

European Union Risk Assessment Report

ALUMINIUM FLUORIDE

CAS No: 7784-18-1

EINECS No: 232-051-1

RISK ASSESSMENT

FINAL APPROVED VERSION

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RISK ASSESSMENT

Final version, March 2008

The Netherlands

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Foreword

We are pleased to present this Risk Assessment Report which is the result of in-depth work carried out by experts in one Member State, working in co-operation with their counterparts in the other Member States, the Commission Services, Industry and public interest groups.

The Risk Assessment was carried out in accordance with Council Regulation (EEC) 793/93¹ on the evaluation and control of the risks of “existing” substances. “Existing” substances are chemical substances in use within the European Community before September 1981 and listed in the European Inventory of Existing Commercial Chemical Substances. Regulation 793/93 provides a systematic framework for the evaluation of the risks to human health and the environment of these substances if they are produced or imported into the Community in volumes above 10 tonnes per year.

There are four overall stages in the Regulation for reducing the risks: data collection, priority setting, risk assessment and risk reduction. Data provided by Industry are used by Member States and the Commission services to determine the priority of the substances which need to be assessed. For each substance on a priority list, a Member State volunteers to act as “Rapporteur”, undertaking the in-depth Risk Assessment and recommending a strategy to limit the risks of exposure to the substance, if necessary.

The methods for carrying out an in-depth Risk Assessment at Community level are laid down in Commission Regulation (EC) 1488/94², which is supported by a technical guidance document³. Normally, the “Rapporteur” and individual companies producing, importing and/or using the chemicals work closely together to develop a draft Risk Assessment Report, which is then presented at a meeting of Member State technical experts for endorsement. The Risk Assessment Report is then peer-reviewed by the Scientific Committee on Health and Environmental Risks (SCHER) which gives its opinion to the European Commission on the quality of the risk assessment.

If a Risk Assessment Report concludes that measures to reduce the risks of exposure to the substances are needed, beyond any measures which may already be in place, the next step in the process is for the “Rapporteur” to develop a proposal for a strategy to limit those risks.

The Risk Assessment Report is also presented to the Organisation for Economic Co-operation and Development as a contribution to the Chapter 19, Agenda 21 goals for evaluating chemicals, agreed at the United Nations Conference on Environment and Development, held in Rio de Janeiro in 1992 and confirmed in the Johannesburg Declaration on Sustainable Development at the World Summit on Sustainable Development, held in Johannesburg, South Africa in 2002.

This Risk Assessment improves our knowledge about the risks to human health and the environment from exposure to chemicals. We hope you will agree that the results of this in-depth study and intensive co-operation will make a worthwhile contribution to the Community objective of reducing the overall risks from exposure to chemicals.

¹ O.J. No L 084, 05/04/199 p.0001 – 0075

² O.J. No L 161, 29/06/1994 p. 0003 – 0011

³ Technical Guidance Document, Part I – V, ISBN 92-827-801 [1234]

General introduction to risk assessment

The concern about the potential environmental effects of the high fluoride (F) concentration in air was the reason why hydrogen fluoride (HF) was initially put on the first EU priority list (1994). In the subsequent EU risk assessment on HF (2001) it was indeed concluded that for a number of HF producing and using sites the local risk characterisation points to risks for the atmospheric compartment (plants, livestock and wildlife exposed via air). In addition, potential risks were identified for the aquatic compartment around some HF production and processing facilities.

The regional exposure assessment was, however, not addressed in the HF risk assessment. The reason was that also other F-containing High Production Volume Chemicals (HPVCs), and so-called unintentional sources, would significantly contribute to the regional emissions of HF into the atmosphere (and water). It was therefore decided to put CaF₂ and AlF₃, being chemicals listed on Annex I of EC Regulation 793/93, on the fourth EU priority list. At that time it was also considered to include other fluoride salts prior to establishing the fourth priority list, but it was decided then to prioritise CaF₂ and AlF₃, only. With the release information of those two additional inorganic F-compounds, a more balanced regional exposure assessment of fluoride could be made.

On the assumption that the limited information provisionally provided about the mass balance of CaF₂ and AlF₃ enables to image the overall environmental fate, it was decided to make a targeted RA for CaF₂ en AlF₃ focusing only on the atmospheric compartment. This will be done at the local scale for CaF₂ and AlF₃, and at the regional scale for the combination of F sources (intentional (CaF₂, AlF₃ and HF) and unintentional). The main reason for ‘targeting’ is that F-emissions to air and their potential effects were the primary reason for addressing these F-compounds under EC Regulation 793/93. In line with the RA for HF the focus on the potential risks for plants via air exposure will be accompanied by specific attention on potential effects of airborne fluoride on livestock and wildlife (contamination of grass via air).

The following arguments have been brought forward for not addressing the water compartment (including sediment and wastewater treatment systems) in the RA of AlF₃ at this stage:

- F-emissions to water from the AlF₃ industry are in general lower than the air emissions;
- no information was received that fluorides constitute a water problem at a regional scale in the EU;
- fluoride emissions from unintentional sources, in particular those from the fertiliser industry (phosphate ore), by far exceed the emissions from the intentional emissions of fluoride to water at a regional scale. The contribution of unintentional sources is also expected to be high for the atmospheric F emissions, but to a relatively lower extent as for water;
- with respect to the potential emissions of AlF₃ complexes it should be realised that the toxicity of these complexes is primarily related to the aluminium (free F has a much lower aquatic toxicity than Al ions). It thus seems more obvious to assess these risks in a possible future RA of aluminium and aluminium compounds.

In the RA of HF the Predicted Environmental Concentrations (PEC) values for the terrestrial compartment (calculated from the deposition of HF) were found to be negligible compared to background concentrations (conclusion ii). For this reason also for AlF₃ a local risk

assessment for the terrestrial compartment is not considered necessary as long as the deposition of F from the different processes, in which AlF_3 is produced or used, are not significantly higher than for HF. Potential effects of the aluminium (from AlF-complexes) on terrestrial ecosystems will not be addressed in the TRA (see water above). The terrestrial ecosystem, plants in particular, will therefore principally be addressed via the route of atmospheric fluoride exposure.

As this RA is targeted on the environmental effects of fluoride emissions to air, the human health risk assessment is limited to man indirectly exposed via the environment. In the HF risk assessment report (2001), all human health protection targets are included.

0 OVERALL RESULTS OF THE RISK ASSESSMENT⁴

CAS Number: 7784-18-1
 EINECS Number: 232-051-1
 IUPAC Name: Aluminium fluoride

Environment

Terrestrial compartment

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

Conclusion (ii) for the terrestrial compartment applies to all EU primary aluminium production sites at a local scale (see risk characterisation for the atmosphere). Also for the AlF_3 producers conclusion (ii) is drawn at a local scale. At the regional scale the PEC derived with EUSES taking into account a higher deposition velocity did not exceed the PNEC (conclusion ii).

Atmosphere

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

For AlF_3 production site 4 and the formulation site 5 conclusion (ii) is applicable, as there is minimal and no emission to air, respectively.

For sites 1, 2 and 3 the PEC local exceeds the PNEC due to the contribution of the regional background concentration. However, in view of the limited contribution of the local air concentration to the exceeding of the PNEC, conclusion (ii) is drawn for these sites.

The regional PEC based on both intentional and unintentional sources is $0.20 \mu\text{g}/\text{m}^3$, which equals the established $\text{PNEC}_{\text{plant-air}} = 0.2 \mu\text{g}/\text{m}^3$. As the Dutch mean measured concentration of $0.07 \mu\text{g}/\text{m}^3$ confirms that the PNEC is not exceeded conclusion (ii) is drawn for the regional scale.

Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Conclusion (iii) applies to all primary aluminium production sites (downstream use of AlF_3) at the local scale. At almost all primary aluminium production sites fluoride monitoring programs are in place. The monitoring programs are not evaluated within the scope of this RAR.

⁴ Conclusion (i) There is a need for further information and/or testing.
 Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.
 Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Non compartment specific effects relevant to the food chain

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

For AlF_3 production sites no risk is indicated for the winter season and the grazing season (conclusion ii) for the non compartment specific effects relevant to the food chain.

Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Local air concentrations around the primary aluminium production sites exceed the atmospheric NOECs for livestock of $0.8 \mu\text{g}/\text{m}^3$ and $0.3 \mu\text{g}/\text{m}^3$ for the grazing season and winter season, respectively (conclusion iii). It is emphasized that wildlife is probably more susceptible to fluorides than livestock.

Since the risk for non compartment specific effects relevant to the food chain is determined by the deposition via the atmosphere any reduction measures needed to reduce the risk for the atmosphere will also reduce the risk for these specific effects.

Human health

Human health (toxicity)

Humans exposed via the environment

The background intake via food and drinking water of the fluoride-ion is circa $85 \mu\text{g F}^-/\text{kg bw}$ day (HF RAR, 2001; Table 4.5, page 56). In analogy with F^- intake via air for HF, the F^- intake via air from AlF_3 use is put into the context of the overall F^- intake. The intake of F^- of $7.7 \mu\text{g}/\text{kg bw}/\text{day}$ is marginal compared to the total daily fluoride intake (**conclusion ii**).

The regional air concentration of F^- is $0.2 \mu\text{g F}^-/\text{m}^3$. This concentration would lead to an intake of $6 \times 10^{-2} \mu\text{g F}^-/\text{kg bw}/\text{day}$ which is negligible compared to overall intake of fluoride via food and drinking water of $85 \mu\text{g F}^-/\text{kg bw}/\text{day}$ (**conclusion ii**).

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EUSES Calculations can be viewed as part of the report at the website of the European Chemicals Bureau:
<http://ecb.jrc.it>

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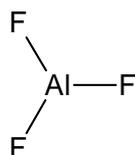
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1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION OF THE SUBSTANCE

CAS Number: 7784-18-1
EINECS Number: 232-051-1
IUPAC Name: aluminium fluoride
Molecular formula: AlF_3
Structural formula:



Molecular weight: 83.98
Synonyms: aluminum fluoride, aluminium trifluoride, aluminum trifluoride

1.2 PURITY/IMPURITIES, ADDITIVES

Purity: >97% (wet production process)
>90% (dry production process)
Impurity: For both qualities the balance is aluminium oxide or aluminium hydroxide depending on the production process used.
Additives: none

1.3 PHYSICO-CHEMICAL PROPERTIES

The data are based on references as mentioned in the IUCLID dataset (11 september 2001), as submitted by the industry.

Table 1.1 Summary of physico-chemical properties

Property	Value	Remarks
Physical state	solid	
Melting point	1257° C	Melting point is not relevant because of sublimation. No decomposition below 600°C.
Boiling point	1537° C	
Relative density	850 or 1,500 kg/m ³ at 20° C ⁽¹⁾	
Vapour pressure	1.3 hPa at 1238° C	
Water solubility	5.3 – 9.4 mg/l at 25° C	pH = 5.9 for saturated solution
Partition coefficient n-octanol/water (log value)	Not applicable	
Granulometry	>0.090 mm 74% >0.063 mm 18% >0.045 mm 4% <0.045 mm 4%	
Conversion factors	Not applicable	
Flash point	Not applicable	
Autoflammability	Not applicable	
Flammability	Non flammable	
Explosive properties	Not explosive	
Oxidizing properties	No oxidising properties	
Viscosity	Not applicable	
Henry's constant	7.03E-06	
Surface tension	Not applicable	
Additional remark	Not combustible/ does not support combustion	

⁽¹⁾ depending on the filling process if shaking is applied or not

1.4 CLASSIFICATION

Current classification: -

Proposal of rapporteur: No Classification

Aluminium chloride, several aluminium alkyls and HF are already listed on Annex I with no classification and labelling for the environment. The aluminium substances were not classified because aluminium precipitates at an environmental pH range. Toxicity is only observed at a low pH. In water with a hardness >50 mg CaCO₃/l, fluoride precipitates with Ca as CaF₂ (especially when pH>4.5), which will reduce the toxicity significantly. In one toxicity study (Rai *et al.* 1996) performed at an environmental relevant pH range toxicities were observed in a classifiable range. However, no information was provided on the hardness of the test medium. Therefore, no classification for the environment is concluded for AlF₃.

2 GENERAL INFORMATION ON EXPOSURE

2.1 PRODUCTION

2.1.1 Production processes

The production of AlF_3 is located at different sites in the European Union (see **Table 2.1**). According to the IUCLID (2001), there were five producers in the EU in 2000. Within industrial category 2, two production processes of AlF_3 can be distinguished:

1. Production in two steps with HF (83,672t):

I: Mixing fluorspar with sulphuric acid producing HF (gas).

II: Formation of AlF_3 out of aluminium oxide (Al_2O_3) or, for one producer, aluminium hydroxide ($\text{Al}(\text{OH})_3$) and HF.

2. Production without HF (23,000t):

AlF_3 (formed out of aluminium hydroxide and fluorosilicic acid), is purified by crystallisation, drying and calcination.

At one site 5 tons of AlF_3 are in fact formulated, since bought AlF_3 and aluminium fluoride-3-hydrate is dried, mixed and packed in bags and no chemical reactions are involved.

2.1.2 Production capacity

The total EU production (2000) of all AlF_3 is 106,677 tonnes, according to exposure information provided by industry. Next to the production in the EU AlF_3 is also imported by two companies (Pechiney in Italy and Alcan Smelting and Power in the U.K.). The total quantity imported for the year 2000 amounts to 14,244 tonnes. A total quantity of 57,095 tonnes is exported (2000) by three manufacturers. The total amount of AlF_3 within the EU for the year 2000 is $(106,677 + 14,244 - 57,095 =) 63,826$ tonnes.

Table 2.1 Production sites of AlF_3 in the EU

Company	Location
Derivados del Fluor SA	Urdiales, Spain
Honeywell Special Chemicals	Seelze, Germany
Alufluor AB	Helsingborg, Sweden
Fluorsid S.p.A.	Assemini, Italy
Boliden Odda AS	Odda, Norway

2.2 USES

Table 2.2 shows the industrial and use categories of AlF_3 as indicated by the downstream users. The main use of AlF_3 is as a temperature-regulating agent, a pH-regulator and as a solubility enhancer of aluminium oxide in the electrolyte solution in the production process of

aluminium. The use of AlF_3 as such results in a lowering of the energy consumption in the aluminium pot. The raw material (aluminium oxide) is melted and split in aluminium and oxygen. **Table 2.3** gives an overview of all primary aluminium smelters in the EU for which the European Aluminium Association (EAA) provided information on HF emission for the year 2002.

The minor downstream uses of AlF_3 , reported by the producers are summarised in **Table 2.4**. Other minor uses of AlF_3 found on the internet are for optical coating as an essential component of anti-reflective coatings and in semiconductors. A total of 52 tonnes of AlF_3 was sold to traders, for which it is also assumed that it is used for other purposes than aluminium production.

Table 2.2 Industrial and use categories of AlF_3 .

Industry category	IC no.	Use category	UC no.
Metal extraction, refining and processing	8	pH regulating agent	40
Metal extraction, refining and processing	8	Process regulators (catalysts)	43

Table 2.3 Users of AlF₃: primary aluminium smelters in the EU.

Company	Location(s)
Elkem Lista	Norway
Elkem Mosj.	Norway
Hydro Årdal ¹	Norway
Hydro Høyen ¹	Norway
Hydro Karm	Norway
Hydro Sund	Norway
Sørval AS	Norway
Trimet Aluminium	Germany
Hydro Stade ²	Germany
Hydro Neuss	Germany
HAW	Germany
Corus Voerde	Germany
Aluminium Delfzijl	Netherlands
PNL Vlissingen	Netherlands
Anglesey Al.	United Kingdom
Alcan Lynem	United Kingdom
Alcan Lochab	United Kingdom
Nordural	Iceland
Alcan Isal	Iceland
Kubikenborg AB	Sweden
Talum	Slovenia
Slovalco	Slovakia
Aluminium of Greece	Greece
Alcan Lannemezan ³	France
Alcan Dunkirk	France
Alcan St. J. De Maurienne	France
Alcoa San Ciprian	Spain
Alcoa Aviles	Spain
Alcoa La Coruna	Spain
Alcoa P. Vesme	Italy
Alcoa Fusina	Italy
Alcan Steg ²	Switzerland

¹ a part of the production plant has been closed

² plant has been closed

³ plant is being closed at the moment

Table 2.4 Reported minor uses of AlF₃.

Use	Tonnage	% of total tonnage
Metal treatment	170	0.16
Unknown (traders)	52	0.05
Soldering of car coolers	50	0.05
Enamelling	48	0.04
Fluxing agent	43	0.04
Production of welding paste	14	0.01
By ceramic industry	7	<0.01
Coating for protection of components	1.35	<0.01
Production of aluminium oxide	1.35	<0.01
Total:	386.7	0.36

As no other significant uses were reported, neither by producers nor by downstream users, it is assumed that the main application is for production of aluminium, which is in general agreement with the information provided by the producers (> 99.6% used for aluminium production). As a consequence the risk assessment will focus on this particular use.

2.3 TRENDS

Very limited data was submitted by the industry on trends and expected production volumes and fluoride emissions in the future. Based on the information provided by two producers it is assumed that the total EU production of AlF₃ will be more or less the same in the next five years (2006 – 2010). In addition, no further reduction in fluoride emissions is expected based on this information.

2.4 LEGISLATIVE CONTROLS

All primary aluminium production plants are according to the European Integrated Pollution Prevention and Control (IPPC) Bureau Directive 96/61/EC as described in the Reference Document on Best Available Techniques in the Non Ferrous Metals Industry (ICCP, 2001) under a permitting process by their national local authorities. The reference document (BREF) prescribes different emission limit values for primary aluminium electrolysis (<0.2 mg HF/Nm³)¹ and primary aluminium smelters (<1 mg total fluoride/Nm³) under application of Best Available Techniques (BAT). However, these standards can not be related to the emission data in this RAR. As indicated by the industry almost all sites do have a monitoring program in place, measuring not only the air concentration of HF in the immediate surroundings of the plant, but also measuring the HF content in vegetation, like grass and pine needles. Next to the fluoride content analysis, the vegetation is also visually inspected in order to check for fluoride-linked vegetation damage. The on-site monitoring programs are not evaluated within the scope of this RAR.

¹ THE EMISSION LIMIT VALUE SHOULD BE CONSIDERED AS A DAILY AVERAGE BASED ON CONTINUOUS MONITORING DATA DURING THE OPERATING PERIOD UNDER STANDARD CONDITIONS OF 273K, 101.3 kPa, MEASURED OXYGEN CONTENT AND DRY GASS, WITHOUT DILLUTION WITH AIR., IN WHICH THE N STANDS FOR NORMALISED.

In addition, OSPAR prescribes an emission limit value for the primary aluminium industry of 0.4 kg HF per ton produced aluminium, which is linked to production (PARCOM, 1994). It should be noted that the current maximum emission under BAT prescribed by OSPAR does not warrant environmental concentrations below the PNEC of 0.2 µg/m³ (see section 3.1.5.1.2, **Table 3.4**), since 21 of the 32 sites fulfil this criterion.

In the WHO Air Quality Guideline for Europe (2000) it is concluded that the available information does not permit the derivation of an air quality guideline value for fluoride(s). In addition, it is recognised that fluoride levels in ambient air should be less than 1 µg/m³ to prevent effects on livestock and plants and that these concentrations will also sufficiently protect human health.

3 ENVIRONMENT

3.1 ENVIRONMENTAL EXPOSURE

3.1.1 Environmental releases

3.1.1.1 Release from production

All production processes applied are continuous and executed in closed systems. Of the total production of 106,677 tonnes of AlF_3 in 2000, the main part is produced with HF (83,672 tonnes). Emission factors derived from the data provided by the producers range from 2.3 to 14.4 g HF per ton AlF_3 for the year 2000 (see **Table 3.1**). Four out of five producers, responsible for almost the total EU production, emitted a total amount of 1,190 kg HF in the year 2000. Location number 5 is in fact a formulation site, since AlF_3 and aluminium fluoride-3-hydrate are dried, mixed and packed in bags without chemical reactions involved. Consequently, no HF emission is expected from this formulation step. The total annual EU emission for AlF_3 production of 1.2 ton HF will be taken forward to the regional risk assessment.

Table 3.1 Emission rates of HF for AlF_3 -production sites for the year 2000.

Location number	Tonnage of AlF_3 (t/year)	Total HF emission in 2000 (kg/year)	Emission rate (g HF/t AlF_3)
1	42,000*	603 ⁽¹⁾	14.4
2	28,372*	227	8
3	23,000	330	14.4
4	13,300*	30 ⁽¹⁾	2.3
5	4.5 ⁽²⁾	0	0
Total emission	106,677	1,190	

* produced with HF

⁽¹⁾ Fluoride emissions reported as kg F/year

⁽²⁾ AlF_3 and aluminium fluoride-3-hydrate are dried, milled and mixed and packed in bags.

3.1.1.2 Release from industrial/professional use

During the electrolytic production process of aluminium, considerable amounts of F-gases (mainly HF) and F-particulates (consisting partly of HF adsorbed on aluminium oxide particles) will escape into the (work) atmosphere. In two reports of the Norwegian Institute for Air Research (NILU) detailed information is given on the emission of fluoride at two Norwegian aluminium production sites between 1990 and 1997. According to the European Aluminium Association (EAA) these sites are representative for other aluminium smelters in Europe, it can be concluded that roughly 10% of all HF is emitted via chimneys of several gas scrubbers, while the main part (approximately 90%) of fluoride is emitted to the atmosphere with ventilation air over a roof of an aluminium electrolysis pot room, which can be up to 1,000 meters in length. In addition, HF is emitted at a height (of both roof and chimney) of at

least 25 m. The release to other environmental compartments (in particular wastewater) is negligible or low compared to the release to the atmosphere. Consequently, the release to other environmental compartments is mainly via atmospheric deposition of HF and fluoride particulates.

The data supplied by the manufacturers and users revealed that over 99.6% of all AlF_3 is used by the aluminium industry. For all aluminium smelters in the EU member states the total F-emission for the year 2002 is available. For 28 out of 32 sites the fraction present in the gaseous HF form is specified. The ratios between total F and HF range from 10.9 to 88.4% (see **Table 3.2**). The average fluoride emission of a primary aluminium smelter within the EU consists for 53% of HF and 47% of particulate fluoride. In cases where the HF emission is not specified, the maximum proportion of HF is taken as a worst-case estimate for the HF emission. The summation of the fluoride emissions results in a total of 4,929 tonnes for the year 2002. Assuming that all of the AlF_3 within the EU (63,826t) is used by the primary aluminium industry this results in a total emission of 2,463 ton HF per year.

According to the International Aluminium Institute (IAI) in the year 2000 3,801,000 ton of aluminium was produced in Western-Europe. Since in **Table 3.2** the reported emissions can not directly be related to production levels (only the production capacity is given), the total HF emission reported for 2002 is considered to be representative for the year 2000.

The emissions resulting from the other minor uses of AlF_3 (approximately 0.4% of 106,677t) in the EU can be considered negligible compared to the use by aluminium smelters.

Table 3.2 Total F and HF emissions for all EU primary aluminium smelters (AlF₃ downstream user sites) for the year 2002

Location number	Production capacity (tons aluminium / year)	Total F-emission (tonnes/yr)	HF emission (tonnes/yr)	Ratio HF of total F-emission (%)
1	300,000	86.7	50.8	58.6
2	281,000	124	47.2	38.1
3	255,000	119.3	68	57
4	229,000 ¹	154.8	136.8*	(88.4)
5	224,000	118.6	35	29.5
6	222,000	60.2	53.2*	(88.4)
7	219,000	174	86	49.4
8	185,000	73.6	47.8	64.9
9	176,000	97.9	69.4	70.9
10	169,000	188	140	74.5
11	166,000	246.7	193.4	78.4
12	164,000	85.9	63.2	73.6
13	158,000	30.1	26.6	88.4
14	151,000	30	10	33.3
15	150,000	505	286	56.6
16	145,000	76.1	50.4	66.2
17	135,000	81.3	51.5	63.3
18	134,000	59.8	52.9*	(88.4)
19	117,000	1,360	420	30.9
20	110,000	103	84	81.6
21	102,000	67.5	10	14.8
22	93,000	39.1	16.7	42.7
23	90,000	79.2	41	51.8
24	90,000	41	29.1	71
25	89,000	288	111	38.5
26	86,000	145.7	66.2	45.4
27	76,000 ¹	39.7	21.6	54.4
28	69,000 ²	110	12	10.9
29	50,000 ³	215	129	60
30	45,000	91.5	29	31.7
31	44,000 ²	13.9	12.3 ⁴	(88.4)
32	41,000	23.4	13.3	56.8
Total	4,565,000	4,929	2,463	

¹ a part of the production plant has been closed

² plant has been closed

³ plant is being closed at the moment

⁴ No data on HF: HF was estimated from location number 13 for which (26.6/30.1) 88.4% (realistic worst-case) of total fluoride emission was reported to be HF.

3.1.1.3 Summary of releases

The total amount of HF released to the atmospheric compartment in the EU during production (1.2 t/y) and industrial use (2,463 t/y) of AlF_3 amounts to 2,464 tonnes HF for the year 2000. It can be concluded that a negligible fraction of HF is released to the atmosphere during the production of AlF_3 (1.2 t/y) compared to the total annual emission of HF within the EU (11,945 t/y; see section 3.1.6.2).

3.1.2 Environmental fate

3.1.2.1 Release and fate of HF

HF may enter the environment from both natural (volcanoes, weathering of minerals and marine aerosols) and anthropogenic sources. The latter includes production of HF itself, but HF is also formed as a by-product during other industrial processes (phosphate fertiliser, aluminium and steel production, ceramic industry etc.).

HF enters the environment via industrial waste water, atmospheric deposition and by the application of sludge and fertilisers. Once released in the environment HF is unlikely to remain in its original form for very long. In air, water and soil HF is transformed to a variety of other F-compounds. An extensive overview of the fate of fluorides is given in the RIVM Criteria Document on Fluorides (Slooff *et al.*, 1988) and in the RAR of HF (2001). In this section an overview is given of the fate of HF in the environment.

Fluorides are emitted to the atmosphere as gaseous compounds (75%) or as solids in the form of aerosols (25%). Gaseous fluorides in the atmosphere are predominantly HF (and SiF_4). HF is removed relatively rapidly from the atmosphere by both dry and wet deposition with a half-life of ca. 14 hours and ca. 12 hours for dry and wet deposition, respectively. Fluoride aerosol is eliminated slowly predominantly (65%) by wet deposition with a half-life of 50 hours. For dry deposition of fluoride aerosol a half-life of 12 days is reported (Slooff *et al.*, 1988).

The dry deposition for the whole Netherlands is calculated to be 30 and 1 mg/m^2 per year for gaseous and aerosol fluoride, respectively (1300 tonnes/year in total). The wet deposition in the Netherlands is calculated to be 13 and 4 mg/m^2 for gaseous and aerosol fluoride, respectively (700 – 1,100 tonnes/ year in total; Slooff *et al.*, 1988). Fluorides in air are deposited in the general vicinity of an emission source (IPCS, 2002).

When HF (F) is released in fresh water at pH above 5, the free ion is the main fluoride species when calcium concentrations are low. At lower pH, the proportion of fluoride ion decreases, while HF_2^- and non-dissociated HF increase. In the presence of phosphate insoluble fluorapatite is formed, a large part of which is transferred to the bottom sediments (Slooff *et al.*, 1988).

AlF_3 can be released during the production process or as a result of industrial use to waste water. At most of the production and downstream user sites for which exposure information is provided free fluoride is removed from waste water by adding calcium. The precipitate CaF_2 is removed and sent to landfill. Even when assumed that fluoride is emitted as free ions to waste water, this emission is not expected to result in considerable atmospheric HF emission,

as only a fraction of fluoride occurs as HF, especially when the pH is above 5. It is however more likely that AlF_3 complexes are released instead of free ions. Therefore it can be concluded that the release of HF to the atmosphere can be considered negligible.

In soils with $\text{pH} < 6$ fluoride is considered to be immobile as it is predominantly occurs in the form of fluoride containing minerals. At a pH above 6, the fluoride ion is the dominant species.

Fluoride accumulates, food-dependently in skeletal tissues of both aquatic and terrestrial vertebrates and invertebrates. Bioaccumulation occurs in marine organisms and, to a lesser extend, fresh water organisms. Reported BCF-values for marine organisms range up to approximately 150 and 60 for fish and crustacea, respectively.

The most important exposure route for plants is uptake from the atmosphere. Concentrations in plants in the vicinity of a HF production plant range up to approximately 200 mg/kg, with mean levels between 20 and 50 mg/kg dry weight. Generally, lowest fluoride levels are found in herbivores and (somewhat) higher levels in predators (Slooff *et al.*, 1988).

3.1.2.2 Fate of aluminium fluoride

AlF_3 is not photodegradable, but abiotic hydrolysis of AlF_3 does occur. Many complexes can be formed and occur in water such as $\text{Al}(\text{OH})_3$, $\text{AlF}_3(\text{OH})^-$, $\text{Al}(\text{OH})_4^-$, AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})\text{F}^+$, AlF_2^+ , AlF_2^{2+} and AlF_4^- . The forming of complexes is dependent on several factors such as pH, water hardness and temperature. In hard water (>50 mg CaCO_3/l), fluoride precipitates with Ca as CaF_2 (especially when $\text{pH} > 4.5$). In water AlF_3 complexes are generally the most dominant inorganic aluminium species (Driscoll *et al.* 1980). Free aluminium and aluminium hydroxide complexes are present in relatively smaller amounts. In the low pH range formation of AlF_3 complexes will dominate, whereas hydrolytic species will predominate at higher pH levels (Sjöberg, 2002). Fluoride ions, being similar in size to hydroxyl ions, will readily substitute in these complexes (EHC 194, 1997), although the complexes formed with OH^- are much stronger than with F^- ions.

3.1.3 Aquatic compartment (incl. sediment)

No risk assessment for the water compartment (including sediment and wastewater treatment systems) was performed based on several reasons explained in the general introduction.

3.1.4 Terrestrial compartment

3.1.4.1 Calculation of $\text{PEC}_{\text{local}}$

In the risk assessment of HF the Predicted Environmental Concentrations (PEC) values for the terrestrial compartment (calculated from the deposition of HF) were found to be negligible compared to background concentrations (conclusion ii). For this reason also for AlF_3 a local risk assessment for the terrestrial compartment is not considered necessary in case the deposition of F from the different processes, in which AlF_3 is produced or used, are not significantly higher than for HF. For the AlF_3 production such is the case. However, it appeared that the downstream users of AlF_3 emitted significantly more HF to the atmosphere than the HF industry (see section 3.1.6.1). It should be noted that potential effects of

aluminium (from AlF-complexes) on terrestrial ecosystems will not be addressed in the TRA (see water section 3.1.3 above). The terrestrial ecosystem, plants in particular, will principally be addressed via the route of atmospheric fluoride exposure.

3.1.4.1.1 Calculation of PEC_{local} for production

For the AlF₃ industry only the atmospheric deposition is used for calculating the concentration in soil. The contribution of STP sludge applied on agricultural soils is not taken into account since it is considered to be negligible. For the production plant with the highest emission to air (plant 1: 603 kg HF/yr (see **Table 3.1**) 1.9 kg/d) a local soil concentration is calculated with EUSES 2.0.3. The fraction of the main source was set to 1, and the number of emission days based on exposure information was set to 320 days. Based on experimental data a higher deposition velocity of 1.4 cm/s (Slooff et al., 1988) was used, in conformity with the RAR on HF (2001) to calculate the deposition flux, which results in a soil concentration of 0.1 mg/kg.

3.1.4.1.2 Calculation of PEC_{local} for industrial/professional use

For the downstream use of AlF₃ the concentration in soil is directly related to the atmospheric deposition of HF, since the contribution of STP sludge applied on agricultural soils is considered to be negligible. Based on a recommended deposition velocity of 1.4 cm/s by Slooff *et al.*, 1988, the atmospheric PNEC of 0.2 µg/m³ results in a soil concentration of 0.035 mg F/kg, which is much lower than the PNEC for soil of 11 mg/kg. For this reason the soil concentrations in the surrounding of the European aluminium smelters have not been worked out in detail, since risks identified for soil will be subordinated to the risks assessed for plants for atmospheric HF concentrations (see section 3.3.1).

3.1.4.1.3 Calculation of PEC_{regional}

Based on a regional air concentration of 0.20 µg HF/m³ (see section 3.1.6) and the higher deposition velocity a regional soil concentration is calculated of 0.04 mg F/kg.

3.1.4.2 Measured levels

3.1.4.2.1 Local near industrial sources

Elevated fluoride soil concentrations are reported near aluminium sites. Within 4 km from an aluminium plant in Greece the average fluoride concentration was 823 mg/kg. Between 5 and 15 km and between 8 and 15 km the total fluoride concentration was 570 and 339 mg/kg, respectively. Within 0.5 km from a former aluminium smelter (closed in 1992) in Ranshofen, Austria water-soluble fluoride concentrations of 84-124 mg/kg (range of means) were measured. At 15 km the concentrations were about 10 times lower: 9.8 –10 mg/kg (Tscherko & Kandeler, 1997). Likewise, in the surrounding of five Norwegian aluminium plants elevated levels of CaCl₂-soluble fluoride in the uppermost soil horizon were measured, with soil concentrations between 15 - 70 mg/kg close to the plants declining to 1-10 mg/kg at a distance of 15 km from the plants (Hydro Aluminium, 1994).

3.1.4.2.2 Regional background

The total fluoride content of organic soils in areas without natural phosphate or fluoride deposits ranges from 20-1000 mg/kg and can be several thousands mg/kg in mineral soils with deposits of fluoride (IPCS, 2002). The clay and organic carbon content as well as the pH of soil are primarily responsible for the origin and retention of fluoride in soils. In the Netherlands, total fluoride concentrations in clay soils range from 330 to 660 mg/kg (dryweight). In soils with higher pH values a higher amount of soluble fluoride complexes is found (Slooff *et al.*, 1989). Soil samples taken from (natural) areas in the Netherlands that are assumed to be not anthropogenically influenced, showed fluoride concentrations of 364-720 mg/kg (total F) and 3.6-4.6 mg/kg (water extractable F) (Joode *et al.*, 1997). In agricultural soils of the Netherlands the total fluoride content ranged from 39-679 mg/kg and the water soluble content ranged from 0.5-13 mg/kg (data from 1971/1972) (Slooff *et al.* 1989).

The fluoride content in groundwater depends on many factors such as geological, chemical and physical characteristics of the water-supplying area, the consistency of the soil, the temperature, the pH, the depth of the well etc. Recent data on the fluoride concentration in groundwater are not available, but it would rarely exceed 0.5 mg/l (Slooff *et al.*, 1989). Mean fluoride concentrations in Dutch groundwater are < 0.01-1.5 mg/l (pH > 6) and < 0.01-0.58 mg/l (pH < 6) (Stuyfzand, 1991). In Germany concentrations of 0.07-0.13 mg/l were measured in the riverbank groundwater of the Rhine. In Finland riverbank groundwater fluoride concentrations ranged from 0.01 to 0.4 mg/l (Slooff *et al.*, 1989).

3.1.4.3 Comparison between predicted and measured levels

Based on the concentration measured in the vicinity of aluminium plants, HF concentrations seem to be elevated close to the aluminium plants. The regional soil concentration resulting from the atmospheric deposition is considered negligible in comparison to the background concentration.

3.1.5 Atmosphere

3.1.5.1 Calculation of PEC_{local}

3.1.5.1.1 Adjustment of defaults

During the evolution of the risk assessment both the AlF_3 and primary aluminium industry provided more detailed information with respect to the production plants, which indicated that some of the default settings in EUSES are not representative for the real situation. Based on this information it was decided to replace these defaults with more realistic data resulting in more realistic calculations of the local air concentrations. These adjustments include the emission height (both for AlF_3 and aluminium producers) and the type of emission (point versus emission over a surface).

In order to demonstrate the impact of the type of emission (point versus multiple source) and emission height, additional OPS-Pro 4.1 calculations were carried out to predict the HF concentrations at 100 and 500 m. distance from the smelter (see **Table 3.3**). These calculations are based on the provided NILU reports, assuming a realistic worst-case emission

height of 25 m., as given for plant 1 (the other plant has an emission height of 50 m.) and emissions to take place from a surface of 500 by 500 m. (representing the emissions from both the roof and gas scrubbers). The HF concentration calculated for the emission of a point source at a distance of 100 m. with an emission height of 10 m. (EUSES defaults) was set to 100%. As input for the model Dutch climatic and environmental parameters are used. The distance from the surface of emission, is the distance measured from the edge of the surface. The concentrations given are in fact averages of all wind directions. These calculations demonstrate that the impact of adjusting the main assumptions results in a reduction of predicted atmospheric concentrations of 91.5%. It should be noted that the old version of OPS (v1.20E) and consequently EUSES, predicts 20 to 25% higher concentrations in comparison to the latest model version (Pro 4.1), which has been left out of the current calculations.

Table 3.3 Ratios between HF concentrations at 100 and 500 m. distance from the emission source in %.

Emission type:	Distance to source (m)	Emission height:		
		10 m	25 m	50 m
Point source	100	100*	15	1.6
	500	15	5.3	1.8
Over a surface of 500 by 500 m.	100	29	8.5	2.6
	500	10	2.8	1.3

* Average HF concentration conform EUSES default settings is set to 100%

This exercise revealed atmospheric concentrations of HF in the same range as the NILU predictions. It can therefore be concluded that by assuming emissions over a surface instead of one point source and a higher emission height will lower the predicted air concentrations significantly. Using a point source and an emission height of 10 m. the OPS model (a component of EUSES 2.0.3.) predicts a concentration at 100 m. distance, roughly 12 times higher than predicted with emission height 25 m. and emissions over a surface of 500 by 500 m. The OPS-Pro 4.1 derived local concentrations are considered to be more realistic and have been taken forward in the risk assessment.

3.1.5.1.2 Calculation of PEC_{local} for production

The highest C_{local} was calculated with EUSES 2.0.3 (2005) for the main production site with a volume of 42,000 tonnes AlF_3 for the year 2000. The fraction of the main source was set to 1. The number of emission days was set to 320 based on emission data provided by the industry. The emission of fluorides for the year 2000 for this production plant is reported to be 603 kg (see section 3.1.1.1). The HF emission per day is calculated to be 1.884 kg/d (603 / 320). This emission resulted in a C_{local} of 0.46 $\mu\text{g}/\text{m}^3$ and 0.069 $\mu\text{g}/\text{m}^3$ (after correction of the emission height). In **Table 3.4** an overview is given of the calculated local concentrations for all production sites, before and after correction of the default emission height from 10 to 25 metres. The industry provided the chimney heights of all production sites (ranging from 26 to 87 metres), from which it could be concluded that it is justified to calculate the C_{local} with a minimum emission height of 25 metres. For the formulation site (location no. 5) no HF emission is expected, therefore the calculation of C_{local} is not applicable.

Table 3.4 Emission rates and C_{local} (HF) for the production sites.

Location number	Tonnage of AlF_3 (t/year)	Total HF emission in 2000 (kg/year)	Emission rate (g HF/t AlF_3)	Number of emission days	C_{local} ($\mu\text{g}/\text{m}^3$)	C_{local}^{**} ($\mu\text{g}/\text{m}^3$)
1	42,000	603	14.4	320	0.46	0.069
2	28,372	227	8	318	0.17	0.026
3	23,000	330	14.4	330	0.25	0.038
4	13,300	30	2.3	300*	0.023	0.003
5	4.5	0	0	-	-	-

* Since no information on the number of emission days was given, the default number of 300 days was taken from Table B1.1 (TGD 2003).

** Based on additional information provided by the industry the emission height was set to 25 meters as the chimney height of the production sites ranged from 26 metres to 87 metres. Therefore, the C_{local} was corrected conform the ratio derived from Table 3.5.

3.1.5.1.3 Calculation of $\text{PEC}_{\text{local}}$ for industrial/professional use

Based on the HF emissions data given for the aluminium smelters in the EU member states, the local concentrations are derived using EUSES 2.0.3 (see **Table 3.5**). One out of six downstream users that provided emission data in an earlier stage reported emission of fluorides to water. As in fresh water at pH above 5, the free ion F^- is the main fluoride species, the evaporation of HF from water is considered negligible. To rule out the evaporation of HF from the STP, the emission to water was set to zero. All downstream users reported 365 emission days.

The calculations in EUSES 2.0.3 are based on an included OPS model assuming 100 metres from one point source at an emission height of 10 m. As mentioned in section 3.1.1.2, according to EAA, a more realistic assumption for the aluminium smelters would be an emission from multiple sources at a height higher than 10 m. This has been modelled by NILU for two Norwegian aluminium smelters for the year 1991, where it is shown that the atmospheric fluor concentrations are significantly lower than those calculated with EUSES 2.0.3, although that HF emissions generally decreased from 1991 to 2002 (the year from which our emission data originates). For illustrative purposes the calculated concentrations are included in **Table 3.5** for the two sites (see values between brackets for sites 1 and 4).

Table 3.5 Total F and HF emissions for all EU primary aluminium smelters for the year 2002, including estimated local air concentrations based on model calculations (EUSES 2.0.3 and OPS-Pro 4.1)

Location number	Production capacity (tons aluminium / year)	Total F-emission (tonnes/yr)	HF emission (tonnes/yr)	HF emission (kg HF/ ton aluminium)	EUSES derived: C _{local} HF (µg/m ³)	OPS-Pro 4.1 derived:* C _{local} HF (µg/m ³)
1	300,000	86.7	50.8	0,17	39	3.3 (5)***
2	281,000	124	47.2	0,17	36	3.1
3	255,000	119.3	68	0,27	52	4.4
4	229,000 ¹	154.8	136.8**	0,60	100	8.5 (3)***
5	224,000	118.6	35	0,16	27	2.3
6	222,000	60.2	53.2**	0,24	41	3.5
7	219,000	174	86	0,39	65	5.5
8	185,000	73.6	47.8	0,26	36	3.1
9	176,000	97.9	69.4	0,39	53	2.4
10	169,000	188	140	0,83	110	9.4
11	166,000	246.7	193.4	1,17	150	13
12	164,000	85.9	63.2	0,39	48	4.1
13	158,000	30.1	26.6	0,17	20	1.7
14	151,000	30	10	0,07	7.6	0.65
15	150,000	505	286	1,91	220	19
16	145,000	76.1	50.4	0,35	38	3.2
17	135,000	81.3	51.5	0,38	39	3.3
18	134,000	59.8	52.9**	0,39	40	3.4
19	117,000	1,360	420	3,59	320	27
20	110,000	103	84	0,76	64	5.4
21	102,000	67.5	10	0,10	7.6	0.65
22	93,000	39.1	16.7	0,18	12.7	1.1
23	90,000	79.2	41	0,46	31	2.6
24	90,000	41	29.1	0,32	22	1.9
25	89,000	288	111	1,25	85	7.2
26	86,000	145.7	66.2	0,77	50	4.3
27	76,000 ¹	39.7	21.6	0,28	16	1.4
28	69,000 ²	110	12	0,17	9.1	0.77
29	50,000 ³	215	129	2,58	98	8.3
30	45,000	91.5	29	0,64	22	1.9
31	44,000 ²	13.9	12.3**	0,28	9.4	0.80
32	41,000	23.4	13.3	0,32	10	0.85
Total	4,565,000	4,929	2,208	0,48		

* Calculations based on emission over a surface of 500x500 m. and an emission height of 25 m.; ** No data on HF: HF was estimated from location number 13 for which (26.6/30.1) 88.4% (realistic worst-case) of total fluoride emission was reported to be HF; *** Between brackets: the HF concentration indicated by the NILU ($\mu\text{g}/\text{m}^3$) at circa 500m. distance from the plant for the year 1991.

¹ a part of the production plant has been closed

² plant has been closed

³ plant is being closed at the moment

3.1.5.2 Measured levels

3.1.5.2.1 Local near industrial sources

Two downstream users supplied air measurements of HF in the vicinity of the aluminium production site. One of these reported a concentration of $< 0.4 \mu\text{g}/\text{m}^3$, while the other reported a mean concentration of $170 \text{ ng}/\text{m}^3$.

For the area of Greater Cologne (671 km^2) in Germany measurements of fluorides (as F⁻) in the air showed values between 0.3 and $1.0 \mu\text{g}/\text{m}^3$ (data from 1980; Luftreinhalteplan Rheinschiene Sud 1982-1986). Levels of fluoride in air in the vicinity of emission sources are generally not higher than $2\text{-}3 \mu\text{g}/\text{m}^3$ (IPCS, 2002). In the Netherlands, fluoride in air is measured in a monitoring program near high fluoride-emitting industrial sources. For the site Nieuwdorp fluctuations in *maximum* daily average fluoride concentrations are corresponding with production levels of local aluminium producers (Hammingh, 2001). The reported *maximum* daily and yearly average fluoride concentrations in air range up to $4.6 \mu\text{g}/\text{m}^3$ and $0.45 \mu\text{g}/\text{m}^3$ (see **Table 3.6** and **3.7**), respectively (Hammingh, 2001, 2002). In additional Polish data of fluoride measurements in air yearly average fluoride concentrations are reported of $0.9 - 1.2 \mu\text{g}/\text{m}^3$ at 20 km distance from a former aluminium smelter, which is comparable to the concentration measured nearby (at an unknown distance) of $1.1 \mu\text{g}/\text{m}^3$ in 1999. It has to be noted that the values at 20 km distance have been measured in the city centre of Krakow, there are therefore not considered representative as regional background values. Other reported average concentrations measured near high fluoride-emitting sources in Poland range from 2.05 to $4.2 \mu\text{g}/\text{m}^3$.

Table 3.3 Maximum daily average fluoride concentrations in air ($\mu\text{g}/\text{m}^3$) measured near high fluoride-emitting industrial sources in the Netherlands.

	1998	1999	2000	2001
Nieuwdorp	4.55	3.78	2.26	3.4
Delfzijl	3.21	0.69	-	-
Sas van Gent	1.74	1.89	2.32	1.6
Vlaardingen	0.79	0.97	-	0.4

Table 3.4 Yearly average fluoride concentrations in air ($\mu\text{g}/\text{m}^3$), measured near high fluoride-emitting industrial sources in the Netherlands.

	1998	1999	2000	2001
Nieuwdorp	0.45	0.42	0.31	0.4
Delfzijl	0.26	0.09	0.12	-
Sas van Gent	0.20	0.21	0.18	0.2
Vlaardingen	0.08	0.09	0.04	0.03

Near various industrial sources in the Netherlands, including brickworks, aluminium plant and a glass fibre factory, annual average fluoride concentrations measured from 1980-1986, ranged from 0.2 to 0.8 $\mu\text{g}/\text{m}^3$ (Slooff *et al.*, 1989). Median concentrations of fluoride in the air surrounding a Norwegian aluminium smelter in the spring and summer of 1994, ranged from 1.3 to 3.8 $\mu\text{g}/\text{m}^3$ (IPCS, 2002). The industry submitted data provided by the NILU (Norwegian Institute of Air Research) from a measuring station about 600 m from the plant fence (and approximately 700 to 800 metres from the nearest emission source) of a aluminium smelter. For the year 2002 measured average fluoride (F^-) levels per month ranged from 0.5 to 3.3 $\mu\text{g}/\text{m}^3$. In addition, the EAA provided monitoring data for location number 10 at 100 metres distance from the boundary of the smelter resulting in an annually averaged monthly concentration of 0.4 $\mu\text{g}/\text{m}^3$. Also the Swedish Chemicals Inspectorate KEMI provided monitoring data with respect to a primary aluminium producer in Sweden. Mean monthly average fluoride concentrations of sites at 2 (W) and 4 km (NW) distance from the aluminium producer were very similar and ranged from 0.21 to 0.28 $\mu\text{g}/\text{m}^3$ (minimum value 0.04, maximum 0.70 $\mu\text{g}/\text{m}^3$) for the years 2002 to 2004.

3.1.5.2.2 Regional background

The natural occurring background concentration of fluoride is calculated to be 0.0005 $\mu\text{g}/\text{m}^3$. The worldwide background concentration is estimated to be 0.003 $\mu\text{g}/\text{m}^3$, taking anthropogenic emissions into account (Slooff *et al.*, 1989). The mean concentrations of fluoride in ambient air are generally less than 0.1 $\mu\text{g}/\text{m}^3$ (IPCS, 2002).

Air concentrations measured in the Netherlands for 1982-1983 range from 0.03-0.1 $\mu\text{g}/\text{m}^3$, with the highest concentrations in the south-west. Mean concentration for the Netherlands is 0.07 $\mu\text{g}/\text{m}^3$ (Slooff *et al.*, 1989). At one non-industrial urban location in the UK the mean fluoride concentrations are below the detection limit of 0.1 $\mu\text{g}/\text{m}^3$, with a range of <0.1-0.17 $\mu\text{g}/\text{m}^3$ (IPCS, 2002).

3.1.5.3 Comparison between predicted and measured levels

The data provided by the downstream users can not be used for deriving a C_{local} as no information was given on the exact position where these measurements were performed (i.e. distance to the emission source).

When the measured data are compared with the calculated data, they seem to differ considerably, at first sight. The range of the calculated data (0.65 to 27 $\mu\text{g}/\text{m}^3$; see section 3.1.5.1.2) is approximately 3 to 6 times higher as the range of measured data (0.2 to 4.55 $\mu\text{g}/\text{m}^3$; see section 3.1.5.2.1). As it is most of the times not clear at what distance from the emission source these concentrations in air have been measured, it seems plausible that this difference can be explained by distance to the emission source. The predicted HF levels are calculated for a distance of 100 metres from the emission source with OPS-Pro 4.1. In **Table 3.5** also the impact of measuring concentrations at greater distance (500 m.) can be derived. From this table it can be concluded that the predicted concentrations at 500 m. distance are an additional factor of 3 lower than the predicted concentrations at 100 m. distance from the site.

For some of the monitoring data for fluoride the distance to the aluminium production plants is known. The NILU (see section 3.1.5.2.1) reported fluoride concentrations in the range 0.5

to $3.3 \mu\text{g}/\text{m}^3$ at approximately 700 metres from the emission source. In 1987 and 1988 at 1.65 km from an aluminium plant in the USA the mean concentration of fluoride was 0.79 and $0.85 \mu\text{g}/\text{m}^3$, respectively (CEPA, 1993). These measurements seem to confirm the assumption that the differences can at least partially be explained by the greater distance.

According to the Norsk Elektro Optikk the typical concentration levels in dry scrubber outlets of aluminium plants is in the range of 0.1 to $10 \text{ mg HF}/\text{m}^3$. Comparable emissions ($2\text{-}4 \text{ mg}/\text{m}^3$), also measured in a chimney, from a HF plant result in mean measured atmospheric fluoride concentrations of $0.3\text{-}0.4 \mu\text{g}/\text{m}^3$ at a distance of 500 metres from this site (RAR HF, 2001). Taking these data into account, it can be concluded that the calculated atmospheric concentrations of HF at a distance of 100 metres from the emission source are in general agreement with monitoring data of aluminium smelters.

With respect to the monitoring data for site 10 a direct comparison with the modelled value of $9.4 \mu\text{g}/\text{m}^3$ (see **Table 3.5**) is not possible since 100 metres from the smelter boundary is not the same as 100 metres from the emission surface upon which the calculation is based.

3.1.6 Calculation of $\text{PEC}_{\text{regional}}$

3.1.6.1 The total emission of production and use of HF, CaF_2 and AlF_3

Approximately 92% of all produced and imported CaF_2 in the EU forms the raw material for the production of HF. Approximately 15% of the total amount of produced HF is in turn used for the production of aluminium fluoride.

It can be concluded that the total continental atmospheric emission for intentional use of HF, CaF_2 and AlF_3 is 3,576 tonnes for the year 2000 (see **Table 3.8**). For the reported emissions with respect to the production of HF and downstream use of CaF_2 is referred to the RAR on CaF_2 (2008).

Table 3.5 Combined continental (EU) atmospheric HF emissions for the year 2000 in tonnes per year.

Chemical:	HF:	CaF_2 :	AlF_3 :	Total:
Production	18 ⁽¹⁾	0	1.2	19.2
Downstream use		1,094 ⁽²⁾	2,463	3,557
Total emission :	18	1,094	2,464	3,576

⁽¹⁾ A total emission is calculated for both production as downstream use (see RAR CaF_2 , 2008).

⁽²⁾ Emissions resulting from downstream use of CaF_2 , other than HF-production (RAR HF, 2001 & RAR CaF_2 , 2008).

3.1.6.2 Summary of exposure and calculation of $\text{PEC}_{\text{regional}}$

In **Table 3.9** atmospheric fluoride emissions for industrial sources have been summarised for Europe in 2001 based on data from the European Pollutant Emission Register (EPER). In addition, in **Table 3.10** atmospheric fluoride emissions for industrial sources have been summarised for The Netherlands for the year 1998 in tonnes/year (LAE, 1998). Emission data with respect to the production and downstream use of HF, AlF_3 and CaF_2 (intentional sources) have been combined with emission data of unintentional sources for the calculation of the $\text{PEC}_{\text{regional}}$.

The total EU emission is compared with the total HF emission in the Netherlands multiplied by a factor 10 (extrapolation from region to EU applying the 10% rule, TGD 2003), resulting in an emission of 9,084 tonnes per year. The total regional emissions of intentional sources have been expressed as a percentage of this total EU emission.

Table 3.9 Fluoride emissions to air in the EU in 2001 in tonnes (European Pollutant Emission Register).

No	Industry	Total EU emission to air (t)	Relative within EU (%)	Relative emission (%) within EU of intentional sources (absolute HF emissions)	Source : RAR of
1	Other raw chemicals	12.1	0.1	0.2 (19.2 t)	HF/AlF ₃ /CaF ₂
2	Basemetals	3,462 ¹	29.0	20.7 (2,476 t)	AlF ₃ /CaF ₂
3	Ceramics, glass and building materials	1,683	14.1	9.0 (1,075 t)	CaF ₂
4	Fertiliser compounds	296	2.5	0	-
5	Coal using power plants	6,361	53.3	0	-
6	Electrotechnical	- ¹	-	0.05 (6 t)	CaF ₂
7	Other: Storage and trans-shipping and waste treatment industry	131	1.1	0	-
	Total	11,945	100	29.9 (3,576 t)	

¹ No distinction between metal industry and electrotechnical industry was made

Table 3.10 Fluoride emissions to air in The Netherlands in 1998 in tonnes.

No	Industry	Total Dutch emission to air (t)	Relative within NL (%)	Relative emission (%) within EU of intentional sources (absolute HF emissions)	Source : RAR of
1	Other raw chemicals	35	3.9	0.2 (19.2t)	HF/AlF ₃ /CaF ₂
2	Basemetals	390	42.9	27.3 (2,476t)	AlF ₃ /CaF ₂
3	Ceramics, glass and building materials	448	49.4	11.8 (1,075t)	CaF ₂
4	Fertiliser compounds	6.0	0.7	0	
5	Coal using power plants	22	2.4	0	
6	Electrotechnical	3.7	0.4	0.07 (6 t)	CaF ₂
7	Other: Storage and trans-shipping and waste treatment industry	3.5	0.4	0	
	Total	908	100	39.4 (3,576 t)	

The differences in calculated emissions based on NL emission data and EPER emission data can partly be explained by the origin of the emission data. The NL data originates from the year 1998, while the EPER data originates from 2001. Taking the total relative emissions within the EU into account, it can be concluded that the contribution of the intentional sources (HF emissions resulting from the production and down stream use of HF, AlF₃ and CaF₂) has significantly decreased over this time span (NL: 39%, EPER: 30%), mainly due to the absolute increase in total HF emission within the EU. The main contributions of this intentional emission can be subscribed to the aluminium industry (EPER: 21 % – NL: 27%) and ceramics, glass and building materials (EPER: 9 % – NL: 12%), respectively.

The main unintentional source within NL or EPER emission data differ. The ceramics, glass and building industry is the main unintentional source within the Netherlands (38% (total: 49.4 – intentional: 11.8) of the total EU emission). While, the EPER data indicate that coal using power plants contribute mostly to the total EU HF emission (53%). It should be noted that the grouping of the industry most probably differs between the NL and EPER data given the fact that the total NL emission resulting from the production of raw chemicals (35 tons of HF in 1998) exceeds the emission reported by EPER (12.2 tons of HF in 2001 for the whole of Europe). Other differences can be observed for the ceramics, glass and building materials (factor 3.7), fertiliser compounds (factor 49), coal using power plants (factor 289) and other: storage and trans-shipping and waste treatment industry (factor 37). The derived contributions of both intentional and unintentional sources should therefore be interpreted with care. Since, the total European emissions of HF are considered fairly consistent, the total value for EU based on EPER data has been taken forward in the risk characterisation to derive the PEC_{regional} . The flow chart in **Figure 3.1** gives an overview of the different sources that contribute to atmospheric emission of F and in which RARs the local and regional F releases are assessed.

The total emission within the EU for 2001 of 11,945 tonnes results in a PEC_{regional} of $0.20 \mu\text{g}/\text{m}^3$ for the atmosphere derived with EUSES 2.0.3 (2005). The calculated PEC_{regional} is in the same order of magnitude as the mean measured concentration for the Netherlands of $0.07 \mu\text{g}/\text{m}^3$ (Slooff *et al.*, 1988).

As the calculated PEC_{regional} is comparable to the mean measured concentration in the Netherlands, it was decided to use this value ($0.20 \mu\text{g}/\text{m}^3$) to derive the PEC_{local} for the aluminium production plants (see current RAR).

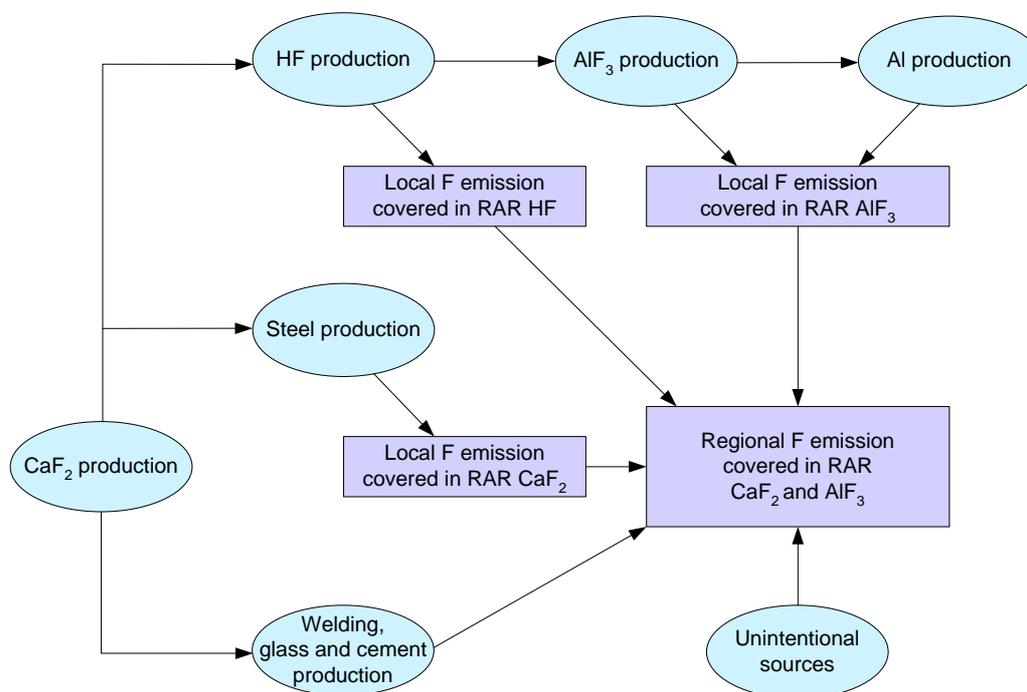


Figure 3.1 Overview of the different sources which contributes to atmospheric emission of fluoride and in which RARs the local and regional fluoride releases are assessed.

3.2 EFFECTS ASSESSMENT: HAZARD IDENTIFICATION AND DOSE (CONCENTRATION) - RESPONSE (EFFECT ASSESSMENT)

3.2.1 Aquatic compartment (incl. sediment)

3.2.1.1 General complexation of aluminium fluoride

All reported tests are performed with AlF_3 . Toxicity can be expected from free Al and F ions, but also from aluminium fluoride-complexes, which will also occur in view of the water solubility (5.3 – 9.4 mg/l; OECD guide-line 105). In water aluminium fluoride-complexes are generally the most dominant inorganic aluminium species (Driscoll *et al.*, 1980). In the low pH range formation of aluminium fluoride-complexes will dominate, whereas hydrolytic species will predominate at higher pH levels (Sjöberg, 2002). Fluoride ions, being similar in size to hydroxyl ions, will readily substitute in these complexes (EHC 194, 1997), although the complexes formed with OH^- are much stronger than with F^- ions.

It has to be noted that there are several factors, which influence the toxicity to a large extent, such as pH, water hardness and temperature. The highest toxicity of aluminium fluoride-complexes is observed at low pH (in general $\text{pH} < 4.5$), in soft water and at higher temperature. In hard water ($> 50 \text{ mg CaCO}_3/\text{l}$), fluoride precipitates with Ca as CaF_2 (especially when $\text{pH} > 4.5$), which will reduce the toxicity significantly. In literature critical levels are often reported for Al^{3+} and F^- only, while many complexes can be formed and occur in water such as $\text{Al}(\text{OH})_3$, $\text{AlF}_3(\text{OH})^-$, $\text{Al}(\text{OH})_4^-$, AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})\text{F}^+$, AlF_2^+ , AlF^{2+} and AlF_4^- . The most toxic forms of aluminium fluoride-complexes are AlF_2^+ and AlF^{2+} , which appeared to be phytotoxic in the aquatic environment. AlF_4^- and $\text{AlF}_3(\text{OH})^-$ form within organisms a functional barrier for ATP-ases and inhibit ATP-ase activity (Strunecká & Patočka, 1999, Husaini *et al.*, 1996 and Rai *et al.*, 1996). In this form the uptake by higher organisms is considered negligible. Free Al and AlOH-complexes, however, are considered to be even more toxic than the aluminium fluoride-complexes (Cameron *et al.*, 1986, Stevens *et al.*, 1997 and Lydersen *et al.*, 1990).

Reference is made to the RAR on HF, which presents toxicity data for the F ion and EHC 194, which presents toxicity data on the Al^{3+} ion.

As no risk assessment for the aquatic environment (both freshwater and marine) is performed, the following aquatic toxicity data are summarised for classification and labelling purposes only. No PNECs will be derived for the aquatic compartment.

3.2.1.2 Toxicity test results

3.2.1.2.1 Fish

The toxicity studies with AlF_3 for freshwater fish are summarised in **Table 3.11**. Results are both expressed as total Al and F concentrations.

Table 3.11 Toxicity data of AlF₃ for freshwater fish

No.	Species	Duration (h)	LC50 (mg/l)	Method	Hardness (mg CaCO ₃ /l)	pH	Reliability	References
1	Brachydanio rerio	96	>7.6 F >3.0 Al (EC50)	OECD 203	250	7.9	2	(Toxicon AB 16/01 – 2001)
2	Salmo salar (yolk-sac larvae)	99	0.41 AlF (LC100)	Other	4.3	5.3	2	(Lydersen <i>et al.</i> 1990)
3	Catostomus commersoni	336	0.48 Al 0.47 F (EC29)	Other	5 – 10	4.4	2	(Driscoll <i>et al.</i> 1980)
4	Catostomus commersoni	336	0.42 Al 0.50 F (EC55)	Other	5 – 10	5.2	2	(Driscoll <i>et al.</i> 1980)

Due to low water solubility no EC₅₀ could be derived in study 1. The reported values of study 2 are based on measured concentrations of natural water sampled in lakes, summarised for all aluminium fluoride-complexes.

In contrast to fresh water, seawater (salinity >32‰) has a constant pH of approximately 8.2. As a consequence aluminium fluoride-complexes will be present in small amounts. In addition the high Ca concentrations in seawater also reduce the toxicity by the formation of complexes with F.

In the RA on HF a long-term NOEC-value of 4 mg F/l for fish has been taken into consideration for the derivation of PNEC for the aquatic environment. In WHO document 194, the lowest reported toxicity value for Al is a 96-h LC₅₀ of 0.095 mg Al/l for the American flagfish. It is also stated that toxicity diminishes if the aluminium is inactivated by complexation with (for example) fluoride.

3.2.1.2.2 Aquatic invertebrates

The short-term toxicity study with AlF₃ for a freshwater aquatic species is summarised in **Table 3.12**.

Table 3.12 Short-term toxicity data of AlF₃ for aquatic invertebrates

No.	Species	Duration (h)	EC50 (mg/l)	Method	Hardness (mg CaCO ₃ /l)	pH	Reliability	References
1	Daphnia magna	48	>7.6 F >3.0 Al (EC50)	OECD 202	250	7.9	2	(Toxicon AB 26/01 – 2001)

Due to low water solubility no EC₅₀ could be derived in study 1. There are no additional tests for aquatic invertebrates, both fresh water as marine, with AlF₃ available.

In the RA on HF a long-term NOEC-value of 8.9 mg F/l for freshwater crustaceans has been taken into consideration for derivation of PNEC for the aquatic environment. In WHO document 194 the lowest reported toxicity value for Al is a 96-h LC₅₀ of 0.48 mg Al/l for the polychaete *Ctenodrilus serratus*.

3.2.1.2.3 Algae

The toxicity studies with AlF₃ for (freshwater) algae are summarised in **Table 3.13**.

Table 3.13 EC₅₀-values of AlF₃ for algae

No.	Species	Duration (d)	EC ₅₀ (mg/l)	Method	Hardness (mg CaCO ₃ /l)	pH	Reliability	References
1	Selenastrum capricornotum	3	0.86 F 0.34 Al (NOEC)	OECD 201	< 60	8.3	2	(Toxicon AB 25/01 – 2001)
2	Nostoc linckia	15	42 AlF	Other	Unknown	7.5	3	(Rai <i>et al.</i> 1996)
3	Nostoc linckia	15	3.36 AlF	Other	Unknown	6.0	3	(Rai <i>et al.</i> 1996)
4	Nostoc linckia	15	1.01 AlF	Other	Unknown	4.5	3	(Rai <i>et al.</i> 1996)

In the toxicity study of Rai *et al.* (1996) the water hardness is not reported and therefore the results are not considered reliable. In addition, the results are expressed as the total sum of Al and F concentrations. No toxicity studies for marine algae have been found. As mentioned before (section 3.2.1.1.1) AlF₃ will be present in marine environment in less toxic forms, and is not expected to have detrimental effects on aquatic organisms.

In the RA on HF the lowest EC₅₀-value of 43 mg F/l for freshwater algae has been taken into consideration for derivation of PNEC for the aquatic environment. In WHO document 194 the lowest reported effect concentration is 5 µg (labile) Al/l in an artificial hard water, which significantly inhibited the growth of the alga *Chlorella pyrenoidosa*. Algae assays are often carried out in culture media containing high concentrations of nutrients, including phosphate, which reduces the availability of aluminium.

3.2.2 Terrestrial compartment

The PNEC for the terrestrial compartment derived in a RAR for HF, will be taken forward without revision in the risk assessment for AlF₃, since no additional data are available. The PNEC for HF of 11 mg/kg was based on the lowest available NOEC, i.e. 106 mg/kg for nitrification divided by an assessment factor of 10. The background F concentrations in the above-mentioned test systems were very low. So theoretically, the PNEC of 11 mg/kg is a concentration that must be added to the neutral background concentration in soil.

3.2.3 Atmosphere

The PNEC derived for plants and atmosphere derived in a RAR for HF, will be taken forward without revision in the risk assessment for AlF_3 , since no additional data are available: $\text{PNEC}_{\text{plant-air}} = 0.2 \mu\text{g}/\text{m}^3$. The PNEC has been derived from the lowest NOEC for highly sensitive plant species, without making use of an extrapolation factor.

3.2.4 Non compartment specific effects relevant to the food chain

The fluoride NOECs, as derived earlier in the HF RAR for both plants (air) and livestock/wildlife (food-air), will be taken forward without revision in the TRA for AlF_3 .

The atmospheric NOECs for livestock (and plants) are $0.8 \mu\text{g}$ and $0.3 \mu\text{g}/\text{m}^3$ (daily averages) for the grazing season and winter season, respectively (see also Slooff *et al.*, 1988), based on a maximum acceptable F level in feed of 55 mg/kg dry weight.

In the RIVM report (Slooff *et al.*, 1988) an annual average NOEC for cattle with respect to the fluoride content in feed (total diet) of 30 mg F/kg feed (dry weight) was derived. In addition, adverse effects on bone structures for wild-life (white-tailed deer) were observed for dietary fluoride concentrations of 25 mg/kg (24 months). It was concluded that wild herbivores are or may be more susceptible to fluoride toxicity than domestic live stock, on a dietary F content basis. This greater susceptibility is probably due to larger variation in F intake by wild animals, in conjunction with the influence of other stress-inducing factors in the environment. This conclusion was supported by the Dutch Health Council (1990).

Thus atmospheric NOECs derived for livestock may provide an insufficient guarantee for the protection of wild fauna.

3.3 RISK CHARACTERISATION

3.3.1 Terrestrial compartment

The potential risk for the terrestrial compartment is caused by the atmospheric deposition of fluoride, which is directly related to the air concentration. As explained in section 3.1.4.1.2, the air concentration causing a risk for the terrestrial compartment via atmospheric deposition is much higher than the one that will cause a risk for the atmospheric compartment. Consequently, the risk for the terrestrial compartment will be subordinated to the risks assessed for plants for atmospheric HF and in concomitant all emission reduction measures necessary to reduce the risk for plants, will automatically reduce the risk for the terrestrial compartment as well. For this reason it is considered redundant to perform a detailed risk assessment for the terrestrial compartment. As an indication all sites with a PEC in the atmosphere higher than $63 \mu\text{g}/\text{m}^3$ result in a soil concentration higher than the PNEC of $11 \text{ mg}/\text{kg}$ (estimated with EUSES 2.0.3). Since the highest calculated local concentration is $27 \mu\text{g}/\text{m}^3$ (see **Table 3.4**), no PEC/PNEC ratios above 1 are expected. The levels for the AlF_3 producers were found to be negligible compared to background concentrations (conclusion ii) (see RAR on HF 2001).

It should be noted that the PNEC used for the terrestrial compartment is based on toxicity data for HF and does not take into account the possible toxicity of aluminium. The risks from aluminium ions for the terrestrial compartment should be considered in a possible future risk assessment for aluminium compounds.

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

Conclusion (ii) for the terrestrial compartment applies to all EU primary aluminium production sites at a local scale (see risk characterisation for the atmosphere). Also for the AlF_3 producers conclusion (ii) is drawn at a local scale. At the regional scale the PEC derived with EUSES taking into account a higher deposition velocity did not exceed the PNEC (conclusion ii).

3.3.2 Atmosphere

The local PEC-values based on EUSES for the AlF_3 producers and the OPS-Pro 4.1 calculations for the primary aluminium smelters and the corresponding PEC/PNEC ratios for air for producers and downstream users are summarised in **Table 3.14** and **Table 3.15**, respectively. The PNEC for plant-air is $0.2 \mu\text{g}/\text{m}^3$ (RAR HF). For the risk characterisation the ambient background F concentration in air ($\text{PEC}_{\text{regional}}$) has been added to the PEC-values. A $\text{PEC}_{\text{regional}} 0.20 \mu\text{g}/\text{m}^3$ has been calculated with EUSES 2.0.3 (see section 3.1.6.2).

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

For AlF_3 production site 4 and the formulation site 5 conclusion (ii) is applicable, as there is minimal and no emission to air, respectively.

For AlF_3 production sites 1, 2 and 3 the PEC local exceeds the PNEC due to the contribution of the regional background concentration. However, in view of the limited contribution of the local air concentration to the exceeding of the PNEC (see **Table 3.14**), conclusion (ii) is drawn for these sites.

The regional PEC based on both intentional and unintentional sources is $0.20 \mu\text{g}/\text{m}^3$, which equals the established $\text{PNEC}_{\text{plant-air}} = 0.2 \mu\text{g}/\text{m}^3$. As the Dutch mean measured concentration of $0.07 \mu\text{g}/\text{m}^3$ confirms that the PNEC is not exceeded conclusion (ii) is drawn for the regional scale.

Table 3.14 Atmospheric local F-concentrations, PEC-values and PEC/PNEC-ratios at production sites

Location number	C_{local} ($\mu\text{g}/\text{m}^3$)	$\text{PEC}_{\text{local}}$ ($\mu\text{g}/\text{m}^3$)	$\text{PEC}/\text{PNEC}_{\text{local}}$
1	0.069	0.27	1.4
2	0.026	0.23	1.2
3	0.038	0.24	1.2
4	0.003	0.20	1.0
5	-	-	-

Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Conclusion (iii) applies to all primary aluminium production sites (downstream use of AlF_3) at the local scale. At almost all primary aluminium production sites fluoride monitoring programs are in place. The monitoring programs are not evaluated within the scope of this RAR.

From **Table 3.15** it can be concluded that by adaptation of the OPS model with more realistic conditions for the primary aluminium smelters (i.e. multiple source emission and higher emission height), the HF air concentrations in the surrounding of all EU primary aluminium smelters still exceed the PNEC.

It is assumed that further refinement of the model calculations based on additional site-specific information (e.g. specific plant configurations and meteorological information) will not lower the $\text{PEC}_{\text{local}}$ sufficiently to affect the conclusion (iii) in the risk characterisation.

Local risk reduction measures should be tailor made, taking into account additional site-specific information (e.g. the specific plant configurations and relevant meteorological information).

Table 3.15 Atmospheric local F-concentrations, PEC-values and PEC/PNEC-ratios for all EU primary aluminium smelters

Location number	OPS-Pro 4.1 derived: C _{local} HF (µg/m ³)/ year)	PEC _{local} (µg/m ³)	PEC/PNEC _{local}
1	3.3	3.5	18
2	3.1	3.3	17
3	4.4	4.6	23
4	8.5 ¹	8.7	44
5	2.3	2.5	13
6	3.5	3.7	19
7	5.5	5.7	29
8	3.1	3.3	17
9	2.4	2.6	13
10	9.4	9.6*	48
11	13	13	65
12	4.1	4.3	22
13	1.7	1.9	9.5
14	0.65	0.85	4.3
15	19	19	95
16	3.2	3.4	17
17	3.3	3.5	18
18	3.4	3.6	18
19	27	27	135
20	5.4	5.6	28
21	0.65	0.85	4.3
22	1.1	1.3	6.5
23	2.6	2.8	14
24	1.9	2.1	11
25	7.2	7.4	37
26	4.3	4.5	23
27	1.4 ¹	1.6	8.0
28	0.77 ²	0.97	4.9
29	8.3 ³	8.5	43
30	1.9	2.1	11
31	0.80 ²	1.0	5.0
32	0.85	1.1	5.5

* For this location monitoring data were provided at 100 metres distance from the boundary of the smelter resulting in an annually averaged monthly concentration of 0.4 µg/m³. It should be noted that a direct comparison between this value and the modelled value of 9.4 µg/m³ (see **Table 3.5**) is not possible since 100 metres from the smelter boundary is not the same as 100 metres from the emission

surface upon which the calculation is based. Based on the measured concentration the PEC/PNEC ratio is still > 1 and consequently conclusion (iii) remains.

¹ a part of the production plant has been closed

² plant has been closed

³ plant is being closed at the moment

3.3.3 Non compartment specific effects relevant to the food chain

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

For AlF₃ production sites no risk is indicated for the winter season and the grazing season (conclusion ii) for the non compartment specific effects relevant to the food chain.

Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Local air concentrations around the primary aluminium production sites exceed the atmospheric NOECs for livestock of 0.8 µg and 0.3 µg/m³ for the grazing season and winter season, respectively (conclusion iii). It is emphasized that wildlife is probably more susceptible to fluorides than livestock.

Since the risk for non compartment specific effects relevant to the food chain is determined by the deposition via the atmosphere any reduction measures needed to reduce the risk for the atmosphere will also reduce the risk for these specific effects.

4 HUMAN HEALTH

4.1 HUMAN HEALTH (TOXICITY)

4.1.1 Exposure assessment

As discussed in the "General introduction to risk assessment", only an exposure assessment for man indirectly exposed via the environment will be performed.

4.1.1.1 Indirect exposure via the environment

The focus of this targeted risk assessment will be on the F⁻ emissions to air. The human health tRA exposure of humans will thus only deal with F⁻ intake via air. Consequently, with the fluoride ion being the only relevant species to consider, it is possible to do a tRA for humans exposed to F⁻ ions via air in the way it was done for HF.

(Hydrogen) fluoride emissions are resulting from AlF₃ use. **Table 4.1** shows the highest local concentration HF derived from aluminum smelters (**Table 3.5** in the environmental section). Pragmatically, the concentration of HF and F⁻ are considered equivalent. For man exposed indirectly, the yearly average concentration is taken, including regional exposure. This concentration would lead to an intake of $27.2 \mu\text{g F}^-/\text{m}^3 \times 20 \text{ m}^3/\text{day}/70 \text{ kg bw} = 7.7 \mu\text{g F}^-/\text{kg bw}/\text{day}$.

Table 4.1 Local and regional concentrations of HF derived from the AlF₃ use and the calculated intake.

Local	Local $\mu\text{g F}^-/\text{m}^3$	Yearly average $\mu\text{g F}^-/\text{m}^3$	Intake in $\mu\text{g F}^-/\text{kg bw}/\text{day}$
Aluminum smelter	27	27.2	7.7
Regional		0.2	0.06

4.1.2 Risk characterisation

As discussed in the "General introduction to risk assessment", only a risk characterization for man indirectly exposed via the environment will be performed, using information from the HF RAR.

4.1.2.1 Man exposed indirectly via the environment

The background intake via food and drinking water of the fluoride-ion is circa $85 \mu\text{g F}^-/\text{kg bw}$ day (HF RAR, 2001; Table 4.5, page 56). In analogy with F⁻ intake via air for HF, the F⁻ intake via air from AlF₃ use is put into the context of the overall F⁻ intake. The intake of F⁻ of $7.7 \mu\text{g}/\text{kg bw}/\text{day}$ is marginal compared to the total daily fluoride intake (**conclusion ii**).

The regional air concentration of F⁻ is $0.2 \mu\text{g F}^-/\text{m}^3$. This concentration would lead to an intake of $6 \times 10^{-2} \mu\text{g F}^-/\text{kg bw}/\text{day}$ which is negligible compared to overall intake of fluoride via food and drinking water of $85 \mu\text{g F}^-/\text{kg bw}/\text{day}$ (**conclusion ii**).

5 RESULTS ⁵

5.1 ENVIRONMENT

Terrestrial compartment

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

Conclusion (ii) for the terrestrial compartment applies to all EU primary aluminium production sites at a local scale (see risk characterisation for the atmosphere). Also for the AlF₃ producers conclusion (ii) is drawn at a local scale. At the regional scale the PEC derived with EUSES taking into account a higher deposition velocity did not exceed the PNEC (conclusion ii).

Atmosphere

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

For AlF₃ production site 4 and the formulation site 5 conclusion (ii) is applicable, as there is minimal and no emission to air, respectively.

For AlF₃ production sites 1, 2 and 3 the PEC local exceeds the PNEC due to the contribution of the regional background concentration. However, in view of the limited contribution of the local air concentration to the exceeding of the PNEC, conclusion (ii) is drawn for these sites.

The regional PEC based on both intentional and unintentional sources is 0.20 µg/m³, which equals the established PNEC_{plant-air} = 0.2 µg/m³. As the Dutch mean measured concentration of 0.07 µg/m³ confirms that the PNEC is not exceeded conclusion (ii) is drawn for the regional scale.

Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Conclusion (iii) applies to all primary aluminium production sites (downstream use of AlF₃) at the local scale. At almost all primary aluminium production sites fluoride monitoring programs are in place. The monitoring programs are not evaluated within the scope of this RAR.

Non compartment specific effects relevant to the food chain

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

⁵ Conclusion (i) There is a need for further information and/or testing.
 Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.
 Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

For AlF_3 production sites no risk is indicated for the winter season and the grazing season (conclusion ii) for the non compartment specific effects relevant to the food chain.

Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Local air concentrations around the primary aluminium production sites exceed the atmospheric NOECs for livestock of $0.8 \mu\text{g}/\text{m}^3$ and $0.3 \mu\text{g}/\text{m}^3$ for the grazing season and winter season, respectively (conclusion iii). It is emphasized that wildlife is probably more susceptible to fluorides than livestock.

Since the risk for non compartment specific effects relevant to the food chain is determined by the deposition via the atmosphere any reduction measures needed to reduce the risk for the atmosphere will also reduce the risk for these specific effects.

5.2 HUMAN HEALTH

5.2.1 Human health (toxicity)

5.2.1.1 Humans exposed via the environment

The background intake via food and drinking water of the fluoride-ion is circa 85 $\mu\text{g F}^-/\text{kg bw}$ day (HF RAR, 2001; Table 4.5, page 56). In analogy with F^- intake via air for HF, the F^- intake via air from AlF_3 use is put into the context of the overall F^- intake. The intake of F^- of 7.7 $\mu\text{g}/\text{kg bw /day}$ is marginal compared to the total daily fluoride intake (**conclusion ii**).

The regional air concentration of F^- is 0.2 $\mu\text{g F}^-/\text{m}^3$. This concentration would lead to an intake of 6×10^{-2} $\mu\text{g F}^-/\text{kg bw/day}$ which is negligible compared to overall intake of fluoride via food and drinking water of 85 $\mu\text{g F}^-/\text{kg bw/day}$ (**conclusion ii**).

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ABBREVIATIONS

BAT	Best Available Techniques
BCF	Bioconcentration Factor
BREF	Best Available Techniques Reference Documents
CA	Competent Authority
CAS	Chemical Abstract Services
CEC	Commission of the European Communities
EAA	European Aluminium Association
EC	European Communities
EC50	median Effect Concentration
ECB	European Chemicals Bureau
EEC	European Economic Communities
EINECS	European Inventory of Existing Commercial Chemical Substances
ENV	Environment
EPER	European Pollutant Emission Register
EU	European Union
EUSES	European Union System for the Evaluation of Substances [software tool in support of the Technical Guidance Document on risk assessment]
HPVC	High Production Volume Chemical (> 1000 t/a)
IAI	International Aluminium Institute
IC	Industrial Category
IPCS	International Programme on Chemical Safety
IPPC	European Integrated Pollution Prevention and Control
IUCLID	International Uniform Chemical Information Database (existing substances)
IUPAC	International Union for Pure and Applied Chemistry
KEMI	Swedish Chemical Inspectorate
LC50	median Lethal Concentration
LD50	median Lethal Dose
NILU	Norwegian Institute for Air Research
NOEC	No Observed Effect Concentration
OSPAR	Oslo-Paris Convention for the protection of the marine environment of the North-East Atlantic Ocean
PEC	Predicted Environmental Concentration
pH	logarithm (to the base 10) (of the hydrogen ion concentration {H ⁺ })
PNEC	Predicted No Effect Concentration
RA	Risk Assessment
RAR	Risk Assessment Report

RCR	Risk Characterisation Ratio
RIVM	National Institute for Public Health and the Environment
SCHER	Scientific Committee on Health and Environmental Risks
TGD	Technical Guidance Document
TNO	The Netherlands Organisation for Applied Scientific Research
TRA	Targeted Risk Assessment
UC	Use Category
WHO	World Health Organization

European Commission

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The report provides the comprehensive risk assessment of the substance Aluminium fluoride. It has been prepared by the Netherlands in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to man and the environment, laid down in Commission Regulation (EC) No. 1488/94.

The evaluation is essentially targeted on the environmental effects of fluoride emissions to air, the human health risk assessment being limited to man indirectly exposed via the environment.

It concludes that there is concern at the local scale for the atmospheric compartment at all primary aluminium production sites (downstream use of AlF_3), together with a concern about non compartment specific effects relevant to the food chain.

There is no concern for the terrestrial compartment, and also not for humans indirectly exposed via the environment