very minor fraction of the total VOCs released from known sources in Canada. As a means of comparison, consider that the highest reported emissions of VOCs at any one location are the 4.62 tonnes released by Falconbridge-Kidd Creek (see Table 6). Considering that the average light-duty gasoline



vehicle emits about 33 kg of VOCs per year (based on sector emissions and number of vehicles in this class obtained from RDIS, 1995), VOC emissions from the Kidd Creek facility are roughly equivalent to those from 140 automobiles.

Therefore, emissions from copper smelters and refineries and zinc plants do not appear to contribute significantly to the formation of ground-level ozone.

## 2.4.2.2 Stratospheric ozone depletion

Certain compounds containing halogen atoms, such as chlorine, bromine, iodine or fluorine, are capable of depleting stratospheric ozone (WMO, 1998). A series of complex reactions occurs in the stratosphere, usually involving chlorinated or brominated molecules, leading to the creation of a reactive ion and ultimately to destruction of stratospheric ozone. Three of the four release constituents considered here —  $CO_2$ , PM and  $SO_2$  — have no halogen atoms in their molecular structure; therefore, they play no role in the depletion of stratospheric ozone. VOCs can contain halogens, but, as noted above, total emissions of VOCs from Canadian copper smelters and refineries and zinc plants are very low.

It should be noted that SO<sub>2</sub> is transformed in the troposphere into sulphate aerosols through a series of oxidative reactions. It is well known that sulphate aerosols facilitate the destructive reaction of chlorine and ozone in the stratosphere, by providing a reactive surface for the heterogeneous (gas-solid) reactions to take place (WMO, 1998). During episodes of volcanic activity, tonnes of sulphur-containing compounds may be injected into the stratosphere. Otherwise, very little of the tropospheric sulphate aerosols migrate to the stratosphere, as their lifetime is too short (4-5 days) to allow their transport to the upper atmosphere. Therefore, it is very unlikely that these stratospheric aerosols are derived from anthropogenic tropospheric sources such as smelting or refining.

Therefore, emissions of copper smelters and refineries and zinc plants do not appear to contribute to the depletion of stratospheric ozone.

## 2.4.2.3 Climate change

Typically, substances that influence or contribute to climate change must be able to absorb and reemit radiant energy from the Earth's surface, within the wavelength range 7–14  $\mu$ m (Wang *et al.*, 1976). Such substances typically must be volatile and sufficiently long-lived to absorb and re-radiate this energy. In relation to emissions from copper smelters and refineries and zinc plants, CO<sub>2</sub> and VOCs are the principal release constituents that fit the physical-chemical profile of substances that can contribute to climate change.

Releases of these substances and other greenhouse gases from the non-ferrous metal sector in Canada (including but not restricted to zinc and copper processing facilities) have been estimated for 1995 and reported as CO<sub>2</sub> equivalents (Table 6). The non-ferrous metal sector is estimated to have released about 2790 kilotonnes of CO<sub>2</sub> equivalents (Jaques, 1997). The total reported from all Canadian sectors in 1995 was 619 000 kilotonnes. Therefore, the non-ferrous metals industry sector as a whole, which includes mining as well as lead and nickel smelting and refining, contributes about 0.5% of the Canadian total of greenhouse gas emissions (Jaques et al., 1997). Contributions from copper smelters and refineries and zinc plants would be significantly lower. Release data for CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> were available from the RDIS for only four of the nine facilities being considered in these assessments. Emissions of these greenhouse gases from these four facilities in 1995 totalled 352 kilotonnes of CO<sub>2</sub> equivalents.

Sulphur dioxide emitted from zinc and copper plants can result in the formation of submicrometre sulphate aerosols. Charlson *et al.* (1992) have described how this aerosol is able to scatter incoming shortwave (solar) radiation in clear sky conditions and improve the reflective properties of cloud surfaces (albedo) in cloudy skies or increase the lifetime of clouds. These ultimately have a cooling effect on the Earth's surface. At present, however, these cooling effects are not sufficiently well understood and fully integrated into global climate change models to quantitatively estimate their impacts on the Earth's climate.

Therefore, based on available information, emissions from copper smelters and refineries and zinc plants do not appear to contribute significantly to climate change.<sup>12</sup>

2.4.3 Effects on human health epidemiological studies of
populations in the vicinity of copper smelters and refineries and zinc plants

In this section, available epidemiological studies of health effects in human populations near copper smelters and refineries and zinc plants are reviewed.<sup>13</sup> As discussed in Section 1.0, the studies considered have been restricted to those in which the population was exposed environmentally (i.e., non-occupationally), as it is these populations that are directly exposed to "releases" from these facilities.

2.4.3.1 Studies of mortality and of cancer incidence

Mortality of humans from various causes, both cancer and non-cancer, as well as cancer incidence in populations in the vicinity of copper smelters or zinc smelters and plants have been examined in a number of studies.

The endpoint most commonly studied was lung cancer. In a number of ecological (correlational) epidemiological studies, mortality from lung cancer was elevated above expectation (usually significantly) in populations near facilities smelting copper and/or zinc (Blot and Fraumeni, 1975; Newman et al., 1975; Pershagen et al., 1977; Cordier et al., 1983; Xiao and Xu, 1985; Semenciw and Manfreda, 1987); these included populations near Canadian smelters in Rouyn-Noranda, Quebec (Cordier et al., 1983), and Flin Flon, Manitoba (Semenciw and Manfreda, 1987). In contrast, lung cancer mortality was not related to residential proximity to U.S. copper smelters in several studies (Polissar et al., 1979; Mattson and Guidotti, 1980; Hartley and Enterline, 1981; Frost et al., 1987), and in a small study of the mortality experience of residents near the lead-zinc smelter in Trail, B.C., lung cancer mortality was not elevated compared to the province as a whole (British Columbia Cancer Agency, 1992).

In most of the ecological studies, some attempt was made to account for the effects of occupational exposure to smelting on lung cancer (usually by excluding smelter employees or by conducting separate analyses for females), although there was no control for occupation in two studies (Polissar et al., 1979; Xiao and Xu, 1985), and the excess observed in males in some studies was at least partly attributable to employment in copper smelting or mining. (Newman et al., 1975; Pershagen et al., 1977). There was also no information on other potential confounders, particularly smoking, or on migration in most of these studies. The study populations were also generally quite small in size (i.e., on the order of several thousand), reflecting the remote location of many of the facilities studied.

Results of more robust case-control studies of lung cancer mortality or incidence in relation to residence near copper smelters or zinc smelters and plants, in which there was some attempt to estimate individual exposure, at least

<sup>&</sup>lt;sup>12</sup> It is nevertheless recognized that efforts to reduce emissions of greenhouse gases from all relevant sectors should be undertaken as part of Canada's overall strategy to minimize climate change.

<sup>&</sup>lt;sup>13</sup> There are a large number of epidemiological studies of Japanese populations that were exposed environmentally to Cd emitted from facilities that produced copper and/or zinc (much of this work has been summarized by Tsuchiya [1978]). However, these studies are considered to be less relevant (the study populations were principally exposed via consumption of local rice grown in paddies contaminated by discharges from smelting and often also from mining) and have not been included.

crudely, are also mixed. Residence near smelters, or cumulative exposure to smelter emissions, was associated with marginally increased relative risks of developing lung cancer, after controlling for occupational exposures, in several studies near copper (Pershagen, 1985; Frost et al., 1987; Xu et al., 1989) or zinc smelters (Brown et al., 1984). In contrast, there was no significant association between lung cancer risk and intervals at increasing distance from U.S. facilities smelting copper or zinc in three studies of similar design (Lyon et al., 1977; Greaves et al., 1981; Rom et al., 1982). There was also no significant association between lung cancer mortality and various measures of residential exposure to smelter emissions (including highest level of exposure, duration of exposure above background, or cumulative exposure above background) in two well-conducted studies in Arizona copper smelter towns (Marsh et al., 1997, 1998; Stone et al., 1997). In the latter studies, extensive efforts were made to reconstruct exposures and to account for possible confounders, using lifetime residential, occupational and smoking histories, time- and location-specific estimates of residential exposures to smelter emissions based on atmospheric diffusion modelling of ambient SO<sub>2</sub> measurements, and application of multivariate statistical techniques.

Although case-control studies are generally considered to be of inherently stronger design than ecological (correlational) studies, the available case-control studies of lung cancer risk in smelter communities are quite limited in a number of respects. As in the ecological studies, exposure was inadequately characterized - few monitoring data were presented for any of the studies, and none from the earliest time periods when exposures would likely have been heaviest. The possible effects of smoking, migration and occupation were not accounted for, and the numbers of cases and controls in the areas nearest the smelters were very small in the studies of U.S. smelters by Lyon et al. (1977), Greaves et al. (1981) or Rom et al. (1982), all of which used a similar design. In addition, in two of these studies (Lyon et al., 1977; Rom et al.,

1982), the method of analysis would have yielded a less powerful test than the standard design (Hughes *et al.*, 1988). In the case of the studies by Marsh *et al.* (1997, 1998), the underlying data were limited by the small number of cases and controls estimated to have had residential exposure above background, and by substantial gaps in the residential and occupational histories for a large proportion of the decedents.

The inconsistent findings with respect to lung cancer risk across the epidemiological studies are perhaps not surprising, given the limitations inherent in the identified studies. While an association with lung cancer is plausible, based on the sufficient weight of evidence for several of the metals emitted from such facilities (Hughes et al., 1994a,b,c; Newhook et al., 1994), exposure of residents to smelter emissions would certainly have been much less than that in the occupational settings where significant excess risks for lung cancer have been observed, with the result that the increased risk, if any, would have been relatively small. In addition, the statistical power of all of the available studies is quite limited. In a review of epidemiological studies of health effects in communities surrounding arsenic-emitting industries, Hughes et al. (1988) estimated the minimum detectable risk for lung cancer near copper and zinc smelters, given the study design and the significance levels used, at 2.0 or more for 8 of the 13 studies they reviewed; the lowest minimum detectable risk was estimated at 1.18. The two case-control studies by Marsh et al. (1997, 1998) also had limited power to detect small increased risks, being designed to have greater than 80% statistical power to detect a relative risk of 2.0 for lung cancer mortality. Moreover, there was limited control for potential confounders, particularly smoking, in the available studies.

The weight of evidence for lung cancer as a result of environmental exposure to smelter emissions is, thus, inadequate. Although an association is plausible, there is little indication of consistency (although statistical power and accounting for potential confounders were limited or inadequate in all studies), strength of association, or an exposure-response relationship (although exposure was only crudely characterized, being most often limited to residence in the surrounding region).

Significant increases in cancers at some other body sites were reported in some studies (Polissar *et al.*, 1979; Lauwerys and De Wals, 1981; British Columbia Cancer Agency, 1992; Kreis, 1992; Wong *et al.*, 1992; Wulff *et al.*, 1996a), but these results were most often based on very small numbers of cases, and there was no consistent increase in any specific type of cancer. Hence, there is no consistent convincing evidence of cancers for sites other than the lung either.

With respect to non-neoplastic causes of death, the only finding with any degree of consistency is mortality from respiratory disease, which was significantly increased in a few ecological studies (Mattson and Guidotti, 1980; Cordier et al., 1983; Semenciw and Manfreda, 1987). Pershagen et al. (1977) also observed a non-significantly increased standardized mortality ratio for respiratory disease mortality in both males and females residing near the Ronnskar copper smelter in northern Sweden. The category of respiratory disease that was affected was not consistent (i.e., acute disease mortality in some studies, chronic in others), although the reliability of the death certificate data on which these distinctions was made in these early studies is unknown. However, there is no reliable information on the levels of smelterrelated substances to which these populations were exposed, and accounting for possible confounders, such as smoking, was inadequate in all of these studies.

#### 2.4.3.2 Non-neoplastic effects

Non-neoplastic effects in populations near copper smelters or zinc smelters and plants have been investigated in numerous studies. Endpoints investigated have most often included blood lead levels and associated effects on the neurological and heme systems. Renal and respiratory effects have also been investigated in a number of studies.

Levels of lead in blood in populations in the vicinity of smelters have been investigated in a large number of studies. Blood lead levels were elevated in most studies of residents near copper smelters and zinc smelters and plants, reflecting the large quantities of Pb released to the environment (Landrigan et al., 1975a, 1976; Roels et al., 1976; Savoie and Weber, 1979; Ewers et al., 1985; Chenard et al., 1987; Cook et al., 1993; Gagné, 1993, 1994; Galvin et al., 1993; Trepka et al., 1997; Hilts et al., 1998). These included the Canadian facilities at Rouyn-Noranda, Quebec (Gagné, 1993, 1994), Murdochville, Quebec (Chenard et al., 1987) and Trail, B.C. (Hilts et al., 1998). [However, blood lead levels were not clearly increased in two surveys of populations residing near a number of U.S. smelters (Baker et al., 1977; Hartwell et al., 1983).] The increased Pb burden was typically most pronounced in young children (Landrigan et al., 1975a, 1976; Savoie and Weber, 1979; Hilts et al., 1998), as a result of such factors as increased contact with house dust or soil. increased hand-to-mouth activity and greater gastrointestinal absorption. The blood lead levels in a number of these studies, particularly the earlier ones, were markedly elevated, with a large proportion of the children near smelters having levels well in excess of 10 µg/dL (Landrigan et al., 1975a, 1976; Roels et al., 1976; Chenard et al., 1987; Cook et al., 1993; Gagné, 1993, 1994; Galvin et al., 1993; Hilts et al., 1998), the currently recommended intervention level (CEOH, 1994).

Reduced environmental exposure to Pb, as a result of one or more of reduced emissions, remediation measures, and education and intervention efforts, resulted in marked reduction in children's blood lead levels in a number of these studies (Yankel *et al.*, 1977; Landrigan and Baker, 1981; Gagné, 1993, 1994; Hilts *et al.*, 1998; Hilts, 2000), including near the Canadian facilities at Rouyn-Noranda (Gagné, 1993, 1994) and Trail (Hilts *et al.*, 1998; Hilts, 2000). The most recent data from populations near copper



smelters or zinc plants in Canada indicate that roughly 10-20% of children surveyed had blood lead levels greater than or equal to  $10 \,\mu g/dL$ (Chagnon and Bernier, 1990; Gagné, 1993, 1994: Hilts, 2000). This compares favourably with earlier surveys at these locations, in which the majority of children studied had blood lead levels greater than or equal to 10 µg/dL (Chenard et al., 1987; Gagné, 1993, 1994; Hilts et al., 1998). No data on blood lead levels in populations in the vicinity of the remaining Canadian copper smelters and zinc plants were identified.

In the studies identified, levels of lead in blood were typically not related to a variety of other possible sources, including Pb from paint, local produce, drinking water or culinary pottery (Landrigan et al., 1975a, 1976; Baker et al., 1977; Cook et al., 1993; Hilts et al., 1998; Meyer et al., 1998), but were instead significantly associated with levels of Pb in ambient air, household dust or soil (Landrigan et al., 1975a, 1976; Roels et al., 1976; Yankel et al., 1977; Cook et al., 1993; Galvin et al., 1993; Hilts et al., 1998; Meyer et al., 1998).

In a number of these populations, elevated levels of lead in blood were accompanied by characteristic effects of Pb on the heme system, including reduced activity of delta-aminolevulinic acid dehydratase (Roels et al., 1976; Savoie and Weber, 1979), reduced hematocrit and increased levels of free erythrocyte protoporphyrin, although the latter effects occurred only at higher exposures (Landrigan et al., 1976; Roels et al., 1976; Savoie and Weber, 1979; Chenard et al., 1987). The nervous system was also affected in two early U.S. studies, in which extremely high blood lead levels in children living near smelters processing copper and/or zinc were accompanied by impaired performance in neuropsychological testing (effects on non-verbal cognitive and perceptual motor skills, fine motor skills and performance IQ) (Landrigan et al., 1975b) and reduced peroneal nerve motor conduction velocity (Landrigan et al., 1976).

The evidence of other non-neoplastic effects in populations with environmental exposure to substances released from copper smelters and zinc smelters and plants is more limited.

Effects on renal function and on calcium metabolism/bone mineralization were observed in three well-conducted cross-sectional studies in regions of Belgium and The Netherlands contaminated with Cd emitted from zinc smelters and plants. In these studies, Cd in urine (a measure of lifetime exposure to Cd) was significantly increased in the contaminated regions, and residence in these regions, proximity of residence to the zinc smelters and plants and/or urinary Cd excretion were significantly associated with increased excretion of various urinary markers of renal proximal tubular function, after adjustment for a wide range of potential confounders (Buchet et al., 1990; Kreis, 1992: Staessen et al., 1994: Hotz et al., 1999). There were also indications of Cd-related alterations in calcium balance in these populations (increased serum alkaline phosphatase activity, decreased serum calcium, increased urinary calcium excretion), perhaps secondary to the renal effects (Staessen et al., 1991a; Kreis, 1992). Urinary excretion of Cd or calcium or residence in the contaminated areas was associated with significantly decreased forearm bone density and increased risk of bone fractures and height loss, after adjustment for confounders (Staessen et al., 1999). There were no clear effects on blood pressure or on the prevalence of hypertension or cardiovascular disease in these populations (Staessen et al., 1991b: Kreis, 1992).

In another well-conducted study, children living near a copper-silver smelter in Germany had small but significantly increased urinary arsenic and cadmium and blood lead levels (Trepka et al., 1996, 1997; Ritz et al., 1998) and increased prevalences of respiratory diseases and allergies (including histories of bronchitis, allergy, eczema and various respiratory symptoms, as well as positive skin prick tests and increases in specific IgE in physical examination)



(Heinrich *et al.*, 1999). There were also increased prevalences of reported cough, but no significant effects on other respiratory symptoms or on lung function in children exposed to high levels of  $SO_2$  emitted from copper smelters in Arizona in two more limited studies (Dodge, 1983; Dodge *et al.*, 1985).

There were no remarkable patterns in medical utilization/hospitalization studies of populations near Canadian copper smelters and zinc plants in Flin Flon, Manitoba (Anon., 1987) and Trail, B.C. (Fisk *et al.*, 1994), although each of these studies was very limited in scope, and the utilization rates would have been affected by other factors in addition to disease prevalence.

2.4.3.3 Effects on reproduction and development

Epidemiological studies of effects on reproduction and development that were

identified are limited to a small number of ecological (correlational) studies of populations residing near a copper smelter in northern Sweden. In these studies, residence in areas near the smelter was significantly associated with an increased frequency of spontaneous abortion (Nordstrom et al., 1978a) and with reduced birth weight in one study (Nordstrom et al., 1978b), but not with reduced weight in another study (Wulff et al., 1995), time to pregnancy (Wulff et al., 1999) or with the frequency of congenital malformations (Nordstrom et al., 1979; Wulff et al., 1996b). However, exposure characterization was limited to residence in a given area, and all of the studies were further limited by one or more of small numbers of cases and inadequate control for other factors that may affect the endpoints examined, such as smoking or parental employment at the smelter.



### 3.0 Assessment of "Toxic" under CEPA 1999

#### **3.1 CEPA 1999 64(a): Environment**

The environmental risk assessment of the PSL substances "Releases from Primary and Secondary Copper Smelters and Copper Refineries" and "Releases from Primary and Secondary Zinc Smelters and Zinc Refineries" is based on the procedures outlined in Environment Canada (1997a).

Because of the evidence of harm from past releases from Canadian copper smelters and refineries and zinc plants (see Sanderson, 1998, for a summary of these effects), an attempt was made to base these assessments of current releases on realistic assumptions and to estimate the probability of adverse effects. The assessments of the impacts of effluents differed in that they were conducted deterministically, and the risk quotients (RQs) derived are in some respects conservative.

As described previously (Section 2.0), an analysis of exposure pathways for individual release constituents and subsequent identification of sensitive receptors were used to select environmental assessment endpoints (e.g., adverse reproductive effects on sensitive fish species in a community). For each combination of endpoint and release constituent, one or more EEVs were determined — expressed either as concentrations of bioavailable chemical species in air, soil or surface water or as rates of deposition of bioavailable forms from air. Whenever possible, EEVs were based on recent empirical data. Models were used to estimate EEVs if suitable empirical data were not available, and as an additional line of evidence to support empirical values.

An ENEV was also determined for each combination of endpoint and release constituent, by dividing a CTV by an application factor. The CTV is typically an estimate of low toxic effects (e.g.,  $EC_{25}$ ) on the most sensitive environmentally relevant species. To increase realism, application factors used in these assessments were very small — usually 1.0 and never more than 2.0. Consequently, when ENEVs are exceeded, there is a significant probability of effects on sensitive organisms. Since all of the constituents of the releases assessed are natural substances --- and some are essential micronutrients — care was taken to avoid ENEVs within normal natural concentration ranges. When exposure values were expressed as deposition rates, ENEVs were converted to critical loads. Critical loads are defined as rates of deposition required for contaminants to reach threshold effect values (i.e., ENEVs) in receiving media. Critical loads were estimated probabilistically using appropriate fate and transport models.

Risk was evaluated for each combination of endpoint and release constituent by calculating one or more risk quotients (i.e., EEV/ENEV or EEV/CL). Effects are considered possible if risk quotients for any release constituent exceeded 1.0. In cases where none of the quotients for individual release constituents exceeded 1.0, their combined effects may be considered. Typically, the releases considered contained various mixtures of metals, and their combined effects may be determined by assuming additivity as described below. Because risk quotients for at least one metal exceeded 1.0 at locations close to most of the facilities examined, potential for harmful effects could generally be established without considering additivity.

Joint effect of metal emissions: Of the various models in the literature describing the joint effect of toxicants on organisms, the additivity model is often the most accurate. In cases where it is not the most accurate, it may still be used because, depending upon how it is

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applied, it may be conservative; that is, it can predict slightly more severe effects than actually occur (Posthuma *et al.*, 1997).

The additivity model is essentially a sum-of-fractions model. The exposure concentration for each toxicant is normalized relative to a standard toxicity endpoint for that toxicant. Typically, this means that for each toxicant, the exposure concentration is divided by a measure of effects, such as an  $EC_{25}$  or an  $LC_{50}$ . The resulting risk quotient is sometimes referred to as the toxic unit (TU). Because these are normalized units (i.e., they represent the fraction of exposure required to experience an effect), they can be added, and the sum is an index of possible toxic effect due to exposure to multiple toxicants. In these assessments, since EEVs were divided by ENEVs, the  $\Sigma TU$  becomes the sum across the metals (subscript "i") of the concentration ("C") of each metal in the mixture of contaminants (EEV<sub>c</sub>) divided by the ENEV concentration for that metal singly ( $ENEV_{C_i}$ ):

 $\Sigma TU = \Sigma (EEV_{C_i} / ENEV_{C_i}).$ 

According to this model, when  $\Sigma TU>1$ , effects are possible.

In cases where effects are expressed as critical loads,  $\Sigma TU$  based on CL ( $\Sigma TU_{CL}$ ) is a ratio of flux densities to the surface at the receptor location:

$$\Sigma T U_{CL} = \Sigma (E E V_{F_i} / C L_{F_i})$$

where  $\text{EEV}_{F_i}$  is the flux density ("F") of metal "i" in the mixture of contaminants, and  $\text{CL}_{F_i}$  is the critical load for that metal. In this case, when  $\Sigma TU_{CL}$ >1.0, effects are possible.

#### 3.1.1 Copper smelters and refineries

#### 3.1.1.1 Releases to air

For the purposes of this assessment, releases from copper smelters and copper refineries are considered together. This was done for two reasons:

- Copper smelters and copper refineries are connected parts of the process of producing metallic Cu. Furthermore, the distinction between smelters and refineries is not always clear. For example, anode casting — the conversion of blister Cu (the impure product of the smelting process) into anodes for use in electrolytic refining — may take place at either a smelter or a refinery. This casting process can result in significant emissions of both metals and SO<sub>2</sub>.
- Of the three copper refineries included in these assessments, only one is a stand-alone facility. The other two are co-located with a smelter operated by the same company. Thus, environmental receptors are often exposed to releases from copper smelters and refineries together.

#### 3.1.1.1.1 Sulphur dioxide

Ambient  $SO_2$ : Data for the monitoring of  $SO_2$  in the vicinity of copper smelters and refineries were provided by companies and provincial governments. These represent exposure of organisms to ambient  $SO_2$  over time scales of the growing season (April to October) as well as over 1 hour. Monitoring data were summarized in Tables 10 and 11, respectively.

The chronic CTV for SO<sub>2</sub> is  $21 \ \mu g/m^3$  for slight effects on forest growth for exposure over the growing season. The acute CTV — for injury to sensitive vegetation — is 900  $\mu g/m^3$  for 1-hour exposure. ENEVs based on these CTVs were estimated to be 10  $\mu g/m^3$  and 450  $\mu g/m^3$ , respectively. Derivation of these values was discussed in Section 2.4.1.1.1, and the values are summarized in Table 29. Table 36 summarizes risk information for ambient SO<sub>2</sub>. As indicated by source attribution information in the first column of this table, of the five facilities (and region, in the case of Sudbury) that include copper smelting/refining, Falconbridge-Kidd Creek is the only one where other metal production operations contribute to SO<sub>2</sub> emissions. Sixty-five percent of the SO<sub>2</sub> released from the Falconbridge-Kidd Creek facility is attributed to the copper smelter. At the other locations, all SO<sub>2</sub> releases are attributed to copper smelting.

In relation to chronic exposure, "growing season average risk quotients" were obtained by dividing the exposure values calculated as averages for the growing season by the ENEV of  $10 \ \mu g/m^3$ . Values in excess of 1 indicate exposure over the growing season to concentrations greater than those believed to cause no harmful effects. Values greater than 2 indicate exposure to concentrations in excess of those reported to have harmful chronic effects on sensitive vegetation (i.e. the CTV). Quotient values between 1 and 2 may be interpreted to indicate that harmful effects are "possible" for sensitive receptors, while those greater than 2 indicate that effects on sensitive receptors are "likely."

It is clear from Table 36 that risk quotients for chronic exposure of 2 or greater occur frequently within a few kilometres of the facilities, with lower risk quotients observed at greater distances. In general, the entire Sudbury region shows risk quotients in the "possible" effects range (RQ between 1 and 2). At most facilities, all monitoring stations are located very close to source, making estimation of the area impacted difficult.

Table 36 also provides information on acute risk for exposure to ambient  $SO_2$  over time scales of 1 hour. The last two columns show the frequencies of exceedence of risk quotients of 1 and 2, respectively, over the growing season. These risk quotients have been calculated by dividing the 1-hour exposure values by the ENEV of 450 µg/m<sup>3</sup>. There are a moderate number of exceedences of the 1-hour RQ=1 level

near all facilities. As may be expected, there are significantly fewer exceedences of the RQ=2 level. The exception to this is one monitoring station located close to the HBM&S facility, where more than half of the 1-hour averages that exceed RQ=1 also exceed RQ=2. The large number of exceedences at monitoring stations close to this facility may indicate that a significant proportion of SO<sub>2</sub> releases are from fugitive sources.

It should be noted that most monitoring stations produce about 5000 valid 1-hour averages over the period of the growing season. Therefore, the number of times these "possible" and "likely" acute risk levels are exceeded represent a relatively small percentage of the total time. However, even a single exceedence could cause damage to sensitive plants, as the ENEV is based on a 1-hour exposure.

The "Maximum" column of Table 36 shows the risk quotient for the highest 1-hour average concentration (measured over the growing season) at each monitoring station. These quotients represent the extreme for  $SO_2$  exposure for vegetation in the vicinity of copper smelting and refining facilities.

It should be noted that all  $SO_2$  monitoring stations near the Noranda-Horne facility are located in the town's residential areas to the northwest, southwest, south and southeast of the smelter. None of the stations is located to the north, northeast or east of the facility, which are the directions typically downwind of the smelter. Risk quotients in these downwind directions would be expected to be somewhat higher.

Quotients for the Noranda CCR facility are not shown in Table 36 because only limited data for  $SO_2$  monitoring in the vicinity of the Noranda-CCR facility were available. Further, source attribution is problematic, as this copper refining facility has relatively minor emissions of  $SO_2$ , while other significant  $SO_2$  sources are present in the same geographical area.

Facility, data year, and	Distance to	Growing season	Risk que	otients for 1-hour a	average
source attribution (%)	nearest facility (km)	average risk quotient <sup>1,2</sup>	Maximum (in growing	No. of times l (in growin	
			season) <sup>1</sup>	RQ=1 (ENEV)	RQ=2 (CTV)
Copper smelters and refir	ieries				
Noranda-Gaspé	1.5	2.6	3.2	58	3
1997 data Copper smelter – 100%	1.7	2.3	3.9	29	8
Noranda-Horne	1.5	1.6	4.9	25	3
1997 data Copper smelter – 100%	1.8	4.0	5.0	42	4
	1.8	0.6	3.7	6	1
	2.3	0.9	1.4	6	0
	2.4	2.4	2.2	31	3
	2.5	2.8	2.6	54	3
	3.2	2.2	1.5	6	0
Sudbury region	0.7	1.3	5.5	15	2
Mostly 1997 data Inco: - Copper smelter – 84%	0.7	0.9– <b>2.2</b>	2.5	11 excee	d RQ=1.5
	3.0	1.3	2.4	11	2
- Copper refinery – 0% - Nickel refinery – 0%	3.5	0.9	2.0	10	1
Falconbridge:	4.0	0.2–1.4	1.0	0 exceed	l RQ=1.5
- Copper smelter – 16%	4.2	0.8	1.5	9	0
	4.9	1.0	2.1	4	I
	5.0	1.4	2.1	15	3
	7.8	0.8	3.5	5	2
	8.5	1.1	1.4	4	0
	9.0	1.5	1.7	11	0
	9.7	0.2-1.4	0.9	0 exceed	1 RQ=1.5
	10.0	1.2	1.9	13	0
	10.8	0.9	3.2	7	1
	13.8	0.4	0.8	0	0
	14.9	0.6	1.1	3	0
Zinc plants					
Noranda-CEZinc,	1.3	2.6	2.8	60	8
1998 data Zinc plant – 100%	1.7	0.3	0.6	0	0

# **TABLE 36**Risk quotients for exposure of vegetation to ambient $SO_2$ as a function of distance from<br/>copper and zinc production facilities



Facility, data year, and	Distance to	Growing season	Risk qu	otients for 1-hour :	average		
source attribution (%)	nearest facility (km)	average risk quotient <sup>1,2</sup>	Maximum (in growing	No. of times RQ exceeded (in growing season)			
			season) <sup>1</sup>	RQ=1 (ENEV)	RQ=2 (CTV)		
Cominco-Trail,	0.8	2.4	1.9	13	0		
1998 data Zinc plant – 85%	1.2	3.0	4.2	6	1		
Lead plant – 15%	1.3	2.7	2.7	28	1		
	1.4	3.4	3.6	13	3		
	2.4	2.3	3.2	16	2		
	3.9	2.6	4.2	4	2		
	4.3	1.4	2.9	2	2		
	10.5	2.1	1.8	4	0		
	12.7	0.8	0.6	0	0		
	19.0	0.4	0.5	0	0		
	27.1	0.6	0.2	0	0		
Facilities having both copp	er smelters and ref	fineries and zinc pla	nts				
HBM&S,	0.7	3.6	5.9	66	35		
1998 data Copper smelter – 100%	1.9	2.0	4.1	51	11		
Zinc plant – 0%	2.1	1.2	2.9	17	4 *		
	2.6	0.9	2.6	17	5		
Falconbridge-Kidd Creek,	0.6	1.7	2.5	18	1		
1997 data Copper smelter – 65%	0.6	0.0–1.2	0.1	0	0		
Copper refinery – 0%	1.4	2.2	1.8	30	0		
Zinc plant – 15% Concentrator – 20%	1.6	0.0– <b>1.2</b>	0.1	0	0		

**TABLE 36** Risk quotients for exposure of vegetation to ambient  $SO_2$  as a function of distance from<br/>copper and zinc production facilities (continued)

<sup>1</sup> Values in bold meet or exceed a risk quotient of 1.0.

<sup>2</sup> In some cases, a range is shown for "Growing season average risk quotient," as insufficient data were available to properly correct for values below the detection limit. The lower value is calculated by letting all values below the detection limit equal zero. The higher value is the sum of the lower value and one-half of the detection limit.

Uncertainties: Uncertainties associated with the estimation of exposure to ambient  $SO_2$ include the placement of  $SO_2$  monitors in locations that may result in overestimation or underestimation of exposure levels typical of the area. An example of underestimation was provided above. Further, the high detection limits of some monitoring instruments necessitated statistical analysis, which likely introduced minor error in estimates of seasonal average  $SO_2$ concentrations. There is also uncertainty associated with selection of CTVs and ENEVs, although the effects information base is relative large for ambient  $SO_2$ .

There is a significant body of evidence of detrimental effects on the environment resulting from fumigations of ambient SO<sub>2</sub> in the vicinity of copper smelting facilities. These are mostly related to the high releases of SO<sub>2</sub> in the past. In particular, damage to the Sudbury region has been extensively documented (see, for example, Linzon, 1999, and references cited therein).

Based on data in Table 36, it may be concluded that there is the possibility for effects on sensitive vegetation from both acute (1-hour) and chronic (growing season) exposure to  $SO_2$ released from the smelting component of copper smelting/refining facilities. Although there are few monitoring stations located further than 3 km from the facilities, data for the Sudbury region indicate that the impacted area may extend to 10 km or more from the source. Distances over which effects on sensitive species are more likely (indicated by risk quotients of greater than 2) are somewhat smaller — generally extending out to 4 km or less from the source, but in some cases extending beyond 10 km.

#### 3.1.1.1.2 Deposited sulphate

Sulphur dioxide emitted from copper smelters and refineries can be oxidized to sulphate in the atmosphere. Both sulphur dioxide and sulphate can be transported long distances from the source, resulting in acidic deposition to soils and lakes over large areas.

The source-receptor model IAM (see Section 2.3.1.1.3) has been used to estimate annual wet sulphate deposition in four regions of eastern Canada. IAM was calibrated to account for oxidation, transport and sulphate deposition based on SO<sub>2</sub> emission sources throughout Canada and the United States for the period 1990–1993. The four receptor regions considered are Algoma, Ontario; Muskoka, Ontario; Montmorency, Quebec; and Kejimkujik, Nova Scotia. Estimates of annual total wet sulphate deposition to the four areas from the period 1990-1993 are shown in Table 37.

TABLE 37	Risk quotients for wet sulphate	deposition for four receptor are	as in eastern Canada
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Parameter		Recep	tor area	
	Algoma	Muskoka/ Sudbury	Montmorency	Kejimkujik
Total wet sulphate deposition from Canadian & U.S. anthropogenic sources and natural background (kg/ha/a) <sup>1</sup>	17.5	22.9 (Muskoka)	18.8	13.9
Critical load for surface waters for 95% protection to pH $\ge 6.0$ (kg/ha/a) <sup>2</sup>	8.0	13.2 (Sudbury)	6.9	<6
Risk quotient	2.2	~1.7	2.7	>2.3
Source attribution: <sup>3</sup>				
Canadian copper smelters	3%	7%	8%	2%
Canadian copper refineries	0.1%	0.01%	0.06%	0.01%
Canadian zinc plants	0.02%	0.01%	0.2%	0.03%

<sup>1</sup> Deposition values were produced by IAM based on emission data for the period 1990-1993.

<sup>2</sup> Critical loads are based on Jeffries et al. (1999).

<sup>3</sup> Source attributions are relative to the sum of anthropogenic and natural deposition.



Critical loads for wet sulphate deposition derived to allow 95% of lakes to maintain a pH of 6.0 or higher are also shown in Table 37. These are based on evaluation of between 200 and 300 lakes in each of the four regions considered (Jeffries *et al.*, 1999). A critical load for Muskoka was not available. Therefore, the value estimated for Sudbury, located about 150 km northwest of Muskoka, was used.

The risk quotients shown in Table 37 were calculated by dividing the estimated total wet sulphate deposition, due to anthropogenic and natural SO<sub>2</sub> sources, by the estimated critical loads for wet sulphate deposition for each of the four areas. At all receptor locations considered, the calculated risk quotient is greater than 1, indicating a potential risk to the environment receiving the deposition. It should be recognized that reductions in SO<sub>2</sub> emissions in Canada and the United States have occurred since the 1990-1993 period on which this evaluation is based. Continued study has shown, however, that despite these reductions, critical loads are likely still being exceeded in these regions (Acidifying Emissions Task Group, 1997). Note that these risk quotients are based on all North American sources of SO<sub>2</sub>.

IAM parameters were scaled based on 1995 emission data for the facilities being considered in these assessments, to estimate incremental contributions to deposition attributable to these sources. Attribution based on source type is shown in Table 37. For example, about 7% of the sulphate deposited at Muskoka is due to SO<sub>2</sub> released from Canadian copper smelters. Although these percentages have been calculated based on releases from all sources of wet sulphate deposition between 1990 and 1993, comparison of sulphate deposition for these years to those for 1995 at monitoring sites in eastern Canada suggests that total wet sulphate deposition in these regions changed relatively little between 1990 and 1995 (Table 14). It is furthermore recognized that SO<sub>2</sub> emissions from several of the facilities being assessed have been reduced somewhat since 1995, the year on which attribution was based. However, anthropogenic

emissions from many sources in Canada and the United States have likely also decreased somewhat. Thus, the relative source attribution percentages presented in Table 37 should be fairly reflective of current conditions.

Uncertainties: There is uncertainty inherent in any modelling exercise, including the detailed evaluation of acid deposition in eastern Canada that led to the source-receptor relationships used in this work (Olson et al., 1983). As pointed out in Section 2.3.1.1.3, however, at sites where comparison was possible, there is good agreement between estimates of acidic deposition and results of monitoring conducted by the OME. There are also uncertainties associated with the estimation of critical loads in the receptor areas, as well as in the comparison of source attribution estimates derived from 1995 emission data with IAM modelling based on the years 1990-1993. As discussed above, however, differences between the two time periods are likely fairly minor.

A significant body of evidence of detrimental effects on the environment resulting from historic acid deposition has been established. In particular, damage to the Sudbury region has been extensively documented (see, for example, Sanderson, 1998, and references cited therein).

There are clearly detrimental effects on lakes in eastern Canada owing to anthropogenic releases of SO<sub>2</sub>. It may be concluded that Canadian copper smelters contribute a moderate portion of the SO<sub>2</sub> leading to this acid deposition (up to 8% at the receptor locations considered). Canadian copper refineries appear to have very minor contributions to acid deposition. It should be recalled, however, that the distinction between emissions from the smelting and refining processes is not always clear. It should also be noted that, based on field studies in the Sudbury region, large emission sources such as copper smelters can contribute a much greater fraction of total sulphate deposited within about 100 km of the source, where dry deposition is a significant factor (Keller and Carbone, 1997).

#### 3.1.1.1.3 Deposited metals

Estimates of annual deposition of the metals Cu, Zn, Ni, Pb, Cd and As, based on monitoring data obtained in the vicinity of copper smelters and refineries, are summarized in Tables 15, 17 and 18. Derivation of critical loads for these metals was discussed in Section 2.4.1.1.3, and annual critical loads were summarized in Tables 31 and 33 for terrestrial and aquatic endpoints respectively.

Table 38 shows risk quotients for metals deposited in the vicinity of copper smelters and refineries. Risk quotients were determined by dividing the exposure (deposition) values by the expected effect (critical load) values. Both deposition and critical load estimates are based on soluble forms of metals. As discussed in Section 2.3.1.2.2, deposition values based on dustfall data are expected to be the most reliable. When data of other types are also available, greater weight is given to dustfall values. Comparison of deposition (and hence risk quotients) for sites located close to facilities where both dustfall and TSP monitoring are conducted indicated that, in general, estimation of total deposition from TSP data underestimated the deposition by a factor of 2-5. The likelihood of TSP-based data to underestimate deposition rates was discussed in Section 2.3.1.2.2.

Critical loads used in determination of the risk quotients are the 25th percentile values, for either sandy soils or circumneutral to acidic lakes. If deposition were to be continued at these rates in a typical Shield area until steady state is achieved, 25% of the sandy soils and lakes would be expected to be adversely impacted. Thus, when the risk quotient for a particular monitoring station is equal to 1.0, there is a 25% chance that sandy soils or soft-water (Shield-type) lakes in the vicinity of the station will be adversely affected by the contaminant. Risk quotients above 1.0 indicate that there is a greater chance of observing effects near that station and that effects may be more severe. Critical loads derived for sandy soils typical of those found on the Canadian Shield were used to calculate risk quotients for the Noranda-CCR and NorandaGaspé facilities. Although these are not located on the Shield, examination of local surface geology and soils maps (Lajoie, 1954; Fulton, 1996; Service des inventaires forestiers, 1995) indicates that sandy soils occur near each of these facilities, making use of soil critical loads suitable for application at these sites. At all other sites, the more sensitive of soil pore water or surface water critical loads were used.

Emission-based source attribution information is also shown in Table 38. Noranda-Gaspé, Noranda-Horne and Noranda-CCR are stand-alone facilities, and all metal emissions may be attributed to copper smelting or copper refining. Most metal emissions in the Sudbury region are attributable to copper processing, although the Inco-Copper Cliff facility also includes a nickel refinery, which contributes to releases of Cu, Ni, Pb and As. The zinc pressure leaching process used at HBM&S-Flin Flon is reported to have insignificant emissions of metals, and emissions from this facility may be fully attributed to the copper smelter. Between 14% and 92% of metal emissions from the Falconbridge-Kidd Creek facility are attributable to copper processing. It should be noted, however, that because these attributions are based on only a partial inventory of sources (e.g., fugitive releases from tailings areas are not included), the relative contributions of smelters and refineries to total metal deposition rates estimated from monitoring data may be somewhat overestimated.

In general, it may be stated that exceedences of 25th percentile critical loads for Cu extend out to greater distances around copper smelters and refineries than those for other metals. The maximum distance at which an exceedence is observed for Cu is 14.0 km, which, assuming symmetrical deposition patterns, equates to an area of greater than 600 km<sup>2</sup>. Exceedences for Cu extend out at least 2 km at all facilities examined except Noranda-CCR. Exceedences of 25th percentile critical loads for Zn, Pb, Cd and As are also observed, typically out to distances of 2-4 km from the facilities.



Distance						mpared	to suitable 25th percentile critical loads) <sup>1,2</sup>						
from nearest		Base	ed on d	ustfall (	lata			T	Base	ed on ot	her dat	a types	
facility (km)	Cu	Zn	Ni	Pb	Cd	As	Cu	Zn	Ni	Pb	Cd	As	Data type
Copper smelte	rs and r	efinerie	s										
Noranda-Gaspé	(Source	e attribut	tion: Co	pper sn	nelter –	100%)							
0.6	61	1.6		4.0	0.3	1.7							
1.3	9.4	0.9		1.6	0.6	0.7							
1.4	7.7	0.9		1.1	0.4	0.5							
1.5	6.2	0.5		0.8	0.1	0.3	1.5	0.1		0.6	0.1	0.2	TSP
1.5	6.8	1.5		0.9	0.1	0.3							
1.6	26	1.1		2.2	0.2	0.8							
- 1.8	6.0	0.5		1.3	0.1	0.3							
3.0	6.7	0.5		1.0	0.1	0.3							
3.8	2.5	0.5		0.4	0.0	0.2							
3.8	3.9	0.4		0.8	0.1	0.2							
6.1	1.2	0.4		0.1	0.1	0.0	1						
6.8	1.2	0.3		0.4	0.0	0.1	1						
7.5	2.5	0.4		0.3	0.2	0.1							
12.5	1.2	0.3		0.2	0.0	0.0							
Noranda-Horne	e (Source	e attribu	tion: Co	pper sn	nelter –	100%)							
0.2								1.0					Snowpack
0.4												1.0	Snowpack
1							52	0.7	0.0	4.1	0.6	0.9	Snowpack
2							33	0.5	0.0	3.0	0.4	0.6	Snowpack
3							22	0.4	0.0	2.2	0.3	0.5	Snowpack
4							15	0.3	0.0	1.6	0.2	0.4	Snowpack
5							10	0.2	0.0	1.2	0.2	0.3	Snowpack
5.8										1.0			Snowpack
10							2.4	0.1	0.0	0.4	0.1	0.1	Snowpack
14.0							1.0						Snowpack
15							0.8	0.1	0.0	0.2	0.1	0.0	Snowpack
20							0.5	0.0	0.0	0.1	0.1	0.0	Snowpack
0.3	[						[			8.9	1.9	4.0	TSP
0.7							21	1.6	0.0	4.8	2.2	1.8	TSP
0.8							l.			2.6	0.9	1.2	TSP
1.8							12	0.8	0.0	2.4	0.9	0.9	TSP
2.9							4.2	0.4	0.0	0.6	0.2	0.2	TSP
3.2	4.7	0.4		0.5	0.3	0.2							
3.2	22	0.9		2.8	0.8	1.1							
3.2	8.7	0.6		0.9	0.3	0.4							
3.2	10.3	0.8		1.4	0.4	0.4							
6.4	2.7	0.3		0.3	0.3	0.1							
6.4	3.7	0.3		0.5	0.3	0.1							

**TABLE 38** Risk quotients for metal deposition as a function of distance from copper and zinc production facilities

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Distance	Risk quotients (compared to suitable 25th percentile critical loads) <sup>1,2</sup>												
from nearest	Based on dustfall data						Based on other data types						
facility (km)	Cu	Zn	Ni	Pb	Cd	As	Cu	Zn	Ni	Pb	Cd	As	Data type
6.4	5.5	0.3		0.6	0.3	0.2		•		•	<b></b> _		L
6.4	3.4	0.4		0.6	0.3	0.2							
Sudbury region													
	Source	attributio	on:										
	- 2 cop	per smelt	ers				73%	100%	70%	81%	_	86%	
		er refiner					13%	0%	0%	0%	_	7%	
	- INICKE	el refinery					14%	0%	30%	19%	-	7%	
0.7							9.7		0.9	0.0		0.0	TSP
0.8							1.5		0.2	0.0	2.1		TSP
1.0							1.5	6.5	0.2	0.0	2.1	0.0	TSP
3.5							1.1	0.0	0.0	0.1	0.1	0.0	Wet + dry
4.9							0.5	0.0	0.0	0.0	0.1	0.0	Wet + dry
6.0							4.8		0.7	0.1	<b>.</b>	0.0	TSP
8.8							0.6	0.0	0.0	0.0	0.1	0.0	Wet + dry
14.9							0.4	0.0	0.0	0.0	0.1	0.0	Wet + dry
22.6				~		0000	0.2	0.0	0.0	0.0	0.0	0.0	Wet + dry
Noranda-CCR	Source	attributi	on: Cop	oper refi	nery – l	00%)				<u> </u>			
0.5							0.8	0.3	0.0	0.1	0.0	0.1	TSP
Zinc plants													
Noranda-CEZir	nc (Sou	rce attrib	ution: 2	Zinc pla	nt – 100	%)							
0.6		39			5.2								
0.7		33			4.8								
1.3		7.5			1.0			16			1.2		TSP
1.4		6.4			0.7								
1.7		2.4			0.2								
1.9		4.5			0.6								
2.2		2.3			0.6								
3.4		3.4			0.6								
3.6		2.2			0.4								
3.8		4.4			0.6								
Cominco-Trail	3												
	Source	attributio	on:										
	- Zinc J	plant					_	90%	_	4%	36%	0%	
	- Lead							10%	_	96%	64%	100%	
0.8		24		6.9	3.2	0.2		3.4		1.3	0.5	0.1	TSP
1.0		21		14	4.2	0.4							
1.2		12		5.0	1.5	0.1							
1.3	3.3	25		8.6	13								

#### TABLE 38 Risk quotients for metal deposition as a function of distance from copper and zinc production facilities (continued)



Distance			Ris	sk quotie	ents (cor	mpared	to suita	ble 25t	h perce	ntile cri	itical loa	ads) 1,2	
from nearest		Bas	ed on d	lustfall o	lata				Base	ed on ot	her dat	a types	
facility (km)	Cu	Zn	Ni	Pb	Cd	As	Cu	Zn	Ni	Pb	Cd	As	Data type
1.4								2.2		1.0	0.5	0.1	TSP
1.5		23		7.2	3.0	0.2							
1.6		16		4.8	1.8	0.1							
2.0		7.8		3.2	1.0	0.1							
2.2		13		3.8	1.9	0.1							
2.4		2.8		1.3	0.8	0.1		1.2		0.6	0.4	0.1	TSP
3.9		13		4.8	1.7	0.1		2.4		1.1	0.5	0.2	TSP
4.3		5.0		2.4	0.9	0.1		1.4		0.9	0.4	0.1	TSP
7.0		2.4		1.2	0.9	0.1							
10.5		7.7		1.5	1.0	0.1		2.6		1.1	0.6	0.1	TSP
12.7								1.0		0.6	0.4	0.1	TSP
19.0								0.3		0.2	0.3	0.1	TSP
Facilities havin	ng both	copper	smelte	ers and r	efinerie	s and z	inc plan	ts					
HBM&S (Sour	ce attrib	ution: C	opper :	smelter –	- 100%;	Zinc pla	int – 0%	)					
0.6							18	3.7		1.3	6.1	0.4	TSP
1.1							10	0.9		0.4	1.9	0.1	TSP
1.9							5.5	0.5		0.3	1.3	0.1	TSP
2.0							12	0.5		0.2	1.1	0.0	TSP
Falconbridge-K	idd Cre	ek											
	Source	attributio	on:										
	- Coppe	er smelte	г				66%	15%	87%	92%	79%	14%	
	- Coppe	er refiner	у				0%	0%	0%	0%	0%	0%	
	- Zinc I	plant					2%	24%	6%	1%	7%	86%	
	- Conce	entrator					32%	61%	7%	7%	14%	0%	
0.3	207	30		1.7	14	0.5							
0.6	e.						50	7.0		1.7	4.2	0.7	TSP
1.2	76	13		0.9	4.5	0.2							
1.4							15	2.6		0.5	1.7	0.3	TSP
1.6							9.0	1.5		0.3	1.0	0.2	TSP
2.0	51	5.8		1.7	3.4	0.1							
2.0	25	3.4		6.8	1.7	0.0							
2.4	23	4.0		0.7	1.2	0.0							
4.2	40	3.9		0.8	2.2	0.3							_

**TABLE 38** Risk quotients for metal deposition as a function of distance from copper and zinc production facilities (continued)

<sup>1</sup> Bolded risk quotients indicate that the EEV equals or exceeds the  $CL_{25}$ .

<sup>2</sup> Risk quotients are based on comparison to soil pore water critical loads for Cominco, CEZinc, Noranda-CCR and Noranda-Gaspé and on the more sensitive of soil pore water or surface water critical loads for HBM&S, Falconbridge-Kidd Creek, Sudbury region and Horne.

<sup>3</sup> Atmospheric emissions from the Cominco facility are expected to be higher in 1999 than in 1998, as the furnaces were brought up closer to capacity operation in 1999 (personal communication with facility operators).



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None of the six risk quotients for the monitoring station at Noranda-CCR exceeded 1.0 individually. It should be noted, however, that the value for Cu (0.8) is close to 1, and also that the sum of the individual quotients is slightly above 1. If the additivity model described at the beginning of Section 3.1 is applicable, it is possible that sandy soils in the vicinity of Noranda-CCR are adversely impacted by the combined loadings of these metals. Furthermore, as indicated earlier, there is a significant probability that risk quotients based on TSP data - such as those for the CCR station - are low by a factor of 2-5. If the quotients for Noranda-CCR were increased by even a factor of 2, the value for Cu would exceed 1.

It may be concluded that there is potential for effects on aquatic and/or soildwelling organisms from exposure to steady-state concentrations of metals in the vicinity of copper smelters and refineries resulting from releases (especially of Cu) from these facilities. Impacted areas appear to extend up to about 14 km from the sources based on comparison to 25th percentile critical loads, which equates to an area of as much as 600 km<sup>2</sup>.

Exceedence radii were also estimated based on the generic deposition modelling described in Section 2.3.1.2.3 and detailed in SENES Consultants (2000).

Although many of the model input parameters are based on data for the facilities being assessed, it is important to recognize that the results of generic modelling do not correspond to any individual facility. In particular, results for a 95th percentile modelled deposition will draw from among the worst of each characteristic (emission rate, stack height, etc.) that has been used as input to the model, irrespective of facility.

The results shown in Table 23 are generally supportive of the deposition data based on monitoring. Maximum radii of exceedence of  $CL_{25}$ s estimated from the empirical data are based on higher emitting facilities, and these radii

generally fall between those determined from the 50th and 95th percentile modelled deposition values. In a number of cases, exceedence radii estimated by deposition modelling are less than those determined from monitoring data. This may be indicative of emissions from sources not being directly considered in these assessments (and therefore not used as model inputs), but which contribute to local background. Such sources may, for example, be due to the production and transport of concentrates or to metal containing dust blown from uncovered tailings areas. One exception is the estimate for Cu emitted from copper refineries. Based on the 50th percentile modelled deposition, the radius of exceedence of the CL<sub>25</sub> for Cu is 7 km. This appears to be somewhat greater than the radii of exceedence indicated by monitoring-based data. This is in part because Cu emissions from the only standalone copper refinery considered in these assessments appear to be quite low. However, as was expressed above and in Section 2.3.1.2.2, values of total deposition calculated by applying a deposition velocity to TSP monitoring data are generally underestimates, especially close to the source. All of the empirically derived deposition estimates for Noranda CCR and the Sudbury region were based either fully or partially (i.e., "wet plus dry") on TSP data. The relatively large modelled radius of exceedence may reflect the fact that essentially all of the metals released from copper refineries are fugitives or are from low-elevation stacks. This suggests that Cu released from the Inco-Copper Cliff copper refinery may also contribute more to locally deposited Cu than the 13% expected based on source attribution (see Table 38). Thus, copper refineries may be more significant sources of local deposition than might be expected based on consideration of emission data alone.

*Uncertainties*: There are relatively minor uncertainties in monitored data and somewhat larger ones in use of the data to estimate annual depositions. In particular, estimation of total metal deposition from measurements of TSP appears to generally underestimate exposure. The relative reliability of results obtained using the different methods was discussed in Section 2.3.1.2.2.

Uncertainties are associated with selection of ENEVs, although care was taken in using high-quality studies focused on realistic (indigenous), most sensitive biological species. There was potential for significant uncertainty through use of the free-ion activity model in this work. While this approach is believed to be an improvement over standard assessment methods that consider exposure to total metal concentrations, it introduces uncertainties related to estimation of free-ion concentration as well as bioavailability. Parameters influencing metal uptake by organisms include free-ion concentration in solution, pH and hardness. The latter two were addressed by selecting effects studies that used pH and hardness conditions similar to those typically found in soft-water, circumneutral to acidic lakes on the Shield. Use of the free-ion activity model approach necessitated that effects studies that did not include sufficient data to allow estimation of free metal ion concentrations be ignored. As a result, some potential "most sensitive" studies may have been excluded from consideration. This approach also ignored ingestion as a pathway for uptake of metals, which may significantly underestimate exposure for some organisms.

There is significant uncertainty owing to assumptions made in using fate and transport models to estimate critical loads. These have been discussed in Section 2.4.1.1.3. One of the most significant ones is the assumption that there is no transfer of metal from catchment areas to lakes. It is believed that this could result in up to about a five-fold underestimation of metal exposure (equivalent to a five-fold overestimate of critical loads) in some realistic worst cases. The extent of underestimation could be even greater for a small percentage of watersheds. Critical load modelling was carried out to steady state in order to avoid complications owing to historic depositions, which have typically been much greater than current depositions. It is again pointed out that, in many cases, exposure levels must decrease over long periods of time to reach these steady-state concentrations. Hence, the potential for effects on organisms in the time

period leading up to steady state may be underestimated.

It should be pointed out that risk quotients derived in this section have been based on comparison to 25th percentile critical loads, rather than on comparison to more protective levels, such as 10th percentiles. Further, the potential for additive effects of exposure of organisms to multiple metals has not been addressed in detail. This potential for additive effects should be kept in mind when considering risk quotients based on exposure to individual metals. Finally, for practical reasons, these assessments considered in detail a limited number of components released from these facilities. It is recognized that there is uncertainty introduced to the overall risk characterization associated with those compounds — such as Hg - that were not assessed.

The estimated range of impact is generally in keeping with results of aquatic and terrestrial field studies of the environmental effects of mostly historic accumulations of metals around copper smelters (see, for example, Freedman and Hutchinson, 1980; Couillard *et al.*, 1993; Borgmann *et al.*, 1998). Other evidence of the impacts of metals on organisms owing to past emissions from copper smelting facilities has been documented (see, for example, Sanderson, 1998, and references cited therein).

#### 3.1.1.2 Releases to water (Noranda-CCR)

*Risks*: A site-specific screening-level risk assessment of releases from Noranda-CCR to surface waters was carried out. Release data were used to estimate the annual average exposure concentrations for organisms in waters receiving effluent from the MUC-WWTP, which receives releases from CCR (Table 26).

Risk quotients for aquatic releases from the MUC-WWTP are shown in Table 39. This table also contains estimates of the proportion of release components attributed to the Noranda-CCR operation. Risk quotients were determined by dividing the exposure values by the ENEVs that were discussed in Section 2.4.1.2.2 and summarized in Table 35. As shown in Table 39, there is a possibility of chronic effects on fish related to Cu and Ag (RO=1.4 and 4.9, respectively) and of acute effects on zooplankton related to Ag (RQ=1.4), in the near-field plume in the St. Lawrence River. Toxicity testing of MUC-WWTP effluent (discussed in Section 2.4.1.2.1) also suggests a potential for aquatic toxicity in the plume, although there are questions about the representativeness of the samples tested. There are no environmental effects monitoring data. The CCR contribution to Cu and Ag in the MUC-WWTP effluent is very small. Thus, the potential for effects that has been identified is mainly attributable to sources other than the copper refinery.

*Uncertainties*: In the assessment of aquatic releases, some uncertainties have been accommodated by making conservative assumptions. These will tend to give high estimates for chemical exposure and low estimates for effect levels, so that potential effects are unlikely to be overlooked.

Conservative exposure assumptions include the assumption that fish with small home ranges are resident in the near-field plume, as well as the use of a two- to four-day exposure period in the acute toxicity benchmarks for zooplankton. In addition, the toxicity benchmarks are based on protection of sensitive species, which may not be present in the local receiving environments.

Alternatively, it should be noted that the discussion of risk considers potential effects of each element in isolation. As noted previously (see discussion of "Joint effect of metal emissions" — Section 3.1), there is the possibility that, due to simultaneous exposure to multiple elements, risks are greater than those predicted. Water/sediment distribution coefficients typically have order of magnitude uncertainty. There are also uncertainties in the appropriateness of the ability of the models applied to estimate the plume dispersion pattern accurately. Model validation was impeded by a shortage of near-field monitoring data.

Risk quotients for biota in the St. Lawrence River based on exposures calculated for
annual average loadings from the MUC-WWTP which receives effluent from the
Noranda-CCR facility

Release		Risk quotient <sup>1,2</sup> (percentage attributable to CCR)										
component	Fish		Zoopl	ankton	Benthic	-epifauna	Benthic-infauna					
Cu	1.4	(1.2%)	0.26	(1.0%)	0.25	(0.9%)	0.40	(0.9%)				
Ni	0.06	(0.6%)	0.001	(0.5%)	0.007	(0.4%)	0.31	(0.4%)				
Pb	0.008	(0.2%)	0.001	(0.2%)	0.03	(0.1%)	0.07	(0.1%)				
Cd	0.14	(0.04%)	0.006	(0.03%)	0.08	(0.02%)	0.35	(0.02%)				
As	0.002	(2.4%)	0.001	(1.5%)	0.001	(0.9%)	0.22	(0.9%)				
Cr	0.08	(0.07%)	0.08	(0.06%)	0.23	(0.04%)	0.02	(0.04%)				
Se	0.07	(73%)	0.001	(61%)	0.04	(49%)	-	(49%)				
Ag	4.9	(0.2%)	1.4	(0.2%)	0.08	(0.2%)	_	(0.2%)				

<sup>1</sup> Risk quotients for zooplankton are based on acute effects. Risk quotients for fish and benthic organisms are based on chronic effects.

<sup>2</sup> Values in bold meet or exceed a risk quotient of 1.0.

With regard to the MUC-WWTP specifically, data were not available to estimate short-term risk quotients (based on maximum monthly or four-day average loadings), which would be expected to be higher than those calculated using annual average loadings. Furthermore, since no data were identified on the chemical forms of releases, all metals were assumed to be in dissolved or adsorbed (i.e., bioavailable) forms.

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3.1.2 Zinc plants

3.1.2.1 Releases to air

#### 3.1.2.1.1 Sulphur dioxide

Data for the monitoring of ambient  $SO_2$  in the vicinity of zinc plants were provided by the companies. These represent exposure to ambient  $SO_2$  over time scales of the growing season as well as over 1 hour. Monitoring data were summarized in Table 10 and Table 11, respectively.

Table 36 shows risk information for ambient  $SO_2$ . Derivation and interpretation of data in the table were described in Section 3.1.1.1.

As indicated in Table 36, four facilities have zinc plants. Release of  $SO_2$  from these plants is typically associated with roasting operations. Noranda-CEZinc is a stand-alone zinc processing facility. Eighty-five percent of  $SO_2$ emissions from Cominco-Trail are attributed to the zinc plant; the remainder are attributed to the lead plant. The zinc plant at Falconbridge-Kidd Creek is responsible for an estimated 15% of  $SO_2$ emissions from that facility. Finally, although HBM&S includes both a copper smelter and zinc plant, the pressure-leach technology used in its zinc plant does not result in the release of  $SO_2$ .

The chronic "growing season average risk quotient" values in Table 36 for the three facilities with measurable  $SO_2$  releases show little similarity. This is in part due to the fact that data in the table have lost some spatial coherence, as sites are listed in increasing order of distance

from the facility irrespective of direction. This obscures trends in the data somewhat, lacking consideration of geographical and meteorological factors.

The clearest trend is observed for Cominco-Trail due to the larger number of monitoring stations operated. Due to the valley location of this facility, most of the monitoring stations are downwind of the complex much of the time (i.e., either up or down the valley from the facility). Although growing season average risk quotients are not overly high (maximum of 3.4), they remain elevated over a significant area. Exceedences of a risk quotient of 2, indicative of "likely" effects on sensitive species, extend out to about 10 km within the confines of the valley.

At the Noranda-CEZinc facility, a relatively high chronic risk quotient (2.6) is observed at one monitoring station located 1.3 km from the plant in what is frequently a downwind direction. At another station located at a similar distance in a direction that is seldom downwind of the plant, the risk quotient is quite low. Insufficient data are available to determine the distance from the facility in the downwind directions that may be impacted.

The environmental impact of  $SO_2$  emitted by the zinc plant at Falconbridge-Kidd Creek is of lesser significance due to the generally lower risk quotients observed for monitoring stations near this facility and to the lower attribution of the zinc plant to total  $SO_2$  emitted by the facility. It should be recognized, however, that only 20% of the  $SO_2$  emitted is from a source not considered as part of these combined assessments, and that at one monitoring station a risk quotient exceeding 2 is observed.

Trends similar to those observed for chronic (growing season) exposure are seen for each facility when considering the risk information for acute (1-hour) exposure. At the Cominco-Trail facility, a moderate number of exceedences of the "possible" effect level (RQ=1) are observed with relatively few exceedences of the "likely" effect level for sensitive species (RQ=2). The observed outer limits for exceedence of these two levels are about 10 km and 4 km, respectively. Acute risk quotients above 1.0 occur relatively frequently at the monitoring station located downwind of the Noranda-CEZinc plant, reinforcing the expectation that the area impacted by ambient  $SO_2$  in the downwind directions extends somewhat further from the source. While there were a moderate number of 1-hour periods where the risk quotient was greater than 1 at some monitoring stations near Falconbridge-Kidd Creek, on only one occasion was RQ=2 exceeded.

The "maximum" risk quotient column shows the extreme values for acute (1-hour) exposure to  $SO_2$  for vegetation near the zinc plants. The highest quotient, 4.2, was calculated for two stations located within 4 km of the Cominco-Trail facility.

It may be concluded that there is the possibility for effects on vegetation from both acute (1-hour) and chronic (growing season) exposure to  $SO_2$  released from zinc plants. Depending upon the facility type ( $SO_2$  releases are typically associated with roasting operations) and local meteorology and geography, the areas impacted may extend to about 10 km from the source.

Uncertainties: Uncertainties in the evaluation of risk to the environment due to ambient SO<sub>2</sub> were discussed in association with releases to air from copper smelters and refineries (see Section 3.1.1.1.1).

#### 3.1.2.1.2 Deposited sulphate

Sulphur dioxide emitted from zinc plants can be oxidized to sulphate in the atmosphere. Sulphur dioxide and sulphate can be transported long distances from the source, resulting in acidic deposition to soils and lakes over large areas.

Information needed for the evaluation of risk due to wet sulphate deposition is shown in Table 37. Derivation and interpretation of data in the table were described in Section 3.1.1.1.2. As was described, model parameters were scaled based on 1995 emission data for the facilities considered in these assessments, to estimate incremental contributions to deposition attributable to these sources. Of the four receiving areas shown in Table 37, the highest relative contribution to wet sulphate deposition from zinc plants was 0.2%, seen for the Montmorency location.

*Uncertainties*: Uncertainties in the evaluation of risk to the environment due to sulphate deposition were discussed in association with releases to air from copper smelters and refineries (see Section 3.1.1.1.2).

Although there are clearly detrimental acidification effects on lakes in eastern Canada owing to anthropogenic emissions of  $SO_2$ , it may be concluded that current emissions from Canadian zinc plants contribute only a minor portion of the  $SO_2$  leading to lake acidification.

#### 3.1.2.1.3 Deposited metals

Estimates of annual deposition of the metals Cu, Zn, Ni, Pb, Cd and As based on monitoring data in the vicinity of zinc plants are summarized in Tables 15, 17 and 18. Derivation of critical loads for these metals was discussed in Section 2.4.1.1.3, and annual critical loads were summarized in Tables 31 and 33.

Table 38 shows risk information for metals deposited in the vicinity of zinc plants. Derivation and interpretation of data in the table were described in Section 3.1.1.1.3.

Critical loads derived for sandy soils typical of those found on the Canadian Shield were used to calculate risk quotients for Cominco-Trail and Noranda-CEZinc. Although these are not located on the Shield, examination of local surface geology and soils maps (Mailloux, 1954; Fulton, 1984, 1996) indicates that sandy soils occur near each of these facilities, making use of soil critical loads suitable for application at these sites. For HBM&S and Falconbridge-Kidd Creek, the more sensitive of soil or surface water critical loads were used.

Emission-based source attribution information is also shown in Table 38. Noranda-CEZinc is a stand-alone facility, and all metal emissions may be attributed to zinc processing. The Cominco-Trail facility also includes a lead plant, which is responsible for large portions of the Pb, Cd and As emissions from that complex. The zinc pressure-leaching process used at HBM&S-Flin Flon results in insignificant emissions of the metals being assessed, excluding it from consideration in this section. The Falconbridge-Kidd Creek facility includes multiple operations. Emissions of Zn and As have significant proportions coming from the zinc plant. It should be noted, however, that because these attributions are based on only a partial inventory of sources (e.g., fugitive releases from tailings areas are not included), the relative contributions of zinc plants to metal deposition rates estimated from monitoring data may be somewhat overestimated.

It is apparent from the data in Table 38 that 25th percentile critical loads for Zn are often exceeded. At the Cominco facility, risk quotients significantly greater than 1 are seen at a monitoring station 10.5 km down the valley from the zinc operations. Considering the TSP-based risk quotient of 1.0 observed at 12.7 km, the impacted area likely extends beyond 13 km. Critical loads for.Pb and Cd are also exceeded beyond 10 km, although only 4% and 36% of these metal emissions, respectively, are attributable to the zinc operations.

At the Falconbridge-Kidd Creek and Noranda-CEZinc facilities, the critical load for Zn is significantly exceeded out to a distance of at least 4 km — the locations of the furthest monitoring stations. At the Falconbridge site, however, only 24% is attributed to the zinc operations, the largest portion being attributed to the concentrator.

It may be concluded that there is potential for effects on aquatic and/or soil-

dwelling organisms from exposure to steady-state concentrations of metals in the vicinity of zinc plants resulting from releases (especially of Zn) from these facilities. Depending upon the facility type (metal emissions from plants relying exclusively on pressure-leach technology may be negligible) and local meteorology and geography, the areas impacted may extend as far as about 13 km from the source.

Exceedence radii were also estimated for zinc plants based on the generic deposition modelling described in Section 2.3.1.2.3 and detailed in SENES Consultants (2000).

Table 23 shows the maximum distance from each facility type, or combination of facilities, where the 50th or 95th percentile estimates of total soluble deposition rates exceeded the benchmark 25th percentile critical load. As discussed in Section 3.1.1.1.3, these results do not correspond to any individual facility or combination of facilities. Again, the results shown in Table 23 are generally supportive of the deposition data based on monitoring, and estimates of exceedence radii based on modelling tend to be lower that those determined from monitoring data. Along with the possible explanation of other sources contributing to local background, it is pointed out that the metal emission values for the Cominco-Trail facility, which were one of the sets of input values used in the model, may have been underestimated (see footnote to Table 4). As was noted for copper refineries, essentially all of the metals emitted from zinc plants are from lowelevation sources, increasing the potential for these operations to contribute significantly to local deposition.

*Uncertainties*: Uncertainties in the evaluation of risk to the environment due to exposure to deposited metals were discussed in association with copper smelters and refineries (see Section 3.1.1.1.3).

## 3.1.2.2 Releases to water (Noranda-CEZinc and Cominco-Trail)

*Risks*: Site-specific screening-level risk assessments of releases to surface waters were carried out for two zinc facilities: Noranda-CEZinc and Cominco-Trail. Release and monitoring data were used to estimate the maximum monthly (chronic) and four-day (acute) exposure concentrations for the CEZinc and Trail facilities, shown in Tables 27 and 28, respectively.

Risk quotients for aquatic releases from the CEZinc and Trail facilities are shown in Tables 40 and 41, respectively. These tables also contain estimates of the proportion of release components attributed to the operations being assessed. Risk quotients were determined by dividing the exposure values by the ENEVs that were discussed in Section 2.4.1.2.2 and summarized in Table 35.

The potential effects of effluents from the CEZinc and Cominco-Trail facilities were evaluated by considering their local impacts on St. Lawrence River and Columbia River receiving waters. As indicated by the risk quotients for CEZinc shown in Table 40, there is a possibility of chronic effects on fish related to Se (RQ=4.9 based on 1995 release data) and Cu (RQ=1.5) under maximum loading conditions. Recent significant reductions in releases of Se, however, have likely reduced the quotient for that element. Toxicity testing of CEZinc effluent (discussed in Section 2.4.1.2.1) does not suggest a potential for aquatic toxicity in the plume given the pH control measures currently in effect. There are no EEM data.

For Cominco-Trail releases related to zinc operations (Table 41), there is a potential for effects on fish related to Cd and Tl (RQ=1.1 and 3.4, respectively) and benthos related to Zn, Cd, As and Hg (quotients up to 4.5). In the case of Cd and As, however, only a relatively small percentage of the exposure is attributable to Cominco's zinc operations. Toxicity testing of Cominco-Trail effluent (discussed in Section 2.4.1.2.1) does not suggest a significant potential for acute toxicity in the plume. Chronic toxicity testing has not been performed. EEM (discussed in Section 2.4.1.2.3) has found sediment toxicity

**TABLE 40**Risk quotients for aquatic biota based on exposures calculated for maximum monthly<br/>or four-day average effluent loadings from the Noranda-CEZinc facility to the<br/>Beauharnois Canal

Release	Risk quotient <sup>1,2,3</sup> (percentage attributable to CEZinc)										
component	Fish		Zooplankton		Benthic-epifauna		Benthic-infauna				
Cu	1.5	(86%)	0.09	(32%)	0.10	(10%)	0.16	(10%)			
Zn	0.44	(82%)	0.03	(50%)	0.05	(8%)	0.85	(8%)			
Cd	0.22	(69%)	0.004	(15%)	0.06	(4%)	0.28	(4%)			
Hg	0.42	(90%)	0.006	(40%)	0.01	(13%)	0.40	(13%)			
Se	<b>4.9</b> <sup>4</sup>	(100%)	0.007	(95%)	0.11	(81%)	_	(81%)			

<sup>1</sup> Risk quotients for zooplankton are based on acute effects. Risk quotients for fish and benthic organisms are based on chronic effects.

<sup>2</sup> Insufficient data were available to evaluate maximum (1-month) exposure concentrations for Pb or ammonia. Of note is that the risk quotient determined for exposure of fish to ammonia was 0.58 (with 97% attributable to CEZinc) based on an annual average EEV (Beak International, 1999). A risk quotient based on a maximum short-term (1-month) EEV could be significantly higher.

<sup>3</sup> Values in bold meet or exceed a risk quotient of 1.0.

<sup>4</sup> Releases of Se from the Noranda-CEZinc facility are believed to have been significantly reduced recently; thus, this quotient likely overestimates risk.



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Release		Risk quotient <sup>1,2</sup> (percentage attributable to Cominco zinc plant)											
component	Fi	ish	Zoopla	ankton	Benthic-	epifauna	Benthic-infauna						
Cu	0.59	(19%)	0.18	(18%)	0.25	(18%)	0.22	(18%)					
Zn	0.85	(74%)	0.18	(74%)	0.45	(70%)	4.0	(70%)					
Pb	0.05	(54%)	0.006	(56%)	0.39	(58%)	0.36	(58%)					
Cd	1.1	(6%)	0.26	(8%)	1.1	(7%)	4.5	(7%)					
As	0.01	(18%)	0.005	(26%)	0.008	(10%)	1.1	(10%)					
Hg	0.38	(58%)	0.04	(61%)	0.07	(52%)	2.3	(52%)					
Tl	3.4	(94%)	0.02	(93%)	0.02	(84%)	_	(84%)					
Ammonia	0.08	(51%)	0.06	(49%)	0.05	(30%)	_	(0%)					
Fluoride	0.05	(46%)	0.03	(40%)	0.04	(23%)	_	(0%)					

**TABLE 41** Risk quotients for aquatic biota based on exposures calculated for maximum monthly or<br/>four-day average effluent loadings from the Cominco-Trail facility to the Columbia River

<sup>1</sup> Risk quotients for zooplankton are based on acute effects. Risk quotients for fish and benthic organisms are based on chronic effects.

<sup>2</sup> Values in bold meet or exceed a risk quotient of 1.0.

and benthic/periphyton community effects in areas directly downstream of the outfalls, although these may have been related at least in part to historical slag deposits.

Uncertainties: As noted previously (see Section 3.1.1.2), in the assessment of aquatic releases, some uncertainties have been accommodated by making conservative assumptions. As a consequence, the potential effects identified may not be realized. For example, it has been conservatively assumed that fish with small home ranges are resident in the near-field plume, and that organisms in local receiving environments are among the most sensitive identified in the literature.

Alternatively, it should be noted that risk quotients for several organism-element combinations were found to be only slightly below 1, and that if the additivity model discussed earlier (see "Joint effect of metal emissions" — Section 3.1) is applicable, it is possible that effects are greater due to simultaneous exposure to multiple elements. In addition, data were not available to calculate a maximum monthly exposure value for ammonia at the CEZinc facility. This omission could be significant given that the risk quotient determined for exposure to fish was 0.58, based on an annual average EEV. A risk quotient based on a maximum monthly EEV could be significantly higher.

Water/sediment distribution coefficients typically have order of magnitude uncertainty. There are also uncertainties related to the ability of the models applied to accurately estimate the plume dispersion pattern. Model validation was impeded by a shortage of near-field monitoring data.

# **3.2** CEPA 1999 64(b): Environment upon which life depends

As described in Section 2.4.2, based on the very small amounts of VOCs included in releases from Canadian copper smelters and refineries and zinc plants, these releases are not expected to contribute significantly to the creation of groundlevel ozone. Similarly, because emissions of VOCs are low, and since sulphate aerosols formed from emitted  $SO_2$  are unlikely to migrate to the stratosphere, such releases are unlikely to contribute to stratospheric ozone depletion. Finally, based on the relatively small amounts of  $CO_2$  and other greenhouse gases included in releases from Canadian copper smelters and refineries and zinc plants, these releases are not expected to contribute significantly to global warming.

### 3.3 CEPA 1999 64(c): Human health

#### 3.3.1 Exposure assessment

Based on the data summarized in Section 2.3.1, the airborne levels of metals, SO<sub>2</sub> and PM are increased by releases from Canadian copper smelters and refineries and zinc plants. For those facilities where there is more than one monitoring site, the mean concentration of As, Cd, Cr, Ni, SO<sub>2</sub> and PM is generally increased in relation to the proximity to the smelter. However, while the levels are elevated in this fashion at most of the copper smelters and refineries and zinc plants, particularly at those monitoring sites situated very close to the facility (i.e., less than 1 km), the mean concentration does not simply decline monotonically as a function of increasing distance. This is likely due to other factors that would influence dispersion of the emissions, including local meteorology and topography, as well as to the limited number of monitoring stations situated near all the facilities. It also appears that monitoring stations are often located in close proximity to local populations, which generally do not reside downwind of the copper smelters and refineries and zinc plants, rather than being situated where dispersion of the emissions can be tracked.

In addition, the airborne levels of each of these substances near Canadian copper smelters and refineries and zinc plants are consistently higher than regional background levels measured in areas removed from point sources. However, it is noted that there is considerable variation in the degree by which levels are increased between both substances and between facilities. Thus, concentrations of As, Cd and Pb are increased by up to approximately three orders of magnitude near some facilities, compared with more modest elevations in SO<sub>2</sub> and in PM near all of the copper smelters and refineries and zinc plants. As well, levels of As, Cd and Pb are generally higher near those facilities where smelting is conducted compared with those where refining alone takes place, reflecting the lesser amounts of these metals emitted from refining (Table 4).

Hence, the results of monitoring near the Canadian copper smelters and refineries and zinc plants indicate that releases from these facilities result in increased potential for inhalation exposure (the route associated with the critical effect for these substances) to these and other substances.

The sizes and locations of local populations have not been characterized as part of this assessment, and the networks of monitoring stations are very limited for all of the facilities. Nonetheless, while the number of sites near each facility is very small, they are generally well situated with respect to local populations. Most of the monitoring stations are located in residential areas, and there is potential for exposure of the general population at the commercial and rural sites that comprise the bulk of the remainder. In addition, the available information indicates that, while the resident populations in many of these relatively isolated locales are not large, there are significant numbers of people (several thousand, and in some cases more than 100 000) residing within a few kilometres of virtually all of these facilities (SENES Consultants, 1996b; Fontana, 2000). In some instances, local communities are located within a few hundred metres of the smelters.

The focus of the health assessment is on evaluating the potential impacts of current releases of substances from copper smelters and refineries and zinc plants in Canada. To that end, the monitoring data from environmental media were restricted to those for ambient air, because levels in air were expected to reflect current releases much better than is the case for other media, which can be strongly influenced by high historical releases. The results of studies of environmental Pb near the Cominco lead smelter and zinc plant at Trail, B.C., provide support for this assumption (Hilts *et al.*, 1998). In these studies, several lines of evidence indicated that air transport of re-entrained historical reservoirs of Pb was minimal compared with current emissions:

- 1) The amount of Pb suspended in air was nearly four times higher when the wind blew predominantly from the smelter toward the sampling station compared with when it blew away.
- 2) While total dustfall increased in summer months, when the ground is bare and the weather dry, the amount of Pb in dustfall was highest in winter months when emission dispersion conditions are poor.
- There were declines of up to 80–90% in airborne Pb and in dustfall Pb during a onemonth shutdown of the smelter.
- 4) Lead concentrations in dustfall were generally very high (>10 000 mg/kg), even higher than in the very fine fraction of soil.

Structural equations pathway modelling in this community explained 71% of the variation in blood lead in local children and indicated that the main direct contributor to blood lead was house dust lead loading and that environmental Pb passed from dust fall through street dust, soil and yard waste into house dust (Hilts *et al.*, 1998). Following the introduction of a new lead smelter in 1997, which reduced emissions of Pb substantially, children's geometric mean blood lead concentrations declined by almost half, from 11.5  $\mu$ g/dL in 1996 to 5.9  $\mu$ g/dL in 1999 (Hilts *et al.*, 1998; Hilts, 2000).

Thus, the results of studies near Trail confirm that both airborne levels and exposure of local populations to particulate metals are strongly influenced by current releases from the smelter. This would be expected to be even more pronounced near some of the other Canadian copper smelters and refineries and zinc plants, from which emissions of Pb and other metals are greater (in some instances, many times) than from the Trail smelter (Table 4).

#### 3.3.2 Effects assessment

The epidemiological studies of human populations exposed to emissions from copper smelters and refineries and zinc plants in the environment are considered most relevant to the determination of "toxic" under Paragraph 64(c) of CEPA 1999, in terms of both the profile of substances to which they would have been exposed and the composition of the study populations (i.e., those exposed in the general environment, including the young, the elderly and compromised individuals).

However, with the exception of increased levels of lead in blood, the weight of evidence for health effects from epidemiological studies of populations in the vicinity of copper smelters and refineries and zinc plants is inadequate (Section 2.4.3). Even in the case of blood lead, while the most recent data from such populations in Canada indicate that roughly 10-20% of children surveyed had blood lead levels greater than or equal to the current intervention level of 10  $\mu$ g/dL, such data are available only for a minority of the Canadian facilities, and most of these are at least several years old. In addition, children's current blood lead levels would reflect unknown contributions from both current and historical emissions of lead.

For these reasons, the results of the available epidemiological studies of populations resident near copper smelters and refineries and zinc plants are considered inadequate to characterize exposure response for both cancer and non-cancer effects.

For the substances for which recent data in ambient air near the Canadian facilities have been compiled in Section 2.3.1 (i.e., As, Cd, Cr, Ni, Pb, SO<sub>2</sub> and PM), health assessments conducted under the PSL program and internationally are available. (These substances comprise the vast majority, on a mass basis, of those released to air from Canadian copper smelters and refineries and zinc plants [Tables 3, 4 and 5], as well as those considered a priori to be most relevant to health.) In selecting from among available health assessments for these substances, the criteria considered included whether the approach taken was consistent with the principles on which the PSL health assessments are based (e.g., whether the assessment was strictly health-based), whether the assessment was specific to the inhalation route of exposure, whether quantitative measures of exposure-response were developed, and how recently the assessment was conducted. On this basis, the assessments selected included those conducted for the PSL program for As (EC/HWC, 1993), Cd (EC/HC, 1994a), Cr (EC/HC, 1994c), Ni (EC/HC, 1994b) and respirable PM (EC/HC, 2000a), and in development of the WHO Air Quality Guidelines for Europe for Pb and SO<sub>2</sub> (WHO, 2000).

In the next section, for each of the metals,  $SO_2$  and PM, a summary of an assessment of the substance under the PSL program or the WHO air quality guidelines program is presented. This includes a summary of the weight of evidence for the critical effect for each substance and the basis for the health-based measure of exposure–response or guidance value for the critical effect. It should be noted that the information provided is based entirely on the reports of these health assessments.<sup>14</sup>

For Priority Substances for which the weight of evidence of carcinogenicity is sufficient, where possible, estimated exposure is compared to quantitative estimates of carcinogenic potency to characterize risk and provide guidance for the establishment of priority for further action (i.e., analysis of options to reduce exposure). Potency is usually expressed as the dose or concentration that induces a 5% increase in the incidence or mortality due to relevant tumours ( $TD_{05}$  or  $TC_{05}$ ), based on data obtained in toxicological studies in experimental

animals or epidemiological investigations in exposed human populations.

3.3.2.1 Exposure-response characterization for selected components of emissions from copper smelters and refineries and zinc plants

#### 3.3.2.1.1 Arsenic

The following text, summarizing the PSL assessment for "arsenic and its compounds" (EC/HWC, 1993), has been taken from Hughes *et al.* (1994a):

An association between inhaled arsenic and increased mortality due to respiratory cancer has been consistently demonstrated in available epidemiological studies. In addition, ingestion of inorganic arsenic in drinking water has been consistently associated with an increased prevalence of skin cancer in exposed human populations with some indication of increases in mortality due to cancers of internal organs. Therefore, based on the weight of evidence of carcinogenicity in humans by more than one route of exposure, the group of inorganic arsenic compounds as a whole is considered to be carcinogenic to humans.

In the case of arsenic, potency estimates were developed for exposure by both inhalation and ingestion, based on epidemiological data. The TC<sub>05</sub> for inhaled arsenic was based on data presented in the large studies of workers at the Tacoma smelter (Enterline *et al.*, 1987), the Anaconda smelter (Higgins *et al.*, 1986) and the Ronnskar smelter (Jarup *et al.*, 1989), for which there was considerable information to serve as a basis for estimates of exposure. A negative exponential growth curve was used to describe the concave-downward relationship between concentrations of arsenic in air and mortality due to respiratory cancer (most of which were cancers of the lung) among workers for the



<sup>&</sup>lt;sup>14</sup> While there was no formal search strategy to identify recent data that may have impacted on the outcome of these assessments, the authors are not aware of new data that would impact significantly on the conclusions drawn under Paragraph 64(c).

Tacoma and Anaconda cohorts. This curve models the difference between a linear effect in exposure and a negative exponential term. A linear model was used to describe the relationship between exposure to arsenic and lung cancer mortality for the Ronnskar cohort. Excess risk of respiratory cancer was obtained using the predicted curves and age-adjusted lung cancer mortality rates for the Canadian population. Based on these data, the TC<sub>05</sub>s for inhaled arsenic were 7.8, 10 and 51  $\mu$ g/m<sup>3</sup> for the Anaconda, Tacoma and Ronnskar smelter workers, respectively.

#### 3.3.2.1.2 Cadmium

The following text, summarizing the PSL assessment for "cadmium and its compounds" (EC/HC, 1994a), has been taken from Newhook *et al.* (1994):

Although an association between inhaled cadmium compounds and increased mortality due to lung cancer has been observed in some epidemiological studies, it is not possible to eliminate the potential influence of exposure to other heavy metals on these results. However, inhalation of cadmium chloride, oxide, sulphate or sulphide has induced lung cancers in several studies in rodents. Each of these compounds has also been carcinogenic in studies involving routes less relevant to environmental exposure i.e., subcutaneous or intramuscular injection, and cadmium chloride was carcinogenic in one of two adequate studies in which the compound was administered to rats in the diet. Concomitant exposure to zinc compounds reduced the carcinogenicity of inhaled cadmium oxide to rats (Glaser et al., 1990), and of cadmium chloride injected subcutaneously in rats and mice (IARC, 1976; Waalkes et al., 1989), indicating that it is most likely the cadmium ion itself which is carcinogenic.

On the basis principally of the results in inhalation studies in animals and supporting data on genotoxicity, inorganic cadmium compounds are considered to be probably carcinogenic to humans.

In the case of cadmium, the  $TC_{05}$  was derived from the data on lung cancers induced in rats by long-term inhalation of cadmium chloride aerosols (Takenaka et al., 1983); these data are considered to provide the most reliable estimate of the  $TC_{05}$ , as a consequence of the clear dose-response relationship observed in this experiment for the incidence of total lung carcinomas (0 µg Cd/m<sup>3</sup>, 0/38; 13.4 µg Cd/m<sup>3</sup>, 6/39; 25.7 µg Cd/m<sup>3</sup>, 20/38; 50.8 µg Cd/m<sup>3</sup>, 25/35). The TC $_{05}$ , estimated by first fitting the multistage model to these data, and subsequently amortizing the exposure over the lifetime of the rat and adjusting to account for the duration of the experiment and the breathing volumes and body weights of rats and humans, is 5.1 µg Cd/m<sup>3</sup>. (TC $_{05}$  values calculated from the total lung tumour incidences observed by Glaser et al. (1990) in rats inhaling cadmium chloride, cadmium oxide dust, cadmium sulphate, and cadmium sulphide are similar, ranging from 2.7 to 12.7 µg Cd/m<sup>3</sup>.)

#### 3.3.2.1.3 Chromium

The following text, summarizing the PSL assessment for "chromium and its compounds" (EC/HC, 1994c), has been taken from Hughes *et al.* (1994b):

On the basis of its documented carcinogenicity in human populations exposed by inhalation in the occupational environment, the group of hexavalent chromium compounds as a whole is considered to be carcinogenic to humans. Available data are insufficient to support a hypothesized threshold for the carcinogenicity of hexavalent chromium, based on exceedence of the extracellular capacity to reduce hexavalent chromium to the trivalent species. Cellular uptake of trivalent chromium has been demonstrated (Alcedo and Wetterhahn, 1990) and the entry of hexavalent chromium into cells is rapid and extracellular reduction in the mucosal lining is incomplete (Witmer, 1991).

The  $TC_{05}$  was estimated on the basis of a study by Mancuso (1975), as this was the study in which the most information on exposure

(inhalation) was provided. Although the cohort in this study was small, workers were classified into several categories of cumulative exposure to total chromium and soluble (principally hexavalent) or insoluble (principally trivalent) chromium. In addition, the period of follow-up was sufficiently long to account for the latency period of development of lung cancer. However, mortality by age group necessary for comparison with the general population was reported for total chromium only. Therefore, an estimate of the carcinogenic potency was derived based on exposure to total chromium.

The age-specific death rate for lung cancer was assumed to be a time-weighted quadratic function of exposure to chromium, which is additive to the death rate for the general population assumed not to be exposed to chromium. The increase in probability of death due to constant lifetime exposure to chromium was determined, based on the assumption that there are no competing causes of death and exposure is constant for a period equal to the median survival time of 75 years. The TC<sub>05</sub> for inhaled chromium (total) was estimated to be 4.6  $\mu$ g/m<sup>3</sup>.

An indirect estimate of the carcinogenic potency of hexavalent chromium may be derived from the study by Mancuso (1975). In an earlier study at the same chromate production plant, it was reported that the proportion of trivalent to hexavalent chromium present in most areas of the plant was about 6:1 or less (Bourne and Yee, 1950), although the number of workers in each area of the plant was not specified. Thus, the concentrations of hexavalent chromium may be estimated to be one seventh (1/7) of the reported concentrations of total chromium. Based on this assumption, the TC<sub>05</sub> for hexavalent chromium has been estimated to be  $0.66 \ \mu g/m^3$ .

#### 3.3.2.1.4 Nickel

The following text, summarizing the PSL assessment for "nickel and its compounds" (EC/HC, 1994b), has been taken from Hughes *et al.* (1994c):

There is sufficient and consistent evidence of the carcinogenicity of each of oxidic, sulphidic and soluble nickel in adequate epidemiological studies in different types of exposed workers and some weak evidence of genotoxicity in limited epidemiological studies. Although there may have been concomitant exposure to other compounds in these studies, the common predisposing factors in the various groups of workers examined appear to be these groups of nickel compounds. In addition, there is some supportive evidence of carcinogenicity and genotoxicity of these forms of nickel in principally limited studies in animal species. Therefore, each of oxidic, sulphidic and soluble nickel is considered to be carcinogenic to humans.

The epidemiological studies which provide sufficient information to serve as a basis for quantitative estimation of the carcinogenic potency of inhaled inorganic nickel are those of large cohorts (n = 3250 to 54 509) of exposed workers at two nickel refineries for whom the most extensive information on exposure is available: the Inco mining, smelting and refinery operations in Ontario and the Falconbridge refineries in Kristiansand, Norway (Doll et al., 1990). Estimates of the carcinogenic potency of oxidic, sulphidic and soluble nickel (combined), based on results at the Inco mining, smelting and refinery operations in Ontario, were considered the most relevant and reliable for several reasons: the cohorts were relatively large (e.g., total expected numbers of death of Copper Cliff sinter plant workers with 15 or more years since first exposure due to lung cancer was approximately 20); there was clear evidence of increased lung and nasal cancer mortality with increasing duration of exposure in the sinter workers and there was not exposure to metallic nickel (i.e., the estimates of total nickel concentrations did not include a form of nickel for which there is no convincing evidence of carcinogenicity). Although the potency of the various species may vary considerably, the TC<sub>05</sub>s estimated on the basis of the Inco cohort are based on oxidic, sulphidic and soluble nickel (combined) since



available data do not permit separate estimates for each of the groups of compounds.

The Kristiansand cohort consisted of two clearly defined working groups (i.e., electrolysis workers with no employment in other high exposure departments and those employed in the roasting, smelting and calcining department). There was little exposure to metallic nickel in both groups. Based on the data presented for these workers, TC<sub>05</sub>s were developed for oxidic, sulphidic and soluble nickel (combined) and soluble nickel (specifically).

The age-specific death rate for lung cancer observed in the cohorts of the Copper Cliff sinter plant and Coniston sinter plant was assumed to be a linear function of the cumulative exposure to total nickel, whereas the age-specific death rate for lung cancer reported in the cohorts of the Port Colborne nickel refinery and Kristiansand nickel refinery was assumed to be an exponential function of the cumulative exposure to total nickel. The age-specific death rate was also assumed to be multiplicative to the death rate for the general population. The increase in probability of death due to a constant lifetime exposure to nickel has been determined, based on the assumption that there are no competing causes of death and a constant exposure for a period equal to the median survival time of 75 years. The estimates of the TC<sub>05</sub> for inhaled oxidic, sulphidic and soluble nickel (combined) for lung cancer mortality ranged from 0.04 to 1.0 mg/m<sup>3</sup>. It should be noted that the TC<sub>05</sub>s based on data for workers in the Clydach refinery (although the numbers of workers in each occupational group were small) would not be substantially different. The  $TC_{05}$  for lung cancer mortality for soluble nickel was within this range of values (i.e., 0.07 mg/m<sup>3</sup>).

#### 3.3.2.1.5 Lead

The following text is based on a recent review of lead produced for the "WHO Air Quality Guidelines for Europe" (WHO, 2000). A variety of effects has been documented in humans exposed to lead, both occupationally and environmentally. In conditions of low-level long-term exposure, as for the general population, the most critical effects include those on heme biosynthesis, erythropoiesis and the central and peripheral nervous systems. The results of animal studies provide support for lead as the causative agent for these effects.

Children up to six years of age are considered to be more at risk for lead exposure and effects compared to adults for several reasons, including their lesser concern for personal hygiene and increased hand-to-mouth activity, substantially higher absorption in the gastrointestinal tract, a less developed blood-brain barrier, and lower thresholds for hematological and neurological effects of lead. In children, Lowest-Observed-Adverse-Effect Levels (LOAELs) for hematological and neurobehavioural endpoints have been summarized as follows. Reduced hemoglobin levels have been observed at blood lead concentrations around 40 µg/dL. Hematocrit values below 35% have not been reported at levels below 20  $\mu$ g/dL; this is also true for several enzyme systems that may have clinical significance. Effects on the central nervous system occur at levels below 20 µg/dL; consistent effects have been reported for measures of cognitive functioning such as the psychometric IQ between 10 and 15 µg/dL, and in some studies below 10 µg/dL.

Based on the above information, the WHO (2000) identified a critical level of lead in blood of 10  $\mu$ g/dL. This value was then used to derive an ambient air quality guideline, as follows. It was recommended that efforts be taken to ensure that at least 98% of the general population, including preschool children, should have blood lead levels that do not exceed 10  $\mu$ g/dL. The corresponding median blood lead level was estimated at 5.4  $\mu$ g/dL, compared with currently measured "baseline" blood lead levels of minimal anthropogenic origin of up to 3.0  $\mu$ g/dL. The air quality guideline was calculated as the concentration of lead in air that



was estimated to yield the difference (2.4  $\mu$ g/dL). Based on regressions between levels of lead in ambient air and in blood, which indicate that 1  $\mu$ g Pb/m<sup>3</sup> directly contributes approximately 1.9  $\mu$ g Pb/dL in blood, and calculating the indirect contribution through dust/soil, it was estimated that 1  $\mu$ g Pb/m<sup>3</sup> would contribute 5  $\mu$ g Pb/dL blood (summarized in WHO, 1995). On this basis, an ambient air guideline of 0.5  $\mu$ g Pb/m<sup>3</sup> (annual average) was derived.

#### 3.3.2.1.6 Sulphur dioxide

The following text is based on reviews of  $SO_2$  produced for the "WHO Air Quality Guidelines for Europe" (WHO, 1987, 2000).

Information on effects of exposure to SO<sub>2</sub> averaged over a 24-hour period is based mainly on epidemiological studies in which the effects of ambient mixtures of SO<sub>2</sub>, PM and other associated pollutants are considered. Respiratory morbidity in patients with pre-existing conditions (asthmatics, bronchitics) was consistently observed when SO<sub>2</sub> concentrations exceeded 250  $\mu$ g/m<sup>3</sup>. This occurred in situations in which the air pollution arose principally from the inefficient burning of coal in domestic appliances. In several more recent studies involving the mixed industrial and vehicular sources that now dominate, increased mortality (total, cardiovascular and respiratory) and increased emergency department admissions for total respiratory causes and for chronic obstructive pulmonary disease (COPD) were observed at lower levels of exposure (mean annual levels below 50 µg/m<sup>3</sup>, and daily levels usually less than 125  $\mu$ g/m<sup>3</sup>). The association with SO<sub>2</sub> levels remained, in some instances, when Black Smoke and TSP were controlled for. There were also small effects on lung function at concentrations of SO<sub>2</sub> below 300 µg/m<sup>3</sup> in some studies, though it was difficult to separate out the effects of other pollutants.

With respect to the effects of longer-term exposures, in earlier studies during the coalburning era, there were increased frequencies of respiratory symptoms and illnesses or effects on lung function associated with annual average concentrations of SO<sub>2</sub> of 100  $\mu$ g/m<sup>3</sup> or more, in combination with other pollutants. The results of more recent studies have indicated adverse effects below this level, though it is not clear to what extent the findings may have been related to the different pollutant profile of earlier years. Cohort studies of differences in mortality between areas with contrasting pollution levels indicate that there is a closer association with particulate matter than with SO<sub>2</sub>.

Applying a two-fold uncertainty factor to the LOAEL reported above yielded ambient air quality guideline values of 125  $\mu$ g/m<sup>3</sup> and 50  $\mu$ g/m<sup>3</sup> for 24-hour and annual periods, respectively (WHO, 1987). In more recent studies, adverse effects were observed at lower levels of exposure. However, these values were retained in the recent revision of the guidelines (WHO, 2000), because of uncertainty as to whether SO<sub>2</sub> was the responsible pollutant or merely a surrogate for some other correlated substance.

#### 3.3.2.1.7 Respirable particulate matter (PM<sub>10</sub>)

The following text, summarizing the PSL assessment for "respirable particulate matter less than or equal to 10 microns," has been taken from EC/HC (2000a):

In numerous epidemiological studies from around the world, including Canada, positive associations have been observed between ambient levels of particulate matter (as PM<sub>10</sub>, PM<sub>2.5</sub> or other particle metrics) and a range of health outcomes, including daily mortality, respiratory and cardiovascular hospitalizations, impaired lung function, adverse respiratory symptoms and medication use, restricted activity days and the frequency of reported chronic respiratory diseases. These associations could not be explained by the influence of weather, season, yearly trends, day-to-day variations or variations due to holidays, epidemics or other non-pollutant factors. While the populations studied were always exposed to other air pollutants in addition

to particulate matter, associations of a similar magnitude were observed across numerous locations with differing air pollutant mixtures, and the association with particulate matter remained in analyses that adjusted for the effects of various other pollutants. These particulate matter-related health effects were observed at ambient concentrations that currently occur in Canada.

Therefore, the epidemiological evidence of mortality and morbidity in response to current levels of particulate air pollution meets a number of the criteria for causality, including consistency, dose–response relationship, coherence, temporal relationship and specificity of both outcome and agent. With respect to the biological plausibility of the association, the results of experimental studies in animals and humans provide some limited support for the epidemiological findings. However, both animal and human experimental work is constrained by the technological difficulties in reproducing environmentally relevant particulate matter, and this work has generally been conducted at high levels with artificial particles. Some of this work, and specifically the most recent work with concentrated ambient particles, has provided initial evidence of particulate matter–induced effects on the cardiorespiratory system, particularly in individuals with pre-existing respiratory and cardiovascular disease, and has provided preliminary indications of possible mechanisms. The database supports, therefore, a causal relation between current ambient  $PM_{10}$  and  $PM_{2.5}$  exposure and adverse health effects.

Table 42 summarizes the magnitude of the health effects associated with ambient particulate matter in the epidemiological studies, as the percentage increase in risk per 10  $\mu$ g/m<sup>3</sup> of PM<sub>10</sub> for each endpoint. The average concentration of PM<sub>10</sub> at which each PM-associated health effect has been observed in the studies reviewed in WGAQOG (1999) and in EC/HC (2000a) is also included.

 TABLE 42
 Summary of adverse health effects associated with particulate matter (epidemiological studies) (modified from EC/HC, 2000a)

Endpoint	% increase of risk per 10 μg/m³ of PM <sub>10</sub>	Average concentrations of $PM_{10}$ (µg/m <sup>3</sup> ) associated with endpoint
Acute increase in mortality	0.8% (unweighted); $0.5%$ (weighted)	18–115 μg/m³
Acute increase in respiratory hospitalizations and emergency department visits	0.35-7.3%	25-55 μg/m <sup>3</sup>
Acute increase in cardiovascular hospitalizations	0.56–1%	48 μg/m <sup>3</sup>
Acute pulmonary function decrements	0.09–0.4%	10–174 µg/m <sup>3</sup>
Acute increase in symptoms	0.6–2.2%	10–174 μg/m³
Acute increase in respiratory symptom- related activity restriction	9.0%	41–51 μg/m <sup>3</sup>
Long-term increase in mortality	10% from cohort studies	18–47 μg/m <sup>3</sup>
Long-term pulmonary function decrements	1.4% increase in odds from cross- sectional studies	24–58 μg/m <sup>3</sup>
Long-term increase in symptoms	From non-significant to 39% increase in odds from cross-sectional studies	20–59 µg/m <sup>3</sup>

#### 3.3.3 Risk characterization

In this section, the risk posed to nearby populations by exposure to the various substances released from Canadian copper smelters and refineries and zinc plants has been characterized, by relating the concentrations in ambient air near these facilities to the healthbased guidelines or measures of exposure-response for each substance. Based on the critical effects for each of the substances summarized in the previous section, the potential risks from As, Cd, Cr and Ni are considered together, followed separately by each of Pb, SO<sub>2</sub> and PM.

Releases from copper smelters and refineries and zinc plants include complex mixtures of substances, including SO<sub>2</sub> and numerous heavy metals. It is known that some of the components of these releases can interact in inducing toxic effects; for example, simultaneous exposure to Zn and a number of other elements is known to protect against the toxicity of Cd, and SO<sub>2</sub> may enhance the respiratory carcinogenicity observed in workers at non-ferrous metal ore smelters (Krishnan and Brodeur, 1991). However, the available data are inadequate to characterize possible interactions among the numerous substances contained in releases from copper smelters and refineries and zinc plants, and in the following risk characterization, it is assumed that there is no interaction. In the case of those substances that are lung carcinogens, this amounts to assuming additivity.

### 3.3.3.1 Arsenic, cadmium, chromium and nickel

As summarized in Section 3.3.2, carcinogenicity is considered to be the critical effect for As, Cd, Cr and Ni, based on the sufficient weight of evidence for pulmonary carcinogenicity in occupational populations or experimental animals following inhalation of inorganic compounds of each of these metals. For such substances, estimates of exposure are compared with quantitative estimates of cancer potency to derive an Exposure Potency Index (EPI), in order to characterize risk and provide guidance in establishing priorities for further action (i.e., analysis of options to reduce exposure) under CEPA 1999 (Health Canada, 1994). The derivation of the relevant potencies (i.e., TC<sub>05</sub>s) for each of the metals is described in Section 3.3.2.

For each monitoring site at each Canadian copper smelter and refinery and zinc plant, a total EPI was developed as a measure of lung cancer risk (Table 43), as follows. A separate EPI was first calculated for each metal, as the ratio of the annual average concentration to the TC<sub>05</sub> for lung cancer mortality/incidence, and then these values were summed for each site. For those metals for which more than one TC<sub>05</sub> was available (i.e., all but Cd), the values presented in the table are based on the lowest value; the impact of using these values on the total EPI was modest (i.e., most often four- to five-fold). The total EPI at a given site included only estimates for those metals for which data were available; based on data from those sites where monitoring was conducted for all four metals, the impact of the data for the individual metals that were most often missing for the other sites (i.e., Cr and Ni) was five-fold or less at most sites. For those facilities that are combined sources (i.e., the Inco nickel-copper smelter, copper refinery and nickel refinery in Sudbury, the Falconbridge-Kidd Creek copper smelter and refinery and zinc plant in Timmins, the Cominco lead smelter and zinc plant in Trail, and the HMB&S smelter in Flin Flon), that portion of the EPI that was attributable to the operation(s) that are the subject of this assessment was estimated, based on the source attribution presented in Table 17.



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Facility	Site	Metals	Total Exposure Potency Index (EPI) <sup>1</sup>	Margin between potency and exposure	Priority for further action
Noranda-Gaspé (copper smelter)	Mines Gaspé	As, Cd	3.8 × 10 <sup>.3</sup>	260	High
Noranda-Horne	Arena Dave Keon	As, Cd, Cr, Ni	$3.3 \times 10^{-2}$	30	High
(copper smelter)	Laiterie Dallaire	As, Cd, Cr, Ni	$4.2 \times 10^{-3}$	240	High
	Hotel de Ville	As, Cd, Cr, Ni	$1.6 \times 10^{-2}$	63	High
	Ecole Notre Dame	As, Cd	$2.3 \times 10^{-2}$	43	High
	250 6 <sup>icme</sup> rue	As, Cd	$7.6 \times 10^{-2}$	13	High
HBM&S (copper smelter and zinc plant)	Barrow Prov. Bldg.	As, Cd	copper smelter <sup>2</sup> $1.4 \times 10^{-2}$ zinc plant 0		High Low
	Ruth Bettes School	As, Cd	copper smelter <sup>2</sup> $3.2 \times 10^{-3}$ zinc plant 0	310	High Low
	FF Sewage Plant	As, Cd	copper smelter <sup>2</sup> $3.2 \times 10^{-3}$ zinc plant 0	310	High Low
Noranda-CCR (copper refinery)	1111 Notre Dame	As, Cd, Cr, Ni	5.8 × 10 <sup>.3</sup>	170	High
Noranda-CEZinc (zinc plant)	Boul. Cadieux	Cd	$3.7 \times 10^{-3}$	270	High
Falconbridge-Sudbury	Edison	As, Cd, Cr, Ni	$2.3 \times 10^{-2}$	43	High
(nickel and copper matte smelter)	Pumphouse	As, Cd, Cr, Ni	$2.3 \times 10^{-2}$	43	High
Inco-Copper Cliff (nickel and copper smelter, copper refinery and nickel refinery)	Copper Cliff	As, Cd, Cr, Ni	copper smelter $1.4 \times 10^{-2}$ copper refinery $5.4 \times 10^{-5}$	71 18 500	High Moderate
	Federal Bldg.	Cd, Cr, Ni	copper smelter $5.5 \times 10^{-3}$ copper refinery 0	180	High Low

TABLE 43 Total Exposure Potency Index for lung cancer mortality at sites near Canadian copper smelters and refineries and zinc plants (continued)

Facility	Site	Metals	Total Exposure Potency Index (EPI) <sup>1</sup>	Margin between potency and exposure	Priority for further action
Falconbridge-Kidd Creek (copper smelter, copper refinery, zinc plant)	1# SMA	As, Cd	copper smelter $2.8 \times 10^{-3}$ copper refinery 0 zinc plant $4.2 \times 10^{-3}$	360  240	High Low High
	AMS #6	As, Cd	copper smelter 7.6 × 10 <sup>-3</sup> copper refinery 0 zinc plant 1.1 × 10 <sup>-2</sup>	130  91	High Low High
	AMS #7	As, Cd	copper smelter $1.8 \times 10^{-3}$ copper refinery 0 zinc plant $3.3 \times 10^{-3}$	560  300	High Low High
Cominco-Trail	West Trail	As, Cd	zinc plant $6.6 \times 10^{-4}$	1500	High
(lead smelter, zinc plant)	Oasis	As, Cd	zinc plant $5.9 \times 10^{-4}$	1700	High
	Warfield	As, Cd	zinc plant $5.0 \times 10^{-4}$	2000	High
	Genelle	As, Cd	zinc plant 4.9 $\times$ 10 <sup>-4</sup>	2000	High
	Glenmerry	As, Cd	zinc plant 6.8 $\times$ 10 <sup>-4</sup>	1500	High
	Downtown	As, Cd	zinc plant 7.1 $\times$ 10 <sup>-4</sup>	1400	High
	Columbia Gardens	As, Cd	zinc plant $8.3 \times 10^{-4}$	1200	High
	Northport	As, Cd	zinc plant $4.3 \times 10^{-4}$	2300	High

The sum of the EPIs (i.e., the annual average concentration in ambient air from Table 24 divided by the TC<sub>05</sub> for lung cancer mortality/incidence) for each of the metals for which monitoring data at the site were available. The TC<sub>05</sub> values were 7.8  $\mu$ g/m<sup>3</sup> for As, 5.1  $\mu$ g/m<sup>3</sup> for Cd, 0.66  $\mu$ g/m<sup>3</sup> for Cr and 40  $\mu$ g/m<sup>3</sup> for Ni. See text for discussion of the basis for the TC<sub>05</sub> values for each metal.

<sup>2</sup> Due to the process used, releases of metals to air from the zinc plant are negligible.

The total EPI values and the corresponding margins between carcinogenic potency and estimated exposure for each monitoring site in the vicinity of Canadian copper smelters and refineries and zinc plants are presented in Table 43. Based on these margins, the priority for investigation of options to reduce exposure is considered to be in the high range for copper smelters, to range from low to high for copper refineries, and to range from low to high for zinc plants. In general, the margins are smallest near copper smelters, largest near copper refineries, and intermediate near zinc plants, although there is considerable variation among facilities of a given type (i.e., two orders of magnitude or more).

#### 3.3.3.2 Lead

Increased exposure of children to Pb has been observed near copper smelters and zinc plants around the world, including some Canadian facilities (Section 2.4.3.2). The concentration of lead in blood is the most widely used and most generally accepted measure of dose, and there is extensive evidence linking blood lead levels to a variety of health effects. However, while there are data on blood lead levels in populations, mostly children, in the vicinity of some facilities in Canada (and some indication that the prevalence of excessive exposures in these populations studied has declined), these are not considered suitable as a basis for assessing risks to health from current releases of Pb. This is principally because the available data are inadequate to distinguish the contribution of current versus historical emissions of Pb to children's current blood lead levels.

Instead, the potential for health effects from exposure to current releases of Pb from Canadian copper smelters and refineries and zinc plants has been assessed by comparing recent data on levels of Pb in ambient air near these facilities to the WHO ambient air quality guideline of 0.5  $\mu$ g/m<sup>3</sup> (annual average). The annual mean concentrations of Pb in ambient air are elevated above regional background near all of the Canadian facilities (Table 24), although

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levels exceeding the WHO guideline occur near just a few of the facilities. These include two of the copper smelters (Noranda-Horne and HBM&S), where mean concentrations of Pb at some sites are elevated above the guideline, sometimes by a considerable margin. This appears to be a combined result of the proximity of these monitoring sites to the smelter and the substantial quantities of Pb emitted from these facilities (Table 4). The guideline is also slightly exceeded at one site near the Falconbridge-Kidd Creek smelting and refining complex. Although this facility also includes a copper refinery, zinc refinery and concentrator, virtually all of the Pb emitted from this facility is released from the copper smelter (Table 4). These results indicate the potential for lead-induced health effects, particularly neurodevelopmental and hematological effects, in populations in the vicinity of certain of the Canadian facilities involved in smelting copper.

#### 3.3.3.3 Sulphur dioxide

The ambient 24-hour concentrations of SO<sub>2</sub> in the vicinity of Canadian copper smelters and refineries and zinc plants are elevated. These increased levels are also reflected in exceedences of the 24-hour WHO Air Quality Guideline for Europe for SO<sub>2</sub> of 125  $\mu$ g/m<sup>3</sup> (WHO, 2000), intended to protect sensitive individuals against health effects. While the guideline is exceeded occasionally near all of the facilities, this occurs most often in the vicinity of certain of those where copper is smelted. (The long-term WHO guideline of 50 µg/m<sup>3</sup> was not exceeded near any of the Canadian copper smelters and refineries or zinc plants.) SO<sub>2</sub> is also oxidized to sulphate particles in the environment, and as noted in the next section, an association between adverse health effects and airborne concentrations of respirable PM similar to those in the vicinity of Canadian copper smelters and refineries and zinc plants has been observed in numerous epidemiological studies. On this basis, there is some potential for SO<sub>2</sub>-induced cardiorespiratory health effects in individuals with pre-existing conditions (e.g., asthmatics) near these facilities. While some of the Canadian facilities include

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process streams that are not the subject of these assessments (e.g., the Cominco lead operations in Trail), the emissions of  $SO_2$  from the combined sources are estimated to be principally or entirely due to the copper smelters or zinc plants (i.e., between 80% and 100%; Table 10).

#### 3.3.3.4 Particulate matter

Given the considerable uncertainties in such factors as the estimates of dose-response for the various health outcomes associated with exposure to PM and the background concentrations of PM in the regions of Canada where copper smelters and refineries and zinc plants are located, no attempt has been made to estimate the potential magnitude of health impacts of PM in the area near these facilities. However, it is noted that the range of annual mean concentrations of PM<sub>10</sub> near the Canadian facilities overlaps the range of mean concentrations (most often averaged over a year or more) from epidemiological studies in which exposure to PM<sub>10</sub> has been associated with a variety of adverse health effects (Table 25 and Table 42). For those facilities that are combined sources, most of the particulate emissions are expected to arise from the copper smelting or zinc plants, with the exception of the Cominco facility in Trail, where 1995 data indicate that approximately 90% was associated with lead processing (RDIS, 1995).

#### 3.3.4 Uncertainties and degree of confidence in human health risk characterization

The exposure assessment was based on recent monitoring data for those substances that comprise the vast majority of current emissions and was specific to the environmental medium most relevant to the critical effects of exposure to these substances.

Nonetheless, there remains a fair degree of uncertainty in the exposure assessment for the health assessment of releases from copper smelters and refineries and zinc plants. The network of monitoring stations is very limited near all of the Canadian facilities, being small in number and apparently located near local populations, rather than being placed at points of impingement or located so as to track the dispersion of the emissions.

In addition, only a small number of substances was considered, limited to those that professional judgement indicated were most likely to be of concern and for which recent relevant assessments were known to be available. A large number of other substances not considered in these assessments are known to be released from these facilities, and risks to health may have been underestimated as a result.

On the other hand, some of the substances, most notably  $PM_{10}$ , are not specific to the facilities that are the subject of these assessments, and some of the facilities, such as the Noranda-CCR copper refinery, are located near other major industrial operations; hence, other sources may have contributed substantially to the concentrations measured near some of the copper smelters and refineries and zinc plants.

Also with respect to  $PM_{10}$ , it should be noted that most of the values used for this variable were estimated from the TSP data, rather than being measured directly; it is likely that the relative size distribution of airborne particles at a given location will vary depending on origin, composition and other factors affecting deposition rates, although the available limited data indicated that the long-term average concentration of  $PM_{10}$  estimated in this fashion was very similar to concomitant measurements of  $PM_{10}$ . Moreover, this would not materially affect the assessment for this parameter, which is somewhat qualitative in any case.

There are no quantitative data on the species of metals present in ambient air near Canadian copper smelters and refineries and zinc plants. It is known that the various chemical species of a given metal can differ markedly in bioavailability and toxicity. Speciation was addressed to the extent possible in the PSL assessments for As, Cd, Cr and Ni and was



clearly identified as an important information gap; however, these data do not appear to have been generated in the interim.

The overall degree of confidence in the exposure assessment is, therefore, moderate, owing principally to the limitations in the existing monitoring network near Canadian copper smelters and refineries and zinc plants.

There is also a fair degree of uncertainty in the characterization of effects for the health assessment of releases from these facilities. The principal uncertainty is the lack of meaningful direct data on effects on local populations of the mixture of substances released from copper smelters and refineries and zinc plants in Canada, which is the reason the scope of the health assessment is necessarily limited. This limited scope involved reliance on other assessments for information on exposure-response for the large number of components of releases that were considered; though these were not updated, the authors of this assessment are not aware of new data for these substances that would impact significantly on conclusions drawn under CEPA 1999 64(c).

With respect to those components of releases that affect the same endpoint (i.e., lung cancer), it has been assumed that there is no interaction among them, even though, for example, there is evidence that  $SO_2$  enhances the respiratory carcinogenicity of As. In addition, there is a lack of monitoring data for some carcinogenic metals (i.e., Cr and Ni) near some Canadian copper smelters and refineries and zinc plants. As a consequence of these factors, risks may have been underestimated. This is offset somewhat by the use of the most conservative  $TC_{05}$  values, though these have only a modest impact on the margin between potency and exposure.

Confidence in the effects assessment is increased by the fact that the critical effects for some substances (i.e., Pb,  $SO_2$  and  $PM_{10}$ ) have been determined based on epidemiological studies that were conducted at ambient levels of

pollutants in the same range as those observed near the Canadian facilities considered in this assessment (though not necessarily the same mixtures of pollutants as for copper smelters and refineries and zinc plants) and on populations that included critical subpopulations in terms of exposure and sensitivity.

While releases from copper smelters and refineries and zinc plants can result in high blood lead levels, there is a lack of recent data on blood lead levels near all but one of the Canadian facilities, and there is inadequate information on the contribution of current emissions versus reentrainment of historical deposits to these levels.

Overall, the degree of confidence in the effects assessment is considered to be low to moderate, owing principally to lack of data concerning the effects of environmental exposure to mixtures of substances emitted from copper smelters and refineries and zinc plants on local human populations.

### 3.4 Conclusions

## 3.4.1 Releases from copper smelters and refineries

CEPA 1999 64(a): Based on available data, it has been concluded that emissions from copper smelters and refineries of metals (largely in the form of particulates) and of sulphur dioxide are entering the environment in quantities or concentrations or under conditions that have or may have an immediate or longterm harmful effect on the environment or its biological diversity. Therefore, metals (largely in the form of particulates) contained in emissions from copper smelters and refineries and sulphur dioxide are considered "toxic" as defined under

Paragraph 64(a) of CEPA 1999.

CEPA 1999 64(b): Based on available data, it has been concluded that emissions from copper smelters and refineries are not entering the environment in quantities or concentrations or under conditions that constitute or may constitute a danger to the environment on which life depends. Therefore, emissions from copper smelters and refineries are not considered "toxic" as defined under paragraph 64(b) of CEPA 1999.

CEPA 1999 64(c): Based on available data concerning the effects of PM<sub>10</sub>, sulphur dioxide and compounds of arsenic, cadmium, chromium, lead and nickel, it has been concluded that emissions from copper smelters and refineries of PM<sub>10</sub>, of metals (largely in the form of particulates) and of sulphur dioxide are entering the environment in quantities or concentrations or under conditions that constitute or may constitute a danger in Canada to human life or health. Therefore, metals (largely in the form of particulates) contained in emissions from copper smelters and refineries, PM<sub>10</sub> and sulphur dioxide are considered "toxic" as defined under Paragraph 64(c) of CEPA 1999.

### Overall

conclusion:

Based on critical assessment of relevant information, metals (largely in the form of particulates) contained in emissions from copper smelters and refineries,  $PM_{10}$ and sulphur dioxide are considered "toxic" as defined in Section 64 of CEPA 1999.

#### 3.4.2 Releases from zinc plants

- CEPA 1999 64(a): Based on available data, it has been concluded that emissions from zinc plants of metals (largely in the form of particulates) and of sulphur dioxide are entering the environment in quantities or concentrations or under conditions that have or may have an immediate or longterm harmful effect on the environment or its biological diversity. Therefore, metals (largely in the form of particulates) contained in emissions from zinc plants and sulphur dioxide are considered "toxic" as defined under Paragraph 64(a) of CEPA 1999.
  - CEPA 1999 64(b): Based on available data, it has been concluded that emissions from zinc plants are not entering the environment in quantities or concentrations or under conditions that constitute or may constitute a danger to the environment on which life depends. Therefore, emissions from zinc plants are not considered "toxic" as defined under paragraph 64(b) of CEPA 1999.

CEPA 1999 64(c): Based on available data concerning the effects of PM<sub>10</sub>, sulphur dioxide and compounds of arsenic, cadmium, chromium, lead and nickel, it has been concluded that emissions from zinc plants of metals (largely in the form of particulates), of PM<sub>10</sub> and of sulphur dioxide are entering the environment in quantities or concentrations or under conditions that constitute or may constitute a danger in Canada to human life or health. Therefore, metals (largely in the form of particulates) contained in emissions from zinc plants, PM<sub>10</sub> and sulphur dioxide are considered "toxic" as defined under Paragraph 64(c) of

CEPA 1999.

Overall conclusion:

Based on critical assessment of relevant information, metals (largely in the form of particulates) contained in emissions from zinc plants, PM<sub>10</sub> and sulphur dioxide are considered "toxic" as defined in Section 64 of CEPA 1999.

# 3.5 Considerations for follow-up (further action)

The assessment of risk to the environment was based on emissions to air of Cu, Zn, Ni, Pb, Cd and As (largely in the form of particulates) as well as SO<sub>2</sub>, while the health assessment included the same metals less Cu and Zn, plus Cr, SO<sub>2</sub> and PM. These constituents were selected for evaluation from the complex combination of substances released from smelters and refineries, as these generally represent the substances released in the greatest quantity. This does not imply that other constituents do not pose a risk. Thus, investigations of options for risk management should also take into consideration other substances of potential concern, some examples of which include Hg, Se, dioxins and furans. It should be noted in particular that, as a class, the facilities considered in these assessments are the largest source of Hg emissions in Canada. In 1995 (the most recent year for which comprehensive Canadian Hg emissions data are available), copper smelters and zinc plants emitted a total of about 3.8 tonnes of Hg. This represents about 35% of the 11 tonnes emitted by all anthropogenic sources in Canada in 1995 (data summarized in CED, 2000).

Risk to the environment due to aquatic releases was evaluated for only three of the facilities considered in these assessments. This was done because restrictions of time and resources precluded site-specific evaluation of aquatic releases from all facilities. In addition, aquatic releases from all six of the facilities not assessed are mixed with mining effluent prior to release to surface waters. As a result, their effluents fall under the Metal Mining Liquid Effluent Regulations and Guidelines (MMLER), passed in 1977 under the Fisheries Act. Currently, these facilities are only subject to Guidelines under MMLER. However, all six facilities will have to conform to the revised Metal Mining Effluent Regulations (MMER), anticipated to come into effect in 2002. The MMER will include a requirement for EEM. It should be clearly stated that the exclusion of these facilities from site-specific risk assessment of aquatic releases does not imply that their effluents do not pose a risk to the environment. It is also of significance that aquatic releases from base metal smelting facilities are the subject of a number of other ongoing and planned risk management initiatives. Any investigations of options to reduce exposure as a result of the assessment of releases from copper smelters and refineries and zinc plants as Priority Substances under CEPA 1999 should also be integrated with these initiatives.

Screening-level risk assessment of aquatic releases from the three facilities evaluated (Noranda-CCR, Noranda-CEZinc and Cominco-Trail) indicated the potential for detrimental effects on the environment. The indicators of risk, based on the limited data available, were relatively low, especially given the slightly conservative nature of the screening assessment. Given existing controls on effluents put in place by the companies or imposed by Provincial governments or other authorities, Federal prevention or control actions under the Canadian Environmental Protection Act, 1999 (CEPA, 1999) are not recommended at this time. It is believed, however, that an increase in contaminant concentrations or loadings or changes in conditions affecting bioavailability (such as pH) have the potential to significantly increase risk to the environment. It is important that facility operators recognize that if information, such as monitoring data, shows a significant increase in contaminant concentrations or loadings or changes in conditions affecting bioavailability, such information may be subject to reporting under Section 70 of CEPA, 1999.

Comparison of estimated exposure to arsenic, cadmium, chromium and nickel in the vicinity of Canadian copper smelters/refineries and zinc plants with the tumorigenic potency indicates that the priority for investigation of options to reduce human exposure to releases from these facilities is considered to be in the high range for copper smelters, to range from low to high for copper refineries, and to range from low to high for zinc plants. Comparison of levels of lead, SO<sub>2</sub> and PM<sub>10</sub> in ambient air with healthbased guidelines or with concentrations at which health effects have been observed also suggests that the priority for options analysis is high, especially for facilities where copper is smelted.

As a result of the Base Metals Smelting Sector Strategic Options Process, there are ongoing toxics initiatives designed to address air and water releases of inorganic As compounds, inorganic Cd compounds, dioxins and furans, Pb, Hg and oxidic, sulphidic and soluble inorganic

Ni compounds from the base metal smelting sector. An assessment of options to reduce exposure as a result of the assessment of releases from copper smelters and refineries and zinc plants as Priority Substances under CEPA 1999 should be integrated with those for this ongoing initiative.

In addition, there are ongoing initiatives to control and reduce emissions of SO<sub>2</sub> from major industrial sources in Canada. Any investigations of options to reduce exposure as a result of the assessment of releases from copper smelters and refineries and zinc plants as Priority Substances under CEPA 1999 should also be integrated with these initiatives.

Respirable PM less than or equal to 10 microns was the subject of a separate PSL risk assessment and was found to be "toxic" as defined in Section 64 of CEPA 1999. It was subsequently added to the list of toxic substances in Schedule 1 of CEPA 1999. As recognized in that assessment,  $SO_2$  is one of the major precursors in the secondary formation of PM<sub>2.5</sub>. Risk from exposure to respirable PM is one consideration that has contributed to the proposal that releases from copper smelters and refineries and zinc plants be considered "toxic" under CEPA 1999. In determining any risk management measures to reduce exposure to respirable PM originating from these facilities, the fact that the facilities are major sources of SO<sub>2</sub> must be recognized.

It should also be noted that since source attribution has been based on an incomplete inventory of emission sources that are not directly associated with copper smelters and refineries and zinc plants, the proportion of emissions estimated to have come from copper smelters and refineries or from zinc plants may be an overestimate. Sources not well represented in current inventories include, for example, emissions related to the production and transport of concentrates, as well as metal-laden dust blown from uncovered tailings piles. These sources augment exposure by contributing to local background metal concentrations. Any



investigations of options to reduce exposure as a result of these assessments should take these other less well characterized sources into consideration. Further, inconsistencies between facilities in reporting of emissions have been a source of uncertainty in these assessments. More stringent standards for reporting, such as is suggested in the "Strategic Options Report for

the Base Metal Smelting Sector" (Environment Canada, 1997b), and perhaps a greater level of industry accountability in future emissions reporting are warranted.



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# APPENDIX A SEARCH STRATEGIES EMPLOYED FOR IDENTIFICATION OF RELEVANT DATA

#### **Environmental assessment**

Data relevant to the assessment of whether releases from copper smelters and refineries and zinc plants are "toxic" to the environment under CEPA 1999 were identified from existing review documents, published reference texts and on-line searches, conducted between January and June 1996. Unless otherwise indicated, no year limits were applied to the databases searched, and databases were searched on the dates shown. The following were searched: Aqualine (Water Research Centre, Buckinghamshire; June 1996), ARET (Accelerated Reduction/Elimination of Toxics, Environment Canada;1995 report), ASFA (Aquatic Sciences and Fisheries Abstracts, Cambridge Scientific Abstracts; June 1996), **BIOSIS** (Biosciences Information Services; June 1996), Business Opportunities Sourcing System (Industry Canada; 1994 issue), CAB (Commonwealth Agriculture Bureau; June 1996), Canadian Research Index (Microlog: CRI, Government Publications/Micromedia Ltd., 1990 - March 1996), CANLIB (Natural Resources Canada), Catalogue of Environmental Data in Atlantic Canada (Environment Canada, Atlantic Region; 1996), CESARS (Chemical Evaluation Search and Retrieval System, Ontario Ministry of the Environment and Michigan Department of Natural Resources; 1996), Chemical Abstracts (Chemical Abstract Services: June 1996), ChemINFO (Canadian Centre for Occupational Health and Safety; 1996), CHRIS (Chemical Hazard Release Information System; up to 1985), CPI Product Profiles (Camford Information Services; 1996), Current Contents (Institute for Scientific Information; 1990–1992, 1996), ELIAS (Environmental Library Integrated Automated System, Environment Canada library; January 1996), ENVIRODAT (Environment Canada; June 1996), Enviroline (R.R. Bowker Publishing Co.; November 1995 - June 1996), Environmental Abstracts (1975 - February 1996), Environmental Bibliography (Environmental Studies Institute, International Academy at Santa Barbara; June 1996), Envirosource (Environment Canada; May 1996), GEOREF (Geo Reference Information System, American Geological Institute; June 1996), HSDB (Hazardous Substances Data Bank, U.S. National Library of Medicine; June 1996), ICAR (Inventory of Canadian Agricultural Research, Canadian Agrifood Research Council; April 1996), Life Sciences (Cambridge Scientific Abstracts; June 1996). Metadex (Cambridge Scientific Abstracts; 1990 - June 1996), NATES (National Analysis of Trends in Emergencies System, Environment Canada; 1996), Northern Info Network (June 1996), NTIS (National Technical Information Service, U.S. Department of Commerce; June 1996), Pollution Abstracts (Cambridge Scientific Abstracts, U.S. National Library of Medicine; June 1996), POLTOX (Cambridge Scientific Abstracts, U.S. National Library of Medicine; 1990-1995), REPEN (Répertoire informatisé des bases de données environnementales sur le Fleuve Saint-Laurent, Environment Canada, Ouebec Region; 1996), RTECS (Registry of Toxic Effects of Chemical Substances, U.S. National Institute for Occupational Safety and Health; 1996), Synopsis of the Northern Contaminants Program (1992/93 and 1993/94 issues), Toxline (U.S. National Library of Medicine; June 1996), TRI93 (Toxic Chemical Release Inventory, U.S. Environmental Protection Agency, Office of Toxic Substances; June 1996), USEPA-ASTER (Assessment Tools for the Evaluation of Risk, U.S. Environmental Protection Agency; up to December 1994), USEPA-ECOTOX (including AQUIRE; U.S. Environmental Protection Agency; up to September 1995), USEPA-National Catalog (U.S. Environmental Protection Agency; February 1996), WASTEINFO (Waste Management Information Bureau of the American Energy



Agency; 1973–September 1995) and Water Resources Abstracts (June 1996).

Two databases were evaluated to quantify releases. These included 1995 and 1996 data collected under NPRI and 1995 data collected under the RDIS. Data were also collected from industry through two questionnaires. Data obtained after fall 1999 were not considered in this assessment unless they were critical data received during the 60-day public review of the report (July 1 – August 30, 2000).

Documents prepared in support of the environmental components of these assessments include:

- Acute and chronic effects of sulphur dioxide on vegetation: Critical Toxicity Values (CTVs) and Estimated No-Effects Values (ENEVs). Prepared by Phytotoxicology Consultant Services Ltd. (cited as Linzon, 1999)
- Assessment of SO<sub>2</sub> releases from copper smelters, refineries and zinc plants. Prepared by SENES Consultants Ltd. (cited as SENES Consultants, 1999a)
- Atmospheric dispersion modelling for the assessment of two Priority Substances — Trace metal releases from primary and secondary copper smelters and refineries and primary and secondary zinc plants. Prepared by SENES Consultants Ltd. (cited as SENES Consultants, 2000)
- Critical load modelling: Cd, Cu, Ni, Pb, Zn and As emitted by smelters and refineries. Prepared by ECOMatters Inc. (cited as Sheppard *et al.*, 1999)
- Effects characterization: Cd, Cu, Ni, Pb, Zn and As. Prepared by ECOMatters Inc. (cited as Bird *et al.*, 1999)
- Estimating bioavailability of trace metals in terrestrial and aquatic ecosystems. Prepared by W. Hendershot, McGill University. (content incorporated into Bird *et al.*, 1999)

- PSL2 assessment of copper and zinc refinery effluents. Prepared by Beak International Inc. (cited as Beak International, 1999)
- Report on site visits to HBM&S Flin Flon, Inco Copper Cliff, Noranda Horne and Noranda Gaspé facilities. Prepared by SENES Consultants Ltd. (cited as SENES Consultants, 1999b)
- A review of the direct and indirect effects on wildlife from copper/zinc smelter and refinery releases into aquatic or terrestrial ecosystems. Prepared by Welbourn Consulting. (cited as Welbourn, 1996)
- Summary of effects related to historic releases from Canadian zinc and copper smelters and refineries. Prepared by J. Sanderson. (cited as Sanderson, 1998)
- Summary of empirical data and data handling methods used in the PSL assessments of releases from copper smelters and refineries and zinc plants. Prepared by the Chemicals Evaluation Division, Environment Canada. (cited as CED, 2000)

#### Health assessment

The focus of the assessment is on evaluating the potential impacts of current releases of substances from copper smelters and refineries and zinc plants in Canada. To this end, the companies operating these facilities were approached in 1998 for recent environmental monitoring data, in order to characterize recent exposure and associated health risks for populations in the vicinity of such facilities. The data requested were the airborne levels of various substances (including several heavy metals, SO<sub>2</sub> and PM) released from these facilities, along with other relevant information.

To identify epidemiological studies of health effects in populations in the vicinity of copper smelters and refineries and zinc plants, literature searches were conducted in April 1996

using the strategy of searching for "smelter\* or refiner\* and (epi\* or morb\* or mortal\*)" in the following databases: Cancerlit (National Cancer Institute's International Cancer Information Centre, U.S.A.), Embase (Elsevier Science), Enviroline (R.R. Bowker Publishing Co.), Environmental Bibliography (Environmental Studies Institute, International Academy at Santa Barbara), Medline (U.S. National Library of Medicine), Pollution Abstracts (Cambridge Scientific Abstracts, U.S. National Library of Medicine), Science Citation Index (Institute for Scientific Information) and Toxline (U.S. National Library of Medicine). In addition to the information identified in these sources, unpublished reports of the studies by Polissar et al. (1979) and by Hartley and Enterline (1981) were kindly provided by J.P. Hughes of the University of Washington.

Epidemiological studies of populations near copper smelters and refineries and zinc plants published after April 1996 were identified by the strategy of searching for "smelter\* or refiner\* and (epi\* or morb\* or mortal\*)" through an SDI (Selective Dissemination of Information) profile run twice yearly in the following databases: Canadian Research Index, CCRIS (Chemical Carcinogenesis Research Information System, U.S. National Cancer Institute), Dialog, EMIC (Environmental Mutagen Information Center database, Oak Ridge National Laboratory) and GENETOX (Genetic Toxicology, Office of Toxic Substances, U.S. Environmental Protection Agency), and by searches of the CD-ROM updates of Medline (monthly) and Toxline Plus (quarterly).

In addition, the reference lists from all reports identified from the above sources were searched manually for relevant studies.

Monitoring and epidemiological data relevant to the assessment of whether releases from copper smelters and refineries and zinc plants are "toxic" to human health obtained after February 2000 have not been included.

Information on health effects and exposure-response for individual substances was taken from other assessments conducted under the PSL assessment program and other national and international programs. In selecting assessments for individual substances, the criteria considered included whether the approach taken was consistent with the principles on which the PSL health assessments are based (for example, whether the assessment was strictly healthbased), whether the assessment was specific to the inhalation route of exposure, whether quantitative measures of exposure-response were developed, and how recently the assessment was conducted. On this basis, the assessments selected included those conducted for the PSL program for As (EC/HWC, 1993), Cd (EC/HC, 1994a), Cr (EC/HC, 1994c), Ni (EC/HC, 1994b) and respirable PM (EC/HC, 2000a), and in development of the World Health Organization (WHO) Air Quality Guidelines for Europe for Pb and SO<sub>2</sub> (WHO, 2000). No attempt was made to identify new data that might impact on the conclusions of these assessments.

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