

Protocol

2F8: SF6 and PFC EMISSIONS FROM THE SEMICONDUCTOR INDUSTRY

IPCC Category:	2F8 Other
NFR Code:	n.a.
NOSE Code:	n.a.
NACE Code 2008	261109, 2612, 331301

FOREWORD

Under the Kyoto Protocol, the Netherlands is required to set up and maintain a national system to monitor its greenhouse gas emissions. One of the elements of this system is a transparent and verifiable description of the methods and processes used in this monitoring system. These methods must meet international guideline criteria, which have been defined by the United Nations (UN) and the European Union (EU).

The Netherlands meets the aforementioned requirement, for example, by defining a series of Monitoring Protocols, which describe the methods and work processes used to determine greenhouse gas emissions and the amounts of carbon sinks available. Protocols have been written for about 40 greenhouse gas sources or sinks. This document describes the protocol for one of these sources or sinks.

The protocols have been compiled in close collaboration with experts from various sectors of society in the Netherlands, particularly experts from the Emissions Registration (ER). The ER is a collaborative group that includes institutions such as CBS, WUR, RIVM and PBL. Until 31 December 2009 this was coordinated by PBL (Planbureau for the Leefomgeving, or the Netherlands Environmental Assessment Agency), but on 1 January 2010 this coordination task was taken over by RIVM (the Netherlands institute for public health and the environment). Other institutions that have contributed to the protocols include NL Agency; Ministry of Agriculture, Nature and Food Quality; and the Ministry of VROM (Housing, Spatial Planning and the Environment).

1 Scope and significance of emission sources/activities

1.1 Scope and definition

This protocol describes the method and working processes used to calculate the emissions figures for SF₆ (sulfur hexafluoride) and PFC (perfluorocompounds) as a result of the use of these gases in the semiconductor industry. This concerns the SBI (industrial) codes 261109, 2612 and 331301.

SF₆ emissions resulting from their use in the manufacture of semiconductors, the high-voltage electricity sector, double glazing and electromicroscopes, are aggregated into a single figure and reported under the CRF (common reporting format) category 2F8 'Other'.

The monitoring procedures for SF₆ emissions during the production of semiconductors and during the manufacture and use of electromicroscopes, double glazing and high-voltage installations, are described in separate protocols. The contribution by the remaining other sources (including the production and use of particle accelerators) currently does not appear to be substantial: 0.2 ton SF₆/year (DHV, 2000) and is therefore not included when determining the total SF₆ emissions.

F-gases (SF₆ and PFCs) are used in the semiconductor industry to clean process rooms and to etch the semiconductors. F-gases are emitted during these processes. The Netherlands has only one semiconductor manufacturer, using only one production location.

1.2 Significance and influences

1.2.1 Contribution to total national emissions

The *PFC* emissions from use of PFCs in the semiconductor industry contribute less than 0.1% to the total annual greenhouse gas emissions from the Netherlands. The total emissions of *SF₆* as reported under sector 2F8 (other) contribute less than 0.5% to the total annual greenhouse gas emissions from the Netherlands.

Aggregated amounts due to confidentiality

SF₆ emissions resulting from their use in the high-voltage electricity sector, plus the manufacture of semiconductors, double glazing and electromicroscopes are all aggregated into a single figure and reported under CRF category 2F8 'Other' (UNFCCC, 2004). This is due to the confidentiality of the figures. If reporting is not implemented in this way, then production information from the (former) Netherlands high-voltage manufacturer, the test laboratory for high-voltage installations, the semiconductor and electromicroscope manufacturers can be immediately deduced from the emission figures, activity data and implied emission figures under the 2F subcategories 6, 7 and 8.

1.2.2 Developments that influence emissions

The methods being developed or currently available to reduce PFC emissions in the semiconductor industry can generally be split into three types of measures:

- A. Reducing the use of etching gases, plus optimising processes and equipment.
- B. Replacing etching gases / using alternative plasma chemistry.
- C. End-of-pipe treatment / abatement.

In 2002 and 2003 PSN (Philips Semiconductors Nijmegen) implemented the project 'Study into the feasibility of reducing PFC emissions through process optimisation', whereby PSN considered modifying a number of processes as part of its PFC reduction plan.

Mass balance calculations and emission measurements showed that C₂F₆ contributed by far the most (>75%) to the greenhouse effect. This process gas is used in PE-CVD (plasma-enhanced chemical vapour deposition) processes. PSN's reduction plans therefore focus on these PE-CVD processes and, in particular, on the C₂F₆ greenhouse gas. Results show that a 30% reduction in PFC emissions can be achieved through process optimisation of the 'chamber cleans' of the PE-CVD nitride and oxide processes within PSN.

In a recently started project, PSN is currently considering how the production machines can best be modified in order to achieve the highest possible PFC reduction (80-95%). This study also evaluates new process developments that will soon work with higher PFC flows, particularly with respect to realising minimum PFC emissions. Up to now, the PFCs used in these processes have largely been emitted directly into the atmosphere. This project focuses on the following five tracks:

- A. Applied Materials Centura: replacing C₂F₆ with NF₃ as etching gas, in combination with remote plasma (with >95% PFC reduction potential).
- B. Novellus Concept 1: replacing C₂F₆ with C₄F₈O in the PE-CVD process (with >80% PFC reduction potential).

- C. Novellus Concept 2: adding a local afterburner HOx Mistral after the PE-CVD process step (with >60% PFC reduction potential).
- D. TEL-unit: using a new plasma etching machine for oxides with or without local plasma abatement (with >99% PFC reduction potential).
- E. LAM-Alliance: adding a new type of plasma abatement (Litmas Blue and Pegasus II) after the existing LAM-plasma oxide/nitride etcher (with >95% PFC reduction potential).

2 Method, emission factors and activity data

2.1 Calculation method

Annual emissions of SF₆ and PFC_{sum} by the semiconductor industry are determined on the basis of a mass-balance method (see formula). This formula is based on the amount of SF₆ and PFC_{sum} used for the production process, plus the emissions of the by-product CF₄ that results from the use of PFC_{sum}. Sections 2.3 and 2.2 of this protocol provide further information on the purchase and sale of gases and emission factors.

$$Emission_{FC_i} = purchase_{of\ FC_i} \cdot C_i \cdot (1 - h) \cdot [(1 - C_i)(1 - a_i \cdot d_i) + B_i \cdot (1 - a_i \cdot d_{CF_4})]$$

Where:

Company-specific information:

Purchase of FC_i Purchase and sale of gases [in kg CF₄, C₂F₆, C₃F₈, c-C₄F₈, CHF₃, NF₃ and SF₆]

a_i Volume fraction of the gas FC_i fed into the emission-reduction process [-]

Standard values conform tier 2c (see Table 1 in Section 2.2):

h Volume fraction of gas FC_i that remains in the gas bottle after use [-]

C_i Volume fraction of the FC_i gas used in the process [-]

d_i Volume fraction of converted/destroyed FC_i gas via the emission-reduction process [-]

B_i kg CF₄ produced per kg gas FC_i [kg/kg]

d_{CF4} Volume fraction of converted/destroyed FC_i gas via the emission-reduction process [-]

- Comparing with IPCC methods

The mass-balance method used to determine the annual emission of F-gases (PFC and SF₆) by the semiconductor industry complies with the tier 2c method as described in equations 3.29 and 3.30 of the IPCC GPG (Good Practice Guidance) 2001, p. 3.72. The tier 2c method is based on company-specific data concerning the purchase and sale of gases and emission-reduction technologies.

2.2 Emission factors

The Netherlands semiconductor manufacturer uses the standard values shown in the following table when implementing the calculations discussed under Section 2.1.

	GWP _i	h _i	1-C _i	d _i	B _i
CF4	6500	0.1	0.8	0.9	n.a.
C2F6	9200	0.1	0.7	0.9	0.1
CHF3	11,700	0.1	0.3	0.9	n.a.
C3F8	7000	0.1	0.4	0.9	0.2
c-C4F8	8700	0.1	0.3	0.9	n.a.
NF3	8000	0.1	0.2	0.9	n.a.
SF6	23,900	0.1	0.5	0.9	n.a.

Table 1. Standard values (conform tier 2c, Table 3.15, IPCC GPG, 2001, p. 3.74)

2.3 Activity data

Within the framework of its environmental permits, the company annually reports its emissions per gas (PFC and SF₆) in kg, plus the method used to calculate these emissions. The Province of Gelderland supplies this information to the ER's (Emissions Registration) ENINA task force before 1 September each year.

The following company-specific information is used by the Netherlands semiconductor manufacturer to calculate these emissions:

Purchase FC_i Purchase and sale of gases [in kg CF₄, C₂F₆, C₃F₈, c-C₄F₈, CHF₃, NF₃ and SF₆]
The purchase figures for PFC and SF₆ are determined by the Netherlands semiconductor manufacturer and are verified by the gas supplier.

a_i Volume fraction of the FC_i gas fed into the emission-reduction process [-]
Up to the end of 2005 the company had no emission-reduction techniques integrated into the production process, so the company-specific volume fraction a_i for this period is zero.

3 Working processes

Process for estimating (t-1)

If preliminary figures are required at any point, the following process is used to estimate the figure for t-1. The preliminary data for the work package leader are calculated by extrapolating them from the previous years' figures, based on prognoses for the developments in the most important activity data (taken from CBS (Statistics Netherlands) or other statistical sources).

INPUT	PROCESS	OUTPUT	BY WHOM
Preliminary data work package leader (t-1)	Include t-1 data in ER database	ER-db with (t-1) data	Work package leader
ER-db with (t-1) data	Check emission figures: compare with previous years (trend), modify if required and document everything	ER-db (t-1) with any modified figures	Task force

Process for final determination of (t-2)

The final emission figures (as described in this protocol) are calculated using the following process.

INPUT	PROCESS	OUTPUT	BY WHOM
Emission figures (and calculation method) determined within the company	Report in AER/MJV (annual environmental report)	MJV	Company
AERs/MJVs	Validate AER/MJV	Validated AER/MJV	Competent Authority (Province)
Validated AER/MJV t-2 Validated AERs/MJVs for previous years	Check emission figures: - Compare with previous years (trend) If unsubstantiated deviations found in AER/MJV, contact the Province and/or Company → if necessary, modify emissions	Approved emission figures (=Final data Work package leader	Work package leader ENINA task force

INPUT	PROCESS	OUTPUT	BY WHOM
	figure and document fully	(t-2)	
Final data Work package leader (t-2)	Include (t-2) data in ER database	ER-db with (t-2) data	Work package leader
ER-db with (t-2) data	Check, and trend analysis of air emissions: explain deviations or modify figures	Final defined emission figures (t-2)	Task forces and PBL experts

Reporting in CRF and NIR

The contribution by the semiconductor industry is reported in the CRF as part of the total SF₆ and PFC emissions under the category 2F8 'Other'. The individual emission figures are considered confidential information.

4 Uncertainty and quality

4.1 Estimating uncertainties

A Tier-1 uncertainty analysis is implemented every year before the NIR is submitted by the ER, based on the greenhouse gas inventory and in compliance with IPCC guidelines. The assumptions used and the results thereof are described in a background report to the NIR. In addition to this, where included in the QA/QC programme for the relevant period, extra analyses are implemented regularly in specific situations, which include any updating of the Tier-2 uncertainty analyses.

The Tier-2 uncertainty assessment was last updated in 2006. This assessment showed that a Tier-1 uncertainty assessment is sufficiently reliable and that Tier-2 uncertainty assessments need only be implemented at periodic intervals of around 5 years, unless a major change in an important source is sufficient to require earlier reassessment.

- Source-specific uncertainty

The uncertainty estimate-totaal concerns the root of the sum of uncertainty in the data sources used (AD_{onz}) in the square and the uncertainty of the emission factor (EF_{onz}) in the square. The extent of the total uncertainty is here primarily determined by the greatest AD or EF uncertainty.

$$\text{Uncertainty estimate}_{\text{total}} = \sqrt{EF_{onz.}^2 + AD_{onz.}^2}$$

The uncertainty estimates concerning the data sources (AD) and emission factors (EF) used, and the total uncertainty estimate, are listed in the following table.

IPCC	Category	Gas	AD _{onz.}	EF _{onz.}	Uncertainty estimates _{tot}
2F	PFC emissions from PFC use	PFC	5	25	25
2F	SF6 emissions from SF6 use	SF6	50	25	56

The uncertainty in SF₆ and PFC emissions from SF₆ and PFC use was estimated to be respectively 56 and 25%. The uncertainty in the activity data for the SF₆ and PFC-sources was estimated at respectively 50 and 5%. For the SF₆ and PFC-emission factors, the uncertainties were both estimated at 25%. These figures were based on expert judgements (Olivier et al, 2009).

4.2 Quality assurance and quality control (QA/QC)

The ER work package leaders check that:

1. the basic data are well documented and adopted (check for typing errors, use of the correct unit sizes and correct conversion);
2. the calculations have been implemented correctly;
3. assumptions are consistent, also whether specific parameters (e.g. activity data) are used consistently;
4. complete and consistent data sets have been supplied.

Any actions that result from these checks are noted on an 'action list'. Before defining the data, supervisors check whether the relevant actions on this list, plus the QC checks, have all been completed. Defining the data is carried out by the WEM (working group on emissions monitoring), and confirmed in writing via an e-mail from the institute representatives to the ER project leader at PBL.

The work package leaders fill out a new documentation sheet when adding new data. For reasons of efficiency a minimum level has been set for obligatory documentation, i.e. 5% changes at target group level, and 0.5% at levels concerning the national total. These documentation sheets form part of the trend analysis, as well as the eventual definition of the data set.

The ER work package leaders communicate by e-mail regarding these QC checks, results and actions. They send a printed copy to the ER secretary, who keeps a logbook and compiles these e-mails into an 'action list'. This shows explicitly that the required checks and corrections have been carried out.

4.3 Verification

In order to check the quality of the emission figures for the sources in this protocol, general QA/QC procedures have been followed that are in line with the IPCC guidelines. These are described further in the QAQC programme used by the National System, and the annual working plans published by the ER.

- Sector-specific QC

No additional specific verification procedures are implemented for the sources defined in this protocol.

4.4 Possibilities for improvement compared to the current calculation method

4.4.1 History

Prior to 2003, the ER's ENINA task force only knew the procurement figures for 1998. The PFC emission is calculated using a small deviation in the volume fraction ($1-C$), and excluding the by-product CF_4 (B_i).

Table 2: parameters used for PFC emissions (1998 compared to IPCC GPG)

	1998	IPCC	
	$1-C_i$	$1-C_i$	B_i
CF4	0.81	0.8	n.a.
C2F6	0.68	0.7	0.1
CHF3	0.28	0.3	n.a.
C3F8	n.a.	0.4	0.2
c-C4F8	n.a.	0.3	n.a.
NF3	0.15	0.2	n.a.
SF6	0.40	0.5	n.a.

The years 1999 and 2000 were estimated based on an average annual growth in the semiconductor industry. In 2002 the Netherlands semiconductor manufacturer supplied ENINA with new emission figures for 1995-2001. These emissions were calculated using the method described in this protocol.

4.4.2 Future

Not applicable

5 Remaining aspects

5.1 Point source criteria

Not applicable

5.2 Substance profiles

Not applicable

5.3 Regionalisation

Not applicable

5.4 Time-based variations in source strength

Not applicable

6 References and additional information

6.1 References

- DHV, 2000: *Identificatie van onbekende bronnen van overige broeikasgassen (Identification of unknown sources of other greenhouse gases)*.
- IPCC, 1997: Revised 1996 IPCC Guidelines for National Greenhouse Gas Emission Inventories, Three volumes: Reference Manual, Reporting Guidelines and Workbook. IPCC/OECD/IEA. IPCC WG1 Technical Support Unit, Hadley Centre, Meteorological Office, Bracknell, UK
- IPCC, 2001: Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories, IPCC-TSU NGGIP, Japan
- Olivier J.G.J., L.J. Brandes and R.A.B. te Molder, 2009 (in print) Uncertainty in the Netherlands' greenhouse gas emissions inventory: Estimate of annual and trend uncertainty for Dutch sources of greenhouse gas emissions using the IPCC Tier 1 approach, PBL-Report 500080013, Bilthoven
- UNFCCC, 2004: *Guidelines for the preparation of national communications by Parties included in Annex I to the convention, Part I: UNFCCC reporting guidelines on annual inventories*, UNFCCC/SBSTA/2004/8, 3 September 2004.

6.2 Additional information

Appendix 1: Terminology

Appendix 1: Terminology

PFK	Perfluorocompounds
SF ₆	Sulfur Hexafluoride
ER	Emission Registration
IPCC	Intergovernmental Panel on Climate Change
RIVM	Rijksinstituut voor Volksgezondheid en Milieuhygiëne (national institute for public health and the environment)
ROB	Reductieplan Overige Broeikasgassen (reduction programme for non-CO ₂ gases)
NIR	National Inventory Report
CRF	Common Reporting Format