European Union Risk Assessment Report

CALCIUM FLUORIDE

CAS No: 7789-75-5

EINECS No: 232-188-7

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) 793/93[1] 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) 1488/94[2], which is supported by a technical guidance document[3]. 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 CaF_2 and AlF_3, 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 CaF_2 and AlF_3, 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 CaF_2 and AlF_3 enables to image the overall environmental fate, it was decided to make a targeted RA for CaF_2 and AlF_3 focusing only on the atmospheric compartment. This will be done at the local scale for CaF_2 and AlF_3, and at the regional scale for the combination of F sources (intentional (CaF_2, AlF_3 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).

With respect to the other compartments, in particular the water compartment (including sediment and waste water treatment systems), the following arguments can be brought forward for not addressing water in the RA of CaF_2 at this stage:

- The F-emissions to water from the CaF_2 industry are in general low; additionally due to its low solubility, CaF_2 dissociation in water is minimal.
- F-emissions to water from the CaF_2 production (i.e. mining companies) may result in levels that exceed the current Predicted No Effect Concentration (PNEC) water for fluoride (one case actually reported). The number of those mining companies, however, is known to be limited and furthermore it is assumed that the emissions from the mining activities are known to (and regulated by) local authorities. It should be borne in mind that high fluoride water levels in mine areas may also be related to high natural background levels in those regions;
- F-emissions to water for the HF production, being the most important use source of CaF_2, were already addressed in the HF report;
- 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;

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 ASSESSMENT[4]

CAS Number: 7789-75-5
EINECS Number: 232-188-7
IUPAC Name: Calcium 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.

For CaF_2 production conclusion (ii) is drawn with respect to HF, since no HF is emitted during this life cycle stage. The downstream use of CaF_2 for the production of HF is covered by the RAR on HF (2001). 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). The same conclusion can be drawn based on the production figures for the year 2000, although the emission is approximately twice as high (see section 3.1.1.2.2).

For the downstream use of CaF_2 by the steel industry as flux agent with respect to HF emissions on a local scale conclusion (ii) is drawn (see section 3.3.1).

For all other minor uses (0.8% of the total EU volume) no conclusion is drawn with respect to HF emissions, since they are considered to be of minor importance.

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 CaF_2 production conclusion (ii) is drawn with respect to HF, since no HF is emitted during this life cycle stage.

The regional PEC derived with EUSES 2.0.3. (2005), combining the fluoride emissions from both intentional and unintentional sources was found to be 0.2 $\mu g/m^3$, which equals the established $PNEC_{plant\text{-}air}$ = 0.2 $\mu g/m^3$. As the Dutch mean concentration of 0.07 $\mu g/m^3$ confirms that the PNEC is not exceeded conclusion (ii) is drawn for the regional scale.

Based on realistic worst-case emission factors provided by the industry, the use of CaF_2 in the metal industry as a flux agent leads to local air concentrations ranging from to 0.032 to 3.05 $\mu g/m^3$. For the class of five steel production sites which use up to 500 tons of CaF_2 a (maximum) C_{local} of 0.095 $\mu g/m^3$ is derived. Adding this maximum local concentration up with the $PEC_{regional}$ (resulting in a PEC_{local} of 0.30 $\mu g/m^3$) leads to a maximum RCR of 1.5.

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.

Since the $PEC_{regional}$ equals the PNEC, each local atmospheric emission of HF leads to exceeding of the PNEC. However, in view of the limited contribution of the local air concentrations to the exceeding of the PNEC, conclusion (ii) is drawn for these five sites.

The use of CaF_2 by the metal industry with respect to welding can be split up in the use for the production of welding consumables and the use as a flux agent for welding. From the latter emissions are considered to be small on a local scale, due to wide distribution of this application across the EU (see section 3.1.1.2.2). In addition, at the production of welding consumables no HF is emitted (see section 3.1.1.2.2). Therefore, conclusion (ii) is drawn at the local scale for both scenarios.

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) is drawn for the following downstream uses of CaF_2:

The local environmental risk characterisation of the main downstream use of CaF_2 (HF production) is described in the RAR on HF (2001). The calculated PEC in atmosphere exceeds the PNEC (conclusion iii).

For the eight steel production sites which use above 500 tons of CaF_2 as a flux agent (classes with upper thresholds ranging from 1,000 to 16,000 tonnes) conclusion iii is drawn. The upper threshold of the class 500 to 1,000 tonnes of CaF_2 results in a C_{local} of 0.19 µg/m^3, a PEC_{local} of 0.39 µg/m^3 and an RCR of 2.0. Since this local air concentration is considered to be equal to the PNEC conclusion (iii) is drawn.

For all other minor uses (0.8% of the total EU volume) no conclusion is drawn with respect to HF emissions, since they are considered to be of minor importance (see last paragraph of section 3.1.5.1.2).

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.

No emissions of HF are expected during the production of CaF_2. Therefore, no specific effects relevant to the food chain are expected (conclusion ii).

Based on realistic worst-case emission factors provided by the industry, the use of CaF_2 in the metal industry as a flux agent leads to local air concentrations ranging from 0.032 to 3.05 µg/m^3. For the five steel production sites which use up to 1,000 tons of CaF_2 a (maximum) C_{local} of 0.19 µg/m^3 is derived. Adding this maximum local concentration up to the $PEC_{regional}$ (resulting in a (maximum) PEC_{local} of 0.39 µg/m^3), the atmospheric NOEC for livestock of 0.3 µg/m^3 for the winter season is exceeded by a factor 1.3. In view of the limited contribution of the local air concentrations to the exceeding of the NOEC, conclusion (ii) is drawn for these sites.

For the ten steel production sites which use up to 3,500 tons of CaF_2 as a flux agent a (maximum) PEC_{local} of 0.87 µg/m^3 (C_{local}: 0.67 µg/m^3 + $PEC_{regional}$: 0.2 µg/m^3) is derived. The NOEC for livestock for the grazing season of 0.8 µg/m^3 is exceeded by a factor 1.08. In view of the marginal exceeding of the NOEC, conclusion (ii) is drawn for these sites.

Steel production: CaF_2 consumption (tonnes/year)	# EU sites	Grazing season	Winter season
0 - < 1,000	5	**conclusion ii**	**conclusion ii**
1,000 - < 3,500	5	**conclusion ii**	**conclusion iii**
3,500 - < 6,500	-	**conclusion iii**	**conclusion iii**
≥ 6,500	3	**conclusion iii**	**conclusion iii**

The use of CaF_2 by the metal industry with respect to welding can be split up in the use for the production of welding consumables and the use as a flux agent for welding. From the latter emissions are considered to be small on a local scale, due to wide distribution of this application across the EU (see section 3.1.1.2.2). In addition, at the production of welding consumables no HF is emitted (see section 3.1.1.2.2). Therefore, conclusion (ii) is drawn at the local scale for both scenarios.

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) is drawn for the following downstream uses of CaF_2:

The local environmental risk characterisation with respect to non compartment specific effects relevant to the food chain of the main downstream use of CaF_2 (HF production) is described in the RAR for HF (2001). The calculated PEC in atmosphere exceeds the atmospheric NOECs for livestock of 0.8 µg/m^3 and 0.3 µg/m^3 for the grazing season and winter season, respectively (conclusion iii). It was emphasized that wildlife is probably more susceptible to fluorides than livestock.

For the eight steel production sites which use above 1,000 tons of CaF_2 as a flux agent (classes with upper thresholds ranging from 1,500 to 16,000 tonnes) conclusion iii is drawn for the winter season. The upper threshold of the class 1,000 to 1,500 tonnes of CaF_2 results in a C_{local} of 0.29 µg/m^3, a PEC_{local} of 0.49 µg/m^3 and an RCR of 1.6. Since this local air concentration is considered to be equal the atmospheric NOEC for livestock of 0.3 µg/m^3 for the winter season conclusion (iii) is drawn.

For the three steel production sites which use more than 6,500 tons of CaF_2 as a flux agent (up to 16,000 tonnes) conclusion (iii) is drawn for the summer season on a local scale, in view of the calculated PEC_{local} of 1.44 µg/m^3 (up to 3.25 µg/m^3).

For all other minor uses (0.8% of the total EU volume) no conclusion is drawn with respect to HF emissions, since they are considered to be of minor importance (see last paragraph of section 3.1.5.1.2).

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 µg/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 for CaF_2 use is put in the context of the daily F^- intake. The intake of F^- of 1 µg/kg bw/day for the flux agent scenario is negligible compared to the total daily fluoride intake (**conclusion ii**).

The regional air concentration of F^- is 0.2 µg F^-/m^3. This concentration would lead to an intake of $6x10^{-2}$ µg F^-/kg bw/day which is negligible compared to an overall intake of fluoride via food and drinking water of 85 µg F^-/kg bw/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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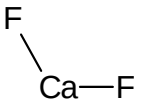
1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION OF THE SUBSTANCE

CAS Number: 7789-75-5
EINECS Number: 232-188-7
IUPAC Name: Calcium fluoride
Molecular formula: CaF_2

Structural formula:



Molecular weight: 78.1
Synonyms: This dossier is also related to calcium fluoride ore (synonyms: fluorspar or fluorit (CAS: 14542-23-5/ EINECS: 238-575-7)).

1.2 PURITY/IMPURITIES, ADDITIVES

Purity: >97%

Impurity: ≤1% silicon dioxide
≤1% calcium carbonate
≤0.6% diiron trioxide
≤0.3% barium suplhate

1.3 PHYSICO-CHEMICAL PROPERTIES

The data are based on references as mentioned in the IUCLID dataset (20 April 2001), as submitted by the industry.

Table 1.1 Summary of physico-chemical properties

Property	Value
Physical state	solid
Melting point	1423°C
Boiling point	2786°C
Relative density	3.18 kg/dm^3 at 20°C
Vapour pressure	10.13 hPa at 2100°C
Water solubility	15 mg/l at 18°C
Partition coefficient n-octanol/water (log value)	Not applicable
Granulometry	Variable
Conversion factors	Not applicable
Flash point	Not applicable
Autoflammability	Not applicable
Flammability	Non flammable
Explosive properties	Not explosive
Oxidising properties	No oxidising properties
Viscosity	Not applicable
Henry's constant	1.04E-04
Surface tension	Not applicable

1.4 CLASSIFICATION

Current classification: -

Proposal of rapporteur: -

In the RAR on HF (2001) several acute aquatic toxicity studies are reported without specification of the water hardness. Nevertheless, in view of the limited water solubility of CaF_2 (15 mg/l; maximum concentration of F^-: 7.3 mg/l), none of the EC50 values for fluoride reported will be reached. Therefore, CaF_2 is not classified for the environment.

2 GENERAL INFORMATION ON EXPOSURE

2.1 PRODUCTION

2.1.1 Production processes

Most of the CaF_2 produced in the EU is obtained from the mineral containing fluorspar (25%-60% CaF_2, next to SiO_2, $CaCO_3$) which is extracted as stones from open-pits and underground mines. There are two concentration processes:

(1) Gravimetric concentration: This is done in water at ambient temperature in closed systems. The water is recirculated in a closed circuit. The washed material is sorted by size (2 mm, 5 mm, 25 mm) and stored outside on concrete surface. The finished product can be sold in wet and dry forms.

(2) Flotation concentration: The stones are crushed and milled to form a pulp. The fluorspar is then separated from other minerals contained by a flotation process. Fluorspar is delivered as a wet filtercake.

A small amount is produced chemically from a reaction between HF and $CaCO_3$ (140 tonnes) or between AlF_3 and $CaCO_3$ in an aqueous solution (5,400 tonnes). The latter process uses the process water from AlF_3 crystallisers to produce CaF_2 and no pure AlF_3.

2.1.2 Production capacity

Table 2.1 lists the production sites of CaF_2 in the EU in 2000.

Table 2.1 Production sites of CaF_2 in the EU in 2000

Company	Country
Philips	Eindhoven, the Netherlands(1)
Minerales y productos derivados	Bilbao, Spain
Sachtleben Bergbau Services	Wolfach, Germany
Sogerem	Le Sequestre, France
Alufluor	Helsingborg, Sweden
Glebe Mines LTD	Hope Valley, United Kingdom
Nuova Mineraria Silius	Italy

(1) Production stopped

Based on the information provided by the producers the total amount produced in 2000 in Europe is 335,546 tonnes.

CaF_2 is also imported into the EU as has been reported by the downstream users (see section 2.2.1). The reported total amount imported in 2000 is 519,636 tonnes. The producers reported an exported quantity of 16,700 tonnes. The export may be higher, as the export data from the producers was not complete. In committant, the total amount of CaF_2 used in the year 2000

may be overestimated, but maximally amounts to 838,482 (335,546 + 519,636 – 16,700) tonnes.

2.2 USES

2.2.1 Introduction

Table 2.2 gives an overview of the companies that provided information about the downstream use of CaF_2 for the year 2000.

Table 2.2 Downstream users of CaF_2 in the EU in 2000

Company	Location
Fluorchemie	Dohna/ Stulln, Germany
MB-Sveda AB	Malmö, Sweden
Bayer	Leverkusen, Germany
Thyssen Sonnenberg Metallurgie	Essen, Germany
Outokumpu Norzink AS	Odda, Norway
INEOS Fluor	Cheshire, United Kingdom
Fluorspid S.p.A.	Assemini, Italy
Honeywell	Weert, The Netherlands
Solvay S.A.	Hannover, Germany
Derivados Del Fluor	Castro Urdiales, Spain
Phosphoric fertilizers industry	Thessaloniki, Greece
Ausimont S.p.A	Milano, Italy
Rhodia Organique Fine Limited	Bristol, United Kingdom
Honeywell Specialty Chemicals Seelze	Seelze, Germany

All kinds of applications have been reported for CaF_2, which have been summarised in terms of industrial and use categories in **Table 2.3**. In the metal industry (for instance steel production) it is used as leaching agent, as a component of electrolyte and fluxing agents, protective and refining salts. In the glass manufacturing it is used for special optical glasses, manufacture of reflection reducing layers and fluorescent lamps, as colouring agent and as fluxing and pre-opacifying agent. For this purpose it is also used in the enamel and glazing frits production. In addition, it is used for the preparation of denture. In the production of welding agents it is used as component of welding rod coatings and welding powders.

Based on the information provided, most of CaF_2 in the EU is used for the production of HF and $CaSO_4$ by the conversion of dried acid spar with concentrated sulphuric acid at elevated temperatures (see **Table 2.4**). Other minor uses are 6.0% as a flux agent (for casting) to reduce melting point and viscosity of slag (UC no. 24), 1.2% for welding, 0.4% in both glass as cement industry and as a colour agent for glasswork (UC no.10). A minor fraction is used for the production of fluorescent powder (0.02%).

Table 2.3 Reported industrial and use categories of CaF_2.

Industry category	IC no.	Use category	UC no.
Chemical industry: Basic chemicals	2	Other (production of HF)	55
Chemical industry: Chemicals used in synthesis	3	Other (fluorescent powder)	55
Metal Industry	8	Flux agents (for casting)	24
Metal Industry	8	Welding and soldering agents	54
Metal Industry	8	Others (leaching agent) (1)	55
Other (glass and enamel industry)	15	Colouring agents(1)	10
Other (glass and enamel industry)	15	Others (flux agent)	55
Other (cement industry)	15	Process regulators	43

(1) No information is given on the absolute quantities involved with this specific use.

All the information provided by producers, importers and downstream users is integrated to quantify the different applications of CaF_2 within the EU for the year 2000 (see columns 2 and 3 from **Table 2.4**). The applications for which the downstream users provided no information on the tonnage of CaF_2 involved have been left out in the overview (columns 4 and 5 from **Table 2.4**). Taking all information into account, for approximately 79% of all CaF_2 the downstream use is covered with the exposure information provided by the companies involved.

Table 2.4 Quantities involved for the use pattern for the year 2000.

Use	Total Tonnage in the EU	% of total tonnage	Tonnage covered by info from users	% of total tonnage in the EU
Basic chemicals: Production of HF	770,930	91.9	641,374	76
Metal industry: Flux agent	50,486	6.0	28,000	3.3
Metal industry: Welding and soldering agents	10,370	1.2		
Cement industry	3,378	0.4		
Glass and enamel industry	3,178	0.4		
Chemicals used in synthesis: Fluorescent powder	140	0.02		
Total:	**838,482**	**100**		**79**

2.3 TRENDS

The production and import data for the period 2000 - 2003 presented in **Table 2.5** are provided by the industry and obtained from CEFIC Fluorspar group and Miller fluorspar report 2003 and deviate from the figures in section 2.1, which are based on information from the producers and down-stream users. It should be noted that the import data given by CEFIC are much lower than the data provided by the questionnaires (375 versus 519 ktonnes). These differences can probably be explained by the fact that not all importers are members of CEFIC.

Table 2.5 Trends in production and import

Year	Production	Imports
2000	339,652	375,784
2001	311,253	408,639
2002	324,130	384,711
2003	310,130	446,024

2.4 LEGISLATIVE CONTROLS

Concerning the production of CaF_2 only dust emissions are expected. In the questionnaires provided by the producers maximum general dust emission limit values in the range of 5 to 10 mg/m^3 per 8 hours are reported. For F^- maximum values of 2 and 2.5 mg/m^3 are reported. If these values are converted to values for CaF_2, also a limit value of approximately 5 mg/m^3 dust is obtained. One producer reported also a limit value for aquatic emission of <10 mg F^-/l.

Since for the downstream use application in the steel industry (flux agent) risks at a local scale considering HF emissions can not be excluded, it should be checked if legislative controls are in place to control these risks and if so, if the risks are controlled sufficiently.

3 ENVIRONMENT

3.1 ENVIRONMENTAL EXPOSURE

3.1.1 Environmental releases

The targeted risk assessment for CaF_2 is focussed on the emissions of gaseous fluorides during the production and downstream use. For the production of CaF_2 solely dust emissions are expected to occur to all environmental compartments (see section 3.1.1.1.2), while for downstream use both gaseous and dust emissions are expected (see section 3.1.1.2.2).

3.1.1.1 Release from production

3.1.1.1.1 Release from production to the aquatic environment

Although the RAR is targeted on the atmospheric release of HF and not on the release to the aquatic environment, for the sake of completeness the following information is given:

Two producers provided information on the fluoride emission to water (as total particles in suspension or unspecified). The calculated emission factors are 28.9 and 233 g/t. Based on a total production in the EU of 335,546 tonnes, the resulting emission of fluoride from CaF_2-production to the aquatic environment will range from 9.7 to 78t.

3.1.1.1.2 Release from production to the atmosphere

The production processes (both gravimetric and flotation method) in which, the natural occurring, raw material containing CaF_2 in the range of 25 – 60% is concentrated (>97%) are not always continuous and not always executed in closed systems. In cases that the concentration process takes place in open systems the fluorspar is wetted to limit dust emissions. The production process using AlF_3 (1.6% of total EU CaF_2 production in 2000) takes place 300 days per year in closed systems. The production process using HF (0.04% of total CaF_2 production in EU in 2000) takes place 325 days per year during 12 hours per day in closed systems. In this production process an overdose of $CaCO_3$ is added to prevent emission of free fluoride.

As the main production process of CaF_2 involves no chemical reactions, but only crushing, milling and flotation of the fluorspar and the chemically derived CaF_2 is produced in closed systems no emission of HF is to be expected. Therefore it can be concluded that the total HF emission for CaF_2 production in the EU is 0 kg. Emissions of CaF_2 (or fluorspar) in the form of dust are summarised in **Table 3.1**. Two companies have no drying facilities and all the production remains in a wet form. Consequently, no CaF_2 dust is emitted. For those companies having drying facilities emission rates were reported of 3.3 and 18.6 g/t resulting in a total emission of 100 and 1,900 kg/y. Using the highest emission rate for the remaining company for which no emission data is available a total emission of 620 kg/y can be estimated. Summarising the emission known from **Table 3.1** and the calculated emission for the producers that did not provide emission data results in a total emission of 2.6 t/y of CaF_2 in the form of dust to the atmosphere. As this risk assessment is focussed on HF, this emission is not further considered.

Table 3.1 Emission rates of CaF_2 to atmosphere for production sites for the year 2000.

Location number	Tonnage of CaF_2 (t/year)	Emission rate (g/t)	Emission rates used for calculations (g/t)	Total emission in 2000 (kg/year)
1	126,000	0	0	0
2	102,159	18.6	18.6	1,900
3	38,492	0	0	0
4	33,355	?(1)	18.6	620
5	30,000	3.3	3.3	100
6	5,400(2)	0	0	0
7	140(2)	0	0	0
Total	**335,546**			**2,620**

(1) No data on dust emission available

(2) CaF_2 was chemically produced with no atmospheric emissions of CaF_2

3.1.1.2 Release from industrial/professional use

3.1.1.2.1 Release from industrial use to the aquatic environment

Although the RAR is targeted on the atmospheric release of HF and not on the release to the aquatic environment, for the sake of completeness the following information is given:

Two of the downstream users that provided exposure information reported a fluoride emission to water (reported as F^- or unspecified). Five downstream users reported their emissions to water to be zero, although it is unclear whether this was estimated or measured. Both users reported as use feedstock for HF-production (representing 14.7% of total downstream use based on volumes). The emission factors derived cover partly one, although the main, specific downstream use, therefore it can only be used as rough estimation of the total emission. The calculated emission factors are 1.16 and 17.8 kg/t. Based on a total use in the EU of 770,930 tonnes, the resulting emission of fluoride from HF-production will range from 890 to 13,720t. In the RAR of HF a total EU emission for 1994 was established of 1,390 tonnes, which is comparable to the minimum amount calculated. It should be noted that the highest factor (17.8 kg/t) is related to an emission to sea.

3.1.1.2.2 Release from industrial use to the atmosphere

<u>HF production</u>

For 83% of the total amount of CaF_2 that is used for the HF production (which, in turn, covers 76% over total CaF_2 that is used in the EU), emission data has been provided. The emission factors for the use of CaF_2 as feedstock for HF-production are given in **Table 3.2**.

Although specified by a limited number of companies (4), the reported emission is assumed be in the form of CaF_2 dust. The emission factors range from 5.1 to 532 g/t. Industry indicated that the highest value was mainly due to equipment failure in the year 2000. Leaving this

emission aside the total emission per site varies between 0.1 – 4 t/y. As the risk assessment is targeted on the release of HF, this emission of CaF_2 is not further considered.

Table 3.2 Emission rates of CaF_2 to atmosphere for downstream users (HF-producers) for the year 2000.

Location number	Tonnage (t)	Fraction of tonnage	Emission rate (g/t)	Total emission (t/y)
1	90,000	0.107	21.5	1.94
2	87,959	0.105	16.8	1.48
3	85,000	0.101	18.8	1.6
4	78,629	0.094	5.1	0.4
5	74,000	0.088	33.8	2.5
6	48,866	0.058	8.3	0.5
7	45,000	0.054	44.4- 88.9	4
8	30,006	0.036	26.7	0.8
9	27,293	0.033	not available	not available
10	24,454	0.029	27.4	0.67
11	19,745	0.024	532	10.5
12	18,500	0.022	20.5	0.38
13	11,922	0.014	11.7	0.14
Total	**641,374**	**0.765**		**24.91**

It was concluded in the RAR of HF (EC, 2001) that for the year 1994 the atmospheric HF emission of the HF industry (producers and downstream users) (9.46 t/a) was less than 0.1% of the total European emission. However, to update this emission data, the emission resulting from production and downstream use is adjusted with a factor derived from the difference in total HF production between the years 1994 and 2000. The risk assessment is based on a total EU production volume of 165,000 to 245,000 tons per year in 1994 (average 205,000 tons per year). Based on the exposure information provided by the CaF_2 industry the total production volume of HF for 2000 can be recalculated. The fraction of total volume of CaF_2 used for HF-production is 92%. In addition, the total volume of CaF_2 within the EU for the year 2000 amounts to 838 kt. From this, 770 kt have been used for the production of HF, which results in a production volume of 395 kt. To take the higher production volume in 2000 into account the emissions from the RAR on HF will be multiplied with a factor 1.9 at a continental scale (395,000/205,000 = 1.9), assumed that the efficiency of the production process of HF remains unchanged.

The continental atmospheric gaseous F emissions (mainly HF) are estimated to be 18 t/y (1.9 * 9.46) for both, production and downstream use, which have been taken forward in the risk assessment.

Other uses: (1) Flux agent and (2) welding applications

As the main application for CaF_2 is the synthesis of HF, the emission of other downstream use seems of minor importance (production volumes 8.0% of total, see **Table 2.4**). However, since these minor uses can still lead to considerable HF emissions at the local and regional

scale, the use of CaF_2 by the metal industry (6.0% of the total EU volume) as a flux agent (for casting) and for welding applications (1.2%) are therefore taken into consideration.

(1): Flux agent

Specific emission information was provided by the steel industry (IC no. 8 and UC no. 24). It was stated that the use of CaF_2 declined in steelmaking over the last years. For the year 2004 a total amount of 44,000 tonnes was reported to be used by 13 steel companies (with the amount of use ranging from 170 – 16.000 tonnes per site per year). For the year 2000 the total use of CaF_2 as a flux agent amounted to 50,486 tonnes (see **Table 2.4**). For two stainless steel plants emission factors (0.25 and 0.23 kg HF per ton CaF_2) were provided, based on calculations taking the detection limit when no HF could be detected. The derived emission factor of 0.25 kg HF per ton of CaF_2 was taken forward to calculate the range in emissions for the steel production plants. Based on the default number of emission days (300), HF emissions are established to range from 0.142 to 13.3 kg/d for the CaF_2 using steel production plants.

The total yearly emission of HF resulting from this use is calculated to be 12.5 tonnes ((6,500 tonnes * 0.23 kg) + ((50,486-6,500 tonnes) * 0.25 kg))), which has been taken forward in the risk assessment.

(2): Welding applications

Production of welding consumables

The European Welding Association (EWA), which covers 90-95% of the production of welding consumables within the EU, provided a statement that no harmful emissions occur by using CaF_2 during the manufacture of welding consumables, using weighing, mixing and binding in closed systems, since it does not involve reactions which lead to any emission of HF. In addition, the EWA confirmed that also during the baking process of welding consumables no HF emissions can occur, since the temperature is too low. The maximum temperature used for the baking process of welding consumables is approximately 720^{o}C, while for HF formation out of CaF_2 a temperature of at least 1350^{o}C is required. This explanation is considered acceptable and it is concluded that no HF emissions occur during the production of welding consumables.

Industrial use (welding):

It was stated by the EWA that during the welding process a limited part of the CaF_2 reacts with hydrogen to HF, but that no EU threshold values are exceeded and no harmful effects to the welder or the environment are known. Based on information found in the literature (Sjögren, 2004) on fluoride emissions (18-20%) during welding, it is obvious that emissions of fluoride occur during welding. However, it is unclear to what extent HF is formed. In addition, it was stated that the emission of CaF_2 during welding is widely spread over the country and thus over the EU over many industries (e.g. automotive industry, building industry infrastructure, shipbuilding, aerospace etc.). This statement is confirmed by the fact that in the Netherlands approximately 1,200 welding companies are present and is therefore considered acceptable. The emissions resulting from welding are therefore not taken into account at the local scale.

The EWA provided an estimation of the total HF emission with respect to welding applications within the EU resulting in a quantity of 1-2 tonnes of HF per year. At first sight, this seems an underestimation given the emission data from the Netherlands for the year 1998

of 3.7 tonnes for the electrotechnical industry. It should however be realised that this emission is in fact the total fluoride emission instead of HF only. The EWA stated that HF-formation is limited by the hydrogen content in the welding electrodes and flux cored wires (0.05%), since during the welding process the electrode is not directly in contact with the open atmosphere. As a consequence HF formation with hydrogen from the atmosphere can be excluded. The total EU estimate of 4 tonnes of HF, based on the hydrogen content of welding consumables in which CaF_2 is being applied, as provided by the EWA is therefore considered acceptable, but has been adjusted to the CaF_2 use level for the year 2000. The EWA reported a total use of CaF_2 of 6,950 tonnes, while for the year 2000 10,370 tonnes of CaF_2 were used for the production of welding consumables (i.e. covered electrodes, flux cored wires and welding fluxes). This results in a correction factor of (6,950/10,370) 1.5. According to the industry a substantial amount (50-75%; 2 to 3 tonnes) of HF is trapped in the ventilation system by reaction with other fume components (e.g. $CaCO_3$). However, as a worst-case estimate it is assumed that the total HF volume is released to the environment, which corresponds to the estimate of 4 tonnes of HF in their calculations. Applying the correction factor results in a total HF emission for the EU of 6 tonnes, which has been taken forward in the regional risk assessment.

It should be noted that the missing part of downstream use (maximally 0.8%), can still result in considerable emissions as calculated in section 3.1.6.1. However, these emissions are characterised as wide dispersive and are therefore not taken into account at the local scale.

3.1.1.3 Summary of releases

Emissions of HF could not be established with the emission data provided and are taken forward from the RAR on HF (2001) applying an extrapolation factor of 1.9, resulting in a total (continental) atmospheric emission for both production as downstream use for the year 2000 of 18 tonnes HF. Applying the 10% rule a total regional emission of 1.8 tonnes HF can be assumed. Assuming 365 production days, the total daily regional emission amounts to 4.9 kg/d, which can be considered negligible compared to a release of 675 kg/d (2,463 tonnes / 365 * 10%) resulting from aluminium production (see RAR on AlF_3).

From the other specified uses the total yearly emissions from the use as flux agent in metal industry (12.5 tonnes of HF for the EU) and the use of CaF_2 for welding (6 tonnes of HF for the EU) has been taken forward.

3.1.2 Environmental fate

3.1.2.1 Release and fate of HF and CaF_2

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.).

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 SiF4). 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 (1,300 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).

CaF_2 is released during production and industrial use to waste water, where it is expected to precipitate, especially when the pH>4.5. Even when 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. Therefore it can be concluded that the release of HF from water to the atmosphere can be considered negligible.

In addition, CaF_2 is also released as dust during the production and downstream use, which is expected to deposit in the vicinity of the production and downstream user sites to both, surface water as soil. In soil CaF_2 tends to accumulate within the surface layer, but maybe displaced throughout the root zone, even in calcareous soils (Polomski *et al*., 1982).

In soils with pH<6 fluoride is considered to be immobile as it 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 extent, 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).

3.1.3 Aquatic compartment (incl. sediment)

The aquatic emissions which have been reported in section 3.1.1 are all CaF_2 emissions, which are independent of HF emissions and also not expected to result in HF emissions. As

HF is the focus of this risk assessment the water compartment (including sediment and waste treatment systems) will not be considered.

3.1.4 Terrestrial compartment

In the RAR on HF (2001), 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. The same conclusion can be drawn based on the HF production figures for the year 2000, although the HF emission is twice as high. The same conclusion can be drawn when the emission of CaF_2 is taken into account, as the emission is comparable to the emission of HF, for which already a high deposition rate was used.

3.1.5 Atmosphere

3.1.5.1 Calculation of PEC_{local}

3.1.5.1.1 Calculation of PEC_{local} for production

As no emissions of HF are expected during the production of CaF_2 (see section 3.1.1.1.2), the calculation of the PEC_{local} is not applicable.

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

The calculation of the PEC_{local} with respect to the HF-production (downstream use of CaF_2) is already covered in the RAR on HF (2001), in which calculated local concentrations of emitting HF production plants ranged from 0.013 to 2.36 µg/m^3. In addition, the emission data provided by the industry, by some of them specified as dust emissions, are most probably related to atmospheric emission of CaF_2 (see section 3.1.1.2.2) instead of HF. With the HF-industry 91.9% of the downstream use of CaF_2 is covered. Approximately 6.8% is used as a flux agent in the metallurgic industry, the glass industry and cement industry. The use as flux agent has partially been covered by the RAR on AlF_3 as CaF_2 is also used for this purpose in the aluminium industry. However, it can not be clearly established to what extent the use of the aluminium industry covers this use of CaF_2 as flux agent in the metal industry.

For the use of CaF_2 as a flux agent (6% of total use) for three sites specific data on HF emissions and all sites general CaF_2 volumes (by assigning them into classes of 500 tonnes) were provided by the industry. These data were used to derive local air concentrations. The calculated C_{local} values of the 13 steel companies ranged from to 0.032 to 3.05 µg/m^3. No local assessment is performed for all other uses (e.g. welding and by cement, glass and enamel industry), since these emissions are considered to be very diffuse and in addition, of minor importance compared to other sources.

3.1.5.2 Measured levels

3.1.5.2.1 Local near industrial sources

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 µg/m^3 (data from 1980; Luftreinhaltplan Rheinschiene Sud 1982-1986). Levels of fluoride in air in the vicinity of emission sources are generally not higher than 2-3 µg/m^3 (IPCS, 2002). In the Netherlands, fluoride in air is measured in a monitoring program near high fluoride-emitting industrial sources. For 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 µg/m^3 and 0.45 µg/m^3 (see **Table 3.3** and **3.4**), respectively (Hammingh, 2001, 2002). In additional Polish data of fluoride measurements in air yearly average fluoride concentrations are reported of 0.9 – 1.2 µg F^-/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 µg F^-/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, they 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 µg F^-/m^3.

Table 3.3 Maximum daily average fluoride concentrations in air (µg/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 (µg/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 µg/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 µg/m^3 (IPCS, 2002).

3.1.5.2.2 Regional background

The natural occurring background concentration of fluoride is calculated to be 0.0005 µg/m^3. The worldwide background concentration is estimated to be 0.003 µg/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 µg/m^3 (IPCS, 2002).

Air concentrations measured in the Netherlands for 1982-1983 range from 0.03-0.1 µg/m^3, with the highest concentrations in the south-west. Mean concentration for the Netherlands is 0.07 µg/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 µg/m^3, with a range of <0.1-0.17 µg/m^3 (IPCS, 2002).

3.1.5.3 Comparison between predicted and measured levels

The emission information derived calculated levels of HF nearby industrial sources range from 0.013 to 3.05 µg/m^3 (section 3.1.5.1.2). It can be concluded that these levels do correspond with the measured data (0.03 to 4.6 µg/m^3).

3.1.6 Calculation of $PEC_{regional}$

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

With the production of CaF_2 out of fluorspar no HF is emitted to the atmosphere (section 3.1.1.1.2). The emissions resulting from downstream use is partially covered with the production of HF, approximately 92% of all produced and imported CaF_2 is used for the production of HF. Approximately 15% of the total amount of produced HF is in turn used for the production of aluminium fluoride. Other emissions resulting from other downstream uses are outlined below.

CaF_2 is also used for the production of glass and cement. Approximately 60% of the fluoride is trapped within the glass during the production, while about 32% of the fluoride, added as CaF_2, is released to the atmosphere (Slooff *et al.*, 1988). No emission data on cement production were found, therefore as worst case the same emission factor was taken as for the production of glass. The realistic worst-case total intentional HF emission resulting from the use of CaF_2 can be calculated as follows:

6,556 t CaF_2 used for glass and cement production

6,556 t * 32% * 0.487 = 1,022 t F.

1,022 t F / 0.95 = 1,075 t HF

The fraction of fluoride in CaF_2 is 0.487 (38/78.1). The use of CaF_2 for the production of glass and cement is 6,556 tonnes in total according to Table 2.4. The fraction of F in HF is 0.95 (19/20).

The total HF emission within the EU resulting from the use of CaF_2 as a flux agent for steel production was calculated to be 12.5 tonnes per year (section 3.1.1.2.2.).

For the use of CaF_2 in the electrotechnical industry (i.e welding) a total yearly HF emission of 6 tonnes was derived for the EU (section 3.1.1.2.2).

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 3.5**). For the reported emissions with respect to the production and downstream use of AlF_3 is referred to the RAR on AlF_3 (2008).

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

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 section 3.1.1.3).

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

3.1.6.2 Summary of exposure and calculation of $PEC_{regional}$

In **Table 3.6** 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 3.7** 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 $PEC_{regional}$.

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.

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, AlF_3 and CaF_2) 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.

Table 3.6 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 3.7 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 (19.2 t)	$HF/AlF_3/CaF_2$
2	Basemetals	390	42.9	27.3 (2,476 t)	AlF_3/CaF_2
3	Ceramics, glass and building materials	448	49.4	11.8 (1,075 t)	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 total emission within the EU for 2001 of 11,945 tonnes results in a $PEC_{regional}$ of 0.20 $\mu g/m^3$ 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 $\mu g/m^3$ (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 µg/m^3) to derive the PEC_{local} for the steel production sites, the production site for welding consumables (see current RAR), the AlF_3 production plants and the aluminium production plants (see RAR AlF_3).

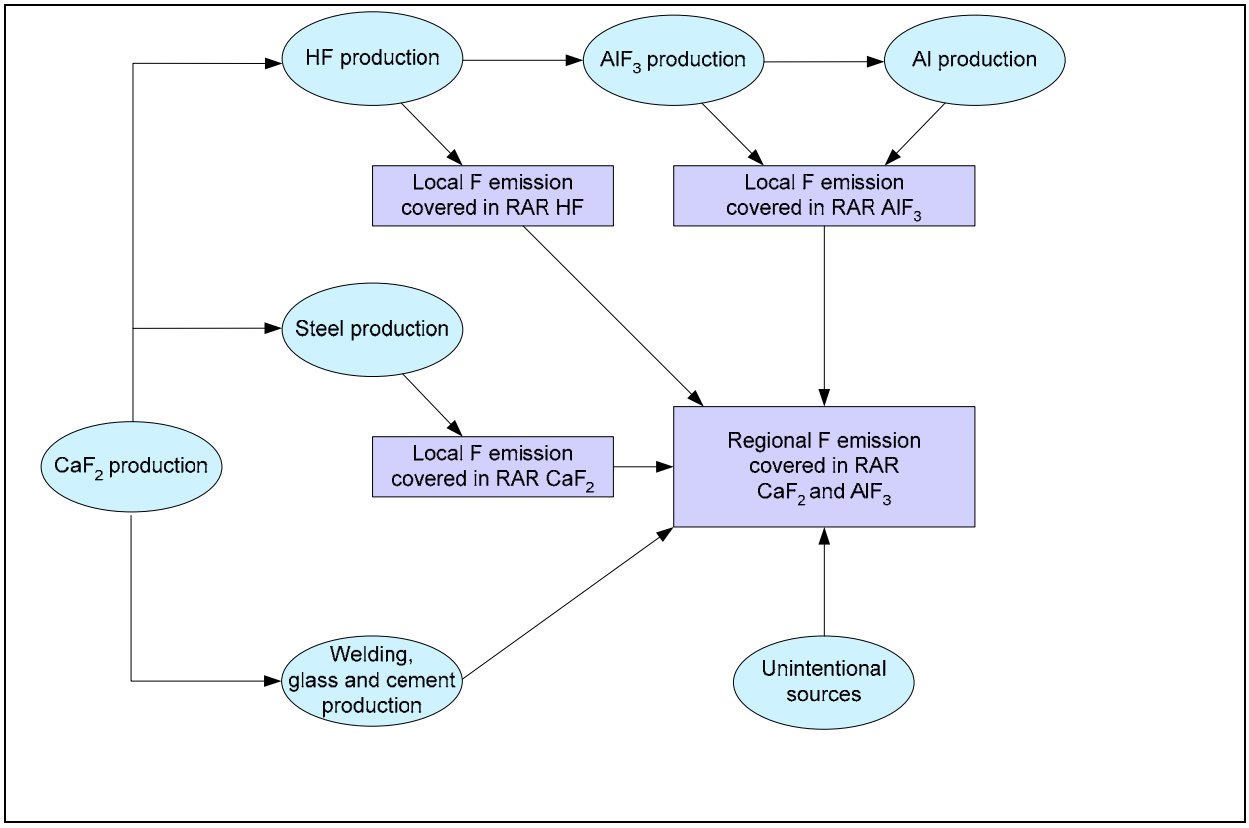


Figure 3.1 Overview of the different sources that contribute to atmospheric emission of fluoride and in which RARs the local and regional fluoride releases are assessed.

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

CaF_2 primary occurs in the environment as a fluoride-containing mineral, called fluorspar. The solubility of CaF_2 in water is poor (about 15 mg/l), therefore toxicity can theoretically be expected from free F^- ions (7.3 mg/l when maximum solubility is achieved), but also from CaF-complexes. In hard and seawater fluoride precipitates with Ca as CaF_2 (especially when pH>4.5).

In this risk assessment reference is made to the RAR on HF, which presents toxicity data for the F^- ion. Most of these tests have been performed with sodium fluoride, which is far more soluble than CaF_2. As the toxicity of CaF_2 is primary expected from the F^- ion, the effect assessment has been based mainly on these data and is therefore quite similar to the RAR on HF.

As no risk assessment for the aquatic environment (both freshwater and marine) is performed, the following aquatic toxicity data are only used for classification and labelling purposes.

3.2.1 Aquatic compartment

3.2.1.1 Toxicity to fish

The short-term toxicity studies with CaF_2 for freshwater fish are summarised in **Table 3.8**.

Table 3.8 Short-term toxicity data of CaF_2 for fish

No.	Species	Duration (h)	LC_{50} (mg/l)	Method	Hardness (mg $CaC0_3$/l)	Reliability	References
1	Tinca vulgaris	48	30000 (LC_{100})	other	unknown	3	(Simonin & Pierron 1937)
2	Cyprinus carpio	24	324-431 (LD_0)	other	10 (ppm)	3	(Loeb & Kelly 1963)
3	Chaenogobius annularis	96	>232 (LC_0)	other	unknown (seawater)	4	(Ishio & Nakagawa 1971)
4	Chrysophrys major	96	>232 (LC_0)	other	unknown (seawater)	4	(Ishio & Nakagawa 1971)
5	Fugu niphobles	96	>232 (LC_0)	other	unknown (seawater)	4	(Ishio & Nakagawa 1971)
6	Halichoeres poecilopterus	96	>232 (LC_0)	other	unknown (seawater)	4	(Ishio & Nakagawa 1971)

The reliability of the available data is very poor as it involves not standardised toxicity studies, in addition few is reported about the test conditions. The concentrations tested are far above water solubility, consequently the short-term effect concentrations are found to be far above water solubility. 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 a PNEC for the aquatic environment. This concentration can occur in the environment, considered the water solubility of CaF_2 of 15 mg/l.

3.2.1.2 Toxicity to aquatic invertebrates (e.g. Daphnia)

The toxicity studies with CaF_2 for freshwater aquatic species are summarised in **Table 3.9**.

Table 3.9 Toxicity data of CaF_2 for marine invertebrates

No.	Species	**Duration (d)**	**NOEC (mg/l)**	**Method**	**Hardness (mg $CaC0_3$/l)**	**Reliability**	**References**
1	Mytilus edulis	20	250	other	unknown (seawater)	2	(Martin et al. 1985)
2	Metapenaopsis barbata	4	232	other	unknown (seawater)	4	(Ishio & Nakagawa 1971)

The first study meets generally accepted scientific principles and resulted in a NOEC of 250 mg/l. However this NOEC exceeds the water solubility of CaF_2. In addition, no EC50 could be derived. 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.

3.2.1.3 Toxicity to algae

The toxicity studies with CaF_2 for algae are summarised in **Table 3.10**.

Table 3.10 Toxicity data of CaF_2 for algae

No.	Species	Duration (d)	NOEC (mg/l)	Method	Hardness (mg $CaC0_3$/l)	Reliability	References
1	Porphyra tenera	30	376	Other	unknown (seawater)	4	(Ishio & Nakagawa 1971)

The applied concentrations exceeded water solubility of CaF_2. Measurements of 1.5 mg/l F^- the highest concentration of 376 mg/l revealed that this study can not be used for the derivation of a PNEC for the aquatic environment.

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.

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 CaF_2, 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 TRA for CaF_2, since no additional data are available.

$PNEC_{plant\text{-}air}$ = 0.2 µg/m^3

The PNEC has been derived form the lowest NOEC for highly sensitive plant species, without using an extrapolation factor.

3.2.4 Non compartment specific effects relevant to the food chain

With respect to secondary poisoning 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 CaF_2.

The atmospheric NOECs for livestock (and plants) are 0.8 µg and 0.3 µg/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 [5]

3.3.1 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.

For CaF_2 production conclusion (ii) is drawn with respect to HF on a local scale, since no HF is emitted during this life cycle stage. For the downstream user of CaF_2 for the production of HF is covered by the RAR on HF (2001). 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). The same conclusion can be drawn based on the production figures for the year 2000, although the emission is approximately twice as high (see section 3.1.1.2.2).

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 the RAR on AlF_3, the air concentration causing a risk for the terrestrial compartment atmosphere is much higher than the one that will cause a risk for the atmosphere. 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, with respect to the use of CaF_2 by the steel industry as flux agent. Therefore, for the downstream use flux agent on a local scale conclusion (ii) is drawn.

For all other minor uses (0.8% of the total EU volume) no conclusion is drawn with respect to HF emissions, since they are considered to be of minor importance.

3.3.2 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 CaF_2 production conclusion (ii) is drawn with respect to HF, since no HF is emitted during this life cycle stage.

The regional PEC derived with EUSES 2.0.3. (2005), combining the fluoride emissions from both intentional and unintentional sources was found to be 0.2 $\mu g/m^3$, which equals the established $PNEC_{plant\text{-}air}$ = 0.2 $\mu g/m^3$. As the Dutch mean concentration of 0.07 $\mu g/m^3$ confirms that the PNEC is not exceeded conclusion (ii) is drawn for the regional scale.

Based on realistic worst-case emission factors provided by the industry, the use of CaF_2 in the metal industry as a flux agent leads to local air concentrations ranging from to 0.032 to 3.05

[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.

µg/m^3. For the class of five steel production sites which use up to 500 tons of CaF_2 a (maximum) C_{local} of 0.095 µg/m^3 is derived. Adding this maximum local concentration up with the $PEC_{regional}$ (resulting in a PEC_{local} of 0.30 µg/m^3) leads to a maximum RCR of 1.5. Since the PEC $_{regional}$ equals the PNEC, each local atmospheric emission of HF leads to exceeding of the PNEC. However, in view of the limited contribution of the local air concentrations to the exceeding of the PNEC, conclusion (ii) is drawn for these five sites.

The use of CaF_2 by the metal industry with respect to welding can be split up in the use for the production of welding consumables and the use as a flux agent for welding. From the latter emissions are considered to be small on a local scale, due to wide distribution of this application across the EU (see section 3.1.1.2.2). In addition, at the production of welding consumables no HF is emitted (see section 3.1.1.2.2). Therefore, conclusion (ii) is drawn at the local scale for both scenarios.

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) is drawn for the following downstream uses of CaF_2:

> The local environmental risk characterisation of the downstream use of CaF_2 (HF production) is described in the RAR on HF (2001). The calculated PEC in atmosphere exceeds the PNEC (conclusion iii).
>
> For the eight steel production sites which use above 500 tons of CaF_2 as a flux agent (classes with upper thresholds ranging from 1,000 to 16,000 tonnes) conclusion iii is drawn. The upper threshold of the class 500 to 1,000 tonnes of CaF_2 results in a C_{local} of 0.19 µg/m^3, a PEC_{local} of 0.39 µg/m^3 and an RCR of 2.0. Since this local air concentration is considered to be equal to the PNEC conclusion (iii) is drawn.

For all other minor uses (0.8% of the total EU volume) no conclusion is drawn with respect to HF emissions, since they are considered to be of minor importance (see last paragraph of section 3.1.5.1.2).

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.

No emissions of HF are expected during the production of CaF_2. Therefore, no specific effect relevant to the food chain are expected (conclusion ii).

Based on realistic worst-case emission factors provided by the industry, the use of CaF_2 in the metal industry as a flux agent leads to local air concentrations ranging from 0.032 to 3.05 µg/m^3. For the five steel production sites which use up to 1,000 tons of CaF_2 a (maximum) C_{local} of 0.19 µg/m^3 is derived. Adding this maximum local concentration up to the $PEC_{regional}$ (resulting in a (maximum) PEC_{local} of 0.39 µg/m^3) the atmospheric NOEC for livestock of 0.3 µg/m^3 for the winter season is exceeded by a factor 1.3. In view of the limited contribution of the local air concentrations to the exceeding of the NOEC, conclusion (ii) is drawn for these sites.

For the ten steel production sites which use up to 3,500 tons of CaF_2 as a flux agent a (maximum) PEC_{local} of 0.87 µg/m^3 (C_{local}: 0.67 µg/m^3 + $PEC_{regional}$: 0.2 µg/m^3) is derived. The

NOEC for livestock for the grazing season of 0.8 µg/m^3 is exceeded by a factor 1.08. In view of the marginal exceeding of the NOEC, conclusion (ii) is drawn for these sites.

Steel production: CaF_2 consumption (tonnes/year)	# EU sites	Grazing season	Winter season
0 - < 1,000	5	**conclusion ii**	**conclusion ii**
1,000 - < 3,500	5	**conclusion ii**	**conclusion iii**
3,500 - < 6,500	-	**conclusion iii**	**conclusion iii**
≥ 6,500	3	**conclusion iii**	**conclusion iii**

The use of CaF_2 by the metal industry with respect to welding can be split up in the use for the production of welding consumables and the use as a flux agent for welding. From the latter emissions are considered to be small on a local scale, due to wide distribution of this application across the EU (see section 3.1.1.2.2). In addition, at the production of welding consumables no HF is emitted (see section 3.1.1.2.2). Therefore, conclusion (ii) is drawn at the local scale for both scenarios.

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) is drawn for the following downstream uses of CaF_2:

The local environmental risk characterisation with respect to non compartment specific effects relevant to the food chain of the main downstream use of CaF_2 (HF production) is described in the RAR on HF (2001). The calculated PEC in atmosphere exceeds the atmospheric NOECs for livestock of 0.8 µg/m^3 and 0.3 µg/m^3 for the grazing season and winter season, respectively (conclusion iii). It was emphasized that wildlife is probably more susceptible to fluorides than livestock.

For the eight steel production sites which use above 1,000 tons of CaF_2 as a flux agent (classes with upper thresholds ranging from 1,500 to 16,000 tonnes) conclusion iii is drawn for the winter season. The upper threshold of the class 1,000 to 1,500 tonnes of CaF_2 results in a C_{local} of 0.29 µg/m^3, a PEC_{local} of 0.49 µg/m^3 and an RCR of 1.6. Since this local air concentration is considered to be equal the atmospheric NOEC for livestock of 0.3 µg/m^3 for the winter season conclusion (iii) is drawn.

For the three steel production sites which use more than 6,500 tons of CaF_2 as a flux agent (up to 16,000 tonnes) conclusion (iii) is drawn for the summer season on a local scale, in view of the calculated PEC_{local} of 1.44 µg/m^3 (up to 3.25 µg/m^3).

For all other minor uses (0.8% of the total EU volume) no conclusion is drawn, since they are considered to be of minor importance (see last paragraph of section 3.1.5.1.2).

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. 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 CaF_2 use. The flux agent scenario shows the highest realistic local HF concentration derived from CaF_2 use (see 3.1.5.1.2). The H atom hardly has any influence on the HF concentration, therefore the concentration of HF and F^- are considered equivalent. For man exposed indirectly, the yearly average concentration is taken, including the regional exposure. This concentration would lead to an intake of 3.25 µg F^-/m^3 x 20 m^3/day/ 70 kg bw= 1 µg F^-/kg bw/day.

Table 4.1 Local and regional concentrations of HF derived from CaF_2 use and the calculated intake

Local scenario's	Local µg F^-/m^3	Yearly average µg F^-/m^3	Intake µg F^-/kg bw/day
Flux agent	3.05	3.25	1
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 µg/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 for CaF_2 use is put in the context of the daily F^- intake. The intake of F^- of 1 µg/kg bw/day for the flux agent scenario is negligible compared to the total daily fluoride intake (**conclusion ii**).

The regional air concentration of F^- is 0.2 µg F^-/m^3. This concentration would lead to an intake of $6x10^{-2}$ µg F^-/kg bw/day which is negligible compared to an overall intake of fluoride via food and drinking water of 85 µg F^-/kg bw/day (**conclusion ii**).

5 RESULTS [6]

5.1 ENVIRONMENT

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.

For CaF_2 production conclusion (ii) is drawn with respect to HF on a local scale, since no HF is emitted during this life cycle stage. The downstream use of CaF_2 for the production of HF is covered by the RAR on HF (2001). 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). The same conclusion can be drawn based on the production figures for the year 2000, although the emission is approximately twice as high (see section 3.1.1.2.2).

For the down stream use of CaF_2 by the steel industry as flux agent with respect to HF emissions on a local scale conclusion (ii) is drawn (see section 3.3.1).

For all other minor uses (0.8% of the total EU volume) no conclusion is drawn with respect to HF emissions, since they are considered to be of minor importance.

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 CaF_2 production conclusion (ii) is drawn with respect to HF, since no HF is emitted during this life cycle stage.

The regional PEC derived with EUSES 2.0.3. (2005), combining the fluoride emissions from both intentional and unintentional sources was found to be 0.2 $\mu g/m^3$, which equals the established $PNEC_{plant\text{-}air}$ = 0.2 $\mu g/m^3$. As the Dutch mean concentration of 0.07 $\mu g/m^3$ confirms that the PNEC is not exceeded conclusion (ii) is drawn for the regional scale.

Based on realistic worst-case emission factors provided by the industry, the use of CaF_2 in the metal industry as a flux agent leads to local air concentrations ranging from to 0.032 to 3.05 $\mu g/m^3$. For the class of five steel production sites which use up to 500 tons of CaF_2 a (maximum) C_{local} of 0.095 $\mu g/m^3$ is derived. Adding this maximum local concentration up with the $PEC_{regional}$ (resulting in a PEC_{local} of 0.30 $\mu g/m^3$) leads to a maximum RCR of 1.5. Since the $PEC_{regional}$ equals the PNEC, each local atmospheric emission of HF leads to exceeding of the PNEC. However, in view of the limited contribution of the local air concentrations to the exceeding of the PNEC, conclusion (ii) is drawn for these five sites.

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[6] 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.

The use of CaF_2 by the metal industry with respect to welding can be split up in the use for the production of welding consumables and the use as a flux agent for welding. From the latter emissions are considered to be small on a local scale, due to wide distribution of this application across the EU (see section 3.1.1.2.2). In addition, at the production of welding consumables no HF is emitted (see section 3.1.1.2.2). Therefore, conclusion (ii) is drawn at the local scale for both scenarios.

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) is drawn for the following downstream uses of CaF_2:

> The local environmental risk characterisation of the downstream use of CaF_2 (HF production) is described in the RAR on HF (2001). The calculated PEC in atmosphere exceeds the PNEC (conclusion iii).
>
> For the eight steel production sites which use above 500 tons of CaF_2 as a flux agent (classes with upper thresholds ranging from 1,000 to 16,000 tonnes) conclusion iii is drawn. The upper threshold of the class 500 to 1,000 tonnes of CaF_2 results in a C_{local} of 0.19 µg/m^3, a PEC_{local} of 0.39 µg/m^3 and an RCR of 2.0. Since this local air concentration is considered to be equal to the PNEC conclusion (iii) is drawn.

For all other minor uses (0.8% of the total EU volume) no conclusion is drawn with respect to HF emissions, since they are considered to be of minor importance (see last paragraph of section 3.1.5.1.2).

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.

No emissions of HF are expected during the production of CaF_2. Therefore, no specific effect relevant to the food chain are expected (conclusion ii).

Based on realistic worst-case emission factors provided by the industry, the use of CaF_2 in the metal industry as a flux agent leads to local air concentrations ranging from 0.032 to 3.05 µg/m^3. For the five steel production sites which use up to 1,000 tons of CaF_2 a (maximum) C_{local} of 0.19 µg/m^3 is derived. Adding this maximum local concentration up to the $PEC_{regional}$ (resulting in a (maximum) PEC_{local} of 0.39 µg/m^3) the atmospheric NOEC for livestock of 0.3 µg/m^3 for the winter season is exceeded by a factor 1.3. In view of the limited contribution of the local air concentrations to the exceeding of the NOEC, conclusion (ii) is drawn for these sites.

For the ten steel production sites which use up to 3,000 tons of CaF_2 as a flux agent a (maximum) PEC_{local} of 0.87 µg/m^3 (C_{local}: 0.67 µg/m^3 + $PEC_{regional}$: 0.2 µg/m^3) is derived. The NOEC for livestock for the grazing season of 0.8 µg/m^3 is exceeded by a factor 1.08. In view of the marginal exceeding of the NOEC, conclusion (ii) is drawn for these sites.

Steel production: CaF_2 consumption (tonnes/year)	# EU sites	Grazing season	Winter season
0 - < 1,000	5	**conclusion ii**	**conclusion ii**
1,000 - < 3,500	5	**conclusion ii**	**conclusion iii**
3,500 - < 6,500	-	**conclusion iii**	**conclusion iii**
≥ 6,500	3	**conclusion iii**	**conclusion iii**

The use of CaF_2 by the metal industry with respect to welding can be split up in the use for the production of welding consumables and the use as a flux agent for welding. From the latter emissions are considered to be small on a local scale, due to wide distribution of this application across the EU (see section 3.1.1.2.2). In addition, at the production of welding consumables no HF is emitted (see section 3.1.1.2.2). Therefore, conclusion (ii) is drawn at the local scale for both scenarios.

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) is drawn for the following downstream uses of CaF_2:

The local environmental risk characterisation with respect to non compartment specific effects relevant to the food chain of the main downstream use of CaF_2 (HF production) is described in the RAR on HF (2001). The calculated PEC in atmosphere exceeds the atmospheric NOECs for livestock of 0.8 µg/m^3 and 0.3 µg/m^3 for the grazing season and winter season, respectively (conclusion iii). It was emphasized that wildlife is probably more susceptible to fluorides than livestock.

For the eight steel production sites which use above 1,000 tons of CaF_2 as a flux agent (classes with upper thresholds ranging from 1,500 to 16,000 tonnes) conclusion iii is drawn for the winter season. The upper threshold of the class 1,000 to 1,500 tonnes of CaF_2 results in a C_{local} of 0.29 µg/m^3, a PEC_{local} of 0.49 µg/m^3 and an RCR of 1.6. Since this local air concentration is considered to be equal the atmospheric NOEC for livestock of 0.3 µg/m^3 for the winter season conclusion (iii) is drawn.

For the three steel production sites which use more than 6,500 tons of CaF_2 as a flux agent (up to 16,000 tonnes) conclusion (iii) is drawn for the summer season on a local scale, in view of the calculated PEC_{local} of 1.44 µg/m^3 (up to 3.25 µg/m^3).

For all other minor uses (0.8% of the total EU volume) no conclusion is drawn with respect to HF emissions, since they are considered to be of minor importance (see last paragraph of section 3.1.5.1.2).

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 µg/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 for CaF_2 use is put in the context of the daily F^- intake. The intake of F^- of 1 µg/kg bw/day for the flux agent scenario is negligible compared to the total daily fluoride intake (**conclusion ii**).

The regional air concentration of F^- is 0.2 µg F^-/m^3. This concentration would lead to an intake of $6x10^{-2}$ µg F^-/kg bw/day which is negligible compared to an overall intake of fluoride via food and drinking water of 85 µg F^-/kg bw/day (**conclusion ii**).

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ABBREVIATIONS

BCF	Bioconcentration Factor
CA	Competent Authority
CAS	Chemical Abstract Services
CEC	Commission of the European Communities
CEFIC	European Chemical Industry Council
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]
EWA	European Welding Association
HPVC	High Production Volume Chemical (> 1000 t/a)
IC	Industrial Category
IPCS	International Programme on Chemical Safety
IUCLID	International Uniform Chemical Information Database (existing substances)
IUPAC	International Union for Pure and Applied Chemistry
LC50	median Lethal Concentration
LD50	median Lethal Dose
NOEC	No Observed Effect Concentration
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 Calcium 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 downstream use sites of CaF_2, 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