Canadian Environmental Protection Act, 1999

PRIORITY SUBSTANCES LIST ASSESSMENT REPORT

FOLLOW-UP TO THE STATE OF SCIENCE REPORT, 2000

Aluminum Chloride
Aluminum Nitrate
Aluminum Sulphate

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LIST OF ACRONYMS AND ABBREVIATIONS

Aβ	amyloid beta
ACH	aluminum chlorohydrate
AD	Alzheimer's disease
AD$_{AF}$	chemical-specific animal to human toxicodynamic adjustment factor
ADP	adenosine diphosphate
ADRDA	Alzheimer's Disease and Related Disorders Association
AK$_{AF}$	chemical-specific animal to human toxicokinetic adjustment factor
AMS	accelerator mass spectrometry
ApoE	apolipoprotein E
ASFA	Aquatic Sciences and Fisheries Abstracts (World Health Organization Food and Agricultural Organization)
ATP	adenosine triphosphate
ATPase	class of enzymes that catalyze the decomposition of ATP into ADP
ATSDR	Agency for Toxic Substances and Disease Registry (U.S. Department of Health and Human Services)
BAF	bioaccumulation factor
BCF	bioconcentration factor
BIOSIS	Biosciences Information Services
CAplus	Chemical Abstracts Plus
CAB	Commonwealth Agricultural Bureaux
cAMP	cyclic adenosine monophosphate
CAS	Chemical Abstracts Service
CASReact	CAS Reaction
CBTB	Canadian Brain Tissue Bank
CEPA	Canadian Environmental Protection Act
CEPA 1999	Canadian Environmental Protection Act, 1999
CESARS	Chemical Evaluation Search and Retrieval System (Ontario Ministry of the Environment and Michigan Department of Natural Resources)
cGMP	cyclic guanosine monophosphate
ChemCats	Chemical Catalogs online
Chemlist	regulated Chemicals Listing
CHRIS	Chemical Hazard Release Information System
CI	confidence interval
CSHA	Canadian Study of Health and Aging
CT	computer tomography
CTV	Critical Toxicity Value
D$_a$	administered dose

D_b	base diet dose
D_c	cumulative dose
DIN	Drug Identification Number
DNA	deoxyribonucleic acid
DOC	dissolved organic carbon
DOM	dissolved organic material
DSM	Diagnostic and Statistical Manual of Mental Disorders (American Psychiatric Association)
dw	dry weight
DWTP	drinking water treatment plant
EC_{50}	median effective concentration
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
EDI	estimated daily intake
EEM	Environmental Effects Monitoring
ELIAS	Environmental Library Integrated Automated System (Environment Canada library)
EPA	Environmental Protection Agency (U.S.)
ETAAS	electrothermal atomic absorption spectroscopy
FAO	Food and Agricultural Organization (United Nations)
GD	gestational day
GEOREF	Geo Reference Information System (American Geological Institute)
GLP	good laboratory practice
GVRD	Greater Vancouver Regional District
GVS&DD	Greater Vancouver Sewerage & Drainage District
HD_{AF}	chemical-specific human variability toxicodynamic adjustment factor
HK_{AF}	chemical-specific human variability toxicokinetic adjustment factor
HSDB	Hazardous Substances Data Bank (U.S. National Library of Medicine)
ICD	International Classification of Diseases (World Health Organization)
IM	intramuscular
IPCS	International Programme on Chemical Safety (World Health Organization)
IV	intravenous
JECFA	Joint FAO/WHO Expert Committee on Food Additives
KASAL	alkaline aluminum phosphate and dibasic sodium phosphate

LC_{50}	median lethal concentration
LD_{50}	median lethal dose
LOAEC	lowest observed adverse effect concentration
LOEC	lowest observed effect concentration
LOEL	lowest observed effect level
LSA	Ontario Longitudinal study of Aging
MEDLINE	Medical Literature Analysis and Retrieval System Online (U.S. National Library of Medicine)
MINEQL+	chemical equilibrium modeling software
MMAD	mass median aerodynamic diameter
MMSE	Mini-Mental State Examination
MOE	margin of exposure
mRNA	messenger ribonucleic acid
MS	multiple sclerosis
MWWTP	municipal wastewater treatment plant
NADPH	nicotinamide adenine dinucleotide phosphate
NATES	National Analysis of Trends in Emergencies System
NEMISIS	National Enforcement Management Information System and Intelligence System
NFT	neurofibrillary tangles
NICNAS	National Industrial Chemicals Notification and Assessment Scheme (Australian Government Department of Health and Aging)
NIH	National Institutes of Health (U.S. Department of Health and Human Services)
NINCDS	National Institute of Neurological and Communicative Disorders and Stroke
NOEC	no observed effect concentration
NOEL	no observed effect level
NTIS	National Technical Information Service (U.S. Department of Commerce)
OECD	Organisation for Economic Co-Operation and Development
OR	odds ratio
p value	the probability of obtaining a value of the test statistic at least as extreme as the one that was actually observed, given that the null hypothesis is true
PAC	polyaluminum chloride
PAQUID	Principle lifetime occupation and cognitive impairment in a French elderly
PAS	polyaluminum sulphate
PASS	polyaluminum silicate sulphate
PEC	Predicted Environmental Concentration

PM	particulate matter
$PM_{2.5}$	particulate matter less than 2.5 micrometers in aerodynamic diameter
PM_{10}	particulate matter less than 10 micrometers in aerodynamic diameter
PND	postnatal day
PNEC	Predicted No-Effect Concentration
POLTOX	Cambridge Scientific Abstracts (U.S. National Library of Medicine)
PPP2	Protein Phosphatase 2
PSL	Priority Substances List
PSL2	Second Priority Substances List
PTEAM	Particle Total Exposure Assessment Methodology
PubMed	free Internet access to MEDLINE
RMOC	Regional Municipality of Ottawa-Carleton
RR	relative risk
RTECS	Registry of Toxic Effects of Chemical Substances (U.S. National Institute for Occupational Safety and Health)
SALP	sodium aluminum phosphate
SOS	State of the Science
$t_{½}$	half-life
TDI	total dietary intake
Tf	transferrin
$TNF^{-\alpha}$	alpha tumour necrosis factor
TOXLINE	toxicology database (U.S. National Library of Medicine)
TRI93	Toxic Chemical Release Inventory (U.S. Environmental Protection Agency, Office of Toxic Substances)
TSS	total suspended solids
USEPA-ASTER	Assessment Tools for the Evaluation of Risk (U.S. Environmental Protection Agency)
V_d	volumes of distribution
WASTEINFO	Waste Management Information (Bureau of the American Energy Agency)
WHAM	Windermere Humic-Aqueous Model software designed to calculate equilibrium chemical speciation in surface and ground waters, sediments and soils
WHO	World Health Organization

SYNOPSIS

The three aluminum salts, aluminum chloride, aluminum nitrate and aluminum sulphate, were included on the Second Priority Substances List (PSL2) under the *Canadian Environmental Protection Act, 1999* (CEPA 1999) in order to assess the potential environmental and human health risks posed by exposure to aluminum derived from these three salts in Canada.

In December 2000, the PSL2 assessment of the three aluminum salts was formally suspended due to limitations in the available data for assessing health effects. At the same time, a State of the Science report (Environment Canada and Health Canada 2000) on the three aluminum salts was released, providing an in-depth review of toxicity and exposure information relating to human health and the environment. During the suspension period, additional health effects information was published in the scientific literature, and they are considered here.

In Canada, municipal water treatment facilities are the major users of aluminum chloride and aluminum sulphate, accounting for 78% of the estimated 16.1 kilotonnes of the 2006 domestic consumption. Industrial water and wastewater treatment, and use in the pulp and paper industry, account for an additional 20 %. Aluminum sulphate and aluminum chloride are also used as ingredients in drugs and cosmetics, such as antiperspirants and topical creams. Aluminum sulphate is permitted as a food additive in a limited number of products. Aluminum nitrate, used in far less quantities than the sulphate and chloride salts, may be used in fertilizers, and as a chemical reagent in various industries.

Aluminum salts occur naturally in small quantities in restricted geological environments and aluminum can be released into the Canadian environment from these natural sources. However, since aluminum is present in relatively large amounts in most rocks, dominantly in aluminosilicate minerals, which weather and slowly release aluminum to the surface environment, the small amounts of aluminum in surface waters resulting from weathering of aluminum salts such as aluminum sulphate cannot be distinguished from other natural aluminum releases.

During their use in water treatment, aluminum salts react rapidly, producing dissolved and solid forms of aluminum with some release of these to Canadian surface waters. The amount of anthropogenic aluminum released nationally in Canada is small compared with estimated natural aluminum releases; however anthropogenic releases can dominate locally near strong point sources. Most direct release into surface waters of aluminum derived from the use of aluminum salts in water treatment processes originates from drinking water treatment plants (DWTPs). However, direct releases of process waters from DWTPs are regulated by many provincial and territorial authorities, and these releases typically occur in circumneutral water, where the solubility of aluminum is minimal. Disposal of sludge produced by municipal and industrial water treatment facilities on land through landfarming practices is a source of aluminum to the terrestrial environment. However, the presence of dissolved organic matter and inorganic chelating agents will lower the amount of bioavailable aluminum in both the terrestrial and aquatic environments.

While extensive recent data on total aluminum concentrations in Canadian surface waters are available, few data exist on levels in areas close to sites where releases occur. The situation for sediment and soil is similar, in that data exist for the Canadian environment in general, but not for areas where releases occur. A large number of environmental toxicity data are available for acidified environments, but relatively few exist for circumneutral environments similar to those where most releases occur.

Based on a comparison of highest measured and estimated aluminum levels present in both aquatic and terrestrial environments in Canada that receive direct inputs of aluminum from the use of the three aluminum salts, and Predicted No-Effect Concentrations (PNECs) derived from experimental data for aquatic and terrestrial biota, it is considered that, in general, it is unlikely that organisms are exposed to harmful levels of aluminum resulting from the use of aluminum salts in Canada. However, it is acknowledged that under some release conditions there is potential for local impacts to benthic organisms related to the settling of aluminum sludge from DWTPs onto the sediment surface. As such, it is proposed that the three aluminum salts (i.e., aluminum chloride, aluminum nitrate, aluminum sulphate) are not entering 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.

With respect to human health, both epidemiological and experimental animal data were reviewed. Considering experimental animal studies, the dose at which neurotoxic, reproductive, and developmental effects have been repeatedly observed was used to establish an exposure level of concern.

General population exposure to total aluminum was quantified. With respect to the three salts—aluminum chloride, aluminum nitrate, and aluminum sulphate—their contribution to total aluminum exposure can only be qualitatively estimated, however, the only media in which the mean concentration may be significantly affected by the use of these salts is drinking water, in which aluminum sulphate or aluminum chloride may be added during the treatment process. As a surrogate for quantitative exposure estimation it was assumed that all aluminum in drinking water is derived from aluminum chloride and aluminum sulphate. Comparison of the exposure level of concern to the age-group with the highest average daily intake of total aluminum from drinking water results in a margin of exposure that is considered adequate.

Based on the information available for human health and the environment, it is proposed that the three aluminum salts, aluminum chloride, aluminum nitrate, aluminum sulphate, are not entering 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 or that constitute or may constitute a danger to the environment on which life depends. It is also proposed that aluminum from aluminum chloride, aluminum nitrate and aluminum sulphate, are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health. It is therefore proposed that aluminum chloride, aluminum nitrate and aluminum sulphate do not meet the definition of "toxic" under section 64 of the *Canadian Environmental Protection Act, 1999.*

1 INTRODUCTION

The *Canadian Environmental Protection Act, 1999* (CEPA 1999) requires the 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 to determine whether they meet or are capable of meeting the criteria as defined in section 64 of the Act. A substance meets the criteria under CEPA 1999 if it is entering or may enter the environment in a quantity or concentration or under conditions that:

(a) 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.

For substances deemed to meet the criteria defined in section 64, risk management measures are identified and implemented in consultation with stakeholders, in order to reduce or eliminate the risks posed to human health or the environment. These measures may include regulations, guidelines, pollution prevention plans or codes of practice to control any aspect of the life cycle of the substance, from the research and development stage through to manufacture, use, storage, transport and ultimate disposal.

Based on initial screening of readily accessible information, the rationale provided by the Ministers' Expert Advisory Panel in 1995 for including aluminum chloride, aluminum nitrate and aluminum sulphate on the Second Priority Substances List was as follows (Environment Canada and Health Canada 2000):

> *"Aluminum, from both natural and man-made sources, is widespread in the Canadian environment. Intakes of aluminum among the human population and ambient airborne concentrations in some parts of the country are close to those that have induced developmental and pulmonary effects in animal studies. Epidemiological studies have indicated that there may be a link between exposure to aluminum in the environment and effects in humans. Aluminum compounds are bioaccumulative, and can cause adverse ecological effects, especially in acidic environments. The Panel identifies three aluminum compounds as being of particular concern. An assessment is needed to establish the weight of evidence for the various effects, the extent of exposure and the aluminum compounds involved. If necessary, the assessment could be expanded to include other aluminum compounds."*

A preliminary report was completed for the three aluminum salts and released as a State of the Science (SOS) report in December 2000. With respect to immediate or long term harmful effects of the three aluminum salts on the environment or its biological diversity, the report proposed that, based on measured and estimated aluminum levels in Canadian aquatic and terrestrial environments receiving direct inputs of aluminum from the use of aluminum salts and on the Predicted No-Effect Concentrations (PNECs) derived from experimental data for aquatic and terrestrial biota, it is in general unlikely that organisms are exposed to harmful levels of aluminum resulting from the use of aluminum salts in Canada.

With respect to human health, a conclusion regarding section 64(c) could not be reached in 2000, owing to the limitations in the available data for assessing health effects. Therefore, the assessment of aluminum salts was suspended in December 2000 for a period of six years to allow for the development of additional human health effects data in order that Health Canada could reach a conclusion on whether aluminum salts (chloride, nitrate and sulphate) should be considered as "toxic" under CEPA 1999.

In terms of this draft PSL2 assessment, the conclusions made under section 64 of CEPA 1999 relate directly to the three aluminum salts nominated by the Ministers' Expert Advisory Panel (chloride, nitrate, and sulphate). However, different approaches are taken by Environment Canada and Health Canada in evaluating the potential for risk.

In characterizing the potential for risk to the environment, data relevant to the entry of the three listed salts into the Canadian environment from local point sources (e.g., drinking water treatment plants) were examined in conjunction with data on environmental fate and exposure. The focus was on assessing potential for effects on the environment near point sources. This evaluation formed the basis for determining whether the three aluminum salts identified by the Ministers' Expert Advisory Panel (chloride, nitrate and sulphate) are "toxic" under section 64 of CEPA 1999.

The human health risk characterization consists of a two-stage evaluation. In the first stage, exposure of the general Canadian population to total aluminum in air, drinking water, diet, and soil is quantified. In the second stage, the relative contribution of each of the three listed aluminum salts (chloride, nitrate, and sulphate) to this total aluminum exposure is qualitatively evaluated, and a recommendation with respect to section 64(c) of CEPA is made for the three salts.

Health Canada chose this two-stage approach on the basis of both scientific and practical considerations. First, overall exposure to the aluminum moiety (Al^{3+}), and not exposure to a particular aluminum compound, is the critical parameter for evaluating potential toxicological risk[1]. Second, concentrations of aluminum in foods, soil, drinking water, and air are generally reported as total aluminum, and not in terms of specific salts, consequently it is difficult to determine with great precision the relative contribution of the three salt forms being considered. Although information on sources and uses of aluminum-containing

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[1] Note, however, that different aluminum salts are absorbed into the bloodstream to different degrees (Yokel et al. 2006) and this aspect is considered in this assessment within section 2.3.3.1.

compounds are used to characterize total aluminum exposure, the risk characterization is limited to the three specific aluminum salts.

The search strategies employed in the identification of relevant data are presented in Appendix A. All original studies that form the basis for decision making have been critically evaluated and are described in the assessment. For issues relevant to the environmental and human health effects of aluminum, but outside the scope of the present assessment, the information is summarized briefly and the reader is referred to recent critical reviews published in the scientific literature for a more detailed discussion.

The human health components of the present document were prepared by the Safe Environments Programme- Quebec Region, in collaboration with the Existing Substances Division of the Safe Environments Programme (National Capital Region) and other Health Canada programs. The environmental components were prepared by the Existing Substances Division of the Science and Technology Branch. While external peer review comments were taken into consideration, the final content and outcome of the risk assessment remain the responsibility of Health Canada and Environment Canada.

The human health components of this assessment have been peer reviewed by the following external experts:

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2 SUMMARY OF INFORMATION CRITICAL TO ASSESSMENT OF "TOXIC" UNDER CEPA 1999

2.1 Identity and physical/chemical properties

Aluminum chloride is also known as aluminum trichloride, aluminum chloride (1:3) and trichloroaluminum (ATSDR 2006). It has the Chemical Abstracts Service (CAS) registry number 7446-70-0 and a chemical formula of $AlCl_3$. In its hydrated form, $AlCl_3 \cdot 6H_2O$, it is called hexahydrated aluminum chloride (CAS No. 7784-13-6). Trade names include Aluwets, Anhydrol and Drichlor.

Synonyms for aluminum nitrate include aluminum trinitrate and aluminum (III) nitrate (1:3). The CAS registry number is 13473-90-0 and the chemical formula is $Al(NO_3)_3$. The nonahydrate aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$ (CAS No. 7784-27-2), is the stable form of this compound.

Aluminum sulphate can also be identified as alum, alumsulphate (2:3), aluminum trisulphate, dialuminum sulphate and dialuminum trisulphate. The CAS registry number for aluminum sulphate is 10043-01-3 and the chemical formula is $Al_2(SO_4)_3$. Alum is often represented as $Al_2(SO_4)_3 \cdot 14H_2O$. It may be found in different hydrated forms. The commercial product, called cake alum or patent alum, is an octadecahydrate aluminum sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$.

In addition to these three compounds, aluminum polymers such as polyaluminum sulphate (PAS) and polyaluminum chloride (PAC) are used in water treatment. The general formula for PAS is $Al_a(OH)_b(SO_4)_c$, where $b + 2c = 3a$; for PAC, the general formula is $Al_a(OH)_bCl_c$, where b/a is usually about 2.5 (e.g., $Al_2(OH)_5Cl$). Mixed aluminum polymers may also be used; their general formula is $Al_a(OH)_bCl_c(SO_4)_d$, and b/a varies between 0.4 and 0.6.

Physicochemical properties of the three aluminum salts are presented in Table 2.1.

Table 2.1 Physicochemical properties of aluminum chloride, aluminum nitrate and aluminum sulphate [1]

Property	Aluminum chloride	Aluminum nitrate	Aluminum sulphate
CAS No.	7446-70-0	13473-90-0	10043-01-3
Molecular formula	$AlCl_3$	$Al(NO_3)_3$	$Al_2(SO_4)_3$
Molecular weight	133.34	213.00	342.14
Colour	White when pure, ordinarily gray or yellow to greenish	Colourless[2]	White, lustrous
Physical state	White hexagonal deliquescent or moisture sensitive plates	Rhombic crystals[2]	Crystals, pieces, granules or powder
Density (g/mL)	2.48	No data	1.61
Melting point (°C)	194 at 527 kPa	73[2]	Decomposes at 770
Boiling point (°C)	182.7 (1.00×10^5 Pa or 752 mm Hg; sublimation temperature)	Decomposes at 135°C[2]	No data, substance has no boiling point
Solubility in water (g/100 mL)	69.86 (15°C) (Reacts violently with water)	63.7 (25°C)	36.4 (20°C)
Solubility in other solvents	Soluble in benzene, carbon tetrachloride, chloroform	Very soluble in alcohol; slightly soluble in acetone almost insoluble in ethyl acetate, pyridine[2]	Insoluble in ethanol
pH	No data	Aqueous solution is acidic	No data
Vapour pressure (Pa)	100 (20°C)	No data	0 (20°C) substance has no vapour pressure

[1] Taken from Perry and Green (1984), Budaveri et al. (1989), Lewis (1992), European Commission (2000a,b) and ATSDR (2006)

[2] Refers to aluminum nitrate nonahydrate (CAS No. 7784-27-2)

2.2 Entry characterization

2.2.1 Production, import, export and use

Aluminum sulphate and aluminum chloride are produced in Canada, while aluminum nitrate is imported. Information on sources and emissions of aluminum salts or aluminum resulting from the use of aluminum salts was initially obtained through an industry survey carried out under the authority of section 16 of CEPA (CEPA 1988; Environment Canada 1997). Information regarding the use of aluminum chloride and aluminum sulphate in water treatment plants was obtained on a voluntary basis from Canadian municipalities with the help of provincial and territorial authorities. In 2007, additional research was conducted in order to review use patterns and quantities of aluminum derived from sources identified in the original assessment, as well as to identify and quantify potential new sources of aluminum to the environment resulting from the application of aluminum salts in Canada (Cheminfo Services Inc. 2008).

Table 2.2 provides estimated production, import, export and consumption values for the year 2006, based largely on input from Canadian aluminum salt producers. Unless otherwise stated, quantities reported in Table 2.2 and the accompanying text represent the amount of elemental aluminum present in the respective salts rather than the total amount of the salt. Polymeric forms of the chloride and sulphate are detailed separately, as these salts were found to be commonly used individually or in combination with other salts in water treatment processes. No producers or users of aluminum nitrate were identified for 2006 and, therefore, while it is likely that very small quantities were being imported into Canada in that year for a variety of low volume applications, no numerical data were available. Total Canadian consumption of aluminum as aluminum salts in 2006 was estimated at 16.1 kilotonnes, with aluminum sulphate accounting for approximately 80% of this demand, and PAC for the majority of the remainder (Cheminfo Services Inc. 2008). Approximately 80% of the total aluminum demand was for the treatment of drinking water and wastewater at municipalities. Industrial fresh water and wastewater treatment facilities accounted for the majority of the remaining demand in Canada.

Table 2.2 Estimated production, import, export and consumption of aluminum in the form of aluminum salts in Canada for 2006
(kilotonnes aluminum; Cheminfo Services Inc. 2008)[1]

	Aluminum Sulphate	**Aluminum Chloride**	**Other[2]**	**Total**
Production	11.9	0.1	4.6	16.6
Imports	0.6	0.2	1.0	1.8
Total supply	**12.5**	**0.3**	**5.6**	**18.4**
Demand				
Municipal Drinking Water Treatment Plants	4.3	0.1	2.4	6.8
Municipal Wastewater Treatment Plants	5.7	0.03	0.07	5.8
Industrial Fresh Water Treatment	0.3	0.03	0.67	1.0
Industrial Wastewater Treatment	0.5	0.03	0.44	0.9
Pulp and Paper Additive	1.1	0.01	0.16	1.3
Miscellaneous	0.1	0.1	0.1	0.3
Total Domestic Consumption	12.0	0.3	3.8	16.1
Exports	0.5	0.0	1.8	2.3
Total Disposition	**12.5**	**0.3**	**5.6**	**18.4**

[1] Quantities reported represent elemental aluminum present in the respective aluminum salts.

[2] This quantity represents the combined total of polyaluminum sulphate, polyaluminum chloride, aluminum chlorohydrate and sodium aluminate.

Five companies produced most of the aluminum salts used in Canada in 2006 (Cheminfo Services Inc. 2008). Imports and exports were roughly in balance, with imports representing approximately 10% of 2006 domestic consumption and exports representing approximately 14% of 2006 production. Alum, PAC and aluminum chlorohydrate (ACH) were the major imported aluminum salts, while PAC and alum were exported.

Total Canadian demand for aluminum salts remained relatively constant between 2000 and 2006 (Cheminfo Services Inc. 2008). Canada's salt producers indicate that the demand for alum and sodium aluminate declined during this period, while PAC, ACH and polyaluminum silicate sulphate (PASS) increased in use. While overall aluminum salts demand for municipal water treatment has increased slightly, use in the pulp and paper industry has dropped. The overall total amount of aluminum contained in the salts used in Canada has remained constant at close to 16 kilotonnes per year (Cheminfo Services Inc. 2008).

2.2.1.1 Aluminum chloride

Aluminum chloride is used in either anhydrous or hydrated form. In the anhydrous form, it is used as a catalyst, in Friedel-Crafts reactions, in the manufacture of rubber, the cracking of petroleum, and the manufacture of lubricants. In its hydrated form, it is used by the pharmaceutical industry as an active ingredient in deodorants and antiperspirants, as well as in wood preservation, and in the manufacture of adhesives, paint pigments, resins, fertilizers and astringents (Germain et al. 2000; Pichard 2005; Merck 2006). Polymeric forms, primarily polyaluminum chloride (PAC) and the more concentrated and highly charged aluminum chlorohydrate (ACH), are used as coagulants and flocculants in water treatment.

PAC has the highest Canadian production and use volumes of the three aluminum chloride salts. PAC demand increased over the period 2000 to 2006, with greatest quantities being used in the treatment of drinking water (Cheminfo Services Inc. 2008). Similar increased demand was evident in other applications, including industrial freshwater treatment, municipal and industrial wastewater treatment, and as a pulp and paper additive (Cheminfo Services Inc. 2008). Production and demand were substantially lower for both aluminum chloride and ACH. Canadian consumption of aluminum chloride remained stable from 2000 to 2006, while ACH demand increased substantially (Cheminfo Services Inc. 2008). Most of the increased demand was associated with increased applications in industrial wastewater treatment, with slower rates of growth in other applications.

2.2.1.2 Aluminum nitrate

Aluminum nitrate is used as a chemical reagent (catalyst), in the leather tanning industry, as an antiperspirant, as a corrosion inhibitor, and in the manufacture of abrasives, refractories, ceramics, electric insulation, catalysts, paper, candles, pots, artificial precious stones and heat-resistant fibres (Budaveri et al. 1989; Pichard 2005). It is also used as an adsorbent in chromatography for the production of filter membranes, in radiation protection dosimetry in the uranium extraction sector, and as a nitrating agent in the food industry (Merck 2006).

There are no known producers of aluminum nitrate in Canada, and only one user was identified in a survey done in 1997 by Environment Canada (1997). This user reported that less than 400 kg of aluminum nitrate was included in fertilizers for export to the United States.

It is likely that very small quantities of aluminum nitrate are being imported into Canada for a variety of low volume applications, including laboratory uses, leather manufacturing, manufacturing of fire works, and other minor applications (Cheminfo Services Inc. 2008).

2.2.1.3 Aluminum sulphate

In Canada, aluminum sulphate is used primarily as a coagulant and flocculant in water and wastewater treatment. There are other applications, however, in the leather industry, the paper industry, as a mordant in dyeing, in the fireproofing and waterproofing of textiles, in resin manufacture, and in the preparation of fertilizers and paint pigments (Germain et al. 2000; Pichard 2005; Merck 2006). The Canadian Fertilizers Product Forum advises that aluminum sulphate (alum) is used as a soil pH adjuster in the Lawn and Garden industry (2008 email from The Canadian Fertilizers Product Forum to J. Pasternak, Environment Canada; unreferenced). Aluminum sulphate can also be used to waterproof concrete, decolorize petroleum products, and as a formulant in antiperspirants and pesticides (Budaveri et al. 1989). Aluminum sulphate or alum is used in the treatment of eutrophic or mesotrophic lakes, to reduce the amount of nutrients present in the water. Both alum ($Al_2(SO_4)_3$) and sodium aluminate ($Na_2Al_2O_4$) are highly effective coagulants and flocculants that adsorb and precipitate soluble phosphorus and other compounds such as organic matter, forming clumps that settle to the bottom of the lake. In saturated solutions, aluminum sulphate is considered a mild corrosive and can be applied to ulcers in concentrations of 5% to 10% to prevent mucous secretion (Pichard 2005). The substance is also used as a food additive and some foods, such as baking powder.

It is estimated that approximately 276 kilotonnes of aluminum sulphate (11.9 kilotonnes on an aluminum basis) were produced in Canada in 2006, 15 kilotonnes (0.6 kilotonnes of aluminum) were imported and 12 kilotonnes (0.5 kilotonnes of aluminum) exported (Table 2.2). Municipal drinking water and wastewater treatment plants were the main users, comprising almost 84% of the total demand for that year. Industrial water treatment facilities and the pulp and paper sector accounted for most of the remaining consumption (15.8%).

2.2.2 Sources and releases

Aluminum sulphate minerals such as aluminite and alunite occur naturally in Canada in certain restricted geological environments. Aluminum chloride and aluminum nitrate do not occur naturally in the environment. Aluminum can be released from natural aluminum sulphate minerals; however, since aluminum is a common constituent of rocks, where it occurs dominantly in aluminosilicate minerals (e.g., kaolinite, boehmite, clay, gibbsite, feldspar, etc.), which weather and slowly release aluminum to the surface environment. Aluminum present in surface waters due to man-made applications cannot be distinguished from natural aluminum released during weathering of aluminum-bearing minerals.

While aluminum chloride, aluminum nitrate and aluminum sulphate have many commercial applications in Canada, releases of aluminum to the environment from most commercial applications are expected to be small. However there is potential for release of relatively large amounts of aluminum resulting from the use of aluminum chloride and aluminum sulphate in water treatment plants (industrial water, drinking water or wastewater).

In this application, aluminum will react rapidly, producing sludge, usually in the form of aluminum hydroxide ($Al(OH)_3$). Most sludge produced by municipal wastewater treatment plants (MWWTPs) or industries is sent to landfills or spread on land, with the remainder being composted, held in permanent lagoons, or incinerated prior to landfilling (Germain et al. 2000). Most provinces control DWTP waste flows through their respective systems of permits and/or approvals. Sludge purged from clarifiers or accumulated in sedimentation basins of drinking water treatment plants (DWTPs) cannot be released directly to the aquatic environment in many provinces. It may be sent to sewers, incinerated with wastewater sludge and landfilled, held in permanent lagoons, spread on land or landfilled. Likewise, backwash waters (used to clean filters) cannot be discharged directly into open water bodies in many provinces where these discharges are often subjected to requirements for pretreatment (e.g., diversion to sedimentation ponds) or diversion to MWWTPs. While many provinces do not generally allow direct discharge to surface water of any DWTP effluents containing sludges or backwash waters (e.g., Alberta, Manitoba, Ontario and New Brunswick), some of their existing plants may continue to discharge effluents directly to surface waters. Communication with provincial agencies indicates that these provinces are generally requiring some type of environmental impact assessments of the subject discharges with consideration of alternatives to direct discharge. Some existing large plants in these provinces have recently removed their DWTP direct discharges from surface water (e.g., Britannia DWTP and Lemieux Island DWTP in Ottawa, ON), or are developing plans for alternatives to direct discharge to surface waters (e.g., certain plants in Alberta). In other provinces, direct discharge may be allowed through provincial approvals systems if it is shown that the discharge results in no adverse effects (defined based on varying criteria) on the receiving body of water (e.g., Saskatchewan, Nova Scotia and Newfoundland). It should be noted that some provinces and territories either do not have any coagulant usage for drinking water treatment, or they only use very small amounts and have requirements for DWTP effluent treatment destined for surface water (e.g., Prince Edward Island, Yukon Territory, Northwest Territories and Nunavut Territory) (Environment Canada unpublished 2008a)

While most aluminum is released in particulate form, a certain proportion occurs as the dissolved metal and it is this form that is considered easily absorbed and therefore bioavailable to aquatic organisms. The following section therefore discusses aluminum releases in general, with additional emphasis given to dissolved forms. This approach was necessary because very few studies examine monomeric aluminum levels in the environment or in anthropogenic releases.

2.2.2.1 Natural Sources

Atmospheric deposition of aluminum on land or water is small compared with internal releases by weathering and erosion of rock, soil and sediment (Driscoll et al. 1994). Weathering and erosion of "alum"-containing rocks will release aluminum into soils and streams, in part as Al^{3+} and other dissolved cationic and anionic species, depending on pH and the availability of complexing ions (Garrett 1998). These releases will be small, however, in relation to releases from weathering and erosion of aluminosilicate minerals.

There are no reliable estimates of the quantities of aluminum released to the environment by natural processes on a global scale, most of which comes from natural aluminosilicate minerals. Quantification of total or dissolved aluminum releases in Canada and elsewhere is very difficult and can provide only a rough estimate. Using Garrels et al.'s (1975) proposed global stream flux of 2.05 g/m^2 per year, total aluminum releases (including particulate material) were estimated to be approximately 20.45 million tonnes per year for Canada. Studies of weathering flux in selected Canadian and U.S. catchments (e.g., Likens et al. 1977; Kirkwood and Nesbitt 1991) yield similar or somewhat lower estimates (2 to 20 million tonnes per year) when extrapolated to the whole of Canada.

2.2.2.2 Anthropogenic sources

Very limited information is available on historical releases of the three aluminum salts. Accidental releases are reported to Environment Canada's National Analysis of Trends in Emergencies System (NATES) database and, more recently, the National Enforcement Management Information System and Intelligence System (NEMISIS). Between 1974 and 1991, 24 events released 316.2 tonnes of aluminum sulphate, mainly to land, and approximately 80% of the spilled material was recovered. Four accidental releases of aluminum chloride occurred in 1986 and 1987, and the product was not recovered on two occasions, resulting in a total release of 18.18 tonnes (Environment Canada 1995). Six spills involving the three aluminum salts subject to this assessment were reported from 1992 to 2008, all for aluminum sulphate. Approximately 40,000 liters of aluminum sulphate were released during these events, to both land and surface water, with no identified recovery of the spilled material. None of the reported incidents related to municipal or industrial effluent discharges (Environment Canada 2008b).

Municipal drinking water and wastewater treatment plants are the main users of aluminum sulphate, aluminum chloride and other aluminum-based polymeric products. Aluminum salts are used as coagulants and flocculants to cause fine materials that are suspended, soluble or both to agglomerate, for subsequent removal via sedimentation and filtration. As part of this agglomeration or coagulation process, most of the aluminum associated with the added aluminum salt hydrolyses to aluminum hydroxide, which precipitates and becomes part of the floc structure. As such, it makes up a part of the sludge generated by the treatment process. A small amount of the aluminum added may stay with the finished water in either colloidal particulate ($Al(OH)_3$) or soluble form (e.g., $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, $Al(OH)_4^-$), dictated by the conditions of the treatment process and in particular, the pH (see Figure 2.1 below and from Stumm and Morgan 1981).

While no comprehensive inventory of releases of aluminum associated with commercial use of aluminum salts exists, order-of-magnitude estimates derived from information provided by Canadian producers and users confirm that most releases are associated with wastewater treatment processes (approximately 43% in 2006), with drinking water treatment plants accounting for the majority of the remainder (about 36%; Table 2.3; Cheminfo Services Inc. 2008). All other sources are relatively minor. Again, most quantities are reported in terms of the elemental aluminum present in the respective salts. Approximately three quarters of the releases are to land, including: landfill, application on farms, and permanent lagoons. It is estimated that 5% of the aluminum used at pulp and paper mills for paper sizing is released to water courses (rivers or lakes), while 95% is contained on the paper, which is assumed to receive eventual disposal to landfills and composting in a minor, but growing proportion (2008 email from Canadian Wastewater Association to J. Pasternak, Environment Canada; unreferenced).

Table 2.3 Estimated total releases in Canada of aluminum from aluminum salts[1] for 2006, by application
(kilotonnes aluminum; Cheminfo Services Inc. 2008)

	Drinking Water	**Receiving Water**	**Storage in Lagoon**	**Landfill**	**Farms**	**Total**
	Water	Water	Land	Land	Land	
Municipal Drinking Water Treatment Plants[2]	0.1	3.2	0.1	2.2		5.7
Municipal Wastewater Treatment Plants[3]		0.4	0.06	2.0	4.5	6.9
Industrial Fresh Water Treatment	0.02	0.5	0.02	0.4		1.0
Industrial Wastewater Treatment		0.06	0.01	0.3	0.6	0.9
Pulp and Paper Additive		0.1		1.2		1.2
Miscellaneous				0.2		0.2
Total	0.12	4.3	0.2	6.3	5.1	16.0
Percent of Total						
Municipal Drinking Water Treatment Plants	1%	20%	1%	14%		36%
Municipal Wastewater Treatment Plants		3%	0.4%	12%	28%	43%
Industrial Fresh Water Treatment	0.1%	3%	0.1%	2%		6%
Industrial Wastewater Treatment		0.3%	0.05%	2%	4%	6%
Pulp and Paper Additive		0.4%		7%		8%
Miscellaneous				2%		2%
Total	1%	27%	1%	39%	32%	100%

[1] Includes aluminum sulphate, aluminum chloride, polyaluminum sulphate, polyaluminum chloride, aluminum chlorohydrate and sodium aluminate.

[2] This excludes aluminum that is contained in effluents sent to wastewater treatment plants

[3] This includes aluminum that is contained in effluents obtained from drinking water treatment plants

Most of the aluminum releases are from the use of aluminum sulphate, which is the aluminum salt having the highest quantity of consumption in Canada (Table 2.4; Cheminfo Services Inc. 2008).

Table 2.4 Estimated total releases of aluminum, by salt, for 2006 (kilotonnes aluminum; Cheminfo Services Inc. 2008)

	Drinking Water	Receiving Water	Storage in Lagoon	Landfill	Farms	Total
Aluminum Sulphate	0.1	3.6	0.2	5.0	3.1	12.0
Polyaluminum Chloride	0.02	0.7	0.03	0.9	0.6	2.3
Aluminum Chlorohydrate	0.01	0.1	0.01	0.2	0.1	0.5
Polyaluminum Sulphate	0.003	0.1	0.005	0.1	0.1	0.3
Sodium Aluminate	0.01	0.2	0.01	0.3	0.2	0.7
Aluminum Chloride	0.004	0.1	0.00	0.1	0.1	0.3
Total	0.2	4.8	0.2	6.6	4.2	16.0

Approximately 2% of the total aluminum used by municipalities for drinking water treatment (6.8 kilotonnes; see Table 2.2) ends up in drinking water (Table 2.3; Cheminfo Services Inc. 2008). A survey of 102 Canadian water treatment facilities conducted in 2006 found that over 80% of drinking water treatment plants (DWTPs) that use aluminum salts as coagulants and flocculants measure the concentration of aluminum in the treated water. The survey considered data from municipal drinking water and wastewater treatment facilities across Canada, primarily from larger municipalities (population > 100,000), although a small sample of small-to-medium sized municipalities was included (population range 20,000-100,000; Cheminfo Services Inc. 2008). Outlet concentrations in drinking water at the surveyed DWTPs which used aluminum ranged from 0.005 to 0.2 mg/L, with an average value of 0.067 mg/L. For comparison, Health Canada's *Guidelines for Canadian Drinking Water Quality* are 0.1 mg/L for conventional treatment plants using aluminum-based coagulants and 0.2 mg/L for other treatment systems using aluminum-based coagulants (Health Canada 2007a).

Less than half of the aluminum used at drinking water plants is released to receiving waters – mostly as solid aluminum hydroxide sludge (Cheminfo Services Inc. 2008). Notable examples of this practice occur in water treatment plants in Toronto. Most of the remaining aluminum is contained in sludge that is sent to landfill. Some of the sludge from drinking water facilities (commonly called "filter backwash solids"), in dilute form, may also be sent to wastewater treatment facilities in the municipality. Results from the 2006 survey suggest that approximately 16% of the aluminum used at drinking water treatment facilities is contained in sludge sent to nearby wastewater treatment facilities. A very small portion (~2%) remains permanently stored in lagoons, which for assessment purposes has been assumed to be a land destination. The 2006 survey did not identify any sludge from drinking water treatment plants going to farms; however, it is possible that some disposal by this method may be occurring in Canada as a small proportion of DWTP sludge was identified for landfarming in the earlier survey conducted for 1995 and 1996 (Germain et al. 2000).

In a study done with sludge from Calgary and Edmonton, AEC (1987) found that less than 0.02% of aluminum bound with sludge (containing 78,187 mg Al/kg dw) was released in water (i.e., 0.20 to 0.32 mg/L). Srinivasan et al. (1998) studied the speciation of aluminum at six different stages of water treatment at Calgary's DWTP. Total aluminum concentrations ranged from 0.038 to 5.760 mg/L, and dissolved inorganic aluminum concentrations varied from 0.002 to 0.013 mg/L. George et al. (1991) measured monomeric aluminum concentrations of less than 0.06 mg/L in alum sludge from ten different DWTPs containing up to a total of 2,900 mg Al/L; Calgary's DWTP was one of the plants studied.

Calgary's DWTP reported the aluminum content in backwash water following the cleaning of its filters. Dissolved aluminum levels ranged from 0.07 to 0.44 mg/L, and total aluminum concentrations varied from 0.76 to 3.3 mg/L. The backwash waters from this DWTP were not released to the river but were treated and sold as fertilizer (Do 1999).

Most of the aluminum discharged from municipal wastewater treatment plants (MWWTPs) surveyed in the 2006 study is associated with sludge. Approximately two thirds of the aluminum in MWWTP sludge is applied to farmland, with most of the balance (around 30%) being sent to landfill. About 5% of total aluminum releases are to surface waters and a very small proportion (less than 1%) is stored permanently in lagoons (Table 2.3). In Quebec City, the sludge from the drinking water treatment plant is directed to MWWTP where the resulting sludge is dried and incinerated with residential waste (co-incineration). The mineral and non-combustible component of the sludge is then landfilled (2008 email from Canadian Wastewater Association to J. Pasternak, Environment Canada; unreferenced). In most cases, the sludge sent to landfills was first sent for anaerobic digestion (where methane gas is generated from the organic content and used for plant energy) and the remaining solids concentrated to remove excess water. Some provinces (e.g., Alberta, Ontario and Quebec) have guidelines for the disposal of sewage sludge on agricultural land; spreading on agricultural land is permitted only when the pH is greater than 6.0 or when liming and fertilization (if necessary) are done. Although not a common practice, a few of the municipalities participating in the 2006 survey provided measured concentrations for aluminum present in sludge solids from their plants. In general, these values were in the range of 10 to 60 mg per gram of solids (dry basis) (Cheminfo Services Inc. 2008).

Final effluent concentrations of aluminum were not always available for MWWTPs participating in the 2006 survey (Cheminfo Services Inc. 2008). Where data were available, reported concentrations ranged from 0.013 to 1.200 mg/L, with an average value (weighted by water volume treated) of 0.816 mg/L. The form of the aluminum measured was not specified. Many of the MWWTPs surveyed relied on substances other than aluminum to treat wastewater, such as iron salts (ferrous and ferric chloride) and/or polyacrylamides, while others did not use any chemicals in their water treatment process.

Only two respondents to the 2006 survey provided information on aluminum concentrations in receiving waters in the vicinity of their effluent outfalls. The typical background level of dissolved aluminum in Lake Ontario in the vicinity of Toronto was reported to be approximately 0.010 mg/L, while typical concentrations in the North Saskatchewan River near Edmonton were 0.020 to 0.040 mg/L (Cheminfo Services Inc. 2008). These data are insufficient to determine in a useful way the contribution of aluminum from aluminum salt consumption in receiving waters. In the original State of the Science (SOS) report (Environment Canada and Health Canada 2000), it was determined that while extensive data on total aluminum concentrations in Canadian surface water are available, few data exist in areas close to sites where releases occur. The situation for sediment and soil is similar, in that data exist for the Canadian environment in general, but not for areas where releases occur. The state of available relevant concentration data has not changed since 2000.

In addition, changes in policies and procedures relating to the direct release of treatment plant effluents into surface waters have occurred since the publication of the original SOS report. In 1993, a total aluminum concentration of 36 mg/L was measured just downstream of the Regional Municipality of Ottawa-Carleton's (RMOC) DWTP discharge pipe, while the concentration 200 m downstream of the plant was 0.5 mg/L (Germain et al. 2000). Similarly, in 1998, sediment concentrations in the Ottawa River were 125,160, 51,428 and 41,331 mg/kg dw at points closest to, 300 m, and 500 m downstream of the DWTP, respectively, and were significantly elevated compared with control and upstream values of 17,543 and 20,603 mg/kg dw, respectively. In 2008, all wastes from the plant were diverted to a nearby MWWTP, effectively eliminating the direct discharge of aluminum-bearing sludge into the river (Environment Canada 2008c). However, it will likely take some time before conditions in bottom sediment in the vicinity of the DWTP outfall return to those in line with non-impacted areas.

Germain et al. (2000) reported mean total aluminum levels in the effluent of some MWWTPs using aluminum salts. Concentrations varied from 0.03 to 0.84 mg/L, and the maximum value reported by one plant reached 1.8 mg/L. These figures are in the same order of magnitude as those reported by Orr et al. (1992) for 10 Ontario MWWTPs and by MEF and Environnement Canada (1998) for 15 Quebec MWWTPs, and agree well with those of Cheminfo Services Inc. (2008) reported above. Some plants do not use aluminum-based coagulants and flocculants but still reported aluminum levels in their effluents; their mean total aluminum levels ranged from 0.003 to 0.90 mg/L (Germain et al. 2000). Many wastewater treatment plants, such as those in Quebec, receive influents from combined sewers which collect both wastewater and stormwater. In these cases, part of the solids content of the influent will come from urban drainage that could contain aluminum-bearing solids from erosion processes and other sources. The content of wastewater treatment plant influents is determined by the nature and proportions of their primary inputs (i.e., residential, commercial, institutional, industrial) and contaminants present in these waters may also appear in the effluent, depending on the treatment process (2008 email from Canadian Wastewater Association to J. Pasternak, Environment Canada; unreferenced).

Federal, provincial/territorial and municipal governments all play a role in managing treated drinking water quality in Canada (Cheminfo Services Inc. 2008). Voluntary guidelines have been established for aluminum concentrations in drinking water, and while provincial/territorial and municipal government authorities recognize these guidelines, they have not been adopted as mandatory standards. For example, in British Columbia, Alberta, Newfoundland and Manitoba, the *Guidelines for Canadian Drinking Water Quality - Technical Documents: Aluminum* as specified by Health Canada (i.e., 0.1 mg/L for conventional treatment plants using aluminum-based coagulants and 0.2 mg/L for other treatment systems using aluminum-based coagulants) are recognized, but specific standards have not yet been fully incorporated into operating permits for treatment facilities. In Ontario, Certificates of Approval with a limit of 0.1 mg/L are issued to drinking water treatment plants; however, this limit is included as a guideline rather than a standard. In Quebec, no limits on aluminum content in drinking water are found in the provincial regulations (including the

Regulation Respecting the Quality of Drinking Water), and operating approvals are not required by wastewater treatment facilities (Cheminfo Services Inc. 2008).

Similarly, no federal legislation specific to municipal wastewater effluent discharges is in place (Cheminfo Services Inc. 2008). The federal government enforces CEPA (1999) that governs the releases of toxic substances to the environment, and the *Fisheries Act* that protects Canadian waters against the deposit of deleterious substances into fish habitat. In recent years, federal, provincial, and territorial governments have been working to develop a *Canada-wide Strategy for the Management of Municipal Wastewater Effluent* through the Canadian Council of Ministers of the Environment (CCME 2008); however, release standards for aluminum are not currently proposed or under development under the Strategy.

Less information is available on industrial releases of aluminum salts. The pulp and paper sector is the primary industrial user of aluminum salts, with applications in water treatment and as a paper additive. Alum is more commonly used for water treatment at mills in the warmer months of the year, while polyaluminum chloride (PAC) and polyaluminum silicate sulphate (PASS) have been found to be more effective winter coagulants. Recent quantitative release data for industrial uses are not available, although average concentrations of residual aluminum in treated water are estimated to be in the range of 0.02 mg/L (Cheminfo Services Inc. 2008). A 35% to 40% decrease in use of aluminum salts as a pulp and paper additive has been reported for the period 2000 to 2006, indicating a significant reduction in demand for this application (Cheminfo Services Inc. 2008).

Germain et al. (2000) reported mean total aluminum levels ranging from 0.46 to 4.8 mg/L in wastewaters released into rivers by the pulp and paper industry over the period 1990 to 1997. Mean total aluminum levels measured for other types of industries ranged from 0.01 to 2.3 mg/L. Since 1995, pulp and paper mills have been subject to the *Pulp and Paper Effluent Regulations* passed in 1992 under the *Fisheries Act*. In Quebec, for example, implementation of these regulations has led to a mean reduction of approximately 60% in total aluminum concentrations present in effluents (Germain et al. 2000). Environmental Effects Monitoring (EEM) reports published by the pulp and paper industry provide information on the distance from point of discharge that is required to dilute an effluent to less than 1% in the receiving water body. In some cases, only a few metres were needed, while in others, up to 300 km was required. In these cases, water input from other watercourses was needed to achieve dilution to 1%.

Sludge containing aluminum from the salts used in industrial water treatment can be sent to landfill or to steam boilers and co-generation units that handle bark, sludge, or other fuels (Cheminfo Services Inc. 2008). Aluminum may be present in the fly ash after burning of the sludge, although a small portion may also be emitted to air along with particulate matter (PM) emissions. No data are available on aluminum concentrations in fly ash; however, potential PM emissions are usually controlled with baghouses, electrostatic precipitators or other PM control systems.

The use of sludge derived from aluminum-based water treatment facilities as a soil amendment is the primary pathway by which aluminum salts enter the terrestrial environment. It is likely that the amount of aluminum added to soil through this practice is small in comparison with aluminum naturally present in soil. Sludge disposal guidelines specifying maximum application rates and soil pH requirements exist for a number of provinces. In Ontario, sludge application rates cannot exceed 8 tonnes solids/ha/5 years and the pH of the receiving soil must be greater than 6.0 or liming is required (ME and MAFRA 1996). Still, potential exists for the release of aluminum into soil due to high amounts of the metal present in sludge residuals (Mortula et al. 2007). In addition, a shift in soil pH at the site of sludge application could mobilize aluminum in the sludge by shifting the chemical equilibrium towards more soluble forms of the metal. Soil acidification may occur during high water discharge events (e.g., storm events), when water entering the sludge deposition area has interacted with organic matter or travelled through more acidic upper mineral soils (Pellerin et al. 2002). Aluminum solubilized in this process is then available to be transported to adjacent soils or water bodies along shallow flow paths in the soil.

2.3 Exposure Characterization

2.3.1 Environmental Fate

The sections below summarize the information available on the distribution and fate of aluminum and the three aluminum salts, aluminum chloride, aluminum nitrate and aluminum sulphate, in the environment. A more detailed discussion on environmental fate can be found in Bélanger et al. (1999), Germain et al. (2000) and Roy (1999a).

2.3.1.1 Air

In air, hydrated aluminum chloride will react with moisture to produce hydrochloric acid and aluminum oxide (Vasiloff 1991). Aluminum nitrate and aluminum sulphate are likely to react in the same way, forming nitric and sulfuric acids, respectively. As the three aluminum salts that are the subject of this assessment are not usually emitted to air, the amount of aluminum present in air due to these salts is expected to be negligible compared with amounts coming from the natural erosion of soil (Environment Canada and Health Canada 2000).

2.3.1.2 Water

Natural sources of aluminum release to aquatic systems include weathering of rocks, glacial deposits and soils and their derivative minerals, and atmospheric deposition of dust particles. The most obvious increases in aluminum concentrations have consistently been associated with environmental acidification (Driscoll and Schecher 1988; Nelson and Campbell 1991). For this reason, recently observed changes in global climate and alterations in the acidity of atmospheric and oceanic systems, both resulting at least in part from human activities, have the potential to influence the presence and mobility of aluminum in the environment (Pidwirny and Gow 2002; Crane et al. 2005). The relationship is complex, however, and more research is needed in order to elicit the nature of potential impacts and their consequences for biota. Crane et al. (2005) postulated that increasingly severe weather patterns occurring as a consequence of global climate change, such as an increased incidence of prolonged heavy rainfall in some areas, may intensify physical and chemical weathering processes. When combined with the effects of acidification of waters, this could lead to significant changes in the speciation and mobility of aluminum and other metals.

Soil minerals such as gibbsite ($Al(OH)_3$) and jurbanite ($AlSO_4(OH)\bullet5H_2O$) are considered the primary sources of aluminum release to the aqueous environment, especially in poorly buffered watersheds (Driscoll and Schecher 1990; Campbell et al. 1992; Kram et al. 1995). In more buffered watersheds, a solid-phase humic sorbent in soil is involved in the release of aluminum (Cronan et al. 1986; Bertsch 1990; Cronan and Schofield 1990; Cronan et al. 1990; Seip et al. 1990; Taugbol and Seip 1994; Lee et al. 1995; Rustad and Cronan 1995).

The three aluminum salts—chloride, nitrate and sulphate—are highly soluble and will form various dissolved species on contact with water. The fate and behaviour of aluminum in the aquatic environment are very complex. Aluminum speciation, which refers to the partitioning of aluminum among different physical and chemical forms, and aluminum solubility are affected by a wide variety of environmental parameters, including pH, solution temperature, dissolved organic carbon (DOC) content, and the presence and concentrations of numerous ligands. Metals in solution may be present as dissolved complexes, as "free" or aquo ions, in association with particles, as colloids or as solids in the process of precipitating. Colloidal particles (i.e., those in the range of 0.001 to 1 µm) are important in the transport of metals in stream ecosystems (Kimball et al. 1995; Schemel et al. 2000), as well as the accumulation of metals in sediment (Church et al. 1997) and biofilm (Besser et al. 2001), and the transfer to biota. Farag et al. (2007) proposed that colloids and biofilm may play critical roles in the pathway of metals to the food chain. The reactivity of aluminum, as well as geochemical behaviour, bioavailability and toxicity, are dependent upon its speciation (Neville et al. 1988; Gagnon and Turcotte 2007).

There are two general types of ligands that can form strong complexes with aluminum in solution. Inorganic ligands include anions such as sulphate (SO_4^{2-}), fluoride (F^-), phosphate (PO_4^{3-}), bicarbonate (HCO_3^-) and hydroxide (OH^-), among others. Organic ligands include oxalic, humic and fulvic acids (Driscoll et al. 1980; Sparling and Lowe 1996). The relative concentrations of the inorganic and organic ligands generally determine the proportions and type of complexes that are formed in solution.

Interactions with pH (Campbell and Stokes 1985; Hutchinson and Sprague 1987; Schindler 1988; Driscoll and Postek 1996) and DOC (Hutchinson and Sprague 1987; Kullberg et al. 1993) are of primary importance to the fate and behaviour of aluminum. DOC will complex with aluminum in water, forming aluminum-organic complexes and reducing concentrations of monomeric forms of aluminum (Farag et al. 1993; Parent et al. 1996). At a pH of 4.5, a concentration of 1 mg DOC/L can complex approximately 0.025 mg Al/L, with this complexing capacity increasing as pH increases (Neville et al. 1988). Fractions of dissolved organic aluminum were estimated for various rivers in Canada using the MINEQL+ (Schecher and McAvoy 1994) and WHAM (Tipping 1994) models; the results suggested that the importance of complexation with dissolved organic material (DOM) decreased over the pH range 7.0 to 8.5, likely due to reduced concentrations of the Al^{3+} and $AlOH^{2+}$ species which can associate with DOM (Fortin and Campbell 1999).

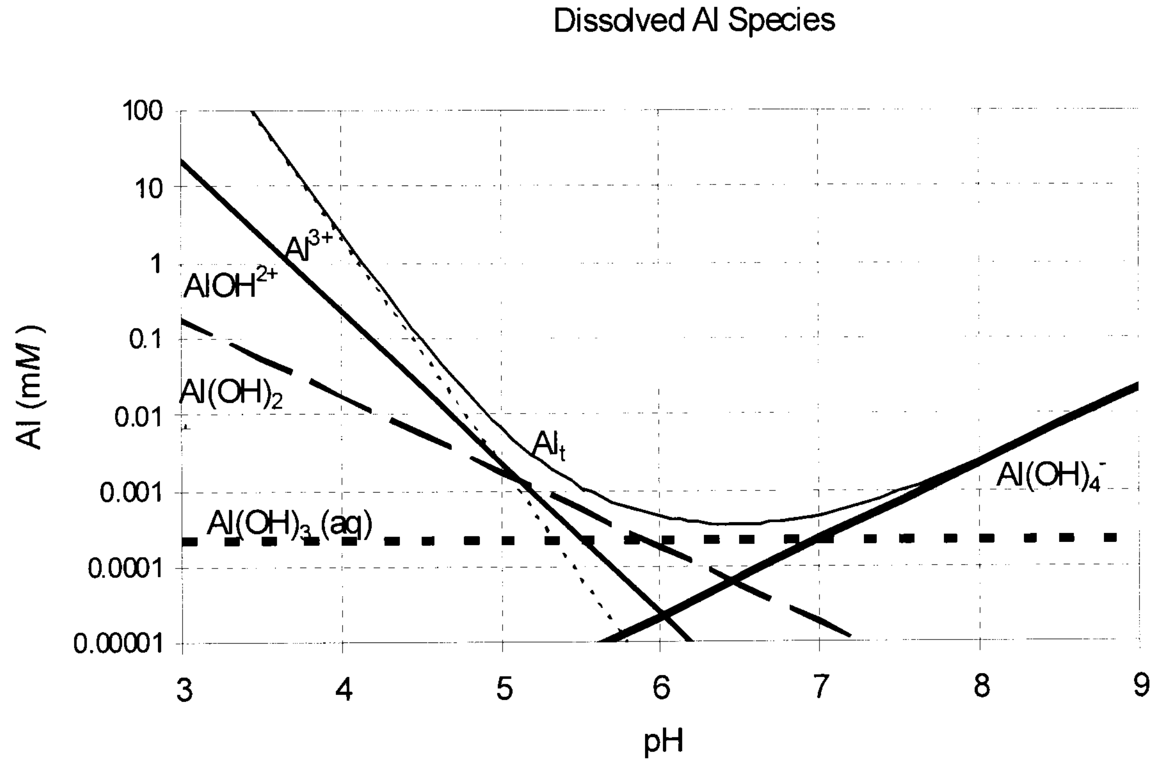
Aluminum is a strongly hydrolysing metal and is relatively insoluble in the neutral pH range (6.0–8.0) (Figure 2.1). In the presence of complexing ligands and under acidic ($pH < 6$) and alkaline ($pH > 8$) conditions, aluminum solubility is enhanced. At low pH values, dissolved aluminum is present mainly in the aquo form (Al^{3+}). Hydrolysis occurs as pH rises, resulting in a series of less soluble hydroxide complexes (e.g., $Al(OH)^{2+}$, $Al(OH)_2^+$). Aluminum solubility is at a minimum near pH 6.5 at 20°C and then increases as the anion, $Al(OH)_4^-$, begins to form at higher pH (Driscoll and Schecher 1990; Witters et al. 1996). Thus, at 20°C and $pH < 5.7$, aluminum is present primarily in the forms Al^{3+} and $Al(OH)^{2+}$. In the pH range 5.7 to 6.7, aluminum hydroxide species dominate, including $Al(OH)^{2+}$ and $Al(OH)_2^+$, and then $Al(OH)_3$. Typically, at a pH of approximately 6.5, $Al(OH)_3$ predominates over all the other species. In this range, aluminum solubility is low, and availability to aquatic biota should also be low. At $pH > 6.7$, $Al(OH)_4^-$ becomes the dominant species. Aluminum-hydroxide complexes predominate over aluminum-fluoride complexes under alkaline conditions. However, the aluminum speciation determined for some rivers in Canada indicated that only one river, of pH less than 7, had a significant concentration (> 1%) of aluminum-fluoride complexes (Fortin and Campbell 1999). It is important to note that the various aluminum species described above are always present simultaneously at any pH value. The influence of pH in aquatic systems is mainly to change the proportion of all the species as the pH changes (2008 email from Canadian Wastewater Association to J. Pasternak, Environment Canada; unreferenced).

Mononuclear aluminum hydrolytic products combine to form polynuclear species in solution (Bertsch and Parker 1996). Aluminum begins to polymerize when the pH of an acidic solution increases to over 4.5:

$$2Al(OH)(H_2O)_5^{2+} \rightleftharpoons Al_2(OH)_2(H_2O)_8^{4+} + 2H_2O$$

Polymerization gradually proceeds to larger structures, eventually leading to the formation of the Al_{13} polycation (Parker and Bertsch 1992a, 1992b). In nature, conditions that favour the formation of polynuclear forms of aluminum can occur during the liming of acidic aluminum-rich watersheds (Weatherley et al. 1991; Lacroix 1992; Rosseland et al. 1992) and possibly during the addition of alum to circumneutral waters (Neville et al. 1988; LaZerte et al. 1997).

Figure 2.1 Solubility of aluminum species (and total aluminum, Al_t) in relation to pH in a system in equilibrium with microcrystalline gibbsite
(0.001 mM = 0.027 mg/L; Driscoll and Schecher 1990)



Temperature has been shown to influence the solubility, hydrolysis and molecular weight distribution of aqueous aluminum species as well as the pH of solutions. Lydersen et al. (1990b) reported a higher degree of aluminum hydrolysis and greater polymerization to high molecular weight species in inorganic aluminum solutions stored for one month at 25°C compared with those stored for an equivalent period at 2°C. The researchers hypothesized that more advanced polymerization evident at the higher temperature resulted in more deprotonation and condensation reactions, possibly accounting for the observed lower pH of the 25°C test solutions (range 4.83 to 5.07 versus 5.64 to 5.78 in the solutions at 2°C). Solubility and sedimentation were significantly higher at 25°C, with dissolution controlled by microcrystalline gibbsite. While substantial amounts of high molecular weight aluminum species were present in the solution at 2°C, little sedimentation was observed. Dissolution at the lower temperature appeared controlled by an amorphous $Al(OH)_3(s)$ with much higher solubility and, therefore, a high proportion of the high molecular weight inorganic aluminum species remained as colloids in the solution. The effects of low temperature on the coagulation efficiency of aluminum sulphate have been studied in relation to water treatment processes (Braul et al. 2001; Wobma et al. 2001; Kundert et al. 2004). The results provide further evidence that temperature-dependent fluctuations in the predominant aluminum species present in an aquatic system may occur in regions of Canada that experience marked seasonal fluctuations in temperature.

When released into water, for example within a drinking water treatment plant (DWTP), most of the aluminum associated with the aluminum salts considered in this report hydrolyses to form aluminum hydroxides (Hossain and Bache 1991). Reactions between aluminum salts, water and associated "impurities" result in the formation of a floc, which separates from the water phase to form alum sludge. A small fraction of the aluminum can stay in the water in either colloidal or dissolved form. Barnes (1985) describes the different reactions involved in the formation of aluminum hydroxide in aqueous solution; the overall reaction can be represented by the following equation:

$$Al_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Al(OH)_3^0 + 3H_2SO_4$$

The aluminum hydroxide present in sludge is expected to remain mostly solid following release into surface water. Ramamoorthy (1988) showed that less than 0.2% of the aluminum hydroxide present in sludge was released in supernatant water at a pH of 6 and less than 0.0013% was released at pH 7.65. In both cases, aluminum hydroxide was present mostly in particulate form. At these pH values, aluminum solubility is low and kinetics favour the formation of solid aluminum hydroxide.

When used to treat sewage water, alum will also react with phosphate, as shown in the following reaction (Romano 1971; Barnes 1985):

$$Al_2(SO_4)_3 + 2PO_4^{3-} \rightleftharpoons AlPO_4(s) + 3SO_4^{2-}$$

This process has been used for many years to treat phosphorus in wastewaters, as well as to reduce phosphorus levels in runoff from land fertilized with poultry litter and restore phosphorus-enriched eutrophic lakes (Lewandowski et al. 2003).

Kopáček et al. (2001) examined the possible role of aluminum in influencing the natural cycling of phosphorus, which is often a limiting nutrient in aquatic systems. The researchers postulated that aluminum from nearby lower pH soils may enter circumneutral water bodies during episodic acidification events, such as spring melt, leading to the formation of colloidal aluminum oxyhydroxide flocs which will strongly adsorb orthophosphate in the water column. The phosphate-bound particulate aluminum settles onto the lake bottom, removing the bioavailability of this phosphorus to organisms in the water column. The increasing sediment concentrations of aluminum-phosphorus floc disrupt the redox-dependent cycling of phosphorus in the lake, indicating that while aluminum does not enter directly into biotic cycles, it is capable of influencing the biogeochemical cycles of substances that are integral to living systems. Based on the solubility characteristics of aluminum (see Figure 2.1), this process may also occur when acidic waters, which generally contain the most aluminum (Gensemer and Playle 1999), enter downstream waters of higher pH.

The cycling and availability of other trace elements (e.g., nitrogen) and of organic carbon may also be influenced by the adsorption and coagulation properties of aluminum (Driscoll and Schecher 1990; Lee and Westerhoff 2006). Dissolved organic carbon (DOC) has been shown to provide an important weak acid/base buffering system that aids in the regulation of pH in dilute acidic waters and removal of DOC by adsorption to aluminum could adversely affect pH conditions in a water body (Johannessen 1980; Driscoll and Bisogni 1984). As well, coagulation and removal of DOC and other light attenuating materials may alter patterns of water column heating, resulting in decreased thermal stability in a water body (Almer et al. 1974; Malley et al. 1982). Changes to the heating pattern and thermal stratification of a lake can profoundly impact ecosystems by altering the vertical transport of solutes and restricting coldwater fisheries (Driscoll and Schecher 1990).

Aluminum is highly reactive in seawater and will be rapidly scavenged by particulate matter when released into this medium (Nozaki 1997). The mean oceanic residence time for aluminum is predicted to be short compared to some other elements, in the range of 100 to 200 years, with vertical distribution dictated by terrestrial and atmospheric inputs at the surface, intense particle scavenging throughout the water column, and some regeneration in bottom waters (Orians and Bruland 1985). The higher ionic strength and relative magnitude of individual ion concentrations in saline waters compared with freshwaters lead to differences in coagulation reactions with aluminum salts. Duan et al. (2002) identified distinctly different characteristics between the two water types with respect to colloid destabilization, coagulation mechanisms, and colloidal removal. These differences can become important when water treatment processes include release of effluent or backwash materials into marine or brackish waters.

2.3.1.3 Sediment

Sediment, where metals are generally considered less biologically available, is nonetheless an important medium for aluminum (Stumm and Morgan 1981; Campbell et al. 1988; Tessier and Campbell 1990). Aluminum occurs naturally in aluminosilicates, mainly as silt and clay particles, and can be bound to organic matter (fulvic and humic acids) in sediments (Stumm and Morgan 1981). At pH > 5.0, dissolved organic matter (DOM) can co-precipitate with aluminum, thereby controlling its concentrations in lakes with elevated concentrations of DOM (Urban et al. 1990). DOM plays a similar role in peatlands (Bendell-Young and Pick 1995). At pH < 5.0, the cycling of aluminum in lakes is controlled by the solubility of mineral phases such as microcrystalline gibbsite (Urban et al. 1990). Lakes receiving drainage from acidified watersheds can act as a sink for aluminum (Troutman and Peters 1982; Dillon et al. 1988; Dave 1992).

Experimental acidification of lakes and limnocorrals has shown that aqueous aluminum concentrations rapidly increase in response to acidification (Schindler et al. 1980; Santschi et al. 1986; Brezonick et al. 1990). Mass-balance studies have demonstrated that retention of aluminum by sediments decreases as pH decreases (Dillon et al. 1988; Nilsson 1988). Under such conditions, sediments in acidified watersheds can provide a source of aluminum to the water column (Nriagu and Wong 1986). Based on calculation of fluxes in acidic lakes, Wong et al. (1989) suggested that sediment is a source of aluminum to the overlying water column.

The release of aluminum hydroxide sludge from drinking water treatment plants (DWTPs) directly to surface waters is the primary pathway by which aluminum from aluminum salts enters sediment. If water velocity is low at the point of discharge, much of the released sludge will settle onto the surface of local sediment. Since, in Canada, the waters receiving such discharges are typically circumneutral, the solubility of aluminum in the sludge will generally be minimal (Environment Canada and Health Canada 2000).

2.3.1.4 Soil

Atmospheric deposition of aluminum to soil is attributed mostly to the deposition of dust particles and is generally low (Driscoll et al. 1994). Volcanic activity can also act as a major natural source of aluminum to soil (Pichard 2005). Aluminum is the third most abundant element in the earth's crust, making up approximately 8% of rocks and minerals and accounting for about 1% of the total mass of the Earth (Landry and Mercier 1992; Skinner and Porter 1989). Approximately 75% of Canada is covered by glacial till (Landry and Mercier 1992); examples of aluminum-bearing minerals inherited from glacial till (i.e., primary minerals) are feldspars, micas, amphiboles and pyroxenes. Transformation of primary minerals by chemical weathering reactions results in new solid phases (i.e., secondary minerals). Aluminum-bearing secondary minerals such as smectite, vermiculite and chlorite are often found in Canadian soils developed on glacial till.

Inputs of aluminum into soil solutions usually occur by mobilization of aluminum derived from the chemical weathering of soil minerals. The most important reaction in the chemical weathering of the common silicate minerals is hydrolysis. However, aluminum is not very soluble over the normal soil pH range; thus, it generally remains near its site of release to form clay minerals or precipitate as amorphous or crystalline oxides, hydroxides or hydrous oxides. Silica is much more soluble than aluminum at normal soil pH and is always in excess of the amount used to form most clay minerals, so that some is removed from the soil system in leachates (Birkeland 1984). In some parts of the world, the extent of chemical transformation by chelation is believed to exceed that by hydrolysis alone. In forest soils of cold and humid regions, such as those of eastern Canada, aluminum is believed to be transported from upper to lower mineral soil horizons by organic acids leached from foliage and the slow decomposition of organic matter in the forest floor (Courchesne and Hendershot 1997). The movement of aluminum-organic complexes stops when the soil solution becomes saturated (or when the aluminum-to-organic-carbon ratio reaches a critical value), thereby reducing their solubility. In pristine conditions, aluminum is normally retained within the B horizon of the soil. A third important reaction involving aluminum is the transformation of one mineral into another through the exchange of interlayer cations (Sposito 1996).

Although the dissolution and precipitation reactions of aluminum-bearing minerals are often good indicators of the solubility of aluminum in soils, they are by no means the only pedogenic processes controlling the concentrations of aluminum in soil solutions. Many other processes may partly control the uptake of aluminum by plants and soil organisms. Aluminum may be 1) adsorbed on cation exchange sites, 2) incorporated into soil organic matter, 3) absorbed by vegetation or 4) leached out of the soil system (Ritchie 1995). Aluminum can form stable complexes with various types of soluble and insoluble organic matter, from simple low-molecular weight organic acids to humic and fulvic acids (Vance et al. 1996; Ritchie 1995). Organic ligands play an important role in the speciation of aluminum in soil solutions (David and Driscoll 1984; Driscoll et al. 1985; Ares 1986).

In eastern Canada, the atmospheric deposition of strong acids, such as nitric acid and sulfuric acid, has accelerated the natural acidification of soil. The increased H^+ activity (lower pH) in the soil solution creates a new equilibrium where more Al^{3+} is dissolved in the soil solution, cation nutrients (Ca^{2+}, Mg^{2+} and K^+) are replaced on the soil exchange complex by Al^{3+} and the base cations are eventually leached out of the soil.

There may be significant variation in Al^{3+} solubility with depth in a soil profile (Hendershot et al. 1995). In the surface horizons, the soil solutions tend to be undersaturated with respect to aluminum-bearing minerals; in the lower B and C horizons, aluminum in soil solutions can be expected to be near equilibrium with some aluminum solids. Although the equilibrium concentration is close to that which would be expected if gibbsite were controlling equilibrium, gibbsite has generally not been identified in Canadian soils. Other forms of aluminum, for example, hydroxy interlayered vermiculite, may control aluminum solubility at values close to those of gibbsite. Amorphous aluminum complexed with organic matter may also have a similar pH solubility curve that is a function of the pH-dependent variation in the number of binding sites.

Fluoride and hydroxide complexes are the two strongest groups of inorganic ion associations with aluminum in soil solutions (Nordstrom and May 1995). In very acidic soils, aluminum in the soil solution is present mainly as free Al^{3+}; as pH increases, free Al^{3+} hydrolyses to form complexes with OH^- ions (e.g., $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$). Near pH 6.5, aluminum solubility is at a minimum, but it increases at neutral to alkaline conditions because of the formation of $Al(OH)_4^-$ (Driscoll and Postek 1996). According to Lindsay et al. (1989), fluorine, the most electronegative and one of the most reactive elements, is released as fluoride ion through the dissolution of fluoride-bearing minerals. In acidic soils ($pH < 5.5$), low-ligand-number complexes such as AlF^{2+} are normally formed. In neutral to alkaline conditions, it is more difficult for F^- to compete with OH^- for aluminum in the soil solution because of the increased level of OH^- and probably the presence of calcium that tends to link with fluoride (CaF_2). Consequently, aluminum-hydroxide complexes predominate over aluminum-fluoride complexes in alkaline conditions.

The complexation of aluminum with sulphate is weaker than that with fluoride. However, in acidic soils where the sulphate concentration is high, aluminum may also form aluminum-sulphate complexes (Driscoll and Postek 1996). At low sulphate concentrations, $AlSO_4^+$ is the dominant aqueous form, whereas $Al(SO_4)_2^-$ is predominant in soil solutions with higher sulphate concentrations. Brown and Driscoll (1992) showed that several aluminosilicate complexes, including $AlSiO(OH)_3^{2+}$, are present in various regions of the eastern U.S. and Canada.

It has been shown that most dissolved aluminum in soil solution of the forest floor is organically bound and that these aluminum-organic complexes become less abundant with increasing soil depth (Nilsson and Bergkvist 1983; David and Driscoll 1984; Driscoll et al. 1985). In the Adirondacks of New York, David and Driscoll (1984) found that 82% and 93% of the total dissolved aluminum in the organic horizons of conifer and hardwood stands, respectively, were organically complexed. The proportion of organic to inorganic aluminum decreased at both sites from the organic to the upper mineral horizons and from the upper to the lower mineral horizons. In the soil solutions of the mineral horizons, aluminum-organic complexes accounted for 67% and 58% of the total aluminum in the conifer and hardwood sites, respectively, which indicates the importance of aluminum-organic complexes in humus-rich forest soils of eastern North America.

2.3.1.5 Biota

In general terms, a substance is considered to be bioavailable if, under the conditions of exposure, it can be taken up by organisms (Environment Canada 1996). The bioavailability of a substance is determined by its chemical form, the physical and chemical characteristics of the media (e.g., water, soil, food) in which it occurs, the receptor species, and the route of the exposure (e.g., dermal contact, ingestion, inhalation). For metals such as aluminum, the "free" or hydrated dissolved ions (i.e., Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^{+}$) are normally considered to be the principal bioavailable forms (Newman and Jagoe 1994). However, there is evidence that some other forms of a metal, such as organometallic compounds (e.g., of mercury and tin), oxyanions of the metal (e.g., CrO_4^{2-}, AsO_4^{3-}), and dissolved organic and inorganic metal complexes (e.g., colloidal and polynuclear aluminum complexes) can also be taken up by organisms (Parker and Bertsch 1992b; Benson et al. 1994; Campbell 1995).

Bioavailability directly influences the potential for bioconcentration, bioaccumulation and biomagnification of a substance in organisms. ICMM (2007) defines bioconcentration as the increase in concentration of a substance in an organism (or specified tissues thereof) relative to the concentration of the substance in the environmental medium (generally water) to which it is exposed, bioaccumulation as the amount of a substance taken up by an organism from water (bioconcentration) as well as through ingestion via the diet and inhalation, and biomagnification as the process by which the tissue concentration of a bioaccumulated substance increases as it passes up the food chain through at least two levels (Parametrix 1995). The three processes are significant indicators of the propensity of a substance to impart toxicity to individual organisms and at higher trophic levels in the food chain. However, bioaccumulation of essential elements (such as some metals) in organisms is typically subject to metabolic regulation (ICMM 2007).

Bioconcentration factors (BCFs) and bioaccumulation factors (BAFs) are unitless values derived by dividing steady state tissue concentrations of a substance by the steady state environmental concentration (ICMM 2007). For synthetic organic compounds, the use of a BCF and BAF threshold value (such as that of 5000 specified in the CEPA 1999 *Persistence and Bioaccumulation Regulations*; Canada 2000) provides valuable information for the evaluation of hazard and risk. Bioaccumulation is more complex for naturally occurring inorganic substances such as metals, however, as processes such as adaptation and acclimation can modulate both accumulation and potential toxic impact (ICMM 2007). All biota will naturally accumulate metals to some degree without deleterious effect and as some metals are essential elements, bioaccumulation does not necessarily indicate the potential for adverse effects (McGreer et al. 2003). While metal bioaccumulation is homeostatically regulated for metals essential to biological function (Adams et al. 2000), non-essential metals may also be regulated to some degree as these homeostatic mechanisms are not metal-specific (ICMM 2007).

Thus, interpretation of the toxicological significance of bioaccumulation data for metals such as aluminum is complex. A more complete discussion of aluminum bioavailability and the implications for bioaccumulation and toxicity can be found in Roy (1999a) and Bélanger et al. (1999).

Few studies have examined the uptake and accumulation of aluminum by algae. While the algal bioassays conducted by Parent and Campbell (1994) were not specifically designed to determine the effect of pH on aluminum bioaccumulation, their data indicated that the accumulation of aluminum by *Chlorella pyrenoidosa* increased with the concentration of inorganic monomeric aluminum. In addition, the comparison of assays performed at the same concentration of aluminum but at different pH values showed that aluminum accumulation was suppressed at low pH (Parent and Campbell 1994). Aquatic invertebrates can also accumulate substantial quantities of aluminum, yet there is evidence that most of the metal is adsorbed to external surfaces and is not internalized (Havas 1985; Frick and Hermann 1990). Using the results of Havas (1985), the bioconcentration factor (BCF) for *Daphnia magna* varied from 10,000 at pH 6.5 down to 0 at pH 4.5. Similar results, i.e., decreasing accumulation of aluminum with decreasing pH, were reported for crayfish (Malley et al. 1988), caddisfly (Otto and Svensson 1983), unionoid clams (Servos et al. 1985) and a chironomid (Young and Harvey 1991). Other studies with clams and benthic insects showed no relationship between water pH and tissue accumulation (Sadler and Lynam 1985; Servos et al. 1985). Frick and Herrmann (1990) found that the largest portion (70%) of the aluminum was present in the exuvia of the mayfly, *Heptagenia sulphurea*, indicating that the metal was largely adsorbed and was not incorporated into the organism.

BCFs for fish were calculated to range from 400 to 1,365 based on results presented in Roy (1999a). Numerous field and laboratory studies have demonstrated that fish accumulate aluminum in and on the gill. It has been suggested that the rate of transfer of aluminum into the body of fish is either slow or negligible under natural environmental conditions (Spry and Wiener 1991). The initial uptake of aluminum by fish essentially takes place not on the gill surface but mainly on the gill mucous layer (Wilkinson and Campbell 1993). Fish may rapidly eliminate mucus and the bound aluminum following the exposure episode. For example, Wilkinson and Campbell (1993) and Lacroix et al. (1993) found that depuration of aluminum from the gills of Atlantic salmon (*Salmo salar*) was extremely rapid once fish were transferred into clean water. The authors suggested that the rapid loss is due to expulsion of aluminum bound to mucus.

Far fewer studies have examined aluminum accumulation in benthic organisms. However, chironomids do not appear to accumulate aluminum to the same degree as other aquatic invertebrates. Krantzberg (1989) reported that the concentration of aluminum in chironomids was < 0.3 nmol/g dw for the entire body and < 0.1 nmol/g dw for the internal structures. Most aluminum is either adsorbed externally or is associated with the gut contents of chironomids (Krantzberg and Stokes 1988; Bendell-Young et al. 1994).

BCFs for terrestrial plants were calculated based on data cited in the review by Bélanger et al. (1999). For both hardwood and coniferous species, the calculated BCF ranged from 5 to 1,300 for foliage and from 20 to 79,600 for roots in studies done with aluminum solutions. For those conducted with soil, BCFs were lower for both foliage (0.03–1.3) and roots (325–3,526). BCFs calculated for grain and forage crops ranged from 4 to 1,260 in foliage and from 200 to 6,000 in roots for experiments done with solutions. For soil experiments, the foliar BCF varied from 0.07 to 0.7.

2.3.2 Environmental concentrations

To determine aluminum concentrations in various environmental media in Canada, the most recent available data in Canada were used where possible, although data from other countries were examined as well. Concentrations in environmental media to be used as input into the human exposure assessment (i.e., air, drinking water, soil, and food) are estimated based on total aluminum. Although other sources of aluminum are also presented (e.g., consumer products) to provide an overview of aluminum exposures, they are not used to estimate general population exposure (see section 3.2.1). Bioavailability of aluminum in different media in relation to absorption in humans is considered separately in section 2.3.3. Data presented below are also relevant to the assessment of ecotoxicological effects.

2.3.2.1 Air

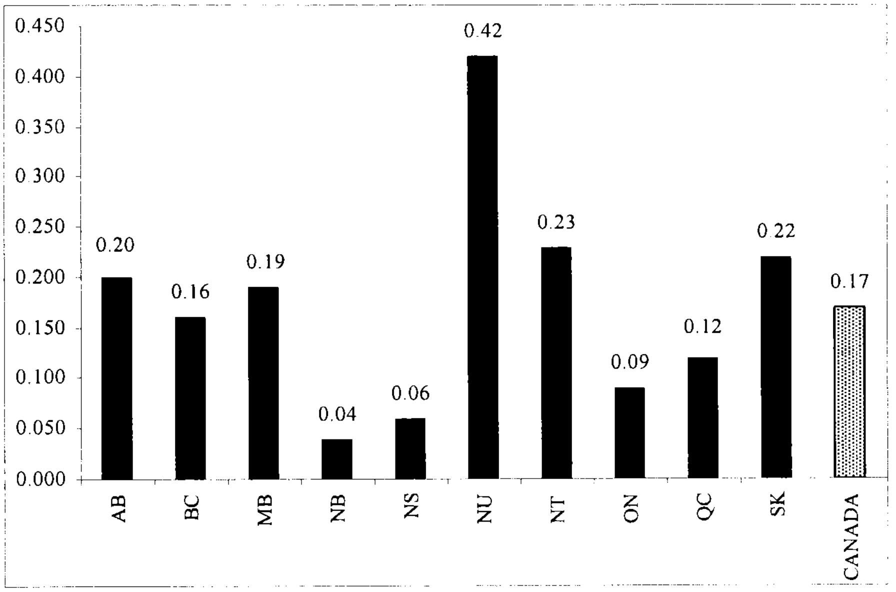
2.3.2.1.1 Ambient air

Ambient air at more than 40 Canadian sites, primarily in urban areas, was sampled over a period of ten years (1996–2006). More than 10,000 samples were measured at different sites throughout Canada, although the number varied from year to year. In 2006, only 25 sites were measured, resulting in 1,400 samples, 96% of which had levels greater than the detection limit (approximately 0.001 $\mu g/m^3$).

Total aluminum concentrations measured in individual samples of PM_{10} (i.e., particulate matter smaller than 10 µm in diameter) ranged from the detection limit to 24.94 $\mu g/m^3$, with the lowest concentration being measured in Saint John, New Brunswick and the highest in Vancouver, British Columbia (Dann 2007).

Figure 2.2 shows estimated mean aluminum concentrations measured in ambient air for all sampling sites by province for the ten-year period. On the basis of these measurements from across Canada, the estimated provincial/territorial mean aluminum concentration in PM_{10} is 0.17 $\mu g/m^3$. This value was used for the purpose of assessing exposure of the Canadian population to aluminum in ambient air.

Figure 2.2 Mean aluminum concentrations in PM_{10} in outdoor air from provinces and territories across Canada (μg/m^3) (1996–2006)



For most of the Canadian sites where PM_{10} measurements were carried out, data were also available for $PM_{2.5}$ particles (i.e., smaller than 2.5 μm in diameter). Close to 20,000 measurements were available from 1998 to 2006, 77% of which had levels greater than the detection limit. Using all available data, the mean aluminum concentration in $PM_{2.5}$ in Canada is approximately 0.069 μg/m^3, with a maximum aluminum concentration of 9.24 μg/m^3 measured in Vancouver, British Columbia (Dann 2007).

No published data were available on aluminum levels in ambient air in the vicinity of aluminum smelters or other industries in Canada, and limited data from other countries were identified. In an industrial area of the province of Turin in Italy, levels of 1.12 and 0.4 μg/m^3 of aluminum were measured during industrial activity and during holidays, respectively, (Polizzi et al. 2007). According to JECFA (2007), the concentration of aluminum in ambient air of industrial areas may range from 25 to 2,500 μg/m^3. It should be noted that the three aluminum salts—chloride, nitrate and sulphate—are unlikely to have contributed significantly to total concentrations measured in ambient air, as their use does not generally result in air emissions of aluminum.

2.3.2.1.2 Indoor air

Few data on aluminum concentrations in indoor air in residential dwellings were identified for Canada. Studies in the U.S. did provide data on aluminum in indoor air. These findings are summarized below.

In 1990, a Particle Total Exposure Assessment Methodology (PTEAM) study was conducted in Riverside, California, in which samples were collected from 178 non-smokers over ten years of age. In addition to the personal sampling (portable sampler), stationary samplers were set up inside the residential dwellings and outside near the entrance door.

Airborne particle (PM_{10} and $PM_{2.5}$) samples were collected for two 12-hour periods (nighttime and daytime), and more than 2,900 samples were analyzed (Clayton et al. 1993; Thomas et al. 1993). In this study, the aluminum concentrations exceeded the reporting limit of 0.5 $\mu g/m^3$ in more than half of the personal PM_{10} samples taken during the two periods. In the case of $PM_{2.5}$, only 20% of the measurements exceeded the reporting limit. Estimated daytime median concentrations of aluminum for the PM_{10} indoor, outdoor and personal exposure monitors were 1.9, 2.5 and 3.4 $\mu g/m^3$, respectively; the corresponding nighttime median concentrations were 0.99, 1.7 and 1.0 $\mu g/m^3$. Based on the average daytime and nighttime concentrations of aluminum in PM_{10} particles, the estimated mean concentration of aluminum in indoor air was about 1.49 $\mu g/m^3$.

For the purpose of assessing exposure for the general Canadian population, this estimated mean concentration of aluminum in PM_{10} particles of 1.49 $\mu g/m^3$ was considered to represent the typical indoor air concentration of aluminum in Canada. As in the case of ambient air, the three aluminum salts—chloride, nitrate and sulphate—are unlikely to have contributed significantly to total aluminum concentrations measured in indoor air.

2.3.2.2 Water

2.3.2.2.1 Surface water

Aluminum is a naturally occurring element and is present in all water bodies in Canada and elsewhere. Aluminum can be analysed under different forms, but historically results were reported mostly as total aluminum because of the low cost and ease of analysis. In many cases, results are also available for extractable or dissolved aluminum. Total aluminum represents all the aluminum present in a water sample, including the particulate fraction. Extractable aluminum includes both the "dissolved" fraction and weakly bound or sorbed aluminum on particles, and "dissolved" aluminum represents the fraction present in a sample filtered through a 0.45 μm membrane. All the bioavailable aluminum is considered to be present in this fraction, but not all the dissolved aluminum is bioavailable. Colloidal aluminum (0.01 to 0.1 μm) and organic aluminum (aluminum bound with soluble organic ligands) that are included in this fraction are generally thought to be less bioavailable than truly dissolved forms of the metal (Roy 1999a).

At reference lake and river sites across Canada that have not been influenced by effluents from facilities using aluminum salts, mean total aluminum concentrations ranged from 0.05 to 0.47 mg/L, with a maximum value of 10.4 mg/L, measured in British Columbia. Mean extractable aluminum concentrations ranged from 0.004 to 0.18 mg/L, with a maximum value of 0.52 mg/L found in a lake in the Abitibi region of Quebec. Mean dissolved aluminum concentrations varied from 0.01 to 0.08 mg/L and the highest dissolved aluminum value reported was 0.9 mg/L in British Columbia (Germain et al. 2000).

Aluminum was measured in water taken both upstream and downstream of facilities using aluminum salts and releasing aluminum or aluminum salts, but sampling stations were typically not located close enough to sources to allow the local impact of the effluents to be assessed. Mean total aluminum levels generally varied from 0.002 to 2.15 mg/L, with a maximum value of 28.7 mg/L, measured in the Oldman River, 40 km downstream of Lethbridge, Alberta. Total aluminum levels are usually higher in the Prairies, in rivers with high total particulate matter content. Mean extractable aluminum concentrations ranged from 0.03 to 0.62 mg/L, and the maximum value of 7.23 mg/L was reached in the Red Deer River, at Drumheller, Alberta. Mean dissolved aluminum concentrations were much lower, ranging from 0.01 to 0.06 mg/L. In surface water, the maximum dissolved aluminum concentration (0.24 mg/L) was measured in the Peace River, Alberta (Germain et al. 2000). Concentrations in downstream locations were not consistently elevated in relation to concentrations in upstream locations, suggesting that the impacts of releases of aluminum salts are mostly local.

Although information on the forms of dissolved aluminum present at these monitoring locations was not identified, results of equilibrium modelling suggest that most dissolved aluminum in waters with pH values of 8.0 and higher is in inorganic monomeric forms (Fortin and Campbell 1999). For the 12 Prairie locations where dissolved and total aluminum levels were reported, pH levels were 8.0 or higher, and dissolved aluminum represented less than 3% of total aluminum (Roy 1999b). The overall average concentration of dissolved aluminum at these sites was 0.022 mg/L, similar to levels of inorganic monomeric aluminum reported in comparatively pristine Adirondack surface waters (pH from ~5.8 to ~7.2), where most values were around 0.027 mg/L (Driscoll and Schecher 1990).

Empirical data indicating an increase in aluminum levels in ambient water receiving inputs of aluminum salts were available for only a few locations. A total aluminum concentration of 36 mg/L was attained just downstream of the discharge pipe of a Regional Municipality of Ottawa-Carleton's (RMOC) DWTP in water samples taken following a rountine release of backwash in 1993; samples taken 200 m downstream of the discharge pipe showed a total aluminum level of 0.5 mg/L In 1994, the total aluminum level reached 11.3 mg/L just downstream of the discharge. In 2008, all wastes previously destined for the Ottawa River from RMOC DWTPs were diverted completely to the local sewage treatment plant for treatment prior to discharge (Wier, pers. comm. 2008). In the Kaministiquia River, the increase in mean total aluminum noted from upstream to downstream stations corresponds approximately to the inputs from the pulp and paper mill located in Thunder Bay, Ontario. The mean difference of 0.071 mg/L observed in total aluminum concentrations for samples taken on the same day at both stations for the period 1990–1996 is equivalent to the predicted aluminum increase of 0.069 mg/L calculated with the aluminum releases reported by the mill (Germain et al. 2000). For the Ottawa and Kaministiquia rivers, estimated dissolved monomeric aluminum levels were 0.027 mg/L and 0.040 mg/L, respectively. These values were obtained using the MINEQL+ model and estimated concentrations in effluents, assuming solubility controlled by microcrystalline gibbsite (Fortin and Campbell 1999). Using boehmite as the controlling phase provides lower dissolved inorganic aluminum levels (0.005 mg/L and 0.007 mg/L, respectively).

The Quebec Environment Ministry, now Ministère du Développement Durable, de l'Environnement et des Parcs, and Environment Canada examined the toxic potential of effluents generated by 15 municipal wastewater treatment plants in Quebec (Ministère de l'Environnement du Québec and Environment Canada 2001). The plants were considered to represent treatment methods used most commonly in Quebec and serviced over 50% of the province's population. Whole effluent sampling was conducted twice a year, during summer and winter operating conditions, over the period 1996 to 1999. Total aluminum concentrations in the effluents ranged from below the detection limit (0.002 to 0.1 mg/L) to 3.57 mg/L in summer and up to 4.25 mg/L under winter operating conditions. Concentrations remained at or below 1 mg/L year-round in all but two of the plants; however, 20 out of 45 summer readings and 25 out of 39 winter readings exceeded the maximum interim water quality guideline of 0.156 mg/L for the protection of freshwater life (water pH equal to or greater than 6.4) as recommended by CCME (2003). The study concluded that ammonia nitrogen and surfactants were mainly responsible for the observed effluent toxicity, with pesticides possibly a factor during summer months; however, the presence of aluminum in the effluents at levels above background may also have contributed to some extent. The results suggest that periodic episodes of aluminum toxicity are possible in some receiving waters; however, the nature of the collected data makes concluding on potential risk to the environment difficult. The study was designed to evaluate the toxic potential of whole effluents and did not include consideration of factors such as dilution effects, interactions between constituents in the effluents, and natural background levels of aluminum in the receiving environments. Therefore, while effluent concentrations may have exceeded the recommended water quality guideline, it is uncertain whether these guidelines were also exceeded in the surface waters receiving these effluents. In addition, it is likely that a large fraction of the total aluminum present in the effluents was associated with particulates that would settle out of the water column upon release into surface waters (Germain et al. 2000). This would substantially reduce the potential for adverse impacts to pelagic organisms, although negative impacts to benthic organisms could still occur. These impacts could relate directly to aluminum toxicity or be associated with physical aspects such as blanketing effects and/or the presence of other toxic contaminants.

Agencies such as the Greater Vancouver Regional District (GVRD; now Metro Vancouver) routinely monitor wastewater products generated at municipal treatment plants, in order to evaluate effluent quality and ensure compliance with provincial regulations such as the Environmental Management Act. Wastewater monitoring in the GVRD is conducted by the Greater Vancouver Sewerage & Drainage District (GVS&DD) and includes determination of total and dissolved aluminum concentrations in wastewater treatment plant influents and effluents, as well as estimates for influent and effluent loading of aluminum. Monthly data summaries are provided on the GVRD website and these are compiled annually into a Quality Control Report (http://www.metrovancouver.org/services/wastewater/treatment /Pages/montoring.aspx). For 2006, the latest report available on the website, influent concentrations measured at the five wastewater treatment plants operating in the GVRD ranged from 0.47 to 2.74 mg/L and 0.04 to 0.25 mg/L for total and dissolved aluminum, respectively (GVRD 2006), while effluent values were 0.05 to 0.97 mg/L and 0.02 to 0.16 mg/L. While influent concentrations of total aluminum were generally comparable between primary and secondary wastewater treatment plants, mean total aluminum concentrations were higher in primary treatment effluents as compared with those from plants using secondary treatment, likely reflecting greater removal of particulate aluminum from the water phase during the coagulation and flocculation process of secondary treatment. In general, influent concentrations of both total and dissolved aluminum were comparable between the two types of wastewater treatment. However, estimated loading rates varied widely between the plants and annually within each plant, with influents ranging from 7.8 to 1,380 kg/d total and 1.0 to 98 kg/d dissolved aluminum, and effluent rates 0.9 to 943 kg/d and 0.2 to 59 kg/d for total and dissolved aluminum, respectively. An analysis of total aluminum concentrations in treatment plant effluents from 1997 to 2006 indicated that levels had remained generally stable around 0.1 to 1.0 mg/L or decreased steadily during this period. A marked reduction in total aluminum was observed at two plants following the implementation of secondary treatment in 1998 and 1999, confirming the efficacy of this process in removing particulate aluminum from water.

2.3.2.2.2 Drinking water

Many drinking water treatment plants in Canada using surface water supplies add aluminum salts (aluminum sulphate, aluminum chloride or polymer forms) as a coagulant/flocculent to eliminate organic compounds, micro-organisms and suspended particulate matter. Treatment with aluminum salts may not necessarily increase the total aluminum concentration in finished drinking water, as the aluminum associated with suspended solids is removed. However, aluminum salt addition does appear to increase the concentration of low-molecular-weight, dissolved aluminum species, which may potentially present a higher bioavailability (Health Canada 1998b). More information on the bioavailability of aluminum from drinking water can be found in section 2.3.3.1.1.

For most provinces and territories, data on concentrations of aluminum in drinking water were obtained directly from municipalities that use aluminum salts in drinking water treatment (Health Canada 2007b). Data were also obtained from monitoring programs carried out in five provinces and territories from 1990 to 1998 (Environment Canada and Health Canada 2000). Over 10,000 drinking water samples from approximately 1,200 sites across Canada were analyzed over the past 20 years. The majority of the data analyzed was collected over ten years, in some cases up to 2007 (Health Canada 2007c).

In drinking water treatment systems in Canada that have surface water sources and use aluminum salts, the mean total aluminum concentration was estimated at 101 µg/L.[2] Mean concentrations for the different provinces (see Figure 2.3) varied from 20.0 µg/L in New Brunswick (between 1995 and 2007) to 174 µg/L in Alberta (between 1990 and 2002).

In addition to the analysis of alum-treated drinking water, more than 2,800 samples of drinking water derived from groundwater sources from various Canadian municipalities were analyzed. Aluminum salts are not used in treatment of groundwater, except in the case of certain sites in the Northwest Territories. New Brunswick private wells had the highest mean total aluminum concentrations at approximately 40.0 µg/L, whereas Ontario had the lowest concentrations of about 10.0 µg/L. On the basis of all the data from about 30 drinking water treatment systems in Canada, the mean aluminum concentration is estimated to be 25.2 µg/L in groundwater sources, which is four times lower than that estimated for surface water treated with alum.

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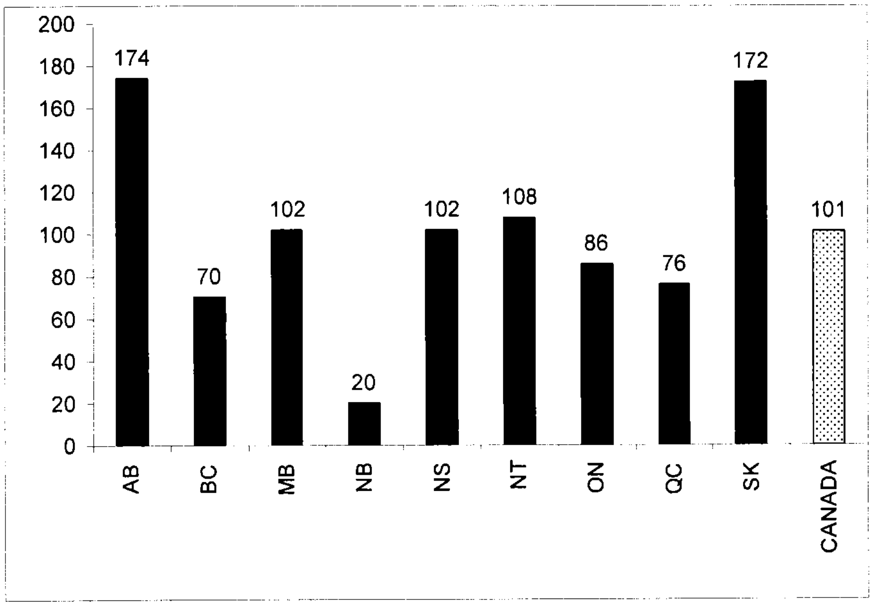
[2] An arithmetic mean was made with all available data per province or territory which provided total aluminum concentrations from water treatment systems that have surface water sources and use aluminum salts. Then an average of these values from the nine provinces/territories was calculated to represent the Canadian average (101 µg/L).

The average value of 101 μg/L, associated with the various aluminum salt-treated water supplies was used for the purpose of assessing exposure of the Canadian population to aluminum in drinking water.

Figure 2.3 Mean total aluminum concentrations in aluminum-treated drinking water from provinces and territories across Canada (μg/L) (1990–2007)



2.3.2.3 Sediment

Based on limited data, total aluminum levels in Canadian sediments are of the same order of magnitude as those measured in soils (see Section 2.3.2.4), with levels varying between 0.9% and 12.8%. The highest levels were found in Lake St. Louis, Quebec. Of particular interest are aluminum levels measured in sediment of the Ottawa River less than 300 m downstream of a location where backwash water (from the Britannia DWTP)_ had been discharged for approximately 27 years (Environment Canada 2008c). In 1989, the mean total aluminum content of sediment collected from a control site situated 100 m off the treatment plant effluent plume was 17,543 mg/kg dw, while the value closest to the outfall was 125,160 mg/kg dw (Germain et al. 2000). Mean concentrations measured 300 m and 500 m downstream of the plant discharge point were 51,428 and 41,331 mg/kg dw, respectively, still elevated compared with the control site and that of an upstream location (mean concentration 20,603 mg/kg dw). In a follow-up study conducted in 2000 (City of Ottawa 2002), sampling confirmed that concentrations of aluminum were highest in riverbed sediment located at the discharge outlet of the Britannia DWTP (approximate mean of 150,000 mg/kg dw), then declined over 500 m to approximately 12,000 mg/kg dw. This concentration was not appreciably higher than the sampling location 150 m upstream from the discharge outlet (10,000 mg/kg). The aluminum concentration then increased to approximately 61,000 mg/kg at the 1,500 m sampling site indicating that this was likely a far-field zone of deposition. Waste discharges of aluminum-bearing sludge from Ottawa DWTPs previously destined for the Ottawa River have been diverted in 2008 to the local WWTP for treatment (Environment Canada 2008c).

2.3.2.4 Soil

Aluminum is the third most abundant element in the earth's crust, after oxygen and silicon, occurring as aluminosilicates and other minerals. The data on soil aluminum concentrations presented below come from soil surveys covering various geographic areas, and generally represent naturally-occurring aluminum concentrations.

In Canada, soil sampling has been carried out since the 1930s, but analysis for aluminum has only occurred in the past 20 years. Data for more than 40 studies based on over 40,000 soil samples across Canada from the past 20 years are thus available and were used to estimate the average total aluminum concentration in soil. Two studies cover all of Canada, while others focus on specific regions such as the Prairies, a province, or a municipality, in connection with local industries, types of soil, soil horizons, soil groups, or land use. In addition, some Canadian data on aluminum in dust from inside residential dwellings were available for consideration. More detailed information describing the available soil concentration data may be found in the supporting documentation for this assessment (Health Canada 2008a).

The estimated exposure to the Canadian population is based on data representing surface soil horizons, or in the first few decimetres, and not on data measured in the C horizon (primary environment; Reimann and Garrett 2005). The surficial concentrations of natural elements are, nonetheless, directly related to their concentration in the primary environment.

Some researchers have maintained that background concentrations[3] should not be expressed as an absolute value but rather a range of values varying by sampling location and scale (Choinière and Beaumier 1997; Reimann and Garrett 2005). For the purposes of the present assessment, however, the concentration of aluminum in surface soil has been based on the arithmetic mean of all available data, and not based on a concentration range.

The mean total aluminum concentration in Canada is estimated to be 41,475 mg/kg[4]. Figure 2.4 summarizes the mean total aluminum concentrations in soils by province and for Canada as a whole. The mean concentrations of total aluminum ranged from 12,000 mg/kg in Nova Scotia to 87,633 mg/kg in British Columbia. While a single estimate of aluminum concentration in soil has been calculated for the purpose of the present assessment, it is important to recognize that aluminum concentrations in soil vary extensively from one region to another.

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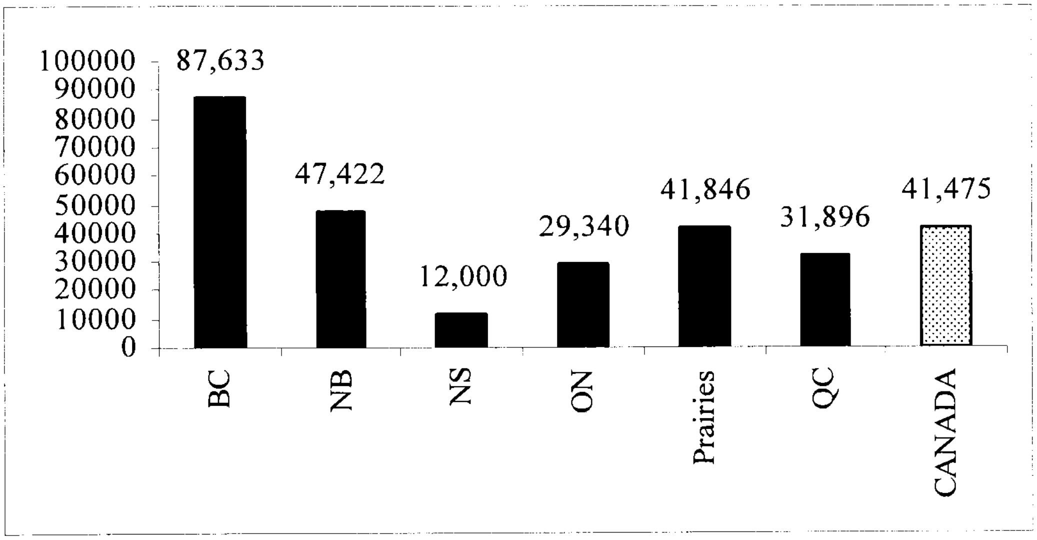
[3] Background concentration is a term used in geochemical exploration that refers to the natural abundance of a sterile element from the Earth's crust (Hawkes and Webb 1962).

[4] Average of the results obtained from over 40 studies covering ten provinces.

In recent years, Health Canada initiated research in the Ottawa region comparing mean aluminum concentrations in residential gardens with concentrations in dust from inside residential dwellings. The results showed that mean aluminum concentrations were about 26,000 mg/kg inside residential dwellings, but more than double that (55,841 mg/kg) in gardens (Rasmussen et al. 2001).

Figure 2.4 Comparison of mean total aluminum concentrations in soils from provinces across Canada (mg/kg) (1987–2007)



Measures of extractable and dissolved aluminum in soil

In general, unless the soil pH falls below 4, levels of the more soluble Al^{3+} form (i.e., the form considered to be more readily taken up by organisms) in the soil pore fluids are likely to be low. Hendershot and Courchesne (1991) measured aluminum in soil solution at St. Hippolyte, Quebec. The median total dissolved aluminum level was 0.570 mg/L, the median inorganic aluminum level 0.190 mg/L and the median Al^{3+} level 0.0003 mg/L in samples collected at a depth of 25 cm (pH = 5.5). Total dissolved aluminum was also measured in soil solution in the Niagara, Ontario, region; its level reached 1.214 mg/L (pH 4.2) in untreated soil. Following treatment with lime, aluminum was not detected in soil pore waters, and the pH increased to 4.8–5.5 prior to planting alfalfa (*Medicago sativa* L.). After three cuts of alfalfa, the pH was elevated to 6.0 in control plots and to 7.5–8.0 in limed plots; the mean total dissolved aluminum level was 0.335 mg/L in pore waters in the control plots and 0.016 to 0.397 mg/L in limed plots (Su and Evans 1996).

Turmel and Courchesne (2007) reported concentrations of 16.5 to 18.5 mg/kg dw total recoverable aluminum (from nitric acid digestion) in surface soil samples (pH 5.2) collected in 2005 from an abandoned agricultural field near a zinc plant in the Valleyfield area of Quebec. Soil collected under a nearby forest stand (pH 6.0) contained from 8.8 to 11.7 mg/kg dw total recoverable aluminum. The water soluble fraction of aluminum for the soils was 0.477 to 0.507 mg/L and 0.403 to 0.424 mg/L for the agricultural and forest soil samples, respectively.

Data relating to aluminum levels in soils treated with aluminum hydroxide sludges are limited. Near Regina, Saskatchewan, 1100 tonnes of alum sludge from a DWTP were spread on 16 ha of soil at a rate of 75 tonnes per hectare. There was no statistical difference in the mean acid-extractable aluminum level in both control (4.0%) and treated (4.1%) soil (Bergman and Boots 1997). In a study done for the American Water Works Association, Novak et al. (1995) measured the aluminum content of soil before (pH 4.7 and 5.5 at two sites) and after application of water treatment residuals. The PAC residual contained 2,330 mg Al/kg dw, and the alum residual, 6,350 mg/kg dw. In cropland soil treated according to the Mehlich III extraction procedure, which estimates the amount of aluminum available for uptake by organisms, concentrations of this available aluminum varied between 405 and 543 mg/kg dw (or 0.04% and 0.05%) before the application of the water treatment residuals. Addition of PAC and alum residuals resulted in an increase of available aluminum to 770 mg/kg dw and 1115 mg/kg dw, respectively. In another experiment, alum residual containing 150,000 mg Al/kg dw was applied to forest soil (pH 4.7). Soil analyses done 30 months later showed no differences between the control and the treatment plots for bioavailable and total aluminum.

2.3.2.5 Biota

Aluminum concentrations in vegetation related to the production or use of the aluminum salts considered in this report were available for only a few locations in Canada. Vasiloff (1991, 1992) reported aluminum levels in bur oak (*Quercus macrocarpa*) foliage collected from trees near an aluminum chloride producer in Sarnia, Ontario. Total aluminum levels ranged from 25 to 170 mg/kg dw in 1989 and from 57 to 395 mg/kg dw in 1991. Levels were higher in the foliage of trees closer to the aluminum chloride plant. These levels were below the Ontario Rural Upper Limit of Normal for aluminum in tree foliage (Vasiloff 1992). Fugitive emissions of aluminum chloride and subsequent hydrolysis, resulting in the formation of hydrochloric acid, were responsible for the damage to trees, including death that was observed at one location. The company ceased its operations in the mid-1990s. No such damage was reported near aluminum sulphate plants.

Novak et al. (1995) measured aluminum levels in soils before (pH 4.7 and 5.5 at two sites) and after the application of water treatment residuals (PAC and alum sludge), as well as aluminum contents in tissues of corn (*Zea mays*), wheat (*Triticum aestivum*) and loblolly pine (*Pinus taeda*) in control and treated soils. Statistical differences in aluminum contents were noted only in corn tissues. Aluminum levels were lower (15.1 mg/kg dw versus 18.6 to 19.6 mg/kg dw) in plants grown in soil treated with 2.5% of PAC water residual than in plants grown in soil treated with 1.34% alum or in controls; however, crop yields (kg/ha) were not lower. Aluminum levels in loblolly pine tissues were not statistically different in trees grown in control (270 mg/kg dw) and treated (152 to 170 mg/kg dw) soil.

No information was found relating concentrations in animals with aluminum entering the environment from direct production or use of the three salts subject to this assessment.

Morrissey et al. (2005) reported mean levels of 55 mg/kg dw in feathers and 2780 mg/kg dw in feces of American dippers (*Cinclus mexicanus*) residing in the Chilliwack watershed of British Columbia. The samples were collected over the period 1999 to 2001, and were considered to represent overall exposure to both natural and anthropogenic sources in the region. Benthic invertebrates (primarily insect larvae) and salmon fry, both key dietary items for the birds, contained mean concentrations of around 1,500 mg/kg dw and 165 mg/kg dw, respectively. Aluminum was present in all invertebrate (n = 30), fish (n = 9) and bird fecal samples (n = 14), but only 16% of the feather samples (n = 82). Based on a calculated total dietary intake (TDI) value of 26 mg/kg bw/d, derived using procedures described in CCME (1998), the researchers hypothesized that dipper populations in the region may be subject to chronic exposure effects of aluminum.

2.3.2.6 Food

Most foods, whether of plant or animal origin, contain a certain amount of aluminum originating from: (a) naturally-occurring aluminum in the soil, (b) the addition of aluminum salt-based food additives, and (c) the migration from aluminum-containing materials in contact with food (InVS-Afssa-Afssaps 2003). More than 80% of total aluminum concentrations found in foods and beverages range from 0.1 to 10 mg/kg wet weight. Some foods containing additives can exceed aluminum concentrations of 100 mg/kg.[5]

Selection of data for foods in Canada

Data on the concentrations of aluminum in Canadian foodstuffs are collected through Canadian Total Diet Studies, carried out by the Health Products and Food Branch of Health Canada, with the fifth Total Diet Study being the most recent. The Total Diet Study estimates the concentrations of more than 15 trace metals (both essential and non-essential) in foods commonly consumed by Canadians.

Estimating quantities of aluminum ingested by an individual is complicated by the fact that foods are composite materials, and the components have very different aluminum concentrations. In the Total Diet studies, foods bought in grocery stores are prepared to reflect the Canadian diet; hence raw meat is cooked, and vegetables are peeled, trimmed or otherwise cleaned for serving, if not cooked. Processed foods or mixes are prepared as directed.

While the Total Diet Study provides data on total aluminum concentrations in foods, it does not allow estimation of the proportion of naturally-occurring aluminum versus the proportion of added aluminum salts. Some qualitative information in this regard is, however, included below.

With respect to aluminum originating from the contact of food with packaging material, this source would be included in the total aluminum concentration measured in the food item in the Total Diet Study. Aluminum utensils, pots and pans are not used to prepare the food, and so this potential source is not reflected in the measured concentrations. Some information on this aspect from other studies is, however, included below.

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[5] Estimate based on data pooled from the fourth and fifth Total Diet Studies.

Estimated exposure in this assessment was based on preliminary data from the first three years of the fifth Total Diet Study (2000–2002) conducted in Ottawa (2000), Saint John (2001) and Vancouver (2002) (Dabeka 2007).

Mean aluminum concentrations in Canadian foods

In Canada, some foods have naturally high total aluminum concentrations, including yeast, raisins, mollusks and shellfish as well as some spices and herbs, where concentrations greater than 400 mg/kg were found (e.g., black pepper and oregano) (Dabeka 1007). Although concentrations in some aromatic herbs and spices may be high, their overall contribution to the daily diet is very low as only small quantities are normally ingested.

Tea is frequently studied by researchers as the plant generally assimilates high concentrations of aluminum (Wu et al. 1997). The fifth Total Diet Study in Canada showed aluminum concentrations of about 4.3 mg/kg in infused tea. This can be compared to the concentrations in other beverages of 0.67 mg/kg in red wine, 0.51 mg/kg in beer and a much lower average concentration of 0.08 mg/kg in coffee (Dabeka 2007). For the Canadian data, all samples were analyzed as prepared for consumption (i.e., brewed tea and coffee).

In addition to natural aluminum in foods, aluminum-containing food additives are permitted for use as a colouring agent, firming agent, stabilizing agent, pH adjusting agent, anti-caking agent, dusting agent, emulsifier, and carrier. Specific maximum levels of use prescribed in the Canadian Food and Drugs Regulations range from 0.036% (or 360 mg/kg) for aluminum sulphate in some egg products to 3.5% (or 35,000 mg/kg) for sodium aluminum phosphate in creamed and processed cheese products (Health Canada 2004).

Table 2.5 summarizes mean total aluminum concentrations found in various food groups in Canada based on the fifth Total Diet Study performed between 2000 and 2002. Certain food groups include diverse items, such that aluminum concentrations may vary considerably within a food group. More detailed information on the concentrations in specific items is presented below.

Cereal products are generally the primary source of dietary exposure to aluminum, followed by sugar-containing foods and dairy products. Other food categories account for less than 10% of the total aluminum dietary exposure. The mean total aluminum concentration in cereal products is a result of higher levels found in retail (ready-to-eat or mix) cakes, pancakes, muffins, Danish pastries, donuts, and cookies (concentrations ranging between 11 and 250 mg/kg). Such levels likely result from the direct addition of aluminum-based food additives, or from the use of baking powder in which aluminum-base food additves are also permitted (baking powder that is purchased in stores and used in home-cooking does not generally contain added aluminum salts.). Lower levels of aluminum are found in pasta, rice, bread, and cooked wheat, oatmeal and corn-based cereals, which are also included in the cereal products category.

Similarly, the mean aluminum concentration in the "Foods, primarily sugar" category is attributed to the level of aluminum found in chewing gum. Most food items included in that particular category such as candy, gelatine desserts, honey, jams, pudding, and syrup, contain very low levels of aluminum.

Table 2.5 Mean total aluminum concentrations in various food groups based on the fifth Canadian Total Diet Study (2000–2002)

Food groups	Mean total aluminum concentration (mg/kg)
Dairy products	0.45
Fats	0.38
Fruits and fruit products	1.35
Vegetables	1.21
Cereal products*	28.8
Meat and poultry	1.42
Fish	2.16
Eggs	0.17
Foods, primarily sugar*	9.36
Mixed dishes and soups	0.49
Nuts and seeds	2.65
Soft drinks and alcohol	1.13

* see text for details on specific food items in this category

Total Diet Studies in Canada have also examined various fast food products, where mean aluminum concentrations exceeding 1 mg/kg were found in french fries and pizza, and up to approximately 50 mg/kg in chicken burger (Dabeka 2007).

Two of the three salts specifically named on the PSL2 (chloride and nitrate) are not used as food additives. Aluminum sulphate (including its potassium and sodium salts) may be used as a food additive, but other aluminum-containing additives (basic and acidic sodium aluminum phosphate, sodium aluminosilicate) are much more widely used[6]. This was confirmed through recent information gathered by Health Canada's Food Directorate from those members of the food industry who manufacture products in which aluminum-based food additives are permitted. This information indicates that aluminum sulphate (and its salts) are used as food additives in a limited number of food items, such as muffins, pizza, tortilla, burritos, egg products and some dry bakery mixes, and in quantities less than 0.5% of the final product weight.

Mean aluminum concentrations in Canadian infant formulas and in breast milk

Health Canada regularly tests infant formulas for metal concentrations as well as the water added to certain formulas as a point of comparison. Available data from the most recent

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[6] Refer to www.hc-sc.gc.ca/fn-an/alt_formats/hpfb-dgpsa/pdf/legislation/e_c-tables.pdf for food-additive uses.

Canada Total Diet Study as well as information from studies conducted by the Health Products and Food Branch are evaluated to estimate aluminum levels in bovine protein and soy-based infant formulas.

According to the fifth Canadian Total Diet Study conducted in 2000–2002, aluminum concentrations of 0.20 and 0.79 mg/kg were measured in the bovine protein and soy-based infant formulas, respectively. These concentrations were measured in the reconstituted infant formulas prepared for consumption.

Aluminum concentrations in several types of bovine protein and soy-based infant formulas were also measured in another Canadian study undertaken between 1999 and 2001 (Health Canada 2003). The mean concentrations in bovine protein formulas were about 0.13 mg/kg in liquid concentrates, 0.18 mg/kg in powdered formula to which a specified quantity of water was added and approximately 0.40 mg/kg in ready-to-use concentrates with iron added. Soy-based infant formulas had mean aluminum concentrations of approximately 0.73 mg/kg in the case of both ready-to-use concentrates and powdered formulas. Again, these concentrations were all measured in the reconstituted infant formulas prepared for consumption.

Two studies were undertaken in Canada to measure levels of aluminum in breast milk. They indicated that mean concentrations of aluminum in breast milk were of the same order of magnitude as elsewhere in the world. In one study in Quebec, which involved only five women, a mean concentration of aluminum in breast milk of 0.34 mg/kg was measured (Bergerioux and Boisvert 1979). In a second study, a median aluminum concentration of 0.014 mg/kg in 12 Albertan women was measured (Koo et al. 1988). Thus, the average concentration of aluminum in breast milk is considered to be approximately 0.11 mg/kg.[7]

Migration of aluminum from materials in contact with food

Aluminum concentrations in food generally increase when there is direct contact with aluminum packaging material or aluminum utensils, pots and pans, especially when food is cooked. Researchers have demonstrated that the migration of aluminum to food could depend on pH, container type, cooking time, purity of the aluminum used in the coating of utensils or aluminum pots, or salt addition to boiling water (Muller et al. 1993; Abercrombie and Fowler 1997; Gramiccioni et al. 1996; Gourrier-Fréry and Fréry 2004; Pennington 1988; InVS-Afssa-Afssaps 2003). For example, aluminum concentrations in coffee, soft drinks and beer increased from 0.02 mg/L to more than 0.25 mg/L when an aluminum percolator was used to brew coffee, or when soft drinks and beer were kept in aluminum cans for more than six months. A level up to 0.87 mg/L in drinks was also observed after 12 months of storage in cans (Muller et al. 1993; Abercrombie and Fowler 1997). Concentrations of up to 35 mg/L

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[7] Weighted mean from the two Canadian studies (Bergerioux and Boisvert 1979; Koo et al. 1988). Human milk density = 1,030 g/L (Health Canada 1998a).

were found in acidified fruit juices after boiling in an aluminum pot (Liukkonen-Lilja and Piepponen 1992).

With respect to the uses of the three salts—aluminum chloride, aluminum nitrate and aluminum sulphate—in food packaging, aluminum sulphate is used as a component in metalized films and aluminum chloride is used as a component in a wax product that is applied as a coating on plastic films. While both of these products may be used in food packaging, the estimated amount of aluminum migrating from these films into the food would be negligible (Health Canada 2008b).

2.3.2.7 Consumer products

2.3.2.7.1 Non-prescription drugs

The major pharmaceutical uses of aluminum are: as an antacid and as phosphate binder for patients with chronic kidney failure (aluminum hydroxide); as a component of the prescription antiulcer medication, sucralfate (sucrose sulfate-aluminum complex), as a component in some vaccines and injections (e.g., alum precipitated allergen extracts, MMR vaccine) (see section 2.3.2.8), as a hemostatic agent to control bleeding from minor cuts (aluminum potassium sulfate (alum), aluminum chloride or aluminum sulfate), as a component in hydrated magnesium aluminum silicate in the antidiarrheal, attapulgite, and as astringents (there are numerous aluminum derivatives in antiperspirants and in some deodorants). Aluminum containing antacids, represent, by far, the largest potential exposure to aluminum in individuals consuming these drug products on a regular, prolonged, basis.

Concentrations of aluminum compounds in over-the-counter products sold in Canada were obtained from the Health Canada Drug Product Database[8]. The Drug Product Database contains brand name, Drug Identification Number (DIN), ingredient and other information for approximately 23,000 drugs approved for use in Canada. Based on the concentrations of specific aluminum compounds, the elemental aluminum contents of orally administered over-the-counter products marketed in Canada are estimated to be 8,700 to 60,000 mg/kg product for antacids (heartburn medication), 30,000 to 50,000 mg/kg product for dental agents, and 3,500 mg/kg product for attapulgite.[9]

2.3.2.7.2 Cosmetics

Compounds such as aluminum chlorohydrate, ammonium aluminum sulphate, aluminum hydroxide, aluminum starch octenylsuccinate, aluminum-based dyes and aluminum silicate are used in deodorants, antiwrinkle preparations, toothpastes, eye and face makeup, shampoo, lipstick, moisturizers and other cosmetic products sold in Canada. Data on concentrations of aluminum compounds in these products are available through Health

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[8] Note that that many aluminum containing products (e.g. antiacids, antiperspirants) are now considered Natural Health Products in Canada

[9] www.hc-sc.gc.ca/dhp-mps/prodpharma/databasdon/index-eng.php

Canada's Cosmetic Notification System, a mandatory system under which manufacturers must submit information including composition data on cosmetics prior to first sale in Canada.

Table 2.6 presents reported ranges of aluminum concentrations that may be contained in a wide variety of cosmetic products sold in Canada. However, it should be noted that the data on concentrations are available with respect to reporting categories (< 0.1%, 0.1% to 0.3%, 0.3% to 1.0%, 1% to 3%, 3% to 10%, 10% to 30% and 30% to 100%). Thus the maximum concentration represents an upper limit of a reporting category, and is therefore very likely an overestimate, by a factor of up to 3.3, of the actual maximum concentration in the product category.

Table 2.6 Range of total aluminum concentrations in various categories of cosmetic products sold in Canada

Product Category	**Range of total aluminum concentration (mg/kg)***	**Product Category**	**Range of total aluminum concentration (mg/kg)**
Hair dye	442–300,000	Lipstick	44–300,000
Antiwrinkle preparation	171–333,000	Manicure preparation	44–300,000
Barrier cream	78–10,377	Baby	78–2,349
Toothpaste	1,588–52,930	Skin cleaner	57–529,300
Deodorant and antiperspirant	171–529,300	Skin moisturizer	42–158,790
Eye makeup	42–NA**	Sun	5,293–15,879
Face makeup	44–NA**	Bath	346–10,000
Fragrance	206–30,000	Shaving	57–157,700
Hair conditioner	78–15,879	Shampoo	309–1,588

* Note that the maximum concentration corresponds to an upper limit for a reporting category (see text) and may thereby overestimate the maximum concentration by up to a factor of 3.3)

** Maximum upper bound not available, as the upper limit of reporting category is 100%

2.3.2.8 Vaccines

Most of the vaccines authorized in Canada contain an aluminum salt adjuvant, according to the systematic vaccination schedule used for infants, young children, adolescents and adults (Canada Public Health Agency 2006). Various types of vaccine adjuvants are used by pharmaceutical companies, such as aluminum hydroxide, aluminum phosphate, aluminum sulphate and aluminum potassium sulphate. The quantity of aluminum ranges between 125 µg and 1,000 µg (aluminum hydroxide) per dose, depending on the vaccine. There is no standard or recommendation available in Canada with respect to the maximum quantity of aluminum or aluminum compound that may be used as an adjuvant in vaccines.

2.3.3 Toxicokinetics: human and experimental animals

An overview of the toxicokinetic processes of aluminum was carried out with the goal of highlighting the various factors influencing its pathway from the environment to target organs. Each toxicokinetic process is described below (absorption, distribution and elimination). Aluminum does not undergo phase I and II biotransformation reactions, occurring only in the +3 oxidation state. The metabolism of aluminum is therefore described in relation to its speciation, in the context of the distribution and elimination processes.

2.3.3.1 Absorption

Even at moderately elevated levels in the environment, exposure of aluminum leads to only small increases of aluminum in human tissues due to its low bioavailability through all routes of exposure. Bioavailability refers to the fraction of the total amount of the substance ingested, inhaled or in contact with the skin that reaches the systemic circulation. In this assessment, emphasis is placed on oral bioavailability, as the estimated daily intake (EDI) of the Canadian population shows that ingestion is the major route of exposure (see section 3.2.1); the bioavailability of aluminum with respect to other exposure routes (inhalation and dermal) is also reviewed. Bioavailability estimates for all exposure routes have been summarized in Table 2.7.

2.3.3.1.1 Oral absorption

The interpretation of aluminum oral bioavailability estimates requires the understanding of: (a) the methods used to calculate oral bioavailability, and (b) the physiological and biochemical factors that influence oral absorption. The ingested matrix to which aluminum is bound likely influences its potential absorption, therefore, the oral bioavailabilities of aluminum from drinking water, food and soil are distinguished.

Methods to calculate oral bioavailability

The methods to calculate the oral bioavailability in experimental studies are: (a) mass balance based on intake, and fecal and urinary excretion; (b) comparison of intake with urinary excretion; (c) concentration in a single blood sample and a calculated volume of distribution; (d) aluminum concentration in tissue; and (e) comparison of areas under the plasma concentration-time curve after oral and intravenous administration (Yokel and McNamara 2000). The most common method is comparison of intake with urinary excretion. This method is the simplest and least invasive, and is relatively reliable provided that the collection period is long enough to measure nearly all the aluminum excreted in the urine.

Prior to 1990, aluminum analyses were based on the quantification of the common isotope ^{27}Al ($\approx$ 100% of the natural isotopes). As ^{27}Al in the environment is ubiquitous, contamination during sampling and analysis may easily occur, leading to overestimation of the tissue concentrations, particularly when the administered amounts of aluminum are near the baseline exposure. The relative contribution from endogenous ^{27}Al is minimized by administering doses that are much higher than the levels encountered in the environment. However, oral absorption may depend on dose. Thus, this approach increases the uncertainty in the estimation of bioavailability of environmental concentrations of aluminum. On this point, the observed relationship between dose and bioavailability is inconsistent: increased dose of aluminum decreased its bioavailability in the experimental studies of Greger and Baier (1983), Weberg and Berstad (1986), and Cunat et al. (2000) while opposite results were observed in other animal studies (Yokel and McNamara 1985; Ittel et al. 1993).

In recent years accelerator mass spectrometry (AMS) has been used to quantify the isotope ^{26}Al, administered as a tracer (Priest 2004). This analytical technique has allowed researchers to more accurately measure bioavailability of aluminum at levels comparable to the levels to which the general population is actually exposed, since it is possible to distinguish the aluminum in the administered dose (^{26}Al) from the aluminum already in the body (^{27}Al). However the cost and small number of facilities limit the sample analyses, which can result in the diminishing of the precision of the estimation and the information concerning the intra-individual variability (Yokel and McNamara 2000).

Factors influencing oral absorption

The principal mechanism of absorption of ingested aluminum seems to be a passive diffusion through the paracellular pathway (Zhou and Yokel 2005). This diffusion occurs predominantly in the small intestine (duodenum and jejunum) and, to a lesser extent, through the gastric mucosa in stomach (Powell and Thompson 1993; Walton et al. 1994). In addition to passive diffusion, Cunat et al. (2000) suggested that absorption of aluminum may occur by a transcellular and saturable route, which may explain the possible dependency of absorption on the dose level.

The rate of uptake, and consequently the cumulative absorption of aluminum, has been shown to vary depending on physiological and chemical factors. Krewski et al. (2007) summarized factors based on findings in both human and animal studies, including:

- Solubility: absorption is greater with more soluble aluminum compounds;
- Gastric pH: absorption is greater at pH 4 compared to pH 7, probably due to the generation of more soluble aluminum compounds;
- Carboxylic acids: increased absorption in the presence of carboxylic acids, particularly citrate that is naturally present in many foods and fruit juices;
- Silicon compounds: decreased absorption in the presence of silicon-containing compounds in the dietary intake, due to a possible formation of hydroxyaluminosilicate.

Among the factors cited above, particular attention has been given to the significant impact of citrate during the ingestion of aluminum. Oral bioavailability has been found to increase by a factor of 5 to 150 when aluminum is ingested with citrate solution, as verified with studies employing the same aluminum complex and under the same experimental conditions (Weberg and Berstad 1986; Yokel and McNamara 1988; Froment et al. 1989; Priest et al. 1996; Drueke et al. 1997; Schönholzer et al. 1997). Citrate probably facilitates the absorption by opening the tight junction between intestinal cells (Froment et al. 1989; Zhou and Yokel 2005). Zhou et al. (2008) recently explored the influence of citrate in drinking water at a similar molar concentration to aluminum. The researchers did not observe a significant enhancement of aluminum absorption for an Al:citrate molar ratio of 1:1, and suggested that aluminum absorption may depend on citrate dose.

The principal biochemical explanation for how the factors listed above influence absorption is the nature of the ligand to which the ion Al^{3+} is associated in the gastrointestinal fluid. In vitro studies using Caco-2 cells derived from the human lower intestine show differences between ligands in the uptake rate of aluminum; aluminum citrate and aluminum nitrilotriacetate were absorbed more rapidly than aluminum lactate (Alvarez-Hernandez et al. 1994) and the uptake rate of aluminum fluoride was higher than that of, in decreasing order, Al^{3+}, aluminum maltolate, aluminum citrate and aluminum hydroxide (Zhou and Yokel 2005). Results from in vivo studies provided evidence for significant differences in the oral bioavailability calculated for different ingested aluminum complexes (Yokel and McNamara 1988; Froment et al. 1989). Cunat et al. (2000) concluded that the organic ligands enhance aluminum absorption, in comparison to the inorganic ligands (citrate > tartrate, gluconate, lactate > glutamate, chloride, sulphate, nitrate), based on the results of a study in which rat intestines were locally perfused with aluminum.

The pH of the exposure media may play an important role in the absorption of aluminum, as it affects aluminum speciation. In aluminum sulphate-treated water with low pH, the aluminum sulphate and Al^{3+} (very soluble) are the predominant forms while, when increasing the pH from 6.3 to 7.8, the predominant complex is aluminum hydroxide (likely insoluble). At pH above 7.8, the solubility in water increased due to the presence of the negative ions of aluminum hydroxyl (Walton et al. 1994). As mentioned in section 2.3.2.2.2, while treatment with aluminum sulphate may reduce the total aluminum concentration in finished water as compared to the untreated water source, through the removal of suspended solids containing aluminum, there is evidence that treatment with aluminum salts also increases the concentration of low-molecular-weight, dissolved aluminum species (Health Canada 1998b).

The low pH of the gastric fluid creates a high potential for transformation of the ingested aluminum complex. This led Reiber et al. (1995) to argue that the aluminum in drinking water would not be more readily assimilated than other forms of aluminum, and that regardless of the form in which the aluminum is consumed, a substantial portion of it will likely be solubilized to monomolecular aluminum in the stomach. Other researchers, however, consider this to be an oversimplication, in light of the observed differences in the oral absorption of different aluminum compounds (Krewski et al. 2007).

Concurrent absorption of aluminum with other dietary nutrients has been shown to influence the intestinal absorption of this metal. For example, the presence of vitamin D likely favours the absorption of aluminum (Adler and Berlyne 1985; Ittel et al. 1988; Long et al. 1991; Long et al. 1994) and the consumption of folic acid supplementation is expected to diminish aluminum absorption and/or its accumulation in various organs (bone, kidney and brain) by a possible formation of folate-Al complex (Baydar et al. 2005). Domingo et al. (1993) investigated the effects of various dietary constituents, such as lactic, malic and succinic acids, on the levels of absorption and distribution of aluminum in drinking water and in the diet of mice, where they observed an enhanced absorption with these concurrent ingestions.

A few studies have been conducted to examine whether food composition or the presence of food in the stomach affect oral aluminum bioavailability, and the results have been mixed. The nature of the contents in the stomach influenced the absorption of aluminum in the study of Walton et al. (1994) in which adult Wistar rats were exposed to water treated with aluminum sulphate along with various beverages and foods. The aluminum concentrations in serum increased when the aluminum sulphate treated drinking water was taken with orange juice; the same phenomenon was observed, but to a lesser extent, with coffee. The authors note that the low levels of aluminum in these two beverages would not have contributed to this increase in aluminum levels. In comparison, when aluminum sulphate treated water was given with beer, tea or cola (beverages that may contain appreciable levels of aluminum) the serum concentration did not markedly rise. Meat and carbohydrate/cereal products decreased aluminum absorption. Drüeke et al. (1997) performed a study in rats using ^{26}Al to examine the effect of silicon contained in drinking water as well as solid food, on the absorption of aluminum. In their study, high Si concentrations in the drinking water failed to depress the ^{26}Al fraction absorbed, as estimated on the basis of skeletal accumulation and urinary excretion. In addition, absorption of ^{26}Al was approximately 15 times higher in the fasted state than in the non-fasted state. As part of a study conducted in rats with ^{26}Al, Yokel et al. (2001a) tested the hypothesis that the stomach contents affect aluminum absorption. According to the authors, although stomach contents delayed aluminum absorption, it did not significantly alter the extent of ^{26}Al absorption.

Estimation of the oral bioavailability of aluminum in drinking water

Experimental data for oral bioavailability of aluminum from drinking water, obtained in studies conducted in humans and animals, and based on varying calculation and quantification methods, were evaluated.

The compilation of central values (mean or median) of the results of different studies in humans results in a range of 0.010% to 0.52% for oral bioavailability of aluminum in drinking water, based on experiments involving more than one volunteer. The lower value is the mean value obtained from the data of two volunteers exposed to ^{26}Al-hydroxide in Priest et al. (1998). This experimental study observed the higher value of 0.52% as well when these two volunteers were exposed to ^{26}Al-citrate. In a much larger study with 29 subjects consuming an aluminum-controlled diet, the oral bioavailability from aluminum sulphate-treated municipal drinking water was estimated at 0.36% to 0.39% (Stauber et al. 1999).

As for the central values for the oral bioavailability for experimental animals, a range of 0.04% to 5.1% is reported in experimental studies with the isotope ^{26}Al, whereas the range based on ^{27}Al is 0.01% to 4.56%. The maximum central value of 5.1% for the animal experiments using ^{26}Al was obtained following ingestion of a concentrated solution of citrate (Schönholzer et al. 1997). The second highest value is 0.97%, based on the exposure to aluminum chloride (Zafar et al. 1997). The maximum central value of 4.56% for ^{27}Al was obtained for aluminum citrate ingested by rats with renal failure (Yokel and McNamara 1988). If only healthy animals had been considered, the maximum value would have been 2.18% for ^{27}Al-citrate.

Krewski et al. (2007) proposed a range for the oral bioavailability of aluminum in drinking water of 0.05% to 0.4% for rats and rabbits, and 0.1% to 0.5% for humans, with a most likely value of 0.3%. The approximate correspondence between the ranges and the most likely estimates in humans and animals for bioavailability from drinking water suggests that there is little interspecies difference in this respect.

Estimation of the oral bioavailability of aluminum in food

In spite of the important contribution of food in the total exposure to aluminum, the database for oral bioavailability of aluminum in food is limited. In an early investigation into the potential for the absorption of aluminum accumulated in food, Jones (1938) demonstrated that a large percentage of aluminum in bread made with aluminum-based baking powder was soluble in the gastric juice of dogs. Several decades later, Yokel and Florence (2006) confirmed that some aluminum from biscuits made with baking powder containing acidic ^{26}Al-sodium aluminum phosphate (SALP) reaches the systemic circulation. In this study, about 0.12% of the ingested aluminum crossed the gastrointestinal tract of exposed rats. Using the same experimental method,[10] Yokel et al. (2008) estimated oral bioavailabilities of ~ 0.1% and ~ 0.3% for basic ^{26}Al-SALP incorporated into cheese at concentrations of 1.5% and 3%, respectively.

The oral bioaccessibility[11] of aluminum encountered in different foods was measured by Lopez et al. (2002) and Owen et al. (1994). It is not possible, however, to directly compare their results, since their methodologies differed. Moreover, the bioaccessibility estimates, ranging from 0.3% to 0.9% by Owen et al. (1994) and 0.85 to 2.15% by Lopez et al (2002), cannot be directly used to estimate the oral bioavailability of aluminum, as the in vitro-in vivo relationship has not been established (Ruby et al. 1999). Nonetheless these bioaccessibility studies do provide evidence that oral bioavailability is low and may change according to the nature of consumed foods. For example, the aluminum in bread, jam and tea appeared to be about 2.7 times more soluble than the aluminum in sponge cake (Owen et al. 1994). It is expected that the actual oral bioavailability of aluminum in food is lower than these bioaccessibility values, as solubility in the intestinal tract would not be the only factor limiting absorption.

The oral bioavailability of aluminum in food has also been estimated based on the comparison of aluminum intake in the general population with the urinary excretion and/or the body burden of aluminum (Ganrot 1986; Priest 1993, 2004; Powell and Thompson 1993; Nieboer et al. 1995). These estimates range from 0.1% to 0.8%. Note that the oral bioavailability estimate of 0.12% of Yokel (2006) for rats fed aluminum-containing biscuits

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[10] Bioavailability is determined by comparing the areas under the serum concentration x time curve (AUC) for the ^{26}Al given orally and the ^{27}Al administered intravenously (Yokel et al. 2008).

[11] The oral bioaccessibility is the soluble fraction of the substance in the gastrointestinal system that is available for absorption (Ruby et al. 1999).

falls in this range, as does the estimate of 0.53% by Stauber et al. (1999), based on a controlled diet in humans.

Bioavailability of aluminum in antacids (aluminum hydroxide) has been estimated in three studies in humans, measured alone or in combination with citrate, orange juice, bicarbonate, or calcium acetate (Mauro et al. 2001; Haram et al. 1987; Weberg and Berstad 1986). These measured bioavailabilities, ranging from 0.001% to 0.2% were generally comparable to the bioavailabilities measured in food.

The limited data concerning the oral bioavailability of aluminum from foods do not allow for the determination, with good predictive value, of the potential absorption of aluminum in food. For the purpose of comparison with other media (Table 2.7), the interval of 0.1% to 0.8% is retained, with a most likely range of 0.1% to 0.3%, based on the recent work of Yokel and Florence (2006) and Yokel et al. (2008).

Estimation of the oral bioavailability of aluminum in soils

Another factor of importance in the human exposure assessment for aluminum is the oral bioavailability of aluminum in ingested soil, as soil ingestion is a significant exposure pathway for the toddler group (see section 3.2.1). No bioavailability data on soil were identified. Limited data, however, were found for the bioaccessibility of aluminum in soil, which, as noted above, is an in vitro measure of the soluble fraction of the substance available for absorption.

Shock et al. (2007) estimated the bioaccessibility of aluminum in different tundra soil samples contaminated by mining waste dust, by simulating gastric fluid in an in vitro experiment. The estimated values varied from 0.31% to 4.0%, according to the grain size and to the solid:fluid ratios used in the experiment. As expected, aluminum in the soil with small sized grains size had the greatest absorption.

As is the case for the bioaccessibility data of aluminum in food, these bioaccessibility estimates for aluminum in soil need to be tied to the *in vivo* bioavailability estimates from appropriate *in vivo* models (Ruby et al. 1999). Even if the experimental protocols used to measure food and soil aluminum bioaccessibility differed slightly, the data of Shock et al. (2007) suggest that the bioaccessibility of aluminum in soil is similar to that in food. In the absence of more relevant data, the range for the oral bioavailability of aluminum in soil is therefore assumed to be similar or less than that of food. The relative oral bioavailability of aluminum in soil is considered to be a major source of uncertainty for this exposure pathway; however, bioavailability from soil is expected to be low.

2.3.3.1.2 Dermal absorption

Utilization of antiperspirant with aluminum would contribute to the body burden if aluminum passes through the skin barrier. There is some evidence from case studies, described below, that small amounts of aluminum do reach the systemic circulation. However, to date, no data for dermal bioavailability are available from controlled studies of more than one or two individuals.

In the study of Flarend et al. (2001), ^{26}Al-chlorohydrate (aluminum complex in antiperspirant) was applied to a single underarm of one man and one woman. The cumulative urinary excretion after 43 days following the application accounted for 0.0082% (male) and for 0.016% (female) of the applied dose. After correcting this fraction for the aluminum not excreted in urine (15% of the absorbed dose), this application was estimated to result in a dermal bioavailability of about 0.012%. On the basis of these data, the authors estimated that the amount of aluminum absorbed from regular use would be 0.25 μg/d.

Guillard et al. (2004) reported on one clinical case in which a woman who used an antiperspirant cream with aluminum chlorohydrate over four years showed elevated levels of aluminum in plasma and urine (10.47 μg/dL in plasma[12]). When the woman discontinued use, concentrations in her urine and plasma dropped to reported normal values after the third and eighth months, respectively.

2.3.3.1.3 Inhalation absorption

The ambient air of multiple occupational environments, such as the aluminum production industry and welders' factory (Priest 2004), may have high levels of aluminum. The higher urinary excretion of aluminum in exposed workers, compared to the general population, demonstrates that some inhaled aluminum can reach the systemic circulation (Sjogren et al. 1985; Sjogren et al. 1988; Pierre et al. 1995). This absorption depends on the form of aluminum in the ambient air (adsorbed to PM, vapour condensation fumes and flakes) and, in the case of particulate matter, also depends on the distribution of the sizes of the aerodynamic diameter of PM ($PM_{2.5}$ versus PM_{10}).

Priest (2004) estimated a deposited pulmonary fraction of 1.9% in a study of two volunteers who inhaled ^{26}Al-oxide adsorbed to particles with a mass median aerodynamic diameter (MMAD) of 1.2 μm. The last value is supported by animal studies showing a deposition of fly ash of aluminum into the lungs from 2% to 12% (Krewski et al. 2007). As well, Yokel and McNamara (2001) have proposed an absorption fraction of about 1.5% to 2%, on the basis of the relationship between the urinary excretion of aluminum-exposed workers and the concentrations of airborne soluble aluminum measured in their environment.

An investigation in New Zealand rabbits exposed via the nasal-olfactory pathway (sponge soaked in aluminum solutions inserted into nasal recess for four weeks) provided evidence that inhaled aluminum in the olfactory tract can cross the nasal epithelium to reach the brain directly through axonal transport (Perl and Good 1987). While an analytical protocol for quantifying the amount of aluminum transported along this pathway under environmental exposure conditions has been described (Divine et al. 1999), further experimental work is required to document transport of aluminum via this pathway to the olfactory bulb, and subsequently to other regions of the brain.

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[12] Guillard et al. (2004) indicated that the normal range of aluminum in blood plasma would be < 1.0 μg/dL.

2.3.3.1.4 Parenteral administration

Intravenous injection of aluminum-containing products (e.g., intravenous feeding solutions) results in complete availability of the aluminum to the systemic circulation (Yokel and McNamara 2001; Priest 2004). In the case of intramuscular injection of aluminum species (e.g., via vaccination), potentially all of the aluminum injected may be absorbed into the bloodstream. However, the uptake rate from the muscle to blood circulation differs according to the aluminum complex. Evidence of this was provided in an experimental study, in which rabbits were injected with ^{26}Al-hydroxide and ^{26}Al-phosphate, two common vaccine adjuvants, at standard dose levels. After 28 days, 17 % of the aluminum hydroxide and 51% of the aluminum phosphate were absorbed (Flarend et al. 1997). The authors estimate that this dose, when administered in humans, would represent an increase of 0.4 μg/dL in plasma (see section 2.3.3.2 on distribution, for estimates of normal plasma concentrations).

2.3.3.1.5 Summary of estimates of aluminum bioavailability

The estimates of aluminum bioavailability presented for the different exposure routes in sections 2.3.3.1.1 to 2.3.3.1.4 are summarized in Table 2.7. The information available to generate these estimates varies considerably depending on the exposure route, and should be considered in any application of these estimates in risk assessment.

Table 2.7 Ranges of estimated aluminum bioavailability for various routes of exposure in humans and/or animals

Route of exposure		Bioavailability (%)
Oral	Drinking water (a)	0.0086 to 0.65 (H) 0.01 to 5.1 (A) Proposed likely estimate: 0.3
	Food (b)	0.10 to 0.80 (H) 0.02 to 0.3 (A) Proposed likely range: 0.1 to 0.3
	Antacids (c)	0.001 to 0.20 (H)
	Soil ingestion (d)	Equal or less than food (default assumption)
Dermal (e)		0.012 (H)
Pulmonary (f)		1.5 to 2.0 (H)
Parenteral (g)		100.0

(H) = data from experimental studies conducted in humans
(A) = data from experimental studies conducted in animals

(a) Ranges based on a compilation of the central values of estimates of the oral bioavailability of aluminum from drinking water, obtained in numerous experimental studies conducted in humans and animals. Proposed likely estimate based on experimental work of Stauber et al. (1999) in humans and the critical review of experimental animal data in Krewski et al. (2007).

(b) Based on comparisons of estimates of aluminum intake and urinary excretion in humans and experimental animal data. The estimate of bioavailablility of aluminum in food is associated with greater uncertainty than that of drinking water, because of the limitations of the database. Proposed likely range based on Yokel and Florence (2006) and Yokel et al. (2008).

(c) Based on human data reported in three studies for the bioavailability of aluminum in antacids alone or in combination with citrate, orange juice, bicarbonate, or calcium acetate.

(d) Assumed to be similar to that in food as a default value in the absence of bioavailability data from soil ingestion; considered to be of low predictive value.

(e) Based on experimental results reported in one study following a dermal exposure in two individuals.

(f) Proposed absorption fraction by Yokel and McNamara (2001) on the basis of the results from two studies in aluminum-exposed workers.

(g) Includes both intravenous (IV) and intramuscular (IM) injection.

2.3.3.1.6 Integrating bioavailability in human health risk assessment

As discussed in previous sections, the generally low oral absorption of aluminum (< 1%) is well recognized. Nonetheless, there is considerable uncertainty associated with differences in oral bioavailability, in relation to:

- the bioavailability of aluminum in different environmental media (soil, different types of food, drinking water, air, dermal application);
- the bioavailability of aluminum in humans versus experimental animal species;
- the influence of dose and dosing regime (bolus dose versus repeated exposure via drinking water or food).

In the characterization of human health risks, relative bioavailability rather than absolute bioavailability is the parameter of greatest interest. Relative bioavailability for a substance may, for example, refer to the ratio of absorbed fractions via two different exposure pathways, or it may refer to the ratio of total absorption by humans (all pathways considered) as compared to the total absorption in experimental animals in the critical study or studies.

Relative bioavailability can be established by directly measuring two absorption fractions and taking the ratio of the two, or potentially indirectly through the measurement of in vitro bioaccessibility and then by comparing in vitro bioaccessibilities (e.g., the fraction of a substance that is extracted through a weak acid solution simulating gastric fluid). In the case of aluminum, bioaccessibility would considerably overestimate bioavailability, as the available evidence indicates that only a fraction of the species dissolved in the stomach is eventually absorbed. However, to the extent that bioaccessibility is proportional to bioavailability, relative bioaccessibility will be approximately equivalent to relative bioavailability.

In the previous sections, experimental data were reviewed with respect to both bioavailability and bioaccessibility of aluminum salts in various media, in humans, and experimental animals. The discussion that follows reconsiders these data from the perspective of relative bioavailability.

The most comprehensive data concerns the bioavailability of aluminum dissolved in drinking water, as measured in both human and animal studies. In humans, measurements of oral absorption of aluminum (citrate, chloride, hydroxide or lactate complexes) generally varies between 0.01% and 0.65%, while in experimental animals the range of reported values is 0.01% to 5.1%. The ranges largely overlap and do not provide evidence for differences between humans and animals in the bioavailability of aluminum in drinking water. The proposed likely estimate for aluminum bioavailability in both humans and animals is 0.3% (see Table 2.7).

The data on bioavailability of aluminum in food are much more limited, both for humans and animals. Section 2.3.3.1.1 proposes a range of 0.1% to 0.8% for the bioavailability of aluminum salts in food (humans) and 0.02 to 0.3 in animals. These ranges have a high level of uncertainty because of the limited database, but do not provide evidence for differences between humans and animals in the bioavailability of aluminum in food.

The bioaccessibilities of aluminum in soil and food were also compared in section 2.3.3.1.1. These very limited data do not provide evidence for a difference in the amount of aluminum available for absorption of aluminum from these two media, and hence do provide a basis for concluding that there are differences in bioavailability between soil and food.

In comparing the bioavailability of aluminum in drinking water and food, in both animals and humans, the ranges of experimental values largely overlap, and the proposed likely value for drinking water is at the upper end of the proposed likely range for food. Thus the available data are insufficient for identifying a difference in bioavailability of aluminum in drinking water and food.

With regard to inhalation absorption of aluminum, there is again significant variability in the available data. These data do indicate that the bioavailability of aluminum from inhalation may be higher than from the oral route; however, since the concentrations of aluminum in ambient and indoor air are low, the absorption factor for the inhalation route would not significantly influence the evaluation of cumulative exposure from soil, air, drinking water, and food.

Although dermal absorption of aluminum salts is thought to be very low, the data is extremely limited (confined to two studies), each involving one or two individuals (see section 2.3.3.1.2). Therefore, no definitive conclusions can be drawn with respect to its relative bioavailability, although the information available suggests that it is lower than for other routes of exposure.

Consideration of bioavailability may considerably influence the conclusions of human health risk characterization if relative bioavailabilities for different salts, different exposure media and different species are greater than or less than one. In this assessment, however, the limited available data did not provide evidence for relative oral bioavailabilities significantly different from one, either with respect to comparisons of humans and experimental animals, or with respect to comparisons of water, food and soil. The bioavailability via inhalation, which is higher than oral bioavailability, would not significantly influence the estimated absorbed dose, because of the low estimated concentrations of aluminum in ambient and indoor air. Dermal exposure, which appears to be associated with a very low absorption, was considered only qualitatively in this assessment. For these reasons, the estimated values of bioavailability for different media were not explicitly integrated into the estimation of population exposure or the characterization of relative contribution of the three salts to overall exposure.

2.3.3.2 Distribution

Once absorbed into the systemic circulation, much of Al^{3+} is readily associated at the binding sites of transferrin (Tf), the plasma protein for iron transport. Since, under normal conditions, Tf in blood is only one-third saturated with iron, binding sites for the absorbed aluminum are available (Harris et al. 1996). Consequently, the Al-Tf complex is the predominant aluminum species in plasma, accounting for approximately 91% of the total aluminum in plasma (7% to 8% of aluminum is associated with citrate and less than 1% with phosphate and hydroxide) (Martin 1996). As well, Day et al. (1994) reported that, one hour after the ingestion of ^{26}Al-citrate, 99% of the ^{26}Al in blood was measured in plasma of which 80% was bounded to Tf, 10% to albumin and 5% to proteins having low molecular weight; after 880 days, 86% of aluminum in blood was bounded to plasma proteins (mostly to Tf) and the rest was associated with erythrocytes.

The major physiological compartment of aluminum is the skeleton. Krewski et al. (2007) suggest that approximately 58%, 26%, 11%, 3%, 0.95%, 0.3%, 0.25% and 0.2% of the aluminum body burden would be in the bone, lung, muscle, liver, brain, heart, kidney and spleen, respectively. Aluminum measured in the lungs may reflect deposition of airborne particles. In addition, a significant amount of aluminum analyzed in skin may result from unabsorbed aluminum deposited on skin surface (Priest 2004).

The transport of aluminum into the body and its deposition into the tissues and organs have been shown to vary widely (Priest 2004). This variability, yielding different aluminum concentrations in tissues and organs, can be explained by some of the same factors influencing aluminum absorption. For example, the presence of citrate seems to enhance the distribution of aluminum into the tissue before being associated with Tf (Quartley et al. 1993; Maitani et al. 1994). According to Jouhanneau et al. (1997), the concomitant ingestion of citrate increases aluminum absorption, but does not appear to modify the relative distribution of ^{26}Al in bone, brain and liver in comparison with ingestion without citrate.

Experimental studies have reported volumes of distribution (V_d) for aluminum, describing its potential to be distributed in tissues and organs. Most of these studies suggested that the initial V_d is approximately the blood volume (Krewski et al. 2007). However, longer collection periods lead to higher V_d, indicating a possible dependency between elimination rate and blood concentrations of aluminum (Krewski et al. 2007) (see section 2.3.3.3). Calculating the oral bioavailability of aluminum using blood volume, instead of V_d, may consequently lead to an underestimation (see section 2.3.3.1).

As neurological and reproductive/developmental endpoints are of greatest concern with respect to the environmental exposures evaluated in this assessment (see section 3.2.3.2), particular attention is paid to the distribution processes leading to accumulation in the brain and in the foetus. As well, aluminum retention in bone was investigated, as it plays an important role in the kinetics of aluminum. The principal observations with regard to retention