ASSESSMENT REPORT ON

HYDROGEN FLUORIDE

FOR DEVELOPING

AMBIENT AIR QUALITY

OBJECTIVES

Alberta Environment

ASSESSMENT REPORT ON
HYDROGEN FLUORIDE
FOR DEVELOPING AMBIENT AIR QUALITY OBJECTIVES

Prepared by
Toxico-Logic Consulting Inc.

for
Alberta Environment

February 2006

ISBN No. 978-0-7785-7651-8 (Printed version)
ISBN No. 978-0-7785-7652-5 (On-line version)
Web Site: http://www3.gov.ab.ca/env/info/infocentre/publist.cfm

Any comments, questions, or suggestions regarding the content of this document may be directed to:

Environmental Policy Branch
Alberta Environment
10th Floor, Oxbridge Place
9820 – 106th Street
Edmonton, Alberta T5K 2J6
Fax: (780) 422-4192

Additional copies of this document may be obtained by contacting:

Information Centre
Alberta Environment
Main Floor, Oxbridge Place
9820 – 106th Street
Edmonton, Alberta T5K 2J6
Phone: (780) 427-2700
Fax: (780) 422-4086
Email: env.infocent@gov.ab.ca

FOREWORD

Alberta Environment maintains Ambient Air Quality Objectives[1] to support air quality management in Alberta. Alberta Environment currently has ambient objectives for more than thirty substances and five related parameters. These objectives are periodically updated and new objectives are developed as required.

With the assistance of the Clean Air Strategic Alliance, a multi-stakeholder workshop was held in October 2004 to s*et al*berta's priorities for the next three years. Based on those recommendations to Alberta Environment, a three-year work plan was developed to review four existing objectives, and create three new objectives.

This document is one in a series of documents that presents the scientific assessment for these substances.

Laura Blair
Project Manager
Environmental Policy Branch

ACKNOWLEDGEMENTS

The authors of this report would like to thank Laura Blair of Alberta Environment for inviting the submission of this assessment report. Toxico-Logic Consulting Inc. would like to acknowledge and thank the following authors who participated in the completion of this report.

Dr. Selma Guigard
Edmonton, Alberta

Dr. Warren Kindzierski
WBK & Associates Inc.
St. Albert, Alberta

Colleen Purtill
Toxico-Logic Consulting Inc.
Calgary, Alberta

Jason Schulz
Edmonton, Alberta

Dr. John Vidmar
Edmonton, Alberta

TABLE OF CONTENTS

LIST OF TABLES

ACRONYMS AND ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
AENV	Alberta Environment
ATSDR	Agency for Toxic Substances and Disease Registry
BMC	Benchmark Concentration
California OEHHA	California Office of Environment and Health Hazard Assessment
CCME	Canadian Council of Ministers of the Environment
CEPA	Canadian Environmental Protection Act
DOAS	Differential Optical Absorption Spectroscopy
EC	Environment Canada
ECB	European Chemicals Bureau
FTIR	Fourier Transform Infrared Absorption
GLP	Good Laboratory Practice
HF	Hydrogen Fluoride
HSDB	Hazardous Substances Database
IARC	International Agency for Research on Cancer
LOAEL	Lowest Observable Adverse Effect Level
MRL	Minimum Risk Level
MOE	Ministry of the Environment
MW	Molecular Weight
NIOSH	National Institute for Occupational Safety and Health
NOAEL	No Observable Adverse Effect Level
NPRI	National Pollutant Release Inventory
NTP	National Toxicology Program
OECD	Organization for Economic Cooperation and Development
OEHHA	Office of Environment and Health Hazard Assessment
OEL	Occupational Exposure Limit
REL	Recommended Exposure Limit (NIOSH) Reference Exposure Level (California OEHHA)
SCE	Sister Chromatid Exchange
STEL	Short-Term Exposure Limit
TDLAS	Tunable Diode Laser Absorption Spectroscopy
TISAB	Total Ionic Strength Activity Buffer
TLV	Threshold Limit Value
TWA	Time Weighted Average
US EPA	United States Environmental Protection Agency
UV/VIS	Ultraviolet/Visible
WHO	World Health Organization

SUMMARY

Hydrogen fluoride (HF) is a highly water soluble gas with a strong, irritating odour. It is used in many industrial processes, including the manufacture of fluorocarbons and the production of aluminum fluorides and synthetic cryolite (aluminum industry). Hydrogen fluoride is also used in the fluoridation of drinking water. Upon release to the atmosphere, hydrogen fluoride will dissolve into atmospheric water (rain, fog, snow and clouds) to form hydrofluoric acid, which is then removed from the air by wet deposition. No data were available regarding the half-life of hydrogen fluoride in air.

Natural sources of hydrogen fluoride include emissions from volcanoes and oceans (marine aerosols), fires, and dusts from soils and rock weathering. Anthropogenic emissions of inorganic fluorides (which include hydrogen fluoride and other fluoride-containing compounds such as sulphur hexafluoride, calcium fluoride, and sodium fluoride) are responsible for most of the hydrogen fluoride present in the atmosphere; these include combustion of fluoride-containing coal for electricity, non-industrial fuel combustion sources, and incineration of fluoride containing wastes. Industrial processes that emit hydrogen fluoride include aluminum smelting (major source), petroleum refining, steel, copper, nickel and magnesium production, brick and clay products manufacturing, and phosphate fertilizer production.

In Canada, anthropogenic hydrogen fluoride emissions are tracked by the Environment Canada (EC) National Pollutant Release Inventory (NPRI) program. The industrial sectors that contribute to hydrogen fluoride emissions in Alberta are the power generation sector, the chemical fertilizer sector and the refined petroleum products sector.

Ambient air concentrations for inorganic fluorides are <0.1 $\mu g/m^3$ in remote areas and rarely exceed 2 to 3 $\mu g/m^3$ in the vicinity of hydrogen fluoride emission sources or in urban areas. Inorganic fluoride air concentrations (predominantly hydrogen fluoride) in the vicinity of aluminum smelters in Quebec ranged from 0.1 to 0.7 $\mu g/m^3$; mean ambient inorganic fluoride air concentrations at other Canadian sites in the vicinity of emissions sources (such as an aluminum plant, a phosphate fertilizer plant, or a brick manufacturing plant), did not exceed 0.85 $\mu g/m^3$.

In humans and animals, toxicity endpoints associated with acute (<24 hours) inhalation exposure to hydrogen fluoride include irritation of the eye and upper respiratory tract and irritation of the lower respiratory tract at higher exposure concentrations (>1000 $\mu g/m^3$). These symptoms were reversible within a week of cessation of exposure. The current Alberta objective for acute exposures to hydrogen fluoride (1-hr average) is 4.9 $\mu g/m^3$. This objective was adopted from Texas and appears to be based on the 15-minute short-term exposure limit (STEL) recommended by the National Institute of Occupational Health and Safety (NIOSH) (*i.e.,* 5 mg/m^3) divided by a safety factor of one thousand.

The subchronic No Observable Adverse Effect Level (NOAEL) for rats exposed to hydrogen fluoride (720 $\mu g/m^3$) was comparable to the lowest acute Lowest Observable Adverse Effect Level (LOAEL) value for mild respiratory effects in humans (*i.e.,* 400 $\mu g/m^3$). Similar LOAEL values were identified for respiratory irritation in humans over a range of exposure durations

(from 1 hour to 6 hr/d, 6 d/wk over a 15 to 50 day period). The lowest acute LOAEL value for mild respiratory effects in humans was selected by the Agency for Toxic Substances and Disease Registry (ATSDR) to develop an acute Minimum Risk Level (MRL) of 16 µg/m^3. Considering the data available for respiratory effects in humans and animals following acute and subchronic exposure to hydrogen fluoride, this MRL is likely protective of the respiratory system in situations of longer (subchronic) exposure durations.

Subchronic and chronic exposure to fluorides (by inhalation or ingestion) results in the uptake of fluoride into bone. High fluoride bone concentrations have been correlated with the occurrence of skeletal fluorosis. One chronic occupational exposure study identified a NOAEL of 480 µg/m^3 fluorides (including hydrogen fluoride) for skeletal fluorosis in workers exposed up to 10 years in the potroom of aluminum smelters. In rats, a subchronic NOAEL of 720 µg/m^3 hydrogen fluoride was reported for the absence of skeletal effects. A NOAEL of 1,070 µg/m^3 was recommended by the California Office of Environment and Health Hazard Assessment (OEHHA) for the occurrence of skeletal fluorosis following occupational (human) exposure to fluorides (including hydrogen fluoride). The California OEHHA developed a chronic Reference Exposure Limit (REL) of 14 µg/m^3 for hydrogen fluoride based on the occurrence of skeletal fluorosis.

Atmospheric hydrogen fluoride is directly deposited on vegetation and can be absorbed by plant roots and translocated to the leaf tissue. Visible symptoms attributed to phytotoxic hydrogen fluoride exposure include chlorosis (degradation of photosynthetic pigments chlorophyll a and b which results in leaf yellowing) and necrosis (cell death) due to loss of cell integrity. Plant growth rate has also been demonstrated to be adversely affected by hydrogen fluoride exposure. Extensive studies on the phytotoxicity of hydrogen fluoride report interspecies and intraspecies differences in sensitivity. Wheat, barley and canola are important agricultural species for Alberta, however, limited data were available for hydrogen fluoride exposure to wheat and barley, and no data on hydrogen fluoride exposure to canola were identified.

Exposure of wheat (*Triticum aestivum* cv. Halberd) and barley (*Hordeum vulgare* cv. Clipper) plants to 0.38 µg/m^3 HF for 90 days decreased the number of barley seeds per tiller (which was offset by an increase of tillers) but did not affect the yield of wheat. A significant reduction in mean dry biomass was reported in wheat (cv. Olaf) exposed to 0.9 µg/m HF for 4 days. Reference air concentrations for hydrogen fluoride in ambient air have been established by the Canadian Council of Ministers of the Environment (CCME) based on the potential for effects in vegetation. Reference levels recommended for 24 hour, 7 day, and 30 to 90 day averages are 1.1 µg/m^3, 0.5 µg/m^3, and 0.4 µg/m^3, respectively.

Air sampling and analytical methods for hydrogen fluoride used by regulatory agencies were included in this assessment. Standard air monitoring methods for hydrogen fluoride are based on active or pump-and-tube sampling approaches that are followed by various analytical techniques. Widely employed and accepted reference air monitoring methods for hydrogen fluoride have been developed, tested and reported by the National Institute of Occupational Safety and Health

National ambient air quality objectives of 1.1 µg/m^3 (24-hour average), 0.5 µg/m^3 (7-day average), and a vegetation limit of 30 µg/g fluoride per gram dry weight have been developed for

hydrogen fluoride by the CCME. Provincial guidelines include an objective of 4.9 $\mu g/m^3$ in Alberta (1-hour average), criteria of 0.85 $\mu g/m^3$ (24-hour average), 0.55 $\mu g/m^3$ (7-day average), 0.35 $\mu g/m^3$ (30-day average), and 0.20 $\mu g/m^3$ (70-day average) in Manitoba, a criterion of 0.86 $\mu g/m^3$ (24-hour average). Ontario has developed nine standards for averageing times of 30 minutes, 24 hours and 30 days for fluorides as HF (refer to Appendix B for details).

The air quality criteria recommended for hydrogen fluoride by the CCME, Manitoba Conservation, and Ontario Ministry of the Environment are based on accumulation and effects in vegetation. Air quality criteria established internationally for hydrogen fluoride (agencies in the United States and the World Health Organization (WHO)) were also reviewed. The ATSDR has developed an acute Minimum Risk Level of 16 $\mu g/m^3$, based on studies of respiratory irritation in humans. The WHO derived an acute (1-hour average) reference exposure level of 600 $\mu g/m^3$ using a benchmark dose approach to a variety of animal and human exposure studies.

The acute exposure guideline for California and Minnesota (240 $\mu g/m^3$ over 1-hour) is based on respiratory irritation effects in humans. California was the only agency to develop a chronic reference exposure level of 14 $\mu g/m^3$ based on an endpoint of increased bone density (skeletal fluorosis) in exposed workers.

In the U.S., six states derived ambient air quality objectives for hydrogen fluoride using occupational exposure limits (OEL). Louisiana, Michigan, and Ohio derived their ambient air guidelines from the American Conference of Governmental Industrial Hygienists (ACGIH) 15-minute STEL of 3.2 mg/m^3 (3 ppm). Massachusetts and Oklahoma derived their ambient air guideline from the NIOSH Recommended Exposure Limit (REL) of 2.5 mg/m^3 (8-hour average). Texas used the NIOSH 15-minute STEL of 5 mg/m^3 to derive ambient air guidelines. The basis for ambient air guidelines derived for eight states (Arizona, New Hampshire, North Carolina, Pennsylvania, Rhode Island, Vermont, Washington, and Wisconsin) could not be identified.

1.0 INTRODUCTION

Ambient air quality objectives are established by Alberta Environment as part of the Alberta air quality management system, Section 14 of the Environmental Protection and Enhancement Act (AENV, 2000). The purpose of this assessment report was to provide a review of scientific and technical information to assist in evaluating the basis and background for an ambient air quality objective for hydrogen fluoride. The following aspects were examined as part of the review:

- Physical and chemical properties;
- Existing and potential anthropogenic emissions sources in Alberta;
- Effects on humans, animals, and vegetation;
- Monitoring techniques, and;
- Ambient air guidelines and objectives in other jurisdictions.

The physical and chemical properties identified for hydrogen fluoride include chemical structure, molecular weight, melting and boiling points, water solubility, density, organic carbon partition coefficient, octanol water partition coefficient, vapour pressure, Henry's Law constant, and odour threshold. A discussion of the atmospheric fate of hydrogen fluoride was also presented.

Existing and potential natural and anthropogenic sources of hydrogen fluoride and inorganic fluoride (which include hydrogen fluoride and other fluoride-containing compounds such as sulphur hexafluoride, calcium fluoride, and sodium fluoride) emissions in Canada and Alberta were examined. Hydrogen fluoride is a reportable substance on Environment Canada's National Pollutant Release Inventory.

Scientific information about the effects of hydrogen fluoride on humans, animals, and vegetation were identified. Toxicity and epidemiology studies were located in peer-reviewed evaluations by the Agency for Toxic Substances and Disease Registry, the World Health Organization and the European Chemicals Bureau. Data on the effects of hydrogen fluoride on vegetation were identified from publications under the Canadian Environmental Protection Act, by the World Health Organization, and from the Web of Science database.

Air sampling and analytical methods for hydrogen fluoride used in practice by regulatory agencies were included in this assessment. Widely employed and accepted reference air monitoring methods for hydrogen fluoride have been developed, tested and reported by the National Institute of Occupational Safety and Health. These methods, as well as alternative, emerging technologies were included in this review.

Ambient air guidelines for hydrogen fluoride are used by a number of jurisdictions in North America for different averaging-time periods. These guidelines were developed using various endpoints, including effects on vegetation, respiratory effects in controlled human exposure studies, or occupational exposure levels adjusted by safety or adjustment factors. The basis for how these approaches are used by different jurisdiction to develop guidelines was investigated in this report.

2.0 GENERAL SUBSTANCE INFORMATION

Hydrogen fluoride (HF) is a colourless gas that fumes in air (O'Neil, 2001) with a strong, irritating odour (Genium, 1999). Anhydrous hydrogen fluoride, one of the most acidic substances known (O'Neil, 2001) is produced by reacting sulphuric acid with fluorspar (CaF_2) (ATSDR, 2003). Hydrogen fluoride is used in many industrial processes, the two most important uses being in the manufacturing of fluorocarbons and in the aluminum industry, for producing aluminum fluorides and synthetic cryolite (Aigueperse, 2001). Hydrogen fluoride is also used as a catalyst in gasoline alkylation, as a pickling agent for stainless steel and as a reactant in the manufacturing of uranium hexafluoride, fluorine containing plastics and other fluorides (Aigueperse, 2001; Genium, 1999). Other uses include in the fluoridation of drinking water; in the etching and frosting of glass and enamel; in the production of ceramics; in the cleaning and polishing of cast iron; and in the enamelling and galvanizing of iron (Genium, 1999).

Table 1 provides a list of important identification numbers and common synonyms for hydrogen fluoride.

Table 1 Identification of Hydrogen Fluoride

Property	Value
Formula	HF
Structure	H – F
CAS Registry number	7664-39-3
RTECS number	MW7875000
UN Number	UN1052 (hydrogen fluoride, anhydrous) UN1786 (Hydrofluoric and sulfuric acid mixtures) UN1790 (hydrofluoric acid solution)
Common Synonyms/Tradenames	anhydrous hydrofluoric acid; anhydrous hydrogen fluoride; antisal 2B; aqueous hydrogen fluoride; EPA pesticide chemical code 045601; fluorhydric acid; hydrofluoric acid gas; hydrofluoride; hydrogen fluoride, anhydrous; rubigine

2.1 Physical, Chemical and Biological Properties

The physical and chemical properties of hydrogen fluoride are summarized in Table 2.

Table 2 Physical and Chemical Properties of Hydrogen Fluoride

Property	Value	Reference
Molecular Weight (MW)	20.006 g/mole	Lide, 2004
Physical state	Colourless gas Colourless, fuming gas or liquid	Lide, 2004 Lewis, 2002
Melting Point	-83.85 ˚C	Lide, 2004
Boiling Point	20 ˚C	Lide, 2004
Density (liquid)	0.991 $g.mL^{-1}$ (at 19.5˚C) 0.970 $g.mL^{-1}$ (at 20˚C) 0.958 $g.mL^{-1}$ (at 25˚C)	ATSDR, 2003 Aigueperse, 2001 Smith, 2003
Density (gas)	0.818 $g.L^{-1}$ (at 25˚C and P=1atm) 0.878 $g.L^{-1}$ (at 25˚C and P=1atm)	Lide, 2004 RSC, 2005
Vapour pressure	122.9 MPa 400 mm Hg at 2.5˚C	Smith, 2003 Lewis, 2000
Solubility in water	very soluble in water	Lide, 2004; O'Neil, 2001
Solubility	very soluble in ethanol slightly soluble in ethyl ether soluble in many organic solvents	Lide, 2004 Lide, 2004 O'Neil, 2001
pKa (in aqueous solution)	3.19	O'Neil, 2001
Henry's Law Constant	0.104 $atm.L.mol^{-1}$	ATSDR, 2003
Octanol water partition coefficient (log K_{ow})	No data 0.23	ATSDR, 2003 MOE, 2005
Organic carbon partition coefficient (K_{oc})	Not relevant	ATSDR, 2003
Flash Point	Not flammable -37.8˚C	ATSDR, 2003 MOE, 2005
Explosive limits	No data	ATSDR, 2003
Autoignition temperature	No data	ATSDR, 2003
Odour threshold	0.5 to 3ppm 30 $\mu g/m^3$	ATSDR, 2003 MOE, 2005
Conversion factors for vapour (at 25 °C and 101.3 kPa)	1 mg/m^3 = 1.223 ppm 1 ppm = 0.82 mg/m^3	ATSDR, 2003

2.2 Environmental Fate

The environmental fate of hydrogen fluoride is described in ATSDR (2003). It should be noted that since hydrogen fluoride is extensively used in industrial processes, hydrogen fluoride is the greatest fluoride air contaminant (WHO, 1984). Once in the air, hydrogen fluoride will dissolve into atmospheric water (rain, fog, snow and clouds) to form hydrofluoric acid, which is then removed from the air by wet deposition (ATSDR, 2003). ATSDR (2003) reports that no data is available regarding possible reactions of hydrogen fluoride with other compounds present in the atmosphere. No data regarding the half-life for hydrogen fluoride in air are available (ATSDR, 2003).

3.0 EMISSION SOURCES AND INVENTORIES

3.1 Natural Sources

Natural sources of hydrogen fluoride include emissions from volcanoes and emissions from oceans in the form of marine aerosols (ATSDR, 2003; United States Environmental Progection Agency (US EPA), 1998; WHO, 2002, 1984). Of these two sources, volcanic eruptions are the largest natural source of hydrogen fluoride, with releases estimated at 0.6 to 6 million metric tones per year (Symonds *et al.,* 1988). It should be noted that volcanic eruptions release hydrogen fluoride directly into the atmosphere but these eruptions also release other fluoride-containing species, which react in the atmosphere to produce hydrogen fluoride (US EPA, 1998). Fluoride emissions from marine aerosols are estimated at 20 kilotonnes per year (Symonds *et al.,* 1988). Other natural sources of hydrogen fluoride include fires (US EPA, 1998) and dusts from soils and rock weathering (US EPA, 1998; WHO, 1984).

3.2 Anthropogenic Sources

Most of the hydrogen fluoride present in the atmosphere is the result of anthropogenic activities (WHO, 1984). Anthropogenic sources include industrial sources, non-industrial fuel combustion sources (ATSDR, 2003; WHO, 1984) and incineration of fluoride containing wastes (ATSDR, 2003). Industrial activities include aluminum smelting; petroleum refining; steel, copper, nickel and magnesium production; brick and clay products manufacturing; and phosphate fertilizer production (ATSDR, 2003; MOE, 2005). Combustion of fluoride-containing coal for electricity generation leads to hydrogen fluoride emissions that have been estimated to range between 0.01 and 0.12 kg of hydrogen fluoride per Mg of coal (ATSDR, 2003). Finally, the incineration of municipal wastes containing fluoride will also release hydrogen fluoride (ATSDR, 2003).

Of these anthropogenic activities, the burning of coal in coal-fired power plants is the single largest anthropogenic source of hydrogen fluoride to the atmosphere in the Unites States (ATSDR, 2003). For Canada, anthropogenic emissions of inorganic fluorides (which include hydrogen fluoride and other fluoride-containing compounds such as sulphur hexafluoride, calcium fluoride, and sodium fluoride) were surveyed under the Canadian Environmental Protection Act (CEPA) by Environment Canada (as cited in EC, 1993) and are summarized in Table 3. It should be noted that the emissions for certain sectors surveyed in Table 3 may be underestimated since a limited number of facilities reported their emissions.

According to the data presented in Table 3, approximately 24% of the total inorganic fluoride emissions are to air (predominantly in the form of hydrogen fluoride), 58% to water and 19% land (EC, 1993). The industrial sectors contributing the most to air emissions of fluoride are aluminum production sector and coal-burning utilities sector.

Table 3 Estimates of Inorganic Fluoride Emissions in Canada according to Environment Canada, 1993 (adapted from EC, 1993)

Industrial Sector	Annual Release (in tonnes)			Total Release	
	Air	Water	Land	In tonnes	% of total
Phosphate Fertilizer Producers	108	10959	75	11141	48
Chemical Producers	305	1362	3077	4745	20
Primary Aluminum Producers	4063	307	NR	4370	19
Coal-Burning Utilities	543	555	NR	1098	5
Steel Producers	239	254	430	922	4
Oil Refining	24	100	784	908	4
Primary Copper and Nickel Producers	26	4	186	216	0.9
Magnesium Producers	100	NR	NR	100	0.4
Clay Products	25	NR	NR	25	0.1
Others	-	1	2	3	0.01
Total	5433	13541	4554	23529	100

NR = not reported

Emissions of hydrogen fluoride in Canada are also provided in the 2003 NPRI database (EC, 2005). Tables 4 and 5 summarize hydrogen fluoride emissions for Alberta: Table 4 summarizes the hydrogen fluoride emissions to air, land and water and Table 5 provides details specifically related to air emissions of hydrogen fluoride. Data for other Canadian provinces are presented in Appendix A. The results in Tables 4 and 5 show that, in Alberta, the NPRI reported emissions of hydrogen fluoride are almost exclusively to air, and these air emissions are predominantly the result of stack or point source emissions. The industrial sectors that contribute to hydrogen fluoride emissions in Alberta are the power generation sector, the chemical fertilizer sector and the refined petroleum products sector.

3.3 Ambient Levels

Ambient air concentrations for inorganic fluorides are presented in ATSDR (2003), WHO (2002), EC (1996), and EC (1993), however no data specific to locations in Alberta were provided. In remote areas, that is, in rural areas or in areas not in the direct vicinity of emission sources, atmospheric fluoride concentrations typically do not exceed 0.1 $\mu g/m^3$ (ATSDR, 2003). Ambient air concentrations in the vicinity of hydrogen fluoride emission sources or in urban areas rarely exceed 2 to 3 $\mu g/m^3$ (ATSDR, 2003). For example, ambient inorganic fluoride air concentrations (predominantly hydrogen fluoride) in the vicinity of aluminum smelters in Quebec ranged from 0.1 to 0.7 μgm^3 (EC, 1993). For several other Canadian sites in the vicinity of emissions sources (such as an aluminum plant, a phosphate fertilizer plant, or a brick manufacturing plant), mean ambient inorganic fluoride air concentrations did not exceed 0.85 $\mu g/m^3$ (EC, 1993).

Table 4 Total Hydrogen Fluoride Emissions in Alberta According to the 2003 NPRI Database (EC, 2005) (in tonnes, ranked by total emissions)

NPRI ID	Company	City	Hydrogen Fluoride Emissions (tonnes)			
			Air	Water	Land	Total
2284	TransAlta Utilities Corporation	Duffield	378.072	0	0	378.072
267	EPCOR Generation Inc.	Warburg	295.191	0	0	295.191
2282	TransAlta Utilities Corporation	Wabamun	145.275	0	0	145.275
2286	TransAlta Utilities Corporation	Duffield	138.495	0	0	138.495
1039	ATCO Power	Grande Cache	69.419	0	0	69.419
1033	ATCO Power	Forestburg	60.03	0	0	60.03
1036	Sheerness Station	Hanna	29.02	0	0	29.02
2134	Agrium Products Inc.	Redwater/Municipal District of Sturgeon	19.4	0	0	19.4
3707	Imperial Oil	Edmonton	0.03	0	0	0.03
3903	Petro-Canada	Edmonton	0	0	0	0.005

Table 5 Hydrogen Fluoride Air Emissions in Alberta According to the 2003 NPRI Database (EC, 2005) (in tonnes, ranked by total emissions)

NPRI ID	Company	City	Hydrogen Fluoride Emissions (tonnes)					
			Stack /Point	Storage /Handling	Fugitive	Spills	Other Non-Point	Total
2284	TransAlta Utilities Corporation	Duffield	378.072	0	0	0	0	378.072
267	EPCOR Generation Inc.	Warburg	295.191	0	0	0	0	295.191
2282	TransAlta Utilities Corporation	Wabamun	145.275	0	0	0	0	145.275
2286	TransAlta Utilities Corporation	Duffield	138.495	0	0	0	0	138.495
1039	ATCO Power	Grande Cache	69.419	0	0	0	0	69.419
1033	ATCO Power	Forestburg	60.03	0	0	0	0	60.03
1036	Sheerness Station	Hanna	29.02	0	0	0	0	29.02
2134	Agrium Products Inc.	Redwater/Municipal District of Sturgeon	4.1	0	15.3	0	0	19.4
3707	Imperial Oil	Edmonton	0	0	0	0	0.03	0.03
3903	Petro-Canada	Edmonton	0	0	0	0	0	0

4.0 EFFECTS ON HUMANS AND ANIMALS

The following is a summary of the available toxicological and epidemiology studies on the health effects of hydrogen fluoride (hydrogen fluoride) focusing on inhalation exposures. The primary literature sources for this assessment of health effects in humans and animals were derived from publications by the Agency for Toxic Substances and Disease Registry (ATSDR, 2003), the World Health Organization International Programme on Chemical Safety (WHO, 2002), and the European Chemicals Bureau (ECB, 2001).

4.1 Overview of Chemical Disposition

The following is a summary of the chemical disposition of hydrogen fluoride in humans and animal systems focusing on the inhalation route of exposure. Because hydrogen fluoride is a very water soluble gas, it is retained by the film of fluid covering the mucosa of the nose, which acts as a "scrubber" protecting the lungs from potentially injurious exposures (Klaassen, 2001). Inhalation studies conducted in rats and humans confirm that hydrogen fluoride is absorbed into the bloodstream via the upper airways following acute exposure periods (40 to 60 minutes) (ECB, 2001 and ATSDR, 2003). In humans, a linear relationship was determined between fluoride exposure and plasma fluoride concentrations at air concentrations greater than 0.7 mg/m^3; maximum plasma concentrations occurred 60 to 120 minutes following the start of exposure (Lund *et al.,* cited in ECB, 2001). In male Long Evans rats exposed via inhalation (head only) to 30 to 176 mg/m^3 (40 minutes intermittent exposure), absorption occurred primarily in the upper respiratory tract (>99%), with very little hydrogen fluoride reaching the lungs (Morris and Smith, cited in ATSDR, 2003; ECB, 2001; and (Hazardous Substances Database) HSDB, 2005). This study also reported a linear relationship between the hydrogen fluoride exposure concentration in air and plasma hydrogen fluoride concentration in rats.

The inhalation of hydrogen fluoride results in increased blood fluoride concentrations and the systemic transport of fluoride. The majority of fluoride is present in the plasma with the remaining associated with red blood cells. About half the serum concentration of fluoride is non-ionic as a result of binding to organic molecules (ECB, 2001).

Free fluoride (unbound) primarily exists as fluoride ion (F^-) at physiological pH (ECB, 2001). The fate or effects of absorbed inorganic fluoride are not affected by the source of fluoride (e.g., hydrogen fluoride, sodium fluoride) (Thiessen, cited in ECB, 2001). Fluoride is distributed throughout soft tissues with approximately half of the absorbed fluoride ion accumulated by the bone structure (ECB, 2001) and the remaining concentrated in the thyroid, aorta, and perhaps the kidney (Hardman *et al*. cited in HSDB, 2005). Fluoride is taken up and stored in the bone matrix (bone and teeth) due to its similarity in size and charge with the hydroxyl ion (OH^-) which results in the displacement of OH^- (and possibly the bicarbonate ion HCO_3^-) in the hydroxyapatite lattice matrix of bone mineral and the formation of hydroxyfluorapatite (Klaassen, 2001; ATSDR, 2003). The degree to which fluoride is stored in the skeleton is related to both intake and age (Hardman *et al.* cited in HSDB, 2005).

Fluoride is transported from the maternal circulation across the placenta to the developing fetus and is readily taken up into fetal bones and teeth (Shen and Taves, cited in WHO, 2002). Fluoride is eliminated in breast milk (Hardman *et al*. cited in HSDB, 2005).

The kidneys are the primary route of fluoride excretion, which can be enhanced by decreased urine acidity (ECB, 2001). Approximately 90% of the fluoride ion filtered by the glomerulus is reabsorbed by renal tubules (Hardman *et al*. cited in HSDB, 2005). Minor routes of fluoride elimination include feces, saliva, sweat, and milk (ECB, 2001; HSDB, 2005). In humans, plasma fluoride half-lives ranging from 2 to 9 hours have been reported while the half-life for bone fluoride is in the range of 8 to 20 years (WHO, cited in ECB, 2001).

4.2 Genotoxicity

The following discussion of genotoxicity includes studies on both hydrogen fluoride and sodium fluoride (NaF) as the data set for hydrogen fluoride was limited and the effects of absorbed hydrogen fluoride and sodium fluoride are both attributable to fluoride (ECB, 2001). Several *in vivo* inhalation studies conducted on *Drosophila*, rats, and mice were identified for hydrogen fluoride.

4.2.1 In vitro genotoxicity

4.2.1.1 Gene mutations

A number of in vitro assays involving exposure of prokaryotic cells (*Salmonella typhimurium*) to fluorides (hydrogen fluoride and sodium fluoride) were negative for gene mutation with and without metabolic activation (Martin *et al.* cited in ATSDR, 2003; Li *et al*.; Tong *et al*.; National Toxicology Program (NTP); Zeiger *et al.* cited in WHO, 2002 and Bayer AG, cited in ECB, 2001).

In eukaryotic cells, an increased frequency of mutations at specific loci (thymidine kinase locus) in cultured mouse lymphoma and human lymphoblastoid cells exposed to sodium fluoride (Cole *et al.*; Caspary *et al.*; Crespi *et al.*; Moore *et al.,* cited in WHO, 2002) was attributed to chromosomal damage rather than point mutations (WHO, 2002).

Sodium fluoride did not increase the frequency of mutations at specific loci (hypoxanthine–guanine phosphoribosyl transferase) in rat liver epithelial cells, Chinese hamster ovary cells or Chinese hamster lung cells exposed under neutral or acidic conditions (Tong *et al.*; Oberly *et al.*; Slamenova *et al.,* cited in WHO, 2002).

4.2.1.2 Clastogenicity

Chromosomal aberrations were reported in many *in vitro* cytogenetic assays involving sodium fluoride; the aberrations were primarily breaks/deletions and gaps, with very few sister chromatid exchanges (WHO, 2002).

An increased frequency in chromosomal aberrations occurred in Chinese hamster lung cells, Chinese hamster ovary cells, Syrian hamster embryo cells, rat vertebral body-derived cells, rat bone marrow cells, human leukocytes, human peripheral blood lymphocytes, human fibroblasts, human amnion (F1) cells, human and chimpanzee lymphoid cells and human oral keratinocytes following sodium fluoride exposure (Bale and Mathew; Aardema *et al*.; NTP; Tsutsui *et al*.; Mihashi and Tsutsui; Khalil; Jachimczak and Skotarczak; Kishi and Tonomura; Albanese; Tsutsui *et al*.; Scott; Scott and Roberts; Suzuki and Tsutsui; Aliev *et al*.; Kishi and Ishida; Tsutsui *et al.* cited in WHO, 2002).

Negative results reported by some authors for chromosomal aberrations in human lymphocytes exposed to fluoride (Gebhart *et al*.; Thomson *et al*.; Gadhia and Joseph, cited in WHO, 2002), may be due to differences in the methodology used to assess clastogenic activity, including chromosomal aberrations, phase of the cell cycle during which the cells were exposed and the concentration of fluoride (WHO, 2002).

An increase in sister chromatid exchange (SCE) was reported in studies on Syrian hamster embryo cells and Chinese hamster ovary cells exposed to sodium fluoride (Tsutsui *et al*.; NTP, cited in WHO, 2002) but not in studies on human peripheral blood lymphocytes, Chinese hamster ovary cells or rat bone marrow cells exposed to sodium fluoride (Kishi and Tonomura; Thomson *et al*.; Tong *et al*.; Gadhia and Joseph; Li *et al*.; Tong *et al*.; Khalil and Da'dara, cited in WHO, 2002). The inconsistency in these results may in part be due to differences in harvest times used to accommodate cell cycle delay (WHO, 2002). Sister chromatid exchange assays indicate mutagen exposure, analogous to DNA damage and repair assays, but are not measures of a mutagenic effect; the uncertainty associated with the mechanisms by which SCEs are formed and how DNA damage or perturbations of DNA synthesis stimulate their formation make the data on SCE less informative than chromosome aberrations (Klaassen, 2001).

Overall, the data available for the clastogenicity of fluoride are consistent with an inhibition of DNA synthesis and/or repair which suggests that fluoride exposure affected the synthesis of proteins involved in DNA synthesis and/or repair, rather than directly acting on DNA (WHO, 2002).

Positive findings occurred at toxic doses of fluoride (ATSDR, 2003). In the case of sodium fluoride, concentrations at or below 10 mg/L did not induce chromosomal aberrations in human fibroblasts, Chinese hamster ovary cells or human diploid lung cells (Scott; Scott and Roberts; Aardema; Oguro; Tsutsui, cited in WHO, 2002). In Chinese hamster lung cells, sodium fluoride concentrations at or below 500 mg/litre did not induce chromosomal aberrations (Ishidate, cited in WHO, 2002).

4.2.1.3 DNA Damage and Repair Assays

Sodium fluoride exposure increased unscheduled DNA synthesis in Syrian hamster embryo cells, human foreskin fibroblasts and human keratinocytes (Tsutsui *et al.* cited in WHO, 2002), however, these results were later determined to likely be the result of the formation of precipitable complexes of magnesium, fluoride and [^{3}H]thymidine triphosphate (Skare *et al.* cited in WHO, 2002).

4.2.2 In vivo genotoxicity

4.2.2.1 Non-mammalian eukaryotes

A study of reproductive parameters in the fly *Drosophila melanogaster* reported significant reductions in the number of eggs per female and male fertility following inhalation exposure to hydrogen fluoride (Gerdes *et al.* cited in ATSDR, 2003), however, the tests were not properly reported and inconclusive in terms of genotoxicity (ECB, 2001). Another test in *Drosophila melanogaster* showed that hydrogen fluoride exposure reduced the viability of F2 offspring homozygous for chromosome II (Mohamed, cited in ECB, 2001) again; these study results could not be interpreted in terms of genotoxicity (ECB, 2001).

4.2.2.2 Clastogenicity

Inhalation exposure of rats to 1 mg/m^3 of hydrogen fluoride (6 hours/day, 6 days/week over 1 month) resulted in chromosomal aberrations (hyperploidy) in bone marrow (Voroshilin *et al.* cited in ATSDR, 2003 and ECB, 2001).

Intraperitoneal injection of sodium fluoride resulted in cytogenetic damage in rodent bone marrow or sperm cells (Ma *et al.*; Pati and Bhunya, cited in WHO, 2002) but did not result in cytogenetic damage in mice (Hayashi *et al.* cited in WHO, 2002).

In many studies involving oral administration of sodium fluoride (acute or chronic) to rodents, no significant effects were reported for sperm morphology, the frequency of chromosomal aberrations, micronuclei, SCE or DNA strand breaks (Martin *et al.*; Skare *et al.*; Albanese; Li *et al.*; Pillai *et al.*; Dunipace; Lu *et al.*; Zeiger *et al.* cited in WHO, 2002). However, other studies on rodents reported positive results for these endpoints following oral exposure to sodium fluoride (Akhundow *et al.*; Aliev and Babaev; Mohammed and Chandler; Ma *et al.*; Pati and Bhunya, cited in WHO, 2002).

No alterations in the occurrence of SCE were observed in humans exposed to high levels of fluoride in their drinking water (4.8 ppm), (Li *et al.* cited in ATSDR, 2003). No increase in SCE was reported in a case-control study of osteoporotic women receiving 23 mg elemental fluoride daily over 18 months (Jackson *et al.* cited in ECB, 2001).

4.2.2.3 Germ cell mutagenesis

An *in vivo* study of C57B1 mice exposed via inhalation to hydrogen fluoride did not detect dominant lethal mutations (Voroshilin *et al*. 1975, cited in ATSDR, 2003).

4.3 Carcinogenicity

There are currently no well-controlled human or animal studies available to assess the carcinogenic potential of hydrogen fluoride via inhalation (ECB, 2001; ATSDR, 2003). Occupational studies have examined the carcinogenicity of hydrogen fluoride and fluoride dust following inhalation by cryolite workers, aluminum industry workers, fluorspar miners, and individuals residing near or working in the steel industry (Grandjean *et al*.; Andersen *et al*.; Gibbs and Horowitz; Milham; Rockette and Arena; deVilliers and Windish; Cecilioni, cited in ATSDR, 2003). An increase in respiratory tract cancer rates was reported in several of these studies (Andersen *et al*.; deVilliers and Windish; Gibbs and Horowitz; Grandjean *et al*.; Milham, cited in ATSDR, 2003). The conclusions of all studies, however, were limited by a lack of adjustments for smoking and exposure to other carcinogenic compounds (ATSDR, 2003).

A number of studies have assessed the carcinogenicity of fluoride in humans following ingestion of drinking water (Cohn; Erickson; Freni and Gaylor; Gelberg *et al*.; Hoover *et al*; Kinlen and Doll; Mahoney *et al*.; McGuire *et al*.; Neuberger; Oldham and Newell; Rogot *et al*; Takahashi *et al*.; Taves; Yiamouyiannis and Burk, cited in ATSDR, 2003). The majority did not find significant increases in cancer risk, although some studies found positive results for bone cancer (Takahashi *et al*.; Yiamouyiannis and Burk, cited in ATSDR, 2003) particularly in young men (Cohn; Hoover *et al.,* cited in ATSDR, 2003). The International Agency for Research on Cancer (IARC, 1987) has determined that the carcinogenicity of fluoride to humans is not yet classifiable (ATSDR, 2003).

In a well-conducted chronic (2-year) ingestion study conducted under the National Toxicology Program (NTP, 1990), a weak, equivocal increase in the occurrence of osteosarcomas was reported for male rats exposed to sodium fluoride in drinking water (NTP, cited in WHO, 2002 and ATSDR, 2003). There was "no evidence of carcinogenic activity" in female rats exposed to sodium fluoride under the same conditions (NTP, cited in WHO, 2002). Pairwise comparison of the incidence of osteosarcomas in the high-dose male group versus the male controls was not statistically significant, however, the osteosarcomas did occur with a statistically significant dose–response trend (NTP, cited in WHO, 2002). In addition, while the incidence of osteosarcomas at any site was not statistically different from historical controls, “the amount of fluoride in the diets in previous National Toxicology Program (NTP) studies of other chemicals was uncontrolled and was estimated to be approximately 3.5- to 5.9-fold higher than in the NTP sodium fluoride study” (NTP, as cited in WHO, 2002). A similar chronic ingestion study of mice exposed to sodium fluoride in drinking water concluded "no evidence of carcinogenic activity" in male and female mice (NTP, cited in WHO, 2002).

A chronic ingestion study exposing Sprague-Dawley rats to sodium fluoride in the diet reported a higher but not statistically significant incidence of bone tumors in exposed rats compared to controls (Maurer *et al.,* cited in ATSDR, 2003). Earlier carcinogenicity bioassays of mice

exposed to sodium fluoride in drinking water or the diet did not report an increased incidence of tumours in exposed mice versus unexposed controls (Tannenbaum and Silverstone; Taylor; Kanisawa and Schroeder, cited in WHO, 2002).

A dose-related increase of fluoride content in bone was reported in all chronic ingestion studies (diet and drinking water) conducted in rats and mice (NTP; Mauer, cited in WHO, 2002). Bone fluoride levels were higher as a result of exposure to fluoride in the diet compared to exposure to fluoride in drinking water (ECB, 2001).

There are currently no well-conducted inhalation studies in animals or humans to determine the carcinogenicity of hydrogen fluoride. Reports of increased respiratory tract cancers following occupational exposures do not adjust for smoking or for concurrent exposure to other carcinogenic compounds in the workplace.

Several assessments of human exposure to high concentrations of fluoride in drinking water correlated fluoride exposure with an increased risk of bone cancer, particularly in young males. In their latest evaluation (1987) IARC determined that the carcinogenicity of fluoride to humans was not yet classifiable.

In well-conducted studies exposing rats and mice to sodium fluoride in drinking water, the NTP (1990) reported that osteosarcomas occurred in male rats with a statistically significant dose–response trend. NTP concluded "equivocal evidence of carcinogenic activity" in male rats, and "no evidence of carcinogenic activity" in female rats or in male or female mice exposed to Na F in drinking water.

The ATSDR (2003) has concluded that additional studies are needed to further evaluate the potential of fluoride exposure to induce bone cancers.

4.4 Acute and Subacute Effects

Acute exposure of experimental animals by inhalation generally refers to continuous exposure for a period of less than 24 hours while subacute exposure involves repeated exposure to a chemical for a period of 1 month or less. The frequency and duration of human exposures are generally not as clearly defined as controlled animal studies, but the same terms can be used to describe exposure situations. An acute workplace or environmental exposures is generally the result of a single incident or episode of exposure (Klaassen, 2001).

4.4.1 Acute and Sub-Acute Human Effects

Table 6 lists some of the reliable LOAEL values reported in humans following controlled acute exposures to hydrogen fluoride.

Table 6 LOAELs for Acute hydrogen fluoride Inhalation (Human)

Effects Reported[1]	Exposure Period	Air Concentration [2] ppm (mg/m^3)	Reference
Respiratory:			
Upper Respiratory Irritation LOAEL (less serious)	1 hr	0.5 (0.4)	Lund *et al*., cited in ATSDR, 2003.
Lower Respiratory Irritation LOAEL (less serious)	1 hr	1.9 (1.6)	Lund *et al*., cited in ATSDR, 2003.
Upper Airway Irritation and Inflammation LOAEL (less serious)	1 hr	4.2 (3.4)	Lund *et al*., cited in ATSDR, 2003.

[1]Less serious LOAEL as identified by ATSDR whereby, "…*less serious* effects are those that are not expected to cause significant dysfunction or death, or those whose significance to the organism is not entirely clear" (ATSDR, 2003)

[2] When both units of concentration were not provided in the literature, the following conversion factor and assumptions were used: 1 ppm = 0.82 mg/m^3 (ATSDR, 2003).

4.4.1.1 Respiratory Effects

Many case reports of human fatality or severe pulmonary effects involved both dermal and inhalation exposure to hydrogen fluoride as a result of splashing to the face and other regions (Bennion and Franzblau; Chan; Chela; Dieffenbacher and Thompson; Kleinfeld; Tepperman, cited in ATSDR, 2003). The effects associated with these fatalities (no exposure concentration estimated) include severe damage to the respiratory tract and lungs as evident by reports of tracheobronchitis, pulmonary edema, pulmonary hemorrhagic edema, and herrhagic alveolitis (ATSDR, 2003).

Symptoms of respiratory irritation (throat burning, shortness of breath, sore throat, and cough) were reported by residents of Texas City, Texas within 24 hours of an accidental release of hydrogen fluoride from a nearby industrial facility. Respiratory effects in "highly" exposed residents included severe breathing, throat, and nose problems; these effects were still prevalent 2 years after the accident (Dayal *et al*.; cited in ATSDR, 2003). This study suggests long-term damage to the respiratory tract resulting from acute exposure to hydrogen fluoride. The study is limited in that the term "severe symptom" was not defined by the authors, nor was there medical confirmation of self-reported symptoms (ATSDR, 2003).

An early study (1934) exposed 2 male volunteers to hydrogen fluoride concentrations of 26 mg/m^3 (32 ppm), 50 mg/m^3 (61 ppm), and 100 mg/m^3 (122 ppm) for periods of several minutes or shorter (Machle *et al.,* cited in ECB, 2001). Mild smarting in the nose and respiratory tract were reported at concentrations of 26 mg/m^3 (32 ppm), marked nasal mucosa irritation at 50 mg/m^3 (61 ppm), and respiratory irritation as well as pain in exposed skin were reported following minutes of exposure to 122 ppm (100 mg/m^3) hydrogen fluoride.

In more recent studies (1997, 1999, 2002), healthy male subjects were exposed under controlled conditions for 1-hour to hydrogen fluoride concentrations ranging from 0.5 ppm (0.4 mg/m^3) to

4.5 ppm (3.7 mg/m^3) (Lund *et al.,* cited in ATSDR, 2003). Males exposed to 0.5 ppm (0.4 mg/m^3) hydrogen fluoride for 1-hour reported symptoms of very mild to moderate upper respiratory irritation. Severe upper respiratory irritation was reported following 1-hour exposure to hydrogen fluoride concentrations from 4.2 to 4.5 ppm (3.4 to 3.7 mg/m^3). Nasal and bronchioalveolar lavage analysis indicated an inflammatory response in the nasal cavity from 1-hour exposure to 4.2 ppm (3.4 mg/m^3) hydrogen fluoride and lower respiratory irritation (bronchial inflammation) following 1 hour exposure to 1.9 ppm (1.6 mg/m^3) hydrogen fluoride. The bronchial inflammation was not associated with any alterations in lung function (ATSDR, 2003) and almost all symptoms were resolved four hours after termination of exposure (ECB, 2001). The results of these studies indicated that acute inhalation of hydrogen fluoride results in irritation of the upper respiratory tract, with higher concentrations causing inflammation of the lower respiratory tract (ATSDR, 2003).

These studies were used by the ATSDR (2003) to develop an acute-duration inhalation minimum risk level (MRL) of 0.02 ppm (0.016 mg/m^3) for hydrogen fluoride. The MRL is based on a LOAEL of 0.5 ppm (0.4 mg/m^3) for upper respiratory tract irritation, divided by an uncertainty factor of 30 to account for the use of a minimal LOAEL (3-fold) and human variability (10-fold) (ATSDR, 2003).

4.4.1.2 OcularEffects

Ocular irritation occurred in male volunteers exposed several minutes to HF concentrations of 32 ppm (26 mg/m^3) (eyes smarting), 61 ppm (50 mg/m^3) (conjunctival irritation), and 122 ppm (100 mg/m^3) (marked conjunctival irritation) (Machle *et al.,* cited in ECB, 2001).

4.4.1.3 Cardiovascular Effects

Cardiac arrhythmias were observed in humans following acute dermal and inhalation exposure to hydrogen fluoride (splashed in the face region) (Chan; Tepperman, cited in ATSDR, 2003).

4.4.1.4 Gastrointestinal Effects

Gastrointestinal effects (nausea, vomiting, and diarrhea) were reported by Texas City residents acutely exposed to hydrogen fluoride following an accidental releases to the air; severe gastrointestinal effects were still reported in a highly exposed group of residents 2 years following the incident (Dayal *et al.,* cited in ATSDR, 2003).

4.4.2 Acute and Sub-Acute Animal Effects

Table 7 lists LC_{50} values for various exposure durations as well as reliable NOAEL and LOAEL values reported in the literature from acute and subacute exposures of experimental animals to hydrogen fluoride. Below is a summary of potential effects associated with acute and subacute

hydrogen fluoride inhalation in animals. Details regarding exposure concentrations, duration of exposure and animal species for cited LC_{50}, LOAEL and NOAEL values are included in Table 7.

4.4.2.1 Death

Inhalation exposure to hydrogen fluoride can result in lethal pulmonary edema and cardiac effects (ATSDR, 2003). Other symptoms in laboratory animals exposed via inhalation to hydrogen fluoride at or near the LC_{50} value include severe ocular and nasal irritation, pulmonary congestion, respiratory distress and erythema of the exposed skin (WHO, 2002).

Lethal concentrations for hydrogen fluoride have been reported for rats, monkeys, mice, and guinea pigs (ECB, 2001; ATSDR, 2003). Based on the LC_{50} values reported in Table 7, mice were the most sensitive species to the acute effects of hydrogen fluoride when compared to the monkey, rat and guinea pig. The 1-hour LC_{50} values reported for rats exposed to hydrogen fluoride ranged from 969 ppm (792 mg/m^3) to 2335 ppm (1909 mg/m^3) (ECB, 2001; ATSDR, 2003). A 1-hour LC_{50} value of 1798 ppm (1470 mg/m^3) hydrogen fluoride was reported for the Rhesus monkey (ECB, 2001). In guinea pigs, the 15 minute LC_{50} was 4237 ppm (3548 mg/m^3) hydrogen fluoride (ATSDR, 2003).

In a range-finding test performed according to Good Laboratory Practic (GLP) standards, male and female rats were exposed via inhalation to hydrogen fluoride concentrations of 0, 1 ppm (0.82 mg/m^3), 8.6 ppm (7.1 mg/m^3), 21.7 ppm (17.8 mg/m^3), 64.9 ppm (53.0 mg/m^3), and 119 ppm (93 mg/m^3) for 14 days (6 hours/day, 5 days/week) (Placke *et al.,* cited in ECB, 2001). Mortality occurred in all female animals exposed to doses of 21.7 ppm (17.8 mg/m^3) hydrogen fluoride or higher; males were slightly more tolerant with mortality occurring in all males exposed to air concentrations of 64.9 ppm (53.0 mg/m^3) or higher. No deaths occurred at the lower exposure levels.

A study by Dalbey *et al*. (cited in ATSDR, 2003) compared the effects of exposure method (i.e., nose-breathing versus mouth-breathing) on the toxicity of hydrogen fluoride in Sprague-Dawley rats. Mouth-breathing exposures resulted in a higher delivery of hydrogen fluoride to the lower respiratory tract. The toxicity of hydrogen fluoride was dramatically greater in rats exposed by mouth-breathing compared to nose-breathing rats. A 10-minute exposure to 3,655 ppm (2997 mg/m^3) or 6,663 ppm (5464 mg/m^3) resulted in a 50 to 80% death rate of the mouth-breathing rats within 2 weeks of the exposure. By comparison, no deaths occurred in the group of rats exposed via nose breathing for 10 minutes to the same concentrations. The higher lethality following mouth-breathing exposure was probably due to a higher dose of hydrogen fluoride in the lower airways. It has been demonstrated in rats exposed to 30 to 176 mg/m^3 for 40 minutes, that >99% of inhaled hydrogen fluoride is absorbed in the upper respiratory tract with very little reaching the lungs (ATSDR, 2003).

4.4.2.2 Respiratory Effects

Several NOAEL and LOAEL values were reported for respiratory effects following acute (2-minutes to 1-hour) inhalation exposure to hydrogen fluoride (see Table 7 for details). Responses

appear to be a function of the product of exposure time and concentration, with the effects reported for very short exposures to high concentrations being similar to those reported for comparatively longer exposure durations to lower concentrations. An exposure concentration at

Table 7 LC_{50}, NOAEL and LOAEL Values for Acute HF Inhalation (Experimental Animals)

Effects Reported[1]	Exposure Period	Air Concentration[2] ppm (mg/m^3)	Species	Reference
Death:				
LC_{50}	1-hour	2236 to 2335 (1828 to 1909)	Rat	Valentine, cited in ECB, 2001
LC_{50}	1-hour	1798 (1470)	Rhesus Monkey	Darmer *et al.,* cited in ECB, 2001
LC_{50}	1-hour	1610 (1320)	Rat	Haskell Laboratory, 1988 cited in ATSDR, 2003.
LC_{50}	1-hour	1325 (1087)	Rat	Wohlslagel *et al.,*1976, cited in ATSDR, 2003
LC_{50}	1-hour	1242 (1018)	Rat Wistar	Rosenholtz *et al*. 1963 cited in ATSDR, 2003
LC_{50}	1-hour	969 (792)	Rat	Vernot *et al.*; MacEwan and Vernot, cited in ECB, 2001
LC_{50}	1-hour	325 (267)	Mouse	Wohlslagel *et al.,* 1976, cited in ATSDR, 2003
LC_{50}	15-min	4327 (3548)	Guinea Pig Hartley	Rosenholtz *et al*. 1963 cited in ATSDR, 2003
100% mortality	14 days 5 d/wk 6 hr/d	21.7 (17.8)	Rat Female	Placke *et al.,* cited in ECB, 2001
100% mortality	14 days 5 d/wk 6 hr/d	64.9 (53.0)	Rat Male	Placke *et al.,* cited in ECB, 2001
Respiratory:				
NOAEL LOAEL (less serious) Mouth-breathing: mid-tracheal Necrosis	2-min	563 (462) 1509 (1237)	Rat Sprague-Dawley	Dalbey *et al.,* cited in ATSDR, 2003
LOAEL (less serious) Nose-breathing: nasal necrosis	2-min	6072 (4979)	Rat Sprague-Dawley	Dalbey *et al.,* cited in ATSDR, 2003
LOAEL (less serious) Mild nasal irritation LOAEL (more serious) Temporary respiratory distress and nasal discharge	5-min	712 (584) 2310 (1894)	Rat	Rosenholtz *et al.,*cited in ATSDR, 2003

Table 7 LC_{50}, NOAEL and LOAEL Values for Acute HF Inhalation (Experimental Animals) (continued)

Effects Reported[1]	Exposure Period	Air Concentration[2] ppm (mg/m^3)	Species	Reference
NOAEL LOAEL (less serious) Mouth-breathing: midtracheal Necrosis	10-min	257 (211) 902 (740)	Rat Sprague-Dawley	Dalbey *et al.,* cited in ATSDR, 2003
LOAEL (less serious) Nose-breathing: nasal necrosis	10-min	1586 (1300)	Rat Sprague-Dawley	Dalbey *et al.,* cited in ATSDR, 2003
NOAEL LOAEL (less serious) Nasal irritation LOAEL (more serious) Temporary respiratory distress and nasal discharge	15-min	292 (239) 357 (293) 1339 (1098)	Rat	Rosenholtz *et al.,* cited in ATSDR, 2003
LOAEL (more serious) Nose-breathing: fibrinonecrotic rhinitis Mouth-breathing: tracheal and bronchial necrosis (also reported a 10% reduction in body weight)	30-min	1235 (1013)	Rat Fischer-344	Stavert *et al.,* cited in ATSDR, 2003
NOAEL LOAEL (less serious) Nasal irritation LOAEL (more serious) Temporary respiratory distress and nasal discharge	1-hour	98 (80) 120 (98) 465 (381)	Rat	Rosenholtz *et al.,* cited in ATSDR, 2003
LOAEL (less serious) Edema of bronchial mucosa (younger rats) and peribronchial hyperplasia (older rats)	1 month 6 hr/d	1.2 (1.0)	Rat (female)	Sadilova *et al.,* cited in ECB, 2001
Ocular:				
LOAEL (less serious) Moderate lacrimation	5-min	712 (584)	Rat	Rosenholtz *et al.,* cited in ATSDR, 2003
NOAEL LOAEL (less serious) Lacrimation	15-min	292 (239) 357 (293)	Rat	Rosenholtz *et al.,* cited in ATSDR, 2003
NOAEL LOAEL (less serious) Lacrimation	1-hour	98 (80) 120 (98)	Rat	Rosenholtz *et al.,* cited in ATSDR, 2003
Haematological:				
NOAEL LOAEL (less serious) Mouth-breathing: increased RBC, hemoglobin, and haematocrit levels	2-min	4643 (3807) 8190 (6716)	Rat Sprague-Dawley	Dalbey *et al.,* cited in ATSDR, 2003

Table 7 LC_{50}, NOAEL and LOAEL Values for Acute HF Inhalation (Experimental Animals) (continued)

Effects Reported[1]	Exposure Period	Air Concentration[2] ppm (mg/m^3)	Species	Reference
LOAEL (less serious) Mouth-breathing: increased hemoglobin and hematocrit levels	10-min	1676 (1374)	Rat Sprague-Dawley	Dalbey *et al.,* cited in ATSDR, 2003
Hepatic:				
NOAEL LOAEL (less serious) Mouth-breathing: increased aspartate aminotransferase activity	2-min	563 (462) 1509 (1237)	Rat Sprague-Dawley	Dalbey *et al.,* cited in ATSDR, 2003
NOAEL mouth-breathing	10-min	1676 (1374)	Rat Sprague-Dawley	Dalbey *et al.,* cited in ATSDR, 2003
Skeletal:				
LOAEL (less serious) Dental enamel damage, irregular cavities in bones	1 month 6 hr/d	1.22 (1.0)	Rat Female	Sadilova *et al.,* cited in ECB, 2001

[1]NOAEL, Less serious LOAEL and Serious LOAEL as identified by ATSDR whereby, "*(s)erious* effects are those that evoke failure in a biological system and can lead to morbidity or mortality …[and] *less serious* effects are those that are not expected to cause significant dysfunction or death, or those whose significance to the organism is not entirely clear" (ATSDR, 2003)

[2] When both units of concentration were not provided in the literature, the following conversion factor and assumptions were used: 1 ppm = 0.82 mg/m^3 and 1 mg/ m^3 =1.223 ppm (ATSDR, 2003).

least one-half (or more) of the LC_{50} value was required to induce acute respiratory effects in experimental animals (Dalbey *et al.*; Rosenholtz *et al.*; Stavert *et al.,* cited in ATSDR, 2003). These acute effects appeared reversible within a week of cessation of exposure (ATSDR, 2003).

In a study which used a tracheal cannula (mouth-breathing) to expose the lower respiratory system of Sprague-Dawley rats to hydrogen fluoride, the LOAEL for mucosal necrosis in the mid-trachea was 1509 ppm (1237 mg/m^3) for a 2 minutes exposure period or 902 ppm (740 mg/m^3) for a 10 minute exposure period (Dalbey *et al.,* cited in ATSDR, 2003). The same authors reported markedly higher LOAEL values for necrosis and acute inflammation of the ventral meatus, nasal septum, and nasoturbinates in rats exposed nose-only to hydrogen fluoride: 6072 ppm (4979 mg/m^3) for 2-minutes or 1586 ppm (1300 mg/m^3) for 10-minutes. The study estimated that mouth-breathing rats inhaled 27% more hydrogen fluoride than the nose-breathing rats based on differences in minute ventilation rates. Fischer-344 rats were exposed to 1235 ppm (1013 mg/m^3) hydrogen fluoride for 30-minutes via the nose or mouth (Stavert *et al.,* cited in ATSDR, 2003). Serious effects were reported in both groups at this exposure concentration and duration, including fibrinonecrotic rhinitis in the nose-breathing rats and tracheal and bronchial necrosis in the mouth-breathing rats (ATSDR, 2003).

Mild nasal irritation was reported in rats exposed via inhalation to 712 ppm (584 mg/m^3) hydrogen fluoride for 5 minutes, 357 ppm (293 mg/m^3) hydrogen fluoride for 15 minutes, or 120 ppm (98 mg/m^3) hydrogen fluoride for 1-hour (Rosenholtz *et al.,* cited in ATSDR, 2003). This study also observed serious respiratory distress following 5 minutes exposure to 2,310 ppm (1894 mg/m^3), 15 minutes exposure to 1,339 ppm (1098 mg/m^3), 30 minute exposure to 1,308 ppm (1073 mg/m^3), or 60 minute exposure to 465 ppm (381 mg/m^3) hydrogen fluoride. No adverse respiratory effects were reported in rats exposed to 292 ppm (239 mg/m^3) or 98 ppm (80 mg/m^3) hydrogen fluoride for exposure durations of 15 minutes or 1-hour, respectively.

Respiratory effects reported in rats exposed via inhalation to hydrogen fluoride for 14 days (6 hours/day, 5 days/week) included clinical signs of discomfort, nasal irritation, and changes in absolute or relative lung weights at exposure concentrations ranging from 1 ppm (0.82 mg/m^3) to 119 ppm (93 mg/m^3) hydrogen fluoride (Placke *et al.,* cited in ECB, 2001).

In a study exposing female rats to 1.22 ppm (1 mg/m^3) hydrogen fluoride for 6 hours a day over a 1 month period, the younger animals (~12 months or less) developed atrophy and local edema of bronchial mucosa, while the older animals (~18 months or more) developed peribronchial hyperplasia (Sadilova *et al.,* cited in ECB, 2001).

4.4.2.3 Ocular Effects

Moderate lacrimation occurred in rats exposed to 712 ppm (584 mg/m^3) hydrogen fluoride for 5 minutes, to 357 ppm (293 mg/m^3) hydrogen fluoride for 15 minutes, or to 120 ppm (98 mg/m^3) hydrogen fluoride for 1-hour (Rosenholtz *et al.,* cited in ATSDR, 2003). No adverse ocular effects were reported in rats exposed to 292 ppm (239 mg/m^3) or 98 ppm (80 mg/m^3) hydrogen fluoride for exposure durations of 15 minutes or 1-hour, respectively.

4.4.2.4 Hematological Effects

Hematological effects related to hydrogen fluoride were only observed in mouth breathing rats following brief inhalation exposures to very high concentrations. Exposure of the lower respiratory system of rats (mouth breathing) to 8190 ppm (6716 mg/m^3) hydrogen fluoride for 2 minutes or to 1676 ppm (1374 mg/m^3) for 10 minutes increased red blood cell, hemoglobin and hematocrit levels (Dalbey *et al.,* cited in ATSDR, 2003). Exposure to 4643 ppm (3807 mg/m^3) hydrogen fluoride for 2 minutes had no effect on these parameters in rats.

4.4.2.5 Hepatic Effects

An increased activity in liver enzyme aspartate aminotransferase was noted following brief exposure of the lower respiratory system of rats (mouth breathing) to very high hydrogen fluoride concentrations (1509 ppm or 1237 mg/m^3) for 2 minutes; however, no effects on liver enzymes were reported following 2 minute exposure to 563 ppm (462 mg/m^3) hydrogen fluoride or 10 minute exposure to 1676 ppm (1374 mg/m^3) hydrogen fluoride (Dalbey *et al.,* cited in ATSDR, 2003).

4.4.2.6 Skeletal Effects

The exposure of female rats to 1 mg/m^3 hydrogen fluoride for 6 hours a day over a 1 month period produced damage to dental enamel (young animals and animals 17-18 months old) and irregular shaped cavities in bones (animals about 12 months old) (Sadilova *et al.,* cited in ECB, 2001).

4.5 Subchronic and Chronic Effects

Subchronic and chronic studies on experimental animal involve repeated exposures for periods of 1 to 3 months (subchronic) or more than 3 months (chronic). Human exposure situations are typically less defined, subchronic workplace or environmental exposures generally occur repeatedly over several weeks or months while chronic exposures occur repeatedly for many months or years (Klaassen *et al.,* 2001).

4.5.1 Subchronic and Chronic Human Effects

Table 8 lists some NOAEL and LOAEL values reported in humans following subchronic and chronic exposures to hydrogen fluoride. Below is a summary of potential effects associated with subchronic and chronic hydrogen fluoride inhalation.

4.5.1.1 Respiratory Effects

Adverse respiratory effects reported for workers occupationally exposed to airborne fluorides (predominately in aluminium smelters) include reduced lung capacity, irritation of the respiratory tract, asthma, cough, bronchitis, shortness of breath and/or emphysema (WHO, 2002).

Respiratory abnormalities (significant increase in the ratio of the closing volume/vital capacity) were reported in male adolescents considered to be in a “high” exposure group for emissions from an aluminium plant near Cornwall, Ontario (Ernst *et al.,* cited in WHO, 2002). The results of the high exposure group (residence within 4 km of the plant for more than 60% of their lives) were compared to a low exposure group (residence within 17 km of the plant for more than 60% of their lives).

Chronic bronchitis, diffuse interstitial fibrosis, and pulmonary emphysema were reported in 45 cases with skeletal fluorosis (bone thickening and exostoses) in an area of China contaminated by coal combustion (Liu, cited in WHO, 2002). Exposure to fluoride in areas of China may be very high as a result of the preparation and consumption of food with water containing high amounts of naturally occurring fluoride as well as the indoor burning of fluoride-rich coal for heating and cooking (WHO, 2002).

Table 8 NOAELS and LOAELs For Subchronic and Chronic HF Inhalation (Human)

Effects Reported[1]	Exposure Period	Air Concentration [2] ppm (mg/m^3)	Reference
Respiratory:			
NOAEL Alterations in pulmonary function	Variable (chronic occupational)	1.03 (0.82) (fluorides, including HF)	ACGIH, cited in ECB, 2001.
LOAEL (less serious) Slight nasal irritation	15-50 days 6 hr/d 6 d /wk	2.98 (2.44)	Largent, cited in ATSDR, 2003
Hematological, Hepatic, Renal:			
NOAEL	Variable (chronic occupational)	0.59 (0.48) (fluorides, including HF)	Chan-Yeung *et al.,* cited in WHO, 2002
Skeletal:			
LOAEL (less serious) Osteosclerosis	Variable (chronic occupational)	3.1 (2.5) (fluorides, including HF)	Hodge and Smith, cited in WHO, 2002
NOAEL Skeletal fluorosis	Variable (chronic occupational)	0.59 (0.48) (fluorides, including HF)	Chan-Yeung *et al.,* cited in WHO, 2002
NOAEL LOAEL Skeletal fluorosis	Variable (chronic occupational)	1.31 (1.07) 2.31 (1.89) (fluorides, including HF)	OEHHA, 2003 (based on Derryberry *et al.,* 1963)

[1]Less serious LOAEL as identified by ATSDR whereby, "…*less serious* effects are those that are not expected to cause significant dysfunction or death, or those whose significance to the organism is not entirely clear" (ATSDR, 2003)

[2] When both units of concentration were not provided in the literature, the following conversion factor and assumptions were used: 1 ppm = 0.82 mg/m^3 (ATSDR, 2003).

The above studies do not provide conclusive evidence for the effect of hydrogen fluoride on respiratory function due to concomitant exposures to other airborne contaminants (WHO, 2002).

No alterations in pulmonary function were observed in workers exposed to an average hydrogen fluoride concentration of 0.82 mg/m^3 (1.03 ppm) and no respiratory complaints were noted in workers to exposed to hydrogen fluoride concentrations below 2.5 mg/m^3 (3.1 ppm) (ACGIH, cited in ECB, 2001).

One controlled exposure study evaluated respiratory effects following hydrogen fluoride inhalation for 6 hrs/day, 6 days/week, for a 15 to 50 day period (Largent, cited in ATSDR, 2003). Slight nasal irritation was reported following exposure to hydrogen fluoride concentrations averaging from approximately 0.85 to 7.7 ppm (0.70 to 6.3 mg/m^3) fluoride (Largent, cited in ATSDR, 2003). Although this study is limited by inadequacies in experiment details and effects reporting, it was the only controlled hydrogen fluoride inhalation study of intermediate exposure

duration and therefore the mean of the average exposure concentrations (2.98 ppm or 2.44 mg/m^3) was identified by the ATSDR (2003) to be a less serious LOAEL.

This LOAEL is within the range of LOAELs reported in *acute* human exposure studies reviewed by the ATSDR (2003) for the establishment of an *acute*-duration inhalation MRL, which suggests that the severity of nasal irritation following the inhalation of hydrogen fluoride may not increase with increasing exposure duration. The similar LOAEL values identified for respiratory irritation in humans over a range of different exposure durations include: 3.22 ppm (2.6 mg/m^3) for 6 hours/day over 10 days (Largent, cited in ATSDR, 2003); 3.8 ppm (3.1 mg/m^3) for 1 hour/day over 1 day (Lund *et al*. cited in ATSDR, 2003), and; 2.98 ppm (2.4 mg/m^3) for 6 hours/day, 6 days/week for 15 to 50 days (Largent cited in ATSDR, 2003).

The ATSDR (2003) did not develop a chronic-duration inhalation MRL. Apart from the single study conducted by Largent over a 15 to 50 day period, no other human studies involving subchronic or chronic exposure to hydrogen fluoride were identified.

4.5.1.2 Gastrointestinal Effects

A higher incidence of nausea and diarrhea was reported in an exposed population near a smelter known to emit hydrogen fluoride and metallic oxide fumes compared to an unexposed control population (Waldbott, cited in ATSDR, 2003). The hydrogen fluoride exposure concentration from the smelter was unknown; however, concentrations of fluoride in plants and animals around the smelter were well above normal.

4.5.1.3 Hematological, Hepatic or Renal Effects

There was no evidence of hemapoetic, hepatic or renal dysfunction in workers exposed to 0.48 mg/m^3 fluoride in the potroom of an aluminum smelter (Chan-Yeung *et al.,* cited in WHO, 2002).

4.5.1.4 Skeletal Effects

Long-term exposure to fluoride (including hydrogen fluoride) by inhalation or ingestion may result in skeletal fluorosis, whereby incorporation of elevated levels of fluoride into the bone renders the bone less soluble and delays or inhibits bone mineralization, reducing bone tensile strength and resulting in brittle bones (Grynpas, cited in WHO, 2002).

The predominance of skeletal fluorosis in individuals residing in certain areas of the world (particularly India and China) may be the result of a very high fluoride intake as a result of naturally occurring, high concentrations of fluoride in water used for drinking and cooking, coal used for heating, and food (Haimanot *et al*.; Krishnamachari; Pettifor *et al*.; Kaminsky *et al*.; Tobayiwa *et al*.; Mithal *et al*.; Wang *et al*.; Abdennebi *et al*.; Liu; Michael *et al*.; Zhao *et al*.; Teotia *et al.,* cited in WHO, 2002). Nutritional status, climate, and factors influencing fluid

intake may also affect the development of skeletal fluorosis (Krishnamachari; Haimanot; Zang *et al.,* cited in WHO, 2002).

The amount of fluoride incorporated into the bone will determine the severity of the effects associated with skeletal fluorosis (WHO, 2002). Factors affecting fluoride deposition into bone include extent and duration of fluoride exposure, as well as age, nutritional status, renal function and calcium intake (US DHHS, cited in WHO, 2002). Impaired renal function (e.g., diabetes) limits the excretion of fluoride (Kaminsky *et al*.; US DHHS, cited in WHO, 2002).

Fluoride concentrations in the bone of individuals in the preclinical stage of skeletal fluorosis may range from 3500 and 5500 mg/kg bone; bone concentrations associated with crippling skeletal fluorosis are greater than 8400 mg/kg bone. These concentrations can be compared to reference values for fluoride concentrations in bone which range from 500 to 1000 mg/kg bone ash weight (US DHHS, cited in WHO, 2002). Average fluoride levels measured in iliac crest biopsies taken from 18–25 individuals with hip fractures living in areas with low fluoride (<0.3 ppm), high fluoride (>1.5 ppm), or fluoridated (1.0–1.2 ppm) water were 450, 3,720, and 1,590 ppm, respectively (Arnala *et al.,* cited in ATSDR, 2003).

Hodge and Smith (cited in WHO, 2002) conducted a review of older occupational studies on the occurrence of skeletal fluorosis in aluminum smelter (potroom) workers which concluded a high incidence of detectable osteosclerosis when fluoride air concentrations (including HF) in the workplace were greater than 3.1 ppm (2.5 mg/m^3) and/or fluoride urine concentrations of exposed workers were greater than 9 mg/L. The authors concluded that years of exposure to airborne fluoride concentrations below 2.5 mg/m^3 (with corresponding urine concentrations below 5 mg/L) did not produce osteosclerosis (WHO, 2002).

No definitive signs of skeletal fluorosis were reported in workers exposed up to 10 years to fluoride concentrations (including HF) up to 0.48 mg/m^3 in the potroom of an aluminum smelter (Chan-Yeung *et al.,* cited in WHO, 2002). The occurrence of fluorosis (multiple joint pain, initial ossification, osteosclerosis) in 2258 workers at an aluminum plant in Poland was reported to increase with increasing duration of employment, with more severe effects observed in older workers (Czerwinski *et al.,* cited in WHO, 2002). Skeletal changes in workers were related to a qualitative "exposure index" based on years of employment and the extent to which the airborne hydrogen fluoride concentrations in the plant exceeded the highest permitted level of 0.5 mg/m^3. A minimal increase in bone density was reported from occupational exposure to hydrogen fluoride concentrations less than 4.3 ppm (3.5 mg/m^3) (ACGIH, cited in ECB, 2001). An intake of between 20 and 80 mg fluoride/day was attributed to skeletal fluorosis in cryolite workers in Copenhagen (Grandjean, cited in WHO, 2002).

A chronic exposure study was conducted on the incidence of minimal osseous changes and occupational exposure to fluorides (including HF) (Derryberry *et al.,* cited in OEHHA, 2003). The California Office of Environment and Health Hazard Assessment (2003) analyzed the data presented in this study and used regression analyses to demonstrate a significant relationship between increasing air concentrations of fluoride and the probability of skeletal fluorosis. The NOAEL and LOAEL values for skeletal fluorosis (defined by the authors as increased bone density) determined from this analysis were 1.07 mg/m^3 (1.31 ppm) and 1.89 mg/m^3 (2.31 ppm),

respectively. A benchmark concentration (BMC_{05}) of 0.37 mg/m^3 was further derived from this data using US EPA software. The BMC_{05} value was adjusted for continuous exposure and a 10-fold uncertainty factor for differences in indivdual sensitivity to develop a chronic Reference Exposure Level (REL) of 0.014 mg/m^3 for fluorides, including hydrogen fluoride. The primary source of uncertainty in the study by Derryberry *et al*. (cited in OEHHA, 2003) was the lack of a comprehensive health effects examination. Another uncertainty associated with the use of an occupational (adult) exposure study for the development of a chronic REL for hydrogen fluoride is the potential for greater susceptibility of children to the effects of inhalaed fluoride (including hydrogen fluoride) during periods of rapid bone growth (OEHHA, 2003).

A delicate balance exists between the prevention of dental caries using fluoride and the occurrence of dental fluorosis (increased porosity or hypomineralization of tooth enamel) from excess exposure to fluoride during tooth development (ages 1–8 years) (ATSDR, 2003). One U.S. study reported a dental fluorosis occurrence of 0.9 and 6.9% in children living in communities with 1 or 4 ppm fluoride in drinking water, respectively (Jackson *et al.,* cited in ATSDR, 2003). Mechanisms associated with dental fluorosis have not been fully elucidated but a number of proposed mechanisms are discussed in ATSDR (2003).

4.5.2 Subchronic Animal Effects

No chronic animal studies and only two subchronic studies of hydrogen fluoride inhalation were identified (ECB, 2001; ATSDR, 2003). Table 8 lists some of the reliable NOAEL and LOAEL values reported in the literature following subchronic inhalation of hydrogen fluoride by experimental animals. Below is a summary of potential effects associated with subchronic hydrogen fluoride inhalation in experimental animals.

4.5.2.1 Death

Rats, mice, guinea pigs, rabbits and dogs were exposed to 8.2 ppm (6.7 mg/m^3 at 47 to 97% humidity) or 31 ppm (25 mg/m^3 at 48 to 66% humidity) hydrogen fluoride for 6 hours/day, 6 days/week over a 5 week period (Stokinger, cited in ATSDR, 2003). At the 31 ppm (25 mg/m^3) hydrogen fluoride exposure level, all of the rats and mice died, but no deaths occurred in guinea pigs, rabbits, or dogs. No deaths were reported in any species following exposure to 8.2 ppm (6.7 mg/m^3) hydrogen fluoride.

Rabbits (n=5), guinea pigs (n=3), and Rhesus monkeys (n=2) were exposed to 18 ppm (15 mg/m^3) hydrogen fluoride for 6 to 7 hours/day, 5 days/week for 50 days (309 hours total) (Machle and Kitzmiller, cited in ASTDR, 2003). Two of the three exposed guinea pigs died as a result of exposure (134 to 160 hours) to 18 ppm (15 mg/m^3) hydrogen fluoride; no other deaths were reported. This is an older study (1935) which is limited by imprecise exposure measurement technology, the evaluation of a small number of animals, and an absence of control data (ATSDR, 2003).

A 91 day subchronic inhalation study conducted according to GLP and Organization for Economic Cooperation and Development (OECD) (413) standards exposed male (n=20) and female (n=20) rats to hydrogen fluoride concentrations of 0, 0.120 ppm (0.098 mg/m^3), 0.88 ppm (0.72 mg/m^3), and 9.20 ppm (7.52 mg/m^3) for 6 hours/day, 5 days/week (Placke and Griffin, cited in ECB, 2001). The highest exposure dose (9.20 ppm or 7.52 mg/m^3) resulted in the death of 5 males and 1 female. A NOAEL of 0.88 ppm (0.72 mg/m^3) was reported based on clinical signs of toxicity and effects on body weights, organ weights, hematology, and histopathology of lung, liver, kidney, testes, spleen, brain, heart, and adrenals.

4.5.2.2 Respiratory Effects

Guinea pigs (n=3) were exposed via inhalation to 18 ppm (15 mg/m^3) hydrogen fluoride for about 35 days (6 to 7 hours/day, 5 days a week); this exposure resulted in the death of two guinea pigs who experienced pulmonary hemorrhage, alveolar inflammation, and hyperplasia of the bronchial epithelium (Machle and Kitzmiller, cited in ASTDR, 2003).

Inhalation exposure to 31 ppm (25 mg/m^3) of hydrogen fluoride for 5 weeks (6 hours/day, 6 days/week) resulted in pulmonary hemorrhaging in dogs, rabbits, and rats (Stokinger, cited in ATSDR, 2003). An exposure of 8.2 ppm (6.7 mg/m^3) hydrogen fluoride over the same time period did not induce pulmonary hemorrhage in rats or rabbits, but did cause localized hemorrhages in 1 out of 5 exposed dogs (Stokinger, cited in ATSDR, 2003).

Clinical effects in male and female rats following 91 days inhalation exposure (6 hours/day, 5 days/week) to 9.20 ppm (7.52 mg/m^3) hydrogen fluoride included a red-coloured discharge from the nose; an increase in relative lung weights was also reported for this exposure group although no histopathological changes were detected (Placke and Griffin, cited in ECB, 2001).

4.5.2.3 Ocular Effects

Repeated exposure of rats and rabbits to 8.2 ppm (6.7 mg/m^3) HF for 5 weeks (6 hours/day, 6 days/week) resulted in subcutaneous hemorrhaging around the eyes (Stokinger, cited in ATSDR, 2003).

A red-coloured discharge was noted in the eyes of rats exposed via inhalation to 9.20 ppm (7.52 mg/m^3) hydrogen fluoride for 91 days (6 hours/day, 5 days/week) (Placke and Griffin, cited in ECB, 2001).

4.5.2.4 Hematological Effects

No hematological effects were observed in dogs, rabbits, and rats exposed to 31 ppm (25 mg/m^3) of hydrogen fluoride for 5 weeks (6 hours/day, 6 days/week) (Stokinger, cited in ATSDR, 2003).

Hematological effects observed in male and female rats exposed via inhalation to 9.20 ppm (7.52 mg/m^3) hydrogen fluoride for 91 days (6 hrs/d, 5 d/wk) included increased platelets and

Table 9 NOAELs and LOAELs for Subchronic Inhalation (Experimental Animals)

Effects Reported[a]	Exposure Period	Air Concentration [2] ppm (mg/m^3)	Species	Reference
Death:				
100% mortality	5 wks 6d/wk 6hr/d	31 (25)	Rat	Stokinger, cited in ATSDR, 2003
100% mortality	5 wks 6d/wk 6hr/d	31 (25)	Mouse	Stokinger, cited in ATSDR, 2003
Respiratory:				
NOAEL LOAEL (less serious) Pulmonary hemorrhage	5 wks 6d/wk 6hr/d	8.2 (6.7) 31 (25)	Rat	Stokinger, cited in ATSDR, 2003
LOAEL (less serious) Pulmonary hemorrhage	5 wks 6d/wk 6hr/d	31 (25)	Dog	Stokinger, cited in ATSDR, 2003
NOAEL LOAEL (less serious) Pulmonary hemorrhage	5 wks 6d/wk 6hr/d	8.2 (6.7) 31 (25)	Rabbit	Stokinger, cited in ATSDR, 2003
NOAEL LOAEL Nasal discharge	91 days 5d/wk 6h/d	0.88 (0.72) 9.20 (7.52)	Rat	Placke and Griffin, cited in ECB, 2001
Ocular:				
LOAEL (more serious) Subcutaneous hemorrhage around the eyes	5 wks 6d/wk 6hr/d	8.2 (6.7)	Rat Mouse	Stokinger, cited in ATSDR, 2003
NOAEL LOAEL Ocular discharge	91 days 5d/wk 6h/d	0.88 (0.72) 9.20 (7.52)	Rat	Placke and Griffin, cited in ECB, 2001
Hematological:				
NOAEL	5 wks 6d/wk 6hr/d	31 (25)	Rat Dog Rabbit	Stokinger, cited in ATSDR, 2003
NOAEL LOAEL	91 days 5d/wk 6h/d	0.88 (0.72) 9.20 (7.52)	Rat	Placke and Griffin, cited in ECB, 2001
Renal:				
NOAEL LOAEL (less serious) Cortical necrosis	5 wks 6d/wk 6hr/d	8.2 (6.7) 31 (25)	Rat	Stokinger, cited in ATSDR, 2003
Skeletal:				
NOAEL LOAEL Dental malocclusions	91 days 5d/wk 6h/d	0.88 (0.72) 9.20 (7.52)	Rat	Placke and Griffin, cited in ECB, 2001

[1]NOAEL, Less serious LOAEL and Serious LOAEL as identified by ATSDR whereby, "*(s)erious* effects are those that evoke failure in a biological system and can lead to morbidity or mortality …[and] *less serious* effects are those that are not expected to cause significant dysfunction or death, or those whose significance to the organism is not entirely clear" (ATSDR, 2003)

[2] When both units of concentration were not provided in the literature, the following conversion factor and assumptions were used: 1 ppm = 0.82 mg/m^3 and 1 mg/ m^3 =1.223 ppm (ATSDR, 2003).

segmented neutrophils (males), decreased lymphocytes and red blood cells (males), and decreased serum albumin (males and females) (Placke and Griffin, cited in ECB, 2001).

4.5.2.5 Hepatic Effects

The exposure of rabbits (n=5), guinea pigs (n=3), and Rhesus monkeys (n=2) to 18 ppm (15 mg/m^3) hydrogen fluoride via inhalation for 50 days (6 to 7 hours/day, 5 days/week) resulted in liver effects in exposed guinea pigs (fatty degeneration of liver parenchyma and focal necrosis) and, to a lesser extent, in rabbits (fatty changes) (Machle and Kitzmiller, cited in ASTDR, 2003). These study results were limited by imprecise exposure measurements, a small number of exposed animals, and an absence of control data (ATSDR, 2003).

4.5.2.6 Renal Effects

Renal cortex degeneration and necrosis occurred in rats (90%) exposed via inhalation to 31 ppm (25 mg/m^3) of hydrogen fluoride for 5 weeks (6 hours/day, 6 days/week) (Stokinger, cited in ATSDR, 2003). No adverse effects were reported in rats exposed to 8.2 ppm (6.7 mg/m^3) for the same time period. Adverse renal effects (degenerative and inflammatory changes) developed in 4 out of 5 rabbits and in 1 out of 2 monkeys exposed to 18 ppm (15 mg/m^3) hydrogen fluoride via inhalation for 50 days (6 to 7 hours/day, 5 days/week) (Machle and Kitzmiller, cited in ASTDR, 2003). Limitations to this study included imprecise exposure measurements, a small number of exposed animals, and an absence of control data (ATSDR, 2003).

4.5.2.7 Organ Weights and Histological Effects

An increase in relative organ weights (kidneys, liver, lung, testes, spleen, brain, heart and adrenals) was reported in male and female rats exposed via inhalation to hydrogen fluoride concentrations of 9.20 ppm (7.52 mg/m^3) for 6 hrs/d, 5 d/wk, over a 91 day period (Placke and Griffin, cited in ECB, 2001). No histopathological changes were found at this exposure dose.

In contrast to the above study, Humiczewska *et al*. (cited in ECB, 2001) reported histological and/or histochemical changes in the liver, lungs, heart, or stomach of rats exposed for 3 months (5 hr/d) to 0.002 ppm (0.0016 mg/m^3) hydrogen fluoride. According to the European Union (ECB, 2001), the reporting in this study was not quantitatively accurate, thus the results were not included in their assessment of hydrogen fluoride effects.

4.5.2.8 Neurological Effects

Albino rats were exposed to 0.02 ppm (0.016 mg/m^3), 0.03 ppm (0.025 mg/m^3) or 0.06 ppm (0.049 mg/m^3) hydrogen fluoride for 24 hours a day over a 5 month period (Sadilova *et al*. cited in ATSDR, 2003). Neurological effects (measured as a change in the threshold of the light adaptive reflex) were reported for 3 rats exposed to 0.03 ppm (0.025 mg/m^3). The toxicological

significance of this response is not clear, in addition, the response may be attributed to mucous membrane irritation rather than an effect on cerebral cortical function (ATSDR, 2003).

4.5.2.9 Skeletal Effects

Increased fluoride levels in teeth (14-fold higher than controls) and bone (6-fold higher than controls) were observed in rats following 5 weeks of repeated (6 hours/day, 6 days/week) inhalation exposure to 8.2 ppm (6.7 mg/m^3) hydrogen fluoride (Stokinger, cited in ATSDR, 2003); however, the study authors did not report if there was any evidence of dental or skeletal fluorosis associated with the increased fluoride levels (ATSDR, 2003). Dental malocclusions were reported in 2 female rats (out of a group of 20 female and 20 male rats) exposed via inhalation to 9.20 ppm (7.52 mg/m^3) hydrogen fluoride for 91 days (6 hrs/d, 5 d/wk) (Placke and Griffin, cited in ECB, 2001).

Animal studies have demonstrated that high fluoride doses increase bone mass, however, a negative association was reported between fluoride-induced new bone mass and bone strength which suggests an impairment of new bone quality by the presence of fluoride (Silva and Ulrich; Turner *et al*.; cited in ATSDR, 2003). More detailed discussions on the possible mechanisms of fluoride toxicity to bone and teeth are provided in ATSDR (2003).

5.0 EFFECTS ON VEGETATION

The following is a review of the literature on the biological effects of hydrogen fluoride on terrestrial vegetation. A number of assessment and reviews on the phytoxicity of hydrogen fluoride on plants were identified. Web of Science database was searched using key words hydrogen fluoride with plant, and vegetation. This review includes a summary of pertinent information presented in the Canadian Environmental Protection Act Report on Inorganic Fluorides (EC, 1993), the Science Assessment Document for hydrogen fluoride developed by Environment Canada (EC, 1996), and the World Health Organizations Environmental Health Criteria 227 for Fluorides (WHO, 2002).

Under the direction of CEPA, Bourgeau and colleagues developed reference levels for hydrogen fluoride in ambient air based on the potential for effects in vegetation (EC, 1996). These levels are 1.1 $\mu g/m^3$ for 24 hours, 0.5 $\mu g/m^3$ for 7 days, 0.4 $\mu g/m^3$ 30 days and 0.4 $\mu g/m^3$ for 90 days. The recommended reference levels were developed from a literature review of numerous studies evaluating the effects of hydrogen fluoride exposure to vegetation. Thirteen studies which analyzed the effect of hydrogen fluoride exposure on vegetation (32 separate effect results) were found to be acceptable. The effect results data set represented 18, 10 and 4 points from horticultural, agricultural and tree species, respectively. The studies evaluated for the development of recommended reference levels for hydrogen fluoride included: Adams *et al*; Solberg *et al*; MacLean *et al*.; Zwiazek; MacLean and Schneider; Madkoar and Weinstein; Coulter *et al*.; McCune *et al*.; Murray; Hitchcock *et al*.; Pack; Mohamed *et al*.; Hill and Park, and; Murray and Wilson, cited in EC, 1996; McCune *et al.,* 1991).

The uptake of hydrogen fluoride in plants involves foliar deposition or root uptake. Gaseous fluoride enters the leaf through the stomata, moves into the transpiration stream (xylem vessels) to sites of accumulation the tips and leaf margins (Treshow, 1984; Garrec and Plebin, 1986). The major pathway for fluoride exposure is direct atmospheric deposition (US EPA, 1998). In addition fluoride is absorbed by roots and translocated to the leaf tissue (Drury *et al.,* 1980). Absorption of hydrogen fluoride is dependent on a number of abiotic factors, which include, air temperature, humidity, wind speed and direction, soil moisture, plant nutrient status, age of plants, exposure levels and duration (EC, 1996). The phytotoxicity of hydrogen fluoride has been extensively studied by Weinstein (cited in EC, 1993; 1996, and WHO, 2002) who reported interspecies and intraspecies differences in sensitivity to airborne hydrogen fluoride. Visible symptoms attributed to phytotoxic hydrogen fluoride exposure are chlorosis and necrosis. Chlorosis occurs due to the degradation of the photosynthetic pigments chlorophyll a and b, and results in the yellowing of leaves and necrosis (cell death) due to loss of cell integrity. Plant growth rate has also been demonstrated to be adversely affected by hydrogen fluoride exposure (EC, 1993; 1996; WHO, 2002).

Stevens *et al*. (1998a) evaluated the phytotoxicity and bioavailability of hydrogen fluoride in solution and hydrogen fluoride uptake into roots of tomatoes (*Lycopersicon esculentum*) and oats (*Avena sativa*). Stevens *et al.,* (1998a) concluded that hydrogen fluoride exposure was more deleterious than H+ ions (pH effect) or F- ions (when compared to Stevens *et al.,* 1998b).

The mechanism of fluoride toxicity is unclear. The physiological effects of hydrogen fluoride on plants are due to fluoride accumulation in plant tissue and growth inhibition. Hydrogen fluoride affects a number of physiological processes, including photosynthesis, respiration, carbohydrate, lipid, and nucleotide metabolism, water transport, acid phosphatase and plasma membrane H^+ATPase (Miller *et al.,* cited in Kamaluddin and Kwiazek 2003; Zwiazek and Shay 1988a; 1988b; Facanha and Meis 1995).

A study by Dogeroglu *et al*. (2002), evaluated the effect of chronic high-level exposure of hydrogen fluoride on tobacco (*Nicotiana tabacum L.*). The authors exposed plants to hydrogen fluoride levels of 262 µg/m^3 for 8 months. Morphological changes observed in hydrogen fluoride treated plants included fading, drying and curling of leaf edges and the development of necrosis lesions. Hydrogen fluoride exposed plants had a decrease in growth rate compared to control plants. The authors measured the effect of growth rate as decrease of stem height (66.15%), stem diameter (68.42%), leaf number (42.61%), leaf area (79.55%), and leaf weight (80.00%). In addition, the study demonstrated that hydrogen fluoride exposure resulted in a decrease of chlorophyll *a* and *b* (proteins involved in photosynthesis) of 38.64% and 51.61%, respectively.

In a subsequent report by Dogeroglu *et al*. (2003) the authors evaluated the effect of short-term hydrogen fluoride exposure at 0.5 and 45 µg/m^3 for 1 or 3 days on 1 month-old tobacco plants. Plants were monitored for 3 weeks after exposure. No visible signs of fluoride symptoms were observed (i.e., chlorosis or necrosis). Fifty and 70% growth rate decreases were observed at 45 µg/m^3 compared to controls, measured as plant height, for 1 and 3 day exposures, respectively, this was accompanied by reductions in chlorophyll content of the plants of 63 and 85%.

Hill and Pack (cited in EC, 1993; 1996, and; WHO, 2002) evaluated the effect of hydrogen fluoride levels ranging from 0.3 to 1.9 µg/m^3 on flower, fruit, vegetable and forage crops in long-term greenhouse experiments. The most sensitive plant species was the snow princess gladiolus (*Gladiolus grandiflorus*), which demonstrate necrosis on 65% of leaves at 0.35 µg/m^3 (following 117 days of hydrogen fluoride exposure over two growing sessions). In addition, apples (*Malis domestica borka*), pole beans (*Phaseolus vulgaris* L.), red clover (*Trifolium pratense*) and alfalfa (*Medicago sativa*) displayed decreased growth rates and/or necrosis when exposed to hydrogen fluoride concentrations of 0.44, 0.54 and 21.3 µg/m^3, respectively.

Plant species that are highly susceptible to fluoride phytotoxicity were barley (seedling stage), blueberries, peach (fruit), grape, plum, prune, sweet corn and tulips. Whereas, alfalfa, asparagus, bean (snap), cabbage, carrot, celery, cucumber, eggplant pea, pear pepper potato, squash, tobacco and wheat display resistance to fluoride toxicity (Griffiths, 2003).

Coniferous trees have been identified as a sensitive species to hydrogen fluoride exposure (EC, 1993). The effect of low exposure levels of hydrogen fluoride (0.4 and 1.6 µg/m^3) on Eastern white pine (*Pinus strobus*) seedlings have been reported (Rakowski and Zwiazek, 1992). Nine-week-old seedlings were treated for 1-28 days. Initial signs of fluoride injury were observed after 20 and 5 d and for 0.4 and 1.6 µg/m^3, respectively; at these levels photosynthesis was not significantly affected. McCune *et al*. (cited in EC, 1993) observed a dose dependent relationship between hydrogen fluoride exposure and necrosis of needles for both black spruce (*Picea*

mariana) and white spruce (*Picea glauca*). Two year-old black spruce and 3 year-old white spruce were exposed for 78h and 50h respectively. The lowest levels of hydrogen fluoride that demonstrated visible effects (necrosis) were 4.4 $\mu m/m^3$ for black spruce and 13.2 $\mu g/m^3$ for white spruce.

Limited information was available for hydrogen fluoride exposure to important agricultural species for Alberta (wheat, barley and canola). In the literature reviewed the effects of hydrogen fluoride exposure on barley were reported by Mandl *et al*. (1975) and Hill and Pack (1983) while hydrogen fluoride effects on wheat were reported by MacLean and Schneider (1981); Hill and Pack (1983); MacLean *et al*. (1984), and; Murray and Wilson (1988). Currently there is no phytoxicity data available for canola (*Brassica rapa* or *Brassica napus*).

The study by Murray and Wilson, (1988) evaluated the effect of hydrogen fluoride on wheat (*Triticum aestivum* cv. Halberd) and barley (*Hordeum vulgare* cv. Clipper). The plants were exposed to hydrogen fluoride at a concentration 0.38 $\mu g/m^3$ for 90 days. The yield of wheat was not affected by the treatment, whereas, in barley there was a decrease of seeds per tiller (6.25%) at this exposure concentration, but this was offset by an increase of tillers. There was a significant increase in the grain protein concentration for fluoride-exposed barley plants. Hill and Pack, (1983) exposed wheat plants for 88 days to 0.38 $\mu g/m^3$ and found no effect. MacLean and Schneider (1981) exposed wheat (cv. Olaf) to 0.9 $\mu g/m^3$ for 4 days. Mean dry biomass of hydrogen fluoride exposed wheat was significantly reduced (20% reduction). The study on wheat conducted by MacLean *et al.,* (1984) used hydrogen fluoride exposure concentrations ranging from 1.6 to 3.3 $\mu g/m^3$. Plants were hydrogen fluoride treated for three successive 3-day periods. Hydrogen fluoride exposure affected anthesis (the maturing of the stamens: site of pollen production), this was observed during the first exposure period. Hydrogen fluoride-induced foliar damage was not observed at these concentrations.

6.0 EFFECTS ON MATERIALS

The result of a literature review undertaken to identify, collect and compile the appropriate information for effects of ambient hydrogen fluoride on materials indicates that no such published literature exists. However, as hydrogen fluoride is an acid gas and is readily dissolvable in water, effects are expected to be similar to those seen from total wet and dry acid deposition. These can range from the corrosion of metals to the deterioration of paint and stone. These effects can seriously reduce the value to society of buildings, bridges, cultural objects and cars. It is difficult; however, to attribute these effects to hydrogen fluoride alone, due to the presence of other atmospheric pollutants.

7.0 AIR SAMPLING AND ANALYTICAL METHODS

7.1 Reference Methods

Air sampling and analytical methods for hydrogen fluoride used by established agencies are reported. In general, standard air monitoring methods for hydrogen fluoride are based on active or pump-and-tube sampling approaches that are followed by various analytical techniques. Widely employed and accepted reference air monitoring methods for hydrogen fluoride have been developed, tested and reported by (NIOSH).

7.1.1 NIOSH Method 7902

The National Institute of Occupational Safety and Health has developed methods for hydrogen fluoride that are suitable for occupational, personal and area monitoring. The first methodology used by the NIOSH to determine hydrogen fluoride in air (NIOSH Method 7902) consists of collecting hydrogen fluoride on cellulose ester membrane filters with sodium carbonate treated cellulose pads, followed by extraction and analysis (NIOSH, 1994a). Sampling is conducted by drawing air through the membrane and filter using a personal sampling pump at a rate of 1 to 2 L/min to collect a volume between 12 to 800 L. Particulate fluorides are fused in sodium hydroxide and then dissolved in 50 mL water and total ionic strength activity buffer (TISAB). Gaseous fluorides (such as hydrogen fluoride) are extracted with 50 mL water and TISAB. The sample is then analyzed with an ion specific electrode. The working range is 0.12 to 8 mg/m³ for a 250 L air sample. This method is most useful for measuring total fluorides (aerosols and gas) and not specifically for hydrogen fluoride alone. If aerosols are present, gaseous fluoride may be underestimated owing to sorption on collected particles, with concurrent overestimation of particulate/gaseous fluoride ratio.

7.1.2 NIOSH Method 7903

The second methodology used by the NIOSH to determine hydrogen fluoride in air (NIOSH Method 7903) consists of collecting hydrogen fluoride on silica sorbent tubes with glass fibre filters, desorbing with a bicarbonate/carbonate buffer solution, and then analyzing by ion chromatography (NIOSH, 1994b). Sampling is conducted by drawing air through a solid sorbent tube (containing washed silica gel with a glass fibre filter plug) using a personal sampling pump at a rate of 0.2 to 0.5 L/min to collect a volume between 3 to 100 L. The sample is subsequently desorbed using a solution of bicarbonate/carbonate buffer and analyzed with ion chromatography. The working range is about 0.01 to 5 mg/m³ for a 50 L air sample. This method measures total concentration of six airborne anions. The corresponding acids may be collected on a single sampler and determined simultaneously.

7.1.3 NIOSH Method 7906

The final methodology used by the NIOSH to determine hydrogen fluoride in air (NIOSH Method 7906) is similar to the first method and consists of collecting hydrogen fluoride on cellulose ester membrane filters with sodium carbonate treated cellulose pads, followed by extraction and analysis (NIOSH, 1994c). Sampling is conducted by drawing air through the membrane and filter using a personal sampling pump at a rate of 1 to 2 L/min to collect a volume between 1 to 120 L. Particulate fluorides are fused in sodium hydroxide and then dissolved in 100 mL water. Gaseous fluorides (such as hydrogen fluoride) are extracted with 100 mL water. The sample is then analyzed with an ion chromatography. The working ranges for hydrogen fluoride are 0.05 to 10 ppm (0.04 to 8mg/m³) for a 250 L air sample.

7.2 Alternative, Emerging Technologies

Reports, journal articles, conference proceedings and other sources known to contain information on ambient measurement methods for chemicals such as hydrogen fluoride were reviewed to determine the current status of alternative and emerging technologies. The results of the review indicate a general lack of technologies for ambient monitoring of hydrogen fluoride beyond the reference methods described earlier. A recent US EPA sponsored survey reinforces this by pointing out the need for methods development for chemicals such as hydrogen fluoride (Mukund *et al.,* 1995). Despite this need, several examples of alternative and emerging technologies have been developed and reported, including alternative active samplers, passive samplers, gas sensors and various spectrometric sampling methods.

Modified active sampling and analytical techniques based on the standard methods previously described have been developed and tested. Hance *et al*. (1997) have tested an active sampler in ambient conditions for an extended period of time to measure hydrogen fluoride. In this method, sampling is conducted by actively drawing air through a tandem filter design (PTFE pre-filter to remove the particulates and a potassium hydroxide treated filter to collected acid gases) using a sampling pump at a rate of 4.9 L/min. Once the sample is collected, the contents of the filter are desorbed using water and the desorbate is subsequently analyzed by ion chromatography. In this study, samples were collected for 24 hours every six days for 8 months in the Southern California atmosphere with good results.

A number of attempts have been made to improve these active sampling techniques by making enhancements to allow for real-time measurements. Hoke and Herud (1993) developed a multigas analyzer to measure hydrogen fluoride in real-time using a continuous-flow miniature impinger with subsequent analysis using ion-selective micro flow through electrodes. Another device was developed using a continuous flow midget impinger but instead of electrodes, real-time analysis was done using ion chromatography (Buffington *et al.,* 1998).

Passive samplers have been explored to measure concentrations of hydrogen fluoride in air as an alternative to the standard active pump sampling techniques. The advantages of these samplers are that there are no moving parts to break down, regular flow calibration is unnecessary, and no bulky, expensive pumps are required. The sampler is exposed to ambient conditions for a set

period of time (usually a much longer period than for active pump sampling) and then analyzed by an appropriate analytical method (Brown and Wright, 1994; Levin and Lindahl, 1994).

Czarnowski *et al*. (2002) tested a passive dosimeter designed to measure exposure to hydrogen fluoride under laboratory conditions. These passive samplers consist of a filter impregnated with dipotassium hydrogen phosphate, which is housed in an open polyethylene holder (protected by a screen). After exposure, the filters are eluted with a solution of sodium citrate and the hydrogen fluoride concentration is determined by a fluoride ion specific electrode. The level of detection for hydrogen fluoride using these passive samplers has not been reported. Although the sampler is ready for use, it requires further testing under various field conditions in the ambient environment to determine its suitability for ambient applications.

There have been some reports of the use of tin-dioxide based gas sensors for the detection of ambient hydrogen fluoride concentrations (Sanchez *et al.,* 2003; Godovski *et al.,* 1994). The main advantages of using such as system are their low cost, small size and low power consumption. These sensors consist of a semi-conducting metal oxide layer and a silicon substrate with an integrated heater. These types of sensors have been recently improved by using a chromatographic column to increase its selectivity for hydrogen fluoride (Sanchez *et al*. 2005). With this configuration it is possible to detect concentrations in the atmosphere as low as 0.8 ppm.

Various spectroscopic techniques have been applied to the measurement of hydrogen fluoride concentrations in air, including differential optical absorption spectroscopy (DOAS), Fourier transform infrared absorption (FTIR), and tunable diode laser absorption spectroscopy (TDLAS) (Ball *et al.,* 2005; Whiteley, 1998; Bomse *et al.,* 1994). The FTIR and TDLAS techniques are based on the measurement of the absorbance due to absorption of infrared radiation by the species under study (i.e., hydrogen fluoride). The DOAS technique uses the same type of measurement but at the UV/VIS regions of the spectrum. These in situ monitoring devices are rapid, real-time, specific, non-destructive and quantitative. However, they require long optical paths or the use of multiple-pass cells to attain adequate sensitivity. In addition, the requirement for large, complex and expensive instrumentation makes these methods unlikely for routine ambient applications. For these reasons, the use of these devices has focused on monitoring hydrogen fluoride at fence lines or for leak detection (usually at fertilizer production facilities or aluminum smelters).

8.0 AMBIENT GUIDELINES OR OBJECTIVES

Current and/or recommended and proposed ambient guidelines of other jurisdictions in Canada, United States and elsewhere were reviewed for hydrogen fluoride. Details about guidelines that exist for each jurisdiction reviewed are presented in tabular format in this section. All jurisdictions have common uses for their guidelines. These uses may include:

- reviewing permit applications for sources that emit air pollutants to the atmosphere,
- investigating accidental releases or community complaints about adverse air quality for the purpose of determining follow-up or enforcement activity,
- determining whether to implement temporary emission control actions under persistent adverse air quality conditions of a short-term nature.

8.1 Hydrogen Fluoride Air Quality Guidelines

Air quality guidelines for hydrogen fluoride are summarized in Table 9. Further details on the development and use of these guidelines or objectives by each jurisdiction are provided in Appendix B. All of the concentrations presented in this table and in text below are expressed as "hydrogen fluoride (HF)." The principal approaches by which guidelines are developed involve using an occupational exposure level (OEL) and dividing it by safety or adjustment factors. A common OEL used by state agencies is the American Conference of Governmental Industrial Hygienists (ACGIH) 15-minute short-term occupational exposure limit (STEL) of 3.157 mg/m3 (3 ppm). Another OEL commonly used is the NIOSH REL of 5 mg/m3 (15-minute STEL) or 2.5 mg/m3 (8-hour time weighted average exposure limit).

The safety or adjustment factors are intended to account for issues such as: differences between eight-hour exposures in the workplace and continuous 24-hour environmental exposures, increased susceptibility of some people in the general population versus the relatively healthy worker, and uncertainty in the margin of safety provided in an occupational exposure limit.

8.1.1 Canada

The Canadian Council of Ministers of the Environment (CCME) has National Ambient Air Quality Objectives of 1.1 µg/m^3 as a 24-hour average and 0.5 µg/m^3 as a 7-day average, based on adverse effects on vegetation (CCME, 1999). Alberta Environment (2005) has a 1-hour Ambient Air Quality Objective of 4.9 µg/m^3.

The Ontario Ministry of the Environment (OME) recently adopted several air standards based on adverse effects on vegetations for the growing and non-growing season (OME, 2005):

- gaseous HF, growing season – 4.3 µg/m^3 as a 30-min. average, 0.86 µg/m^3 as a 24-hour average, and 0.34 µg/m^3 as a 30-day average;

- total HF, growing season – 8.6 µg/m^3 as a 30-min. average, 1.72 µg/m^3 as a 24-hour average, and 0.69 µg/m^3 as a 30-day average; and
- total HF, non-growing season – 17.2 µg/m^3 as a 30-min. average, 3.44 µg/m^3 as a 24-hour average, and 1.38 µg/m^3 as a 30-day average.

Manitoba Conservation (2005) has criteria for different averaging time based on vegetation end-points (0.85 µg/m^3 as 24-hour average, 0.55 µg/m^3 as a 7-day average, 0.35 µg/m^3 as a 30-day average, and 0.20 µg/m^3 as a 70-day average).

8.1.2 United States

The US Agency for Toxic Substances and Disease Registry (ATSDR, 2005) adopted an acute inhalation minimum risk level of 16 µg/m^3 based on an acute human exposure study. Sixteen US states reviewed had air quality guidelines for various averaging times:

- Texas Commission on Environmental Quality (CEQ) uses a 3-hour effects screening level of 5 µg/m^3 (Texas CEQ, 2003)
- Eight states use a 1-hour guideline with values ranging from 20 to 562.5 µg/m^3
- Louisiana Department of Environmental Quality (DEQ) uses an 8-hour ambient air standard of 61.9 µg/m^3 (Louisiana DEQ, 2003)
- Nine states use a 24-hour guideline with values ranging from 0.68 to 187.5 µg/m^3
- Four states use an annual guideline with values ranging from 0.34 to 14 µg/m^3

The basis for derivation of ambient air guidelines was not identified during the review for eight of the states– Arizona, New Hampshire, North Carolina, Pennsylvania, Rhode Island, Vermont, Washington, and Wisconsin. The American Conference of Governmental Industrial Hygienists 15-minute short-term occupational exposure limit (STEL) of 3.157 mg/m^3 (3 ppm) was used to derive ambient air guidelines for three states (Louisiana, Michigan, and Ohio).

The NIOSH REL of 2.5 mg/m^3 (8-hour time weighted average exposure limit) was used to derive ambient air guidelines for two states (Massachusetts and Oklahoma). The NIOSH 15-minute short-term exposure limit (STEL) of 5 mg/m^3 was used to derive ambient air guidelines for Texas. California derived a 1-hour reference exposure level of 240 µg/m^3 (California OEHHA, 1999). This guideline is also used in the state of Minnesota (Minnesota DOH, 2005).

8.1.3 International Agencies

The New Zealand Ministry of Environment and Ministry of Health and the Netherlands National Institute of Public Health (RIVM, 2001) do not have air quality criteria for hydrogen fluoride. The World Health Organization (2000) adopted a 1-hour reference exposure level of 630 µg/m^3 derived by applying a "benchmark dose" approach to a variety of animal and human exposure studies.

8.2 Use of Occupational Limits for Ambient Air Quality Guidelines

Although widely practiced, there are several limitations in the direct and indirect application of occupational limits for ambient air quality guidelines:

- Occupational limits are based on the information gathered in workplace, through experience from medical research and practice, from experimental human and animal studies, and from a combination of these sources. Often they are based upon averaged tolerated doses from actual repeated industrial exposures. In this respect, they would be considered very accurate at predicting human adverse health effects in industrial exposure situations.

- Occupational limits are determined for a population of workers who are essentially healthy and who fall within a working age group of about 17 to 65 years. These individuals are supposedly in the prime of life, and potentially less susceptible to the effects of hazardous substances than other members of the public. Individuals vary in sensitivity or susceptibility to hazardous substances; with the elderly and infants in general being more susceptible than healthy workers.

- For most substances, a worker during a normal work schedule (8 hours per day, 5 days per week) receives 40 hours of exposure per week with daily breaks and extended weekend periods in which the body may rid itself of the accumulated substances before elevated levels are reached. For a person living continuously in an environment containing such substances, however, these recovery periods do not exist.

For these reasons, agencies using occupational limits have a policy of adjusting them downward with the use of safety or adjustment factors to derive guidelines for environmental (ambient) settings. The occupational limits are considered surrogates for benchmark values for ambient exposures only because they tend to be based upon a large body of toxicological, epidemiological, and/or clinical evidence pertaining to human exposure (albeit in the workplace). Uncertainty exists in terms of whether too little (or too much) safety is inherent in ambient air guidelines developed from occupational limits.

Table 10 Summary of Air Quality Objectives for Hydrogen Fluoride

Agency *	Guideline Title	Guideline Value [µg/m^3] Averaging Time: 1-hr	24-hr	Annual
CCME	National Ambient Air Quality Objective		1.1	0.5 (7-day)
Alberta Environment	Ambient air quality objective	4.9		
Manitoba Conservation	Ambient air quality criteria		0.85	0.75 (7-day) 0.35 (30-day) 0.20 (70-day)
Ontario MOE	Standard – gaseous, growing season Standard – total, growing season Standard – total, non-growing season	4.3 (30-min) 8.6 (30-min) 17.2 (30-min)	0.86 1.72 3.44	0.34 (30-day) 0.69 (30-day) 1.38 (30-day)
US ATSDR	Chronic inhalation MRL			16 (14-day)
US EPA	No guideline exists			
Arizona DEQ	Ambient air quality guideline	562.5	187.5	
California EPA	Reference exposure level	240		14
Indiana DEM	No guideline exists			
Louisiana DEQ	Ambient air standard	61.9 (8-hr)		
Massachusetts DEP	Threshold effects exposure limit Allowable ambient limit		0.68	 0.34
Michigan DEQ	Initial threshold screening level	26		
Minnesota DOH	Acute health risk value	240		
New Hampshire DES	Ambient air limit		8.2	5.5
North Carolina ENR	Acceptable ambient level	250	30	
Ohio EPA	Maximum acceptable ground-level concentration	43		
Oklahoma DEQ	Maximum acceptable ambient concentration		50	
Pennsylvania DEP	Ambient air quality standard		5	
Rhode Island DEM	Acceptable ambient level	21	3.2	
Texas CEQ	Effects screening level	5 (3-hour)		0.5
Vermont ANR	Hazardous ambient air standard		59.5	
Washington DOE	Acceptable source impact level		9.2	
Wisconsin DNR	Ambient air concentration	246		
New Zealand MOE	No guideline exists.			
The Netherlands (RIVM)	No guideline exists.			
World Health Organization	Reference exposure level:	630		

* See Appendix B for full name of agency names that have been abbreviated.

9.0 REFERENCES

Agency for Toxic Substances and Disease Registry (ATSDR). 2003. *Toxicological Profile for Fluorides*, Hydrogen Fluoride and Fluorines. ATSDR, Public Health Service, US Department of Health and Human Services. Atlanta, GA. September 2003. 356 pp. (available at http://www.atsdr.cdc.gov/toxprofiles/tp11.html).

ATSDR. 2005. *Minimal Risk Levels (MRLs) for Hazardous Substances*. ATSDR, Public Health Service, US Department of Health and Human Services. Atlanta, GA. (available at http://www.atsdr.cdc.gov/mrls.html).

Aigueperse, J. 2001. Fluorine Compounds, Inorganic. In *Ullman's Encyclopedia of Industrial Chemistry (On-line Edition)*, Wiley-VCH Verlag GmbH & Co. KGaA.

Alberta Environment. 2005. *Alberta Ambient Air Quality Objectives*. Alberta Environment, Environmental Policy Branch, Edmonton, AB. April 2005. 4 pp. (available at http://www3.gov.ab.ca/env/protenf/approvals/factsheets/ABAmbientAirQuality.pdf).

Arizona Department of Environmental Quality (DEQ). 2005. *Arizona Ambient Air Quality Guidelines*. Arizona DEQ, Air Quality Division, Phoenix, AZ. 10 pp. (available at http://www.azdeq.gov/environ/air/index.html).

Ball, M., D. Howe and J. Bauer. 2005. *Measurement and Speciation of Fluoride Emissions at a Phosphate Fertilizer Manufacturing Plant Using Open-Path FTIR and TDL* (available at http://www.boreal-laser.com/docs/HF%20monitoring%20in%20Phosphates%20manufacture%20-%20Ball%20et%20al.pdf).

Bomse, D.S., J.A. Silver and A.C. Stanton. 1994. Hydrogen Halide Trace Detection Using Diode Lasers. *National Institute of Standards and Technology Special Publication 984-1*: 543-549.

Brown, R.H. and M.D. Wright. 1994. Diffusive Sampling Using Tube-type Samplers. *Analyst* 119: 75-79.

Buffington, C.O., S.C. Kneiss, J.L. Hornsby and S.H. Hoke. 1998. Evaluation of Tubing Losses during Field Sampling for Hydrogen Halide Gases. *Field Analytical Chemistry and Technology* 2(4): 231-240.

California Office of Environmental Health Hazard Assessment (OEHHA). 1999. *Acute Toxicity Summary: Hydrogen Fluoride*. Cal OEHHA, Sacramento, CA. 8 pp. (available at http://www.oehha.ca.gov/air/acute_rels/allAcRELs.html).

California Office of Environmental Health Hazard Assessment (OEHHA). 2003. *Chronic Toxicity Summary: Fluorides including Hydrogen Fluoride*. Cal OEHHA, Sacramento, CA. 16 pp. (available at http://www.oehha.ca.gov/air/chronic_rels/AllChrels.html).

Canadian Council of Ministers of the Environment (CCME). 1999. *Canadian National Ambient Air Quality Objectives: Process and Status*. *In*: Canadian Environmental Quality Guidelines. CCME, Winnipeg, MB. 8 pp.

Czarnowski, W., B. Wielgomas and J. Krechniak. 2002. A Passive Dosimeter for Evaluating Exposure to Hydrogen Fluoride. *Fluoride* 35(1): 22-27.

Dogeroglu, T., A. Cicek, and S. Kara. 2002. Impacts of a Chronic High-Level Exposure to HF on Nicotiana tabacum L.: Morphological and Physiological Changes. *Fen. Envir. Bull*. 11: 18-21

Dogeroglu, T., A. Cicek, and S. Kara. 2003. Short-term Effects of Hydrogen Fluoride on *Nicotiana tabacum* L *.J. Envir. Scien. Health*. B38:561-570

Drury, J.S., J.T. Ensminger, A.S. Hammons, J.W. Holleman, E.B. Lewis, E.L. Preston, C.R. Shriner, L.E. Towill. 1980. *Reviews of Environmental Effects of Pollutants. IX. Fluoride*. Health Effects Research Laboratory. US Protection Agency, Ohio, pp 106-175

Environment Canada (EC). 1993. *Priority Substances List Assessment Report: Inorganic Fluorides*. Canadian Environmental Protection Act, Environment Canada/Health Canada, 72 p.

EC. 1996. *National Ambient Air Quality Objectives for Hydrogen Fluoride (HF)*. Science Assessment Document. A Report by the Federal-Provincial Working Group on Air Quality Objectives and Guidelines. Environment Canada, Ottawa, On. July 1996. 105 pp.

EC. 2005. *National Pollutant Release Inventory 2003 Database (Access Format)* (available at http://www.ec.gc.ca/pdb/npri/npri_dat_rep_e.cfm#highlights)

European Chemicals Bureau (ECB), 2001. *European Union Risk Assessment Report: Hydrogen Fluoride,* CAS No.: 7664-39-3, EINECS No.: 231-634-8. Institute for Health and Consumer Protection, Existing Substances. European Communities, 2001. ISBN 92-894-0485-X. (available at http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT /REPORT/ hydrogen fluoridereport002.pdf)

Facanha, A.R., L. deMeis. 1995. Inhibition of Maize Root H+ATPase by Fluoride amd Fluoroaluminate Complexs. *Plant Physi*ol. 108:241-149

Garrec, J.-P., R. Plebin. 1986. Permeabilite au Fluoride D'Hydrogen (HF) des Cuticule Avec ou Snas Stomates de Feuilles: Influence de la Presence des Stomates et Comparaisons Avec la Permeabilite a L'Eau. *Envir. Exp.. Bot*. 26:229-308

Genium Publishing Corporation (Genium). 1999. *Genium's Handbook of Safety, Health and Environmental Data for Common Hazardous Substances*, McGraw Hill, New York, New York.

Godovski, D.Y., A.A. Vasiliev and E.V. Dorofeev. 1994. Analysis of Hydrogen Fluoride with SnO_2 Gas Sensors. *Sensors and Actuators B* 18-19: 483-485.

Griffiths, H. 2003. *Effects of Air Pollution on Agricultural Crops*. (available at: http://www.omafra.gov.on.ca/english/crops/facts/01-015#fluoride).

Hance, C.D., P.A. Solomon, L.G. Salmon, T. Fall and G.R. Cass. 1997. Hydrofluoric Acid in the Southern California Atmosphere. *Environmental Science & Technology* 31(4): 956-959.

Hazardous Substances Data Bank (HSDB). 2005. *Hazardous Substances Data Bank*. Toxicology and Environmental Health Information Program, National Library of Medicine, Bethesda, MD (available at http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB.

Hoke, S.H. and C. Herud. 1993. Real-Time Analysis of Halon Degradation Products. *National Institute of Standards and Technology Special Publication 984-1*: 185-190.

Indiana Department of Environmental Management (DEM). 2002. Office of Air Quality Programs. Indiana DEM, Office of Air Quality. Indianapolis, IN. (available at http://www.in.gov/idem/air/programs/modeling/policy.html).

Kamaluddin, M., J.J. Zwiazek. 2003. Fluoride Inhibits Root Water Transport and Affects Leaf Expansion and Gas Exchange in Aspen (*populus tremuloides*) Seedlings.*Physiol. Plant*. 117:368-375

Klaassen, C. (ed), 2001. *Casarett and Doull's Toxicology: The Basic Science of Poisons*. McGraw-Hill Medical Publisher Division. pgs 14 and 155. ISBN: 0071347216.

Levin, J.O. and R. Lindahl. 1994. Diffusive Air Sampling of Reactive Compounds – A Review. *Analyst* 119: 79-83.

Lewis, R.J. Sr. 2000. *Sax's Dangerous Properties of Industrial Materials 10th Edition (On-line Edition)*, John Wiley & Sons, Inc.

Lewis, R.J. Sr. 2002. *Hawley's Condensed Chemical Dictionary 14th Edition (On-line Edition)*, John Wiley & Sons.

Lide, D.R. (ed.). 2004. *CRC Handbook of Chemistry and Physics, 85th Edition*. CRC Press, Boca Raton, FL.

Louisiana Department of Environmental Quality (DEQ). 2003. Louisiana Administrative Code (LAC). Title 33 Environmental Quality, Part III Air, Chapter 51. Comprehensive Toxic Air Pollutant Emission Control Program. Louisiana Department of Environmental Quality. Baton Rouge, LA. (available at http://www.state.la.us/osr/lac/lac33.htm).

Manitoba Conservation. 2005. *Objectives and Guidelines for Various Air Pollutants: Ambient Air Quality Criteria* (updated July, 2005). Manitoba Conservation, Air Quality Section, Winnipeg, MB. (available at http://www.gov.mb.ca/conservation/airquality/aq-criteria/ambientair_e.html).

Massachusetts Department of Environmental Protection (DEP). 1990. Chemical Health Effects Assessment Methodology & Method to Derive Allowable Ambient Limits (CHEM/AAL). Massachusetts DEP, Boston, MA. February 1990. (available at http://www.mass.gov/dep/air/laws/policies.htm).

Massachusetts Department of Environmental Protection (DEP). 1995. Revised air guidelines [updated list of 24-hour average Threshold Effects Exposure Limit (TEL) values and annual average Allowable Ambient Limit (AAL) values]. Memorandum. Massachusetts DEP, Boston, MA. 6 December 1995. (available at http://www.mass.gov/dep/air/aallist.pdf).

McCune, D.C. Lauver, T.L., Hansen, K.S., (1991) Relationship Between Concentration of Gaseous Hydrogen Fluoride to Incidence and Severity of Foliar Lesions in Black Spruce *Can. J. Forest. Res*. 21:756-761

Michigan Department of Environmental Quality (DEQ). 1998. Michigan Administrative Code (MAC). Air Pollution Control Rules. Part 2 Air Use Approval, R 336.1201 - 336.1299. Air Quality Division, Department of Environmental Quality. Lansing, MI. (available at http://www.state.mi.us/orr/emi/admincode.asp?admincode=Department&Dpt=EQ).

Michigan Department of Environmental Quality (DEQ). 2005. Initial Threshold Screening Level (ITSL) / Initial Risk Screening Level (IRSL) Glossary. Michigan DEQ, Air Quality division, Lansing, MI. (available at http://www.michigan.gov/deq/0,1607,7-135-3310_4105-11754--,00.html).

Minnesota Department of Health (DOH). 2005. Health Risk Values for Air. Minnesota DOH, St. Paul, MN. (available at http://www.health.state.mn.us/divs/eh/air/hrvtable.htm#chronic).

Mukund, R., T.J. Kelly, S.M. Gordan, M.J. Hays and W.A. McClenny. 1995. Status of Ambient Air Measurement Methods for Hazardous Air Pollutants. *Environmental Science & Technology* 29 (4): 183-187.

Murray, F., S. Wilson. 1988. The Joint Action of Sulphur Dioxide and Hydrogen Fluoride on the yield and quality of wheat and barley. *Environ. Pollut*., 55: 239–249.

New Hampshire Department of Environmental Services (DES). 2005. New Hampshire Administrative Rule. Chapter Env-A 1400. Regulated Toxic Air Pollutants. New Hampshire Department of Environmental Services. Concord, NH. (available at http://www.des.state.nh.us/rules/env-a1400.pdf).

New Zealand Ministry for the Environment and Ministry of Health (New Zealand). 2000. *Proposals for Revised and New Ambient Air Quality Guidelines*. Discussion Document. Air Quality Technical Report No 16. Prepared by the Ministry for the Environment and the Ministry of Health. December 2000. 79 pp.

NIOSH (National Institute for Occupational Safety and Health). 1994a. *NIOSH Manual of Sampling and Analytical Methods – 4th Edition, Method 7902, Issue 2*. US Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, Cincinnati, OH, 1994.

NIOSH. 1994b. *NIOSH Manual of Sampling and Analytical Methods – 4th Edition, Method 7903, Issue 2*. US Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, Cincinnati, OH, 1994.

NIOSH. 1994c. *NIOSH Manual of Sampling and Analytical Methods – 4th Edition, Method 7906, Issue 2*. US Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, Cincinnati, OH, 1994.

North Carolina Department of Environment and Natural Resources. 2005. North Carolina Administrative Code (NCAC). North Carolina Air Quality Rules 15A NCAC 2D.1100 – Air Pollution Control Requirements (Control of Toxic Air Pollutants). North Carolina Department of Environment and Natural Resources, Raleigh, NC. (available at http://reports.oah.state.nc.us/ncac.asp).

O'Neil, M. (Ed.). 2001. *The Merck Index, 13th Edition*, Merck Research Laboratories, Division of Merck & Co., Inc. Whitehouse Station, N.J.

Ohio Environmental Protection Agency (EPA). 2005. Air Toxics Policy – Option A: Review of New Sources of Toxic Emissions. Air Toxics Unit, Division of Air Pollution Control, Ohio EPA. Columbus, OH. 11 pp. (available at http://www.epa.state.oh.us/dapc/atu/atu.html).

Ohio Environmental Protection Agency (Ohio EPA). 1994. Review of New Sources of Air Toxic Emissions. Proposed for Public Comment. Division of Air Pollution Control, Ohio EPA. Columbus, OH. January 1994. 31 pp. (available at http://www.epa.state.oh.us/dapc/atu/atu.html).

Oklahoma Department of Environmental Quality (DEQ). 2002. Air Toxics Partial Listing [maximum acceptable ambient concentrations (MAAC) for air toxics]. Oklahoma City, OK. (available at http://www.deq.state.ok.us/AQDNew/toxics/listings/pollutant_query_1.html).

Oklahoma Department of Environmental Quality (DEQ). 2005. Oklahoma Administrative Code (OAC). Title 252. Chapter 100. Air Pollution Control. 100:252-41 - Control of Emission of Hazardous and Toxic Air Contaminants. Oklahoma DEQ, Oklahoma City, OK. (available at http://www.sos.state.ok.us/oar/oar_welcome.htm).

Ontario Ministry of the Environment (OME). 2005. Summary of O. Reg. 419/05 Standards and Point of Impingement Guidelines and Ambient Air Quality Criteria (AAQCs). Standards Development Branch, Ontario Ministry of the Environment, Toronto, ON. December 2005. 16 pp. http://www.ene.gov.on.ca/envision/air/airquality/standards.htm (accessed 3 February 2006).

Ontario Ministry of the Environment (OME). 2004. *Rationale for the Development of Ontario Air Standards for Hydrogen Fluoride*. Standards Development Branch, Ontario Ministry of the Environment, Toronto, ON. June 2004. 121 pp. (available at http://www.ene.gov.on.ca/envision/env_reg/er/documents/2005/airstandards/PA02E0019.pdf).

Pennsylvania Department of Environmental Protection (DEP). 2005. Pennsylvania State Code, Article III Air Resources, Section 131.1, Ambient Air Quality Standards. Pennsylvania DEP, Bureau of Air Quality, Harrisburg, PA. (available at http://www.pacode.com/secure/data/025/articleICIII_toc.html).

Rakowski, K.J., J.J. Zwiazek. 1992. Early Effects of Hydrogen Fluoride on Water Relations, Photosynthesis and Membrane Integrity in Eastern White Pine (Pinus strobus) Seedlings. *Environ. Exp. Bot*. 32:377-382.

Rhode Island Department of Environmental Management. 2004. Air Pollution Control Regulation #22, Air Toxics. Division of Air and Hazardous Materials, Rhode Island Department of Environmental Management. Providence, RI. Amended 27 April 2004. (available at http://www.state.ri.us/dem/pubs/regs/index.htm#Air).

Sanchez, J.B., F. Berger, M. Fromm and M.H. Nadal. 2005. Use of a Chromatographic Column to Improve the Selectivity of the SnO_2 Gas Sensors: First Approach Towards a Miniaturised Device and Selective with Hydrogen Fluoride Vapours. *Sensors and Actuators B* 106: 823-831.

Sanchez, J.B., F. Berger, M. Fromm, M.H. Nadal and V. Eyraud. 2003. Tin Dioxide-Based Gas Sensors for Detection of Hydrogen Fluoride in Air. *Thin Solid Films* 436: 132-136.

Smith, R.A. 2003. Fluorine Compounds, Inorganic, Hydrogen. In *Kirk-Othmer Encyclopedia of Chemical Technology (On-line Edition)*, John Wiley & Sons, Inc.

Stevens, D.P., M.J. McLaughlin, A.M. Alston. 1998a. Phytotoxicity of Hydrogen Fluoride and Fluoborate and Their Uptake from Solution Culture by *Lycopersicon esculentum* and *Avena sativa*. Plant and Soil. 200:175-184

Stevens, D.P., M.J. McLaughlin, A.M. Alston. 1998b. Phytotoxicity of fluoride ion and its uptake from solution culture by Lycopersicon esculentum and Avena sativa. *Plant and Soil.* 200:119-129

Symonds, R.B., Rose, W.I., Reed, M.H. 1988. Contribution of C1- and F-bearing gases to the atmosphere by volcanoes. *Nature* 334(6181):415-418.

Texas Commission on Environmental Quality (CEQ). 2003. Effects Screening Levels. TCEQ Toxicology Section, Austin, TX. (available at http://www.tceq.state.tx.us/implementation/tox/esl/list_main.html).

The Netherlands National Institute of Public Health and the Environment (RIVM). 2001. Re-evaluation of human-toxicological maximum permissible risk levels. RIVN Report 711701 025. RIVN, Bilthoven, The Netherlands. March 2001. 297 pp.

Treshow, M. 1984. Effects of air pollutants on plants. *In* Calvert, S., and England, H. M., (EDs). Handbook of Air Pollution Technology, John Wiley and Sons, New York pp7-24.,

US Environmental Protection Agency (EPA). 2005. Integrated Risk Information System. (available at http://www.epa.gov/iris/).

US EPA. 1998. Study of Hazardous Air Pollutant. Emissions from Electric Utility Steam Generating Units -- Final Report to Congress. Volume 1., US EPA, Office of Air Quality Planning and Standards, EPA 453/R-98-004a, February 1998 (available at http://www.epa.gov/ttn/atw/combust/utiltox/eurtc1.pdf).

Vermont Agency of Natural Resources (ANR). 2001. Air Pollution Control Regulations. State of Vermont Agency of Natural Resources, Air Pollution Control Division, Waterbury, VT. (available at http://www.anr.state.vt.us/air/AirToxics/docs/apcregs.pdf).

Washington State Department of Ecology (DOE). 2005. Washington Administrative Code (WAC). Chapter 173-460 WAC. Controls For New Sources Of Toxic Air Pollutants. Washington State DOE, Olympia, WA. (available at http://www.leg.wa.gov/wac/).

Whiteley, K. 1998. Continuous Long Path Gaseous HF Monitoring in a Potroom Roof Vent. *Proc. 6th Aust. Al Smelting Workshop1998*: 659-676.

World Health Organization (WHO), 2002. *Environmental Health Criteria 227: Fluorides.* International Programme on Chemical Safety, World Health Organization, Geneva, Switzerland (available at http://www.inchem.org/documents/ehc/ehc/ehc227.htm).

WHO. 1984. *Environmental Health Criteria 36: Fluorine and Fluorides.* International Programme on Chemical Safety, World Health Organization, Geneva, Switzerland (available at http://www.inchem.org/documents/ehc/ehc/ehc36.htm).

WHO. 2000. *Air Quality Guidelines for Europe*, 2nd Edition. WHO Regional Publications, European Series, No. 91. WHO Regional Office for Europe, Copenhagen. 273 pp.

Wisconsin Department of Natural Resources (DNR). 2005. Wisconsin Administrative Code (WAC). Air Pollution Control Rules. Chapter NR 445. Control of Hazardous Pollutants. Wisconsin DNR, Madison WI. (available at http://www.legis.state.wi.us/rsb/code/nr/nr445.pdf).

APPENDIX A
Hydrogen Fluoride Emissions
2003 NPRI Database

Table A-1 Total Hydrogen Fluoride Emissions According to the 2003 NPRI Database (EC, 2005) (in tonnes, ranked by province and by total emissions)

NPRI ID	Company	City	Province	Hydrogen Fluoride Emissions (in tones)			
				Air	Water	Land	Total
2284	TransAlta Utilities Corporation	Duffield	AB	378.072	0	0	378.072
267	EPCOR Generation Inc.	Warburg	AB	295.191	0	0	295.191
2282	TransAlta Utilities Corporation	Wabamun	AB	145.275	0	0	145.275
2286	TransAlta Utilities Corporation	Duffield	AB	138.495	0	0	138.495
1039	ATCO Power	Grande Cache	AB	69.419	0	0	69.419
1033	ATCO Power	Forestburg	AB	60.03	0	0	60.03
1036	Sheerness Station	Hanna	AB	29.02	0	0	29.02
2134	Agrium Products Inc.	Redwater/Municipal Diistrict of Sturgeon	AB	19.4	0	0	19.4
3707	Imperial Oil	Edmonton	AB	0.03	0	0	0.03
3903	Petro-Canada	Edmonton	AB		0	0	0.005
2788	Alcan Primary Metal - British Columbia	Kitimat	BC	449.167	0	0	449.167
1708	New Brunswick Power Corporation	New Castle Creek	NB	31.9	0	0	31.9
1696	New Brunswick Power Corporation	Saint John	NB	20.19	0	0	20.19
3071	Suncor Energy Products Inc.	Sarnia	ON	43.185	0	0	43.185
1861	Ontario Power Generation	Nanticoke	ON	42.2	0	0	42.2
1236	Falconbridge Limited	Falconbridge	ON	35.187	0	0	35.187

Table A-1 Total Hydrogen Fluoride Emissions According to the 2003 NPRI Database (EC, 2005) (in tonnes, ranked by province and by total emissions) (continued)

NPRI ID	Company	City	Province	Hydrogen Fluoride Emissions (in tones)			
				Air	Water	Land	Total
2844	Ontario Power Generation	Mississauga	ON	28.9	0	0	28.9
1809	Ontario Power Generation Inc	Courtright	ON	15.493	0	0	15.493
7302	Brampton Brick Ltd.	Brampton	ON	2.99	0	0	2.99
10765	MTI	Mississauga	ON	1.344	0	0	1.344
2815	Falconbridge Ltd-Kidd Metallurgical Div.	Timmins/District of Cochrane	ON	0.925	0	0	0.925
1145	Cameco Corporation - Port Hope Facility	Port Hope	ON	0.537	0	0	0.537
3141	Tower Automotive	Toronto	ON		0	0	0.207
3803	Ontario Clean Water Agency	Mississauga	ON	0.139	0	0	0.139
5655	Honeywell ASCa Inc.	Amherstburg	ON	0.073	0	0	0.073
10980	Metrophotonics Inc.	Orleans	ON	0.004	0	0	0.004
1401	Henkel Canada Corporation	Toronto	ON	0.002	0	0	0.002
3406	Alcan Groupe Métal Primaire	Jonquière	QC	301.12	0	0	301.12
2038	ALCOA Ltd.	Baie-Comeau	QC	258.63	0	0	258.63
5510	Alcan inc.	Alma	QC	146.21	0	0	146.21
1071	Aluminerie de Bécancour inc.	Bécancour	QC	138.2	0	0	138.2
3060	Alcan Métal Primaire	Laterriere	QC	131.3	0	0	131.3
4778	Aluminerie Alouette Inc.	Sept-Îles	QC	111.32	0	0	111.32
3062	Alcan Métal Primaire - Québec	Ville De La Baie	QC	82.78	0	0	82.78

Table A-1 Total Hydrogen Fluoride Emissions According to the 2003 NPRI Database (EC, 2005) (in tonnes, ranked by province and by total emissions) (continued)

NPRI ID	Company	City	Province	Hydrogen Fluoride Emissions (in tones)			
				Air	Water	Land	Total
3057	Alcan Métal Primaire	Shawinigan	QC	74.95	0	0	74.95
4782	Compagnie de Gestion Alcoa-Lauralco	Deschambault	QC	61.5	0	0	61.5
639	Hanson Brick Ltd.	La Prairie	QC	60.63	0	0	60.63
4808	Alcan Métal Primaire	Melocheville	QC	23	0	0	23
2978	ALCAN	Jonquière	QC	7.76	0	0	7.76
3953	Acier Inoxydable Slater Incorporée	Sorel-Tracy	QC	0.505	0	0	0.505
2079	SaskPower	Coronach	SK	73.8	0	0	73.8

Table A-2 Hydrogen Fluoride Air Emissions in Alberta According to the 2003 NPRI Database (EC, 2005) (in tonnes, ranked by province and by total emissions)

NPRI ID	Company	City	Province	Hydrogen Fluoride Emissions (tonnes)					
				Stack /Point	Storage /Handling	Fugitive	Spills	Other Non-Point	Total
2284	Transalta Utilities Corporation	Duffield	AB	378.072	0	0	0	0	378.072
267	Epcor Generation Inc.	Warburg	AB	295.191	0	0	0	0	295.191
2282	Transalta Utilities Corporation	Wabamun	AB	145.275	0	0	0	0	145.275
2286	Transalta Utilities Corporation	Duffield	AB	138.495	0	0	0	0	138.495
1039	ATCO Power	Grande Cache	AB	69.419	0	0	0	0	69.419
1033	ATCO Power	Forestburg	AB	60.03	0	0	0	0	60.03
1036	Sheerness Station	Hanna	AB	29.02	0	0	0	0	29.02
2134	Agrium Products Inc.	Redwater/Municipal District Of Sturgeon	AB	4.1	0	15.3	0	0	19.4
3707	Imperial Oil	Edmonton	AB	0	0	0	0	0.03	0.03
2788	Alcan Primary Metal - British Columbia	Kitimat	BC	12.839	0	0	0	436	449.167
1708	New Brunswick Power Corporation	New Castle Creek	NB	31.9	0	0	0	0	31.9
1696	New Brunswick Power Corporation	Saint John	NB	20.19	0	0	0	0	20.19
3071	Suncor Energy Products Inc.	Sarnia	ON	41.943	0	1.24	0	0	43.185
1861	Ontario Power Generation	Nanticoke	ON	42.2	0	0	0	0	42.2
1236	Falconbridge Limited	Falconbridge	ON	35.187	0	0	0	0	35.187
2844	Ontario Power Generation	Mississauga	ON	28.9	0	0	0	0	28.9

Table A-2 Hydrogen Fluoride Air Emissions in Alberta According to the 2003 NPRI Database (EC, 2005) (in tonnes, ranked by province and by total emissions) (continued)

NPRI ID	Company	City	Province	Hydrogen Fluoride Emissions (tonnes)					
				Stack /Point	Storage /Handling	Fugitive	Spills	Other Non-Point	Total
1809	Ontario Power Generation Inc	Courtright	ON	15.493	0	0	0	0	15.493
7302	Brampton Brick Ltd.	Brampton	ON	1.27	0	0	0	1.72	2.99
10765	MTI	Mississauga	ON	1.344	0	0	0	0	1.344
2815	Falconbridge Ltd-Kidd Metallurgical Div.	Timmins/District Of Cochrane	ON	0	0.925	0	0	0	0.925
1145	Cameco Corporation - Port Hope Facility	Port Hope	ON	0.537	0	0	0	0	0.537
3803	Ontario Clean Water Agency	Mississauga	ON	0.139	0	0	0	0	0.139
5655	Honeywell Asca Inc.	Amherstburg	ON	0.073	0	0	0	0	0.073
10980	Metrophotonics Inc.	Orleans	ON	0	0	0	0	0	0.004
1401	Henkel Canada Corporation	Toronto	ON	0.002	0	0	0	0	0.002
3406	Alcan Groupe Métal Primaire	Jonquière	QC	301.12	0	0	0	0	301.12
2038	Alcoa Ltd.	Baie-Comeau	QC	47.78	0	211	0	0	258.63
5510	Alcan Inc.	Alma	QC	7.353	0	139	0	0	146.21
1071	Aluminerie De Bécancour Inc.	Bécancour	QC	32.5	0	106	0	0	138.2
3060	Alcan Métal Primaire	Laterriere	QC	13.1	0	118	0	0	131.3
4778	Aluminerie Alouette Inc.	Sept-Îles	QC	7.91	0	0	0	103	111.32
3062	Alcan Métal Primaire - Québec	Ville De La Baie	QC	26.9	0	55.9	0	0	82.78
3057	Alcan Métal Primaire	Shawinigan	QC	47.437	0	27.5	0	0	74.95

Table A-2 Hydrogen Fluoride Air Emissions in Alberta According to the 2003 NPRI Database (EC, 2005) (in tonnes, ranked by province and by total emissions) (continued)

NPRI ID	Company	City	Province	Hydrogen Fluoride Emissions (tones)					
				Stack /Point	Storage /Handling	Fugitive	Spills	Other Non-Point	Total
4782	Compagnie De Gestion Alcoa-Lauralco	Deschambault	QC	20.1	0	41.4	0	0	61.5
639	Hanson Brick Ltd.	La Prairie	QC	60.63	0	0	0	0	60.63
4808	Alcan Métal Primaire	Melocheville	QC	0	0	23	0	0	23
2978	Alcan	Jonquière	QC	7.76	0	0	0	0	7.76
3953	Acier Inoxydable Slater Incorporée	Sorel-Tracy	QC	0.505	0	0	0	0	0.505
2079	Saskpower	Coronach	SK	73.8	0	0	0	0	73.8

APPENDIX B
Air Quality Guidelines for Hydrogen Fluoride Development and Use

Agency:

Canadian Council of Ministers of the Environment (CCME).

Air Quality Guideline:

Canadian National Ambient Air Quality Objective (NAAQO):

1.1 µg/m^3 as HF (24-hour average)

0.5 µg/m^3 as HF (7-day average)

30 µg Fluoride /g dry weight – maximum level of accumulated fluoride in vegetation

Averaging Time To Which Guideline Applies:

Various averaging times indicated above.

Basis for Development:

The guidelines for levels in ambient air are based on adverse effects on vegetation, the level in vegetation is to protect livestock and wildlife.

Date Guideline Developed:

1997.

How Guideline is Used:

NAAQOs are the benchmark against which Canada can assess the impact of anthropogenic activities on air quality and ensure that current emission control policies are successfully protecting human health, vegetation, materials, and/or aesthetic air quality parameters. The objectives are designed to facilitate air quality management on a regional scale.

Additional Comments:

NAAQOs are national goals for outdoor air quality that protect public health, the environment, or aesthetic properties of the environment. They are targets for air quality, measured at relevant receptors (e.g., persons, plants, animals, materials).

Reference and Supporting Documentation:

Canadian Council of Ministers of the Environment (CCME). 1999. Canadian National Ambient Air Quality Objectives: Process and Status. *In*: Canadian Environmental Quality Guidelines. CCME, Winnipeg, MB. 8 pp.

EC, 1996. National Ambient Air Quality Objectives for Hydrogen Fluoride (HF). Science Assessment Document. A Report by the Federal-Provincial Working Group on Air Quality Objectives and Guidelines. Environment Canada, Ottawa, On. July 1996. 105 pp.

Agency: Alberta Environment (AENV)
Air Quality Guideline: Ambient Air Quality Objective (AAQO) = 4.9 µg/m^3 as HF.
Averaging Time To Which Guideline Applies: 1-hour averaging time.
Basis for Development: Adopted from Texas.
Date Guideline Developed: 1999.
How Guideline is Used: Used by Alberta Environment to establish approval conditions and can be used to assess compliance and evaluate performance at industrial facilities.
Additional Comments:
Reference and Supporting Documentation: Alberta Environment. 2005. Alberta Ambient Air Quality Objectives. Alberta Environment, Environmental Policy Branch, Edmonton, AB. April 2005. 4 pp. http://www3.gov.ab.ca/env/protenf/approvals/factsheets/ABAmbientAirQuality.pdf (accessed 8 October 2005).

Agency:

Manitoba Conservation.

Air Quality Guideline:

Ambient Air Quality Criteria – maximum acceptable level concentrations for fluorides as HF:

0.85 µg/m^3 as 24-hour average

0.55 µg/m^3 as a 7-day average

0.35 µg/m^3 as a 30-day average

0.20 µg/m^3 as a 70-day average

Averaging Time To Which Guideline Applies:

Various averaging times indicated above.

Basis for Development:

Adverse effects on vegetation.

Date Guideline Developed:

Unknown.

How Guideline is Used:

Used by Manitoba Conservation to serve as a guide for the evaluation of air quality and for planning purposes.

Additional Comments:

Maximum acceptable level concentrations are deemed by Manitoba Conservation as essential to provide adequate protection for soils, water, vegetation, materials, animals, visibility, personal comfort and well-being.

Reference and Supporting Documentation:

Manitoba Conservation. 2005. Objectives and Guidelines for Various Air Pollutants: Ambient Air Quality Criteria (updated July, 2005). Manitoba Conservation, Air Quality Section, Winnipeg, MB. http://www.gov.mb.ca/conservation/airquality/aq-criteria/ambientair_e.html (accessed 8 October 2005).

Agency:

Ontario Ministry of the Environment (OME).

Air Quality Guideline:

30-minute standard: 4.3 µg/m^3 for fluorides (as HF) – gaseous (growing season)
8.6 µg/m^3 for fluorides (as HF) – total (growing season)
17.2 µg/m^3 for fluorides (as HF) – total (non-growing season)
24-hour standard: 0.86 µg/m^3 for fluorides (as HF) – gaseous (growing season)
1.72 µg/m^3 for fluorides (as HF) – total (growing season)
3.44 µg/m^3 for fluorides (as HF) – total (non-growing season)
30-day standard: 0.34 µg/m^3 for fluorides (as HF) – gaseous (growing season)
0.69 µg/m^3 for fluorides (as HF) – total (growing season)
1.38 µg/m^3 for fluorides (as HF) – total (non-growing season)

Averaging Time To Which Guideline Applies:

Various averaging times indicated above.

Basis for Development:

All of the guidelines are based on adverse effects on vegetation and accumulation in forage by this compound.

Date Guideline Developed:

2004.

How Guideline is Used:

The standards are used by Ontario Ministry of Environment (OME) to represent human health or environmental effect-based values not expected to cause adverse effects based on continuous exposure.

Additional Comments:

Reference and Supporting Documentation:

Ontario Ministry of the Environment (OME). 2005. Summary of O. Reg. 419/05 Standards and Point of Impingement Guidelines and Ambient Air Quality Criteria (AAQCs). Standards Development Branch, Ontario Ministry of the Environment, Toronto, ON. December 2005. 16 pp. http://www.ene.gov.on.ca/envision/air/airquality/standards.htm (accessed 3 February 2006).

Agency: US Agency for Toxic Substances and Disease Registry (ATSDR).
Air Quality Guideline: Acute inhalation minimum risk level (MRL) = 16 µg/m^3 as HF.
Averaging Time To Which Guideline Applies: ≤14 continuous exposure.
Basis for Development: Acute inhalation MRL of 16 µg/m^3 (20 ppb) was calculated by dividing a minimal LOAEL of 0.5 ppm (acute human exposure study) by an uncertainty factor of 30 (3 for use of a minimal LOAEL and 10 to account for human variability).
Date Guideline Developed: September 2003.
How Guideline is Used: MRLs are intended to serve as a screening tool to help public health professionals decide where to look more closely. Inhalation MRLs are exposure concentrations that, based on current information, might cause adverse health effects in the people most sensitive to such substance-induced effects for exposure durations described above.
Additional Comments: Inhalation MRLs provide a basis for comparison with levels that people might encounter in air. If a person is exposed to hydrogen fluoride at an amount below the MRL, it is not expected that harmful (noncancer) health effects will occur. Because these levels are based only on information currently available, some uncertainty is always associated with them. Also, because the method for deriving MRLs does not use any information about cancer, an MRL does not imply anything about the presence, absence, or level of risk for cancer.
Reference and Supporting Documentation: Agency for Toxic Substances and Disease Registry (ATSDR). 2005. Minimal Risk Levels (MRLs) for Hazardous Substances. ATSDR, Public Health Service, US Department of Health and Human Services. Atlanta, GA. http://www.atsdr.cdc.gov/mrls.html (accessed 8 October 2005).

Agency: US Environmental Protection Agency (EPA).
Air Quality Guideline: US EPA does not have an air quality guideline for this chemical.
Averaging Time To Which Guideline Applies: n/a
Basis for Development: n/a
Date Guideline Developed: n/a
How Guideline is Used: n/a
Additional Comments: n/a
Reference and Supporting Documentation: US Environmental Protection Agency (EPA). 2005. Integrated Risk Information System. http://www.epa.gov/iris/ (accessed 8 October 2005).

Agency: Arizona Department of Environmental Quality (DEQ).
Air Quality Guideline: Arizona Ambient Air Quality Guidelines (AAAQGs): 1-hour AAAQG: 562.5 µg/m^3 as HF. 24-hour AAAQG: 187.5 µg/m^3 as HF.
Averaging Time To Which Guideline Applies: See above.
Basis for Development: 1-hour AAAQG: Unknown. 24-hour AAAQG: Unknown.
Date Guideline Developed: Unknown.
How Guideline is Used: AAAQGs are used by Arizona DEQ to review permit applications for sources that emit hydrogen fluoride to the atmosphere and as criteria to investigate complaints and violations of Arizona's air quality laws.
Additional Comments: The Arizona Ambient Air Quality Guidelines (AAAQG) are acceptable concentration levels for hazardous air pollutants that are regulated by the State of Arizona.
Reference and Supporting Documentation: Arizona Department of Environmental Quality (DEQ). 2005. Arizona Ambient Air Quality Guidelines. Arizona DEQ, Air Quality Division, Phoenix, AZ. 10 pp. http://www.azdeq.gov/environ/air/index.html (accessed 8 October 2005).

Agency: California Environmental Protection Agency (Cal EPA).
Air Quality Guideline: Acute reference exposure level (REL) = 240 µg/m^3 as HF. Chronic reference exposure level (REL) = 14 µg/m^3 as HF.
Averaging Time To Which Guideline Applies: Acute REL: 1-hour averaging time. Chronic REL: Continuous (daily) exposure over a lifetime.
Basis for Development: Acute REL: The acute REL is based on an extrapolated 1-hr exposure concentration of 2.4 mg/m^3 (3 ppm) resulting in upper respiratory tract membrane irritation in healthy volunteers and a cumulative uncertainty factor of 10. Chronic REL: The chronic REL is based on a benchmark dose (BMD)-modeled exposure concentration of 140 µg/m^3 resulting in increased bone density (skeletal fluorosis) in occupational workers and a cumulative uncertainty factor of 10.
Date Guideline Developed: Acute REL: March 1999. Chronic REL: August 2003.
How Guideline is Used: Acute and chronic RELs are for use in facility health risk assessments conducted for the AB 2588 Air Toxics "Hot Spots" Program.
Additional Comments: n/a
Reference and Supporting Documentation: California Office of Environmental Health Hazard Assessment (OEHHA). 1999. Acute Toxicity Summary: Hydrogen Fluoride. Cal OEHHA, Sacramento, CA. 8 pp. Available at: http://www.oehha.ca.gov/air/acute_rels/allAcRELs.html (accessed 8 October 2005). California Office of Environmental Health Hazard Assessment (OEHHA). 2003. Chronic Toxicity Summary: Fluorides including Hydrogen Fluoride. Cal OEHHA, Sacramento, CA. 16 pp. Available at: http://www.oehha.ca.gov/air/chronic_rels/AllChrels.html (accessed 8 October 2005).

Agency: Indiana Department of Environmental Management (IDEM).
Air Quality Guideline: IDEM does not have an air quality guideline for this chemical.
Averaging Time To Which Guideline Applies: n/a
Basis for Development: n/a
Date Guideline Developed: n/a
How Guideline is Used: n/a
Additional Comments: n/a
Reference and Supporting Documentation: Indiana Department of Environmental Management (DEM). 2002. Office of Air Quality Programs. Indiana DEM, Office of Air Quality. Indianapolis, IN. http://www.in.gov/idem/air/programs/modeling/policy.html (accessed 8 October 2005).

Agency: Louisiana Department of Environmental Quality (DEQ).
Air Quality Guideline: Ambient air standard (AAS) for toxic air pollutants = 61.9 µg/m^3 as HF.
Averaging Time To Which Guideline Applies: 8-hour averaging time.
Basis for Development: The AAS is equivalent to the American Conference of Governmental Industrial Hygienist (2003) Short Term Exposure Limit (STEL) of 3 ppm as fluoride (3.2 ppm or 2.6 mg/m^3 as hydrogen fluoride) divided by a factor of 42. The factor of 42 is a common adjustment representing a safety factor of 10 and 8/24 and 5/7 multipliers to convert 8-hour per 24-hour day and 5-day per 7-day week occupational exposures to continuous exposures.
Date Guideline Developed: December 2003.
How Guideline is Used: AASs are used by Louisiana DEQ to review permit applications for stationary sources that emit hydrogen fluoride to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Louisiana Department of Environmental Quality (DEQ). 2003. Louisiana Administrative Code (LAC). Title 33 Environmental Quality, Part III Air, Chapter 51. Comprehensive Toxic Air Pollutant Emission Control Program. Louisiana Department of Environmental Quality. Baton Rouge, LA. http://www.state.la.us/osr/lac/lac33.htm (accessed 8 October 2005).

Agency:

Massachusetts Department of Environmental Protection (DEP).

Air Quality Guideline:

Threshold Effects Exposure Limit (TEL) = 0.68 µg/m^3 as HF [24-hour averaging time].
Allowable Ambient Limit (AAL) = 0.34 µg/m^3 as HF [annual average].

Averaging Time To Which Guideline Applies:

See above.

Basis for Development:

The TEL was derived by taking 20% of an adjusted "most appropriate occupation limit" (MAOL) to represent the portion of a person's total exposure through inhalation. The MAOL used by Massachusetts DEP was the NIOSH 8-hour time weighted average (TWA) REL of 2.5 mg/m^3. The "adjusted MAOL" was derived by adjusting the MAOL downward by: an uncertainty factor (UF) of 4.2 for continuous exposure [168 hours/week ÷ 40 hours/week], a factor of 1.75 for adult-child differences [(10 m^3/day)/20 kg ÷ (20 m^3/day)/70 kg], a factor of 10 for sensitive individuals, and a factor 10 for adequacy of toxicity data. This resulted in the MAOL being divided by 735. The resultant TEL (20% of the adjusted MAOL) is 0.68 µg/m^3 as a 24-hour average concentration.

The AAL was obtained by deriving a non-threshold effects exposure limit (NTEL) by dividing the adjusted MAOL by a non-threshold effects uncertainty factor (NTEUF) of 10. The resultant AAL is 0.34 µg/m^3 as an annual average concentration.

Date Guideline Developed: Unknown.

How Guideline is Used:

Information could not be obtained to identify how the guideline is used in practice, but it is expected that the guideline is used in some manner to meet state level permitting.

Additional Comments: n/a

Reference and Supporting Documentation:

Massachusetts Department of Environmental Protection (DEP). 1995. Revised air guidelines [updated list of 24-hour average TEL values and annual average AAL values]. Memorandum. Massachusetts DEP, Boston, MA. 6 December 1995. http://www.mass.gov/dep/air/aallist.pdf (accessed 8 October 2005).

Massachusetts Department of Environmental Protection (DEP). 1990. Chemical Health Effects Assessment Methodology & Method to Derive Allowable Ambient Limits (CHEM/AAL).

Massachusetts DEP, Boston, MA. February 1990.
http://www.mass.gov/dep/air/laws/policies.htm (accessed 8 October 2005).

Agency:

Michigan Department of Environmental Quality (DEQ).

Air Quality Guideline:

Initial threshold screening level (ITSL) = 26 $\mu g/m^3$ as HF.

Averaging Time To Which Guideline Applies:

1-hour averaging time.

Basis for Development:

The ISTL is based on the American Conference of Governmental Industrial Hygienist (2003) Short Term Exposure Limit (STEL) of 3 ppm as fluoride (3.2 ppm or 2.6 mg/m^3 as hydrogen fluoride) divided by a safety factor of 100.

Date Guideline Developed: 1992.

How Guideline is Used:

There are two basic requirements of Michigan air toxic rules. First, each source must apply the best available control technology for toxics (T-BACT). After the application of T-BACT, the emissions of the toxic air contaminant cannot result in a maximum ambient concentration that exceeds the applicable health based screening level for non-carcinogenic effects (ITSL). Application of an ITSL is required for any new or modified emission source or sources for which a permit to install is requested and which emits a toxic air contaminant.

Additional Comments:

The applicable air quality screening level for chemical treated as non-carcinogens by Michigan DEQ is the ITSL. There are two health based screening levels for chemical treated as carcinogens by Michigan DEQ: the initial risk screening level (IRSL) – based on an increased cancer risk of one in one million, and the secondary risk screening level (SRSL) – based on as an increased cancer risk of 1 in 100,000.

Reference and Supporting Documentation:

Michigan Department of Environmental Quality (DEQ). 2005. Initial Threshold Screening Level (ITSL) / Initial Risk Screening Level (IRSL) Glossary. Michigan DEQ, Air Quality division, Lansing, MI. http://www.michigan.gov/deq/0,1607,7-135-3310_4105-11754--,00.html (accessed 8 November 2005).

Michigan Department of Environmental Quality (DEQ). 1998. Michigan Administrative Code (MAC). Air Pollution Control Rules. Part 2 Air Use Approval, R 336.1201 - 336.1299. Air Quality Division, Department of Environmental Quality. Lansing, MI.

http://www.state.mi.us/orr/emi/admincode.asp?admincode=Department&Dpt=EQ (accessed 8 November 2005).

Agency: Minnesota Department of Health (DOH).
Air Quality Guideline: Acute Health Risk Value (HRV) = 240 µg/m^3 as HF.
Averaging Time To Which Guideline Applies: 1-hour averaging time.
Basis for Development: The HRV for hydrogen fluoride was adopted directly from the California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Acute reference exposure level (REL) of 240 µg/m^3.
Date Guideline Developed: March 2002.
How Guideline is Used: HRVs are used by the Minnesota Department of Health and sister agencies such as the Minnesota Pollution Control Agency, to assist in the assessment of potential health risks associated with chemicals in ambient air. HRVs can be used as one set of criteria for assessing risks in the environmental review process, issuing air permits, risk assessments and other site-specific assessments.
Additional Comments: The Inhalation Health Risk Values are "concentrations of chemicals or substances in the air that are estimated to produce no significant increased risk of harmful effects for specific lengths of exposure."
Reference and Supporting Documentation: Minnesota Department of Health (DOH). 2005. Health Risk Values for Air. Minnesota DOH, St. Paul, MN. http://www.health.state.mn.us/divs/eh/air/hrvtable.htm#chronic (accessed 8 November 2005).

Agency: New Hampshire Department of Environmental Services (DES).
Air Quality Guideline: 24-hour ambient air limit (AAL) = 8.2 µg/m^3 as HF. Annual ambient air limit (AAL) = 5.5 µg/m^3 as HF.
Averaging Time To Which Guideline Applies: See above.
Basis for Development: 24-hour Ambient Air Limit – Unknown. Annual Ambient Air Limit – Unknown.
Date Guideline Developed: Unknown.
How Guideline is Used: AALs are used by New Hampshire DES to review permit applications for sources that emit hydrogen fluoride to the atmosphere. Sources are regulated through a statewide air permitting system and include any new, modified or existing stationary source, area source or device.
Additional Comments: n/a
Reference and Supporting Documentation: New Hampshire Department of Environmental Services (DES). 2005. New Hampshire Administrative Rule. Chapter Env-A 1400. Regulated Toxic Air Pollutants. New Hampshire Department of Environmental Services. Concord, NH. http://www.des.state.nh.us/rules/env-a1400.pdf (accessed 8 November 2005).

Agency: North Carolina Department of Environment and Natural Resources (ENR)
Air Quality Guideline: Acceptable ambient level (AAL): 1-hour averaging time – 250 $\mu g/m^3$ as HF 24-hour averaging time – 30 $\mu g/m^3$ as HF
Averaging Time To Which Guideline Applies: See above.
Basis for Development: Unknown
Date Guideline Developed: Unknown.
How Guideline is Used: A facility emitting hydrogen fluoride must limit its emissions so that the resulting modeled ambient levels at the property boundary remain below the health-based acceptable ambient level (AAL).
Additional Comments: n/a
Reference and Supporting Documentation: North Carolina Department of Environment and Natural Resources. 2005. North Carolina Administrative Code (NCAC). North Carolina Air Quality Rules 15A NCAC 2D.1100 – Air Pollution Control Requirements (Control of Toxic Air Pollutants). North Carolina Department of Environment and Natural Resources, Raleigh, NC. http://reports.oah.state.nc.us/ncac.asp (accessed 8 November 2005).

Agency:

Ohio Environmental Protection Agency (EPA).

Air Quality Guideline:

Maximum acceptable ground-level concentration (MAGLC) = 43 $\mu g/m^3$ as HF.

Averaging Time To Which Guideline Applies:

1-hour averaging time.

Basis for Development:

$$\text{MAGCL} = \frac{\text{TLV}}{10} \times \frac{8\ \text{hr}}{24\ \text{hr}} \times \frac{5\ \text{d}}{7\ \text{d}} = \frac{\text{TLV}}{42}.$$

The Threshold Limit Value (TLV) is the American Conference of Governmental Industrial Hygienist short-term occupational exposure limit (STEL) of 3 ppm as fluoride (2.58 mg/m^3 as hydrogen fluoride) adjusted with a factor of 0.737 (Spires (1999) as cited in OME (2004)). The TLV is further adjusted by a safety factor of 10 to take into account greater susceptibility of the general population in comparison to healthy workers. The 8/24 and the 5/7 multipliers are used to relate the exposure to longer than 40-hour time periods and ascertain that the individual's total exposure will be no greater than that allowed by the TLV.

Date Guideline Developed: January 1994.

How Guideline is Used:

Used by Ohio EPA to review permit applications for sources that emit vanadium to the atmosphere.

Additional Comments: n/a

Reference and Supporting Documentation:

Ohio Environmental Protection Agency (EPA). 2005. Air Toxics Policy – Option A: Review of New Sources of Toxic Emissions. Air Toxics Unit, Division of Air Pollution Control, Ohio EPA. Columbus, OH. 11 pp. http://www.epa.state.oh.us/dapc/atu/atu.html (accessed 8 November 2005).

Ohio Environmental Protection Agency (Ohio EPA). 1994. Review of New Sources of Air Toxic Emissions. Proposed for Public Comment. Division of Air Pollution Control, Ohio EPA. Columbus, OH. January 1994. 31 pp. http://www.epa.state.oh.us/dapc/atu/atu.html (accessed 8 November 2005).

Ontario Ministry of the Environment (OME). 2004. Rationale for the Development of Ontario Air Standards For Hydrogen Fluoride. Standards Development Branch, Ontario Ministry of the Environment, Toronto, ON. June 2004. 121 pp.http://www.ene.gov.on.ca/envision/env_reg/er/documents/2005/airstandards/PA02E0019.pdf (accessed 8 October 2005).

Agency: Oklahoma Department of Environmental Quality (DEQ).
Air Quality Guideline: Maximum acceptable ambient concentration (MAAC) = 50 µg/m^3 as HF.
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: The MAAC is the NIOSH 8-hour TWA REL of 2.5 mg/m^3 for hydrogen fluoride divided by a factor of 50. In this case, the factor of 50 is applied to substances that are considered by Oklahoma DEQ to be of moderate toxicity.
Date Guideline Developed: Not stated.
How Guideline is Used: MAACs are used by Oklahoma DEQ to review permit applications for sources that emit molybdenum to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Oklahoma Department of Environmental Quality (DEQ). 2005. Oklahoma Administrative Code (OAC). Title 252. Chapter 100. Air Pollution Control. 100:252-41 - Control of Emission of Hazardous and Toxic Air Contaminants. Oklahoma DEQ, Oklahoma City, OK. http://www.sos.state.ok.us/oar/oar_welcome.htm (accessed 8 November 2005). Oklahoma Department of Environmental Quality (DEQ). 2002. Air Toxics Partial Listing [maximum acceptable ambient concentrations (MAAC) for air toxics]. Oklahoma City, OK. http://www.deq.state.ok.us/AQDNew/toxics/listings/pollutant_query_1.html (accessed 8 November 2005).

Agency: Pennsylvania Department of Environmental Protection (DEP).
Air Quality Guideline: Ambient air Quality standard (AAQS) = 5 µg/m^3 (total soluble hydrogen fluoride)
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: Unknown.
Date Guideline Developed: Unknown.
How Guideline is Used: Used by Pennsylvania DEP to review permit applications for sources that emit hydrogen fluoride to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Pennsylvania Department of Environmental Protection (DEP). 2005. Pennsylvania State Code, Article III Air Resources, Section 131.1, Ambient Air Quality Standards. Pennsylvania DEP, Bureau of Air Quality, Harrisburg, PA, http://www.pacode.com/secure/data/025/articleICIII_toc.html (accessed 8 November 2005).

Agency: Rhode Island Department of Environmental Management (DEM).
Air Quality Guideline: Acceptable ambient level (AAL) for fluorides and compounds, including hydrogen fluoride: 1-hour averaging time – 20 µg/m^3 as fluoride (F) (equivalent to 21 µg/m^3 as HF) 24-hour averaging time – 3 µg/m^3 as F (equivalent to 3.2 µg/m^3 as HF)
Averaging Time To Which Guideline Applies: See above.
Basis for Development: Not stated.
Date Guideline Developed: April 2004.
How Guideline is Used: AALs are used by Rhode Island DEM to review permit applications for sources that emit manganese to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Rhode Island Department of Environmental Management. 2004. Air Pollution Control Regulation #22, Air Toxics. Division of Air and Hazardous Materials, Rhode Island Department of Environmental Management. Providence, RI. Amended 27 April 2004. http://www.state.ri.us/dem/pubs/regs/index.htm#Air (accessed 8 November 2005).

Agency:

Texas Commission on Environmental Quality (CEQ) – formerly Texas Natural Resource Conservation Commission (TRNCC).

Air Quality Guideline:

Short-term effects screening level (ESL) = 5 $\mu g/m^3$ as HF.

Long-term effects screening level (ESL) = 0.5 $\mu g/m^3$ as HF.

Averaging Time To Which Guideline Applies:

3-hour averaging time for short-term ESL.

Annual averaging time for long-term ESL.

Basis for Development:

Short-term Effects Screening Level – Unknown, however the short-term ESL is equivalent to the National Institute for Occupational Safety and Health (NIOSH) 15-minute short-term exposure level (STEL) of 5 mg/m^3 for hydrogen fluoride is divided by a factor of 1000.

Long-term Effects Screening Level – Unknown, however the long-term ESL is equivalent to the National Institute for Occupational Safety and Health (NIOSH) 15-minute short-term exposure level (STEL) of 5 mg/m^3 for hydrogen fluoride is divided by a factor of 10,000.

Date Guideline Developed:

Not stated.

How Guideline is Used:

ESLs are used to evaluate the potential for effects to occur as a result of exposure to concentrations of constituents in air. ESLs are based on data concerning health effects, odor nuisance potential, effects with respect to vegetation, and corrosion effects. They are not ambient air standards. If predicted or measured airborne levels of a chemical do not exceed the screening level, adverse health or welfare effects would not be expected to result. If ambient levels of constituents in air exceed the screening levels, it does not necessarily indicate a problem, but rather, triggers a more in-depth review.

Additional Comments:

n/a

Reference and Supporting Documentation:

Texas Commission on Environmental Quality (CEQ). 2003. Effects Screening Levels. TCEQ Toxicology Section, Austin, TX. http://www.tceq.state.tx.us/implementation/tox/esl/list_main.html (accessed 8 November 2005).

Agency: Vermont Agency of Natural Resources (ANR).
Air Quality Guideline: Hazardous ambient air standard (HAAS) = 59.5 µg/m^3 as HF.
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: Unknown
Date Guideline Developed: Not stated.
How Guideline is Used: HAASs are used by Vermont ANR to review permit applications for stationary sources that emit hydrogen fluoride to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Vermont Agency of Natural Resources (ANR). 2001. Air Pollution Control Regulations. State of Vermont Agency of Natural Resources, Air Pollution Control Division, Waterbury, VT. http://www.anr.state.vt.us/air/AirToxics/docs/apcregs.pdf (accessed 8 November 2005).

Agency: Washington State Department of Ecology (DOE).
Air Quality Guideline: Acceptable source impact level (ASIL) = 8.7 µg/m^3 as F (equivalent to 9.2 µg/m^3 as HF).
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: Unknown.
Date Guideline Developed: Unknown.
How Guideline is Used: ASILs are used by Washington State DOE to review permit applications for sources that emit hydrogen fluoride to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Washington State Department of Ecology (DOE). 2005. Washington Administrative Code (WAC). Chapter 173-460 WAC. Controls For New Sources Of Toxic Air Pollutants. Washington State DOE, Olympia, WA. http://www.leg.wa.gov/wac/ (accessed 8 November 2005).

Agency: Wisconsin Department of Natural Resources (DNR).
Air Quality Guideline: Ambient air concentration (AAC) = 246 µg/m^3 as HF.
Averaging Time To Which Guideline Applies: 1-hour averaging time.
Basis for Development: Unknown.
Date Guideline Developed: November 2004.
How Guideline is Used: AACs are used by Wisconsin DNR to review permit applications for sources that emit molybdenum to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Wisconsin Department of Natural Resources (DNR). 2005. Wisconsin Administrative Code (WAC). Air Pollution Control Rules. Chapter NR 445. Control of Hazardous Pollutants. Wisconsin DNR, Madison WI. http://www.legis.state.wi.us/rsb/code/nr/nr445.pdf (accessed 8 November 2005).

Agency: New Zealand Ministry for the Environment (MOE) and New Zealand Ministry of Health (MOH).
Air Quality Guideline: New Zealand MOE and MOH does not have air quality criteria for hydrogen fluoride.
Averaging Time To Which Guideline Applies: n/a
Basis for Development: n/a
Date Guideline Developed: n/a
How Guideline is Used: n/a
Additional Comments: n/a
Reference and Supporting Documentation: New Zealand Ministry for the Environment and Ministry of Health (New Zealand). 2000. Proposals for Revised and New Ambient Air Quality Guidelines. Discussion Document. Air Quality Technical Report No 16. Prepared by the Ministry for the Environment and the Ministry of Health. December 2000. 79 pp.

Agency: The Netherlands National Institute of Public Health and the Environment (RIVM)
Air Quality Guideline: RIVM does not have air quality criteria for hydrogen fluoride.
Averaging Time To Which Guideline Applies: n/a
Basis for Development: n/a
Date Guideline Developed: n/a
How Guideline is Used: n/a
Additional Comments: n/a
Reference and Supporting Documentation: The Netherlands National Institute of Public Health and the Environment (RIVM). 2001. Re-evaluation of human-toxicological maximum permissible risk levels. RIVN Report 711701 025. RIVN, Bilthoven, The Netherlands. March 2001. 297 pp.

Agency: World Health Organization (WHO)
Air Quality Guideline: Ambient air reference exposure level for general population = 600 µg/m^3 as F (equivalent to 630 µg/m^3 as HF).
Averaging Time To Which Guideline Applies: 1-hr averaging time.
Basis for Development: The reference exposure level was derived by applying a "benchmark dose" approach to a variety of animal and human exposure studies by the WHO (2000).
Date Guideline Developed: 2000.
How Guideline is Used: The guideline is intended to provide background information and guidance to governments in making risk management decisions, particularly in setting standards.
Additional Comments: n/a
Reference and Supporting Documentation: World Health Organization (WHO). 2000. Air Quality Guidelines for Europe, 2nd Edition. WHO Regional Publications, European Series, No. 91. WHO Regional Office for Europe, Copenhagen. 273 pp.