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INTEGRATED CRITERIA DOCUMENT FLUORIDES

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SUMMARY

This document on the subject of inorganic fluorides contains data concerning their sources and distribution pattern (soil, water, air, biota), the risks based on a careful consideration of exposure levels and toxic concentrations, the technical possibilities of reducing these risks and the economic consequences of any measures taken or proposed. This information provides the scientific basis for the formulation of the effect-directed standardization policy.

Further study of the inorganic fluorides is called for because, for the time being, the extent and scale of their effects on public health, ecosystems, cultivated plants and livestock are not sufficiently well known. The extent to which fluoride accumulates and causes (more) problems in the long term is also not sufficiently clear.

A general summary of the emissions and transport of fluorides to the environmental compartments in the Netherlands is given in figure A.

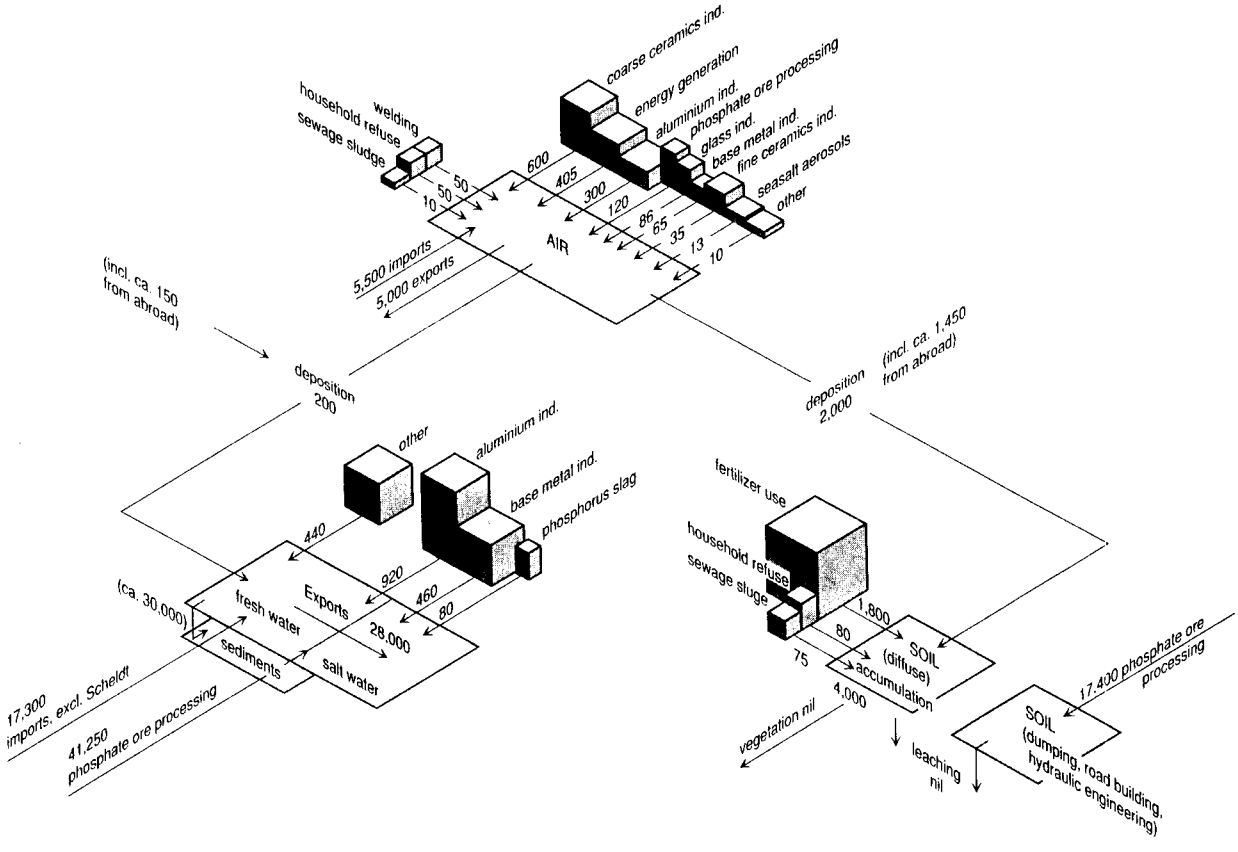


Figure A: Fluoride flows in the Dutch environment (in tonnes per year, with 1985 as reference year)

The emission of fluoride into the atmosphere amounts to more than 1700 tonnes per year, the major sources being the coarse ceramics industry, energy generation and the aluminium industry. Quantitatively, the principal source of fluoride to water is the processing of phosphate ore, discharging into brackish/salt water, but in view of the forms of occurrence and, thereby, the biological availibility of fluoride, the smaller discharges from the aluminium and base metals industries are relatively more important. Fertilizer use and deposition account for the greater part of the diffuse input of fluoride to the soil. Deposition is important the more so because this process eventually leads to the most critical effects. It has been estimated that, on the average, about 75% of the deposition in the Netherlands comes from abroad. The influence of foreign emissions is greatest in South Limburg and Zeeuws Vlaanderen. The main sources of fluoride emissions in the Netherlands are in East Groningen, the Rhine-Meuse area, the Sloe area and the Rijnmond area.

Fluorine is a very reactive halogen which, because of its strong affinity to other elements, is not found in the free state in nature. The behaviour and biological availability of the numerous fluoride compounds can differ widely, making an overall evaluation difficult.

In man, fluoride plays a role in the development of dentition and the skeleton. Low F intake helps to prevent dental caries, whilst high F intake can cause dental lesions (dental fluorosis) and bone structural changes (osteofluorosis). The available data lend support to the assumption that the current oral exposure to fluoride generally does not entail a risk to the population in the Netherlands.
Although the data are insufficient for making a statement about the possibly maximum acceptable atmospheric fluoride concentrations for man, it can nevertheless be concluded that the current concentrations indoors as well as outdoors (also around sources) will have no adverse effects on human health.

A maximum concentration of 1.5 $mg.l^{-1}$ in fresh surface water (dissolved amount) has been proposed for aquatic organisms, on the basis of long-term toxicity studies. This level is also considered to be the maximum acceptable toxicant concentration for humans with regard to the occurrence of dental fluorosis, and has been proposed by the EEC as an upper limit for

surface waters intended for the production of drinking water. Both this ceiling and the standard for drinking water in force in the Netherlands are lower, viz., 1.0 and 1.1 $mg.l^{-1}$, so that the range of the maximum permissible level lies between 1.0 and 1.5 $mg.l^{-1}$.
Since 1980, the number of water bodies exceeding the level of 1 $mg.l^{-1}$ in fresh surface water has fallen sharply. Quarterly averages are below this limit, except in the Ghent-Terneuzen Canal (a decrease from about 8 to 1.5-2 $mg.l^{-1}$ during the past decade) and, possibly, a number of smaller water bodies in areas of industrial F emissions. Adverse effects cannot be excluded in these areas. In accordance with recent policy premises, the target value has been set at 1% of the maximum acceptable level (i.e., 0.01-0.015 $mg.l^{-1}$), or at the background level (0.01-0.3 $mg.l^{-1}$) when the target value to be derived is lower than the natural background concentration. The range of the lower limit therefore lies between 0.01 and 0.3 $mg.l^{-1}$.

In the marine environment, fluoride occurs naturally in high concentrations and accordingly belongs to the macrocomponents of seawater. Studies with a limited number of species of organisms support the assumption that intolerable effects are not to be expected when the concentration is less than 5 $mg.l^{-1}$. The current levels, also in coastal waters, lie below this value.

Data on terrestrial ecosystems necessary for establishing a permissible concentration for soil or air are insufficient. For plants, the most critical route is exposure to atmospheric fluoride, while for animals the main intake source of fluoride is the diet.
In view of the relatively high natural F concentrations in soil, the effect of F pollution on the soil flora and fauna does not appear to be the most critical consideration. However, when in the long term, as a result of prolonged excessive loading of the soil with fluoride, the adsorption complex reaches an equilibrium with the soil solution, the fluoride concentration in the ground water may locally exceed the reference value (0.5 $mg.l^{-1}$) and even the current drinking-water standard (1.1 $mg.l^{-1}$).
The recommended values for the atmospheric fluoride concentrations are provisionally the same as those established for the protection of cultivated plants and domestic livestock. These recommended values have been derived indirectly from observed effects or damage. The uncertainty in

these values is great and, because of the economic interests involved, require further study.

As with surface water, a range of maximum concentrations has provisionally been given, within which different levels of protection can be distinguished:

- 0.05 μg $F.m^{-3}$, as a maximum annual average (pH 1 soluble fraction) during the whole year (thus also in winter) to protect flora and fauna,
- 0.13 μg $F.m^{-3}$, as a maximum annual average (pH 1 soluble fraction) to protect (most) cultivated plants and wild flora,
- 0.18 μg $F.m^{-3}$ as a maximum annual average (seasonal average 0.13 $\mu g.m^{-3}$; pH 1 soluble fraction) to protect cattle and wild fauna during the grazing season.

Measurements made near sources indicate that the fluoride concentrations generally have fallen during the past few years. The current interim ceiling (seasonal average 0.4 $\mu g.m^{-3}$) is still being exceeded around a limited number of sources. A further decrease in the concentrations is expected after implementation of proposed measures, in this case the application of flue-gas scrubbers in coal-fired power stations and waste incinerators (reducing emissions by more than 400 tonnes annually). By taking additional measures, the emissions of fluoride in the Netherlands can be cut by nearly 1000 tonnes at most, albeit not without economic consequences for most of the companies concerned. When these measures are implemented, the current interim limit can be met in the areas with a fluoride pollution problem, except close to emission sources in East Groningen and the Sloe area. According to estimates, a maximum annual average of 0.2 μg $F.m^{-3}$ (roughly equivalent to the highest recommended concentration) is then probably not attainable in East Groningen and Zeeuws Vlaanderen, while this maximum will certainly be exceeded in the Sloe area. Application of air-purification techniques is accompanied by chemical waste when dry systems are employed (over 1000 tonnes a year), with uncertain prospects for its reuse, and by a slight rise in F concentration in surface waters when wet systems are used, the effect of which may be assumed to be not measurable.

For terrestrial ecosystems, the no-effect levels are exceeded everywhere except in the NW of the Netherlands. However, it is not possible to indicate the severity and extent of the ecological damage taking place. As regards cultivated plants, there is yield reduction for flowers, bulbs, trees and pot plants, but it generally appears to be limited. Damage to

cattle in terms of reduced milk production occurs locally and in some degree regionally in a few areas with a fluoride pollution problem. An estimated 2000 head of cattle are exposed locally to (too) high F levels. In Zeeuws Vlaanderen, the Sloe area and the Rijnmond area, anti-fluoride pellets are administered to the cattle to keep fluoride toxicosis within acceptable limits. In a number of cases there are compensation schemes for damage to both cultivated plants and farm animals.
There are no data indicating that fluorides are involved in pollutant damage to materials at current atmospheric concentrations. The contribution of hydrogen fluoride to the total F deposition is also negligible. The stratospheric contribution to the hydrogen fluoride concentrations in the troposphere due to CFCs could increase to approximately 0.001 $\mu g.m^{-3}$ in the next 50 years. In view of the no-effect levels, worldwide effects on the biosphere are not to be expected for the time being.

It can be concluded that the fluoride concentrations in water and air have fallen in the Netherlands during the past few years. The fluoride level in nearly all surface waters lies below the toxic level, while it is assumed that the fluoride loading of soil in the areas with industrial emissions has not (yet) led to toxic levels in the groundwater. Nevertheless, the atmospheric fluoride concentrations are such that, with the exception of the NW of the Netherlands, damage to ecosystems, agriculture and livestock farming cannot be excluded; there is demonstrable damage in emission areas. However, the proposed air quality objectives are based on transfer factors and dose-response relationships, whereby assumptions have been made including a number requiring a sounder underpinning. Various recommendations for research have been made.

INTRODUCTION

Environmental policy at government level is first of all aimed at attaining and maintaining an air quality which ensures the general health and wellbeing of man and the preservation of animals, plants and goods, as well as specific uses of the substance in question (Indicative Multi-year Programme - Environmental Management 1986-1990). However, with insufficient knowledge it is impossible for the time being to describe fully the overall environmental quality in view. Attention is therefore being concentrated on factors which probably entail considerable risks, including environmentally harmful substances. A selection has been made of the many substances of relevance, because of emission or use, and a priority list compiled. In principle, so-called integrated criteria documents are drawn up for most of the priority substances.
Integrated criteria documents contain, per substance or substance group, data on the sources and the distribution pattern (soil, water, air, biota), the risks of actual exposure concentrations for man, (parts of) ecosystems and materials, and the technical possibilities and economic consequences of reducing these risks. This information serves as the scientific basis for formulating the effect-directed environmental policy. This may lead to environmental quality criteria and a general task-setting for the emission reductions per source.

This document deals with fluorides, specifically the inorganic fluorides. This implies, among other things, that the chlorofluorocarbons (CFCs) will not be considered. The inorganic fluorides require further study because of their effects on man, natural ecosystems, agriculture, horticulture, forestry and livestock farming, thus raising the question of to what extent the problems are only localized, and whether accumulation occurs in the environment. Unlike previous integrated criteria documents, it emerged during the exploratory meeting that most of the usual topics considered in an integrated criteria document were important, but the emphasis will be mainly on describing as fully as possible the sources and emitted compounds, behaviour in air, multicompartmental transport, possibilities of emission reduction and measuring techniques. The description of effects on a global scale, production and applications are considered to be relatively less important.

This document was prepared by the National Institute of Public Health and Environmental Protection (RIVM) with the cooperation of, and contributions from, DHV Consulting Engineers BV, the Netherlands Organization for Applied Scientific Research (TNO) and the Research Institute for Plant Protection (IPO), as well as contributions from the Institute for Environmental Issues (IvM), the Agricultural Economic Institute (LEI) and the consulting firm Milvetox.

For some sections, such as emission-control techniques and their costs, valuable information was obtained from relevant industrial sectors; their valued cooperation was procured through the Office of Environment and Physical Planning of the Council of Dutch Employers' Unions, VNO and NCW.

The document has been checked in its entirety by a Review Committee of the RIVM and submitted to interest groups and advisory bodies for comments.

An Advisory Board comprising staff from the Ministry of Housing, Physical Planning and the Environment, the Department of Inland Waterways/National Institute for Waste Water Research (DBW/RIZA) and the Ministry of Agriculture and Fisheries also gave guidance in the preparation of this document.

1. PROPERTIES AND EXISTING STANDARDS

1.1. PROPERTIES

For the description of the properties, only those fluorine compounds which are relevant within the framework of this integrated criteria document have been selected.

1.1.1. Nomenclature and registration numbers

The various names, the registration number and molecular formula of the main forms of occurrence of fluorine are given in table 1.1.

Table 1.1. Nomenclature, CAS registration and molecular formula of several forms of fluorine (compounds)

Dutch name	CAS registration name	English name	CAS reg.no.	Mol.formula
Fluor	fluorine	fluorine	7782 -41-4	F_2
Fluor atoom	atomic fluorine	atomic fluorine	63241-95-2	F
Fluoride	fluoride	fluoride	16984-48-8	F^-
Waterstoffluoride	hydrofluoric acid	hydrogen fluoride	7664 -39-3	HF
Waterstoffluoride-ion	fluoride	hydrogen fluoride ion	18130-74-0	H_2F^+
Natrium fluoride	sodium fluoride	sodium fluoride	7681 -49-4	NaF
Natriumwaterstoffluoride	sodium fluoride	sodium hydrogen fluoride	1333 -83-1	$NaHF_2$
Kaliumfluoride	potassium fluoride	potassium fluoride	7789 -23-3	KF
Kaliumwaterstoffluoride	potassium fluoride	potassium hydrogen fluoride	7789 -29-9	KHF_2
Aluminiumfluoride	aluminium fluoride	aluminium fluoride	7784 -18-1	AlF_3
Ammoniumfluoride	ammonium fluoride	ammonium fluoride	12125-01-8	NH_4F
Ammoniumwaterstoffluoride	ammonium fluoride	ammonium hydrogen fluoride	1341 -49-7	$(NH_4)HF_2$
Siliciumtetrafluoride	tetrafluorosilane	silicon tetrafluoride	7783 -61-1	SiF_4
Calcium fluoride	calcium fluoride	calcium fluoride	7789 -75-5	CaF_2
Natriummonofluorfosfaat	phosphorofluoridic acid	sodium monofluoro-phosphate	10163-15-2	$Na_2FH_2PO_3$
Natriumaluminiumfluoride	trisodium hexafluoro-aluminate	sodium aluminium fluoride	13775-53-6	Na_3AlF_6
Fluorine-containing minerals				
Vloeispaat	fluorite	fluorspar	14542-23-5	CaF_2
Kryoliet	cryolite	cryolite	15096-52-3	Na_3AlF_6
Fluorapatiet	fluorapatite	fluorapatite	1306 -05-4	$Ca_5F(PO_4)_3$
			58051-82-4	Ca_2FPO_4
			12525-40-5	$Ca_7F_2(PO_4)_4$

1.1.2. Physical and chemical properties

- Fluorine and fluorine compounds

The univalent element fluorine is a halogen which, because of its strong affinity to other elements, is not found in the free state in nature (Waldbott, 1963). It is the most reactive chemical element and reacts directly with all other elements except oxygen and nitrogen (Banks and Goldwhite, 1966). In aqueous solution, fluoride ions form complexes with metal ions, such as FeF_6^{-3}, AlF_6^{-3}, MnF_5^{-2} and MnF_3^-. The toxicity of inorganic fluorides is determined primarily by this behaviour and the formation of insoluble fluorides. The fluoride ion forms complexes with metals which usually have the ionic form, both in the crystalline state and in solution. Most of these fluorides are readily soluble in water; lithium, aluminium, strontium, barium, lead, magnesium, calcium and manganese fluorides are insoluble or sparingly soluble. A few fluorides with a high melting point are not even completely decomposed by boiling sulphuric acid. Fluorine and hydrogen fluoride form covalent compounds with nonmetals, such as fluormonoxide, silicon tetrafluoride and sulphur hexafluoride. Covalent compounds generally have low melting points and high volatilities (Durrant and Durrant, 1962; WHO, 1984).

- Hydrogen fluoride

Hydrogen fluoride is the most toxic fluorine compound known. At room temperature hydrogen fluoride is a colourless liquid or gas with an irritating odour. Its freezing point is -83°C and boiling point 19.5°C. It fumes in air and is completely soluble in water below 20°C. Hydrogen fluoride in liquid form is one of the best known strong acids (Horton, 1962); even such nonbasic compounds as alcohols, ketones and mineral acids are protonated and dissolved. It is a strong dehydrant; it chars wood and paper, and aldehydes undergo condensation through elimination of water (Gall, 1966; WHO, 1984). HF dissolved in water is however a weak acid.

- Alkali fluorides

The alkali fluorides have high melting and boiling points and are moderately to very soluble in water. All alkali fluorides, except for the lithium salt, absorb hydrogen fluoride with the formation of acid fluorides of the MHF_2 type, where M is the alkali metal (Banks and Goldwhite, 1966).

- Silicon tetrafluoride and fluorosilicates

Silicon tetrafluoride is a colourless and strong poisonous gas with an irritating odour. Its boiling point is -86°C and melting point -90°C. The gas reacts with water producing hexafluorosilicate ion, which is very poisonous. Most fluorosilicates are soluble in water (WHO, 1984a).

Fluoride can form readily to sparingly soluble minerals. The solubility heavily depends on other components and the pH (see subsection 3.2.2.). Table 1.2. lists the solubility of the most relevant fluorine salts. The log Ks associated with the various equilibrium reactions differ widely (log K ranges from -30 to +30; Elrashidi and Lindsay, 1986; Wibowo and Zielhuis, 1986).

Table 1.2. Solubility of F compounds (in $g.l^{-1}$) at different temperatures (Dean, 1985)

Compound	*0°C*	*10°C*	*20°C*	*25°C*	*30°C*
Aluminium fluoride	*5.6*	*5.6*	*6.7*	-	*7.8*
Barium fluoride	-	*1.6*	*1.6*	-	*1.6*
Carbon tetrafluoride (ml/l)	-	*5.5*	*4.9*	-	*4.2*
Copper fluorosilicate	*735*	*765*	*816*	*841*	-
Iron(II) fluorosilicate	*721*	*744*	-	*770*	-
Lead(II) fluorosilicate	*1900*	-	*2220*	-	-
Magnesium fluorosilicate	*263*	-	*308*	-	-
Manganese fluoride	-	-	*10.6*	-	-
Nickel fluoride	-	*25.5*	*25.6*	-	-
Potassium fluoride	*447*	*535*	*949*	-	*1080*
Potassium silicate	*0.77*	*1.02*	*1.51*	-	*2.02*
Potassium hydrogen fluoride	*245*	*301*	*392*	-	*468*
Sodium fluoride	*36.6*	-	*40.6*	-	*42.2*

The odour threshold for F_2 is 0.15-0.30 $mg.m^{-3}$ (van Gemert et al., 1984). The odour threshold for hydrogen fluoride is 0.03 $mg.m^{-3}$ (Health Council, 1981) and the concentration at which irritation occurs is about 4 $mg.m^{-3}$ (Rush, 1982).

1.2. STANDARDS AND RECOMMENDED VALUES

1.2.1. Soil

For a multifunctional soil, the reference value for fluorine is calculated according to [F] = 13 C + 175, where C is percent clay (diameter < 2 μm) by weight. For a standard soil with a clay content of 25%, [F] = 500 $mg.kg^{-1}$.

It has been reported that this or lower values are not expected to cause adverse effects. The reference value for fluorides in groundwater is 0.5 $mg.l^{-1}$; however, higher values occur naturally in areas which are under strong marine influence (see chapter 4) (MPV/88, 1987). A reference value of 175 $mg.kg^{-1}$ is in force for soil with very little or no clay (such as, for example, sandy soils and peat soils, which together make up about 50% of the Dutch land area).

A test framework for the assessment of concentration levels in soil has been given in the Soil Cleanup Guide (VROM, 1983) (see table 1.3.). The values mentioned in this guide should not be regarded as standards but as an assessment framework, which distinguishes the following values: A: reference value, B: test value for the purpose of (further) research, and C: test value for the purpose of soil-cleanup research. The concentrations are considered in relation to the function of the soil and the local contamination situation. In the assessment of cases of soil contamination, the differentiated reference values will replace the current A values in the Soil Cleanup Guide (MPV/88, 1987). At present, however, it is not clear to what extent the A values are still in force. Replacement of the A values as suggested in MPV/88 (1987) may lead to discrepancy with respect to the B and C values.

In Switzerland, the recommended guideline for the total fluoride content of soil is 400 mg $F.kg^{-1}$ dry matter and that for the soluble fluoride content 25 mg $F.kg^{-1}$ dry matter (SCMO-TNO, 1986).

Table 1.3. Test framework for the assessment of the concentration levels of fluorides in soil with respect to soil cleanup

Matrix	*A*	*B*	*C*
Soil (mg/kg dry matter)	*200 (500*)*	*400*	*2000*
Groundwater (µg/l)	*300*	*1200*	*4000*

** see text*

1.2.2. Water

Surface water intended for the production of drinking water has to meet a number of quality criteria (see table 1.4.)

Table 1.4. Quality criteria for surface water (mg F/l) intended for the production of drinking water

Country/river	*Extent of purification*	*Max. conc.*	*Status*	*Ref.*
EEC	*simple*	*0.7-1 **	*guideline*	*1*
		1.5	*ceiling*	
	normal	*0.7-1.7**	*guideline*	
	thorough	*0.7-1.7**	*guideline*	
NL	*simple*	*1.0*	*ceiling*	*2*
	normal	*1.0*	*guideline*	
	thorough	*1.0*	*guideline*	
Rhine (FRG)		*1*	*ceiling*	*3*

* *Maximum values depend on the average annual temperature*
1: EEC (1975)
2: Water Board Decree (1984)
3: IAWR (1986)

1.2.3. Air

Tables 1.5 and 1.6 present the quality criteria for the work environment and ambient air, respectively.

Table 1.5. Air quality in the workplace (MAC values, time-weighted averages (TWAs) for an 8-hour day, 40-hour workweek, in mg $F.m^{-3}$)

Country	*MAC values*	*Comment*	*Reference*
The Netherlands	*2*	*fluorine*	*National MAC*
	2.5	*fluorides;under consideration*	*list (1986)*
	2	*hydrogen fluoride*	
US, ACGIH	*2*	*fluorine*	*Wibowo and*
	4	*fluorine (10 min)*	*Zielhuis (1986)*
	2.5	*fluorides*	
	2.5	*hydrogen fluoride (10 min)*	
USSR	*0.5*	*hydrogen fluoride*	
West Germany	*0.2*	*fluorine*	
	2.5	*fluorides*	
	2.5	*mixture of fluorides and hydrogen fluoride*	
Sweden	*2*	*hydrogen fluoride*	*TNO (1977)*
East Germany	*1*	*hydrogen fluoride*	

The Working Group of Experts published a concept report in August 1987, proposing the following composition for the MAC-TWA 15-minute values:

Fluorine	0.5 mg $F.m^{-3}$
Hydrogen fluoride	1 mg $F.m^{-3}$
Soluble fluorides	2 mg $F.m^{-3}$

As a result, the MAC-TWA 8-hour values would no longer apply (WGD, 1987). For Germany, standards and guidelines for fluoride emissions are incorporated in the TA Luft (1986). For emissions of particulates containing readily soluble fluorides (e.g. NaF), a maximum emission concentration of 5 $mg.m^{-3}$, at a mass flow of over 25 g per hour, is in force. The same emission concentration applies to emissions of fluorine and fluorine compounds, insofar that they are present in the vapour or gaseous phase, but with a mass flow exceeding 50 g per hour. Installations emitting fluorine or gaseous fluorine compounds amounting to more than 0.5 kg per hour (as HF) have to be monitored continuously. The measuring technique must meet VDI guidelines 2470 and 2286; measurements in ambient air should be made in accordance with VDI guideline 2452. Emission control in the manufacture of HF is provided for in VDI guideline 2296.

1.2.4. Food and drinking water

Estimates have been made in the foreign literature of the safe and - on the basis of its anticaries activity - desirable daily fluoride intake. This is dependent upon age (see table 1.7.).

Ekstrand et al. (1981) recommended a daily intake of 0.05-0.07 mg F per kg body weight.

The drinking-water standards are given in table 1.8. Natural mineral and spring waters should contain no more than 2 mg $F.l^{-1}$. In Austria, the maximum permissible F content in mineral water is 1.5 $mg.l^{-1}$.

Table 1.6. Air quality criteria for ambient air in mg $F.m^{-3}$ (IDC, 1985)

Country	Concentration	Comment
The Netherlands	0.0028	daily average
(interim ceilings)	0.0008	monthly average
	0.0004	growing-season average (April to November) (as HF and inorganic gaseous fluorine compounds, as F^-)
West Germany	0.001	arithmetic mean of 30-minute values over a year
	0.003	98th percentile of 30-minute values over a year (as HF and inorganic fluorine compounds, as F^-)
Bruges (Belgium)	0.004	daily average
	0.002	annual average (as F)
USSR	0.02	maximum
	0.005	daily average, gaseous compounds (HF, SiF_4)
	0.03	maximum
	0.01	daily average (as readily soluble inorganic compounds; NaF, Na_2SiF_6)
	0.2	maximum
	0.03	daily average (sparingly soluble inorganic compounds; AlF_3, Na_3AlF_6, CaF_2)
	0.03	maximum
	0.01	daily average (as a mixture of fluorine and fluorine compounds)
US- Montana	0.007	daily average (as HF)
- New York	0.007	daily average, rural area (as HF)
	0.0013	daily average, city (as HF)
	0.0026	daily average , industrial area (as HF)
- Pennsylvania	0.005	daily average (as HF)
Canada	0.085	daily average
	0.055	weekly average
	0.035	monthly average
	0.02	70-day average
- Ontario	0.0026	daily average, rural area (as HF)
	0.007	daily average, city (as HF)
	0.07	30-minute average
China	0.02	maximum, as F
	0.007	daily average

Table 1.7. Proposed daily fluoride intake (mg)

Age	Amount	Reference
children aged 1-3 years	0.5-1.5	Food and Nutrition
adolescents	1.5-2.5	Board (1980)
adults	2.5-4.0	
0.5-1 year	0.3-0.4	Smith (1984)
1.5-2 years	0.5-0.7	
3 years	0.7-1.0	
4 years	0.9-1.2	
6 years	1.2-1.6	
8 years	1.4-2.0	
12 years	1.8-2.5	
16 years	2.3-3.3	
<0.5 year	0.1-0.5	LSI (1985)
0.5-1 year	0.2-1.0	
1 - 3 years	0.5-1.0	
4 - 6 years	1.0-2.5	
7 years up to adulthood	1.5-2.5	
adults	1.5-4.0	

Table 1.8. Drinking-water standards ($mg.l^{-1}$)

Country	Max. conc.	Comment	Reference
The Netherlands	1.1		Water Board Decree (1984)
EEC	0.7-1.7	temperature-dependent	Contaminants Booklet (1987)
Germany	1.5		TNO (1977)
WHO	1.5		WHO (1984b)

1.2.5. Other

The standards for forage crops are given in table 1.9. (Health Council, 1981).

Table 1.9. Recommended values for forage intake

Age	Per year	2 months	1 month	Feed per day (kg d.m.)
	(mg F/kg dry matter, unwashed material)			
Cattle up to 1 year	30	45	55	3 - 4.5
Over 1 year	35	50	65	4.5-10
Adults	40	60	75	10 -17

The Cosmetics Decree (1980) specifies that a total of 0.15% F is permitted in oral hygiene products, and 0.5% F in topical applications for teeth. Fluorine-containing waste is defined as chemical waste when the fluorine content is more than 5 $g.kg^{-1}$ or when the concentration of fluorine compounds exceeds 20 $g.kg^{-1}$ (Chemical Waste Act, 1984; Concept Decree "Specification of chemical waste products" of 2 May 1989).

2. PRODUCTION, APPLICATIONS, SOURCES AND EMISSIONS

2.1. PRODUCTION, IMPORTS AND EXPORTS, AND APPLICATIONS

In the Netherlands, inorganic fluorides are not produced as a marketable product, although fluosilicic acid (H_2SiF_6) is recovered as a by-product of the manufacture of phosphate-containing fertilizer and as far as possible sold as such. Also, chlorofluorocarbons are made at two locations, producing hydrogen fluoride as an intermediate.
Imports and exports of fluorine and inorganic fluorine compounds, and of fluorine-containing raw materials and fuels are given in tables 2.1. and 2.2., respectively.

Table 2.1. Imports and exports of fluorine and inorganic fluorine compounds in 1985 (tonnes) (CBS, 1985)

Compound	*Imports*		*Exports*	
Fluorine	*4*	*(4)***	*-*	
*Hydrogen fluoride (0.95)**	*x ****		*822*	*(781)*
Ammonium and sodium fluorides (0.49)	*645*	*(310)*	*209*	*(100)*
Aluminium fluoride (0.68)	*5,282*	*(3592)*	*490*	*(333)*
Other fluorides (ca. 0.55)	*297*	*(163)*	*21*	*(12)*
Na_2 and K_2 hexafluorosilicate (0.56)	*123*	*(69)*	*1960*	*(1098)*
K_2 hexafluorozirconate (ca. 0.40)	*19*	*(8)*	*-*	
Na_3 hexafluoroaluminate (0.54)	*1,028*	*(555)*	*122*	*(66)*
Natural cryolite and chiolite (0.54)	*33*	*(18)*	*2*	*(1)*
Fluorspar (CaF_2) (0.49)	*27,200*	*(13,328)*	*220*	*(109)*
Other fluorosilicates, Fluoroborates and other fluorine salts (ca. 0.55)	*1,793*	*(986)*	*1758*	*(967)*
Total (as F)	*>>19,000*		*3,500*	

* *the figure in brackets is the F content (kg F/kg compound)*
** *the figure in brackets is the estimated or calculated amount of F*
*** *x = confidential information (only one or a few importers)*

Table 2.2. Imports and exports of fluorine-containing raw materials and fuels in 1985 (CBS, 1985)

Material	*F (%)*	*Total (1000 tonnes)*		*F (tonnes)*	
		imports	*exports*	*imports*	*exports*
Coal	*0.02*	*6,843*	*1,469*	*1,370*	*290*
Coke	*0.02*	*4,903*	*996*	*980*	*200*
Iron ore	*0.023*	*8,507*	*56*	*1,960*	*13*
Phosphate ore	*3.8*	*2,388*	*57*	*90,740*	*2,170*
Total (approx.)				*95,000*	*2,700*

- Applications

Inorganic fluorine compounds are used in the Netherlands chiefly for the manufacture of aluminium and as a flux in the steel and glass-fibre industries. In 1985, the primary aluminium industry consumed over 5000 tonnes of AlF_3 and more than 2000 tonnes of cryolite. Of the fluorspar, over 12,000 tonnes were used in the secondary aluminium industry, and further in the glass-fibre and base-metal industries.

2.2. SOURCES AND EMISSIONS

2.2.1. Processing of phosphate ores

Phosphate ore is processed in the Netherlands for the manufacture of polyphosphates, phosphoric acid and superphosphate, among other products. Polyphosphates are used for the production of detergents. Phosphoric acid is used in the production of commercial fertilizer and phosphate animal feed. The composition of phosphate ore varies from one deposit to another, and is approximately as follows: 33% P_2O_5, 51% Ca, 3-4.5% F (average 3.8%) in the form of calcium fluoride (CaF_2), and 12% other elements.
Polyphosphates are produced from phosphate ores by an electrolytic process followed by a wet-chemical process. In 1985, 80,000 tonnes of phosphate ore were used to manufacture polyphosphates.

Warehouse of phosphate ore (Kemira Pernis BV, RIVM photograph)

Filter system (about 200 m^2) for the processing of phosphate ore intended for the manufacture of phosphoric acid (Kemira Pernis BV, RIVM photograph)

The sources of F emissions to the atmosphere are the electrolysis furnace, where pure phosphorus is produced, the removal of phosphorus slag, and the burning of the phosphorus to make - very pure - phosphoric acid. Gaseous and particulate fluoride compounds are separated from the exhaust gases by means of cloth filters, electrostatic precipitators and scrubbers. The wash water from the scrubbers is recycled. The surplus is partly taken up in other waste streams. Insofar that the wash water consists of sea water, the surplus is discharged, resulting in a discharge into salt water of about 200 tonnes F per year. The residual F emission into the air is not fully known. It is assumed to be 30 tonnes, but recent experimental measurements indicated that especially during slag removal, not yet included in this figure, the F emissions may be considerable. The remaining fluoride, over 29 ktonnes, ends up almost exclusively in the phosphorus slag, about 550 tonnes of which were produced in 1985 (700 in 1987).

The slag is used in the building of roads and hydraulic structures, about 80% of the latter category in salt water. The release of F from phosphorus slag into salt water has been assessed at 4000 mg per tonne per 24 hours during the first few years and at 50 mg per tonne thereafter (Dijkzeul, 1979). Assuming that the average rate of release is 50 mg F per 24 hours, it can be estimated that nearly 80 tonnes of F per year are released from the more than 4.7 million tonnes of phosphorus slag used up to 1985 inclusive. The release from roads into the soil is believed to be less.

The phosphoric acid used for the manufacture of fertilizer is made by a wet-chemical process. The extraction with sulphuric acid, in particular, produces a F-containing waste-gas stream, which is treated in scrubbers, leading to discharge of F (into brackish water near the sea). Additionally, large amounts of phosphorus gypsum are produced, also containing F and currently discharged.

The phosphoric acid produced also still contains some F. The fluoride entering the waste water during the manufacture of fertilizer is partly derived from this, and partly from phosphate ore used directly in the production process. The fertilizer produced in the Netherlands contains about 6850 tonnes F, of which 5050 tonnes are exported and 1800 tonnes end up on the Dutch soil as a result of fertilizer application. Because of the production methods used, normal and triple superphosphate contain different amounts of F (HML, 1986). HML (1986) reported that the former contains on average 75 kg F per tonne of P_2O_5 and the latter 110. It is assumed, however, that the F content is considerably lower, on average 18-22 kg per

tonne of P_2O_5. In the Netherlands, much more triple superphosphate is used than normal superphosphate.

In the manufacture of feed phosphates, the acid also undergoes a defluorination step. Consequently, feed phosphates have low F concentrations, so that the maximum concentration permitted in phosphate animal feed is not exceeded. The total amount of F present in phosphate animal feed is estimated at 20 tonnes per year, which ends up for the most part in manure.

Table 2.3. summarizes the atmospheric F emissions into the air from factories manufacturing polyphosphate, phosphoric acid and inorganic fertilizer. As far as is known, it mostly concerns emitted gaseous F. A large part of this consists of residual emissions after passage through gas scrubbers.

Table 2.3. Emissions into the atmosphere as a result of the processing of phosphate ores

Production category	*Emission (tonnes F/year)*	*Number of companies*
*Polyphosphates **	*60*	*1*
*Phosphoric acid ***	*20*	*3*
*Other fertilizer ****	*10*	*5*
Total	*90*	*9*

* *fairly large uncertainty, the emissions resulting from slag removal in particular are not known; reference year 1986 (licensing authority)*
** *reference year 1986 (Berenschot/Tebodin, 1987, and licensing authority)*
*** *reference year 1982 (Emissions Registration), and reference year 1986 (licensing authority)*

As mentioned already, all the above factories also discharge into water (table 2.4.), but the form in which the fluoride is discharged is not fully known. A large proportion is probably present as free ion in water from scrubbers. Both Ca and phosphate can be expected in gypsum, and consequently a large part of the F should be present as calcium fluorapatite.

As far as is possible, the fluorine balance sheet of the phosphate ore-processing industry in the Netherlands is shown in figure 2.1., which also shows the emissions which may occur during the storage and transshipment of fluorine-containing bulk products.

Table 2.4. Emissions into water as a result of the processing of phosphate ores

Production category	Emission (tonnes F/year)	Number of companies
Phosphoric acid, in gypsum *	34,500	
idem , in waste water *	3,500	3
Polyphosphates **	200	1
Other fertilizer **	3,050	5
Total	41,250	9

* reference year 1986 (Berenschot/Tebodin, 1987)
** reference period 1979-1982 (Emissions Registration)

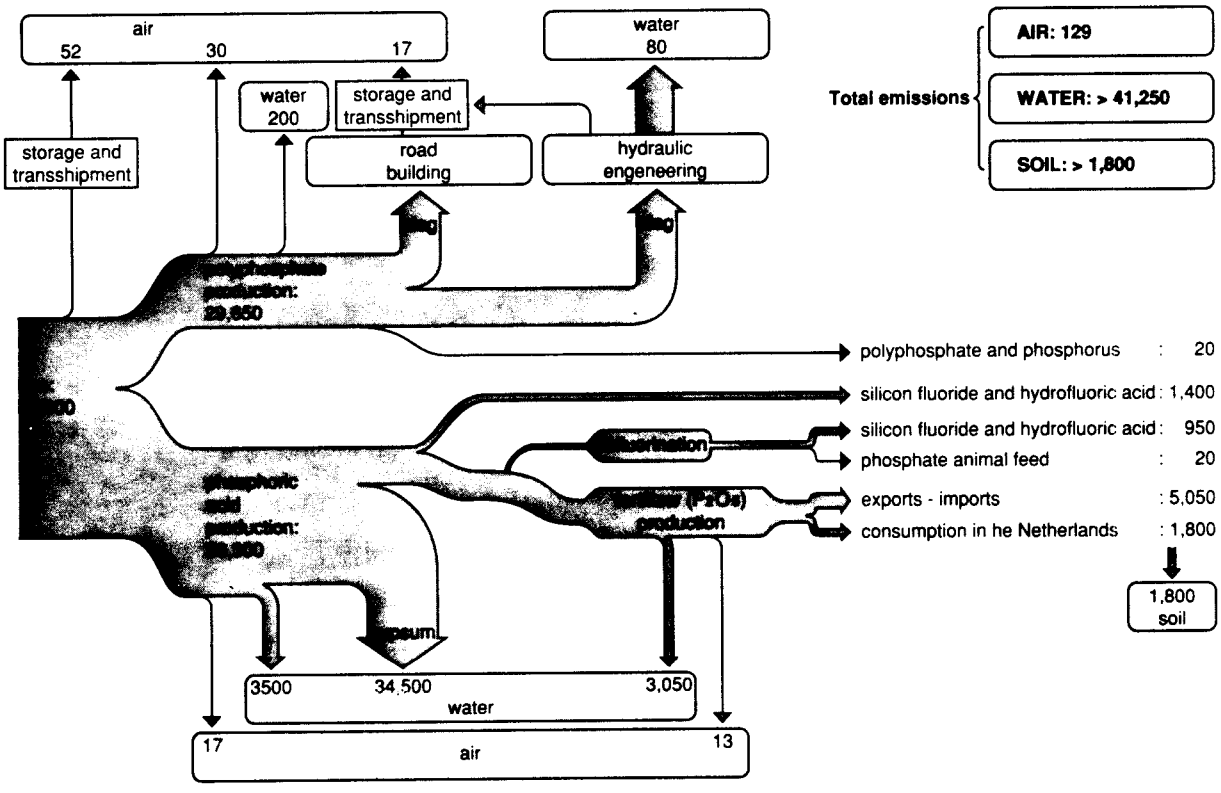


Figure 2.1. Fluorine balance sheet of the phosphate ore-processing industry in the Netherlands (1985), expressed in tonnes of F

Dust is dispersed during the unloading of seagoing vessels, the handling of the ore in the storeyard, and the loading of river barges, involving substantial emissions of fluoride. The phosphate ore is not damped down, because a high moisture content (>1%) adversely affects further processing of the phosphate ore. Emissions of fluoride during storage and transshipment of phosphate ores occur at three companies, one of them accounting for about 80% of the total. In addition, emissions occur at one firm as a result of the storage and transshipment of phosphorus slags. The emissions have been estimated on the basis of emission factors, but the uncertainty in these factors is great. Total emission into the air is around 60 tonnes of F per year, including 53 tonnes of F per year from the storage and transshipment of phosphate ore (reference year 1982; Rijnmond, 1984) and 7 tonnes of F per year from the storage and transshipment of phosphorus slags (reference year 1979; Emissions Registration) in the form of particulates.

2.2.2. Processing of minerals (ceramics, glass and glass fibre)

Fluoride compounds are emitted into the air when clay is heated. Considering the amount of clay that is processed, the principal source is the coarse ceramics industry, but emissions also occur in the fine ceramics and glass(-processing) industries.

- Coarse ceramics industry

The information on this industrial sector is for the most part derived from the survey by Haskoning (1987). A breakdown by region is given in table 2.5.

The manufacture of coarse ceramic products is, broadly speaking, as follows: the clay is dug out, usually in the immediate vicinity (within 20 km) of the factory; the digging and storage of the clay should yield a homogeneous mixture. After storage, pretreatment and forming, the product is dried in order to lower the moisture content from an average of 32% to 2-5%. Next, the product is baked (also called burning, sintering or firing). The chemical and physical changes taking place during this heat treatment are such that the end product has the desired properties.

Table 2.5. Regional distribution of the ceramics industry (ERL, 1979-1983 and Haskoning, 1987)

Province	Estimated emission (tonnes F per year)	
	coarse ceramics	fine ceramics
Groningen	36	-
Friesland	3	-
Drente	-	< 1
Overijssel	7	-
Gelderland	320	8
Utrecht	49	< 1
Noord-Holland	-	< 1
Zuid-Holland	15	< 1
Zeeland	< 1	< 1
Noord-Brabant	50	3
Limburg	120	19
Total	600	35

The chemical conversions give rise to the formation of fluorides, which end up in the flue gases. The fluorine in clay is chiefly in the form of fluorspar (CaF_2), but aluminium fluoride (AlF_3), sodium fluoride (NaF), cryolite ($3NaF.AlF_3$) and fluorapatite ($CaF_2.3Ca_3(PO_4)_2$) are also present. The F concentrations in clay vary widely between the clay-producing areas, and large differences are also found within each location. In the Netherlands, the level ranges from 330 to 660 $mg.kg^{-1}$ with an average of around 500 $mg.kg^{-1}$. The concentration in the fired product averages 272 $mg.kg^{-1}$ dry matter (35-400 $mg.kg^{-1}$ dry matter). Ten to 90 per cent disappears during the firing process. It is not known what causes this wide variation in the volatilization of fluoride during firing. A number of factors (lime content of the clay, heating-up time, maximum temperature) are known to play a role in this variation, but how they act and to what extent is not clear. Part of the volatilized fluoride is not emitted but adsorbed onto furnace walls, is present in dust adhering to the product, wagons, etc., and is estimated at 25 mg F per kg dry matter. The emission factor calculated from the above data is, on average, 206 mg F per kg dry matter.

However, an emission factor can also be calculated on the basis of measurements in flue gases, resulting in an average of 192 mg F per kg product, with a minimum of 65 and a maximum of 385 mg F per kg dry matter. The proportion of gaseous fluorides of the total emission varied between 44% and 91%; the proportion of solid fluorides averaged 22 % (with a

scatter of about 16%). Of the total content of particulates, fluorine compounds constitute an average of 58%, consisting of calcium fluoride, potassium fluoroaluminate ($KAlF_4$, K_3AlF_6) and compounds present in the raw material. The emission factor chosen is 200 mg F per kg product, which is approximately the average of the measured and calculated emission factors. This means that, on the basis of production data of 1984, total F emissions by the coarse ceramics industry can be calculated at 600 tonnes per year, emitted by some 80 plants, with individual emissions varying from about 0.01 to more than 18 tonnes per year. It is believed that the number of companies has further decreased since then, but that production has remained roughly the same.
In the late 1970s, the brick works switched from the old tall chimney-stacks (essential for inducing a natural draught) to low chimneys following the introduction of flue-gas ventilators. Since the F emissions caused damage, it was nevertheless necessary to emit the flue gases at greater heights, some tens of metres, although not all plants have implemented this. A survey of factories in the province of Gelderland indicated that about half the plants emit at a height of 30 m or lower, and the other half higher, usually at 50 to 60 m, but a clear relationship with the emissions was not found. The heat content of the outgoing air also affects the dispersion, and is assumed to lie between 0.1 and 1 MW, based on twenty practical data.

- Fine ceramics industry

There are about 30 fine-ceramics enterprises, about one-third located in Limburg, one-third in Zuid-Holland and the remaining third in the rest of the Netherlands. The emissions are produced in a similar manner to those in the coarse ceramics industry. The clay used for the manufacture of fine ceramics is imported, and contains an average of 250 mg $F.kg^{-1}$ dry matter. Lime is added to the clay, which reduces the F emissions. This industrial sector emits 30-40 tonnes of F annually, two-thirds of which is in Limburg (see also table 2.5.).

- Glass and glass-fibre industry

Within the glass industry, fluoride is emitted in the manufacture of glass, glass fibre, glass wool and rock wool. In all, eight companies are concerned.

The principal emissions occur as a result of the use of the F-containing additive alumite (blast-furnace slag, about 7.5 tonnes of F), the reuse of F-containing cullet from the East bloc, and fluorspar (CaF_2), which is used to speed up the melting process, particularly in the manufacture of glass fibre. About 60% of the fluorspar is retained in the glass and the rest is emitted into the air (about 32%) and water (around 8%). The emission from the major glass-fibre producer is, as a point source, clearly the largest within this industrial sector. Although recent limitation of the use of fluorspar has resulted in a lowering of the emission factor, this was offset by an increase in production so that F emissions in 1987 were similar to those in 1985.
Table 2.6. summarizes the emissions into the atmosphere from the heating of minerals.

Table 2.6. Emissions into the atmosphere from the heating of minerals

Production category	*Emission (tonnes F/year)*
*Coarse ceramics industry**	*600*
*Fine ceramics industry***	*30*
Glass, glass-fibre, glass- and rock-wool industry	*102*
Total	*732*

** based on production data of 1984 and an emission factor*
*** data from Emissions Registration (1979-1983)*

2.2.3. Metal industry

- Manufacture of aluminium

In connection with the manufacture of aluminium, there are three sources of F emissions:

- primary aluminium production
  production of carbon anodes for the aluminium industry
- secondary aluminium smelters

The first two processes are closely related, and are both carried out by one of the two aluminium manufacturers. Figure 2.2. shows schematically at which steps in the processes the emissions arise and how the companies concerned control them at present. The orders of magnitude of the F flows

related to Al manufacture are also included in this figure, both estimated for the Dutch situation and as reported in the literature.

F is released into the atmosphere during exhausting of the electrolysis furnaces, exhausting of the rooms, and from diffuse sources. At present, the exhaust gases of the electrolysis furnaces are cleansed of gaseous fluoride by injection of alumina. Next, cloth filters remove particulates with a high efficiency. Captured alumina is used in the process. The ventilation air of the rooms is cleaned in gas scrubbers. Since the efficiencies of these scrubbers, especially for particulates, are much lower than those of the cloth filters (with adsorption onto alumina), the so-called encasement efficiency (the fraction exhausted into the dry filters) is a major factor in determining overall efficiency.

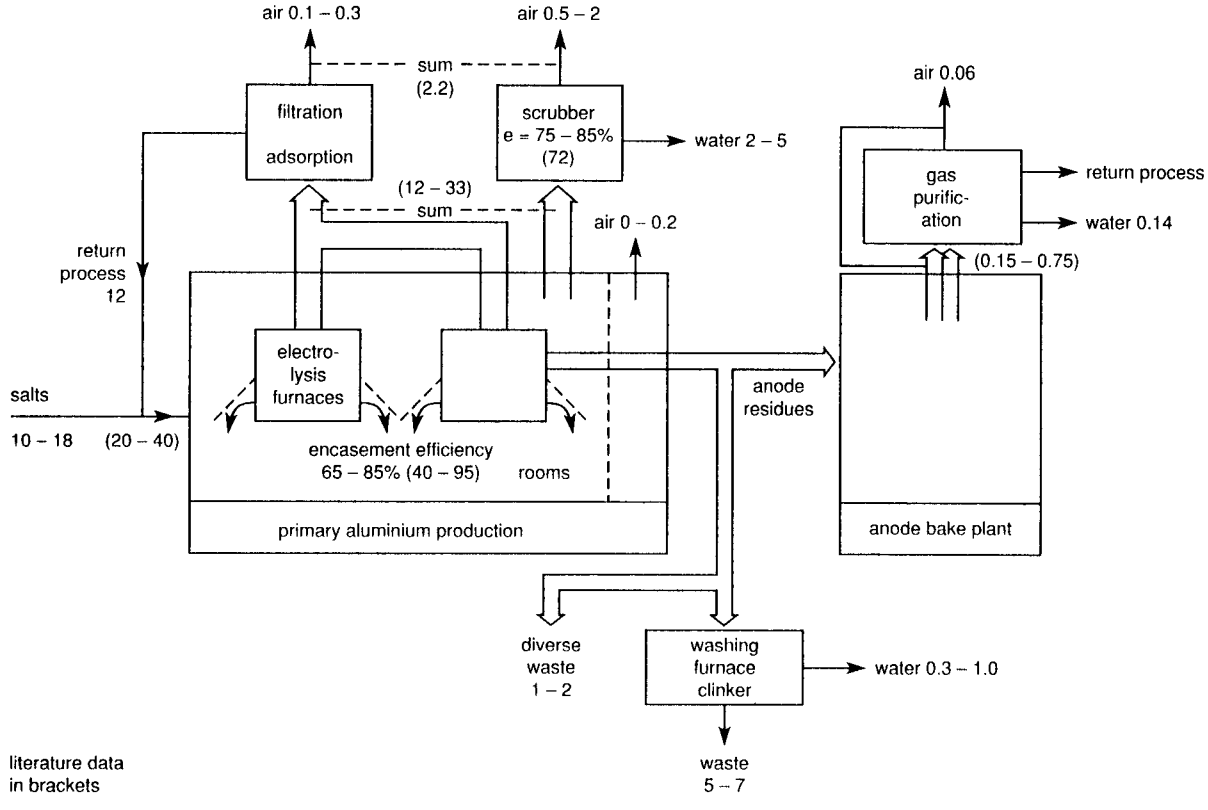


Figure 2.2. Diagrammatic representation of the flows and their fluoride contents (in kg F per tonne of Al), in primary aluminium production

Diffuse sources occur, for example, during the storage and transshipment of fluorine-containing raw materials, the spillage of fluorine-containing products in the electrolysis room, and during slag processing. Total emissions into the air are given in table 2.7. (Bijl, 1986; Bootsma, 1988; Aluminium producers, 1988).

Table 2.7. Emissions into the air as a result of aluminium manufacture

Source	*Emission (tonnes F/year)*		
	gaseous	*solid*	*total*
Electrolysis furnaces	*22*	*11*	*33*
Ventilation air of rooms	*37*	*184*	*221*
Diffuse	*2*	*27*	*29*
Anode bake plants	*14*	-	*14*
Total	*75*	*222*	*297*

The differences in the final emissions from the Dutch plants are determined by differences in F losses from the furnaces, differences in the encasement efficiency and, to a somewhat lesser degree, in the efficiency of gas purification. The wash water from the scrubbers is a source of emissions into water, and is estimated at 780 tonnes of F. In addition, the wash water from the furnace slag also contains fluoride, approximately 140 tonnes of F.

Gaseous fluoride (HF) is released during the baking of anodes. The total emission into the air is estimated to have been 14 tonnes F in 1983 (Bijl, 1986).

Apart from Al manufacture from alumina, Al-containing scrap is processed in secondary Al production. The scrap is smelted in furnaces, using a F-containing flux to remove unwanted substances (e.g. magnesium). The flux contains 2% F. An estimated 100-200 kg F in flux are utilized per tonne of aluminium produced.

It has been estimated that some 40,000 tonnes of reclaimed scrap were processed in the Netherlands in 1985, for the most part by one company. In addition, the primary and secondary aluminium industry also processes revert scrap (around 70,000 tonnes). The licensing authority estimated the total emission into the air by the secondary smelters to have been 1.5 tonnes of F in 1985. At two plants it concerns residual emissions after

application of lime injection and cloth filters as emission-control techniques. The filter dust is disposed of as chemical waste.
A new scrap processor became operational in 1987. It employs a production method in which a flux is not used, so that F emissions do not occur.
Table 2.8. summarizes the emissions from the aluminium industry.

Table 2.8. Emissions into air and water from the aluminium industry

Production category	*Emissions (tonnes/year)*		*Number*
	air	*water*	
Aluminium manufacture	*297*	*920*	*2 ****
Production of carbon anodes	*14 **	*-*	*2*
Secondary Al manufacture	*1.5 ***	*-*	*3*

* *reference year 1983*
** *reference year 1985*
*** *1 company also produces carbon anodes and thus has been counted twice*

- Manufacture of iron and steel

Fluorides are released in the manufacture of iron and steel, because iron ore and recycled iron-containing processing waste contain fluorine. In the sintering process, the iron ore and iron-containing processing waste are heated to a high temperature in a blast furnace with coke and limestone. This results in decomposition of the fluorine compounds, so that (besides emissions into water) fluorine is emitted into the air (mostly in the form of HF). In addition to being sintered, the ore mixture is also pelletized. The emissions from this process are controlled with a gas scrubber, with consequent emissions into water. Sodium fluoride is used as an additive in the manufacture of steel, and is partly emitted into the air during the casting process. Total fluoride emissions are given in table 2.9.

Table 2.9. Emissions into air and water by the aluminium industry

Source	*Emission (tonnes F/year)*			
	*air**			*water****
	Gaseous	*Solid*	*Total*	
Sintering plant	*40*	*-*	*40*	*160*
Pelletizing plant	*1*	*4*	*5*	*302*
Oxy-steel plants	*-*	*20*	*20***	*-*
Total	*41*	*24*	*65*	*462*

* *reference year 1985 (licensing authority)*
** *fairly large uncertainty, because the data are not recent (licensing authority)*
*** *reference year 1982 (Emissions Registration)*

- Other metal industry

Foundries also emit fluorine, which is estimated to be several tonnes a year. Fluorine compounds are used and discharged by many metal-processing plants, for example, during surface treatment, but the magnitude of the emissions is not known. The total emission from unspecified companies and industrial sectors has been estimated on the basis of the Emissions Registration as 430 tonnes of F per year (ER 1979-1983).

2.2.4. Other chemical industry

A relatively large emission occurs at one plant during the production of pigment. About 500 tonnes of F were emitted into the air in 1981 (Emissions Registration). A flue-gas scrubber was installed in 1982, so that F emissions fell to about 60 tonnes in 1983 and, after optimization of the scrubber, to 6 tonnes in 1985.
According to the licensing authority, the plants producing hydrogen fluoride and chlorofluorocarbons emitted about 6 tonnes of F in 1985. Part of this is residual emissions after passage through a scrubber.

2.2.5. Energy generation

In the Netherlands, the burning of coal is the major source of the emissions from the combustion of fossil fuels. The F content of coal can be determined in various ways. The percentage entering the gas phase during coal combustion is related to the measurement technique used.
As part of the National Coal Research Programmme (NOK), research has been conducted into the emissions from the combustion of coal (PEO, 1986a,b). On the basis of measurements and literature data, it is assumed that the concentration of fluorine and the percentage in the gas phase vary as shown in table 2.10.

Table 2.10. Emissions of F from the combustion of coal

Conc. in coal (mg F/kg)	*In gas phase (%)*	*Emission (mg F/kg coal)*	*Concentration in flue gas (mg F/m^3)**
190	*20*	*38*	*3.8*
250	*25*	*63*	*6.3*
320	*35*	*110*	*11*
*80 ***	*90*	*72*	*7*

* *standard conditions (0°C; 101.3 kPa, dry)*
** *average, after digestion in an aqueous medium (Mey et al., 1985)*

At present, the bulk of the coal is burned in power stations, and a small fraction in industrial installations (table 2.11.).

Table 2.11. Coal consumption in the Netherlands (ktonnes per year) (DHV, 1986; Jeuring, 1987)

Source	*1984*	*1985*	*1987*
Power stations	*5,032*	*4,900*	
Industrial installations	*335*	*774*	
Total	*5,367*	*5,674*	*5,822*

The reader is referred to chapter 6 for an estimate of the future consumption of coal. At present, there are 3 coal-fired power stations: in Geertruidenberg (with a generating capacity of 1131 MWe today, 1284 MWe in 1995), Nijmegen (855 MWe today, 609 MWe in 1995), and Buggenum (526 MWe today, 222 MWe in 1995). Two more coal-burning plants came on stream in mid-1988, namely, in Rotterdam (1034 MWe) and Borssele (408 MWe). The (average) F emissions are estimated on the basis of an emission factor of 72 mg per kg of coal (table 2.12.). This corresponds with 2.7 $g.GJ^{-1}$ (gaseous).

Table 2.12. Fluoride emissions (in tonnes of F per year) from coal-fired power stations and industrial installations

Year	*Power stations**	*Industrial units***	*Total*
1984	*360*	*25*	*385*
1985	*350*	*55*	*405*
1987	*420*		

** These estimates do not take into account flue-gas desulphurization*
*** There are 3 large and about 40 small installations in the Netherlands*

2.2.6. Diffuse emissions

Fluorides can be emitted as a result of using fluorine-containing products in:

- Fertilizer and feed phosphates; see 2.2.1.
- Glass treatment

  Solutions of hydrogen fluoride or ammonium fluoride are used in the etching of glass, whereby fluorides may be released. It probably concerns application in special cases only and the total emission is not large. Emission data are not published.

- Welding

The electrodes used in welding contain fluorides. F may be emitted with the waste gases produced during welding operations. The fluoride concentration in the waste gases depends, among other things, on the welding technique used. A few measurement data are available (Donaldson-Torit BV) and are summarized in table 2.13. The total emission can only be estimated when electrode consumption figures in the Netherlands are known. However, pertinent information has not been found. A very rough estimate of the emission from welding operations can be made using an emission factor of 10 mg F per capita per day (Handbook of Emission Factors, 1983), giving a total emission in the Netherlands of about 50 tonnes of F per year.

Table 2.13. Emissions as a result of welding operations

Source	*Concentration in waste gas from welding (mg F/m^3)*	
	average	*(range)*
Autogenous welding	*0.01*	
Arc welding		
- manual arc welding	*1.5*	*(0.01-3)*
- gas-shielded arc welding	*0.01*	
Plasma welding	*2.5*	*(0.02-5)*

- Dental uses

F may be emitted into surface waters via direct discharges of sewage and via sewage treatment plants, as a result of the use of fluorides in toothpaste, in fluoride tablets and in fluorine applications for teeth. In the Netherlands, fluoride consumption via tooth paste was less than 0.5 kg in 1986, that via tablets about 45 kg in 1985. The amount used in gels and solutions is estimated to be about the same as that in toothpaste. The emission is estimated to be of the order of 50 kg per year.

2.2.7. Waste processing

Fluorides may be present in dredged materials, sewage sludge, and household and industrial wastes. The principal industrial waste products have already been discussed in the preceding subsections.

The F content of dredged spoil is not known. It has already been mentioned

in 2.2.1. that the gypsum produced in the manufacture of phosphoric acid contains a considerable amount of F. This is probably discharged in the form of an insoluble compound, which makes it likely that it is also present in dredged materials.

The F concentration in sewage sludge is not measured in the Netherlands. According to English literature ((Water Research Centre, 1980), the average concentration is 250 mg $F.kg^{-1}$ dry matter, with a large range. Translation of this datum to the Dutch situation is too uncertain, so the F load in sewage sludge is not further quantified.

The F content of household refuse and similar industrial waste is not known, but the part that may be released can be estimated. Incineration of this waste results in an emission of 15-20 g F per tonne of waste (RIVM, 1987). A total of 6,500 ktonnes of domestic and industrial wastes were produced in 1985, about 2,500 ktonnes of which were incinerated. According to this division, about 50 tonnes of F were emitted into the atmosphere and 80 tonnes of F ended up on the waste dumps in 1985.

2.3. SOURCES IN AND IMPORTATION FROM FOREIGN COUNTRIES

2.3.1. Foreign emissions into the air

Emission data on emissions in other countries are not available, and have been estimated from production figures (Eurostat, 1985 and 1986; Industrial Statistics Yearbook, 1983; FAO, 1985; IEA Coal Information, 1986) and emission factors (Handbook of Emission Factors, 1983). In view of the variation in the emission factors, however, the uncertainty in these estimates is great. Sources of fluoride emissions (table 2.14.) are:

- the crushing and milling of phosphate ores and the processing of the products
- the heating of fluorine-containing minerals (clay)
- metal industry
- energy generation: combustion of coal
- the use of fluorine-containing products and waste processing.

Table 2.14. Foreign emissions into the atmosphere (period 1983-1986)

Emission source	*Emission factor (kg F/1000 tonnes)*		*Emission (tonnes F per year)*		
	range	*representative*	*Belgium*	*West Germany*	*Britain*
Aluminium manufacture	*700-3000*	*2000*	*580*	*2,280*	*740*
Coarse ceramics ind.	*-*	*200**	*260*	*462***	*4,160*
Crude steel manufacture	*200- 400*	*200*	*2,400*	*8,100*	*3,140*
Fertilizer production	*70- 400*	*200*	*100*	*100*	*70*
Coal combustion	*-*	*63**	*920*	*7,520*	*5,480*
Waste incineration	*-*	*20**	*?*	*160*	*680*
Total (approximate)			*4,000*	*23,000*	*14,000*

** Based on information given in subsection 2.2.1.*
*** The influence of flue-gas scrubbing is not known and has not therefore been taken into account. The actual emission will thus be less than 462 tonnes of F per year.*

2.3.2. Transboundary loads

The importation into and exportation from the Netherlands of fluorine compounds via the air can only be estimated on the basis of model calculations (chapter 3). Imports are estimated to be 5500 tonnes annually, and exports around 5000 tonnes a year.
The Rhine and the Meuse are the principal conveyances of imports via water. The Westerscheldt is considered to have only a small influence on the quality of fresh surface waters in the Netherlands. The available data are summarized in table 2.15.

Table 2.15. Imports via surface water in 1985 (Dept. of Public Works, 1985)

River	*Imports (tonnes F/year)*
Rhine	*13,250*
Meuse	*4,020*
Total	*ca. 17,300*

Exports via surface water take place via the Noordzeekanaal, IJsselmeer, Nieuwe Waterweg, Haringvliet and the Ghent-Terneuzen Canal. However, the fluoride exports as a result of importation via the large rivers, and the F emissions into surface waters cannot be accurately determined. The reason is that, because of the longitudinal dispersion caused by the tide, mixing of seawater and river water takes place over long distances. The

concentration in seawater is about 1.3 $mg.l^{-1}$, and that in the Rhine at Lobith around 0.2 $mg.l^{-1}$ (see chapter 4). Furthermore, close to the mouth of the Nieuwe Waterweg, in the area of tidal movement, the manufacture of phosphoric acid is a large source of F emission. However, this emission is not reflected in a rise in concentration at measurement locations downstream of the source. It is assumed, partly on the basis of visual observations, that a large portion of the fluoride emission settles very rapidly (see chapter 3).
In addition, fluorine-containing waste products are partly exported (see also 2.2.7.). The estimated amounts are given in table 2.16.

Table 2.16. Estimated exports of solid fluorine-containing waste products

Industry	*Product*		*F*	*Exports*
	Type	*Quantity (tonnes)*	*(%)*	*(tonnes)*
Phosphate ore processing	*phosphorus slag*	*100,000*	*5*	*5000*
Aluminium	*furnace slag*	*3000-4000*	*10-20*	*325-650*
	waste material	*500-1500*	*15*	*75-225*

2.4. SUMMARY AND CONCLUSIONS

Table 2.17. summarizes all the emission data on fluorides in the Netherlands, but any flows with unknown quantities (dredged spoil, sewage sludge) are not included.

Table 2.17. Summary of fluoride emissions (tonnes per year) into the various environmental compartments in the Netherlands (1985)

Emission cause/source	*Soil*	*Water*	*Air*	*Waste*
Phosphate ores				
- industrial		*41,250*	*120*	*17,400*
- application of phosphorus slag		*ca. 80*		
- fertilizer use	*1,800*			
- use of phosphate animal feed	*20*			
Mineral processing				
- coarse ceramics industry			*600*	
- fine ceramics industry			*35*	
- glass industry (total)		*16*	*86*	
Metal industry				
- primary aluminium manufacture		*920*	*298*	*2,000*
- secondary aluminium manufacture			*1*	*6,000*
- base metals iron and steel		*462*	*65*	*?*
Other industry		*430*	*10*	*?*
Energy generation (coal)			*405*	*1,600*
Welding			*50*	
Dental uses		*0.05*		
Domestic waste processing	*1*	*1*	*50*	*78*

Figure 2.3. gives an idea of the geographical distribution of the emissions into the atmosphere in the Netherlands. Most emissions into the air occur at a height of several tens of metres. Only a small fraction of the industrial emissions of fluorides is discharged from chimneys more than 60 m high. For coal-fired power stations (indicated in figure 2.2.) and waste incinerators, the situation is different. In all, over 1700 tonnes of F are emitted into the atmosphere. Much more enters the water, although it should be noted that this gives rise to fewer problems than the air emissions. Almost the entire load is discharged into brackish or salt water, or reaches this through leaching.

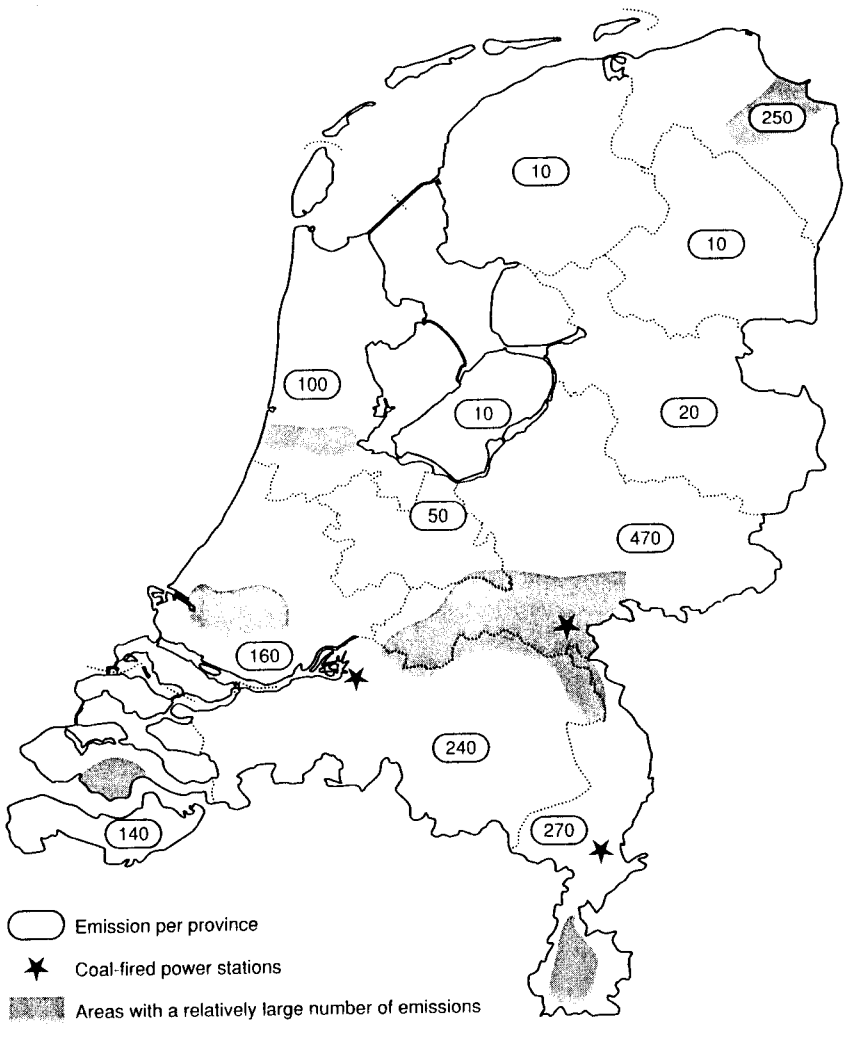


Figure 2.3. Chart showing the geographical distribution of the Dutch F emissions into the atmosphere, for 1985 (F in tonnes)

3. FORMS OF OCCURRENCE, CONVERSION AND DISPERSION

3.1. BEHAVIOUR IN THE SOIL

3.1.1. Forms of occurrence

Fluorine occurs in the soil largely in the bound form. At a pH below 6, most of the dissolved fluorine is in complexes. The main complexes are AlF complexes (AlF_2^+, AlF_3^0 and AlF_4^-) and FeF complexes (FeF_2^+ and FeF_3^0) (Elrashidi and Lindsay, 1986, a and b). At a pH above 6, the fluoride ion is the dominant species. A direct consequence of the strong complexation properties of fluoride is, among other things, that with increasing F concentration in soil water or groundwater, the Al and Fe concentrations also increase (Peek and Volk, 1986). In addition, a positive correlation was found between the concentration of fluoride and that of organic carbon in the soil solution, which may indicate that fluoride also forms complexes with carbon.

3.1.2. Retention

The binding of fluorides to soil material can take place by one of several mechanisms:

- Adsorption (anion exchange)

Barrow and Ellis (1986) found maximum adsorption of fluoride at pH 5.5; at a pH below 5.5, adsorption is lower due to the formation of AlF complexes, and at a pH above 5.5 it is lower because of a lower electrostatic potential of the charged clay surfaces. Omueti and Jones (1977) studied the adsorbing capacity of various soil types and found a strong correlation with the concentration of amorphous aluminium oxides in the soil, and a correlation with the pH and the clay (diameter <2 μm) content (see also figure 3.1.). The adsorbing capacity was not correlated with the organic matter content of the soils.

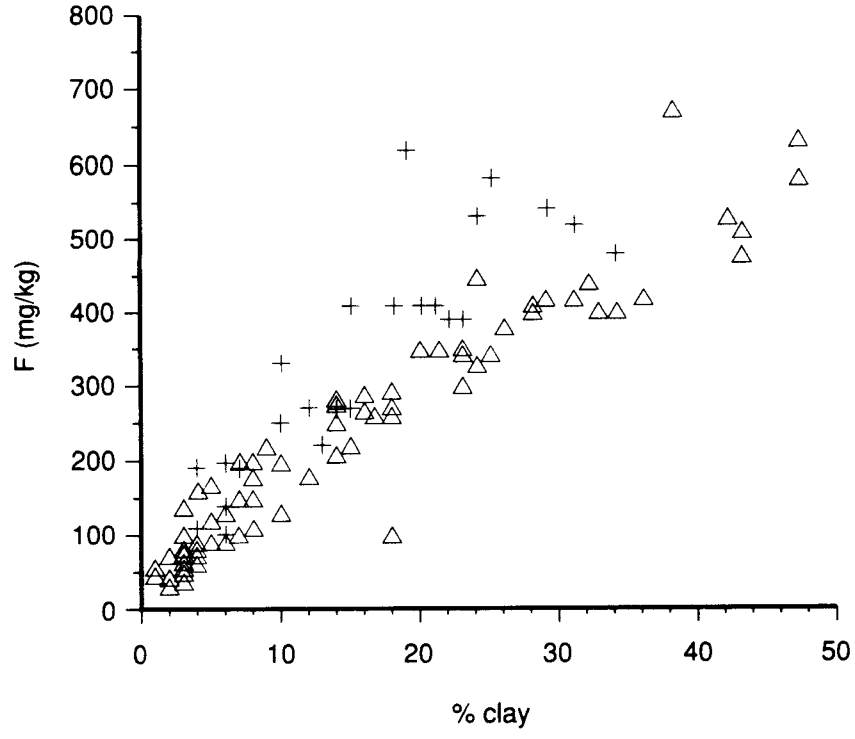


Figure 3.1. Relationship beteen the concentrations of total fluoride (mg/kg) and % clay (diameter <2 μm) in soil (Roorda van Eysinga, 1974): [F] = 48 + 12.3 % clay

At higher concentrations, the F ion also changes place with OH ions on the surface of the clay minerals (Huang and Jackson, 1965). This type of adsorption was most pronounced at pH 3 and 4, and decreased strongly at pH values above 6.5 (Slavek et al., 1984). Here, the F ion changes place with the OH ions in amorphous materials such as Al oxides (Perrott et al., 1976). The adsorption of fluorine in soil can be described by a Freundlich isotherm, up to a concentration of 20 mg $F.l^{-1}$ in acidic soils (Chabra et al., 1980; Omueti and Jones, 1977), and up to 10 mg $F.l^{-1}$ in alkaline soils (Bower and Hatcher, 1967). At higher concentrations, description of the behaviour of fluorine in soil is no longer possible because of precipitation.

Precipitation

Fluorspar (CaF_2) precipitates in the presence of excess Ca^{2+} ions. The solubility product is $3.4x10^{-11}$ at 18°C (Roorda van Eysinga, 1974). This reaction is pH-dependent. Tracy et al. (1984) irrigated a loamy soil with fluoride-containing water (7 $mg.l^{-1}$) and noted precipitation of fluorspar after saturation of the adsorption complex. As a result of this precipitation, the concentrations of labile F in calcareous soils are low (see figure 3.2.).

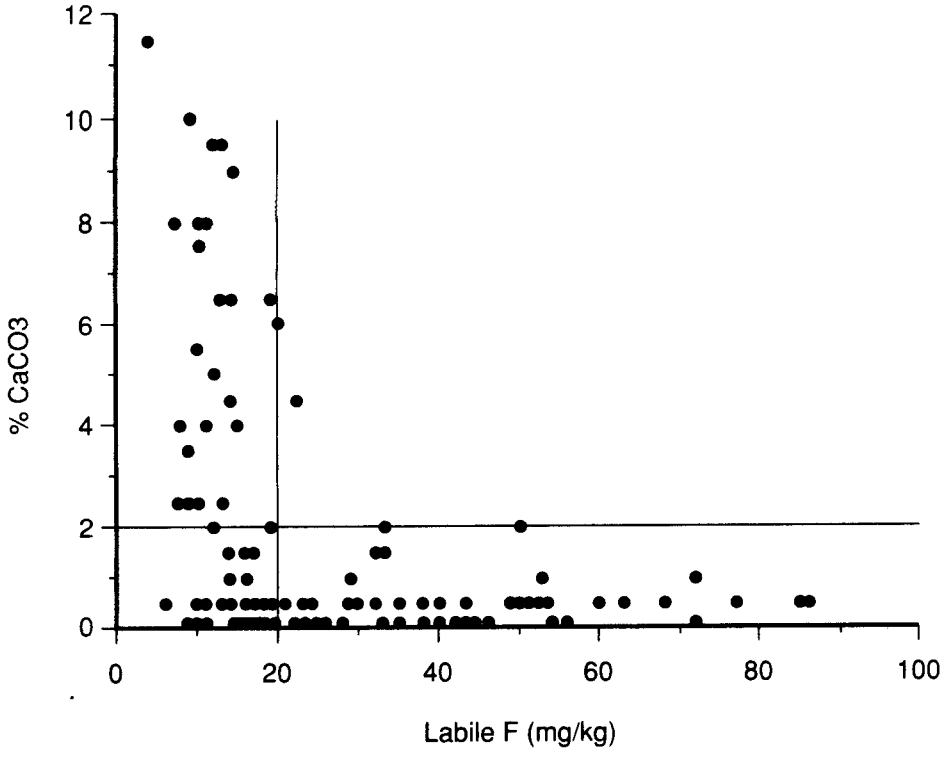


Figure 3.2. Relationship between the concentrations of labile F (mg/kg) and % calcium carbonate in soil (Roorda van Eysinga, 1974)

3.1.3. Leaching

Behaviour studies are relatively scarce. MacIntire et al. (1955) performed a few lysimeter experiments and noted that fluoride is extremely immobile within the soil. Although this immobility is a result of adsorption and precipitation, little leaching was also observed from low-clay dune soil; 5% leaching at F concentrations of up to 80 $mg.dm^{-3}$ (Murray, 1983). Fluoride was taken up primarily in the B-horizon. Polomski et al. (1982) reported that leaching of aluminium, iron and organic material occurred simultaneously with leaching of fluoride.

3.1.4. Accumulation

No research has been conducted in the Netherlands into accumulation of fluoride in topsoil. A number of studies are known from the literature. Polomski et al. (1982) measured F concentrations of 2000 to 3000 $mg.kg^{-1}$ in the topsoil at a distance of 0.5 to 1.0 km from an aluminium smelter, a relatively large fraction of which was water-soluble. This indicates that a considerable portion of the accumulated fluoride was present as CaF_2. The

experiments by Tracy et al. (1984; see 3.1.2.) showed CaF_2 formation after the adsorbing capacity was exceeded. It can be calculated from the solubility product of CaF_2 that precipitation does not occur below a concentration of 5 to 10 mg $F.l^{-1}$, and that in these cases fluoride is retained in the soil chiefly by adsorption to clay minerals or to Al and Fe oxides. At these F concentrations, the concentration in the topsoil will not increase further when the F concentrations in solution and in the soil are in equilibrium. Enhanced leaching of fluoride may then present a problem in the long run.

3.2. BEHAVIOUR IN WATER

3.2.1. Seawater

Fluoride is one of the macrocomponents of seawater, and has a residence time of 1,000,000 years. The following distribution of the total dissolved fluoride can be calculated: $[F^-]=4.1x10^{-5}$ $mol.l^{-1}$ (51%), $[MgF^+]=3.7x10^{-5}$ $mol.l^{-1}$ (47%), $[CaF^+]=1.6x10^{-6}$ $mol.l^{-1}$ (2%) and $[HF]=3x10^{-10}$ $mol.l^{-1}$ (Stumm and Morgan, 1981). An equilibrium is assumed to exist between input of fluoride via rivers and removal of fluoride from seawater in the form of insoluble compounds (Stumm and Morgan, 1982). It is not clear whether, as is often supposed, aerosols play an important role in the geochemical cycle of fluoride. Based on measurement data and a rough estimate of the mass balance, Barnard and Nordstrom (1982) stated that fluoride should not be viewed as a cyclic sea salt. Calculations indicated that approximately 10 tonnes of fluoride enter the Dutch environment each year from sea aerosol. This is less than 1% of the anthropogenic fluoride input to the atmosphere in the Netherlands.

3.2.2. Fresh water

Although numerous complexes of fluoride exist, in surface water with pH > 5, dissolved F is mainly in the free ion form, F^-. This follows from stability diagrams constructed from thermodynamic data (Elrashidi and Lindsay, 1986). These considerations also show that fluorapatite $Ca[PO_4]_3F$ or $Ca_{10}[PO_4]_6F_2$) is a sparingly soluble mineral. It can be deduced from the equilibrium reaction:

$$Ca_5(PO_4)_3F + 6H^+ = 5Ca^{2+} + 3H_2PO_4^- + F^- \qquad \log K = -1$$

that the solubility product is extremely low:

$Ca_{10}(PO_4)_6F_2 = 10Ca^{2+} + 6PO_4^{3-} + 2F^-$ log K = -119

Golterman (1971) reported a solubility product of 10^{-107}. Since the concentration of calcium in the Rhine is about $3x10^{-3}$ mol.l^{-1} and since $[PO_4^{3-}] = 10^{-5}xPO_4$-P at pH 7.6, this implies that at a phosphate level of 0.3 mg.l^{-1} PO_4-P (=10^{-5} mol.l^{-1}), the F^- concentration must be less than $2.5x10^{-4}$ μg.l^{-1}, i.e., surface water would contain virtually no F^- at these calcium and phosphate levels. Elrashidi and Lindsay (1986) stated that in water of a pH above 5.6, the fluoro-hydroxy-apatite system is dominant:

$Ca_5(PO_4)_3F + H_2O = Ca_5(PO_4)_3OH + F^- + H^+$

With log K = -15.14, the concentration of free fluoride is:

log $[F^-]$ = -15.14 + pH, or a concentration of less than 0.2 μg.l^{-1} at pH 7. However, it is unlikely that the F/OH-apatite system determines the ionogenic fluoride content of surface water to such an extreme degree.

Van Eck (1982) demonstrated that if the similarly sparingly soluble hydroxy-apatite (log K = -114) were to control the concentration of free orthophosphate, this would be 100 to 1000 times lower than is generally being measured in Rhine water. Kinetic barriers are assumed to prevent the formation of the hydroxy-apatite (Ferguson and McCarthy, 1971). This is very likely also true for fluorapatite. This is because the concentration of labile F, the sum of $[F^-]$ and (less important at pH > 5.5) the complexes of F, as measured by the Department of Public Works (1976-1986), was 0.2 mg.l^{-1} or more in Dutch surface waters (see subsection 4.2.2.), i.e., likewise three orders of magnitude greater than calculated thermodynamically.

3.2.3. Sediments

The Health Council (1981) reported values of up to 200 mg F.kg^{-1}or marine sediments, and of up to 450 mg F.kg^{-1} for river sediments, on a dry matter basis (see also ch. 4). It can be inferred from the preceding subsection that insoluble fluorapatite may be formed locally and as such accumulate in some locations, especially in the sediments. This is also the case when fluorine is discharged in the form of fluorapatite as, for example, at points of discharge of phosphate ore-processing plants (see ch. 2). However, more insight into the distribution between labile and insoluble F is needed to give a decisive answer.

3.2.4. South Holland and Zeeland water bodies

The F balance sheet for the compartment fresh water in the Netherlands does not tally with the facts.. Exports have been estimated at around 28,000 tonnes of F per year and imports at 17,300 tonnes per annum (ch. 2). The difference between exports and imports does not agree with the total emissions into water (55,000 tonnes annually). It should be noted that the major source of this emission is the processing of phosphate ore in the Botlek area, discharging fluorine mainly in the form of the insoluble fluorapatite. Measurements taken by the Department of Public Works are consequently less suitable for estimating imports and exports, because undissolved F is not included in the calculation. The transport of insoluble fluorapatite to the sea and sediments could play an important role, as is shown schematically in figure 3.3. Although the discharges of fluoride-containing compounds to the Zeeland waters are small compared with the inputs to the Botlek area, they do lead to locally elevated concentrations of labile fluoride (chapter 4). The form in which the fluorine is discharged is probably more important for the quality of the receiving surface waters than the magnitude of the emissions.

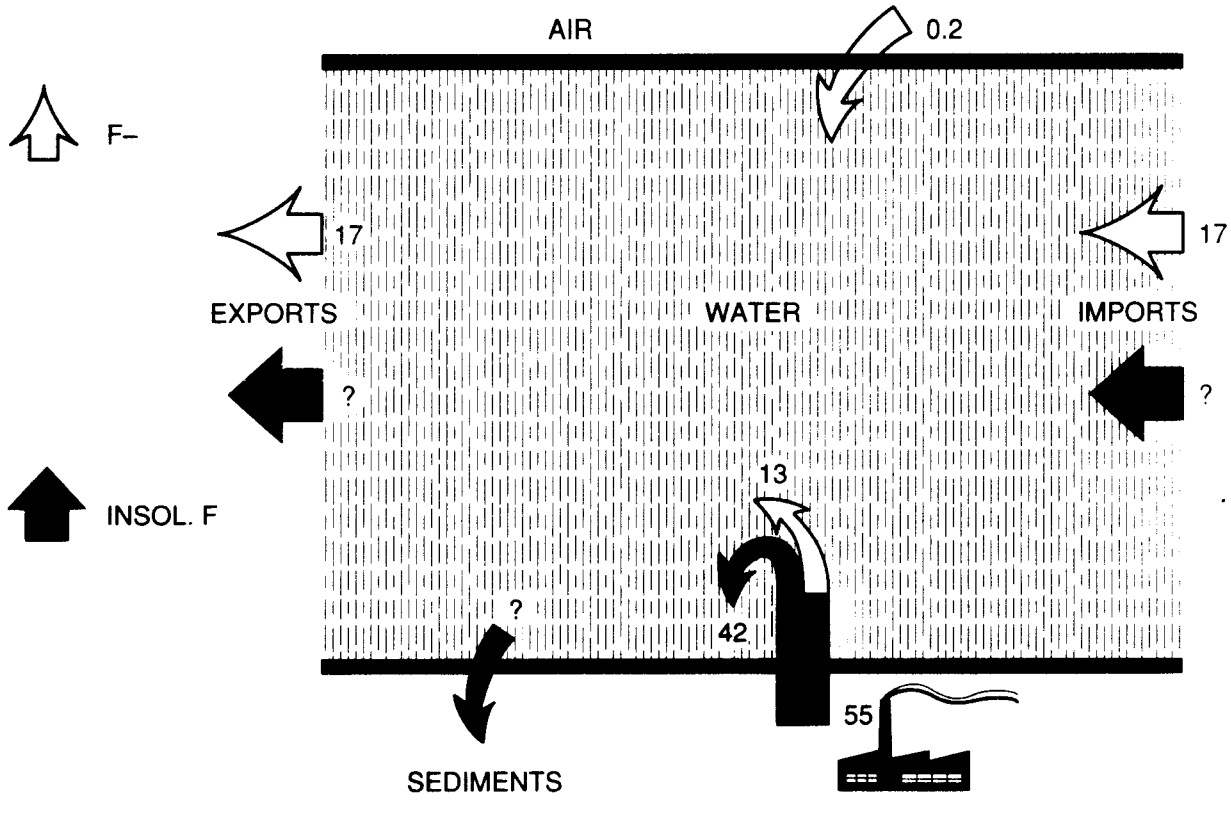


Figure 3.3. Estimated emissions into water and the imports and exports of fluoride via water in the Netherlands (in ktonnes per year)

3.3. BEHAVIOUR IN AIR

Fluorides are emitted as gaseous compounds and as particulate matter in aerosol form (chapter 2). A few of the emitted compounds are given in table 3.1.

Fluorine in the form of F_2 will be rapidly converted to HF in the atmosphere, and this is also true for the silicon fluorides, H_2SiF_6 and SiF_4, which are hydrolyzed in the atmosphere to HF and silicon oxide (SiO_2); SiO_2 particles can act as HF carriers.

Table 3.1. Species of fluoride in emissions from industrial sources (Harrison and Perry, 1986)

Industry	*Fluoride*	
	gaseous	*particulate*
Aluminium	HF	Na_3AlF_3
		AlF_3
		$Na_5Al_3F_{14}$
Steel	HF	CaF_2
	SiF_4	
Glass	SiF_4, HF	CaF_2, NaF
	F_2, BF_3	Na_2SiF_6
	H_2SiF_6	PbF_2
Phosphate	HF, SiF_4	$Ca_5(PO_4)_3F$
	F_2	CaF_2

On the basis of thermodynamic data it may be assumed that the readily soluble fluorides in aerosols are eliminated as HF by reaction with other gaseous (acid) components such as HNO_3, H_2SO_4 and HCl present in the atmosphere. For a substance such as ammonium fluoride (or ammonium bifluoride) too, when present at an average concentration of 5 $\mu g.m^{-3}$ ammonia in the atmosphere, ammonia and hydrogen fluoride constitute over 90% of the equilibrium mixture. It is estimated that 200 ktonnes of HF per year enter the global atmosphere from sea-salt aerosols; this is about 50% of the total natural input of HF from volcanism (Clegg and Brimblecombe, 1988). For the Netherlands, this contribution is at most 13 tonnes a year.

The gaseous fraction constitutes about 75% of the more than 1700 tonnes of fluoride released annually into the Dutch atmosphere. Assuming that approximately 70% of the total atmospheric fluoride is comes from abroad (see chapter 4), and taking into account the high deposition rate of HF, it can be calculated that around 60% of the fluorides in the atmosphere in the Netherlands is in the gaseous state. This percentage may be somewhat higher in practice because of the above-mentioned elimination effect.
Fluoride in aerosol form especially can be dispersed over large distances by the action of wind or as a result of atmospheric turbulence. The deposition velocity of both the gaseous HF and the particulate F determines the distances over which fluoride is dispersed in the atmosphere. With large particles (diameter >10 μm), this distance will be determined mainly by the (large) particle falling speed, and dispersion will be confined to the immediate vicinity of the source. With smaller particles, the falling speed will be less important, the deposition velocity lower and the area over which they are dispersed larger. Fluoride is removed from the atmosphere by two mechanisms: dry and wet deposition.

3.3.1. Dry deposition

The rate (the mass deposited per unit of surface area and per unit of time) is the product of the dry deposition velocity (Vg) and the concentration in the air (C). The deposition velocity depends on the atmospheric stability, the surface area and the properties of the component concerned:

$$Vg = (Ra+Rd+Rc)^{-1} \qquad (1)$$

where:

- Ra (in $s.m^{-1}$) describes the diffusion of the material from the free atmosphere to the laminar surface layer,
- Rd describes the diffusion through the laminar layer (0.1-0.01 cm thick), and
- Rc is a measure of the uptake capacity of the surface for the component concerned.

For large-scale dispersion, an average (surface) roughness and atmospheric stability have been assumed. The deposition velocities used for fluoride are:

gaseous fluoride : 2 $cm.s^{-1}$ (PEO, 1986)
fluoride aerosols (<7μm) : 0.1 $cm.s^{-1}$ (Sehmel, 1980)

The high deposition velocity for HF can be explained largely by its good solubility in water, resulting in a low Rc value for HF (approximately 12 $s.m^{-1}$).

Measurements (see chapter 4) indicated that about 70% of the soluble fluoride is in a gaseous state. Based on this information, the average large-scale deposition velocity for total soluble fluoride is taken to be 1.4 $cm.s^{-1}$.

The effect of the dry deposition on the decrease in the amount of fluoride in the atmosphere can be expressed in terms of a characteristic residence time, T. This time is the ratio between the height of the mixing layer (taken to be 1000 m) and the deposition velocity. From the assumed values for the deposition velocities, residence times of $5x10^4$ s = 14 hours (gas) and 10^6 s = 12 days (aerosol) have been calculated.

An average deposition velocity cannot be applied for the area surrounding a point source. For example, when atmospheric conditions are stable, a low deposition velocity will be accompanied by high air concentrations. Because of the low Rc value, the deposition velocity of HF in particular depends heavily on the atmospheric conditions; it can be gleaned from table 3.2. that the deposition velocity for HF can differ by a factor of 7 as compared with less than 10% for particulate fluoride. For example, at low point-source heights, the contribution of stability class F to the annual average concentration is large, and the deposition velocity for this class is small. The yearly average effective deposition velocity (sum of the deposition rates divided by the sum of the concentrations) will then be relatively small, of the order of 1.2 $cm.s^{-1}$. At high source heights, and for stability class F, the plume will increasingly no longer reach the ground as the height of the source increases. In these cases the average deposition velocity of HF is actually higher, of the order of 2.5 $cm.s^{-1}$.

The roughness of the terrain and the transition from one terrain to another also play an important role. Erisman et al. (1987), for instance, calculated that the atmospheric deposition rate of HNO_3, a component comparable to HF, is approximately 1.8 greater along forest edges than over heather or grass.

Table 3.2. Deposition velocity under different atmospheric conditions (chimney height, 5 m; surface roughness length, 0.15 m; meteorological situation at Eindhoven). The grouping into stability classes is based on the RIVM dispersion and deposition model (Van Jaarsveld, 1988)

Stab class	Freq. (%)	Vg (HF) (cm/s)	Vg (particles)** (cm/s)	Deposition ($mg/m^2/day$)* NE of source	SW of source
ABC	10	2.2	0.21	8.7	9.8
D1	25.6	1.0	0.20	12.5	6.7
Dm	29.7	2.4	0.21	20.6	7.4
Dh	19	3.0	0.21	21	7.0
E	3.5	1.2	0.20	14	13
F	12.1	0.4	0.19	16	15

* *Effective deposition velocity for NE: 1.3 cm/s, SW: 1.0 cm/s*
** *The percentage of coarse particles (>7.2 μm) is larger close to the source, resulting in a higher average deposition velocity*

3.3.2. Wet deposition

The wet deposition rate is the product of the annual rainfall (760 mm in the Netherlands) and the concentration in rainwater. Where open rain gauges were used (i.e., those not protected against dry deposition), a correction was applied to eliminate the contribution from the dry deposition. An average correction factor of 0.5 to 0.7 for fluoride was obtained from comparative measurements (see chapter 4). For a model description, the wet deposition process can be separated into two main processes:

- washout from plumes below the cloud
- rainout of particulates taken up by clouds

The washout process is important for readily soluble substances (HF, aerosols) especially at a short distance from the source. For irreversibly soluble gases such as HF, it is assumed that all the gaseous HF is washed out during the shower. Fluoride aerosol is washed out from a plume as a result of raindrops scavenging particles out of the plume on their way down. The washout coëfficient is described by (Janssen and Brink, 1985):

$$\Lambda d = \epsilon . \lambda_o . R^{1-\beta} [h^{-1}] \qquad (2)$$

The RIVM dispersion and deposition model (Van Jaarsveld, 1988) uses for ϵ (the particle-size dependent collision probability) the value given by

Slinn (1977). The data of Best (1950) were used for λ_o and β (parameters for the droplet-size distribution). Averaged over all the model classes, the washout coëfficient for fluoride aerosol is 0.4% per hour.

The rainout process is important especially at a larger distance from the source when the plume is situated wholly or partially in the clouds. The rainout velocity for particles is usually described by an effective washout coeëfficient: $\Lambda d = WR/H$, where R is the rain intensity and H the mixing layer height. The quantity W (scavenging ratio) is the average ratio between the measured rainwater concentrations and the air concentrations. The scavenging ratio for fluoride aerosol is 0.15×10^6.

To calculate an overall annual deposition rate, information is required about the rain probability, average shower duration and rain intensity for the separate stability classes and wind directions. For large-scale dispersion, the annual average wet deposition is 1.4% per hour for fluoride aerosol and 5.9% per hour for gaseous fluorides. It can be deduced from these values that the residence time of gas is 12 hours and that of particulates 50 hours.

For HF, the half-times for wet and for dry deposition are thus approximately the same. With large-scale dispersion, fluoride aerosol will be removed largely by wet deposition. For the Netherlands the average contribution of wet deposition to the removal of fluoride aerosol is about 65% (Van Jaarsveld et al., 1988b).

Locally, around a point source, the deposition of both gaseous and particulate fluoride is determined mainly by dry deposition owing to the relatively high ground concentrations.

3.4. BEHAVIOUR IN BIOTA

The data in this subsection are based on chapter 5.

- Uptake by plants

Under the conditions pertaining in the Netherlands, the principal source of contamination of plants is airborne F. Compared with other plant species, grass absorbs fluoride at a relatively high rate; equilibrium between airborne and grass fluoride is generally attained within 24 hours and is proportional to the atmospheric F concentration.

Plants can also take up fluoride from the soil. The availability of soil fluoride to plants is however low, certainly when the soil naturally

contains fluoride and/or when fluoride has been added to it gradually, for example, through atmospheric deposition. On the other hand, the addition of F-containing sludge or a phosphate fertilizer can lead to a considerable rise in the F concentrations in plants, in any case soon after application; the availability appears to decrease with time after application. The degree of accumulation depends, among other things, on the soil type. Of the soil factors influencing F accumulation, the pH plays a prominent role; up to a pH of around 7 there is a negative relationship between the fluoride concentration in soil and that in crops.

- Uptake by aquatic organisms

Aquatic organisms exposed to relatively high concentrations (10-50 mg $F.l^{-1}$) accumulate fluoride to only a slightly greater extent than those exposed to background concentrations. In both plants and animals (crustaceans, fish), at concentrations of up to 50 mg $F.l^{-1}$, bioconcentration factors of <10 have been calculated (on a fresh weight basis). The limited data available indicate that accumulation through food chains (biomagnification) is of little significance.

- Uptake by terrestrial organisms

Terrestrial organisms accumulate more fluoride when exposed to high concentrations than when exposed to background concentrations. Invertebrates and vertebrates exhibit the same food-dependent relationship: the lowest levels in herbivores and (somewhat) higher levels in predators. The relatively high concentrations in predators indicate a moderate degree of biomagnification, but the data are ambiguous.

3.5. SUMMARY AND CONCLUSIONS

Fluorine occurs in the environment in a variety of physicochemical forms. Within the soil, fluoride is extremely immobile and at pH below 6 it exists mainly as an aluminium fluoride complex. In seawater, fluoride belongs to the macrocomponents, and the dominant species are the free fluoride ion (51%) and MgF^+ (47%). In fresh water at pH above 5, the free ion is the main fluoride species. In the presence of phosphate, among other substances, insoluble fluorapatite is formed, a large part of which is transferred to the bottom sediments. Most of the fluoride in the atmosphere is of anthropogenic origin. Approximately 25% of the fluoride is emitted as particulate fluoride and the rest as gaseous fluoride (mostly HF). HF is removed relatively rapidly from the atmosphere by both wet and dry deposition (half-time about 13 hours). In contrast, fluoride aerosol diappears only slowly from the atmosphere, mainly by wet deposition (half-time 50 hours).

Plants only take up the fairly small, water-soluble and labile fractions. The major source of fluoride to plants is atmospheric deposition on and in the plant. The bioconcentration factor in water is less than 10 for both plants and animals. The limited data available indicate that terrestrial animals bioaccumulate fluoride to a small extent. Biomagnification is of no significance.

4. CONCENTRATIONS IN THE ENVIRONMENT AND EXPOSURE LEVELS

4.1. MEASUREMENT TECHNIQUES

Fluoride can exist in many forms: from gaseous to particle-bound fluoride (air) and from sparingly to readily soluble fluoride (water). Of these compounds, the soluble compounds in particular are relevant for the environment. It is important therefore to know which species of fluoride are determined with the measurement techniques in use. This is because the measurement techniques described here differ, primarily in the sampling and destruction procedures employed. After pretreatment, the released fluorides are generally transferred into the liquid phase. The next step is decomplexation followed by determination of the F ion. The F ion is currently usually measured with a fluoride ion-selective electrode.

4.1.1. Soil

- Digestion

For the analysis of fluoride in soil material, the particular method used to solubilize fluorides is of paramount importance. Determination of the total fluoride content is less important because the fluorides occurring naturally in the soil matrix, and which are not available to plants and animals, are also solubilized with this method. The most widely used methods can be divided into four categories (see also table 4.1.):

Table 4.1. Scheme of the species which are determined with the various methods for analyzing fluorides in soil

Form of fluoride	*Analysis method*			
	water-sol. F	*Labile F*	*acid-extr. F*	*total F*
Adsorbed onto:				
- Al and Fe hydroxides	*+/-*	*+*	*+*	*+*
- clay minerals	*+/-*	*+*	*+/-*	*+*
Precipitate of:				
- AlF_3	*+*	*+*	*+/-*	*+*
- CaF_2	*-*	*+/-*	*+/-*	*+*
- fluorphlogopite	*-*	*-*	*-*	*+*
- alkaline F minerals	*-*	*-*	*+*	*+*
- other F minerals	*-*	*-*	*-*	*+*

- Extraction with a solution of 0.01 M $CaCl_2$ (water-soluble F). Reproducible results are obtained with a shaking time of 16 hours and a soil/water ratio of 1:3 (Larsen and Widdowsen, 1971). When high fluoride concentrations are expected, a $MgCl_2$ solution is frequently used instead of a $CaCl_2$ solution (Barrow and Ellis, 1986), or distilled water (Polomski et al., 1982) to prevent fluorspar (CaF_2) precipitate formation.

- Extraction with an anion exchanger (labile F). This method releases all the fluoride from the soil without decomposition of the soil matrix. A strong-base anion exchanger is shaken with soil and distilled water (ratio by weight, 5:1:50; shaking time, 16 hours); the anion exchanger is separated from the slurry by filtration over a 0.25 mm filter (Larsen and Widdowsen, 1971; Roorda van Eysinga, 1974; Supharungsun and Wainwright, 1982).

- Alkali destruction (total F). 4.5 Grams of NaOH are added to 0.5 g of soil which has been dried at 105 ^{o}C, followed by heating for 20 minutes. After cooling, the mixture is dissolved in distilled water (Polomski et al., 1982; Hani, 1975).

- Analysis

After their extraction, fluorides can be determined with an ion-specific electrode (see 4.1.2.). Data on the accuracy and detection limit of this method have not been reported in the literature. On the basis of the standard guideline for fluoride determination in water, the following detection limits have been estimated for the various extraction/destruction procedures:

Water-soluble F : 0.1 mg $F.l^{-1}$
Labile F : 0.5 mg $F.l^{-1}$
Total F : 1.0 mg $F.l^{-1}$

The accuracy of the analyses is estimated to be around 10%. Their cost is determined chiefly by the labour costs for the destruction or extraction procedure.

4.1.2. Water

- Digestion

Although in water fluoride usually exists in ionic form, it may be necessary to separate the fluoride from the matrix, depending on the composition of the latter. When insoluble fluorides are present, an alkaline digestion procedure followed by steam distillation has to be carried out, as described by "The Analytical Working Group of the Comité Technique Européan du Fluor" (1986). The steam distillation technique, as introduced by Willard and Winter (1933), is based on the volatilization of H_2SiF_6 with perchloric acid and sulphuric acid vapours at 135 ^{o}C. Separation by HF diffusion is employed especially in clinical chemistry and biochemistry, and is based on conversion of F to HF by reaction with perchloric acid and sulphuric acid, which is then collected in a sodium hydroxide solution (Singer and Armstrong, 1965).

- Analysis

Determination with the fluoride ion-selective electrode is a direct method, (Frant and Ross, 1966) and the one most widely used. The electrode potential is related to the F concentration via the law of Nernst (measurement quantity is proportional to the log concentration). This electrode permits the measurement of the total content of free and complex-bound fluoride dissolved in water (NNI, 1982). The addition of "Total Ionic Strength Adjustment Buffer" (TISAB reagent) ensures that the variations in ionic strength between different samples become negligible, the pH is optimal and interfering metal ions are masked. This method is applicable to all types of water containing at least 20 $\mu g\ F.l^{-1}$. Barnard and Nordstrom (1982) reported for rainwater a reproducibility of 5% at concentrations of 10 $\mu g\ F.l^{-1}$ and a detection limit of 1 $\mu g\ F.l^{-1}$. In this concentration range the electrode no longer behaves according to the law of Nernst, making it necessary to include additional standard solutions in the analysis. It is estimated that the accuracy of the potentiometric method is around 10% at concentrations ordinarily found in rainwater. The analysis is cheap because the procedure is not very labour-intensive and requires only simple equipment. The price per analysis will rise substantially as soon as a digestion procedure has to be carried out.

4.1.3. Air

- Sampling

The methods for sample collection can be divided into dynamic and static (= without the drawing in of air) techniques. The dynamic techniques make it possible to express the analytical result in a unit of concentration (e.g., ug $F.m^{-3}$); the static methods yield an immission load (e.g., mg $F.cm^{-2}$ per 24 hours) or a F content of crops (μg $F.kg^{-1}$ of crop). The measurement of biological effects can also be included in the static methods. The methods described here usually determine a different fraction of the total range of fluorine compounds.

Dynamic sampling techniques

Sampling on filters is preferred to absorption in fluids because of its simplicity and the limited precautions required.

- Single-filter method

  To determine the total F content or the concentration of "readily soluble fluorides" in air, it is not necessary to distinguish between gaseous fluorides and fluorides in aerosol form. The fluorides can then be collected on a lime-impregnated filter. Sampling times usually range from 1 hour to 24 hours, and the air flow is set at between 0.3 and 1.0 m^3 per hour.

- Double-filter method

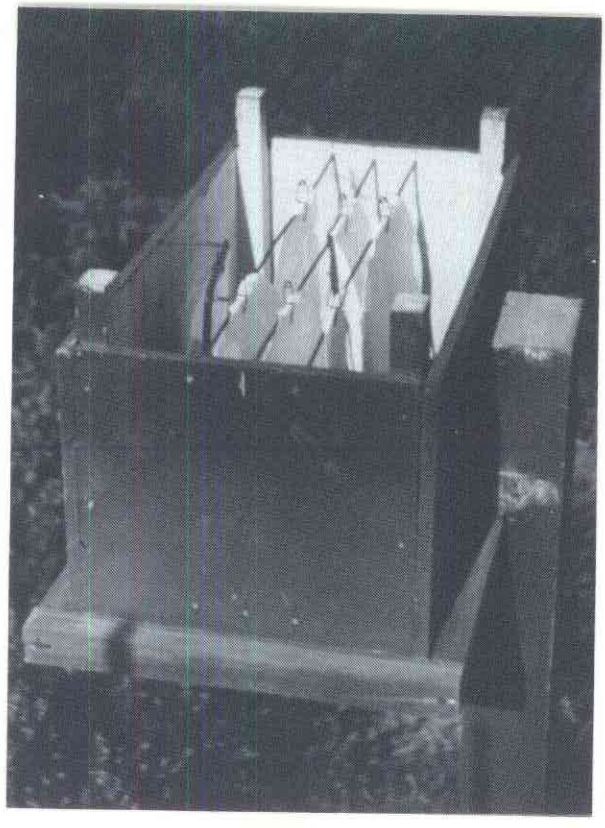
  When it is important to distinguish between fluorides in the gaseous phase and those in the aerosol phase (e.g., for determination of the deposition velocity, effects, or model calculations), the aerosols are collected on a heated inert dust filter which allows the gaseous fluorides to flow through. The gaseous fluorides are collected on a second, lime-impregnated filter. There is a Dutch practical guideline for the double-filter method (NNI, 1983). The dust filter and the gas filter are fitted into the same filter holder. The sampling time and air flow are the same as for the single-filter method. The filters should be transferred to (separate) sealable polyethene flasks as soon as possible after the samples have been obtained. The filters must be analyzed within six weeks of sampling.

A study comparing the two methods was carried out in Vlaardingen in 1982/83 (Bikker, 1985). The low correlation coëfficient (0.5) found for concentrations below 1 μg $F.m^{-3}$ is probably due to the greater inaccuracy of the single-filter method. Bikker and De Leu (1986) do not, therefore, recommend this method for low-fluoride pollution areas.

Static sampling techniques

- Impregnated filter (limed paper method)

  In this method, entrained F compounds are absorbed by impregnated filter papers. In general, three parallel rows with two filters each are hung vertically in a housing mounted about 1.5 m above ground level (see photograph). Exposure lasts from 1 to 4 weeks. The sampling efficiency is heavily dependent upon the meteorological conditions and the physicochemical properties of the fluoride.



Experimental setup of the determination with the limed paper method in practice (derived from IPO)

Comparison of the single- and double-filter methods (Bikker and De Leu, 1986) yielded the following relationships:

C on single-filter = 0.09 C on limed paper + 0.09 (n=24, R=0.62)

C on double-filter = 0.13 C on limed paper (n=4)

C on limed paper is expressed in μg F per gram of limed paper per exposure day.

In view of its simplicity, the method can be used for indicative measurements. However, the correlation is too low to permit estimation of the atmospheric concentrations with sufficient precision.

- Precipitation collector

The precipitation (rain, snow, hail) is collected via a polyethene funnel in polyethene bottles over a period of 2 to 4 weeks. Given the surface area of the funnel, the volume of the precipitation and the sampling time, the F content can then be expressed in mg $F.m^{-2}.day^{-1}$. The "open-top" collector most widely used to date determines both the fluorides washed out by the precipitation (wet deposition) and the fluorides accumulated in the rain collector via diffusion from the air (dry deposition). The dry deposition measured with this collector and the (higher) dry deposition on natural surfaces are not comparable. The new generation of "closed" rain collectors determines wet deposition only.

- Grass

Grass has been analyzed for its F content in the Netherlands since the 1960s (Tesink, 1982; Van der Eerden, 1983). Once a month, sixteen handfuls of grass are cut per area of 9x9 m^2, particular care being taken that soil particles are not included. The grass is analyzed as soon as possible after the samples have been obtained. The F contents are calculated in mg F per kg dry matter. Van der Eerden (1983) has studied the relationship between grass and ambient air F concentrations. The following formula was derived from this study:

$[G] = 90\ K_s\ [L] \cdot e^{-(0.1\ K_s \times [T])}$, where

[G] = F content of grass

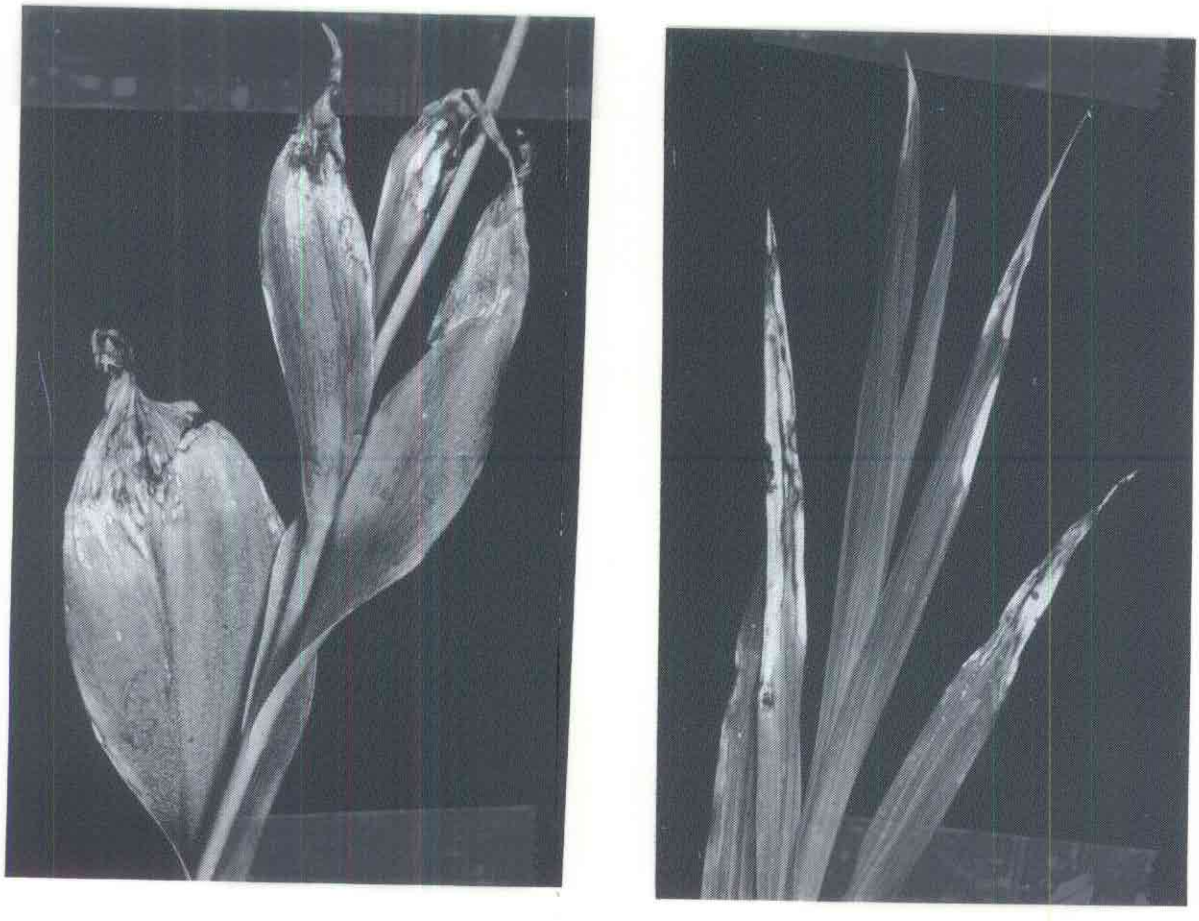
[L] = maximum 24-hour average F concentration in the ambient air, after the last shower at least 2 mm of rain

Ks = seasonal factor, ranging from 0.6 (summer) to 1.4 (winter)

T = number of days between observed [L] and sample collection

Several field experiments conducted around local point sources showed that the correlation of this regression generally varied between 0.7 and 0.8, and that there was, on the average, good agreement between the measured and calculated [G] values. Although the explained variance (approximately 60%) is too low for calculation of individual [G] and [L] values, it is nevertheless considered suitable for establishing a relationship between the maximum allowable fluoride content of grass and the resultant maximum acceptable atmospheric fluoride concentration (see also Appendix).

- Tulips and gladioli (biomonitoring)
  Apart from resulting in accumulation of fluorides in relatively insensitive plants (such as grass), an elevated concentration of airborne fluoride also has adverse effects on susceptible plants such as some varieties of tulip and gladiolus. A striking effect in the latter is necrosis of the tips of leaves (see photograph).



Analysis method based on biomonitoring: tip necrosis of leaves (Source: IPO)

As part of the National Airquality Monitoring Network, folial injury, in cm, is measured on tulips (in spring) and gladioli (in summer and autumn) in standard culture trays. This method gives an idea of the spatial distribution of fluoride effects. However, the magnitude of the effect depends in part on the overall nutritional status of the plant and is sometimes also not readily distinguishable from other causes, such as drought, wind, hail, salt, SO_2, NO_2, etc. Furthermore, the difference between acute and chronic effects must also be taken into account (see chapter 5).

- Digestion

The digestion procedure determines the percentage of the collected fluorides that will be measured. The "concentration of readily soluble fluorides" therefore requires translation in terms of extracting agent, temperature, pH and extracting time.

Single- and double-filter method

The digestion procedure as proposed in the practical guideline involves extracting the (dust) filter with 0.5 M sulphuric acid (pH 0) for two minutes. This treatment releases all the readily soluble fluorides and a small fraction of the insoluble fluorides. The gas filter (double-filter method only) is extracted with 0.03 M hydrochloric acid.

Limed paper method

The filters (with mostly HF) are ashed at 600 ^{o}C for two hours, followed by the addition of concentrated sulphuric acid. The fluorides (for determination of total content) are subsequently distilled off as HF.

Grass

After drying and grinding, the grass is ashed at 520 ^{o}C and fused with NaOH at 500 ^{o}C for 4 to 10 minutes. The fluorides (determination of total content) are distilled off in an sulphuric acid medium at 180 ^{o}C.

- Analysis

The most widely used method of analysis is based on the measurement of the potential with a fluoride ion-selective electrode (see 4.1.2.). The detection limit of the single-filter method is approximately 0.05 $\mu g\ F.m^{-3}$, and for the double-filter method according to the Dutch practical

guideline, it is around 0.1 $\mu g\ F.m^{-3}$. The detection limit can be lowered to 0.04 $\mu g\ F.m^{-3}$ by applying the modifications proposed by Joziasse and Bikker (1986). At a concentration of 2 $\mu g\ F.m^{-3}$ (24-hour sampling and an air flow of 0.5 m^3 per hour), the standard deviation reported for the Dutch practical guideline is 0.3 $\mu g\ F.m^{-3}$ (15%) for both gaseous and particulate fluorides.
Only part of this deviation is attributable to the analytical method, namely, 0.1 $\mu g\ F.m^{-3}$ (5%).

4.1.4. Cost of analysis

When measurement data are required on a continual basis, the concentrations in air and water can be recorded with monitors, which determine fluorides by a wet-chemical process. Wet-chemical monitors are usually maintenance-intensive. The lowest price per measurement result is obtained with a monitor. For small numbers of samples (a few dozen), analyzed by a double-filter method, the cost per sample is approximately f 80.-. The price of a continuous 24-hour measurement taken at about ten stations of the National Airquality Monitoring Network will be around f 150,000.- on an annual basis (about f 40.- per sample), exclusive of the capital outlay for the equipment.

4.2. CONCENTRATIONS IN THE ENVIRONMENT

4.2.1. Occurrence in the soil

Fluoride is found in nature in minerals such as fluorspar and fluorapatite, and in the lattices of micas (clay minerals). In addition, fluoride exists in the soil adsorbed onto the surfaces of clay minerals and onto aluminium and iron oxides. In soil water at a pH below 6, fluorides are present mainly in the form of complexes, while at a pH above 6 the fluoride ion is the dominant species.

Table 4.2. gives the F content of soil at various locations in the Netherlands. F concentrations in clay soil range from 330 to 660 mg $F.kg^{-1}$, with an average of over 500 $mg.kg^{-1}$. These variations exist not only between the clay-producing areas for the coarse-ceramics industry, but also within the same location. The concentration of total F in Dutch agricultural soils (excluding greenhouse soils) is correlated with the clay content (particle size <2 μm) according to:

[F] = 48 + 12.3% clay (Roorda van Eysinga, 1974),

where [F] is expressed in $mg.kg^{-1}$ of dry soil (R=0.96; n=72). Samples of greenhouse soil may have slightly higher F contents as a result of fertilization with fluorine-containing phosphate (see figure 3.1.). A correlation was also found between the F content and the pH; as the pH increased, the concentration of soluble F also increased. The concentration of labile F in Dutch agricultural soils (open field and greenhouse) ranged from 3.4 to 140 $mg.kg^{-1}$, the low values being found particularly in calcareous soils (see figure 3.2.).

Data on fluorine in contaminated soils have been reported in the foreign literature. Total fluoride concentrations in such soils did not exceed 2000 $mg.kg^{-1}$ (Gisiger, 1968; Sidhu, 1979; Polomski et al., 1982; Supharungsun and Wainwright, 1982; Braen and Weinstein, 1985). In the vicinity of F emitting sources, the F concentration in soil water may be noticeably increased for a distance of up to several kilometres from the source (see figure 4.1.).

Recent data on the F concentration in groundwater in the Netherlands are not available. According to old data, it would rarely exceed 0.5 mg $F.l^{-1}$ (Stas, 1945, and Lehr et al., 1955; cited by Breimer, 1986). Riverbank groundwater along the Lower Rhine (West Germany) contained between 0.07 and 0.13 mg $F.l^{-1}$ (Kussmaul, 1979); in Finland, concentrations in riverbank groundwater ranged from 0.01 to 0.4 $mg.l^{-1}$ and in areas with rapakivi from 0.5 to 6 $mg.l^{-1}$ (Vuorinen, 1986).

Table 4.2. F concentrations in soil at various locations in the Netherlands

Year	Location/soil type	F concentration (mg/kg)*				Ref.
		Total	pH 2 extractable F	pH 7	water	
1971/72	agricultural soil- open field	39-679 (n=72)			0.5-13	1
1971/72	agricultural soil- greenhouse	65-570 (n=32)			0.5-13	1
1952	W. Utrecht/peat grassland	84 (n=4)				2
1953	Kralingse Veer/peaty clay	91 (n=4)				2
1980/81	S.Vlaanderen/diluvial sandy clay	180 (n=3)				2
1980/81	Sloe area/alluvial marine clay	281 (n=20)				2
1980/81	Hansweert/alluvial marine clay	258 (n=2)				2
1980/81	Gravenpolder/diluvial sandy clay	138 (n=2)				2
1090/81	Bruinisse/alluvial marine clay	250 (n=2)				2
1980/81	NE Polder/alluvial marine clay	432 (n=2)				2
1980/81	Rijnmond/peaty clay	100 (n=1)				2
1988	Bilthoven/humous sand	60	27	6	(n=4)	3
1988	Heteren/river clay	550	45	4	(n=4)	3
1988	Houten/river clay	370	25	3	(n=4)	3

* *Data reported in the literature are not strictly comparable owing to possible differences between the extraction procedures used*

1) *Roorda van Eysinga (1974)*
2) *Tesink (1982)*
3) *Van den Berg et al. (1988)*

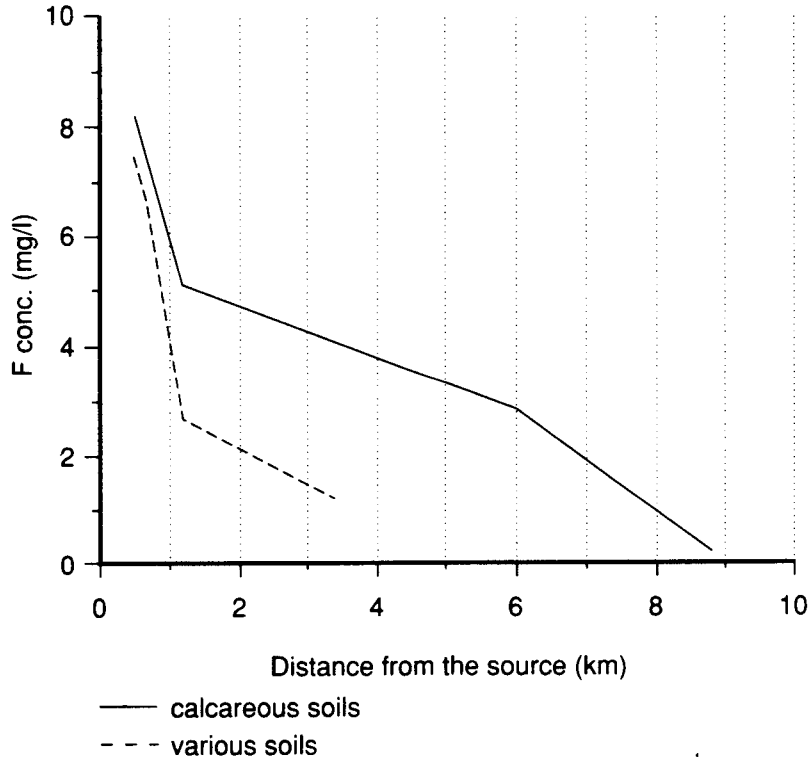


Figure 4.1. Distribution pattern of fluoride in soil water in the vicinity of a source. Soil solutions were squeezed from soil material under a pressure of 15 bars (adapted from Polomski et al., 1982)

4.2.2. Occurrence in water

- Seawater

Fluorine is one of the 14 elements present in seawater at a concentration of more than 1 $mg.l^{-1}$. Stumm and Morgan (1981) reported the total F concentration as 1.3 $mg.l^{-1}$.

- Inland water bodies

The natural F concentration in surface waters depends on local geological, physical and chemical characteristics. The natural concentration in surface waters not affected by F-rich rock varied between 0.01 and 0.3 mg $F.l^{-1}$ (Gabovic, 1957).

Examination of the data on the Dutch state-owned water bodies covering the past 10 years (Department of Public works, 1976-1986) yielded the following information. The concentrations in the Rhine-IJssel-IJsselmeer system fell in the period 1986-1980 from 0.3-0.4 mg $F.l^{-1}$ to 0.2 mg $F.l^{-1}$. The quarterly average concentrations have remained at the 0.2 $mg.l^{-1}$ level since 1980. Seasonal variations were not observed.

Conversely, the data on the Meuse water (see figure 4.2.) revealed that seasonal variations did occur in the Meuse. These were strongest at Eijsden and damped out downstream (Lith and Keizersveer).

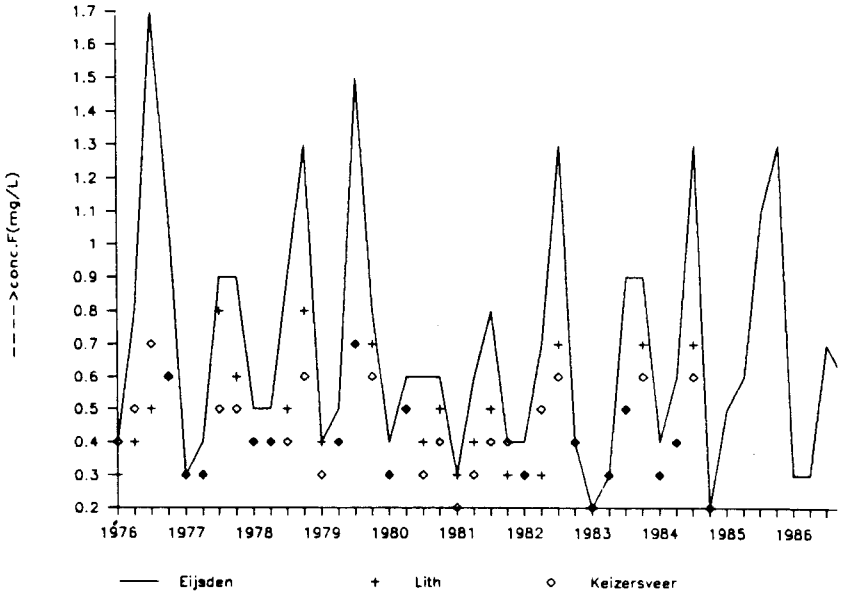


Figure 4.2. F concentrations in the Meuse, measured at Eijsden, Lith and Keizersveer during the period 1976-1986 (quarterly averages; Department of Public Works)

Figure 4.3. summarizes the F loads for the period 1973-1980 (RIZA, 1981). A striking feature is the lower loads in 1976 and 1977. The Water Companies Rhine Committee (1978-1980) attributed this mainly to the treatment of the effluent from one industrial operation in the Belgian part of the river basin. When this cleanup effort was discontinued, the load increased again to the 1975 level. High concentrations were measured in the Ghent-Terneuzen Canal (Department of Public Works, 1976-1986).

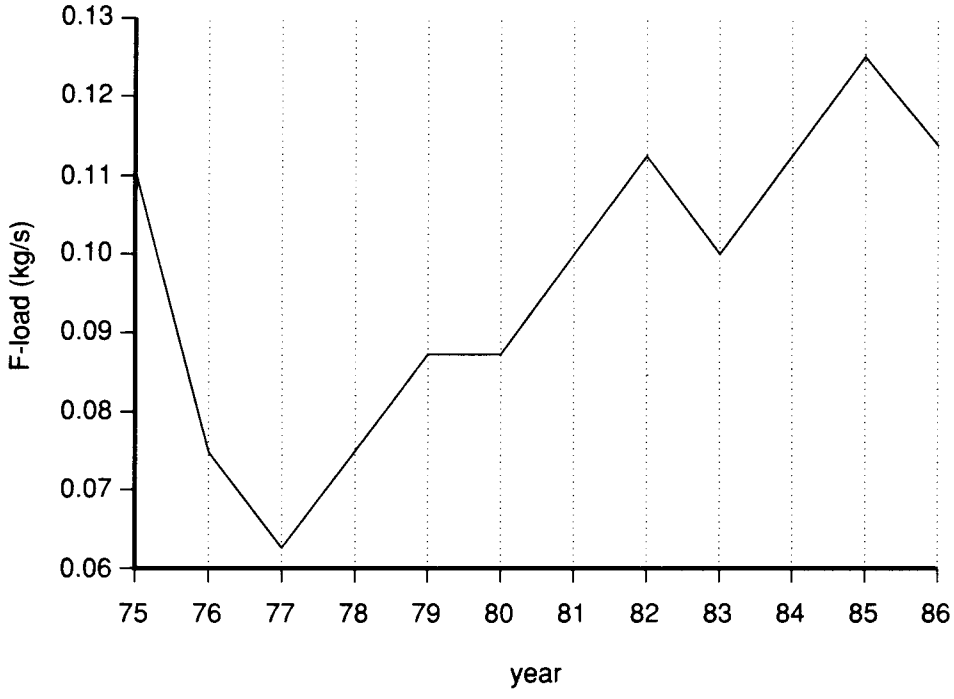


Figure 4.3. F load in the Meuse at Eijsden during the period 1975-1986 (Department of Public Works)

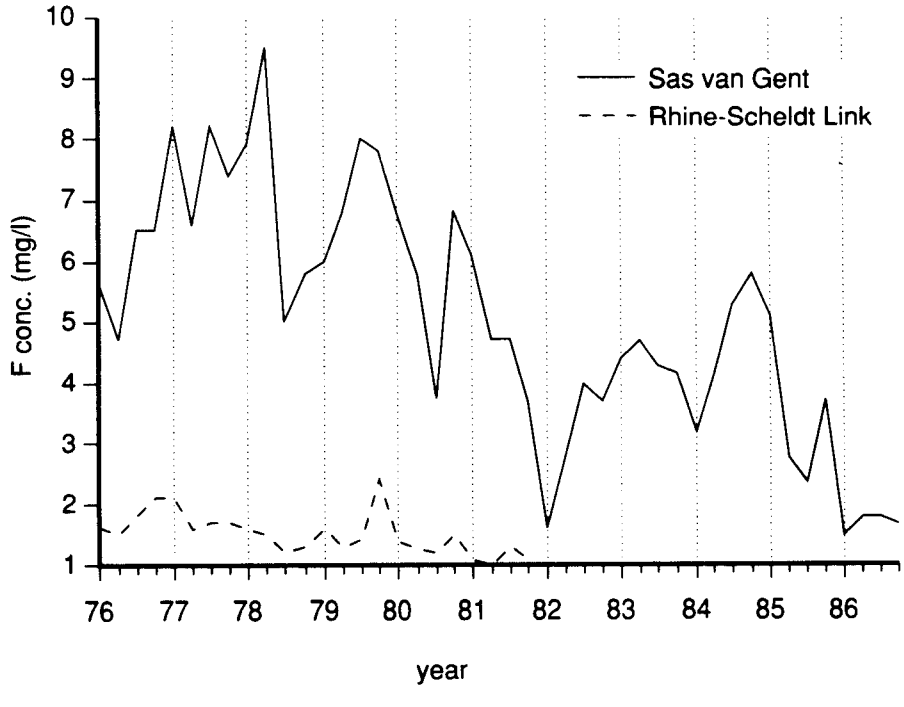


Figure 4.4. Fluoride concentrations at two locations in the Zeeland waters (quarterly averages; Department of Public Works)

Figure 4.4. shows the quarterly averages at two locations in this area. Since 1982, fluoride analyses are no longer carried out at the sampling site SR24 Belgian Border (Rhine-Scheldt Link).
High F concentrations were also observed in ditches in areas with F-emitting sources (up to 1.5 $mg.l^{-1}$; Health Council, 1981).

4.2.3. Occurrence in air

The atmospheric F concentrations can be regarded as the result of dispersion on different scales:
- dispersion on a large scale (national or per province)
- dispersion on a regional scale (part of a province)
- dispersion on a local scale (in the vicinity of a source)

- Large-scale dispersion

Large-scale concentrations (measured)
The large-scale atmospheric F concentrations in the Netherlands derived from the measurements made by Thijsse and Huygen (1985) are presented in figure 4.5. (Bikker and De Leu, 1986). It shows that the concentration in the part of the Netherlands with few sources ranged from 0.03 to 0.04 $\mu g.m^{-3}$, and also that the measured national average large-scale concentration was 0.07 $\mu g.m^{-3}$. The highest concentrations were observed in the South-west of the Netherlands, indicating the presence of many and/or large sources in this region or in NW Belgium. In addition, numerous measurements were made via the National Airquality Monitoring Network using the limed paper method described in 4.1. (RIVM, 1986). The concentrations thus measured are given in figure 4.6., and exhibit a similar pattern.

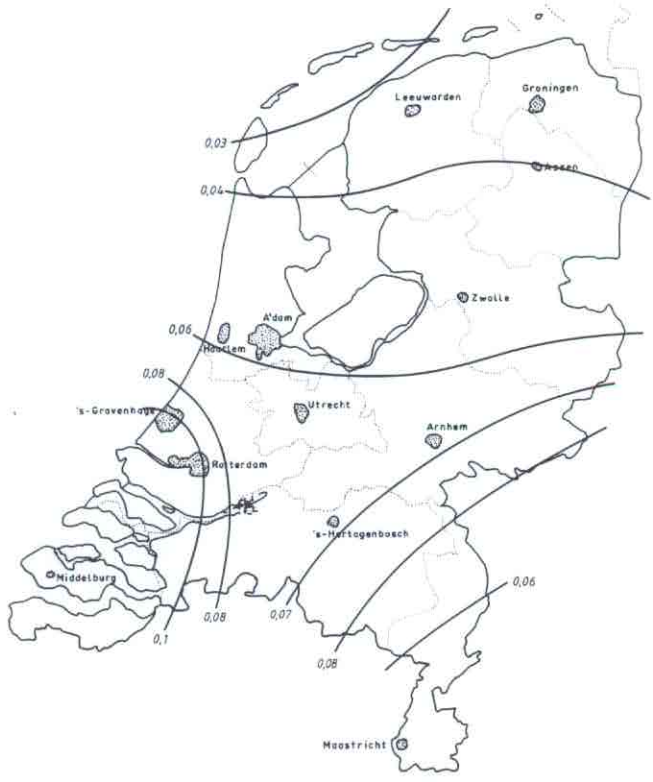


Figure 4.5. Large-scale concentrations of fluoride in the gaseous and in the aerosol state ($\mu g.m^{-3}$), measured in the period October 1982- October 1983 (Bikker and De Leu, 1986)

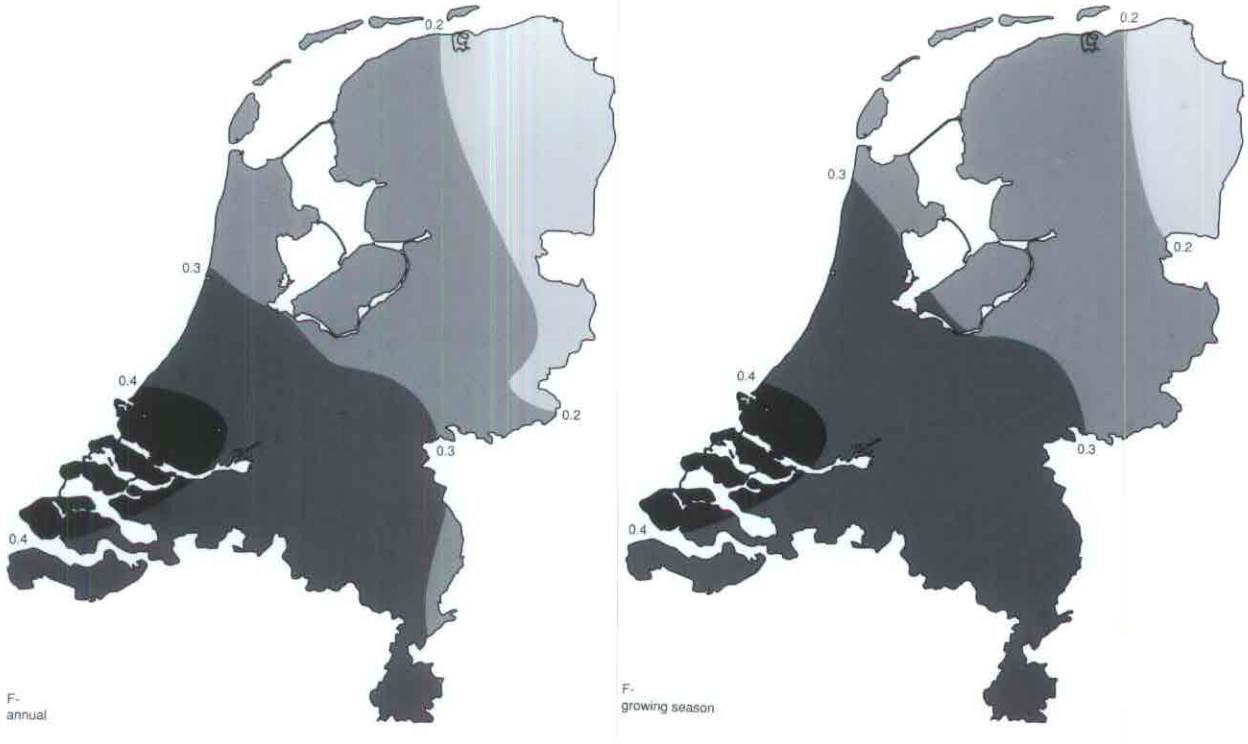


Figure 4.6. Seasonal and annual average fluoride accumulations on lime-impregnated paper in 1987 (RVM, 1988)

Figure 4.7. gives an idea of the variation of the concentration, based on the results obtained with this method over a 10-year period (RIVM, 1988). Averaged over the 24 measuring stations (since 1986: 16), the annual average (large-scale) fluoride accumulation on limed paper has remained approximately constant since 1982. The relatively high value in 1984 is most likely attributable to unfavourable dispersal conditions in that year.

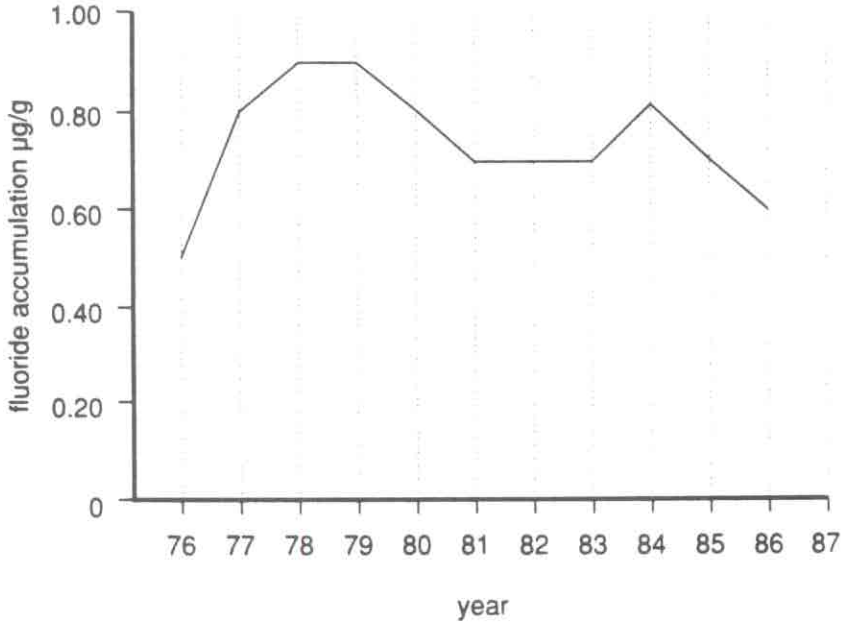


Figure 4.7. Fluoride accumulation as measured by the limed paper method, 1976-1986

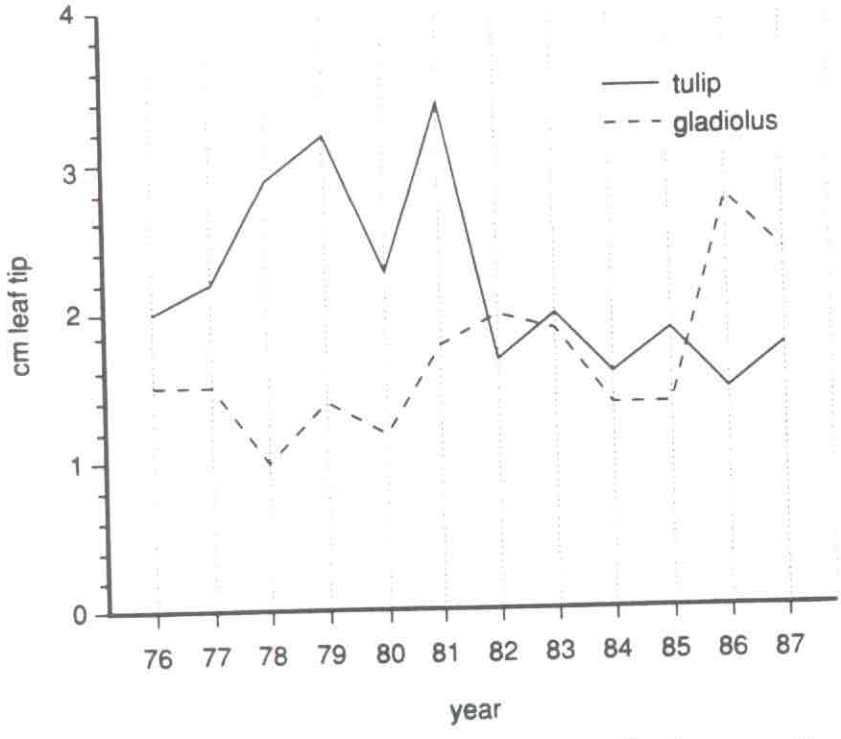


Figure 4.8. Seasonal averages of tip necrosis of leaves in tulip and gladiolus during 1976-1986 (RIVM, 1987; 1988)

The seasonal averages of necrosis of leaf tips in tulip and gladiolus have also not increased or decreased significantly since 1982 (figure 4.8.). The geographical patterns of this biological effect were each year reasonably well related to the accumulation of fluoride (RIVM, 1986), but may have a different form owing to differences in weather conditions.

Large-scale concentrations (calculated)

Most of the atmospheric fluoride is the result of human activities. It has been calculated that the natural background concentrations are of the order of 0.0005 $\mu g.m^{-3}$. When taking into account the anthropogenic emissions, the global background concentrations are of the order of 0.003 $\mu g.m^{-3}$.

The gaseous and particulate fluoride concentrations over the Netherlands have been calculated (Eerens et al., 1988) with the aid of the RIVM's Operational Priority Substances (OPS) model (Van Jaarsveld and Onderdelinden, 1988) and using the emission data given in chapter 2 (see figures 4.9 and 4.10.).

Figure 4.9. Calculated concentration of fluoride aerosol in the Netherlands

Figure 4.10. Calculated HF concentration in the Netherlands

Table 4.3. Comparison of calculated and measured fluoride concentrations

Location	*HF(meas)*	*HF(calc)*	*ΔHF%(calc)*	*Aer(meas)*	*Aer(calc)*	*ΔAer(calc)*
Witteveen	*0.035*	*0.036*	*3*	*0.011*	*0.030*	*170*
Bilthoven	*0.048*	*0.059*	*19*	*0.021*	*0.043*	*100*
B-Houtakker	*0.055*	*0.073*	*33*	*0.026*	*0.050*	*92*
Rekken	*0.058*	*0.066*	*14*	*0.024*	*0.036*	*50*
Vlaardingen	*0.33*	*0.100*	*-30*	*0.066*	*0.068*	*4*

The calculated average concentration of gaseous and particulate fluoride is 0.057 and 0.042 $\mu g.m^{-3}$, respectively. The calculated and measured values are compared in table 4.3. When Vlaardingen, which is subject to F pollution from a local source, is discounted, the calculated HF concentrations are on average 17% too high. Considering the uncertainty in the emissions, the agreement between measured and calculated HF concentrations is reasonable to good. Particulate fluoride presents a different picture, the calculated concentrations being, on the average, 100% higher than those measured. There are two explanations for this discrepancy: (a) the method used does not extract all the particulate fluoride (see 4.1.), and (b) part of the soluble particulate fluoride will be released as HF by reaction with acid gaseous components present in the atmosphere. The contribution from abroad to the fluoride concentration is substantial, of the order of 70% (see table 4.4.).

Table 4.4. Origin of the fluoride concentrations in the Netherlands

Country	contribution (%) HF	aerosol
The Netherlands	*32*	*29*
West Germany	*42*	*9**
Belgium	*15*	*20*
Britain	*5*	*13*
Others	*6*	*29*

* *Source emission control (cloth filters) in West Germany is assumed to capture around 80% of the particulate fluoride*

- Large-scale deposition

The annual input to the Dutch soil and water bodies is the product of the surface area of the Netherlands ($4.1x10^{10}$ m^2) and the deposition rate. The OPS model was used to calculate the average large-scale deposition rate for HF. The resulting large-scale dry deposition rate of gaseous and particulate fluorides is 30 mg and 1 $mg.m^{-2}$ per year, respectively. Multiplying this figure with the surface area yields an annual loading of 1300 tonnes by dry deposition.

The average large-scale wet deposition rate is the product of the average annual rainfall (760 mm) and the average concentration of fluorides in it. The measured concentrations in the collected rainwater are usually higher than in the rainwater itself because most rain collectors are not "protected" against dry deposition (see chapter 3). During a study conducted by Ridder (1984), the F concentrations in rainfall collected in an open-top collector were found to be about 30% higher than in rain collected in a wet-only collector. This implies that wet deposition would constitute about 70% of the total deposition in an unprotected collector. After correction, the wet deposition in the Netherlands over the period 1983-1986 would have been 14, 13, 15 and 13 $mol.ha^{-1}year^{-1}$, respectively. This works out at an average of 14 $mol.ha^{-1}.year^{-1}$ (26 $mg.m^{-2}$). Comparison of the amounts of fluorides collected near Lelystad in 1983 in a protected and an unprotected collector, 5.6 and 13 $mol.ha^{-1}$ respectively (PEO, 1986; KNMI and RIVM, 1983), shows that wet deposition accounted for only 43% of the measured deposition. If this were to obtain nationwide, then 8.5 $mol.ha^{-1}.year^{-1}$ (16 $mg.m^{-2}.year^{-1}$) should be taken to be wet deposition. The average wet deposition rate calculated with the OPS model was 7 $mol.ha^{-1}.year^{-1}$ (13 $mg.m^{-2}.year^{-1}$) for HF (see figure 4.11.) and 2 $mol.ha^{-1}.year^{-1}$ (4 $mg.m^{-2}.year^{-1}$) for fluoride aerosol.

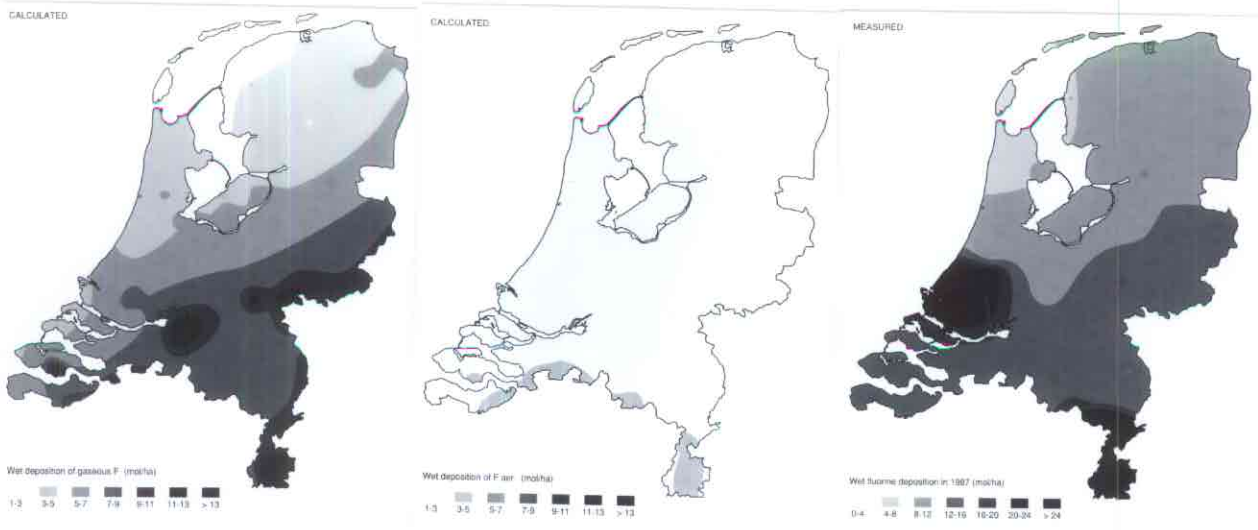


Figure 4.11. Calculated (HF) and measured (uncorrected) wet deposition in the Netherlands

The calculated total wet deposition was 9 $mol.ha^{-1}.year^{-1}$ (17 $mg.m^{-2}.year^{-1}$), which is in reasonable agreement with the measured values. According to these three calculations, the annual input to the Dutch soil and water bodies by wet deposition ranges from 700 to 1100 tonnes of F per year. The actual load is assumed to lie between these values. The wet deposition rate decreases from south to north. It is twice the national average in the Rijnmond area, in South Limburg and near Flushing. Sea-salt aerosol has no influence on the values in coastal regions. The total deposition in the Netherlands (wet + dry) is therefore 2000-2400 tonnes per year (including about 200 to 250 tonnes on surface waters). Table 4.5. indicates that about 70% of the dry and around 80% of the wet deposition originate abroad, so that the contribution from this source is about 1600 tonnes. Approximately 65% (1100 tonnes) of the 1700 tonnes of fluoride emitted in the Netherlands is exported.

Table 4.5. Contribution made by other countries to the fluoride deposition levels in the Netherlands

Country	Contribution (%)			
	dry (HF)	dry (aerosol)	wet (HF)	wet (aerosol)
The Netherlands	31	33	22	14
Belgium	17	23	23	29
West Germany	39	10	34	7
Britain	5	13	11	21
Others	8	21	10	29

- Dispersion on a regional scale

The Rhine-Meuse area

In the Netherlands, 33 brick works are situated in the region between the Rhine and Meuse over a relatively short distance. The OPS model was used to calculate the contribution made by the emissions from these sources to the annual average concentration (Eerens et al., 1988), incorporating the following assumptions (average per plant):

Emission : 8 tonnes per year
Chimney height : 25 m (50%) and 50 m (50%)
Heat emission : 0.6 MW
Gaseous F (HF) fraction : 70%

The meteorological data came from the National Airquality Monitoring Network, period 1976-1986. The results of the calculation are given in figure 4.12. It shows that the maximum contribution from the brick works is 0.18 $\mu g.m^{-3}$ (averaged over an area of 2 by 2 km around the source); averaged over the entire Rhine-Meuse area, this contribution increases the annual average concentration by 70% (0.044 $\mu g.m^{-3}$). The emissions from other industries in this area, such as a glass factory, a coal-fired electrical generating plant and a waste incinerator, are taken to be part of the emissions determining the background concentration contribution.

An idea of the variation of the concentrations (i.e., the emissions from the brick plants together with those causing the large-scale concentration) can be obtained from the accumulation observed on limed paper at the Puiflijk and Wageningen measuring stations of the National Airquality Monitoring Network during the period 1976-1985 (figure 4.13.). According to the relationship established by Bikker and De Leu (1986), the accumulations, averaged over the past few years (0.8 and 1.1 μg per gram of

paper per day, respectively), correspond to annual average concentrations of 0.16 and 0.19 $\mu g.m^{-3}$. This is in line with the calculated values (0.15 and 0.18 $\mu g.m^{-3}$, including the large-scale background concentration of approximately 0.06 $\mu g.m^{-3}$.

As regards the deposition rates, these are also higher in the Rhine-Meuse region than the national average values. Using the above-mentioned Operational Priority Substances (OPS) model, it was calculated that the deposition rates in this area (42x82 km) are approximately 40% (8.4 $mol.ha^{-1}.year^{-1}$ (dry) and 1.3 $mol.ha^{-1}.year^{-1}$ (wet)) higher than the national averages. This means an additional loading of the soil with 65 tonnes of fluoride per year, about 25% of the locally emitted amount.

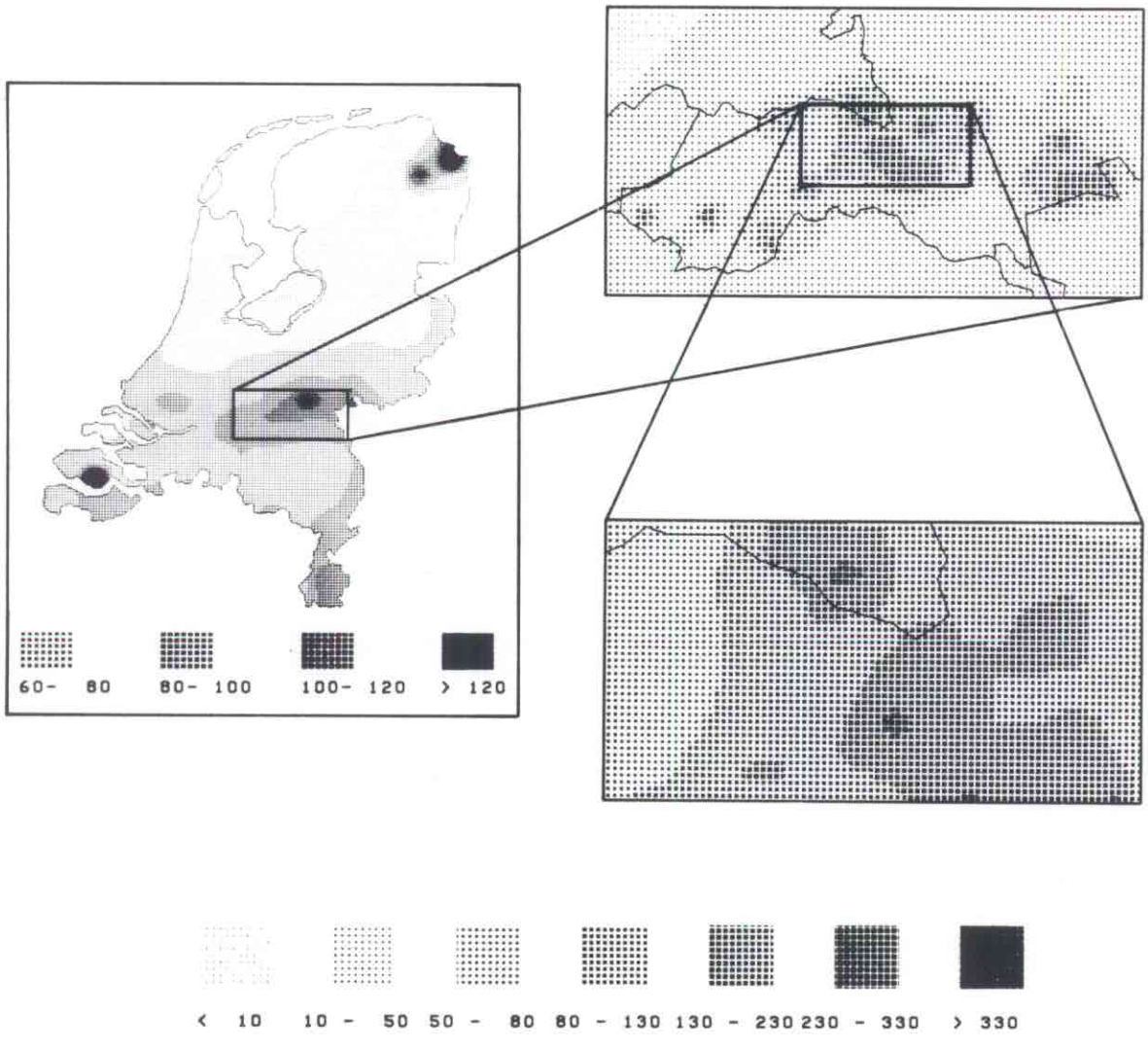


Figure 4.12. Calculated contribution to the annual average fluoride concentration by the emissions from 33 brick works in the Rhine-Meuse region (in $\mu g.m^{-3}$)

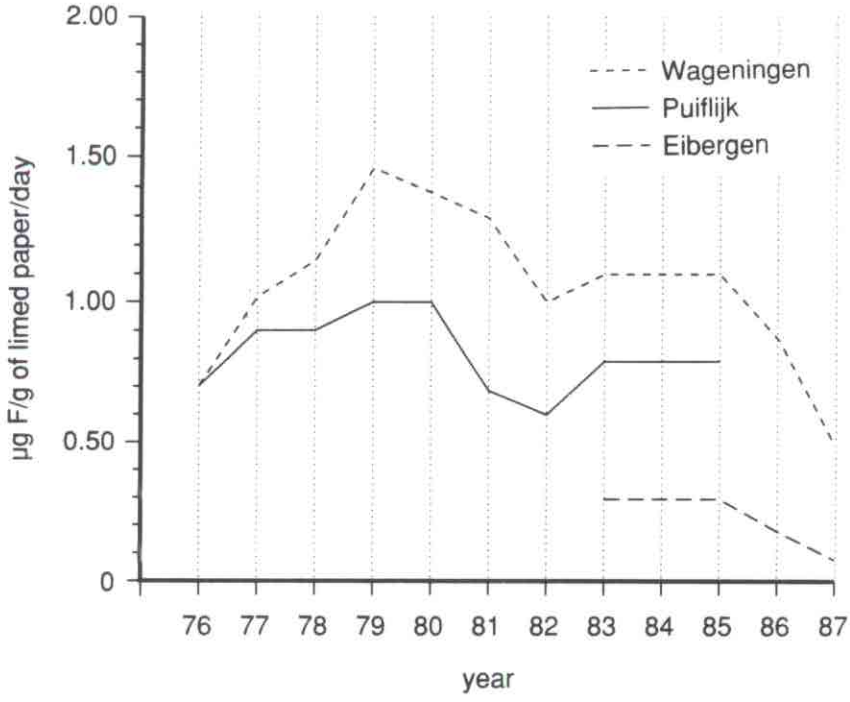


Figure 4.13. Annual average fluoride accumulations on limed paper at the Puiflijk, Wageningen and Eibergen measuring stations of the National Airquality Monitoring Network for the years 1976-1986 (CBS, 1986; RIVM, 1988)

East Groningen

As well as a number of smaller F-emitting brick works, the province of Groningen has an aluminium plant and a glass-fibre factory discharging relatively large amounts of fluoride into the atmosphere. Calculations made with the OPS model (figure 4.14.) over areas of 5x5 km indicate that the concentrations increased by about 160 % (0.08 $\mu g.m^{-3}$), on average, over the region as a whole (50x55 km). The maximum annual average concentration was 1.9 $\mu g.m^{-3}$. The dry and wet deposition rates increased by 10 and 1.8 $mol.ha^{-1}.year^{-1}$, respectively, and in the maximum by 260 and 15 $mol.ha^{-1}.year^{-1}$, respectively. This gives an additional F input to the soil of 32 tonnes.

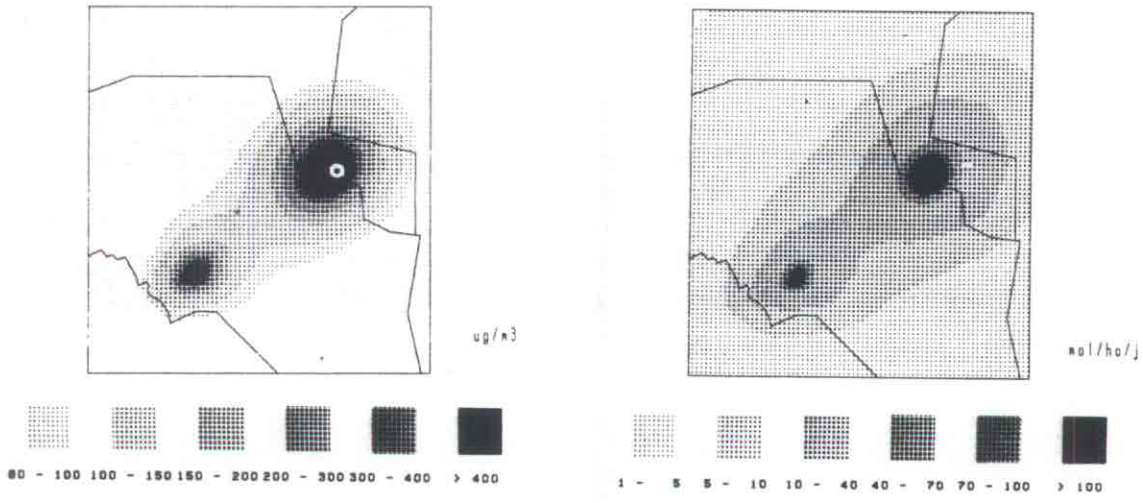


Figure 4.14. Contribution to the annual average F concentrations and deposition rates as a result of the emissions from two factories in East Groningen (Eerens et al., 1988)

Zeeland (Sloe area)

As in East Groningen, the fluoride pollution load in the vicinity of Flushing is relatively large, due to two industrial sources, including an aluminium plant. Using the OPS model, an annual average concentration of 1.3 $\mu g.m^{-3}$ (soluble + insoluble fluoride) was calculated for the maximum (4x4 km) (see figure 4.15.). Averaged over the area (42x28 km), the F concentration increased by about 50% (0.065 $\mu g.m^{-3}$).

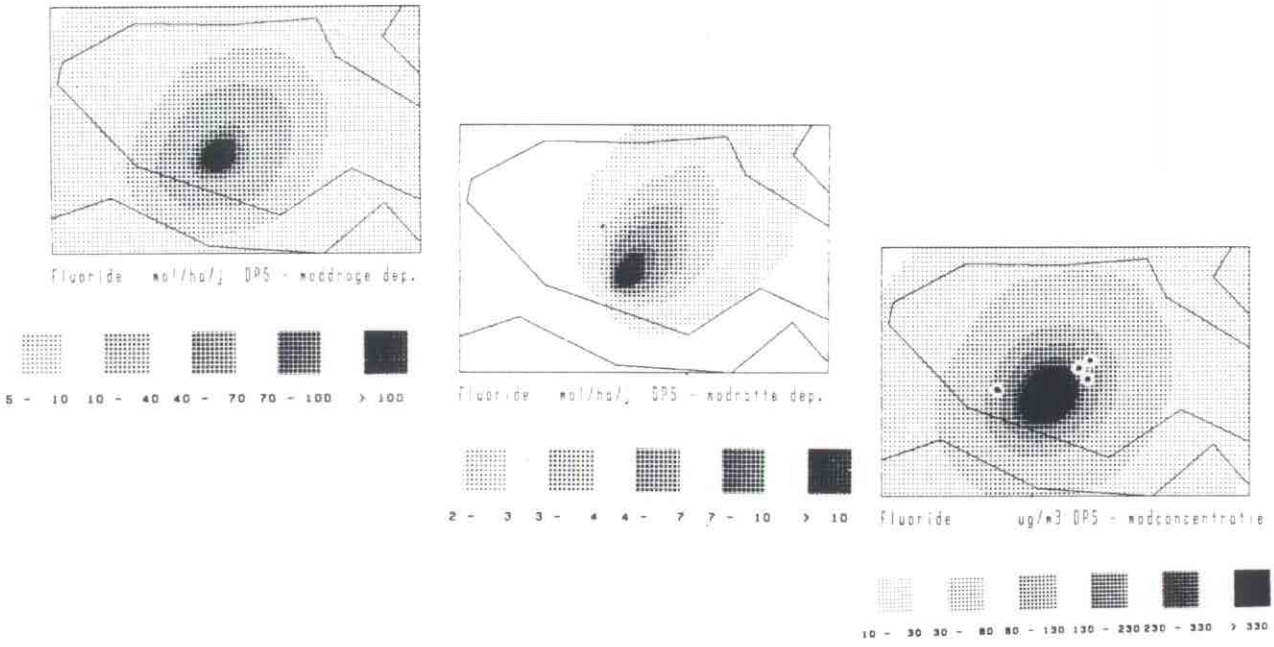
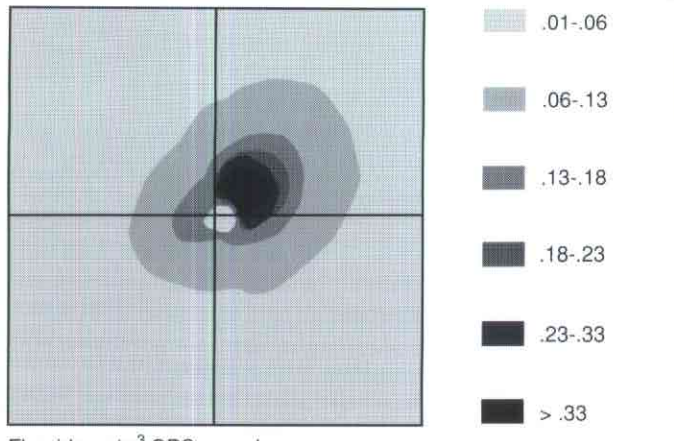


Figure 4.15. Contribution to the annual average F concentrations and deposition rates as a result of the emissions from two factories in the vicinity of Flushing (Sloe area) (RIVM, 1988)

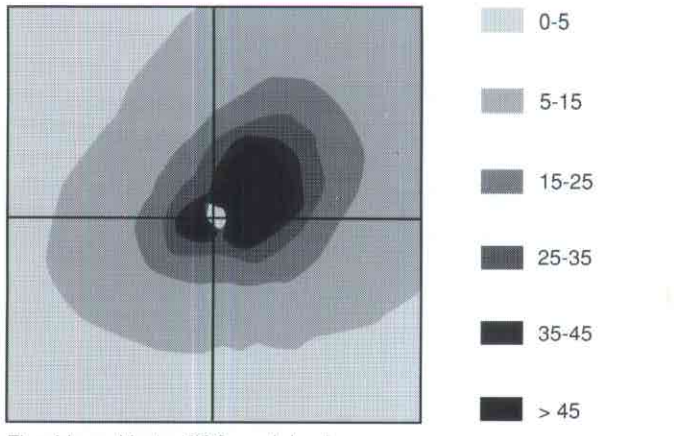
- Dispersion on a local scale

Local concentrations (calculated)

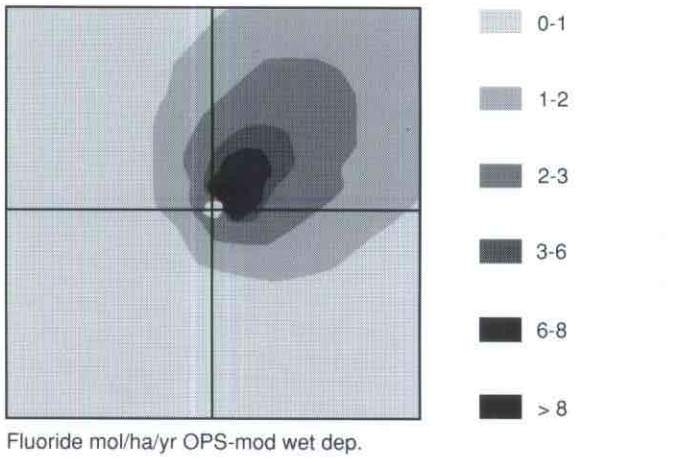
The magnitude of the industrial fluoride emissions can vary widely and is generally insufficiently known. The inaccuracy in the estimate can easily be a factor of 2. To illustrate the concentrations which may be observed near such sources, a medium-sized source was chosen, with an assumed emission of 1 kg F per hour. Calculations were made for chimney heights of 15 and 35 metres and for heat emissions of 0.5 and 1.5 MW. In addition, a "worst case" was further worked out (brick works emitting 14 tonnes of F per year). The results are given in figures 4.16-4.18. and in table 4.6.).



Fluoride µg/m^3 OPS – mod conc.

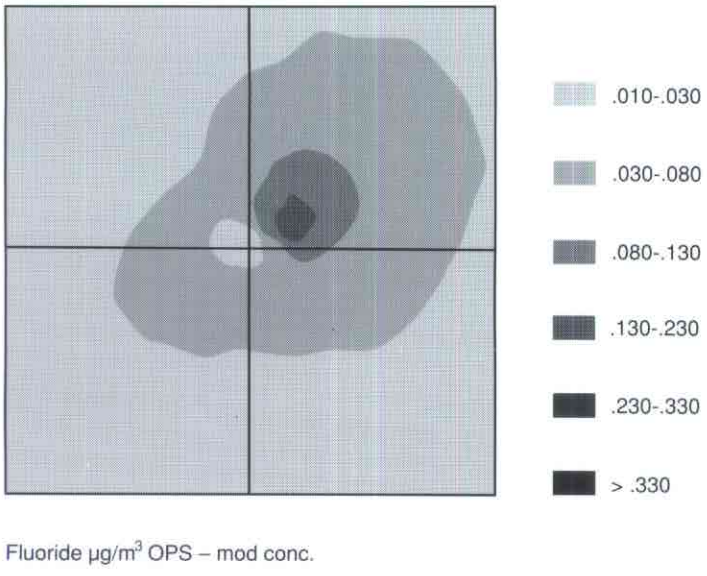


Fluoride mol/ha/yr OPS-mod dry dep.

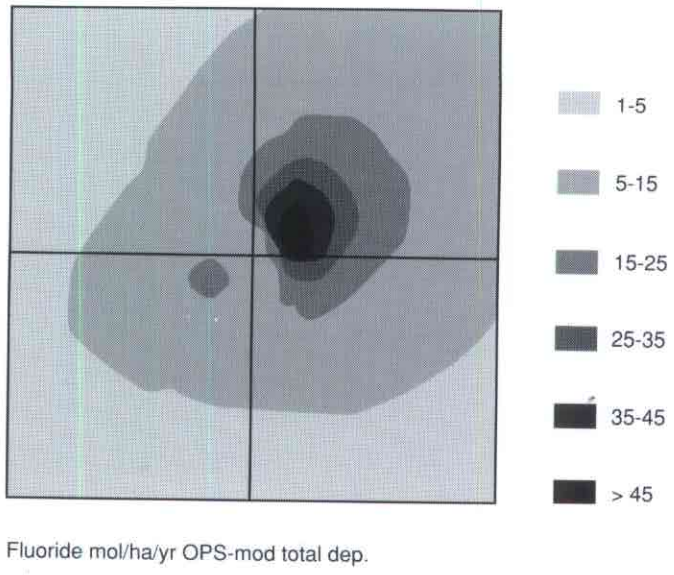


Fluoride mol/ha/yr OPS-mod wet dep.

Figure 4.16. Contribution to the annual average F concentrations (in µg.m^{-3}) and deposition rates (in mol per ha per year) from a 35-m-high source with a continuous F emission of 1 kg per hour and a heat emission of 0.5 MW; meteorological data from the NAMN, 1976-1986 (RIVM)

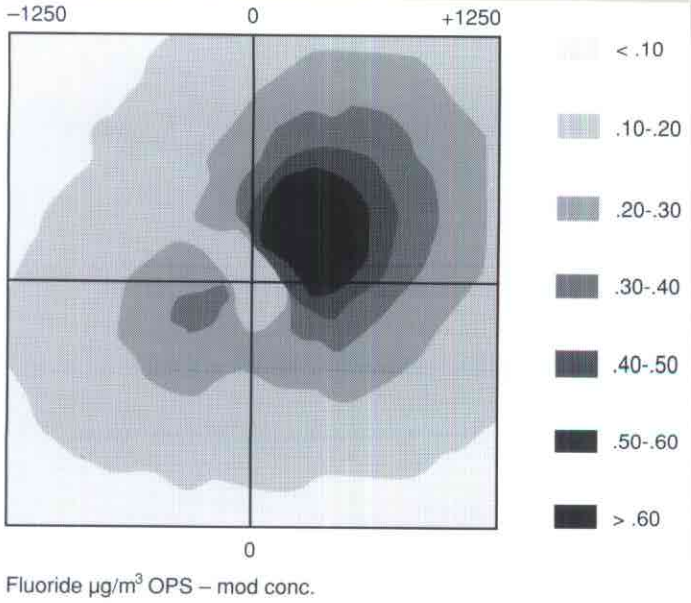


Fluoride µg/m^3 OPS – mod conc.

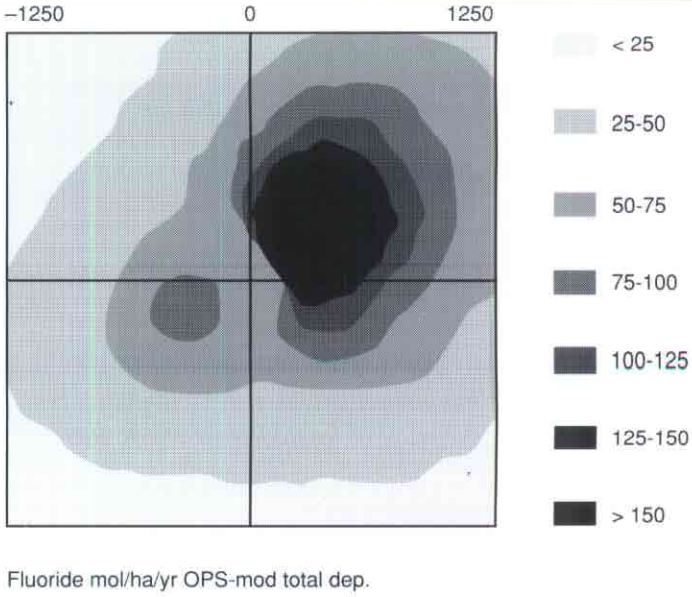


Fluoride mol/ha/yr OPS-mod total dep.

Figure 4.17. Contribution to the annual average F concentrations (in µg.m^{-3}) and deposition rates (in mol per ha per year) from a 5-m-high source with a continuous F emission of 1 kg per hour and a heat emission of 1.5 MW; meteorological data from the NAMN (RIVM)



Fluoride µg/m^3 OPS – mod conc.



Fluoride mol/ha/yr OPS-mod total dep.

Figure 4.18. Contribution to the annual average F concentrations (in ug/m3) and deposition rates (in mol/ha/yr) from a 10-m-high source with a continuous F emission of 14 tonnes per year and a heat emission of 0.65 MW; meteorological data from the NAMN (RIVM)

Table 4.6. Calculated contributions to the annual average F concentrations and deposition rates from a medium-sized source (emitting 1 kg of F per hour, 70% as HF and 30% as aerosol) for different discharge heights and heat emissions; meteorological data from the NAMN (RIVM)

Discharge height (m)	Heat emission (MW)	Max. concentration (at approx. 1 km) ($\mu g/m^3$)	Deposition rate (mol/ha/year) dry	wet
15	0.5	0.50	160	9
15	1.5	0.16	50	8
35	0.5	0.16	55	8
35	1.5	0.07	24	8
10	0.65	0.88*	300	18

* "worst case" maximum at 600 m, F emission of 14 tonnes per year

Table 4.6. shows that the maximum concentration is heavily dependent on the discharge height and heat emission; the influence of these parameters is small at greater distances. For the medium-sized source, the annual average concentration, including the large-scale contribution, will range from 0.14 to 0.57 $\mu g.m^{-3}$ in the maximum. The maximum annual average concentration, including the background contribution, is approximately 0.95 $\mu g.m^{-3}$ for the "worst case".

According to Bikker and De Leu (1986), the maximum daily average concentration in "background" areas is roughly a factor of 6 to 7 higher than the annual average. The maximum daily average would then be 0.4 to 3.5 $\mu g.m^{-3}$ for a medium-sized source, and 5 to 6 $\mu g.m^{-3}$ for the "worst case". The maximum of the growing-season average is about 75% of the annual average concentration, giving a maximum daily average of 0.3 to 2.6 $\mu g.m^{-3}$ during the growing season and 4 to 4.5 $\mu g.m^{-3}$ in the "worst case".

Local concentrations (measured)

Bikker and De Leu (1986) reported that annual average concentrations ranging from 0.2 to 0.4 $\mu g.m^{-3}$ have been measured at distances from 1.5 to 5 km from F-emitting industrial plants, which broadly agrees with the calculated values. Also, the interim F ceilings for the growing-season average (0.4 $\mu g.m^{-3}$) and the monthly average (0.8 $\mu g.m^{-3}$) may be exceeded regularly and the daily average (2.8 $\mu g.m^{-3}$) occasionally at a distance of 1500 m from industrial sources (Janssen, 1987). Table 4.7. summarizes the levels measured in the Netherlands.

Table 4.7. Fluoride concentrations ($\mu g.m^{-3}$) in the Netherlands (Bikker and De Leu, 1986)

Concentration	National	Industry up to 1500m	Industry 1500-5000m	Town centre residential area
Annual average	0.03-0.1	0.3-0.6	0.2-0.4	0.1-0.2
Growing-season av.	0.03-0.1	0.3-0.6	0.2-0.4	0.1-0.2
Monthly maximum	0.05-0.2	0.5-1	0.3-0.6	0.2-0.3
Daily maximum	0.2- 0.6	2 -5	0.8-2	0.5-0.8

The trend of the fluoride accumulations on limed paper near industrial operations in several locations is presented in table 4.8. The table shows that the accumulations have been static during the past 5 years, i.e., an average of 2.3 and 1.4 μg F per gram of limed paper per day for the locations in the Rijnmond area and the Sloe area, respectively. These amounts would (according to the relationship established by Bikker and De Leu, 1986) correspond to concentrations of 0.30 and 0.22 $\mu g.m^{-3}$, respectively. The corresponding maximum daily average would then be 2.1 and 1.5 $\mu g.m^{-3}$, respectively.

Table 4.8. Fluoride accumulations in μg F per gram of limed paper per day (IPO) (CBS, 1986)

Year	Vlaardingen	Spijkenisse	Sas van Gent
1977	2.8	3.9	2.0
1978	4.0	2.1	1.8
1979	3.2	1.8	1.6
1980	2.4	2.1	0.5
1981	1.8	2.5	1.2
1982	2.0	2.3	1.3
1983	2.1	2.2	1.5
1984	2.7	3.1	1.5
1985	2.1	1.9	1.4

Direct measurements (single-filter method; TNO) have also been made during the past ten years. The F concentrations have been measured over the past few years at two locations in N-East Groningen, at two locations in the Sloe area and at Sas van Gent. The annual averages are presented in table 4.9.

Table 4.9. Annual average F concentrations (in $\mu g.m^{-3}$) near industries in N-East Groningen, in the Sloe area and at Sas van Gent (CBS, 1986)

Year	N-East Groningen		Sloe area		Sas van Gent
	1.3 km SE	0.37 km NW*	6 km W	5 km NE	
1978-1979	0.6			0.21	0.29
1979-1980	0.6			0.20	0.36
1980-1981	0.54		0.24	0.28	0.39
1981-1982	0.46		0.17	0.22	0.27
1982-1983	0.32		0.20	0.24	0.25
1983-1984	0.22	0.8	0.19	0.22	0.28
1984-1985	0.42	0.5	0.24	0.25	0.26
1985-1986	0.40	0.6	0.25	0.25	0.34

* annual average, for 1985 the first 8 months only

Local depositions (calculated)

For a medium-sized F-emitting source, the maximum deposition rate varies between 32 and 170 $mol.ha^{-1}.year^{-1}$ (61 and 320 $mg.m^{-2}.year^{-1}$, see figures 4.15-4.18 and table 4.6.). The wet and dry deposition rates near a modern coal-fired power station have also been measured (PEO, 1986). The deposition maximum was found to be determined by the wet deposition rate (5 $mol.ha^{-1}.year^{-1}$, or 110 $mg.m^{-2}.year^{-1}$). This is more than twice the ional background deposition (dry + wet). It was also calculated that domestic coal-fired power stations contributed about 9% and those in other European countries around 40% to the fluorides deposited in the Netherlands.

Local depositions (measured)

Van Giezen (1982, 1984) reported monthly average deposition rates, determined with an open-top rain collector at several measuring sites in Zeeland. The highest rates were observed in the Sloe area, viz., an average of 9.1 $mg.m^{-2}.month^{-1}$ (4.8 $mol.ha^{-1}.month^{-1}$; 58 $mol.ha^{-1}.year^{-1}$) and a maximum of 20 $mg.m^{-2}.month^{-1}$ (11 $mol.ha^{-1}.year^{-1}$). On an annual basis, the deposition in Beek and Rotterdam is higher than in Flushing (table 4.10.)

*Table 4.10. Fluoride deposition rates in $mg.m^{-2}.year^{-1}$ ($mol.ha^{-1}.year^{-1}$) at three locations in the Netherlands **

Year	Beek	Rotterdam	Flushing
1983	80 (42)	73 (38)	70 (37)
1984	72 (38)	48 (25)	41 (22)

* Determined with an open-top rain collector, which includes only part of the dry deposition

The KNMI and RIVM (1983) have also determined deposition rates with an open rain collector in several locations. The highest values were found near Flushing: an average of 5.7 $mg.m^{-2}.month^{-1}$ (3 $mol.ha^{-1}.month^{-1}$; 36 $mol.ha^{-1}.year^{-1}$) and a maximum of 19.6 $mg.m^{-2}.month^{-1}$ (10 $mol.ha^{-1}.month^{-1}$).

- Indoor air

Occupational setting

In the period 1976-1980, F concentrations were determined from personal samples taken on operators of welding equipment in 7 machine shops and shipyards. The results are presented in table 4.11.

Table 4.11. F concentrations (in $\mu g.m^{-3}$) in machine shops and shipyards (Ministry of Social Affairs and Employment, 1987)

Plant	*Year*	*Concentration*	*Comment*
1	*1976*	*190- 1250*	*particulate only*
2	*1977*	*2200-16500*	
3	*1978*	*560- 6700*	*without exhaust*
3	*1978*	*500- 4300*	*with exhaust*
3	*1978*	*220- 1110 **	*background, particulate only*
3	*1978*	*30- 70 **	*background, gaseous only*
4	*1978*	*300- 400*	
5	*1979*	*1000- 2200*	
6	*1979*	*600- 2000*	
7	*1980*	*200- 1400*	

** Static measurements (i.e., not taken on equipment operators)*

The average F concentration in an aluminium plant in Sweden was 900 $\mu g.m^{-3}$ during working hours, 34% of which was in gaseous form (Ehrnebo and Ekstrand, 1986).

During welding operations in large rooms, average daily (workday) concentrations ranged from 30 to 200 $\mu g\ F.m^{-3}$ at a distance of 1 to 2 m from the welders. Higher averages were measured during welding activities in small, enclosed spaces: 500-6300 $\mu g\ F.m^{-3}$. Averages of 230 and 330 $\mu g\ F.m^{-3}$ were measured locally in an iron ore-processing plant (depending on sampling time, 12 minutes and 1 hour respectively).

Nonoccupational setting

As well as through transport from outdoors, fluorides may also be present in indoor air as a result of the use of fluoride-containing materials. In 1985 and 1986, following complaints about etched glass, HF measurements were made in five so-called Scandinavian wooden dwellings treated with a wood preservative (Improsol, containing 56% F) (see table 4.12.). After seven years the concentration measured was still as high as 22 $\mu g\ HF.m^{-3}$ (sampling time, 6-10 hours). No noticeable fall in the HF concentration was observed during the two-year-long investigation (Van der Wal, 1987; Neele, 1986; Barelds and Meijer, 1986). The concentrations in the rooms of a dwelling in which all the wood had been treated with a F-containing preservative were approximately 50 $\mu g\ F.m^{-3}$ (Van der Wal, 1987).

Table 4.12. Measurements made in five dwellings into which Improsol-treated wood had been incorporated

Location	*Date of building*	*HF concentration* $\mu g.m^{-3}$
Apeldoorn *	-	*11-49*
Oosterhout	*1984*	*18-37*
Rhoon	*1984*	*< 2*
Nieuw Beijerland	-	*38*
Rijnsburg	*1979*	*19-22*

* *the average concentration of 21 measurements was 23* $\mu g.m^{-3}$

4.2.4. Food, drinking water and dental preparations

- Food

The Memorandum on Fluoridation of Drinking Water (1973), the Health Council Recommendation (1981) and the Contaminants Booklet (Staarink and Hakkenbrak, 1987) mention a few F concentrations found in foods (table 4.13.).

Table 4.13. Fluoride concentrations (mg/kg^{-1}) in foods

Food	*Fluoride content*
Cereal products	*0.6 - 1*
Potatoes	*0.1 - 0.4*
Vegetables	*0.1 - 1.8*,***
Tea	*0.5 - 2.4*
Beer, wine	*0.06 - 6****
Meats	*0.22 - 1**
Milk (products)	*0.05 - 0.49*
Fish	*4.6 - 30**
Eggs	*1.2*
Miscellaneous (fruit, etc.)	*0.1 - 2*****

* *foreign data (mg F/kg): vegetables, 6.4; meats, 0.2-10; fish, 84.5; (McClure, 1949)*

** *contaminated areas in the Netherlands (mg F/kg of fresh product): kale, 40; endive, 5.5*

*** *the Memorandum on Fluoridation of Drinking Water (1973) reports (without citing sources) concentrations of up to 70 mg/l in wine. Note that the higher values in the table refer to wine; beer has relatively lower levels*

**** *F concentrations in "miscellaneous" are estimated values*

In 1973 and 1974, Biersteker and Zielhuis (1975) measured the F concentrations in vegetables grown in the vicinity of Borssele (table 4.14.). The F contents of unwashed products decreased with distance from the source. Of the ready-to-ate vegetables, endive and kale were the main sources of an increased F intake. Cooking did not appear to affect the F content.

Table 4.14. Fluoride concentrations (mg/kg) in vegetables grown in the vicinity of Borssele, measured in 1973 and 1974 (Biersteker and Zielhuis, 1975)

Vegetable	*Treatment received*	*F concentration*	
		dry weight	*wet weight*
Lettuce	*outer leaves, unwashed*	*52 - 146*	
	edible part, washed	*1 - 2*	*0.2 - 0.3*
Endive	*edible part, unwashed*	*6 - 72*	
	edible part, washed	*2 - 16*	*0.3 - 2.8*
Kale	*washed*	*7 - 46*	
	washed and cooked	*11 - 33*	*1.9 - 5.6*
Brussels sprouts	*unwashed*	*4 - 12*	
	edible part, washed	*1 - 8*	*0.2 - 1.4*

The F contents of endive and kale grown in the Sloe area were measured in the years 1975 and 1976 (Van Raay, 1977). The concentrations in endive were

similar to those in the study at Borssele, whereas kale was found to contain as much as 200 $mg.kg^{-1}$ dry matter. With a dry substance content of 14%, kale contained 40 mg $F.kg^{-1}$ fresh product. The F content of washed control crops from Zierikzee was 9 and 2 $mg.kg^{-1}$ dry matter for kale and Brussels sprouts, respectively.

There is little relationship between the F concentration in milk and that in the cow's diet. Recent data are not available: in 1973, milk was found to contain 0.2-0.4 mg $F.l^{-1}$ at concentrations in drinking water varying between 0.2 and 500 $mg.l^{-1}$ (Memorandum on Fluoridation of Drinking water, 1973), while in 1972 fluoride was measured in milk from a control and a fluoride-polluted farm (grass contained 82 mg $F.kg^{-1}$ dry matter) (table 4.15.).

Table 4.15. Fluoride content of milk ($mg.l^{-1}$), measured in 1972 in milk derived from 3 cows on a control farm and 3 cows on a fluoride-polluted farm, using the fluoride ion-selective electrode method (Tesink, 1982)

Origin of milk	*Fluoride content*	
	morning milk	*evening milk*
Fluoride-uncontaminated farm	*0.08*	*0.12*
Fluoride-contaminated farm	*0.27*	*0.34*

The data on wine are also for the most part out of date. According to information provided by the Amsterdam Food Inspection Department, the F concentration in wine varies between 0.06 and 0.5 $mg.l^{-1}$ (Hennig and Villforth, 1938; Fischler and Kretzdorn, 1942). The WHO (1970) reported that wine may contain up to 6 $mg.l^{-1}$, and according to the Memorandum on Fluoridation of Drinking Water (1973), without citing sources, it may contain as much as 70 $mg.l^{-1}$ (average, 60), depending on the use of fluoride compounds in spraying or winemaking.

Tea may contain high F concentrations naturally or as the result of additions during cultivation or fermentation. According to the Memorandum on Fluoridation of Drinking Water (1973), the F content of dry tea ranges from 3 to 300 $mg.kg^{-1}$ (average, 100) and 2 to 3 cups of tea contain an estimated 0.4 to 0.8 mg. Staarink and Hakkenbrak (1987) reported concentrations ranging from 1.2 to 2.4 $mg.l^{-1}$ for tea as a solution, based on German data of 1984. Singer et al. (1967) reported 52 to 161 $mg.kg^{-1}$ for five varieties of black tea and 336 $mg.kg^{-1}$ for a green tea. The Medicins

Bulletin (1982) assumes a value of 0.5 to 1 $mg.l^{-1}$ of tea infusion, the WHO (1970) 1 $mg.l^{-1}$.

Fluoride is concentrated in the calcified tissues of animals. Consequently, high F concentrations are found in chicken soup, bone meal, fish meal, fish protein concentrate, fish (canned sardines) and baking powder containing calcium phosphate. Mineral water and sea salt may also have high natural F levels (Memorandum on Fluoridation of Drinking Water, 1973) (table 4.16.). The WHO (1970) reported F concentrations in mineral water of up to 10 $mg.l^{-1}$.

Table 4.16. Fluoride contents ($mg.kg^{-1}$) of foods with a relatively high natural F level

Food	*Fluoride content*
Fish	*6 - 30*
Bone meal	*300 - 800*
Calcium phosphate	*600 - 1000*
Sea salt	*40 - 300*

High F levels (10 to 14 $mg.kg^{-1}$) have occasionally been found in rice and peas, depending on the use of F-containing abrasive in the polishing process.

Baby food contained between 0.04 and 0.20 mg $F.kg^{-1}$.

- Drinking water

Table 4.17. gives the F concentrations in Dutch drinking water per province. The maximum levels in Overijssel, South Holland, Zeeland and North Brabant and the average concentrations in South Holland and Zeeland are significantly higher than in the rest of the Netherlands.

Table 4.17. Fluoride concentrations in 1985, annual average for all pumping stations per province (in mg/l)

Province	Annual average concentrations	
	range	average
Groningen	0.04-0.14	0.10
Friesland	0.07-0.29	0.14
Drenthe	0.04-0.14	0.08
Overijssel	0.03-0.40	0.11
Gelderland	0.02-0.18	0.07
Utrecht	0.02-0.23	0.07
Flevoland	0.04-0.05	0.04
North Holland	0.04-0.21	0.12
South Holland	0.07-0.41	0.19
Zeeland	0.14-0.35	0.23
North Brabant	0.06-0.41	0.11
Limburg	0.03-0.30	0.12

- Dental preparations

Fluoride preparations for dental use are distinguished into low-F and high-F preparations (Medicins Bulletin, 1984). Preparations with low F concentrations are:

- fluoride tablets: 0.25 mg F per tablet;
- fluoride-containing toothpaste: 1000-1500 mg $F.kg^{-1}$;
- dental rinses for use once a week: 1000 mg $F.kg^{-1}$;

Preparations with high F concentrations are:

- solutions for topical application: 10,000 mg $F.l^{-1}$;
- gels for topical application: 4000-6000 mg $F.kg^{-1}$.

- Fodder

Table 4.18. lists the F content of uncontaminated forage (Health Council, 1981).

Table 4.18. Average fluoride content of forage (mg.kg^{-1} dry matter)

Forage	Content
Grass	15 *
Leguminous plants (clover, alfalfa)	8
Beet leaf	9
Mangel-wurzel	2

* *refers to English rye-grass; concentrations in other grass varieties generally ranged from 1 to 5 mg/kg dm (Tesink, 1982)*

At least once a month, fluoride concentrations are determined in grass samples taken in the vicinity of Sas van Gent, Delfzijl and Dordrecht, and in the Sloe and Rijnmond areas. In every case, the grass had an elevated F content. Figure 4.19. shows the concentration profiles of F in grass during the past few years. It is apparent that the F content is less in spring and summer when the grass is growing rapidly.

Rainfall or spray-irrigation may lower the F content since this washes off a proportion (varying from a few percent to several tens percent) of the fluoride deposited on grass surfaces. On the other hand, the F content of grass can increase through the use of commercial fertilizer. Fertilization with 4 kg of 18% superphosphate powder (1.7% F, by weight) per ha and with 12 kg of diammonium phosphate (2.45% F, by weight) per ha increased the concentrations to 1600 and over 500 mg F per kg of dry grass, respectively. They fell, partly due to showers, within 2 to 3 weeks to the pre-fertilization levels (study caried out in 1964; Tesink, personal communication).

In 1983, the fluoride levels were measured in fodder and soil in the canal zone near Sas van Gent and in the Sloe area (table 4.19.).

Table 4.19. Fluoride concentrations in fodder and soil (mg.kg^{-1} dry matter) measured in 1983 on livestock farms in the canal zone near Sas van Gent and in the Sloe area

Crop	*Canal zone*	*Sloe area*
Hay	*4 - 18*	*1 - 37*
Alfalfa		*3 - 13*
Bean-, pea- and barley straw	*4 - 10*	*2 - 17*
Maize silage		*9*
Grass silage	*17*	*7 -152*
Fresh beet leaf		*8 - 72*
Beet leaf silage	*42 - 72*	*33 -173*
Soil	*188 -310*	*205 -512*

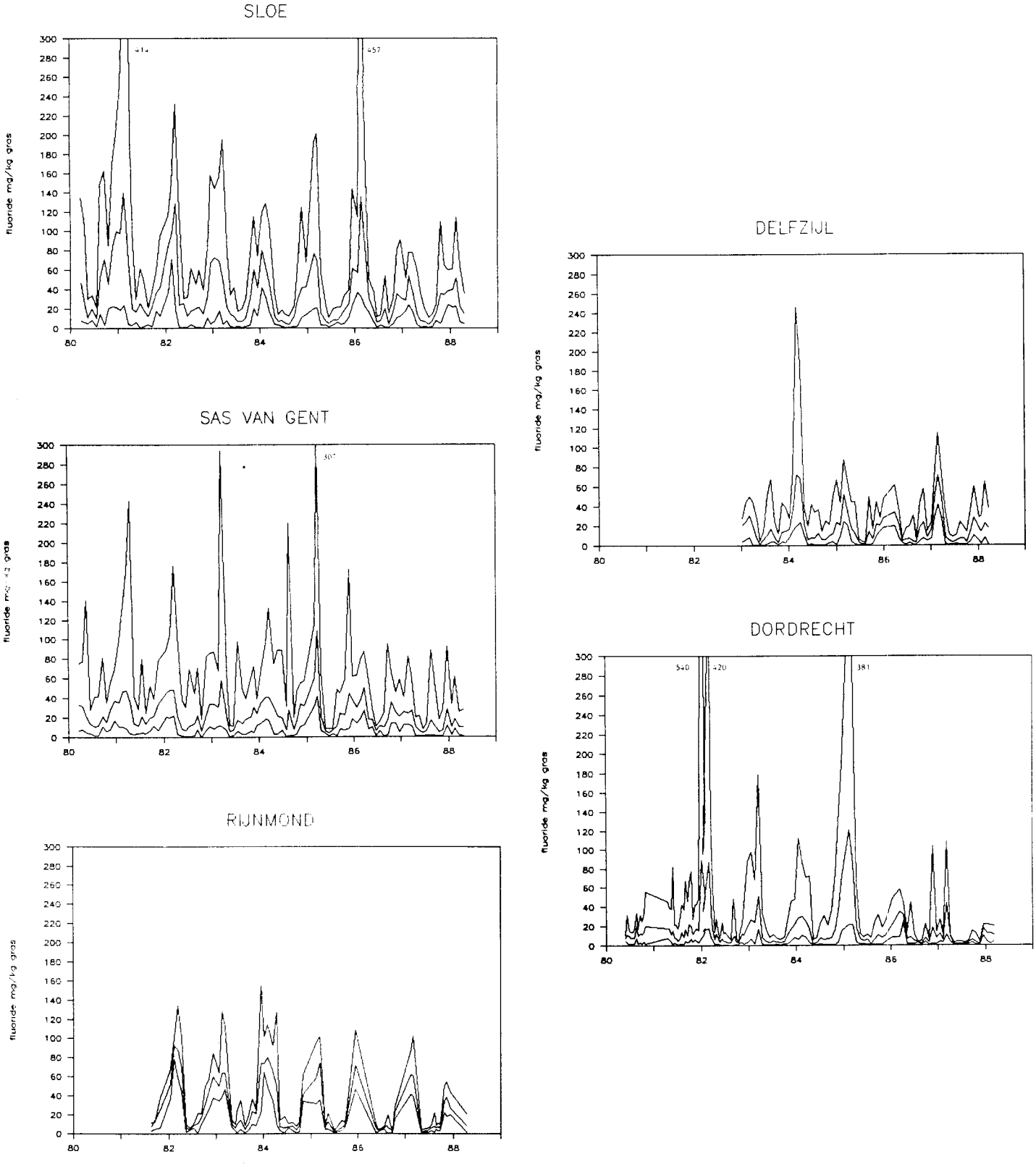


Figure 4.19. Concentration profiles of F in grass (mg/kg dry matter) in areas with emission sources. The average, maximum and minimum contents are given for each area

4.3. EXPOSURE LEVELS

4.3.1. Man

- Food

The exposure of man to fluoride via the diet is given in table 4.20. The average daily consumption of food is based on figures of the Ministry of Agriculture and Fisheries (concerning the consumption of foods, 1970-1977).

Table 4.20. Average daily consumption of various foods and beverages, their F content and the average daily F intake

Food	*Daily consumption (g)*	*F content (mg/kg)*	*F intake (mg/day)*
Cereal products	*161*	*0.6 - 1*	*0.10 - 0.16*
Potatoes	*165*	*0.1 - 0.4*	*0.02 - 0.07*
Vegetables	*157*	*0.1 - 1.8*,***	*0.02 - 0.28*
Tea	*350*	*0.5 - 2.4*	*0.18 - 0.84*
Beer	*235*	*0.2*	*0.47*
Wine	*26*	*0.06- 6*	*0.16 - 1.56*
Meat	*150*	*0.22- 1**	*0.03 - 0.15*
Milk (products)	*420*	*0.05- 0.49*	*0.02 - 0.21*
Fish	*16*	*4.6 - 30**	*0.07 - 0.48*
Eggs	*29*	*1.2*	*0.04*
Miscellaneous (fruit, etc.)	*349*	*0.1 - 2****	*0.04 - 0.70*
Total			*1.2 - 5.0*

** : foreign data (mg/kg): vegetables, 6.4; meat, 0.2-10.1; fish, 84.5 (McClure, 1949)*

*** : contaminated areas in the Netherlands (mg/kg of fresh product): kale, 40; endive, 5.5*

**** : F content of "miscellaneous" is an estimated value*

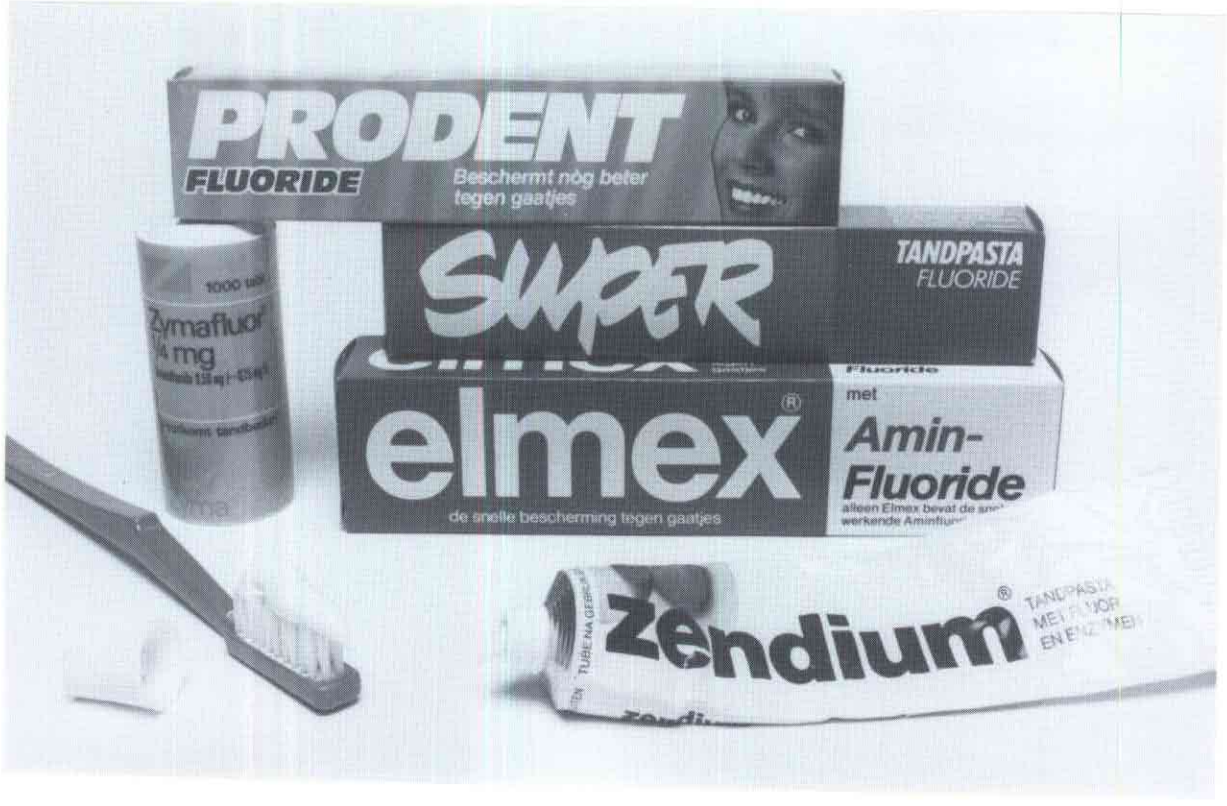
The Health Council (1981) estimated the daily dietary intake at 0.5 mg and the Memorandum on Fluoridation of Drinking Water (1973) at 0.4 mg, while the CIVO (1976-1981) (Staarink and Hakkenbrak, 1987) reported that the diet contains up to 3 mg of F per day. The data used in this document, however, indicate that this level may be appreciably higher.

- Drinking water

The amount of fluoride ingested in drinking water ranges from 0.03 to 0.68 mg per day with an average consumption of 1.65 l per day (excl. tea). The Health Council (1981) takes the fluoride intake from drinking water to be 0.5 mg per day.

- Dental preparations

It is estimated that 10% of toothpaste is ingested. At a daily consumption of 2.25 g of toothpaste, this works out at 0.2-0.3 mg F per day.



Fluoride in dental preparations: deliberate increase of F intake by man (photograph RIVM)

Eikman et al. (1960) reported that adults ingest 6-12% of the 1 to 2 g of toothpaste used per day. The calculated F intake is then 0.06-0.36 mg per day. A study of a group of children found that 7% swallowed 1-2 g of toothpaste per day, resulting in a dose of 1-3 mg F per day. Children on 2 fluoride tablets daily ingest 0.5 mg F per day.
The Health Council (1981) assumes the extra F intake by children via tablets and toothpaste to be 1 mg per day. The magnitude of exposure from the use of other dental preparations is not known (see subsection 4.2.4.).
The daily F intake by infants eating 0.8 kg of baby food per day ranges from 0.03 to 0.17 mg.

- Air

Indoor air

An average concentration of 0.02 mg $F.m^{-3}$ was mentioned in subsection 4.2.3. in dwellings where a wood preservative had been used. The maximum inhalatory intake by an individual breathing in 12 m^3 of air in a 24-hour period has been calculated at 0.2 mg F per day. In the workplace this may be a factor of 100 higher.

Outdoor air

The annual average intake via outdoor air (mg F per day) is (12 x 0.07 μg=) 0.0008 on a national scale, (12 x 0.12-0.18 μg=) approximately 0.001-0.002 on a regional scale, and (12 x 0.3-0.6 μg=) about 0.004-0.007 around sources. The maximum monthly and daily averages are higher by a factor of roughly 2 and 5-8, respectively.

- Total human exposure

Table 4.21. indicates that man takes into his body from 1.4 to 6.0 mg F per day, and that this comes mainly from food sources.

Table 4.21. Intake of fluorides by man in the Netherlands

Route	*Intake (mg F/day)*	*Contribution (%)*
Foods	*1.15 - 4.96*	*80 - 85*
Drinking water	*0.03 - 0.68*	*5 - 10*
Air	*< 0.01*	*< 1*
Toothpaste	*0.2 - 0.3*	*5 - 15*
Total	*1.4 - 6.0*	

Fluoride intake by children is lower because they consume less food than adults, especially wine, and higher because they swallow toothpaste and take fluoride tablets (an increase of up to 3.5 mg F per day).

A survey conducted in Borssele in 1973 (Biersteker and Zielhuis, 1974) revealed that:

- one third of the children took fluoride tablets;
- one third of the children cleaned their teeth with fluoride-containing toothpaste;
- two thirds of the households regularly ate vegetables from their own garden.

However, since it concerns here a risk area and as well as 15-year-old data, it is assumed that this exposure pattern is not representative of the Netherlands in 1988.

4.3.2. Aquatic life

The concentrations in water are important for aquatic organisms. The concentration in fresh waters varies between 0.01 and 1.3 mg $F.l^{-1}$. However, levels of 1.5-6 mg $F.l^{-1}$ have been measured in the Zeeland polder water and in the Terneuzen-Ghent Canal. The F concentration in the marine environment is 1.3 $mg.l^{-1}$.

4.3.3. Terrestrial life

Table 4.22. gives an indication of the difference in the amount of F ingested by cattle in uncontaminated and contaminated areas. It concerns an estimated 2000 head of cattle in the 5 problem areas, including 1000 in the Rijnmond area and 100-200 in each of the other areas. To convert the monthly average contents of grass (silage), hay and other components into annual average contents, the annual average levels were multiplied by a factor of 1.9 derived from the recommended guidelines given in table 1.9. As part of this integrated criteria document, an exploratory study was made of the percentage of absorption from soil particles (Van den Berg et al., 1988). It could be deduced from the simulation experiments that, at pH 2 and 35°C, the maximum amount of F available to cattle was 40 $mg.kg^{-1}$ of soil, that there were no significant differences attributable to variation in soil type and time of year, and that this level was relatively independent of the total F contents of the soil.
Table 4.22. shows that the difference in the amounts of fluoride ingested is a factor of 3 between F-polluted and F-unpolluted areas. Fluoride intake during the indoor period is approximately a factor of 2 lower than during the grazing period; the amount ingested may increase by 25 to 50% in cattle at pasture during the winter months. It might be concluded from this that, when the cattle are grazed in winter, the internal exposure level resulting from the basic feed of grass silage and hay will be no higher than in the summer period.
A different situation obtains with wildlife, particularly with ruminants such as stag deer and roe deer, which do rely on the natural vegetation as a source of food in winter. Moreover, these animals often graze along forest edges where the deposition level and, consequently, the F content of the vegetation is relatively high. The vegetation consumed may also exhibit a different accumulation profile than grass (see chapters 3 and 5). The

extent to which these wild ruminants graze in the vicinity of F-emitting sources is not known. However, F concentrations have been found to be higher in wildlife in areas with relatively high F levels than in unpolluted areas.

Table 4.22. Fluoride intake of mature cows via the diet (monthly average), in unpolluted (u.) and polluted (p.) areas (average values)

Feed product	Consumption (kg d.s./day)	Content (mg/kg d.s.)		Absorption (%)	Intake (mg F/day)	
		u.	p.		u.	p.
Grazing period (15/4-1/11)						
Grass	13	5	25	95	62	309
Concentrate (phosphatic minerals)	3	30	30	50	45	45
Water (l/day)	60	0.25	2	100	15	120
Soil	1	not significant (see text)			40	40
Total					ca.160	ca.515
Indoor period (1/11-15/4)						
Grass silage, hay	14.5	4	20	95	55	275
Concentrate	1.5	30	30	50	22	22
Water (l/day)	50	0.2	0.2	100	10	10
Total					ca. 85	ca.305
Grazing during indoor period						
Grass silage, hay	13	4	20	95	49	247
Concentrate	1.5	30	30	50	22	22
Grass	1.5	5	50	95	7	71
Water (l/day)	50	0.2	0.2	100	10	10
Soil	1	not significant (see text)			40	40
Total					ca.130	ca.390

4.4. SUMMARY AND CONCLUSIONS

Because of the different forms of occurrence of fluoride, a large number of analytical methods have been developed. Depending on the method selected, the total fluoride, the labile, the water-soluble, the gaseous, or the particulate fraction, or combinations thereof (biomonitoring), are determined. The most widely used method involves determination of the fluoride concentration with the fluoride ion-selective electrode, after preparation of the sample if required. Because of the differences in the available methods, the concentrations in the various environmental

compartments (as given in table 4.23.) are not strictly comparable. Concentrations in air higher than 0.1 $\mu g\ F.m^{-3}$ are readily measurable.
Food is the main source (about 80-85%) of fluoride intake in man, and varies between approximately 1.2 and 5.0 mg F per day. The F intake may be increased by 0.03-0.7 mg per day from the consumption of drinking water, and by less than 0.01 mg per day via inhalation. The use of F-containing toothpaste and other oral hygiene products may further increase the intake. The exposure level for most aquatic organisms can be equated with the concentration in the surface water (see table 4.23.); only predators at the top of the food chain may be subject to somewhat higher exposure levels because of bioaccumulation of fluoride in food organisms. For terrestrial organisms, the exposure level is much more strongly related to the type of species. The exposure levels vary with the season: during the summer period, aquatic organisms take in relatively more fluoride (because of reduced water flow) and terrestrial herbivores relatively less (because forage growth causes dilution of fluoride) than in winter. The F intake of cows in areas with low fluoride pollution is estimated at 85 to 160 mg per day; in areas with high fluoride pollution it is roughly 300 to 500 mg per day at most.

Cows grazing near a brick works (photograph RIVM)

Table 4.23. Indicative summary of fluoride levels in soil, water, air and food in the Netherlands

Soil				
- clay	80 - 700	mg/kg d.m.	(total F)	
	25 - 45	mg/kg d.m.	(pH 2 extractable)	
	3 - 4	mg/kg d.m.	(pH 7 extractable)	
- sand	60	mg/kg d.m.	(total F)	
	27	mg/kg d.m.	(pH 2 extractable)	
	6	mg/kg d.m.	(pH 7 extractable)	
- groundwater	0.07- 0.13	mg/l	(West Germany)	
Water				
- seawater	1.3	mg/l		
- fresh water				
natural	0.01- 0.3	mg/l		
Rhine (branches)	0.2	mg/l		
Meuse, Westerscheldt	0.2 - 6	mg/l		
ditches (polluted areas)	1.5	mg/l		
Air				
- concentration				
national	0.04- 0.1	$\mu g/m^3$	(HF)	
regional	0.1 - 0.2	$\mu g/m^3$		
local -annual av.	0.1 - 2	$\mu g/m^3$	(calculated)	
-monthly av.	0.2 - 1.0	$\mu g/m^3$	(measured)	
-daily av.	0.5 - 5.0	$\mu g/m^3$	(measured)	
- deposition				
national	31	mol/ha/year		
regional	31 - 60	mol/ha/year		
local	31 - 400	mol/ha/year		
Miscellaneous				
- food	0.2 - 30	mg/kg d.m.		
- drinking water	0.02- 0.4	mg/l		
- grass (unpolluted area)	1 - 10	mg/kg d.m.		
- grass (polluted area)	10 - 150	mg/kg d.m.		

5. EFFECTS

The data in sections 5.1. (human toxicity) and 5.2. (ecotoxicity) are a summary of a background report on the effects of fluorides. This report, which also contains the references discussed in these two sections, has been appended to this document (Janssen et al., 1988).
All the data processed concerning the effects on cultivated plants and livestock (5.3.) and the effects on materials, and on a global scale (5.4.), have been included in this integrated criteria document, with the exception of a concept publication on the derivation of atmospheric F concentrations on the basis of F concentrations in grass, which has been included in the above-mentioned report.

5.1. HUMAN TOXICITY

5.1.1. Metabolism

The degree of absorption of fluorides following ingestion and inhalation depends on the form of occurrence of fluoride. Water-soluble species (NaF, HF) are almost completely absorbed from the gastrointestinal tract, whereas the absorption percentages are considerably lower for sparingly soluble species. As regards the biological availability of fluoride to man, the increased solubility of fluoride compounds in the stomach, caused by the high acidity (pH = 1-3) prevailing in this organ, should be taken into account. Overall, an individual absorbs at least 45% of the fluoride present in food, but the proportion absorbed can also be as high as 100%.
Blood acts as the transport medium for fluoride. After long-term ingestion of F-containing drinking water, the plasma F concentration is approximately equal to the concentration in the drinking water, up to about 10 mg $F.l^{-1}$ of drinking water. Part of the fluoride absorbed by the body is deposited in the calcified skeletal and dental tissues. The storage capacity of these tissues is large. Children incorporate fluoride into their bones and teeth to a much greater extent than adults. After cessation of exposure, fluoride is slowly mobilized from the skeleton, and probably also from the teeth. Fluoride is excreted in urine, faeces and sweat, the urinary route being the most important. After long-term ingestion of F-containing drinking water, the F concentration in the urine is approximately the same as that in the drinking water, up to about 10 mg $F.l^{-1}$ of drinking water. The

mechanism of fluoride excretion via the kidneys consists of glomerular filtration followed by incomplete tubular reabsorption. Patients with chronic kidney dysfunction have a reduced capacity for excreting fluoride. In addition to excretion of unabsorbed fluoride in the faeces, some excretion of absorbed fluoride probably also occurs by this route. Only a few percent of the absorbed fluoride is usually excreted in sweat, but this may be as much as 30% when sweating is excessive.

5.1.2. Effects on laboratory animals

The available animal toxicity data give only a fragmentary picture of the dose-response relationship for the toxic action (oral and inhalatory) of inorganic fluorides. [Animal studies focusing on effects in specific organs are not discussed here but in 5.1.3.: "Effects on man", when they provide supporting information about comparable effects in man].

Gaseous fluorides (F_2, HF, SiF_4) severely irritate (etch) the skin, nasal mucous membranes and the respiratory passages. The LC50 values in rats for HF and F_2 were 1070 and 287 $mg.m^{-3}$, respectively (1016 and 143 mg $F.m^{-3}$, respectively), after exposure for 60 minutes. In mice and rats, the oral LD50's for NaF ranged from 32 to 52 $mg.kg^{-1}$ body weight (14 to 23 mg $F.kg^{-1}$).

Adequate subacute or (semi-)chronic studies in animals by oral or inhalation administration do not exist. The available carcinogenicity studies are too limited to permit an evaluation of the possible carcinogenicity of fluorides in laboratory animals. An oral carcinogenicity study with NaF is in progress in the United States as part of the "National Toxicology Program", the results of which are expected to be published in 1988.

There is no paucity of mutagenicity data. These concern for the most part studies with NaF. Data on other inorganic fluorine compounds are very scarce, if at all available. Sodium fluoride did not have any mutagenic effects in bacteria and Drosophila sp.. Sodium fluoride induced chromosomal aberrations in in vitro mammalian cells, but only when tested at cytotoxic concentrations, i.e, 10 $mg.l^{-1}$ and higher (4.5 mg $F.l^{-1}$).

Genetic mutations and DNA damage or SCEs (sister chromatic exchanges) have been observed in several in vitro systems exposed to NaF concentrations of 30 $mg.l^{-1}$ and higher; these concentrations also induced noticeable cytotoxic effects. No increase in chromosomal aberrations was observed in

several in vivo studies with mice. The available in vivo tests for DNA damage or SCEs were also negative. It can be concluded that NaF may cause genetic damage in in vitro systems exposed to high, cytotoxic concentrations. The mechanism by which fluoride exerts its toxic effect under these conditions is not understood. There are indications that fluoride, which inhibits many enzymes, interferes with the metabolism of DNA. There is no reason to expect that fluoride-DNA interaction occurs under physiological conditions, not even when the level of fluoride intake is relatively high. The occurrence of genetic damage does not therefore appear to be relevant in actual exposure situations.

Experiments aimed at establishing the teratogenicity and reproduction toxicity of fluoride are scarce. Adequate studies in commonly used laboratory animals are not available.

In reproduction studies with birds, toxic effects were observed in both the young and the parent animals fed diets containing 40 mg $F.kg^{-1}$ or more. Cows given 5 mg $F.l^{-1}$ or more in the drinking water produced fewer calves (according to Tesink - personal communication - this effect is not known in Dutch veterinary practice). Reproduction was not impaired in sheep given up to 20 mg $F.l^{-1}$ in the drinking water.

5.1.3. Effects on man

- Acute effects

Gaseous fluorides severely irritate the skin and pulmonary tract. F_2 had the greatest effect, followed in decreasing order by HF, BF_3 and H_2SiF_6. Some studies with HF have been conducted in volunteers, but were very limited as regards both set-up and reporting. The duration of exposure in these studies varied between 1 and 5 minutes. Concentrations of 13 mg $F.m^{-3}$ and higher were experienced as intolerable (the test subjects requested termination of the exposure); concentrations of 40 mg $F.m^{-3}$ and above produced severe irritation of the mucous membranes, while 2 mg $F.m^{-3}$ probably still had a mildly irritating effect. A 1967 study found that dark adaptation of the eye was affected at an exposure level of 28.5 μg $F.m^{-3}$, an effect which could also be produced by as little as 14 μg $F.m^{-3}$ when there was simultaneous exposure to 300 μg $SO_2.m^{-3}$.

The acute oral toxicity of fluorides varies with their solubility: the sparingly soluble calcium and aluminium salts are less toxic than the more

soluble sodium, potassium and magnesium salts. The lowest toxic dose reported for readily soluble fluorides was 1 mg $F.kg^{-1}$ body weight.

- Chronic effects

Effects on the teeth and skeleton

A large number of studies on the relationship between F content of drinking water and the occurrence of caries showed that fluoride prevents dental caries, particularly in children. The protective action of fluoride is observed at concentrations of 0.5 mg $F.l^{-1}$ and more in the drinking water, and increases with the concentration up to 2 mg $F.l^{-1}$. The symptoms of dental fluorosis begin to appear at 1.5 to 2 mg $F.l^{-1}$, caused by excessive F uptake by the dental enamel during its formation. Dental fluorosis is characterized by white patches in the enamel (mottling), and in more severe forms the teeth may be stained yellow to dark brown. The imperfect enamel is subject to more rapid attrition so that the dental pulp becomes (almost) exposed.

The ingestion of excessive amounts of fluoride may also lead to osteofluorosis, with the development of an abnormal bone structure and, possibly, exostoses. The maximum daily intake for prolonged exposure without any risk of osteofluorosis is 5 mg F. In non-tropical areas, no cases of fluorosis (absence of clinical symptoms) have been reported after ingestion of drinking water containing less than 4 mg $F.l^{-1}$.

In regions with a temperate climate, such as the Netherlands, the optimum drinking-water concentration is 1 mg $F.l^{-1}$; this level affords protection against caries without causing skeletal and dental fluorosis.

Carcinogenicity, teratogenicity and reproduction toxicity

A large number of epidemiological studies on a possible relationship between the incidence of cancer and exposure to fluorides via drinking water have been conducted in a variety of countries. The results of these studies indicated that fluoride is not carcinogenic in humans. The findings of the (less numerous) epidemiological studies aimed at investigating a possible teratogenic effect of fluoride were also negative. The available studies concerning occupational fluoride exposure did not provide sufficient evidence that fluoride is carcinogenic or impairs reproduction.

Effects on the respiratory tract

Adequate studies to assess the chronic toxicity of inhaled fluorides are not available. The lowest reported effect concentration in man was found in a study among aluminium smelter workers: pulmonary function was affected when the total F concentration was 500 $\mu g.m^{-3}$ (of which 200 $\mu g.m^{-3}$ gaseous components and 300 $\mu g.m^{-3}$ particulates).

However, a confounding factor here was the simultaneous presence of CO_2, SO_2 and benzo(a)pyrene, at concentrations of 11 $mg.m^{-3}$, 2 $mg.m^{-3}$ and 3.5 $\mu g.m^{-3}$, respectively.

Effects on the thyroid gland

The available human data do not indicate that the thyroid is adversely affected. The effect found in a recent, limited animal study is as yet insufficient reason for deviating from this conclusion.

Effects on the kidneys

In animal experiments, high oral dosages (22.5 mg $F.kg^{-1}$ body weight, acute; 22 and 100 mg $F.l^{-1}$ in drinking water, semichronic study in mice and rats, respectively) led to histopathological changes in the kidneys. The available data are too limited for establishing a no-effect level for this effect. The available human studies do not permit an unambiguous conclusion to be drawn.

Effects in kidney patients

Fluoride excretion in patients with renal insufficiency is below normal and they are consequently at increased risk when chronically exposed to fluorides. A limited study attempted to quantify this greater susceptibility. Fluoride retention in patients with renal insufficiency was the same as in healthy individuals at oral intake levels which were a factor of 3.25 lower.

Effects in residents near fluoride-emitting industries

Several studies focused on possible effects in residents near F-emitting plants. In only a few instances have the exposure levels been measured. A Russian study found in children an increased frequency of changes in the respiratory tract, with F concentrations varying between 98 and 485 $\mu g.m^{-3}$;

the results did not indicate whether these concentrations referred to gaseous fluoride or to total fluoride.
A limited Dutch study found no effect of F in lung function tests in children living near a HF-emitting factory exposed to measured concentrations (4-hour averages) of from 3 to 16 $\mu g\ F.m^{-3}$.

5.2. ECOTOXICITY

5.2.1. Aquatic organisms

- Accumulation

Fluoride is accumulated by aquatic organisms when exposed to both background and elevated concentrations.
At raised F concentrations, aquatic plants accumulate fluoride to a significant degree (relative to the background level) only when the exposure level is at least 10 to 50 $mg.l^{-1}$. The limited data available on F contents of plants growing in water with elevated F concentrations (10 to 50 $mg.l^{-1}$) yielded BCF values (bioconcentration factor, defined as the ratio of concentration in organism to concentration in water) ranging from < 1 to 7.5.
The limited data available on F contents of animals (crustaceans, fish) exposed to elevated F concentrations in the water yielded similar BCF values, calculated as fresh weight of whole organisms. The BCF values calculated on a dry ash-weight basis ranged from 50 to 150. Fluoride is accumulated mainly in the endoskeleton or exoskeleton. Muscle generally has the lowest F content. Nevertheless, the muscle of some types of aquatic organisms can accumulate fluoride to relatively high levels (in relation to average content of food). For example, in studies on bioaccumulation, the - edible - muscle of crabs (crustaceans) exposed to 10-30 mg $F.l^{-1}$ in seawater for 12 to 13 weeks contained 10-20 mg $F.kg^{-1}$ (fresh weight).
Mussels exposed to "undissolved" fluoride (CaF_2; phosphorus gypsum) accumulated significantly more fluoride than mussels exposed to "dissolved" fluoride (NaF).
Data on the movement of fluoride through food chains are very scarce. The available data indicate that biomagnification (accumulation through food chains) is insignificant.

It can be concluded that no considerable accumulation of fluoride by aquatic organisms is to be expected with elevated F concentrations (up to approximately 50 $mg.l^{-1}$) in the aquatic environment.

- Toxicity to freshwater organisms

The abiotic factors "hardness" and "temperature" have been shown qualitatively to have a distinct influence on the toxicity of fluoride to various types of aquatic organisms (crustaceans, fish). The toxicity is positively correlated with the temperature and negatively with the hardness. Because of the species-specific differences, it is not possible to give a generally applicable quantification of the effect of these parameters. Most of the data on the effect of hardness and temperature concern short-term tests: the observed LC50's usually differed by a factor of no more than 2 to 3 when either one of these parameters was changed. The effect of hardness on the toxicity of fluoride appeared to be greatest in relatively soft water, with a hardness of up to about 50 $mg.l^{-1}$ as $CaCO_3$. Unless indicated otherwise, the following data are based on nominal, total F concentrations. The concentrations have been expressed in the amount of fluoride present (mg $F.l^{-1}$).

Acute toxicity of fluoride

In single-species tests with the readily soluble sodium fluoride as the test substance, the 48 to 96-h L(E)C50 values for algae, crustaceans and fish ranged from 43 to 460 mg $F.l^{-1}$. Tests with ammonium fluoride and sodium hexafluorosilicate gave LC50's of the same order of magnitude. LC50 values varying between 2.7 and 5.4 mg $F.l^{-1}$ were found in tests with cryolite and F-containing effluent; the greater degree of toxicity of these compounds (based on measured F) is most likely due to the presence of aluminium, or one or more other substances.

Chronic toxicity of fluoride

In single-species tests conducted with sodium fluoride in the test water, the NOEC values for algae, protozoa, rotifera, crustaceans and amphibians varied between 3.7 and 370 mg $F.l^{-1}$. NOEC's [no-observed-effect concentration] and MATC's [maximum acceptable toxicant concentration] for species of fish are not available. With regard to the available NOEC values, relatively low effect concentrations (0.45-8.5 mg $F.l^{-1}$) were

measured especially in tests conducted in very soft water with a hardness of less than 20 $mg.l^{-1}$ as $CaCO_3$.

Field observations

Field data are not available except for one report of "healthy" populations of trout in surface waters containing up to 14 mg $F.l^{-1}$. Further information, for example, about the parameters, the fraction analyzed (dissolved, total) and the hardness of these waters was not given. Nor was it reported whether the above concentrations were the maximum concentrations measured or average values.

- Toxicity to marine organisms

Acute toxicity of fluoride

In single-species tests with sodium fluoride, 96 to 120-h L(E)C50's for algae, molluscs, crustaceans and fish varied between 10 and 500 mg $F.l^{-1}$. Only five L(E)C50 values are available. The LC50's measured in tests with ammonium fluoride and sodium hexafluorosilicate were of the same order of magnitude.

Chronic toxicity of fluoride

In single-species tests with sodium fluoride, the NOEC values were 50-200 mg $F.l^{-1}$ for algae (12 species), 60 mg $F.l^{-1}$ for molluscs (2 species) and 11 mg $F.l^{-1}$ for crustaceans. The effect concentrations were 5 mg $F.l^{-1}$ for crustaceans and 10 mg $F.l^{-1}$ for molluscs.

In long-term tests with experimental ecosystems - one consisting of nematoda, turbellarians, polychaetes and crustaceans, and the other of plants, crustaceans and fish - the observed NOEC's ranged from 4.1 to 5.9 $mg.l^{-1}$, based on measured F.

Field observations

Field studies indicated that both the number and the diversity of marine organisms may be adversely affected by effluent containing relatively low F levels. However, suitable data on exposure levels are not available; moreover, it is not clear to what extent these observations were influenced by other effluent parameters such as pH and/or the presence of other substances.

5.2.2. Terrestrial organisms

This subsection discusses only data on wild animals. The reader is referred to section 5.3. for data on farm animals.

- Accumulation

The F contents of both invertebrates and vertebrates were significantly higher in areas with relatively high F pollution than in unpolluted areas. Data on F concentrations in invertebrates indicate that the type of food plays an important role in F accumulation by these organisms. Several field studies showed that herbivores such as locusts had the lowest F contents and the lowest "accumulation factors" (defined here as concentration in organism from polluted area : concentration in organism from control area); pollinators (honeybees, bumblebees) and predators such as spiders had the highest values. The relatively high F levels in predators point to biomagnification in food chains consisting of invertebrates, but the data are ambiguous.

Vertebrates accumulate fluoride chiefly in the skeletal tissue. The skeletal fluoride concentration increases with age. The distribution of F in the skeleton of wild ungulates is similar to that in other mammals.

The bone fluoride content of mammals with symptoms of fluorosis derived from polluted areas was up to 100 times higher than that of comparable mammals from unpolluted areas. Data on F concentrations in the skeletal tissues of birds and mammals show the same food-dependent trend as was found for invertebrates: the lowest concentrations in herbivores and somewhat higher levels in omnivores and carnivores.

Based on the available data, biomagnification of fluoride through terrestrial ecosystems appears to be insignificant.

- Toxicity - experimental data

By far the majority of the available data concern experiments in which fluoride was administered in the diet, usually in the form of a readily soluble compound such as sodium fluoride. Most experiments were conducted with insects.

In experiments with insects, concentrations of 190 mg $F.kg^{-1}$ feed and higher, or 45 mg $F.l^{-1}$ of nutrient solution produced (sub)lethal effects. The readily soluble sodium fluoride was more toxic than sparingly soluble compounds such as calcium and magnesium fluoride. Fluoride incorporated in

plant tissue after fumigation of the plants with hydrogen fluoride, was less toxic than fluoride in the form of a readily soluble compound. This is consistent with the lower availability of plant fluoride to animals.

In several experiments in which insects were cultured on hydrogen fluoride-fumigated plants, the lowest plant F concentration which had no effect was 200 $mg.kg^{-1}$ dry weight. Concentrations of 400 $mg.kg^{-1}$ dry weight and higher had adverse effects on the insects.

A concentration of 6 mg $F.m^{-3}$ was lethal to fruit flies exposed to gaseous hydrogen fluoride for short periods of time. On long-term exposure, a concentration of 1.4 mg $F.m^{-3}$ adversely affected reproduction.

In an experiment in which Japanese quail were exposed for 6 weeks to varying amounts of sodium fluoride in the drinking water, 50 mg $F.l^{-1}$ had no effect on mortality, growth, skeletal parameters or egg shell thickness.

In a 2-year-long feeding experiment with deer aged 4 to 6 months, both exposure levels (25 and 50 mg $F.kg^{-1}$ of feed, nominally; measured concentrations, 44-50 and 69-75 $mg.kg^{-1}$ of feed) adversely affected the teeth and bones and, possibly, weight gain. According to the researchers, the dental lesions were more severe and the osseous lesions less severe than was expected on the basis of feeding experiments in cattle. The fluoride was administered as sodium fluoride.

A very high mortality rate among young foxes on several breeding farms due to reduced milk production by the mothers was ascribed to fluoride in the mothers' diet, ranging from 98 to 137 mg $F.kg^{-1}$.

- Toxicity - field data

Field studies showed that elevated atmospheric F concentrations may both decrease and increase insect populations. Honeybees are among the most sensitive insects, which is consistent with the relatively high degree of F accumulation by them.

In the vicinity of an aluminium plant, house martins were extremely rare in a zone with atmospheric F concentrations above 100 $\mu g.m^{-3}$ as compared with zones where the air contained from 60 to 100 μg $F.m^{-3}$, and less than 30 μg $F.m^{-3}$. It was not stated whether these concentrations related to total fluoride, nor whether other substances were also being emitted. A few other bird species were present in similar numbers in all three zones.

In areas with relatively high F concentrations of natural or anthropogenic origin, fluorosis has been described in several species of mammals (rodents, moles, ungulates). The dental and osseous lesions observed in

wild ungulates were broadly similar to those in domestic livestock suffering from fluorosis.

The major sources of fluoride to herbivores are vegetation and drinking water. Because of the large variation (found) in F concentrations in vegetation (range 2.5 to 900 $mg.kg^{-1}$ dry weight; unwashed) and water (range 0.5 to 24 $mg.l^{-1}$) in areas with cases of fluorosis in ungulates, it is not possible, on the basis of these field studies, to establish levels at which effects are or are not observed. Although sufficient data are available to justify direct extrapolation of data derived from experimental studies in domestic livestock to wild herbivores, cases of fluorosis have been reported in the latter group at lower skeletal F contents than was expected on the basis of studies with farm animals. Assuming a similar accumulation pattern, this implies that wild herbivores are or may be more susceptible to fluoride toxicity than domestic livestock, on a dietary F content basis. This greater susceptibility is probably due to the large variation in F intake by wild animals, in conjunction with the influence of other stress-inducing factors in the environment.

5.3. EFFECTS ON PLANTS AND LIVESTOCK

5.3.1. (Cultivated) plants

By far the majority of the data concern cultivated plants; data on "wild" plants are scarce.

- Uptake and accumulation

Uptake from the air

Plants take up fluoride mainly from the air. Atmospheric fluorides enter the plant through the stomata of the leaf as well as the cuticles and epidermis (Benedict et al., 1965; McCune et al., 1977). The HF molecule can penetrate more easily than the F ion (Collet et al., 1969; Chamel and Garrec, 1977; Kronberger, 1983). Since the pH of both the foliar surfaces and the plant liquids is rarely below 4, F compounds which are only soluble at lower pH's are not relevant to effects on plants because they are not absorbed.

In connection with fluoride toxicosis in cattle, the uptake of fluoride by grass has been studied quite extensively (De Temmerman, 1984; Van der

Eerden, 1986, 1988). Fluoride uptake and accumulation by grass proceeds until an equilibrium is attained, usually within 24 hours, and which is directly proportional to the atmospheric F concentration. The main process by which the F content of grass (Fg) decreases is dilution by plant growth, but F is also lost through desorption and death. Under dry conditions the half-time of fluoride in grass is approximately 4 days in summer and 12 days in winter. Rain can cause a sharp fall in the fluoride content of grass. This holds not only for fluorides deposited as particulates but also for the fluorides deposited in gaseous form. In species of plants other than grass, the rate of F absorption is usually lower and the residence time longer. A striking feature is that susceptible plant species accumulate less fluorides from a given dose than more resistant species.

Uptake from the soil

A large number of studies showed that plants can also take up fluoride through their root system. Soil pH is an important environmental determinant of fluoride accumulation: in several studies, the F content of plants was negatively correlated with the pH of the soil, at least up to a pH of about 6.5. Several other studies could not establish a significant relationship between the F content of crops and the total-F concentration in the soil; the F content of crops was sometimes correlated with a particular F fraction in the soil. Under normal conditions (i.e., without the application of an external F source such as a phosphate fertilizer or sludge), the availability of the fluoride present in soil to plants is low (Roorda van Eysinga, 1974; Hani, 1975; Davis, 1980). In a study in which freesias and oat plants were grown in a F-free atmosphere on 102 different Dutch agricultural soils with total-F levels ranging from 39 to 679 $mg.kg^{-1}$ dry weight, the concentration in freesias was nearly always less than 0.5 $mg.kg^{-1}$ dry weight (detection limit), a factor of 3 to 10 lower than with exposure in the field. This illustrates the relatively large contribution of F uptake from the atmosphere to the accumulation in the plant compared with F uptake from the soil. The F concentration in 75% of the oat plant samples varied between 0.5 and 1.0 $mg.kg^{-1}$ dry weight. The uptake of F from soil by grasses was also low (De Temmerman, 1984).

A laboratory experiment with Italian ryegrass grown in river clay with a total-F level of 150 $mg.kg^{-1}$ dry weight, or mixtures of this clay and F-contaminated sludge (giving maximum substrate concentrations of 450 $mg.kg^{-1}$ dry weight), showed that the F content of the grass may be considerably

increased (up to tenfold) in the presence of sludge, in any case soon after its application. Later grass crops generally had lower fluoride levels, the leaf lengths being equal, which can be ascribed to reduced availability and/or to a difference in growth conditions. Considering the test conditions (light, temperature) under which this study was conducted, its results may lead to overestimation of fluoride accumulation by this crop in field situations, exposure levels being equal (Davis, 1980).

- Effects

Atmospheric exposure

Once fluoride has entered the cells, it affects numerous physiological processes because it induces changes in the structure of chloroplasts, mitochondria and plasmalemma (Chang, 1975; Soikeli and Paakunaimen, 1981). Higher light intensity, higher relative humidity and higher temperature render the plant, up to certain limits, more susceptible to HF toxicity (Guderian, 1977). Young leaves, plants in the exponential growth phase, and plants about to flower are often relatively susceptible. The effect is partly determined by the availability of nutrients (EPA, 1978).

Although considerable research has been carried out on the effects of atmospheric fluoride pollution on plants, the available information is one-sided:

- for the most part, studies have focused on the effects of fluoride on the organ and organism. The lower levels of biological organization (biochemistry and cell) have received little attention, and the higher levels (vegetation and ecosystem) even less. However, there are indications that F-containing air pollution may adversely affect forests and other ecosystems (Niklfeld, 1967; Sidhu, 1978; Carlson and Hammer, 1974; Guderian and Ruppers, 1980), but as yet this information is not usable for establishing recommended levels.
- most studies were conducted under "laboratory" conditions and involved constant exposure levels. Fumigation experiments lasting more than a few months are exceptional.
- nearly all experiments involved exposure of plants to HF as the test substance; other F compounds were only occasionally tested.

Of the many hundreds of published fumigation experiments with plants, only twenty are of direct relevance for the establishment of a maximum permissible atmospheric F level. These relevant experiments are described

in Adams et al. (1956), Guderian et al. (1969), McCune (1969), Wolting (1978), Brandt (1981), Weinstein and Alscher-Herman (1982), and Murray (1983). On the basis of effect concentrations and no-effect concentrations found in these experiments, a relationship was derived between the NOEC (in $\mu g\ HF.m^{-3}$) and the exposure time T (in days):

$$NOEC = 0.76 \times T^{-0.22}$$

All the experiments (exposure periods ranging from about 1 day to 3 months) from which this expression was derived were carried out in cultivated plants (ornamental plants, fruiters and conifers), with foliar and floral lesions and growth reduction as effect parameters. The resultant calculated NOEC values (in $\mu g\ F.m^{-3}$) for exposure periods of 1 day (24 hours), 1 month and 3 months are given in table 5.1.

Table 5.1. NOEC's (in $\mu g\ F.m^{-3}$) for plants, derived from fumigation experiments with HF

	Duration of exposure		
	1 day	*1 month*	*3 months*
NOEC	*0.76*	*0.34*	*0.27*

In the afore-mentioned derivation of NOEC values, the results of two fumigation experiments, in which relatively low F concentrations already had an effect after exposure for a short period, were disregarded because of the difference between these results and those of the other experiments. In one of these, 15 different cultivars of hothouse tulips were fumigated intermittently (6 hours per 48 hours), resulting in foliar injury in 4 of these 15 cultivars after the third treatment; the average F level during the three fumigation periods was 0.10, 0.11 and 0.25 $\mu g.m^{-3}$, respectively (Wolting, 1978). In the other experiment, exposure of gladioli to approximately 0.15 $\mu g\ F.m^{-3}$ for 9 days damaged 6% of the leaf area (McCune, 1969).

The remaining published fumigation experiments were likewise disregarded in the above-mentioned derivation of NOEC values on the ground that they were performed at exposure levels which were either very high or poorly defined. Thus far, only the effects of HF on plants have been discussed. Too little information is available to permit derivation of NOEC values for other F compounds, but it is known that HF is the most phytotoxic of them all. The

differences in toxicity are strongly related to differences in rates of uptake (De Temmerman, 1984).

Exposure from the soil

Studies investigating the sensitivity of plants to soil fluoride are scarce.

In a pot experiment in which some 35 monocotyledonous and dicotyledonous cultivated plants were grown on in peat treated with fluoride-contaminated phosphate fertilizers, all the dicotyledons were resistant as well as several monocotyledons. Monocotyledonous bulbous plants and tuberous plants were found to be the most sensitive. The F concentration used in these pot experiments was not given.

In other experiments with freesia cultivars performed by the same author, fertilization with triple superphosphate (resulting in F concentrations of 18-74 $mg.kg^{-1}$ of peat, dry weight) caused more serious foliar injury than fertilization with monocalcium phosphate (giving F concentrations of 3-5 $mg.kg^{-1}$ of peat, dry weight). Fumigation with concentrations of HF ranging from 0.5 to 1.4 $\mu g.m^{-3}$ for at least 6 days resulted in a relatively high degree of foliar injury as compared with fertilization with triple superphosphate (Roorda van Eysinga, 1974). In another pot experiment, Roorda van Eysinga (1974) found weak, positive correlations between foliar injury and F contents (water-soluble F, "labile" F and total F) when freesias were grown in 102 Dutch agricultural soils (total F: 39-679 $mg.kg^{-1}$ dry weight; water-soluble F: 0.46-12.60 $mg.kg^{-1}$ dry weight). In addition to fluoride, other soil factors, especially the nitrate concentration, also played a part in foliar injury. In a pot experiment with Italian ryegrass, F levels in the substrate (mixtures of river clay and F-contaminated sludge; pH about 7) of up to 450 $mg.kg^{-1}$ dry weight had no effect, despite an increase in the F content of the crop from 6 to 60 $mg.kg^{-1}$ dry weight (Davis, 1980).

The idea that, with a high deposition rate of fluorides, soil processes will change in the course of decades as a result of the elevated F level so that the vegetation also becomes affected (Polomski et al., 1979; see also 8.2.1.) is of only hypothetical value. This is illustrated by a study in which the application of fluoride (as NaF) to a mineral soil reduced the yield of maize, starting with added F concentrations of about 200 $mg.kg^{-1}$ (equivalent to 24 $mg.kg^{-1}$ water-soluble F), possibly due to a secondary effect of aluminium which, the concentration of which, like that of

fluoride, was also increased in the plants (Hani, 1975). The reader is referred to chapter 3 for the behaviour of fluoride in the soil, and the effects of elevated F concentrations in soil on abiotic processes therein. In hydroponic cultures, foliar lesions were observed in susceptible crops (lily, freesia) starting with added fluoride concentrations of 1 $mg.l^{-1}$ (Roorda van Eysinga, 1974).

5.3.2. Livestock

- Intake and accumulation

Under normal conditions, the diet is the major source of fluorides in livestock; the direct inhalation of fluorides from the atmosphere contributes a negligible amount to the total fluoride intake, even in an area of relatively high atmospheric fluoride pollution (Rao and Friedman, 1975; Health Council, 1981; see also chapter 4, exposure levels). The ingested fluorides enter the stomach of the ruminant. The pH in the rumen varies between approximately 5 and 7, and in the abomasum between about 2 and 4 (Van den Berg et al., 1988). Regarding the toxicity of fluoride to livestock, it is therefore useful to distinguish between F compounds that are soluble at pH 2 and those that are not.

It is assumed that 90 to 95% of the fluoride incorporated in forage is absorbed; an absorption percentage of 30 to 35% has been reported for fluorides adhering to the foliage of plants, depending on solubility. In many instances, more than 90% of the fluoride intake from drinking water is absorbed. Cattle also ingest soil when grazing forage too closely, an average of 1 kg per day by a mature cow, thus contributing to the F intake (Health Council, 1981). However, only about 40 mg F is absorbed through the rumen wall from every kg of soil ingested, irrespective of soil type (Van den Berg et al., 1988), so that the intake from soil is insignificant compared to that from feed (and possibly drinking water). Also, livestock may temporarily ingest larger amounts of F when the pasture has been fertilized with a high-fluoride phosphate fertilizer.

After the fluoride has been absorbed by the body, a proportion of it is incorporated into the bones and teeth; the remainder is excreted, for the most part via the urine and a small fraction via the milk. F does not accumulate in soft tissues (Health Council, 1981; see also chapter 4). When cows were fed a ration (hay with added sodium fluoride) containing an average of 109 mg $F.kg^{-1}$ for 7 years, the fluoride levels in the milk

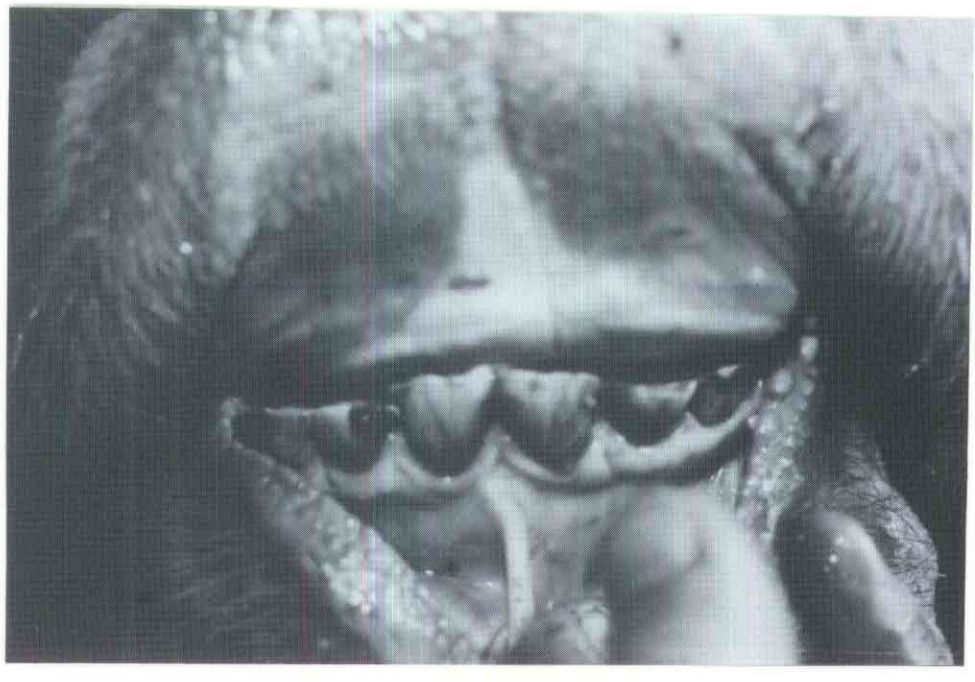
ranged from 0.1 to 0.2 $mg.l^{-1}$; the control group receiving untreated hay (10 mg $F.kg^{-1}$) produced milk containing between 0.04 and 0.06 $mg.l^{-1}$ (Stoddard et al., 1963).

- Effects

Absorbed fluorides can induce various types of effects:

- Impairment of the rumen flora and reduced enzyme activity in the gastro-intestinal tract. As a result, digestion and consequently food utilization are inhibited. This effect is characterized by abnormally thin faeces containing undigested forage residues.
- The enamel being formed during the period of tooth development is of inferior quality (therefore, only young animals are sensitive to excessive fluoride ingestion), resulting in an increased rate of wear, suboptimal mastication, and impaired (pre-)digestion.
- Enhanced bone dissolution and delayed bone formation. The tissues formed are deficient in calcium and phosphorus. Symptoms include stiffness, lameness, reluctance to stand.

All these effects eventually lead to loss of body weight and diminished meat and milk production.



Fluorotic lesions in dentition of a 4-to 5-year-old cow (source: Tesink)

Table 5.2. gives an idea of the sensitivity of different species of farm animals to fluoride, present in absorbable form (US NAS, 1974).

Table 5.2. "Tolerance levels" for domestic livestock, expressed in mg F per kg of dietary dry matter (US NAS, 1974)

Animal	*Pathological changes*	*Change in behaviour, decrease in agricultural value*
Young cattle	*30*	*40*
Mature cattle	*40*	*50*
Sheep	*not known*	*60*
Horses	*40*	*60*
Pigs	*100*	*150*
Poultry	*not known*	*300*

See text for details

Cattle are the most sensitive of domestic animals to dietary fluoride, particularly young animals. The long-term ingestion of fluorides by animals in excess of the indicated F levels in animal feed leads to the development of associated symptoms. The table distinguishes between "pathological changes" and "change in behaviour, decrease in agricultural value". The former category includes discolouration of the dental enamel and reduced enzyme activity in the gastrointestinal tract or bone marrow. Such changes do not naturally lead to a discernible change in behaviour or a decrease in meat or milk production (agricultural value), but they are indications of the occurrence of some effect. The latter category includes food intake repression, weight loss, diminished milk and/or meat production, and dental and skeletal lesions.

The maximum permissible concentration in the diet has been reported in the literature as 50 $mg.kg^{-1}$ (Hapke, 1977) and 80 $mg.kg^{-1}$ (Suttie, 1969). An in vitro study showed that at concentrations of about 80 $mg.l^{-1}$ and higher in the ruminal juice (which, according to the author, result from a F intake of about 2.5 mg and more per kg body weight; mature cattle ingest this amount when their diet contains about 80 mg $F.kg^{-1}$), fermentation was strongly inhibited, resulting in a reduced energy and protein supply (Prins, 1973). These acute effects, caused by an imbalance in the bacterial flora, lead directly to a decrease in milk and meat production (Tesink, personal communication).

On the basis of these literature data as well as feeding experiments conducted in the Netherlands and Dutch veterinary practice, the Health Council (1981) has established recommended limits for the maximum

concentration of readily absorbable fluorides in the total diet (see chapter 1, table 1.9.) to prevent adverse effects. For the most sensitive category (young cattle up to 1 year old), the recommended levels are 55, 45 and 30 $mg.kg^{-1}$ of forage (dry weight), not to be exceeded for more than one month, 2 consecutive months and one year, respectively).
In connection with the sampling frequency of grass in problem areas in the Netherlands (once a month), the monthly average of 55 mg $F.kg^{-1}$ of forage is adopted in practice as a maximum permissible level which should not be exceeded. These concentrations have not caused problems in practice (Tesink, 1968-1983).

Effect on milk production
In a feeding experiment, in which 3-to 4-month-old cows (8 per dosage group) were exposed continually to sodium fluoride-treated hay for about 7 years, the lowest dose (average F concentration 27 $mg.kg^{-1}$ of hay, on a dry weight basis) reduced the average daily milk production per cow by 7% in the first four lactations and by 4% in all lactations, compared with a control group fed untreated hay containing 12 mg $F.kg^{-1}$. This statistically not significant reduction is considered by the authors to fall within the normal biological variation (Stoddard et al., 1963). Such an effect on milk production is not measurable with normal management practices. In the same study, an average concentration of 49 mg $F.kg^{-1}$ in the diet had also no statistically significant effect on the average daily milk production per cow (a reduction of 10% and 8%, respectively), but this level did induce skeletal lesions and reduced the number of lactations, so that total milk yield fell by 18%. Data on the F contents of the concentrates fed to these animals (all dosage groups) in this study were not given.
Eckerlin et al. (1986) concluded, on the basis of a comparison of the experimental data of Suttie et al. (1957) and Stoddard et al. (1963) and their own results, that milk production by cattle already begins to fall at an average F level in the diet below the "tolerance level" of 40 mg $F.kg^{-1}$ dry weight adopted by the US NAS (1974) for productive ability, including milk production, at least, with continuous ingestion of F by the animals from a very early age. According to these authors, there is no reason for assuming that a "background" level of approximately 10 $mg.kg^{-1}$ dry weight guarantees optimal milk production.

NOEC values

On the basis of all available data, the following NOEC's have been derived for cattle in relation to the F content of the total diet (table 5.3.). These values are in accordance with the recommended concentrations set by the Health Council (1981) for young cattle on the understanding that the value of 55 $mg.kg^{-1}$ is taken to be a maximum and not a monthly average, this in connection with the sampling practice.

Table 5.3. NOEC values (in mg F/kg dry weight) for cattle with respect to the fluoride content of feed (total diet)

Criterion	*mg F/kg of feed (dry weight)*
Annual average	*30*
2-Monthly average	*45*
Maximum	*55*

When the amount of F emitted is more or less constant, an annual average concentration of 30 mg $F.kg^{-1}$ dry weight in grass corresponds to a grazing-season average of about 20 mg $F.kg^{-1}$ dry weight. With this annual average concentration, the levels in the winter season can be as high as about 100 $mg.kg^{-1}$ dry weight (Van der Eerden, 1988).

In deriving the NOEC's for cattle (table 5.3.), no account was taken of several factors which could possibly favour an extra safety margin:

* the proportion of stored silage in the ration of cattle is greater now than has been the case in the past, possibly causing a slight fall in the ruminal pH as compared with the pH with normal grazing. As a result, a somewhat larger fraction of the ingested fluoride may be absorbed by the animal.
* The Dutch dairy herd now produces much more milk owing to inbreeding. This high milk yield makes great demands on the animal and renders it more susceptible to external factors.
* Relatively little veterinary research has been conducted into the effects of fluoride, particularly on milk production. (On the other hand, the few experimental studies which have been performed, concerned, almost without exception, animals stall-fed the relatively readily soluble sodium fluoride; their relevance to the field situation has been questioned by Krook and Maylin (1979).

Relationship between NOEC's in grass and in soil

The ingestion of a certain amount of soil by grazing animals contributes to the total F intake. An exploratory study into the availability to cattle of soil fluoride, conducted by the RIVM as part of this integrated criteria document, estimated that the absorption of fluoride from river clay was about 10% and that from humous sand 50%. From the samples examined, 40 ± 10 mg $F.kg^{-1}$ were extracted at pH 2 (pH in the rumen), irrespective of soil type (Van den Berg et al., 1988). On the basis of these absorption percentages and an estimated 95% absorption of the fluoride present in grass, estimates can be made, using the formulas drawn up by Van der Eerden (1986), of acceptable F concentrations in soil, presupposing certain levels in grass. It is assumed here that the animals are not fed supplementary foods (even in winter, although this is done in practice), and a distinction has been made between the summer and winter seasons concerning the difference in soil intake during grazing (an estimated 5% in summer and 20% in winter of the total feed intake). These estimates indicate that, compared to the F level in grass, relatively high to very high F concentrations in soil are required to reach the maximum acceptable concentration of 55 mg of absorbable fluoride per kg dry weight in the total diet (grass + soil), especially in the summer season. This information leads to the conclusion that soil is not an important source of F intake (see also table 4.22. and accompanying text).

Relationship between NOEC's in grass and atmospheric F concentrations

With the help of the formula drawn up by Van der Eerden (1983) (see 4.1.3.), atmospheric F concentrations can be derived from F concentrations in grass (see also the concept publication by Van der Eerden, included in the Appendix). The relationship between these two concentrations is strongly determined by the amount of biomass, and therefore heavily dependent upon the season. When the afore-mentioned NOEC of 55 mg $F.kg^{-1}$ dry weight is used as the maximum content of grass (see table 5.3.), it can be calculated that the atmospheric F concentrations (as 24-hour averages) should not exceed 0.8 $\mu g.m^{-3}$ during the grazing season and 0.3 $\mu g.m^{-3}$ at other times. If the year were to be divided into more than two parts, then these maximum daily values for the atmospheric F concentrations would be somewhat higher: here, the least favourable period in each part (both parts) of the year has been chosen. In any case, with the common frequency distributions for atmospheric F concentrations, both upper limits are more

than sufficient to ensure that even the annual average NOEC (30 mg $F.kg^{-1}$ dry weight) is not exceeded.

Relationship between NOEC's in grass and atmospheric F deposition

The relationship between atmospheric wet and dry deposition rates of F and F levels in grass is difficult to qualify: F uptake by grass is "more efficient" at high than at low atmospheric concentrations, and can even be negative (elimination instead of accumulation). In addition, deposition velocities from F contents of grass can only be derived when measurements or assumptions are made with respect to the amount of above-ground biomass, removal of fluorides by mowing and grazing, and the residence times of F in grass. The deposition velocities obtained from grass sampling (De Temmerman, 1984; Davison, 1982), 1 $cm.s^{-1}$ in summer and 0.3 $cm.s^{-1}$ in winter, are probably gross underestimations of the actual deposition velocities (see chapter 3).

On the basis of certain assumptions (Van der Eerden, unpublished) and the afore-mentioned maximum permissible atmospheric F concentrations (maximum daily values), maximum permissible deposition rates can be calculated which, in view of the uncertainties about the parameters involved, are only indicative. These calculated maximum permissible deposition rates are 7 g F per ha per day during the grazing season and 0.7 g F per ha per day during the winter season.

5.4. EFFECTS ON MATERIALS AND ON A GLOBAL SCALE

5.4.1. Effects on materials

Solutions of hydrogen fluoride are known for their aggressive properties and are therefore often used as a strong solvent for sparingly soluble substances (digestion procedures in analytical chemistry). Although the concentrations in rainwater and in moisture films on surfaces of materials are much lower, HF may be expected to damage materials because of its aggressiveness. Both the acid properties of HF and the more specific influence of the F ion may play a part in this.

However, in the literature on pollutant damage to materials, HF and other fluorine compounds have received very little attention. A literature search yielded only a few qualitative indications about possible effects of HF in particular. Concentrations of 1000 $\mu g\ F.m^{-3}$ in combustion gases are

reportedly harmful to reinforced concrete (Rabald, 1968). In extremely high concentrations, HF and SiF_4 can etch glass and other Si-containing materials (Yocom and Stankunas, 1982). Under these conditions, other effects would also be expected, such as corrosion of metals. Ceramics, glass and enamelled or glazed materials have been described as the most sensitive materials (Yocom and Baer, 1984; Yocom et al., 1986).

Doyle and wright (1982) reported relatively rapid damage to aluminium following exposure to HF-containing fumes from aluminium smelters. Luckat (1973, 1974) suggested a contribution to the corrosion of iron and damage to stonework (Cologne Cathedral), based on data on exposure to fluorides, among other substances, in conjunction with data on damage to these materials. However, the role of fluorides in this was not made explicit, either qualitatively or quantitatively.

Yocon has remarked in several of the cited reports that the strict control of fluoride emissions, in connection with the susceptibility of vegetation, has virtually eliminated possible damage to materials at the current atmospheric F concentrations. This view is in line with the experience in the Rijnmond area where the complaints about damage to glass in the vicinity of HF sources have now ceased (Besems, 1987). Measurements have been made following complaints about etched glass in "Scandinavian" wooden dwellings. It appeared that the wood had been treated with the preservative Improsol which contains 56% fluoride. The concentrations measured in these dwellings varied between 11 and 49 $\mu g\ F.m^{-3}$, with an average of 23 $\mu g\ F.m^{-3}$ (Barelds and Meyer, 1986).

Insofar that the damage by HF is due exclusively to its acid properties, it can be noted that the contribution of HF to the total acid deposition is very small (of the order of 1%).

5.4.2. Effects on a global scale

Zander et al. (1987) estimated the amount of HF in a column of air up to 100 km above the Earth's surface to be 7.5×10^{14} molecules per cm^2 (in the year 1986). This corresponds to an average concentration, at 1 atmosphere, of about 20 $ng.m^{-3}$. The principal HF source in the stratosphere is the photodissociation of chlorofluorocarbons (CFCs) at an altitude above 25 km. In 1982-1984, the proportion of fluoride in the production of CFCs amounted to some 300 ktonnes (table 5.4.). This is of the same order of magnitude as the anthropogenic fluoride emission. The production (in F) of the major CFCs (F-11 and F-12) in 1952, 1960 and 1970 was 60 (15), 120 (30) and 550 (130) ktonnes, respectively; the emissions of these two substances were within the same range. The half-life of these compounds is 65 and 120 years, respectively (table 5.4.). The HF formed is very stable and does not play an important role in the stratospheric chemistry. The only mechanism for removing HF is diffusion to the troposphere, followed by rainout.
Measurements made during the past eight years showed that the amount of HF has increased by an average of 8.5% per year, equivalent to a doubling of the concentration over this period. In view of the half-life of HF and the emission figures presented in table 5.4., it may be assumed that the HF concentration will increase a further tenfold in the next 30 years.

Table 5.4. Production and half-life of several fluorine-containing CFCs (WMO, 1986)

Compound		*Conc. (pptv)*	*Half-life (in years)*	*% F*	*Production (ktonnes)**	
					CFC	*F*
CCl_2F_2	*(F-12)*	*320*	*120*	*31*	*400*	*120*
CCl_3F	*(F-11)*	*200*	*65*	*14*	*310*	*43*
$CHClF_2$	*(F-22)***	*52*	*20*	*44*	*210*	*91*
CF_4	*(F-14)*	*70*	-	*82*	-	-
$C_2Cl_3F_3$	*(F-113)***	*32*	*90*	*29*	*140*	*41*
$C_2Cl_2F_4$	*(F-114)*	*13*	*180*	*44*	*14*	*6*

* *annual production figures, period 1982-84*
** *some substances, especially F-22 and to a lesser extent F-113, are reused in part as a raw material for subsequent production; only part of the amount produced will reach the air in the long term*

The stratospheric HF concentration can be regarded as a source of HF in the troposphere. Its significance is difficult to assess owing to the lack of data on the exchange velocity between stratosphere and troposphere. If, with some caution, the exchange velocity is assumed to be 1/5 (about 24

ktonnes) of the total HF load in the column per year, then this gives a source contribution of 0.048 $mg.m^{-2}$ a year. Because of the high deposition velocity of HF, its concentration falls rapidly with decreasing height. At an average deposition velocity of 1.5 $cm.s^{-1}$, the contribution of HF to the large-scale F background level (ca. 3 $ng.m^{-3}$) is about 0.1 $ng.m^{-3}$. Without any loss, and assuming that the relative proportion of HF in the air was the same over the entire column, the concentration at sea level would be around 20 $ng.m^{-3}$. The sum of the wet and dry deposition rates is almost the same as the flux to the troposphere, 0.048 $mg.m^{-2}.year^{-1}$ (0.03 $mol.ha^{-1}.year^{-1}$).

It can be concluded that the contribution of the stratospheric HF to the HF concentration in the troposphere is only very small under current circumstances (about 3%). However, in view of the trend in the CFC emissions over the past 30 years and the long life of CFCs, their contribution to the tropospheric HF concentration could increase to 20 to 30% (about 1 $ng.m^{-3}$) over the next 50 years and to about 50% (about 3 $ng.m^{-3}$) in the still longer term. Compared with the no-effect level of approximately 30 $ng.m^{-3}$ (annual average), no effects are to be expected on a global scale for the present.

5.5. RISK ASSESSMENT

5.5.1. Man

There are indications that fluoride is an essential nutrient, but conclusive evidence is still lacking. It has been shown that fluoride plays a role in the development of dental enamel and the skeleton. A minimum F requirement cannot be given.

The available experimental data from animal toxicity studies give only a fragmentary picture of the dose-response relationship, after both ingestion and inhalation. For the effects of fluoride on the thyroid and kidneys observed in laboratory animals, human studies provided no evidence and insufficient evidence, respectively.

The available carcinogenicity data are too limited for an evaluation of the possible carcinogenicity of fluorides in laboratory animals. In mutagenicity studies in in vitro systems, performed mostly with sodium fluoride, high cytotoxic concentrations caused genetic damage. All in vivo mutagenicity studies were negative.

The results of epidemiological studies, both in the general population and among occupationally exposed persons, do not suggest that fluoride is carcinogenic in man.
The contribution of inhaled fluoride to the total F intake is negligible compared with the amount ingested.

A large number of human studies have shown that the consumption of F in drinking water prevents dental caries, especially in children, at a concentration of 0.5 $mg.l^{-1}$ or higher. The symptoms of dental fluorosis begin to appear at 1.5 to 2.0 mg $F.l^{-1}$. The contribution of the diet to the effect of fluoride on dentition is insufficiently known. It can be deduced from these studies that the optimal F concentration in drinking water in the Netherlands (with a temperate climate) is about 1 $mg.l^{-1}$. At this F concentration, there is effective inhibition of dental caries while the occurrence and severity of dental fluorosis remain within acceptable limits. The maximum acceptable F concentration in drinking water with respect to the occurrence of dental fluorosis appears to lie between 1.5 and 2 $mg.l^{-1}$.
The ingestion of excessive quantities of fluoride may also cause skeletal fluorosis. The available human studies indicate that osteofluorosis does not occur with long-term ingestion of a total daily amount (from food and water) of up to 5 mg; this is therefore considered to be the maximum acceptable concentration with respect to this effect, for lifetime exposure.
Kidney patients constitute a possible risk group for the development of osteofluorosis because of increased retention of ingested F. On the basis of the (average) difference in F retention found in a study between healthy persons with normal kidney function and patients with chronic renal insufficiency, the maximum acceptable total daily intake for the latter category appears to be 1.5 mg. In view of the limitation of this comparative study and the individual differences in retention and susceptibility, this value should only be regarded as indicative.

Gaseous fluorides primarily affect pulmonary function. Insufficient data are available to derive a recommended concentration for fluoride in the ambient air. However, an indication can be obtained from several studies into the lung function of children exposed to elevated F concentrations for long periods as a result of industrial F emissions. A Russian study found

effects on pulmonary function at F concentrations of 98 $\mu g.m^{-3}$ and higher; it is not clear whether these concentrations relate to gaseous fluorides only or to total fluoride. In a study in the Netherlands, gaseous fluorides up to a concentration of 16 $\mu g\ F.m^{-3}$ had no measurable effect on the lung function of children.
As regards short-term exposure to atmospheric fluoride, dark adaptation of the eye appears to be the most sensitive criterion: as little as 30 $\mu g\ HF.m^{-3}$ (equivalent to 28.5 $\mu g\ F.m^{-3}$) still had an effect.

5.5.2. Aquatic organisms

At present there are no generally accepted methods for extrapolation of the results of laboratory (mostly single-species) tests to natural ecosystems. Provisionally, therefore, different theoretical procedures will be used to calculate concentrations in water which are "safe" for the aquatic organisms present, with long-term exposure. The Health Council is currently preparing a recommendation ("ecotoxicological risk assessment of substances") on the use of these methods. In anticipation of the definitive recommendation, the concept has been used as a guide in deriving recommended levels.
In the methods according to the U.S. Environmental Protection Agency (EPA, 1984) and Slooff et al. (1986), one toxicity value, either an L(E)C50 from a short-term test or an NOE(L)C from a long-term test, is used to calculate a safe level. In both cases, the value chosen is the lowest "reliable" value found in the literature. In the method according to Kooijman (1985, 1987), either all available L(E)C50's from short-term tests or all available NOE(L)C's from long-term tests are used. In the first case, a HCS (hazardous concentration for sensitive species, an approximation of the L(E)C50 for the most sensitive species in the ecosystem) is calculated, and in the second case a safe concentration for long-term exposure. In the method according to Van Straalen (1986), which has been derived from Kooijman's method, all available NOE(L)C's are used to calculate a safe concentration for long-term exposure.
Tables 5.5 (fresh water) and 5.6 (seawater) summarize the results of these methods of extrapolation. Only the data from tests with the readily soluble sodium fluoride have been used. The L(E)C50 and NOE(L)C values used in the extrapolation methods according to Van Straalen (1986) and Kooijman (1985, 1987) are printed in bold type in tables 2.1. to 2.4. inclusive of the

Appendix. The results of tests with combined compounds such as cryolite were disregarded because of possible combination effects.

Table 5.5. "Safe" fluoride concentrations (in µg F/l) in fresh water according to the methods proposed by EPA (1984), Kooijman (1985, Slooff et al. (1986) and Van Straalen (1986)

Hardness (mg/l) (as $CaCO_3$)	*"soft" (H < 50)*	*"hard" (H > 50)*	*"soft" + "hard"*
1. L(E)C50 (short-term)	*51,000* **	*97,000* *	
Slooff et al.			
1. --> calculated $NOEC_{ss}$	*1,557*	*2,867*	
UF = 25.6 ---> "safe"	***61***	***112***	
--> calculated $NOEC_{eco}$	*1,833*	*3,085*	
UF = 85.7 ---> "safe"	***21***	***36***	
EPA			
AF = 100 ---> "safe"	***510***	***970***	
2. NOEC (long-term)	*5,000* *	*3,700* *	
Slooff et al.			
--> calculated $NOEC_{eco}$	*5,945*	*4,602*	
UF = 33.5 ---> "safe"	***177***	***137***	
EPA			
AF = 10 ---> "safe"	***500***	***370***	
3. NOE(L)C values			
Kooijman			
(10 species) ---> "safe"	***193***	***553***	***1,040***
(100 species) --->	***8***	***84***	***151***
(1000 species) --->	***0.4***	***13***	***22***
Van Straalen			
---> "safe"	***1,015***	***1,554***	***3,181***

AF) "Assessment Factor
UF) "Uncertainty Factor"
ss) "single-species";
eco) "ecosystem"
**) Nominal concentration, total fluoride*
***) Measured concentration, total fluoride*

Table 5.6. "Safe" fluoride concentrations (in μg F/l) in seawater according to the methods proposed by EPA (1984), Kooijman (1985, 1987), Slooff et al. (1986) and Van Straalen (1986)

1. L(E)C50 (short-term)		30,000 *	
Slooff et al.			
--> calculated $NOEC_{ss}$		940	
UF = 25.6	---> **"safe"**	**37**	
--> calculated $NOEC_{eco}$		1,193	
UF = 85.7	---> **"safe"**	**14**	
EPA			
AF = 100	---> **"safe"**	**300**	
2. NOLC (long-term)**		2,400 *	
Slooff et al.			
2. --> calculated $NOEC_{eco}$		3,185	
UF = 33.5	---> **"safe"**	**95**	
EPA			
AF = 10	---> **"safe"**	**240**	
3. NOE(L)C values			
Kooijman			
	---> **"safe"**	**1,910**	(10 species)
		349	(100 species)
		64	(1000 species)
Van Straalen			
	---> **"safe"**	**5,490**	

AF) "Assessment Factor"
UF) "Uncertainty Factor"
ss) "single-species";
eco) "ecosystem"
*) Nominal concentration, total fluoride
**) NOLC for Mytilus edulis, derived from a 6-week test;; all available NOEC values are higher than this value

- Fresh water

The HCS calculated according to Kooijman (on the basis of the short-term L(E)C50's) is 4.8 $mg.l^{-1}$ in soft water (hardness < 50 $mg.l^{-1}$ as $CaCO_3$) and 26.2 $mg.l^{-1}$ in hard water (hardness > 50 $mg.l^{-1}$ as $CaCO_3$). Using all available values, the calculated HCS is 13.6 $mg.l^{-1}$. In all three cases the HCS is higher than the exposure concentration (see chapter 4), which, according to the concept proposal of the Health Council, should result in a recommended concentration equal to the HCS. For fluoride, however, long-term studies are available from which, using the different methods of extrapolation, safe concentrations have been calculated which are lower than the HCS. For this reason, the recommended concentration is primarily established from data from long-term studies, in accordance with the Health Council's concept proposal, using the method according to Van Straalen. Since the hardness of most surface waters in the Netherlands lies around 200 $mg.l^{-1}$ as $CaCO_3$, the recommended concentration is set at the safe concentration calculated by this method: 1.5 $mg.l^{-1}$, total F.

On the basis of a few tests with the rainbow trout Salmo gairdneri, in deionized water with a hardness below 20 $mg.l^{-1}$ as $CaCO_3$, and the increasing toxicity of F to several single species with decreasing hardness of the water, it cannot be ruled out that, in soft water with F levels approaching the recommended concentration, adverse effects occur in the most sensitive species. However, this is not considered relevant in view of the hardness of Dutch surface waters. Moreover, because of the limited nature of the data on the relationship between hardness and toxicity, and because the species-specific differences make a generally valid quantification of this relationship impossible, an acceptable concentration with different hardness values cannot be established.

Owing to the absence of data on (experimental) ecosystems in fresh water, it is not possible to verify the recommended concentration against them.

Mussels exposed to insoluble fluorides (calcium fluoride or phosphorus gypsum) have been found to accumulate considerably more fluoride than mussels exposed to soluble (sodium) fluoride. As a result, the F levels in the soft parts can be very high (more than 200 $mg.kg^{-1}$ dry weight), which may involve a risk to consumers of these organisms.

- Seawater

The HCS calculated according to Van Straalen (from short-term L(E)C50's) is 1.1 mg $F.l^{-1}$. This is lower than the exposure level (which in this case is

equated to the background concentration) of 1.3. mg $F.l^{-1}$, so that the recommended concentration has been calculated on the basis of data from long-term studies. The safe concentrations calculated using the methods of Van Straalen and Slooff et al. are 5.5 and 0.1 mg $F.l^{-1}$, respectively; according to the Health Council's concept proposal, "further research is needed into the cause of this difference". Since the latter concentration is more than a factor of ten lower than the background level, 5 $mg.l^{-1}$ has been proposed as the maximum acceptable concentration for total F in seawater. It should be noted here that this concentration is based on studies with a limited number of different species, i.e., relatively many species of algae and not a single fish species.

5.5.3. Terrestrial organisms

The data on the toxicity of fluoride to wild organisms (5.2.2.) are for the most part unusable and the remaining suitable data are too limited for establishing acceptable concentrations in soil and air.

- Soil

It is not possible to establish a maximum acceptable F concentration for soil from the available plant data (5.3.1.), but accumulation and adverse effects of soil fluoride are not considered to be significant for plants at the current levels (see chapter 4).

Neither can an acceptable F concentration for soil, which is sufficiently underpinned, be established from data on livestock (5.3.2.). However, the available data indicate that the current levels generally will not cause problems.

- Air

The atmospheric NOEC values for plants and livestock are summarized in table 5.7.

The atmospheric NOEC's for plants are based on results of fumigation experiments in which cultivated plants were exposed to HF, the most phytotoxic F compound. This is a "worst-case" situation, because under field conditions fluoride may also be present in the form of other, less phytotoxic compounds.There are no data from which NOEC's for these other F compounds can be derived.

Table 5.7. Atmospheric NOEC's with respect to adverse effects in plants and livestock

"Target group"	Criterion	Concentration in $\mu g\ F.m^{-3}$			
		24-hour	monthly average	3-monthly	
Vegetation	Protection of plants, excluding a few very susceptible species	0.76	0.34	0.27	*
Livestock	Prevention of pathological changes, abnormal behaviour and decrease in agricultural value	0.8 (grazing season) 0.3 (winter season)			** **

* Based on fumigation experiments carried out with HF
** Based on atmospheric concentrations of fluoride soluble at pH ≥ 2

Since in the derivation of these NOEC's two experiments were disregarded, in which a lower effect concentration was found (an average of 0.15 $\mu g\ F.m^{-3}$) in certain cultivars of hothouse tulips and in gladioli exposed to HF for only a relatively short period (varying from 4 to 9 days), effects on the most sensitive species of plant may be expected at the indicated NOEC values.

The atmospheric NOEC's for cattle have been derived from the relationship between F content of animal feed and (the absence of) effects on the one hand, and from the relationship between F contents of feed (grass) and atmospheric F concentrations on the other. Both values are based on a maximum acceptable F level in feed of 55 $mg.kg^{-1}$ dry weight. No allowance has been made for a possible increase in F intake from drinking water, because the ingestion of F from feed contributes by far the largest amount to the total F intake of animals. The concentration given for the winter season is of little relevance to farm animals in practice, because nearly all cattle are kept indoors in winter and receive feed grown in summer (see chapter 4). Sheep, which are out almost all the year round, are usually also fed supplementary forage crops grown in summer.

Based on this information, 24-hour average atmospheric concentrations (maximum daily averages) of 0.3 and 0.8 $\mu g\ F.m^{-3}$ during the winter season and grazing season, respectively, are considered "safe" for both livestock (including the most susceptible category, viz. young cattle) and plants (with the exception of the most sensitive species).

The very limited information on wildlife suggests that the above-mentioned atmospheric NOEC values will also be safe for these animals.
As regards wild plants, there is no real basis for assuming that wild plants are more susceptible to the adverse effects of fluoride than the cultivated plants tested, so that the indicated NOEC values will probably provide the same degree of protection to both types of plants.

5.5.4. Materials

There are no data indicating that fluorides play a role in the damage to materials at current atmospheric fluoride concentrations. Inanimate materials are adequately protected at F concentrations causing no injury to susceptible plants.
The contribution of hydrogen fluoride to the total acid deposition is negligible, as therefore also its effect on materials.

5.5.5. Global scale

The HF concentration in the stratosphere is increasing largely due to the photodissociation of CFCs. The contribution of this potential source to the F concentration in the troposphere will be negligible for the time being. Although this contribution will increase considerably in the coming decades (more than tenfold), effects on a global scale are not expected for the present.

6. POSSIBILITIES AND COSTS OF EMISSION REDUCTION

6.1. PURIFICATION TECHNIQUES

6.1.1. Air purification

Fluorides are emitted as gaseous components or as particulate matter in aerosol form. In most instances, both forms of fluoride are present simultaneously and emission control must be directed at both. There are a number of techniques available for this purpose, which can be divided into wet and dry systems. Wet systems generate a wastewater stream and dry techniques produce waste, which can be reused in a few cases.
Gaseous fluorides can be effectively removed from the air by a wet scrubber. Efficiencies of 99% are feasible and often achieved. In practice, the wash water is mostly recycled in order to decrease the wastewater output, but as a result the driving force from air to water becomes weaker. This driving force can be increased by using wash water with a high pH, if required. Fluoride-containing particulates can also be removed in a wet scrubber quite efficiently. The operating efficiency is heavily dependent on the technical set-up and is accordingly much lower in some cases.
Dry systems are based on a combination of adsorption and separation of particles. They too find application at various locations in the Netherlands or abroad. The combinations employed are adsorption onto alumina followed by cloth filters (primary aluminium industry), lime injection followed by cloth filters (secondary aluminium industry) or by electrostatic precipitators (coal-fired power stations). A filter bed with calcium carbonate has also been reported as an option. In general, very high efficiencies are achieved, higher than with scrubbers.

6.1.2. Wastewater treatment

As mentioned earlier, the treatment of outgoing air in wet systems generates a wastewater stream. If the F load or concentration in this waste water presents problems, a switch to a dry air-treatment system could first be considered. It is true that a waste stream remains, but this waste also arises during wastewater treatment, in the form of sludge.
Particulates can be removed from the waste water by sedimentation. This is applied in practice, especially when the opportunity for recovering the

separated material presents itself. When F ion is the dominant species, it is converted to insoluble particulates by adding a calcium compound.

6.1.3. Waste processing

Solid materials, which result from the industrial processes and cannot be reused, are usually dumped. In a few cases (furnace slag in the aluminium industry), the readily soluble compounds are first removed. This is only done when the discharge of the water is considered to be less problematical (e.g., to the sea) than is the dumping of untreated waste.

6.2. EMISSION REDUCTION IN PRACTICE

6.2.1. Phosphate ore processing

In the manufacture of phosphoric acid, the fluoride emitted into the atmosphere consists mostly of residual emissions from gas scrubbers. Emissions have fallen considerably since 1981 as a result of improvement of the gas scrubbers and better process management (Tebodin, 1987). It is anticipated that a further reduction of 1 tonne per annum will result from increased measures, involving capital investments totalling f 1.5 million.
The main sources of emissions into water in the manufacture of phosphoric acid are by-product gypsum (CaF_2), process condensate and wash water from the gas scrubbers. The fluoride present in the process condensate is recovered in the form of aqueous fluosilicic acid (H_2SiF_6), so that the residual emission still taking place is small. One factory defluorinates a portion of the manufactured phosphoric acid to make it suitable for feed phosphate. Fluosilicic acid is also produced during the defluorination process. Currently, the fluosilicic acid is sold as a by-product but is discharged when this is not possible. There are plans to build a new plant for the processing of fluosilicic acid into silica, so that the total input to water will fall by about 2,400 tonnes of F per annum at most. The total capital outlay required is estimated at f 3 to f 5 million (Berenschot, 1987), but it is not only the emitting industry which decides in this matter.
The by-product gypsum is a serious problem especially because it is contaminated with cadmium. Much research has already been conducted into the possibilities of using by-product gypsum as a substitute for the

natural product, but as yet the prospects for doing so are poor (Ross, 1987).

The principal source of fluoride discharged into water from fertilizer production is wash water from the gas scrubbers. As with the emissions from the manufacture of phosphoric acid, the fluoride will combine with added calcium ions to form CaF_2, provided that the fluoride ion concentration is not too high. The extent of emission reduction into water resulting from the optimization of the scrubbers (e.g., the use of an alkaline solution instead of water) has not been examined.

The input to the soil from phosphate fertilizer application can in principle be reduced by introducing a defluorination step in the conversion of phosphoric acid, as is done in the manufacture of feed phosphate. This has not been considered because the F content of commercial fertilizer has not yet proved a problem in practice.

In the manufacture of polyphosphates, gas scrubbers have been installed to deal with the large point sources, with two scrubbing units in series for the major ones. Measurements made up to 1987 showed that these sources emit about 22 tonnes of F per year. Further emission reduction might be achieved by using (dry) systems with a higher efficiency, which would possibly also reduce the discharge into water. At present, however, the main aim is to gain more insight into the emissions from the slag removal process, and measurements are currently being made to that end.

6.2.2. Processing of minerals

- Coarse ceramics industry

In principle, there are two methods of controlling the emissions of fluoride from the coarse ceramics industry: process-integrated measures and flue-gas treatment. The Netherlands has no experience with either measure. However, much is known about possible emission reduction in West Germany (Haskoning, 1987). The information given below is based on West German data, whereby it should be noted that allowance has to be made for differences between the Dutch and German coarse ceramics industries.

Process-integrated measures

The addition of lime to the clay could cut the emission of fluoride through the formation of (stable) CaF_2. Dutch clay contains naturally more lime than German clay, so that the German brick works emit on average more fluoride than the Dutch ones (about 345 mg F per kg of clay). It is therefore not clear by how much this measure would reduce the emissions in the Netherlands. One problem with adding lime may be the possible colour change (from red to yellow) as the colour is determined by the ratio of the Fe_2O_3 and CaO contents.

Reducing the outflow of air (volume of air per kg of product) cuts the emission of fluoride. However, a certain minimum excess of air is required to promote the transfer of heat to the clay. No survey has been made of the extent of further emission reduction in the Netherlands resulting from measures of this type.

The direct utilization of flue gases as drying air will cut fluoride emissions if the clay contains sufficient lime.

In general, the above-mentioned process-integrated measures have not been sufficiently researched for them to be directly applicable to the Dutch situation.

Flue-gas treatment

In principle, the following techniques can be employed to clean up flue gases:

- Wet systems:
  * spray tower
- Dry systems:
  * injection of CaO or $Ca(OH)_2$, capture with a cloth filter
  * bed packed with $CaCO_3$ granules

West Germany has gained experience with all these systems. Corrosion problems arose as a result of staying below the acid dew-point. Possibly this can be prevented by raising the temperature of the exhaust gases, the cost of which can be readily estimated (Haskoning, 1987). The annual costs and the cost per tonne of product and per kg of fluoride removed are given in table 6.1. The estimation is based on the following basic assumptions:

Fluorine concentration (mg $F.m_o^{-3}$):

* after treatment : 5

Dust (mg $F.m_o^{-3}$):

* before treatment	:	150
* after treatment	:	50
Dumping cost of chemical waste	:	f 250.- per tonne
Depreciation period	:	10 years
Interest rate	:	5 %
Annual depreciation charge + interest:		13 %

Any costs for the treatment of wash water in the case of a spray tower (certainly not negligible) have not been taken into consideration. An evaluation of systems in West Germany showed that the capital investments proved in the end to be somewhat higher than has been assumed in this document (TNO, 1987), but the difference falls within the pertinent inaccuracy margins.

Table 6.1. Annual costs of flue-gas treatment in the coarse ceramics industry

Costs	*Situation 1*			*Situation 2*			*Situation 3*		
	Wet	*Dr(a)*	*Dr(b)*	*Wet*	*Dr(a)*	*Dr(b)*	*Wet*	*Dr(a)*	*Dr(b)*
Per annum (tot.) (kf.)	*84*	*45*	*63*	*113*	*61*	*89*	*171*	*87*	*145*
f./tonne product	*6.5*	*3.5*	*5.0*	*4.4*	*2.4*	*3.5*	*2.2*	*1.2*	*1.9*
f./kg F removed	*20*	*11*	*15*	*21*	*12*	*17*	*190*	*90*	*165*

situation 1: small plant, high emission: 5000 m^3 per hour, 100 mg $F.m^{-3}$
situation 2: medium plant and emission : 10000 m^3 per hour, 65 mg $F.m^{-3}$
situation 3: large plant, low emission : 30000 m^3 per hour, 15 mg $F.m^{-3}$
Wet : spray tower (without wash-water treatment)
Dry (a) : column packed with $CaCO_3$ granules
Dry (b) : adsorption and capture with cloth filters

The annual costs vary between about f 1.20 and f 6.90 per tonne of product, depending on the technique employed and the size of the plant. Total estimated annual costs are of the order of f 10 million if all plants implement the measure. As a result, the annual emission into the atmosphere will be cut by about 95%, from 600 to 30 tonnes of F.

- Fine ceramics industry

According to the Emissions Registration, none of the approximately 30 fine ceramics plants has installed emission control equipment. If it is assumed that the fluoride concentrations in the flue gases are similar to those

produced in the coarse ceramics industry, and that the same emission-control techniques were to be applied, then an estimate can be made of the annual costs. The annual costs of flue-gas treatment are f 7 to f 25 per kg of fluoride captured, resulting in total annual costs to the fine ceramics industry of some f 500,000. Emissions will be cut from 30 to 2 tonnes of F per year.

- Glass industry

According to the licensing requirements, the largest glass-fibre producer has to cut its emissions by approximately another 30 tonnes of F annually in the coming years. In the first instance, the company will try to achieve this by introducing process-integrated measures, as it has done on several occasions in the recent past. Should this not lead to the afore-mentioned reduction, the company has meanwhile planned to fit a gas scrubber to at least one furnace, using an alkaline solution as the washing liquid. The effluent is transported to the sea via a sewer system. There are currently three furnaces in operation. The capital outlay per scrubbing unit (per furnace) is estimated at f 4.5 million, the annual costs at some f 2.5 million. The application of gas scrubbing to all the furnaces is expected to result in a residual stack emission to the atmosphere of about 4 tonnes of F a year. Dry systems can be chosen if discharging F into the sea is considered undesirable. The annual emission of 18 tonnes of F from the glass factories can mostly be eliminated by using fluor-free or low-fluoride cullet and potassium alum. At present, the glass industry and the suppliers of alum are in consultation over a reduction in the F content of this material.

6.2.3. Metal industry

- Aluminium manufacture

The two aluminium producers in the Netherlands currently control the emission of fluoride by what could be regarded as the latest state of technology pertaining to the type of furnace employed. The TA-Luft, for example, stipulates that aluminium plants are not permitted to emit more than 0.7 kg of gaseous inorganic fluoride compounds (as HF) per tonne of Al, and the Dutch plants meet this emission requirement.
Further measures can be aimed at three aspects, namely:

- reducing the amount of F that evaporates from the liquid and which depends on the extent to which the liquid surface is broken
- achieving a greater encasement efficiency
- employing gas scrubbers with a higher operating efficiency

As far as the two first aspects are concerned, the differences between the Dutch plants already show that, from a technical point of view, a further reduction should be considered feasible at at least one of the plants. However, this can probably only be achieved by building a new factory. An assessment of the costs has not been made. The company concerned is considering this possibility for several reasons. In such a new situation, technically more advanced furnaces can be used, making a higher encasement efficiency achievable; figures of 95% and even 93 to 99% have been reported (OECD, 1977).

A quantitative prediction of the emission in such a new situation is hard to make. Figure 6.1. shows how the emission factor should be viewed in relation to the encasement efficiency, the degree of purification of the air drawn from the halls, as well as the amount of F and the associated gaseous/particulate ratio of the portion that "volatilizes" in the furnaces. It can also be gathered from this figure that, with high encasement efficiencies, gas scrubbers for the air exhausted from the halls may not be necessary.

Assuming an emission factor of 12 kg of F per tonne of Al, and an encasement efficiency of 90%, then F emissions would be more than 100 tonnes per year lower than in the present situation, given the same gas-purification systems. This is a theoretical value and serves only as an indication.

At both plants, the air exhausted from the halls can be treated with systems having higher efficiencies than the spray systems currently in use. Particle-bound fluoride especially can be removed more efficiently. For other wet systems, such as a packed bed (cross flow), efficiencies of on average 84% for particulates and 99% for gaseous components have been reported (OECD, 1977). In the Dutch situation, such efficiencies, achieved with an improved scrubbing device, would reduce emissions by a total of about 120 tonnes of F per year. The costs are estimated to be roughly two to three times higher than those for the spray systems, or capital investments amounting to f 70 to f 100 million and annual costs of around f 20 million.

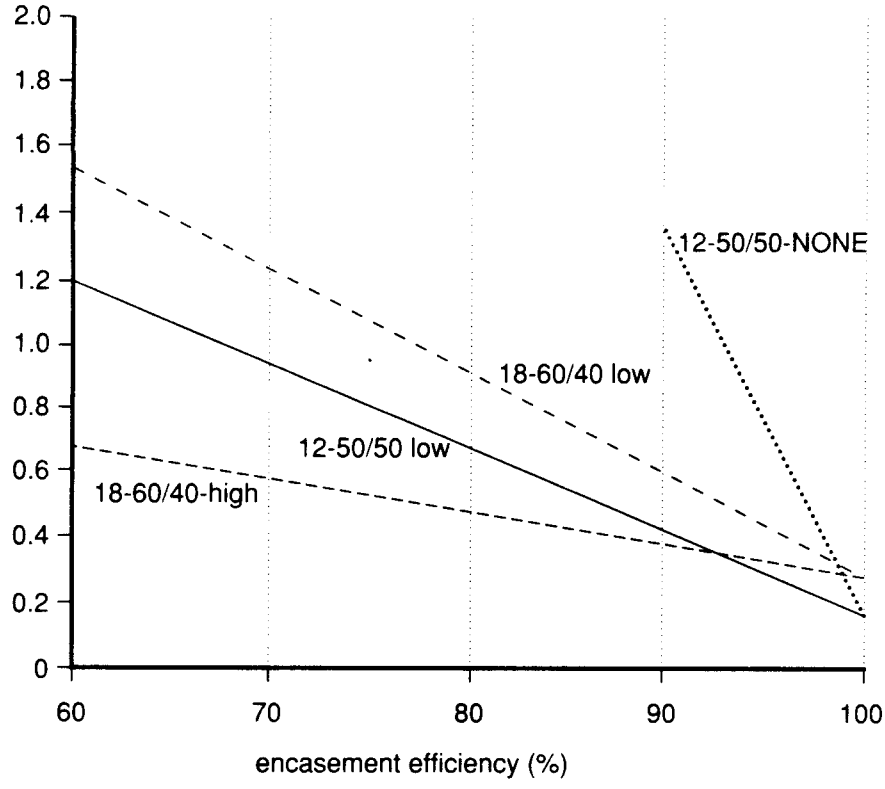


Figure 6.1. Theoretical consideration of the emission factor in primary aluminium manufacturing (furnaces and halls) in relation to the encasement efficiency in the following situations:

Volatilization in the furnace (kg F/tonne Al)	*ratio gaseous/part.*	*Application/efficiency (%) gas scrubbers room exhaust gaseous*	*particulate*
18	*60/40*	*95*	*60 (low)*
18	*60/40*	*99*	*84 (high)*
12	*50/50*	*95*	*60 (low)*
12	*50/50*	*0*	*0 (none)*

Efficiency of cloth filters for furnace exhaust is 98% for gaseous F and 99% for particulates

At present, one plant has a spray tower to treat the exhaust gases resulting from the manufacture of carbon anodes. At another plant where, except for electrostatic precipitators to remove dust particles, there is no equipment to remove the gaseous F components in exhaust gases, the same system could be installed. Another possibility is adsorption onto alumina and capture with a cloth filter. This would enable the plant to cut its emissions from 13 to about 1 tonne of F per year.

The capital outlay for a system with adsorption onto alumina and a cloth filter is estimated at f 4 million and the annual costs at f 0.5 million.

- Iron and steel manufacture

Part of the fluoride emitted by the base metal industry into the air is residual emission from a gas scrubber (pelletizing plant). Only minor improvement in efficiency will be achievable here. The sintering plant has not been fitted with fluoride emission-control equipment. The need for a gas scrubber is currently under consideration, especially because of sulphur dioxide emissions, which in any case have to be considerably reduced within 5 years. If a gas scrubber is installed, fluoride will also be captured, with an efficiency of about 70-90%, thus reducing emissions by over 30 tonnes per year.

The capital outlay for these possible measures is estimated to be of the order of f 150 million. Sintering plants abroad are usually fitted with a combination of an electrostatic precipitator and an SO_2 scrubber.

Fluoride emissions from the steel plants will decline in the future as a result of process modifications, but by how much is not known.

6.2.4. Other chemical industry

As has been mentioned in chapter 2, F emissions from the manufacture of pigments have already been considerably reduced. Increased measures for the chemicals industry have not been considered.

6.2.5. Energy generation

At present, the fluoride emissions resulting from the burning of coal are not controlled in the Netherlands. However, in connection with more stringent emission requirements for sulphur dioxide in particular, wet scrubbers will be installed in the coming years in existing and new coal-fired power stations. This will also cut fluoride emissions. Wet scrubbers are estimated to remove about 70% of the fluoride.

On the other hand, it is expected that considerably more coal will be consumed in the years ahead. Several scenarios have been drawn up for the future coal consumption, which have also been worked out within the acidification framework. Figure 6.2. shows the magnitude of the F emissions in the next few decades within the basic assumptions of the so-called Medium Coal scenario, including planned flue-gas treatment. Figure 6.3. indicates what can be achieved with additional measures involving lime

dosage in one form or another, and which therefore have a positive effect not only on sulphur dioxide but also on fluoride emissions. However, recent developments make it likely that in the near future another scenario will be more consistent with actual practice, the Low Gas scenario. The emissions from power stations within these scenarios are compared in figure 6.4.

It is still not clear whether coal will be gasified for energy generation in the Netherlands in the future. The atmospheric fluoride emission from coal gasification is expected to be small because the gas is cooled with water, which removes Cl and F.

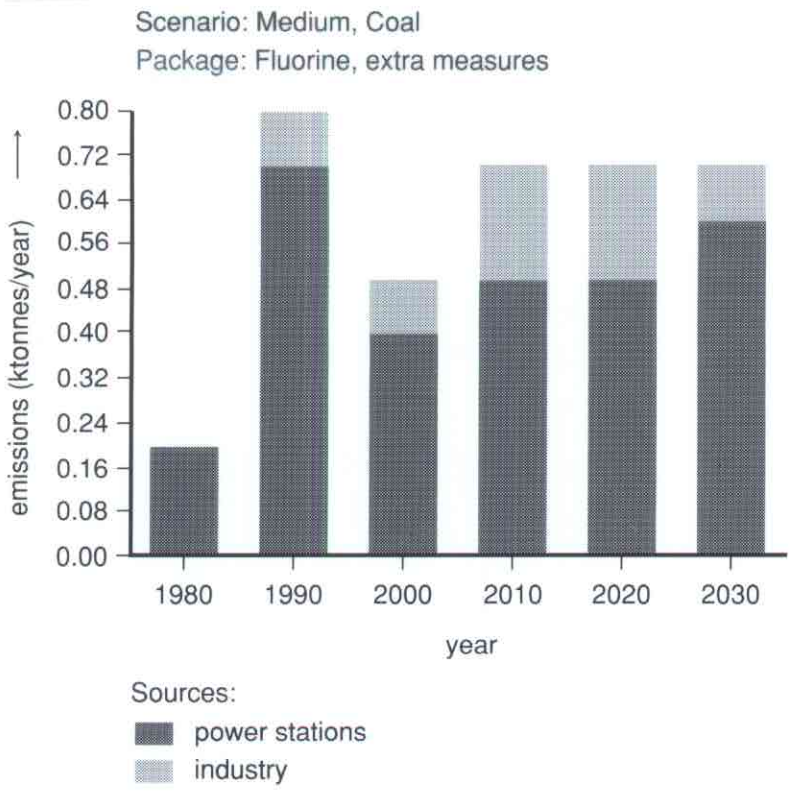


Figure 6.2. Predicted F emissions resulting from energy generation in accordance with the Medium Coal scenario, including planned flue-gas treatment (RIVM/RIM)

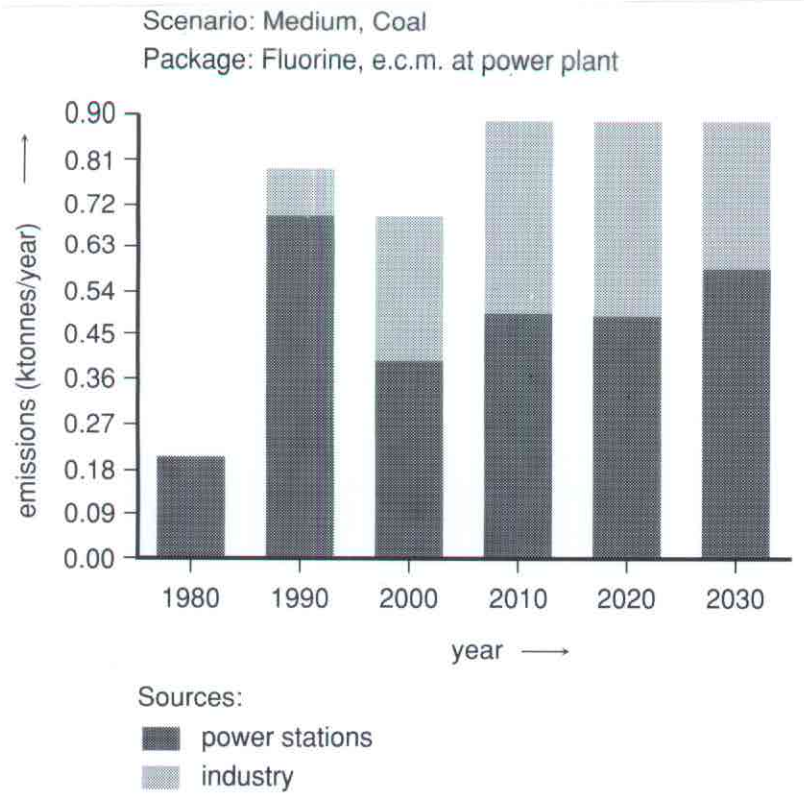


Figure 6.3. Effect of extra measures (lime dosage) on the predicted F emissions resulting from energy generation as described in figure 6.2.

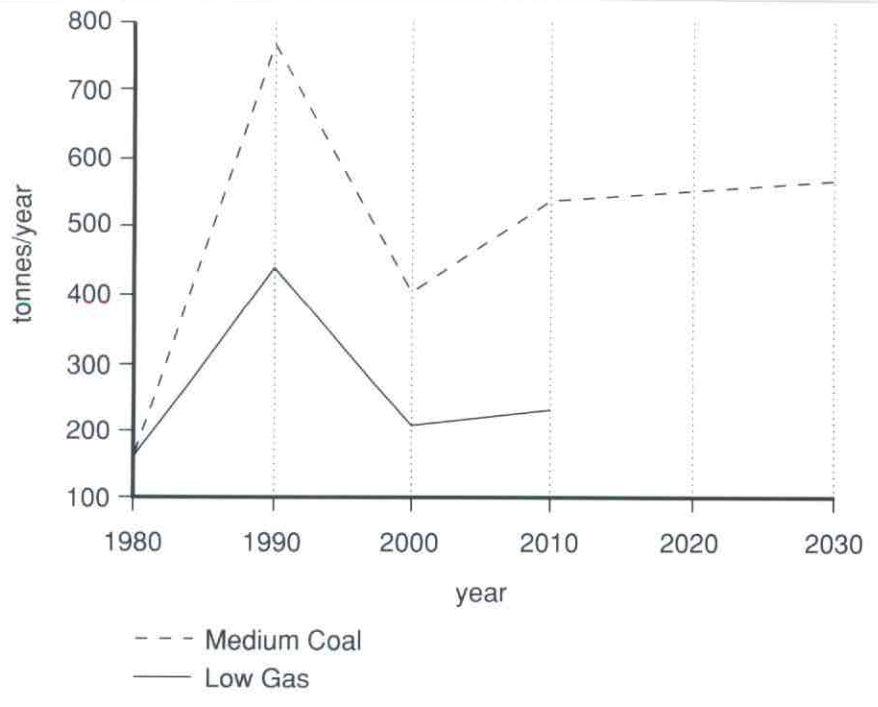


Figure 6.4. Comparison of the fluoride emissions from power stations within the Low Gas and Medium Coal scenarios

6.2.6. Diffuse emissions

The possible reduction of F emissions from glass treatment processes and welding operations has not been studied in this context. Reduction of F emissions from dental uses is not under consideration. Possibly the installation of a third cleanup stage to remove phosphates in sewage treatment plants will lead to further fluoride removal.

6.2.7. Waste processing

In waste incineration, the major emission sources are the eleven (large) waste incinerators. The literature (Haskoning, 1984) indicates that gaseous fluoride (HF) accounts for the greater part of the F emission. The current emission-control systems do not separate the fluoride out, except in one case where gas scrubbing is applied and part of the emitted fluoride enters the water. In the coming years, emission control at new and existing incinerating facilities will become necessary because of more stringent emission requirements.
The atmospheric emissions from incinerators can be further reduced by installing separate post-incineration flue-gas scrubbing systems. Wet, semi-dry and dry systems are in principle available. One drawback of the wet system is that it generates a wastewater stream. An advantage, however, is the guarantee that stringent emission requirements (particularly for heavy metals) can be met, whereas this is uncertain with dry systems. Emission control can be regarded as an autonomous development. On the basis of the 1985 situation, about 45 tonnes of F will be removed from the air streams. The future emission from this source depends in part on the volume of waste to be incinerated.

6.3. SUMMARY AND CONCLUSIONS

Table 6.2. summarizes the afore-mentioned possibilities and costs of reducing fluoride emissions. A number of measures should (also) be viewed in the light of other problems. This applies to any measures at coal-fired power stations, in waste incineration and in the base metal industry. The first two can be regarded as proposed measures. The emission reductions given in this table have been calculated for the year 1985.

Fluorides are for the most part discharged into salt or brackish waters. This has always been regarded as unproblematical, and for this reason there are almost no detailed plans to control these discharges. In general, it can be stated that discharges of wash water from wet scrubbers can be prevented by switching to dry gas scrubbers. If this generates a product that is not suitable for reuse, the residual product is usually chemical waste.

Table 6.2. Possibilities and costs of reducing emissions to the atmosphere

Emission source	*Measures*	*Emission reduction (tonnes F/year)*	*Costs (f mln) investment*	*annual*
Industrial				
- phosphate ore processing	*various in phosphoric acid manufacture*	*1-5*	*> 1.5*	*?*
- coarse ceramics industry	*flue-gas treatment **	*570*	*ca. 30*	*ca. 10*
- fine ceramics industry	*idem*	*28*	*ca. 1.5*	*ca. 0.5*
- glass-fibre industry	*process modifications, if required, with limited flue-gas treatment (scrubbers)*	*30* *60*	*autonomous* *13.5*	*7.5*
- glass industry	*change raw/auxiliary materials*	*18 (max.)*	*?*	*low or nil*
- aluminium industry	*- improve scrubbing of ventilation air of halls*	*120*	*70-100*	*20*
	- new electrolysis process (+ more advanced furnaces)	*100*	*?*	*?*
	- adsorption onto alumina and cloth filter in anode bake plants	*12*	*4*	*0.5*
- base metal industry	*gas scrubber in sintering plant*	*30*	*ca. 150*	*?*
Energy generation	*flue-gas treatment**	*380 (av)*	*autonomous*	
Household waste incineration	*idem**	*45*	*autonomous*	

* *These measures are in principle taken to control the emission of substances other than fluorides (especially sulphur dioxide). Their costs cannot therefore be solely ascribed to the reduction of fluoride emissions*

7. FINANCIAL CONSEQUENCES

7.1. BRICK WORKS

Unless indicated otherwise, the data in this section have been taken from Haskoning (1986).

In the past 25 years, the number of brick works has fallen sharply, from 238 in 1961 to 64 in 1985 (CBS, 1987). Total sales of paving and building bricks fell by 35% in the past ten years. This decline is due to the collapse of the construction market in the years 1980-1982. In the period 1982-1986, sales fluctuated around 2700 ktonnes per annum. Turnover in 1985 was f 408 million (CBS, 1987). Employment in this sector fell by over 10% per year, from more than 11,000 in 1961 to 2,000 persons in 1985. Production capacity was cut by 35% during the reorganization period 1980-1982, which made more than half of the original 4,600 employees redundant. Three-quarters of the plants employ fewer than 50 persons, and have an average annual turnover of f 10 million.

Brick sales depend very heavily on the cyclical building market. The Royal Association of Dutch Brick Manufacturers (KNB, 1987) expects a very small rise in domestic sales up till the year 1990, while the Central Planning Office (CPB, 1985) foresees that growth of building activities will also be very low in the longer term: 0-2% up to the year 2000. Export prospects are reasonably good. In 1984, 23% of production was exported, chiefly to West Germany. However, construction activities are also declining there, and there is increasing competition. The sector expects to keep its export level up and hopes to achieve some growth (KNB, 1987). Brick imports have been low for years, indicating a strong position on the domestic market (EZ, 1980).

In 1979, the financial position of the brick industry was satisfatory: profits were good and ownership capital was on average over 50% of total capital (EZ, 1980). Earnings per brick dropped between 1979 and 1983 by 20% and did not reach the 1979 level again until 1985. On the cost side, the rise in energy prices in 1979 had a negative effect. Brick firing is an energy-intensive process, which is reflected in the 30% contribution made by energy costs to the total production costs. As a result, the selling prices in the years 1980-1985 were on average 5 to 15% below the cost price. However, there are differences between the enterprises. In general, the more capital-intensive, more energy-efficient tunnel-kiln plants can

produce economically, provided that they have sufficient ownership capital. Because of a stable market in conjunction with falling energy prices, the average profits in 1986 have again reached an acceptable level (KNB, 1987). The application of flue-gas scrubbing using the dry system means a 1-5% increase in costs to the brick works. By making possible (cheap) dumping or reuse of the HF-containing lime grit and lime powder produced during flue-gas scrubbing, the extra costs can be cut by about 15%. The required capital expenditure of f 14 million is equivalent to 35% of the average investment budget of the brick industry in the years 1981-1985 (KNB, 1987) as also of the expected investment level. The sector as a whole can probably afford this capital outlay, albeit with difficulty. In view of the differences in production methods and profitability however, it is likely that relatively outmoded plants will run into problems.

7.2. PHOSPHATE FERTILIZER INDUSTRY

The phosphoric acid-producing plants are currently receiving a lot of attention because of discharges of by-product gypsum into the Nieuwe Waterweg. This slurry is contaminated with cadmium, copper and fluorides, among other substances.
In the integrated criteria documents Cadmium and Copper (RIVM, 1987), as well as in the environmental study "Fertilizer Industry" (Berenschot/Tebodin, 1987), much attention has already been paid to the financial consequences of reducing the cadmium discharges in particular. The costs involved amount to f 15 million per annum and mean an increase in cost price of about 5%. The financial consequences are determined mainly by the pace at which the discharges have to be cut back, the possible sale of gypsum blocks to the building industry (depending on the future building products decree), and the question of whether anything is also being done on a European level about the reduction of cadmium in fertilizers.
The phosphate industry is an internationally oriented sector with a saturated market and stiff competition. It is very sensitive to price changes. In view of the fluctuating profitability in the past few years, the staying power of both companies is weak. Their closure will result in the loss of 1300 jobs and a drop in national income of f 200 million. New investment plans for the processing of fluoride-contaminated waste streams (silica and hydrofluoric acid production) will then also become uncertain.

To date, atmospheric fluoride emissions have only led to relatively low claims by cattle farmers for compensation. In the Rijnmond area it involves a sum of less than ten thousand guilders for each emitting plant, excluding the veterinary-technical consulting and administrative expenses. It seems likely that any increases in cost resulting from measures taken in the storage and transshipment of phosphate ore will be passed on to the customers.

7.3. PHOSPHATE DETERGENTS INDUSTRY

The use of phosphate-containing detergents is still under discussion because of the overfertilization problem. Environmental policy is aimed at drastically cutting the production and use of these products, and replacing them by phosphate-free detergents. As a result, fluoride discharges and emissions will probably also decrease.
Adequate assessment of the financial consequences of fluoride emission reduction is not possible in view of the uncertainty about the emissions. It can be noted, however, that the compensation paid to cattle farmers at present is a not inconsiderable sum (more than a hundred thousand guilders per year).

7.4. PRIMARY ALUMINIUM INDUSTRY

The aluminium industry is an intermediary sector. Production is heavily dependent on developments in the raw materials market (prices, instability in supply) and on developments in various outlets. The major customers of aluminum are the transport industry (cars, trains, aircraft), the electrotechnical industry, the building industry (windows and doors), and the (beverages and preserved foods) packaging industry. The economic development differs in each of these markets.
Although aluminium consumption is still growing, its production is lagging behind because of increasing recovery of aluminium from waste. In 1984, about 15% of the aluminium used in the Netherlands was reclaimed. It is assumed that this proportion could rise to 50-60% (TNO Metal Institute, 1984). The aluminium industry operates internationally at a high level, and is multinationally organized. About 90% of the volume produced in the Netherlands is exported. There is strong competition in the export markets, to an increasing extent with East European and developing countries.

Because of this, the Dutch industry will have to specialize in high-value-added products. Following a 10% decline in output between 1980 and 1983, the trend is now moving upwards again and the industry is even operating at almost full capacity. With an annual production worth nearly f 1.4 billion and a workforce of over 2,000 people, the aluminium industry belongs to the large-scale industrial sectors. Energy and raw materials account for 70-80% of the cost price. Because of the very energy-intensive nature of the production process, this sector is vulnerable to competition from countries with cheap energy. Incidentally, twenty years ago, low energy costs were an important reason for the location of the industry in the Netherlands. The staying power of this sector is reasonably strong.
The improved gas scrubbing proposed in chapter 6 involves annual costs of nearly 8% of the value added. This will considerably weaken the position of the enterprises compared to those abroad.

7.5. IRON AND STEEL INDUSTRY

The iron and steel industry is an internationally oriented sector, which has contended with a large over-capacity for years. At the European level, efforts are being made to restructure the industry and to curtail production. By reducing costs, the Hoogovens, the Dutch blast-furnace concern, will still be capable of producing economically. After a few years in which operating profits were reasonably good, the industry expects to suffer losses in 1987, due to the low dollar exchange rate. Future cuts in cost will cause a loss of about 3,500 jobs by the year 1990, or 20% of the workforce. The industry is currently being confronted with cost increases arising from stricter emission-control requirements. In 1985, the estimated total environmental costs amounted to f 125 million, or 1.5-2% of the total production costs. Emission-control equipment for SO_2, NO_x, benzene, cadmium and fine dust requires capital spending totalling over f 20 million annually. The proposed measures are also quite efficient in reducing F emissions. In addition, environmental expenditure is required for the reduction of wastewater discharges and the processing of chemical waste (lime sludge, blast-furnace slag, captured fly ashes and combustion residues).

7.6. GLASS-FIBRE INDUSTRY

The products of the glass-fibre industry are used to reinforce synthetic materials, with applications in bodywork, yachts, silos, piping and the like. The outlook for the glass-fibre industry is bright.
The glass-fibre industry is a relatively large-scale sector concentrating its production in the international market. A low dollar exchange rate leads to pressure on prices and operating results, and weakens the industry's international competitiveness (AKZO, 1986). It is a moderately labour-intensive sector with reasonably strong staying power.
The most comprehensive package of measures involves annual costs of f 7.5 million. This is estimated to be 10% of the value added and is, undoubtedly, a large financial burden. However, the growth and capital investment in the industry indicate a certain amount of confidence in the future, and it is therefore not clear whether or not this expenditure will be prohibitive.

7.7. WASTE INCINERATION

Environmental costs incurred by waste-processing companies are usually passed on to the waste producers, either giving them an economic incentive to reduce waste at the source, or causing them to look for cheaper ways to dispose of their waste. Economic consequences can be expected in indirect terms, for example, in enterprises producing much waste, rather than at the waste-incineration plants themselves.

7.8. AGRICULTURE

Financial consequences for the agricultural sector are not related to the cost of possible emission-control measures, but are the result of damage by fluorides to the product. The methods used to make an estimate of the economic damage to agricultural production from air pollution in the Netherlands were the limed paper and effect measurements made within the National Air Pollution Network (Van der Eerden et al., 1986). They indicate that the damage on a local scale is only a fraction of that on a national scale, f 3 million and f 650 million respectively. The fluoride contribution to this is estimated at f 1.5 million and f 50 million. It should be noted here that "damage on a local scale" refers to damage in the

vicinity of about 10 large sources. In practice, however, there are more point sources causing local damage.

This damage is mainly attributable to effects in the ornamental plant sector and to deterioration of the consumption quality of grass and other forages. Calculations using new measurement data and recent information about the toxicity of fluoride provide concrete indications that the above-mentioned damage on a national scale is an underestimation and is more likely to be of the order of f 90 million annually. Between 50% and 150% of the average exposure level (hereinafter referred to as "current" level), the damage increases approximately linearly with increasing fluoride pollution:

$S = - 34.8 + 1.28\% F$

where S is the damage on a national scale in million guilders and %F is the percentage of the fluoride pollution with respect to the current level. Nearly half the damage occurs in South Holland (24% caused by fluoride-contaminated grassland and 25% by damage to agriculture and horticulture). Of the total fluoride damage, 23% occurs in Gelderland (21% in grassland areas and 2% in agriculture and horticulture). When fluoride pollution is over 150% of the current level, the damage increases more than proportionally with increasing contamination. Incidentally, the damage calculations discussed here can only be made if a considerable amount of expert judgement is added to the present knowledge about fluoride effects. At present, the reliability of the results is still difficult to check. What is certain is that the results expressed in percentage points are more reliable than those expressed in absolute financial terms. The sums mentioned for damage are directly related to production losses. As a rule, these are passed through to the prices, so that the financial consequences are very small from the national point of view.

In addition to economic damage, there are fluoride effects on agricultural production which are difficult to express in terms of money. For example, there is a compensation scheme in the areas near the Hoogovens, but it excludes very susceptible plant species. Although the scheme functions to the satisfaction of both parties, it does impose limitations on the range of products the horticulturist can grow, and for which he receives no financial compensation. A comparable situation obtains with livestock farming: in some areas fluoride toxicosis in cattle is kept within acceptable limits by regularly feeding the animals anti-fluoride pellets. However, the cattle farmers often have difficulty in accepting the fact

that their animals have to swallow "medicines" for long periods. Furthermore, this administration (twice daily) is labour-intensive, and the labour-costs are not reimbursed.
A reduction of the fluoride emissions will of course limit the damage mentioned, but in view of the many assumptions made in quantifying it, no attempt has been made to weigh these benefits against the costs to other industrial sectors.

7.9. SUMMARY AND CONCLUSIONS

Table 7.1. summarizes the most important data concenrning the industrial sectors discussed.

Table 7.1. Summary of relevant characteristics of the industrial sectors

Industrial sector	*Structure (size)*	*Market situation*	*International competition*	*Staying power*
Brick industry	*small*	*fairly good*	*little*	*moderate*
Phosphate fertilizer	*large*	*bad*	*much*	*weak*
Aluminium industry	*large*	*fairly good*	*much*	*moderate*
Iron and steel ind.	*large*	*bad*	*much*	*moderate*
Glass-fibre industry	*medium*	*good*	*considerable*	*moderate*

It can be concluded that the increases in environmental costs are relatively substantial for the aluminium and glass-fibre industries. It is true that the latter sector is probably in a better position to meet these costs, but this cannot be stated with certainty.
The Hoogovens is faced with a cumulation of extra environmental requirements at a time when it is trying to retain its market share by cutting production costs. About 3,500 jobs will be lost even without these extra environmental requirements.
The brick industry, which, after a reorganization period, appears to have found a new balance, can ill afford the additional expenditure. Financially weak plants with outmoded furnaces may run into problems.
In the phosphate fertilizer industry, the pace at which new environmental requirements have to be met is crucial to the survival of the sector. Here, the major factor is the environmental policy concerning cadmium pollution. Closure of the industry will result in a loss of at least 1,300 jobs. The possible consequences of future measures in the manufacture of polyphosphates are not known.

The consequences for agriculture are mainly local (around point sources) and occasionally regional, and consist of damage to ornamental plants and reduced milk production. In practice, there is a compensation scheme in a number of areas.

8. EVALUATION

8.1. RISKS AND RISK GROUPS

8.1.1. Risks to man

The diet is the main source of fluoride intake in man; the contribution of inhaled fluoride is negligible, even in an area of relatively high atmospheric F pollution. There are indications that fluoride is an essential nutrient, which in any case plays a role in the development of dentition and the skeleton. Low fluoride intake prevents dental caries, particularly in children. Excessive fluoride intake can cause dental fluorosis (dental lesions) and osteofluorosis (bone structural changes).
The information about the risks to man from both low and elevated F concentrations is limited. The available data are insufficient for establishing a minimum F requirement. The optimal F concentration in drinking water in the Netherlands is considered to be 1 $mg.l^{-1}$; at this concentration, there is effective inhibition of dental caries while the occurrence and severity of osteofluorosis remain within acceptable limits. The maximum acceptable F concentration in drinking water at which dental fluorosis does not develop lies between 1.5 and 2 $mg.l^{-1}$. With respect to the occurrence of skeletal fluorosis, a total daily oral intake of 5 mg F (from all sources) is taken to be the lifelong acceptable maximum. The data are considered to be too limited for differentiating the minimum amount required and the maximum acceptable amount according to age. It is estimated that the Dutch population ingests daily a minimum of 1.4 mg and a maximum of 6.0 mg F per person. In view of this range, it has been concluded that the current exposure level generally entails no risk to the population, the more so because the indicated minimum and maximum levels are based on a cumulation of "worst-case" situations. Kidney patients constitute a possible risk group with respect to the effects of excessive F intake; because of increased F retention, the maximum acceptable total oral intake is a factor of approximately 3 lower than for healthy people. It is not known how many persons in the Netherlands are involved. Because of the variation in F contents of foods and drinking water, and the use or nonuse of fluoride-containing toothpaste and other dental preparations, it is possible in principle that some of the population ingests either too little

or too much fluoride. However, there are no indications that this is actually the case in practice.
As regards exposure to atmospheric fluoride, it can be concluded that the current concentrations (also around sources) will have no adverse effects on human health. This is also true for the concentrations indoors; only under very special circumstances (living in wooden dwellings treated with a fluorine-containing wood preservative) can an effect on pulmonary function and on dark adaptation of the eye possibly occur.

8.1.2. Cultivated plants and livestock

- Cultivated plants

The maximum annual average concentration proposed in chapter 5 is locally exceeded in the Netherlands as well as regionally. Consequently there is fluoride-caused yield reduction for flowers, bulbs, trees and pot plants grown under glass. Besides damage to grassland (deterioration of consumption quality of grass and other forages), damage in the form of yield reduction also occurs in agriculture and horticulture (ornamental plants). On a provincial scale, the damage is greatest in South Holland, followed by Gelderland and Zeeland. The percentage of yield reduction is negligible in the provinces of Groningen, Friesland, Drente, Overijssel, North Holland, North Brabant and Flevoland. These differences are caused not only by differences in the level of atmospheric fluoride pollution but also by differences in production value of the crop per unit of surface area (it should be noted here that, apart from fluoride - particularly HF -, sulphur dioxide and ozone are chiefly responsible for the yield reduction caused by air pollution; thus, for a proportional decrease in concentration, ozone has an effect on crop production approximately five times greater than HF.
In some cases there is a compensation scheme which functions to the satisfaction of the parties concerned, but which does impose a restriction on the range of products the horticulturist can grow, and for which he receives no financial compensation.

- Livestock

On the basis of a maximum acceptable concentration of 55 mg $F.kg^{-1}$ of forage (dry weight), an atmospheric NOEC of 0.8 μg and 0.3 $\mu g.m^{-3}$ (daily averages) has been derived for the grazing season and winter season,

respectively. In practice, the value derived for the winter season is of little relevance to cattle, because nearly all cows are kept indoors in winter and receive feed grown in summer (livestock such as sheep are less susceptible to fluoride effects). In the grazing season, the recommended concentration is exceeded locally, but also on a regional scale in the areas with a fluoride pollution problem mentioned earlier. When the contribution from other sources (consumption of contaminated ditch water) is taken into account, it is possible that cattle in these areas suffer adverse effects. It should be mentioned that no allowance has been made in the derived NOEC value for this contribution (about 20% at most) to the total F intake; this is considered to be of little relevance in view of the great uncertainties in the derivation.
An estimated 2000 cows are exposed locally to elevated F concentrations. Here, too, there are compensation schemes in a number of cases, and anti-fluoride pellets are administered to the animals to keep fluoride toxicosis within acceptable limits.

8.1.3. Risks to ecosystems

- Aquatic environment

With respect to aquatic organisms and ecosystems, total F concentrations of 1.5 $mg.l^{-1}$ in fresh water and 5 $mg.l^{-1}$ in seawater are considered to be the maximum permissible levels, for long-term exposure.
The quarterly average F concentrations in most Dutch inland water bodies are several times less than 1.5 $mg.l^{-1}$, so that no adverse effects are expected in these waters at current F levels. In the Meuse near the frontier and in water bodies in areas of industrial fluoride emissions, the maximum acceptable concentration is approached or exceeded, depending on the season (the highest levels are observed in the summer season when, with the higher temperature of the water, fluoride is more toxic). It is assumed that this is also true for the Westerscheldt. In the Ghent-Terneuzen Canal and in some ditches in emission areas, the concentration usually exceeds 1.5 $mg.l^{-1}$. However, a decrease in total F concentrations in the Ghent-Terneuzen Canal has been observed during the past decade: whereas quarterly average concentrations of around 8 $mg.l^{-1}$ have regularly been measured between 1978 and 1980, these levels have fallen from 4 mg to 1.5-2 $mg.l^{-1}$ since 1985, possibly owing to the cessation of phosphoric acid manufacture. These F levels may have adverse effects.

On the basis of the limited data, it is not possible to indicate specifically susceptible species.
Data on F concentrations in coastal waters are not available, so that a risk evaluation cannot be made. However, in view of the natural F levels in seawater and the concentration in the inflowing fresh water, it is assumed that the F concentration is not a critical factor here.

- Terrestrial environment

Data on wild terrestrial organisms and ecosystems necessary for establishing a permissible concentration for air and soil are insufficient. No data are available concerning effects on soil organisms and processes, but in view of the relatively high natural F concentrations in soil, this exposure route appears to be relatively less critical to terrestrial ecosystems. Nevertheless, this assumption requires a sounder underpinning (see 8.6.).
Data on higher "wild" plants are scarce so that their susceptibility to excessive fluoride exposure can only be based on the data obtained from experiments with cultivated plants. They indicate that the uptake and effects of soil fluoride are of minor importance and that exposure to atmospheric fluoride (especially HF) is the critical factor. On the basis of fumigation experiments with cultivated plants, it was established that a 24-hour average and a monthly average concentration of 0.8 μg and 0.3 $\mu g.m^{-3}$, respectively, causes no damage to most of the plants. These levels are exceeded in the Netherlands in several regions, but certainly on a local scale. Based on this, it can be assumed that the natural vegetation is damaged by the current fluoride levels. This assumption is strengthened by the fact that the derived concentrations do not provide full protection to very susceptible ornamental plants. However, the extent of the damage and the consequences for the environment cannot be assessed.
Regarding fauna, sufficient indications are available to assume that the fluoride tolerance established for the most important farm animals is partly translatable to wild ruminants (red deer and roe deer). On the basis of the atmospheric NOEC values as proposed for livestock (0.8 μg and 0.3 $\mu g.m^{-3}$; maximum daily averages for the grazing season and winter season, respectively), it can be stated that in winter this value is exceeded on a national scale, and that in the grazing season it is exceeded in some regions, but certainly on a local scale. It cannot be excluded that wild

animals develop fluoride toxicosis sooner than farm animals. Factors playing a part here are:

- the relatively higher deposition rate along forest edges (a factor of approximately 1.8 higher compared with pastures) and concomitant higher F levels in vegetation grazed by red deer and roe deer,
- wild animals are (usually) not fed supplementary foods in the winter period, and
- the effect of other stress-inducing factors in the environment.

The population density of these animal species in areas with high fluoride emissions is not known. Although the population density may be assumed to be low in view of the biotope characteristics, no statement can be made about the severity of the effect.

8.1.4. Materials

There are no indications that the current atmospheric F concentrations cause damage to materials. Etching of glass has occasionally been observed in wooden dwellings treated with a fluorine-containing wood preservative.

8.1.5. Other effects

Worldwide effects on the biosphere are not to be expected at current atmospheric F concentrations. Possibly fluorides play a part in observed large-scale effects such as deterioration of forests. However, the available data cannot be used to relate the effects to atmospheric F concentrations. The contribution of stratospheric HF (with CFCs as the source) to the F concentrations in the troposphere does not lead to effects on the biosphere even in the longer term.

8.2. EXCEEDING OF THE EXISTING STANDARDS AND RECOMMENDED VALUES

8.2.1. Soil and groundwater

A reference value of 175 mg $F.kg^{-1}$ is in force for a multifunctional soil with very little or no clay (diameter < 2 μm); for a standard soil with 25% clay it is 500 mg $F.kg^{-1}$ (see 1.2.1.). Average total F levels ranging from about 60 to 550 $mg.kg^{-1}$ of soil have been measured in the Netherlands, without characterization of the soil with respect to the clay content.

Table 8.1. gives a rough estimate of the maximum fluoride accumulation in soil with constant emissions, assuming that the fluoride ends up on the soil as a result of deposition and is retained in the top layer (upper 20 cm), and that leaching, removal by plants or ploughing activities do not take place.

Table 8.1. Maximum fluoride accumulation in the top layer of the soil after 25 years, with constant emissions

Scale	*Deposition ($mg\ F/m^2/year$)*	*Increase in F content in 25 years (mg F/kg)*	*% of the reference value*	
			standard soil with 25% clay	*soil without clay*
National	*60*	*5*	*1*	*3*
Regional	*60 - 110*	*5 - 10*	*1 - 2*	*3 - 6*
Local	*60 - 750*	*5 - 60*	*1 -12*	*3 -34*

The significance of such an increase for the environment, and for agriculture and horticulture, is not known. However, it may be assumed that a considerable part of it is immobile and not biologically available, due to adsorption and precipitation. If the level and duration of F exposure is such that the adsorption complex is in equilibrium with the soil solution, then all the fluoride which is deposited on the soil can move to the groundwater. This may result in the following concentrations in the groundwater:

on a national scale: about 0.2 $mg.l^{-1}$
on a regional scale: about 0.2-0.4 $mg.l^{-1}$
on a local scale : about 0.2-2.4 $mg.l^{-1}$

This implies that in the long term the F concentrations in the groundwater may locally exceed the reference value (0.5 $mg.l^{-1}$) and even the existing drinking-water standard (1.1 $mg.l^{-1}$). The time scale is heavily dependent on the type of soil (content of aluminium oxides, pH, clay content; see section 3.1.).

8.2.2. water

Since 1980, the number of water bodies exceeding the proposed limit of 1 $mg.l^{-1}$ in fresh surface water intended for the production of drinking water (see table 4.1.) has fallen sharply. The quarterly averages are below this

limit, except in the Zeeland waters (Sas van Gent) and, possibly, a number of smaller water bodies in areas of industrial F emissions.

8.2.3. Air

Measurements made near sources indicate that the F concentrations generally have fallen during the past few years. The current interim ceiling is still being exceeded around a limited number of sources (East Groningen, Sloe area and, to a smaller extent, in the Rijnmond area; see table 8.2.). The concentrations in indoor air will generally not lie above those outdoors. The MAC value, based on total F concentration, applying in the workplace is exceeded in a number of cases. The extent to which this is also true for the recently proposed MAC value based on water-soluble fluorides is not known.

8.2.4. Miscellaneous

The total daily intake by man is similar to the doses previously recommended in the foreign literature. The drinking-water standard is not exceeded. In the winter months, grass F levels exceed the standard for feed in all the contaminated areas discussed, and the same is true in a number of cases for grass silage. The amounts by which the standard is exceeded show a slightly downward trend.

8.3. MEASURING STRATEGY

8.3.1. Soil

A measuring strategy for soil does not appear to be essential despite a possible accumulation effect. This is because of the limited bioavailability of fluorides in soil (Van den Berg et al., 1988).

8.3.2. Water

The current monitoring network activities concerning the state-owned water bodies are judged to be amply sufficient; possibly a reduction in the number of measurement stations can be considered. Measurements are recommended in the smaller (particularly the isolated) water bodies around

local sources, to supplement the grass analyses, in order to gain more insight into the exposure levels to the cattle grazing in the area.

8.3.3. Air

Two measuring strategies can be followed for the compartment air: (a) a measuring strategy aimed at determining the concentration in air, and (b) a more effect-directed measuring strategy (analysis in grass and limed paper, related to effects on cattle and plants respectively, or biomonitoring on tulips and gladioli).
As has been mentioned earlier, there are a number of uncertainties surrounding the derivation of an air concentration standard. Nevertheless, the Advisory Board of the Ministry of VROM has declared that it prefers a concentration standard to a deposition or an effect standard. The advantage of choosing this approach to the air quality criterion is that an unambiguous relationship can be established between the atmospheric concentration and the emission of fluoride. Moreover, if the emission has been clearly characterized, relatively inexpensive dispersion models can be used which also provide a clear insight into the spatial dispersal pattern and the consequences of possible emission reductions. For the determination of national and regional background concentrations, measurement of fluoride at about 10 stations of the NAMN, to supplement model calculations, is sufficient. In connection with the desired accuracy and the differentiation into gaseous and particulate fluoride, the double-filter method is recommended for this purpose. By introducing the modifications proposed by Joziasse and Bikker (1986), a sufficiently low detection limit can be achieved (about 0.04 $\mu g.m^{-3}$). Additionally, the F content of grass can be determined at 3 stations for validation purposes. To be able to compare these total F contents with the atmospheric fluoride concentration, the total F concentration in the air must also be determined at these stations. The currently used methods for determining fluoride can then be cut back (tulip, gladiolus), or abandoned altogether (limed paper method).

8.4. Proposal for environmental quality criteria

As regards the protection of the environment, neither science nor policy has developed an unambiguous philosophy concerning the desired protection level. It is therefore not yet clear which effects can be regarded as

unacceptable, and which risks are acceptable in terms of the degree of probability of these effects occurring. This problem arises especially with fluorides. Also, the emission-effect relationships are not always sufficiently known. For this reason, not one recommended limit but several alternative values have been given for the compartments water and air.

8.4.1. Soil and groundwater

Because of the absence of data, it is not possible to make a proposal for an environmental quality objective for the compartment soil. However, it is assumed that the effect of fluoride on soil flora and fauna is not the most critical factor, partly because it is not accumulated to any great extent. Therefore, there is as yet no reason for deviating from the reference values proposed earlier for soil and groundwater. In keeping with the proposals for standards for the other environmental compartments, it could be considered to express the reference values in the soluble (biologically available) fraction, depending in part on the simplicity and cost of the analysis procedure and its practicability.

8.4.2. Surface water and sediment

A maximum total F concentration of 1.5 $mg.l^{-1}$ in fresh surface water has been derived for aquatic organisms, on the basis of the available toxicity data. This value is exclusively founded on tests conducted with the readily freshwater-soluble sodium fluoride, so that it may be equated to 1.5 $mg.l^{-1}$ dissolved fluoride. Since only this F fraction (NEN 6453: determination of total free and complexed fluorides, dissolved) is determined within the monitoring network for water-quality research in the state-owned water bodies, a maximum concentration of 1.5 $mg.l^{-1}$ dissolved fluoride has been proposed for fresh surface waters. A concentration of 1.5 $mg.l^{-1}$ corresponds to the maximum acceptable toxicant concentration for humans in drinking water with respect to the occurrence of dental fluorosis (see 8.1.1.) and to the upper limit proposed by the EEC for surface waters intended for the production of drinking water (see table 1.4.). On the other hand, both the upper limit for surface water intended for the production of drinking water and the standard for drinking water in force in the Netherlands are lower, viz., 1.0 mg and 1.1 $mg.l^{-1}$ respectively, so

that the range of the maximum permissible level lies between 1.0 and 1.5 $mg.l^{-1}$.

In accordance with recent policy premises, the target value has been set at 1% of the maximum acceptable level (i.e., 0.01-0.015 $mg.l^{-1}$), or at the background level (0.01-0.3 $mg.l^{-1}$) if the target value to be derived is lower than the natural background concentration. The range of the lower limit therefore lies between 0.01 and 0.3 $mg.l^{-1}$.

The current reference value for groundwater (0.5 $mg.l^{-1}$) lies between the ranges of the proposed upper limit and target value.

8.4.3. Air

Standards and recommended limits for the atmospheric fluoride concentrations have been derived directly from observed effects or damage. The uncertainty in these values is great and requires further study. One factor in choosing the type of quality criterion is also that, depending on the effect, a variable fraction of the fluoride present is involved. In the case of a quality criterion intended to protect plants, it concerns especially gaseous and the pH 4-soluble fluorides; for a quality criterion aimed at the protection of cattle, the pH 2-soluble fluorides are also important. As regards the recommended values derived in chapter 5, the maximum daily average values are the most restrictive, in view of the concentrations occurring in the air. In addition to the daily average, the scheme below also gives, in brackets, the annual average or seasonal average approximately corresponding to this (soluble at pH 1, on measurement-technical grounds), and indicates the type of protection provided:

- 0.3 $\mu g.m^{-3}$ (0.05 $\mu g.m^{-3}$), as a maximum daily average during the whole year (thus also in winter) to protect wild fauna (red deer and roe deer).
- 0.8 $\mu g.m^{-3}$ (0.13 $\mu g.m^{-3}$) as a maximum daily average to protect (most) cultivated plants and wild flora.
- 0.8 $\mu g.m^{-3}$ (seasonal average 0.13 $\mu g.m^{-3}$; annual average 0.18 $\mu g.m^{-3}$) as a maximum daily average to protect livestock and wild fauna (red deer and roe deer) during the grazing season.

8.5. REQUIRED AND ATTAINABLE EMISSION REDUCTIONS

8.5.1. Soil

The risks to livestock and other animals are to a considerable extent determined by the F contents of the crops and to a much smaller extent by the soil F concentration. For vegetation, the principal route is exposure to atmospheric fluoride. A reduction in fluoride input to the soil could be achieved by lowering the F content of commercial fertilizer, but this has not been considered because of the small economic interests involved.

8.5.2. Water

The F concentrations at which effects occur are hardly exceeded at all in the Dutch water bodies. Even a possible small increase in freshwater levels would present no problems, which may be an important factor in choosing air-purification techniques. Regarding the residual stream, there is a difference between the wet and dry systems for air purification.
Wet systems generate waste water: if it is discharged into surface water, its F concentration will increase. The proposed maximum F level may be exceeded when discharge takes place into a small water body, but in most cases the waste water will be discharged into the large rivers. Thus, application of wet systems in the ceramics industry, with discharge of the wash water, increases the F concentration in the large rivers by less than 5% when mixed well. In view of the difference between the current concentrations in the large rivers (about 0.2 $mg.l^{-1}$ in the Rhine and its branches, and about 0.2-1.3 $mg.l^{-1}$ in the Meuse) and the maximum acceptable toxicant concentration (1.5 $mg.l^{-1}$), such a small increase may be assumed to have no demonstrable effect.
Dry systems are accompanied by a (chemical) waste problem. In any case the application of dry systems produces over 1000 tonnes of chemical waste, with uncertain prospects for its reuse.

8.5.3. Air

An attempt has been made to gain some insight into the contribution from the various sources to the current F concentrations in different areas, in order to be able to estimate the F concentrations attainable with particular measures.

Distinctions have been made between area sources, Dutch sources outside the area and foreign sources. The contribution from each of these sources separately cannot be determined equally well in all cases. The figures, presented in table 8.2., should therefore be regarded as indicative. The attainability of certain values for the F level in outdoor air can only be roughly tested, whereby possible changes in the foreign emissions are disregarded. This has been worked out for each area, with brief mention of the situation around individual sources in a few cases. The target values used for the discussion are 0.05 $\mu g.m^{-3}$ (the level at which man and, to a considerable extent, the environment are protected), 0.2 $\mu g.m^{-3}$ (approximately corresponding to the level at which cattle are protected during the grazing season), and the current draft limit, 0.4 $\mu g.m^{-3}$ (annual averages; see also 8.4.3.). The contribution from Dutch sources located outside the specific areas also includes the influence of coal-fired power stations. Despite proposed measures, an increase in emissions is to be expected as a result of increasing use of coal (Medium Coal scenario). Its average contribution to the atmospheric F concentration is of the order of 0.001 $\mu g.m^{-3}$.

Table 8.2. Rough indications of the contributions to the F concentrations (in $\mu g/m^3$; annual average) in several Dutch areas from foreign sources, domestic sources outside the area and the sources in the area itself (the last-mentioned are given in peak values for the averages per km^2)

Area	*Background concentration*		*Contribution from sources in the area (peak values) **	*Total*
	Abroad	*At home*		
East Groningen	*0.03-0.04*	*0.006-0.01*	*0.4 -1.9*	*0.4 -2.0*
Gelderland (riv.)	*0.06-0.08*	*0.02 -0.03*	*0.15-0.2*	*0.2 -0.3*
South Limburg	*0.08-0.12*	*0.005-0.01*	*0.1 -0.2*	*0.2 -0.3*
Zeeuws Vlaanderen	*0.07-0.1*	*0.05 -0.2*	*0.03-0.05*	*0.15-0.35*
Sloe area	*0.07-0.09*	*0.01 -0.015*	*0.4 -1.3*	*0.5 -1.4*
Rijnmond	*0.06-0.08*	*0.02 -0.04*	*0.1 -0.2*	*0.15-0.3*

** calculated; includes an unknown fraction of insoluble fluoride*

- East Groningen

The atmospheric F concentrations in this area are mainly determined by two factories which interact to a small extent as regards the prevailing F concentrations. It should be noted that even higher levels have been measured over the Wadden Sea, near one of the plants. In principle, emission reduction is possible to a considerable extent in the manufacture of glass fibre and to a smaller extent in aluminium production. It is unlikely (if the emitted fluoride consists largely of soluble fluoride) that, with the limited emission reduction, the F concentration will fall below 0.2 $\mu g.m^{-3}$ in the area around the plant, possibly to just below 0.4 $\mu g.m^{-3}$, averaged over one km^2 (this would have to be worked out specifically for this situation).

- Gelderland (river area)

Although outside influences on this area are not negligible, it is affected chiefly by the brick works situated here. The contribution from these plants to the atmospheric F concentration is such that the value of 0.2 $\mu g.m^{-3}$ will possibly not be attained everywhere. Increasing the stack height is not the solution, which means that the plants will have to switch to flue-gas scrubbing. In principle, all the scrubbing techniques discussed in chapter 6 are suitable. The atmospheric F concentrations will then no longer be exceeded regionally, nor in specific locations near individual plants, except when the target value is set at 0.05 $\mu g.m^{-3}$. The cost of these techniques may be prohibitive for a certain number of weaker plants. In the present situation, a concentration of 0.4 $\mu g.m^{-3}$ poses no problems on a regional scale, but it is conceivable that it is exceeded around individual sources. It will then be sufficient for most brick works to increase their stack height.

- South Limburg

The atmospheric F concentration in this area, which borders on several other countries, is strongly influenced by emission sources in Belgium and West Germany. Nevertheless, the approach used in the coarse and fine ceramics industries, as described for Gelderland, possibly supplemented with measures in coal combustion, should here also be adequate to reduce the atmospheric F concentration to below 0.2 $\mu g.m^{-3}$, but a level of 0.05 $\mu g.m^{-3}$ is not attainable.

- Zeeuws Vlaanderen

The background concentration in Zeeuws Vlaanderen is strongly influenced by sources in both Belgium and the Sloe area. Local plants make only a limited contribution. Insofar that it can be assessed, the value of 0.4 $\mu g.m^{-3}$ is attained, but the peak values are only just below this. Further reduction requires cleanup of the "outside" sources (see Sloe area).

- Sloe area

The Sloe area is affected by two sources, of which one is probably much larger than has hitherto been assumed (manufacture of polyphosphates: slag removal). In both cases, no significant improvement is to be expected from the emission-control measures elaborated in chapter 6. Polyphosphate manufacture is at a source-investigation stage, with the known sources already having been dealt with. Emission reduction at the aluminium plant is possible, but will be small in view of the present fairly low emission factor. It is therefore unlikely (if the emitted fluoride consists largely of soluble fluoride) that the value of 0.2 $\mu g.m^{-3}$ is attainable, and even the twofold higher concentration is difficult to realize. This is partly because the two plants are situated close to each other.

- Rijnmond

In the 1980s, considerable reductions in F emissions have been achieved in this area so that the outside contributions (Belgium, Sloe area, coal-fired power stations) are now of the same order of magnitude. The F concentrations, calculated for areas of 1 km^2, are less than 0.4 $\mu g.m^{-3}$. A major source is the storage and transshipment of phosphate ore. However, it concerns here particulates containing sparingly soluble F compounds. There are limited possibilities for further emission reductions (phosphoric acid plants, waste incineration). These may reduce the atmospheric F concentration to below 0.2 $\mu g.m^{-3}$, but more calculations and measurements in this field are required, to be to certain about this.

Table 8.3. summarizes the attainability of the three F concentrations discussed.

Table 8.3. Rough indications of the feasibility of F concentrations (in $\mu g/m^3$; maximum annual averages) in several areas, with implementation of the measures described in chapter 6 (see also table 8.2.)

Area	Feasibility			
	average per km^2			in 1 location
	0.05	0.2	0.4	0.4
East Groningen	--	-	+	-
Gelderland	--	++	*	++
South Limburg	--	++	*	++
Zeeuws Vlaanderen	--	-	*	*
Sloe area	--	--	+	--
Rijnmond	--	+	++	++

-- *not attainable*
- *attainability is unlikely (depends on the soluble/insoluble fluoride emission ratio of the plants concerned)*
\+ *possibly attainable*
* *already attained*

8.6. CONCLUSIONS AND RECOMMENDATIONS

As regards the recommended values formulated on the basis of toxicological data, the following conclusions can be drawn:

- The ecotoxicological data on soil and groundwater necessary for deriving a recommended limit are insufficient. However, there are indications that effects on soil flora and fauna are not the most critical consideration. There is therefore as yet no reason for deviating from the reference values proposed earlier.
- As regards fresh surface water and sediments, the gravity of the emission sources in the Netherlands appears to differ widely because of the difference in the emitted F species. A concentration ranging from 1.0 to 1.5 $mg.l^{-1}$ dissolved F has been recommended as an upper limit, and a concentration of from 0.01 to 0.3 $mg.l^{-1}$ as a lower limit.
- As regards outdoor air, the toxicological recommended values are lower than the current interim ceiling (0.4 $\mu g.m^{-3}$). This limit is attainable throughout the Netherlands, except near a few sources (East Groningen, Sloe area). Nevertheless, it is expected that the range of the recommended values (0.05-0.2 $\mu g.m^{-3}$, annual average) will then still be exceeded nationally and regionally, respectively; an international approach is required to achieve the lower limit. However, the proposed recommended concentrations are based on transfer factors and dose-

response relationships, whereby assumptions have been made including a number requiring a sounder underpinning, certainly in view of the possible severity and extent of the effects on the one hand, and the not inconsiderable financial consequences of possible emission-control measures on the other.

More knowledge is desirable concerning:

* in particular the relationship between the F emissions, air concentrations, and contents of grass and other crops for consumption,
* corroboration of the speculative assumption that the effects of F on the soil flora and fauna are not very critical, also in the light of the weak accumulative nature of fluoride and its limited bioavailability,
* The dispersal pattern and the foraging behaviour of red deer and roe deer, a possible major risk group, and the role of the associated relevant factors mentioned earlier,
* the possibly greater sensitivity of evergreen plants to fluoride and thereby the possible contribution of the current F concentrations to the deterioration of forests,
* the slag removal process as an emission source in the manufacture of polyphospates in the phosphate ore-processing industry.

9. REFERENCES

9.1. REFERENCES CHAPTER 1

Banks, R.E. and H. Goldwhite (1966)
Fluorine chemistry
Handbook of experimental pharmacology (F.A. Smith ed.), 20, 1
Springer Verlag, New York

Chemical Waste Act (Wet Chemische Afvalstoffen) (1984)
Bijlage van het Koninklijk Besluit van 26 mei 1977
Staatsblad 435, Staatsuitgeverij, 's-Gravenhage

Contaminantsbooklet (Contaminantenboekje) (1987)
Staatsuitgeverij, 's Gravenhage

Cosmetics Decree (Stoffenbesluit Cosmetica) (1986)
Cosmeticabesluit (Warenwet) 1979
Staatsblad 1980, 256

Durrant P.J. and B. Durrant (1962)
Introduction to advanced inorganic chemistry
Longman Group Limited, London

EEG (1975)
Publikatieblad van de Europese Gemeenschappen
Nr. L 194

Ekstrand, J., L.O. Boreus and P. de Chateau (1981)
Br. Med. J., 283, 761-762

Elrashidi and Lindsay (1986)
Food and Nutrition Board USA (1980)
Recommended dietary allowances, 9th edition
National Academy of Sciences, Washington D.C.
(Voeding, 1986, nr.6)

Gall, J.F. (1966)
Hydrogen fluoride
Kirk-Othmer encyclopedia of chemical technology, 2nd ed., 9, 610-625
John Wiley & Sons, New York

Gemert, L.J. van, et al. (1984)
Compilation of odour threshold values in air
Supplement V, CIVO-TNO rapport no. A 84

Health Council (Gezondheidsraad) (1981)
Advies inzake advieswaarden voor anorganische fluoriden in de buitenlucht

Horton, C.A. (1962)
Fluorine
Practice of analytical chemistry (J.M.Kolthoff en P.J.Elding, eds.)
7, [2], 207-334

IAWR (1986)
Rijn memorandum 1986
Internationale Arbeitsgemeinschaft der Wasserwerke im Rheineinzugsgebiet
ISBN 90 70071 04 2

IDC (1985)
Overzicht normen luchtkwaliteit MIC-waarden
3de aanvulling, maart 1985
Interprovinciaal Documentatiecentrum

Largent, E.G. (1983)
Fluorine and compounds
Encyclopaedia of occupational health and safety
Col. 1, Geneva, ILO

LSI (1985
Drinking water criteria document for fluoride
Life Systems Inc. Cleveland OH., NTIS PB 86-118163
Marktl, W. von (1986)
Mineralwässer und Heilwässer in Osterreich
Wasserwirtschaft, 38, Heft 3/4
MPV/88 (1987)
Milieuprogramma 1988-1991, voortgangsrapportage
Tweede Kamer, vergaderjaar 1987-1988, 20202, nrs. 1-2
National MAC list (Nationale MAC-lijst) (1986)
Directoraat Generaal van de Arbeid
Voorburg
Rusch, G.F. and L.R. Willis (1982)
Renal tubular effects of sodium fluoride
J. Pharmacol. Exp. Ther., 223, 275-279
Smith, G.E. (1984)
Toxicity of fluoride-containing dental preparations: a review
The Science of the Total Environment, 43, 41-61
Elsevier Science Publishers B.V., Amsterdam
Stephen, H. en T. Stephen (1963)
Solubilities of inorganic and organic compounds
Pergamon Press
TA Luft (1986)
Technical constructions on air quality control
Federal Ministry for Environment Nature Conservation and Reactor Safety
TNO (1977)
Milieunormen en criteria
Delft
VAR (1976)
Eisen te stellen aan het oppervlaktewater waarin waterdieren leven die voor menselijke consumptie kunnen dienen
Interim-rapport van de commissie van de Gezondheidsraad
Verslagen Adviezen Rapporten, VROM, Leidschendam
VROM (1983)
Soil Cleanup Guide (Leidraad bodemsanering)
VROM, Staatsuitgeverij, 's-Gravenhage
Waldbott, G.L. (1963)
Fluoride in food
Am. J. Clin. Nutr., 12, 455
Waterboard Decree (Waterleidingbesluit) (1984)
Staatsblad 345, 7 juni 1960, inclusief wijzigingen in werking getreden op 1 juli 1984
Weast, R.C., H.J. Astle and W.H. Beyer (1986)
CRC-Handbook of chemistry and physics
Boca Raton, Fla., CRC Press, 1985-1986
WGD (1987)
Concept rapport van de Werkgroep van Deskundigen
WGD rapport 87-49-4, augustus 1987
WHO (1984a)
Fluorine and fluorides
Environmental health criteria nr.36
World Health Organization, Geneva
WHO (1984b)
Guidelines for drinking-water quality
WHO, Geneva 1984

Wibowo, A.A.E. and R.L. Zielhuis (1986)
A health-bases recommended occupational exposure limit for fluorine, hydrogen fluoride and inorganic fluoride compounds, on behalf of the Group of Experts of the Directorate-General of Labour
Coronel Laboratorium, Academic Medical Centre, Faculty of Medicine, University of Amsterdam
Report No. 8605 R, August 1986

9.2. REFERENCES CHAPTER 2

Alluminium producers (1988)
Personal communication
Aronds, C.A. (1976)
De massastroom van fluor door Nederland
Werkgroep Fluor, Sectie Milieuchemie KNCV, 1976
Berenschot/Tebodin (1987)
Milieustudie van twee fosforzuurfabrieken in Rijnmond
Basisdocument Cadmium (1987)
(J.Ros en W.Slooff, eds.) Chapter 8 and 9
RIVM report nr. 758476002
Bijl, P. en H.J. Huldy (1986)
Onderzoek naar bestrijding fluoremissies bij de non-ferro-metaal-industrie
Report R 86/065 (confidential), TNO
CBS (1985)
Maandstatistiek van de buitenlandse handel per goederensoort c.q. per land
Department of public works (Rijkswaterstaat), Rijksinstituut voor Volksgezondheid en Milieuhygiëne
Kwaliteitsonderzoek in de rijkswateren, Verslag van de resultaten over de kwartalen van 1985
DHV (1986)
Kolenreststoffen in Nederland: produktie, afzet en overschot
Eurostat (1985)
Industry Statistical Yearbook. Theme 4 Energy and Industry, Serie A, Yearbooks 1985
Eurostat (1986)
Industrial Production, Quarterly statistics, Theme 4 Energy and industry, Serie B, Short-term trends 1986
FAO (1986)
Fertilizer yearbook
Vol. 35, FAO Statistics Series No. 71
Food and Agriculture Organization of the United Nations, Rome 1986
Haskoning (1984)
Beperking luchtverontreiniging veroorzaakt door verbranding van afval
Ministerie van VROM
Haskoning (1986)
Fluor- en stofuitworp van de grofkeramische industrie (concept)
Ministerie van VROM
Handbook of Emission Factors (1980)
Staatsuitgeverij, 's Gravenhage
Handboek Modelvoorschriften Luchtverontreiniging (1986)
Hoofdstuk Ammoniak-, salpeterzuur- en kunstmestfabrieken
Staatsuitgeverij, 's Gravenhage
Handbook of emission factors (1983)
Part 1, Non Industrial Sources and Part 2, Industrial Sources
Ministerie van VROM

Industrial Statistics Yearbook (1983)
Volume II, Commodity Production Statistics 1974-1983
Department of International Economic and Social Affairs
Statistical Office of the United Nations, United Nations New York 1983
International Energy Agency (1986)
Coal information, 1986
Integrated criteria document nitrate (1989)
Chapters 2 and 7
RIVM report no. 758473012
Jeuring, Z. (1987)
Ministerie van Economische Zaken, hoofdafdeling kolen
personal communication
Jonge, L.S. de (1985)
Baksteenindustrie en luchtverontreiniging
Lucht en omgeving, 162-165
LEI (1986)
Jaarstatistiek van de kunstmestoffen (1984/1985)
Landbouw-Economisch Instituut
N.V.S.E.P. (1987)
Elektriciteitsplan 1987-1996
Mey, R. et al. (1985)
Emissions and control of particulates of coal-fired power plants
In: proceedings of the second US-Dutch International Symposium on aerosols, Williamsburg, VA, USA, May 1985, chapter 29, 427-440
PEO (1986a)
Air pollution as a result of the emission from coal fired power stations
Stichting Projectbeheerbureau Energie Onderzoek
Project no. 20.70-004.11
PEO (1986b)
De emissie van luchtverontreinigende componenten door met kolen gestookte elektriciteitscentrales
Stichting Projectbeheerbureau Engergie Onderzoek
projectnr. 20.870.-012.40
RIVM-LAE (1985)
Inventarisatie beperkingen verwijderingsmethoden
Deelproject 4 van het project klein chemisch afval (concept)
Ministerie van VROM
Somers, W. (date unknown)
Lasrook, Donaldson-Tonit B.V.
Tjioe, T.I. (1986)
Nieuwe technologie fosforzuurproces
PT/Procestechniek 41, 11, 28-31
TNO (1985)
Review of literature data on hydrogen fluoride
Recycling (1986)
nr. 5, 20e jaargang, 133-137
Water Research Centre (1980)
Control of contamination: problems in the treatment and disposal of sewage sludge
TR 156, 1980, WRC Process Evaluation, Stevenage
Wei, M.W. (1975)
The Alcoa 446 process for the control of anode baking furnace fumes
Light Metals Proceedings Sess., New York, 261-268

9.3. REFERENCES CHAPTER 3

Barnard W.R. and D.K. Nordstrom (1982)
Fluoride in Precipitation - I. Methodology with Fluoride-selective Electrode
Atmospheric Environment, 16, 99

Barrow, N.J. and A.S. Ellis (1986)
Testing a mechanistic model - III. The effects of pH on fluoride retention by a soil
J. of Soil Sci., 37, 287-293

Blokzijl, P.J. (1977)
Meting van fluoriden in de buitenlucht
Publicatie TNO-IMG nr. 590
PT/Procestechniek 32 (7), 392-398

Bower, C.A. and J.T. Hatcher (1967)
Adsorption of fluoride by soils and minerals
Soil Sci. 103, 151-154

Braen, S.N. and L.H. Weinstein (1985)
Uptake of fluoride and aluminum by plants grown in contaminated soils
Water Air Soil Poll., 24, 215-223

Clegg, S.L. and P. Brimblecombe (1988)
Hydrofluoric and hydrochloric acid behaviour in concentrated saline solutions
J. Chem. Soc. Dalton Trans., 705-710

Chabra, R., A. Singh and I.P. Abrol (1979)
Fluorine in sodic soils
Soil Sci. Soc. Am. J., 44, 33-36

Department of Public Works (Rijkswaterstaat) (1976-1986)
Kwaliteitsonderzoek in de Rijkswateren
Verslag van de resultaten in de kwartalen van 1976 tot 1986

Eck, G.T.M. van (1982)
Geochemie van zwevend materiaal in het Hollands Diep/Haringvliet
Proefschrift R.U. Utrecht

Elrashidi, M.A. and W.L. Lindsay (1986a)
Solubility of aluminum fluoride, fluorite and fluoriphlogopite minerals in soils
Soil Sci. Soc. Am. J. 50, 594-598

Ferguson, J.F. and P.L. McCarthy (1971)
Effects of carbonate and magnesium on calcium phosphate precipitation
Environ. Sci. Technol., 5, 534

Fluhler, N.K., J. Polomski and P. Blaser (1982)
Retention and movement of fluoride in soils
J. Environm. Qual., 11, 461-468

Golterman, H.L. (1971)
Het voorkomen van fluoride en eventuele interacties met het eutrofiëringsproces in oppervlaktewateren
Water, 55, 309

Harrison, R.M. and R. Perry (1986)
Handbook of air pollution analysis
University Press, Cambridge, 425

Health Council (Gezondheidsraad) (1981)
Advies inzake advieswaarden voor anorganische fluoriden in de buitenlucht
Verslagen, Adviezen, Rapporten (VAR) no. 50
Ministerie van Volksgezondheid en Milieuhygiene, Leidschendam

Huang, P.M. and M.L. Jackson (1965)
Mechanism of reaction of neutral fluoride solution with layer silicates and oxides of soil
Soil Sci. Soc. Am. Proc., 29, 661-665
McIntire, W.H., A.J. Sterges and W.M. Shaw (1955)
Rate and effects of hydrofluoric acid added to four Tennissee Soils in a 4 year lysimeter study
Agric. Food Chem., 3, 777-782
Murray, F. (1983)
Fluoride retention in sandy soils
Water, Air and Soil Poll., 20, 361-366
Omueti, J.A.I. and R.L. Jones (1977)
Fluoride content of soil from morrow plots over a period of 67 years
Soil Sci. Soc. Am. J., 41, 1023-1024
Peek, D.C. and V.V. Volk (1986)
Composition and speciation of sodium fluoride extracted soil solutions
Commun. in Soil Sci. Plant Anal., 17 (7), 741-759
Perrott, K.W., B.F.L. Smith and R.H.E. Inkson (1976)
The reaction of fluoride with soils and soil minerals
J. Soil Sci., 27, 58-67
Polomski, J., H. Fluhler and P. Blaser (1982a)
Accumulation of airborne fluoride in soils
J. Environm. Qual., 11, 457-461
Polomski, J., H. Fluhler and P. Blaser (1982b)
Aluminium
J. Environm. Qual., 11, 452-457
Roorda van Eysinga, J.P.N.L. (1974)
De opname van fluoride door de wortel en de gevolgen voor diverse gewassen, in het bijzonder de fresia
Proefschrift, Uitg. PUDOC Wageningen
Slavek, J., H. Farrah and W.F. Pickering (1984)
Interaction of clays with dilute fluoride solutions
Water Air Soil Poll., 23, 209-220
Stumm, W. and J.J. Morgan (1981)
Aquatic chemistry
2nd Edition, J.W. & S., N.Y. Chichesterm Brisbane, Toronto, 376
Supharungsun, S. and M. Wainwright (1982)
Determination, distribution and adsorption of fluoride in atmospheric-polluted soils
Bull. Environm. Contam. Toxicol., 28, 632-636
Tracy, P.W., C.W. Robbins and G.C. Lewis (1984)
Fluorite precipitation in a calcareous soil irrigated with high fluoride water
Soil Sci. Soc. Am. J., 48, 1013-1016

9.4. REFERENCES CHAPTER 4

Amsterdam Food Inspection Department (Keuringsdienst van Waren Amsterdam) (1987)
Personal communication
Backer Dirks, O. and J. Tesink (1972)
Unpublished data
Barelds, A.J. and D.H. Meijer (1986)
Onderzoek naar de uitdamping van HF in van geïmprosoleerd hout gebouwde woningen
Keuringsdienst van Waren Assen, 1986

Barnard W.R. and D.K. Nordstrom (1982a)
Fluoride in precipitation
I. Methodology with fluoride-selective electrode
Atmospheric Environment, 16, 99

Barrow, N.J. and A.S. Ellis (1986)
Testing a mechanistic model. III
The effects of pH on fluoride retention
J. of Soil Sci., 37, 287-293

Berg, R. v.d., H. Mesters-Bakhuijs, J.J. van Staden and S. v.d. Berg (1988)
Extractie fluoride uit rivierklei. Simulatie van de beschikbaarheid in de koemaag
RIVM rapport nr. 758474006

Belcher R., M.A. Leonard and T.S. West (1959)
Submicro-methods for the analysis of organic compounds
Part X. Determination of fluorine
J. Am. Chem. Soc., 81, 3577

Biersteker, K. and R.L. Zielhuis (1975)
De fluoridenbelasting in Borsele in 1974

Bikker, M and L.Th. de Leu (1986)
Fluoriden in de buitenlucht, een overzicht van de meetgegevens in Nederland
Rapport MT-TNO, R86/108

Braen, S.N. and L.H. Weinstein (1985)
Uptake of fluoride and aluminum by plants grown in contaminated soils
Water Air Soil Poll., 24, 215-223

Centraal Bureau voor de Statistiek (CBS) (1986)
Luchtverontreiniging, metingen buitenlucht april 1985 - maart 1986
Staatsuitgeverij, 's Gravenhage

Davison, A.W. and J. Blakemore (1980)
Rate of deposition, and resistance to deposition, of fluorides on alkali-impregnated papers
Environ. Pollut. (ser. B), 305-319

Department of Public Works (Rijkswaterstaat) (1976-1986)
Kwaliteitsonderzoek in de Rijkswateren
Verslag van de resultaten in de kwartalen van 1976 tot 1986

Dienst Centraal Milieubeheer Rijnmond (DCMR) (1986)
Jaarverslag 1984

Eerden, L.J. van der (1983)
Fluoride-accumulatie in gras (voortgangsverslag II, 1983)
Instituut voor Plantenziektenkundig Onderzoek

Eerden, L.J. van der, A.E.G. Tonneijck and J.H.M. Wijnands (1985)
Schade door luchtverontreiniging aan de agrarische produktie in Nederland
Instituut voor Plantenziektenkundig Onderzoek, Concept 14-5-1985

Eerens, H.C., H. Schokkin and J.A. van Jaarsveld (1988)
Berekening van concentratie en depositie van fluoride in Nederland
RIVM, in preparation

Eikmann, Th. et al. (1984)
The burden of population with fluoride - I. Communication: occurrence and effects on man (a survey of literature)
Wissenschaft und Umwelt, 3, 170-181

Egmond, N.D. van, and C. Huygen (1979)
Evaluation of a meso-scale model of the dispersion of sulphur dioxide
Proc. 10th NATO/CCMS Intern. Techn. Meeting on Air Pollution Modeling and its Application (Rome)

Ehrnebo, M. and J. Ekstrand (1986)
Occupational fluoride exposure and plasma fluoride levels in man
Int. Arch. Occup. Environ. Health 58, 179-190
Elrashidi, M.A. and W.L. Lindsay (1982)
Chemical equilibria of fluorine in soils
A theoretical development
Soil Science, 141, 274-280
Fischler, M. and H. Kretzdorn (1942)
Wein und Rebe, 24, 69
Fonds, A.W. (1987)
Personal communication
RIVM
Frant M.S. and J.W. Ross (1968)
Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies
Analyt. Chem., 40, 1169
Gabovic, R.P. (1957)
Fluoride and its hygienic importance
Karan, USSR (russian)
Giezen, J.J. van (1982, 1984)
De verontreiniging van de buitenlucht in Zeeland
Rapporten IMG-TNO G 1039 (oktober 1982) en G 1135 (januari 1984)
Gisiger, (1968)
Fluoriden, 1, 21
Hani, H. (1975)
Wechselwirkung von Fluorid mit einem mineralischen, illitachtigen Boden und Veränderung in den darauf wachsende Maispflanzen
Schweiz. Landwirtsch. Forsch., 14, 189-210
Health Council (Gezondheidsraad) (1981)
Advieswaarden voor anorganische fluoriden in de buitenlucht
Hennig, K. and F. Villforth (1938)
Vorratspflege und Lebensmittelforschung, 1, 653
Hout, K.D.van den, C. Huygen, W.A.M. den Tonkelaar and N.D.van Egmond (1983)
Stikstofoxiden in de Nederlandse buitenlucht/ Stikstofdioxide
Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer
Rapport Lucht 15
Jaarsveld, J.A. van, and D. Onderdelinden (1988)
RIVM, in preperation
Jansen, J. (MT-TNO, Delft) (1986)
Personal communication
Joziasse, J. and M.A. Bikker (1986)
Evaluatie van meetmethoden voor fluoriden in de atmosfeer
Rapport nr. 86-014071 MT-TNO, Apeldoorn
KNMI en RIVM (1983, 1984, 1985 en 1986)
Chemical composition of precipitation over the Netherlands
Annual report ISSN 0169-1759 PEO
Stichting Projectbeheerbureau PEO
Kussmaul, H. and D. Muhlhausen (1979)
Hydrologische und hydrochemische Untersuchungen zur Uferfiltrationen, Teil 3: Veränderungen der Wasserbeschaffenheit durch Uferfiltrationen und Trinkwasseraufbereitung
GwF-Wasser/Abwasser, 120, 320-329
Larsen. S. and A.E. Widdowson (1971)
Soil Fluorine
J. of Soil Sci., 22, 210-221

Lavado, R.S. and N. Reinaudi (1979)
Fluoride in salt affected soils of La Pampa (Argentinië)
Fluoride, 12, 28-32
Manley, T.R., D.J. Stewart, D.A. White and D.L. Harrison (1975)
Natural fluorine levels in the Bluff area, New Zealand
Part 2. concentrations in pasture, soil, water, and urine of sheep and cattle
New Zealand J. of Sci., 18, 433-440
McClure, F.J. (1949)
Publ. Hlth. Rep. (Wash.), 64, 1061
Medecins Bulletin (Geneesmiddelenbulletin) (1982)
Fluoriden voor tandheelkundig gebruik
Jaargang 16, 14, 7 oktober 1982
Memorandum on Fluoridation of Drinking Water (Nota fluoridering drinkwater) (1973)
Provinciale staten van Zeeland
Vergadering 23 november 1973, nr. 1764/222
Min. van S.Z. and W., Directoraat van de Arbeid, Directie Gezondheid (1987)
Brief aan Dr. W. Slooff (RIVM), 23 okt. 1987
Neele, J. (1986)
Resultaten van vergelijkingsmetingen van fluorverbindingen uit houtconserveringsmiddelen in een woning te Apeldoorn
NNI NEN 6483 (1982)
Water - Potentiometrische bepaling van het totale gehalte aan fluor
Nederlandse Normalisatie Instituut, Delft
NNI (1983)
Nederlandse Praktijkrichtlijn NPR 2790
Luchtkwaliteit - Buitenlucht - Monsterneming en bepaling van anorganische gasvormige fluoriden met behulp van de dubbelfiltermethode
Nederlands Normalisatie Instituut, Delft 1
Analyse van fluor in grond
Polomski, J., H. Fluhler and P. Blaser (1982)
Accumulation of airborne fluoride in soils
J. Environm. Qual., 11, 457-461
Projectbeheerbureau Energieonderzoek, PEO (1986)
Air pollution as a result of the emission from coal-fired power stations, 17 (table 5)
Raay, A. van (1977)
Onderzoek naar de fluorhoudende luchtverontreiniging in het Sloegebied in de periode 19-10-1975 tot 17-10-1976
Instituut voor Plantenziektenkundig Onderzoek, oktober 1977
Ridder, T.R. et al. (1984)
De invloed van monstermethoden en analysetechnieken op gemeten chemische concentraties in regenwater
KNMI, 1984
Roorda van Eysinga, J.P.N.L. (1974)
De opname van fluoride door de wortel en de gevolgen voor diverse gewassen
Proefschrift, Uitg. PUDOC Wageningen
RIVM (1986)
Luchtkwaliteit, Jaarverslag 1984 en 1985
RIVM (1987)
Luchtkwaliteit, Jaarverslag 1986
RIVM (1988)
Luchtkwaliteit, Jaarverslag 1987

Sehmel, G.C. (1980)
Particle and gas dry deposition: A review
Atmos. Environm., 14, 983-1011
Sholtes, R.S., E.H. Meadows Jr. and J.B. Koogler (1973)
Evaluation and modification of fluoride sampling and analytical methods
Washington CD, US EPA, 84 (EPA-650/2-73-007)
Sidhu, S.S. (1973)
Fluoride levels in air, vegetation and soil in the vicinity of a phosphorus plant
Air Poll. Contr. Ass., 29, 1069-1072
Singer, L. and W.D. Armstrong (1965)
Determiniation of fluoride, procedure based upon diffusion of hydrogen fluoride
Anal. Biochem., 10, 495-500
Singer, L., W.D. Armstrong and G.T. Vatassery (1967)
Econ. Bot., 21, 285-287
Staarink, T. and P. Hakkenbrak (1987)
Het Contaminantenboekje
Een overzicht van stoffen die drink- en eetwaren verontreinigen
Staatsuitgeverij, 's Gravenhage
Stumm W. and J.J. Morgan (1981)
Aquatic Chemistry, 2nd Edition, John Wiley & Sons, N.Y. Chichester, Brisbane, Toronto
Supharungsun, S. and M. Wainwright (1982)
Determination, distribution and adsorption of fluoride in atmospheric-polluted
Bull. Environm. Contam. Toxicol., 28, 632-636
The Analytical Working Group of the Comité Technique Européan du Fluor (1986)
The determination of fluoride in environmentally relevant matrices
Anal. Chem. Acta, 182, 1
Tesink, J. (1982)
collected reports 1968-1982
Raadgevend Bureau Milvetox, Goes
Thijsse, Th.R. and C. Huygen (1985)
Onderzoek naar de grootschalige achtergrondconcentraties van spoor-elementen en -verbindingen in de Nederlandse buitenlucht
Rapport MT-TNO, R 85/272
Tromp, L.M. (Silenka N.V.) (1987)
Personal communication
Vuorinen, A., P. Lahermo and T. Hatva (1986)
In press
Wal, J.F. van der (1987)
Personal communication
Water Companies Rhine Committee (Rijncommissie Waterleidingbedrijven)
Jaarverslag (1977, 1978 en 1979)
deel B: de Maas, Amsterdam, 1978, 1979, 1980
Willard H.H. and O.B. Winter (1933)
Volumetric method for determination of fluorine
Ind. Eng. Chem., 5, 7
WHO (1970)
Fluorides and human health
Geneva

9.5. REFERENCES CHAPTER 5

Adams, D.F., C.G. Shaw, R.M. Gnagy et al. (1956)
Relationship of atmospheric fluoride levels and injury indexes on gladiolus and ponderosa pine
J. Agr. Food Chem., 4, 64-66

Barelds, A.J. and D.H. Meyer (1986)
Onderzoek naar de uitdamping van HF in van geïmprosoleerd hout gebouwde woningen
Keuringsdienst van Waren, Assen

Benedict, H.M., J.M. Ross and R.W. Wade (1965)
Some responses of vegetation to atmospheric fluorides
IAPCA, 15, 253-255

Berg, R. van den et al. (1988)
Extractie fluoride uit rivierklei. Simulatie van de beschikbaarheid in de koemaag
RIVM Rapport nr. 758474006

Besems, A. (1987)
Personal communication

Bikker, M. and L.Th. de Leu (1986)
Fluoriden in de buitenlucht, een overzicht van de meetgegevens in Nederland
Rapport TNO-MT, R 86-108, 45

Brandt, C.J., (1981)
Untersuchungen über Wirkungen von Fluorwasserstoff auf Lolium Multiflorum und andere Nutspflanzen
LIS-Bericht, 14, 1-140

Carslon, C.E. and W.P. Hammer (1974)
Impact of fluorides and insects on radial growth of Lodgepole Pine near an aluminum smelter in North Western Montana
Rep. no. 74-25
For. Env. Prof., Missoula, USA, 14

Chamel, A. and J. Garrec (1977)
Penetration of fluorine through isolated pear leaf cuticles
Environ. Poll., 12, 307-310

Chang, C.W. (1975)
Fluorides
In: Mudd, J.B. and Kozlowski, T.T. (eds.)
Responses of plants to air pollution
Acad. Press., N.Y., 57-95

Collet, G.F., J.P. Quinche and R. Zuber (1969)
Role de la composition chimique des sels fluorés dans leur penetration, accumulation et action biologique chez les végétaux
Recherche Agronomique en Suisse, 8, 1, 65-79

Davis, R.D. (1980)
Uptake of fluoride by ryegrass grown in soil treated with sewage sludge
Environ. Pollut. (Ser. B), 1, 277-284

Doyle, D.P. and T.E. Wright (1982)
Rapid methods for determining atmospheric corrosivity and corrosion resistance
in: W.H. Ailor (ed.) Atmosheric corrosion p. 22
John Wiley and Sons, New York

Eckerlin, R.H., G.A. Maylin and L. Krook (1986)
Milk production of cows fed fluoride contaminated commercial feed
Cornell Vet., 76, 403-414

Eerden, L.J. van der (1986)
Fluoridegehalten in gras
Rapport IPO, Wageningen, 329, 53

Eerden, L.J. van der (1988)
Fluoride contents in grass related to atmospheric fluoride concentrations (concept)

Eerden, L.J. van der and H. Floor (1984)
Fluorideverontreiniging als oorzaak van gewasschade en inferieur veevoer
Bedrijfsontw. 15, 5, 444-449

EPA (1978)
Environmental Protection Agency
Diagnosing vegetation injury caused by air pollution
Lacasse, N.L. and M. Treshow (eds.)
Superint. of Docum., US gov. print. off Washington D.C. 20402
EPA series 450/3-78-005, 250

EPA (1984)
Estimating "concern levels" for concentrations of chemical substances in the environment
Environmental Effects Branch, Health and Environmental Review Division, Environmental Protection Agency

Guderian, R.H., R.H. van Haut and H. Stratmann (1969)
Experimentele Untersuchungen über pflanzenschädigende Fluorwasserstoffkonzentrationen
Forsch. Ber. des Landes Nordrhein-Westf. Nr. 02017
Westdeutscher Verlag, Köln

Guderian, R.H. (1977)
Phytotoxicity of acid gases and its significance in air pollution control
Springer Verlag, Berlin

Guderian, R.H. and K. Rüppers (1980)
Responses of plant communities to air pollution
Proc. of Symp. on Effects of Air Pollutants on Mediterranean and Temperate Forest Ecosystems
Juni 22-27, Pacific. South west Forest and Range Experiment Station
Berkely. General Technical Report, PSW-43, 187-199

Häni, H. (1975)
Wechselwirkungen von Fluorid mit einem mineralischen illithaltigen Boden und Veränderungen in den darauf wachsenden Maispflanzen
Schweiz. Landwirtsch. Forsch., 14, 189-201

Hapke, H.J. (1977)
Immissionswirkungen bei Tieren
Uschau, 77, 15, 517

Health Council (Gezondheidsraad) (1981)
Advieswaarden voor anorganische fluoriden in de buitenlucht
Rapport VAR, 50 , Min. VROM, Leidschendam

Janssen, P.J.C.M. (1988)
Integrated Criteria Document Fluorides - Effects
Appendix to RIVM-Report 758474005

Kooijman, S.A.L.M. (1985)
Een veiligheidsfactor voor LC50-waarden met betrekking tot de variatie tussen soorten
TNO-rapport R 85/49, Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek, Den Haag

Kooijman, S.A.L.M. (1987)
A safety factor for LC50-values allowing for differences in sensitivity among species
Wat.Res., 21, 269-276
Kronberger, W. (1983)
pH-dependency of fluorine uptake by different plants
IUFRO-meeting, Oulu, Finland, Aquilo Ser. Bot., 19, 304
Luckat, S. (1973)
Die Wirkung von Luftveruntreinigungen beim Steinzerfall
Staub-Reinhalt, Luft, 33, 283
Luckat, S. (1974)
Beziehungen zwischen der Korrosionsrate von Stahl und der Immissionsrate verschiedener Schadstoffen
Staub-Reinhalt. Luft, 34, 209
McCune, D.C. (1969)
On the establishment of air quality criteria, with reference to the effects of atmospheric fluorine on vegetation
Air Quality Monograph, 69-3
Am. Petr. Inst. New York, 33
McCune, D.S., D.H. Silberman and L.H. Weinstein (1977)
Effects of relative humidity and free water on the phytotoxicity of hydrogen fluoride and cryolite
Proc. Inst. Clean Air Cong., 2, 292-295
Murray, F. (1983)
Response of grape vines to fluoride under field conditions
Amer, J., Soc. Hort. Sci. 108, 4, 526-295
Niklfeld, H. (1976)
Pflanzensoziologische Beobachtungen in Rauchschadensgebiet eines Aluminiumwerkes
Cbl. ges. Rorstwes., 84, 318-329
Polomski, J., H. Flühler and P. Blaser (1979)
Verändert Fluor den Boden?
Bull. Bodenk. Ges. Schweiz, 3, 51-62
Rao, G.S. and E.A. Friedman (1975)
Fluoride and bone disease in uremia
Kidney International., 7, 125-129
Rabald, E. (1968)
Corrosion guide, second revised edition, 377
Elsevier scientific publishing company, Amsterdam
Roorda van Eysinga, J.P.N.L. (1974)
De opname van fluoride door de wortel en de gevolgen daarvan voor de diverse gewassen, in het bijzonder fresia (proefschrift)
Centrum voor Landbouwpublicaties en Landbouwdocumentatie (PUDOC) Wageningen
Sidhu, S.S. (1978)
Patterns of fluoride accumulation in forest species as related to symptoms and defoliation
Proc. Air Poll. Contr. Ass., Houston, USA, 1-16
Slooff, W. et. al. (1986)
Margins of uncertainty in ecotoxicological hazard assessment
Environ. Toxicol. Chem., 5, 841-852
Soikeli, S. and T. Paakkunainen (1981)
The effect of air pollution on the ultrastructure of the developing and current year needles of Norway spruce
Mitt. Forstl. Bundes-Versucheanstalt Wien, 137, 159-163

Stoddard, G.E., G.Q.Bateman, L.E. Harris, J.L. Shupe and D.A. Greenwood (1963)
Effects of fluorine in dairy cattle. IV, milk production
J. Dairy Sci., 46, 720-726

Suttie, J.W. et al. (1957)
Studies on the effect of dietary sodium fluoride on dairy cows. II. Effect on milk production
J. Dairy Sci. 40, 1485-1491

Suttie, J.W. (1969)
Air quality for the protection of farm animals from fluorides
J.A.P.C.A., 19 (4), 239-242

Temmerman, L. de (1984)
Invloed van atmosferische fluorideverontreiniging op kulturen van Engels Raaigras (Lolium perenme L.) en op artificiële grasland-associaties
Diss. Univ. Gent (België), p. 297

Tesink, J. (1982)
Collected reports 1968-1982
Raadgevend Bureau Milvetox, Goes

US NAS (1974)
Effects of Fluorides in animals
Washington D.C., Nat., Acad. od ci., p. 70

Van Straalen, N.M. (1986)
Stofgehalten in de bodem - (geen) effecten op bodemdieren
In: symposium Bodemkwaliteit, 10 december 1986, Ede, 75-84
VTCB (Voorlopige Technische Commissie Bodembescherming), Leidschendam

Weinstein, L.H. and R. Alscher-Herman (1982)
Physiological responses of plants to fluorine
In: Effects of gaseous air pollution in agriculture and horticulture
M. Unsworth en D.P. Butterworth (eds.), Sci. London

WMO (1986)
Atmospheric ozone 1985; Assessment of our understanding of the process controlling its present distribution on change
WMO, Global ozone research and monitoring project
Report 16, Vol. I, p. 70

Wolting, H.G. (1978)
Gevoelighied van kastulpen voor chronische inwerking van fluorhoudende luchtverontreiniging
Bloembollencultuur, 31, 728-730

Yocom, J.E. and A.R. Stankunas (1982)
A review of air pollutant damage to materials
EPA report 600/8-83-016, 54

Yocom, J.E. and N.S. Baer (1984)
Effects on materials
In: A.P. Altshuller and R.A. Linthurst (ed.)
The acidic deposition phenomenon and its effects: assessment review papers. vol II, 7-27
EPA report 600/8-83-016

Yocom, J.E., N.S. Baer and E. Robinson (1986)
Air Pollution effects on physical and economic systems
In: A.C. stern (ed.) Air poliution vol IV, 166
Academic press Inc. New York

Zander, R. et al. (1987)
Monitoring of the integrated column of hydrogen fluoride above Jungfraujoch Station since 1977 - the HF/HCL column ratio
J. Atmospheric Chemistry, 5, 385-394

9.7. REFERENCES CHAPTER 7

Akzo (1986)
Jaarverslag 1986

Berenschot/Tebodin (1987)
Bedrijfstakgewijze milieustudie kunstmeststoffenindustrie, deelrapportage fosforzuurproducenten

CBS (1987)
Produktiestatistiek van de aardewerk-, baksteen- en dakpannenindustrie 1985

CPB (1985)
De Nederlandse economie op langere termijn
Werkdocument, no. 1

EZ (1980)
Ministerie van Economische Zaken
Bedrijfstakverkenning 1980, nr. 9
Bouwmaterialen, aardewerk- en glasindustrie

Haskoning (1984)
Beperking luchtverontreiniging veroorzaakt door verbranding van afval
Ministerie van VROM

Haskoning (1987)
Fluor- en stofuitworp van de grofkeramische industrie; bestrijdingsmaatregelen en toepassingsmogelijkheden ervan in de Nederlandse grofkeramische industrie

KNB (1987)
Royal Association of Dutch Brick Manufacturers (Koninklijke Verbond van Nederlandse Baksteenfabrikanten)
Jaarverslag 1986

Metaalinstituut TNO (1984)
Inventarisatie afvalstoffen in de basismetaalindustrie, de metaalproduktenindustrie en de machineindustrie (vogelvluchtverkenning)

OECD (1977)
Pollution control costs in the primary aluminium industry, Parijs

Ros, J.P.M. and W. Slooff (1987)
Basisdocument Cadmium, chapter 8 en 9

TNO (1987)
Rapport rookgasreinigingsinstallaties, 753.202/C, Technisch-fysische Dienst (A.H. de Vries) i.o.v. Koninklijk Verbond van Nederlandse Baksteenfabrikanten

Water Research Centre (1980)
Control of contamination: problems in the treatment and disposal of sewage sludge, TR 156, 1980, WRC Process Evaluation, Stevenage

ADDENDUM INDUSTRY

VNO/NCW ad hoc Working Group

The following comment focuses especially on the way various No Observed Effect Concentrations (NOEC) have been chosen. There is also additional comment on the text dealing with the coarse ceramics industry. Finally, a note is made on a differentiated limits policy.

Comments on the NOEC for plants and livestock

Chapter 5, section 5.3. of the integrated criteria document describes the effects on plants and livestock. At two places so-called No Observed Effect Concentrations are given, namely, on page 102 for cultivated plants and on page 118 for forages. Furthermore, on page 120, using an empirical relationship between F concentrations in the atmosphere and in grass developed by the Research Institute for Plant Protection (IPO) in Wageningen, the NOEC values for forage have been converted to an NOEC for air.

Cultivated plants

On the NOEC for cultivated plants, it is stated that its underpinning should have been made clear in the integrated criteria document itself, as was done in the Recommendation of the Health Council (1981) (see page 46 of the "Recommendation"). The integrated criteria document lacks grounds for an NOEC which is a factor of 3.7 lower for the daily value and a factor of 2.35 lower for the monthly average than the recommended limit set by the Health Council (1981). Figures 10 to 15 inclusive reveal that the scatter in the results of the fumigation experiments is very large indeed, and that the NOEC given in the integrated criteria document is very low when compared to the clusters of points shown in these figures. It is obvious that the NOEC for crops is an arbitrary choice with a large margin of uncertainty which does not justify conversion to a definite standard.

Livestock

A similar comment is valid for the NOEC values in forages (see page 118). In particular, it is not clear why the monthly average of 55 mg $F.kg^{-1}$ (maximum permissible concentration) as recommended by the Health Council has been converted into an absolute maximum. It is not appropriate to use the sampling practice as a reason for this drastic step, because neither the table nor the text contains instructions on this matter.
All that is under discussion here is whether the fluoride present in fodder does or does not have adverse effects. The integrated criteria document should have demonstrated that a 2-monthly average has to be equated, as regards its effect, with a maximum of 55 mg $F.kg^{-1}$ not to be exceeded for two consecutive months. The text on page 118 says that during the winter months, with a seasonal average of 20 mg $F.kg^{-1}$, i.e. a value below the annual average NOEC (namely, 30 $mg.kg^{-1}$), levels of as high as 100 mg $F.kg^{-1}$ in grass are found, so there is no basis for setting the maximum at 55 mg $F.kg^{-1}$.

Conversion of F concentrations

An old issue is the question of whether F levels in pasture grass can be derived from atmospheric F concentrations. The Health Council states on page 68 of its Recommendation that, on an annual basis, no clear correlation exists between the two. Chapter 4 of the integrated criteria document returns to this relationship. Page 50 presents a formula drawn up by the IPO (incidentally, it was incorrectly copied from the Appendix, pages 81 and following), which describes the relationship between the maximum 24-hour average (after a shower of at least 2 mm rainfall) and the F content of grass. Admittedly, this formula takes account of the strong wash effect of rainwater and vegetation growth, but not of the desorption effect of the wind, that is, a decrease in the F content after the atmospheric F concentration has reached its maximum. According to the text on page 51, the correlation coefficient between the values calculated using this formula and those measured in the field lies between 0.7 and 0.8, with an explained variance of 60%. Upon checking these data against the figures of the IPO as presented on pages 81 and following of the Appendix, we found, after making a necessary logarithmic transformation of the presented F concentrations, a correlation coefficient of 0.73 with an explained

variance of 54%. The Appendix does not give any figures which might point to a stronger correlation. The text on page 51 says that the model cannot be used for calculation of individual values, but is nevertheless considered suitable for establishing a relationship. However, the point at issue is the way this relationship may be used. We are of the opinion that no reasonably accurate NOEC values can be established using this relationship, because the unexplained standard deviation is too large. The fact is, a simple calculation shows that, if the unexplained portion of the variance is 40%, the standard deviation is 63%. With an unexplained portion of 46%, as exists in the figures of figure 4 on page 95 of the Appendix, the standard deviation is 69%. This implies that 30% of the individual values calculated using the model can deviate more than 63% and 69%, respectively, from the average value. The result is, for instance, that the calculated summer value for the atmospheric NOEC on the basis of an NOEC of 55 mg $F.kg^{-1}$ in fodder works out at 0.8 + 0.5 $\mu g.m^{-3}$, with a 30% probability that the margin of uncertainty is even greater. This does not really suggest that a reliable estimate of the atmospheric NOEC values can be made from F levels in grass, and for this reason, we reject the proposed conversion method.
Summarizing this paragraph, we state that:

- the NOEC values for plants and livestock proposed in the integrated criteria document require a sounder underpinning
- the conversion of atmospheric NOEC values via grass samples should be rejected as being too unreliable to date.

However, we can concur with the statement on page XII of the Summary of the integrated criteria document, namely, that the uncertainties in the recommended limits for ambient air fluoride concentrations are great, but not with the "provisionally" recommended range of maximum concentrations.

Coarse ceramics industry

In view of the fact that the central government is preparing an Order in Council to reduce the fluoride emissions from the coarse ceramics industry, comments on and supplementation of the text of section 2.2. of the integrated criteria document (pages 18 to 20 inclusive) are in order. It is mentioned on page 19 that it is not known what causes the strong variation

in the volatilization of fluoride during brick firing. This statement suggests that it would be impossible to influence the F emissions through modifications to the firing process. However, research has shown that the quantity of F compounds emitted is related to the lime content of the clay, the rate of raising the temperature in the warming-up phase from 700 to 1000 ^{o}C, and the air excess. A significant reduction of 30% to 40% in F emissions has been produced by alterations to the last two parameters. Changing the lime content of the clay may offer additional opportunities for reducing emissions, but this has not yet been studied. Research has also been carried out into the nature of the emitted F compounds. In addition to hydrogen fluoride, silicium and aluminium compounds are also present, which are considerably less toxic to crops than HF. There are even indications that the F emissions from a large number of plants consist of solid CaF_2 which is relatively harmless to plants and animals. Given the fact that neither damage to crops nor fluorosis in cattle has been observed in the vicinity of brick works, it is reasonable to ask on what ground a reduction in fluoride emissions is necessary and justified. We advocate a rational standard which takes into consideration the toxic properties of the specific fluorine compounds which are not classed with those of hydrogen fluoride.

Differentiated limits policy

Knowledge of the relationship between effect and exposure is needed in order to be able to apply a limit judiciously. A limit is often based on a safe concentration for the most sensitive organism. We think that it is unnecessary to adopt this limit for an area that is not a habitat for this organism and in all probability never will be. In that case, we request urgently that a differentiated limits policy be pursued for the area in question based on dose-response relationships for the organisms living in the location. This policy will then lead to separate limits, for example, for urban, agricultural or nature areas.

Yours faithfully,

L.S. de Jonge (Fluorides Coordinator)