

CHAPTER 8

OTHER PRODUCT MANUFACTURE AND USE

[Parts in yellow – comments from Authors/issues that will be refined further]

[Parts shaded in grey – the unchanged text from 2006 IPCC Guidelines]

8

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8 OTHER PRODUCT MANUFACTURE AND USE

8.1 INTRODUCTION

No refinement

8.2 EMISSIONS OF SF₆ AND PFCs FROM ELECTRICAL EQUIPMENT

No refinement

8.3 USE OF SF₆ AND PFCs IN OTHER PRODUCTS

[This section is being updated to include new guidance for estimating fluorochemical emissions from textile manufacturing and electronics waterproofing].

8.3.1 Introduction

This source category excludes the following source categories that are addressed elsewhere in the *2006 Guidelines*:

- Production of SF₆ and PFCs (Section 3.10);
- Production and use of electrical equipment (Section 8.2);
- Primary and secondary production of magnesium and aluminium (Chapter 4); and
- Semiconductor and flat panel display manufacturing (Chapter 6).

Identified remaining applications in this source category include:

- SF₆ and PFCs used in military applications, particularly SF₆ used in airborne radar systems, e.g., AWACS (Airborne Warning and Control System), and PFCs used as heat transfer fluids in high-powered electronic applications;
- SF₆ used in equipment in university and research particle accelerators;
- SF₆ used in equipment in industrial and medical particle accelerators;
- ‘Adiabatic’ applications utilising the low permeability through rubber of SF₆ and some PFCs, e.g., car tires and sport shoe soles;
- SF₆ used in sound-proof windows;
- PFCs used as heat transfer fluids in commercial and consumer applications;
- PFCs used in cosmetics and in medical applications;
- Other uses e.g. gas-air tracer in research and leak detectors.
- PFCs and other fluorochemicals in the manufacturing of textiles and waterproofing of electronic circuits

8.3.2 Methodological issues

8.3.2.1 CHOICE OF METHOD

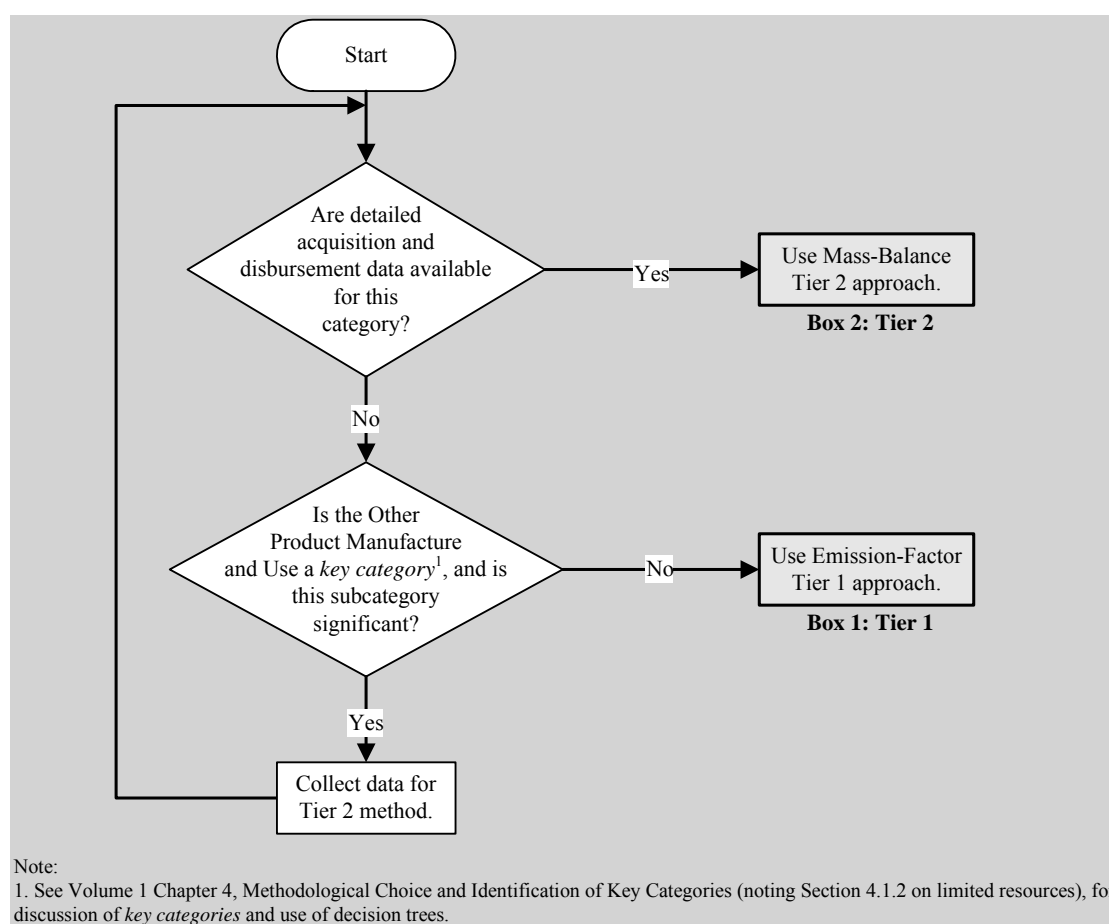
The *good practice* method is to use either consumption data from users of SF₆ or PFCs or top-down import, export and consumption data from national SF₆ producers and distributors, disaggregated by major type of SF₆ or PFC application. Acquiring this data will entail a survey of all producers and distributors of SF₆ and PFCs to identify total net SF₆ and PFC consumption. Once the data are obtained, the amount of SF₆ and PFC consumed by application in this source category should be estimated.

MILITARY APPLICATIONS

SF₆ EMISSIONS FROM OPERATION OF AWACS

SF₆ is used as an insulating medium in the radar systems of military reconnaissance planes of the Boeing E-3A type, commonly known as AWACS. The purpose of the SF₆ is to prevent electric flashovers in the hollow conductors of the antenna, in which high voltages of more than 135 kV prevail. When the plane ascends, SF₆ is automatically released from the system and into the atmosphere to maintain the appropriate pressure difference between the system and the outside air. When the plane descends, SF₆ is automatically charged into the system from an SF₆ container on board. Most emissions occur during the pressure-balancing process on ascent, but emissions from system leakage can also occur during other phases of flight or during time on the ground. Annual emissions per plane have been estimated to be 740 kg, while the charge of each system is approximately 13 kg.

Figure 8.2 Decision tree for SF₆ from AWACS



Tier 1 method – SF₆ emissions per plane

If a country does not have data on SF₆ consumption by its AWACS, it may use a per-plane emission factor to estimate emissions. An emission factor of 740 kg per plane per year is presented in Table 8.7 below; this figure is based on estimates of SF₆ emissions from NATO Boeing E-3As. Note that actual emissions per plane are strongly influenced by the average number of sorties (take-offs) per plane per year. More frequent sorties will raise the emission rate above 740 kg/plane; less frequent sorties will lower it. Leakage rates during flight or during time on the ground will also affect the emission rate.

EQUATION 8.12

EMISSIONS FROM AWACS (DEFAULT EMISSION ACTOR)

$$\text{User Emissions} = 740 \text{ kg} \cdot \text{Number of planes in AWACS fleet}$$

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TABLE 8.7 SF ₆ EMISSIONS PER PLANE PER YEAR	
Emissions per plane per year (kg SF ₆)	Uncertainty
740 kg	±100 kg
Source: Schwarz (2005)	

Table 8.8 includes information on national AWACS fleets world wide (Boeing, 2005); like other activity data, it may quickly go out of date. Countries are in the best position to know the numbers of planes in their AWACS fleets.

TABLE 8.8 NATIONAL AWACS FLEETS							
Country/ Organisation	USA	Japan	France	UK	Other NATO	Saudi Arabia	Total
No. AWACS	33	4	4	7	17	5	70
Source: Boeing (2005)							

Tier 2 method – user mass-balance method

The most accurate method for estimating SF₆ emissions from AWACS is to track SF₆ consumption by the systems. To do so, the following equations, which are similar to the utility-level variant of the Tier 3 method for electrical equipment, may be used. Note that for AWACS, acquisitions and disbursements of SF₆ containers are likely to be considerably more important to the result than acquisitions and retirements of operating systems.

<p style="text-align: center;">EQUATION 8.13</p> <p style="text-align: center;">EMISSIONS FROM AWACS (USER MASS-BALANCE)</p> <p style="text-align: center;">User Emissions = Decrease in SF₆ Inventory + Acquisitions of SF₆ – Disbursements of SF₆ – Net Increase in AWACS Fleet Charge</p>

Where:

Decrease in SF₆ Inventory = SF₆ stored in containers at the beginning of the year – SF₆ stored in containers at the end of the year

Acquisitions of SF₆ = SF₆ purchased from chemical producers or distributors in bulk + SF₆ purchased from AWACS manufacturers or distributors with or inside of new planes + SF₆ returned to site after off-site recycling

Disbursements of SF₆ = SF₆ contained in AWACS that are transferred to other entities + SF₆ returned to suppliers + SF₆ sent off-site for recycling + SF₆ destroyed

Net Increase in AWACS Fleet Charge = 13 kg • (New AWACS – Retiring AWACS)

SF₆ AND PFC EMISSIONS FROM OTHER MILITARY APPLICATIONS

There is wide range of military applications using PFCs or SF₆.¹ Military electronics are believed to be an important and growing application of PFC heat transfer fluids, which are valued for their stability and dielectric properties. The fluids are used in ground and airborne radar (klystrons), avionics, missile guidance systems, ECM (Electronic Counter Measures), sonar, amphibious assault vehicles, other surveillance aircraft, lasers, SDI (Strategic Defense Initiative), and stealth aircraft. PFCs may also be used to cool electric motors, particularly in applications where noise reduction is valued, e.g., in ships and submarines. The specific PFCs used in these applications are believed to be similar to those identified as heat transfer fluids in electronics manufacturing in Chapter 6. Spray cooling, jet impingement cooling, and pool boiling appear to be the favoured systems for heat

¹ David Harris and James Hildebrandt, "Spray Cooling Electrical and Electronic Equipment," *COTS Journal*, November 2003; C. Shepherd Burton, "Uses and Air Emissions of Liquid PFC Heat Transfer Fluids from the Electronics Sector," Draft report prepared for Scott C. Bartos, U.S. Environmental Protection Agency.

removal. In all of these cooling applications, the PFC is contained in a closed system, and neither replacement nor replenishment of the PFC liquid appears to be required. Thus, the greatest opportunities for emissions are the manufacture, maintenance, and, especially, the disposal of the equipment.

SF₆ is used in high-performance ground and airborne radar systems in their hollow conductors for transmission of high-frequency energy pulses at high voltages from the klystron. Another application of SF₆ is as an oxidant of lithium in Stored Chemical Energy Propulsion System (SCEPS), e.g., in naval torpedoes and in infrared decoys (Koch, 2004). Apparently, these applications of SF₆, like those of the PFC heat transfer fluids enumerated above, are generally more or less enclosed, but servicing and testing procedures may lead to emission. The use of SF₆ for the quieting of torpedo propellers has also been reported (NIST, 1997).

In addition, SF₆ may be emitted as a by-product of the processing of nuclear material for the production of fuel and nuclear warheads. SF₆ is known to be emitted from neutralising excess fluorine during the production of nuclear fuel for civilian applications (AREVA, 2005).

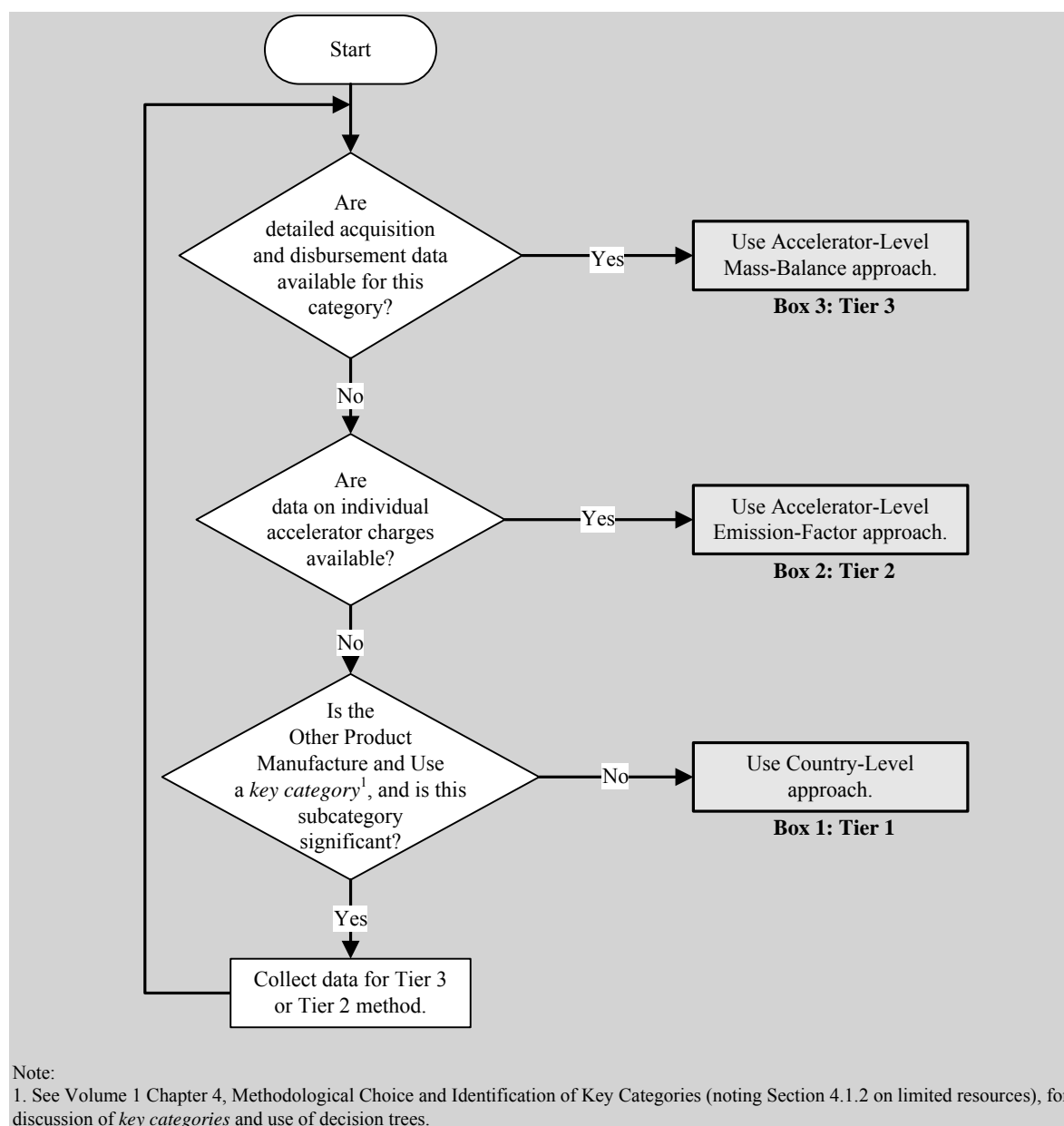
Although it is believed that the total amounts of SF₆ and PFCs consumed and emitted in this sector may be significant, no data on quantities are publicly available so far. Therefore, inventory compilers should try to collect further information from the relevant authorities and, if possible, their suppliers. As noted above, the greatest opportunities for emissions from many of these applications appear to be the manufacture, maintenance, and disposal of the equipment. Thus, if inventory compilers can acquire information on emission rates during the manufacture, maintenance, and disposal of the equipment, along with the quantities of equipment manufactured, in use, and disposed, they can use the Tier 2 or Tier 3 method for electrical equipment to estimate emissions. For applications with different emissions profiles (e.g., prompt emissions), the appropriate equation from Section 8.2 may be used.

SF₆ EMISSIONS FROM UNIVERSITY AND RESEARCH PARTICLE ACCELERATORS

SF₆ is used in university and research operated particle accelerators as an insulating gas. Typically, high voltage equipment is contained and operated within a vessel filled with SF₆ at a pressure exceeding atmospheric pressure. Charges range from five kilograms to over ten thousand kilograms, with typical charges falling between 500 and 3 000 kg. When the equipment requires maintenance, the SF₆ is transferred into storage tanks. SF₆ losses occur primarily during gas recovery and transfer, when pressure relief valves are actuated, and through slow leaks.

Based on two recent studies annual SF₆ losses range between 5 and 7 percent of vessel capacity per year and generally depend on the vessel opening frequency plus the efficiency of the recovery and transfer equipment. World banked capacity is roughly estimated to be 500 tonnes with annual SF₆ emissions of 35 tonnes.

Switzerland has developed a voluntary program to reduce SF₆ emissions from particle accelerators. Suggestions and techniques for reducing SF₆ emissions from these sources exist.

Figure 8.3 Decision tree for SF₆ from research accelerators**Tier 1 method – country-level method**

In cases where individual user accelerator charge data is unavailable, one extremely rough method involves determining the total number of university and research particle accelerators in the country and using several factors to determine the country-level annual emission rate as noted in Equation 8.14. For this Tier 1 method, the only data that requires collection is the total number of university and research particle accelerators in the given country.

EQUATION 8.14**UNIVERSITY AND RESEARCH PARTICLE ACCELERATOR EMISSIONS (COUNTRY-LEVEL)**

Emissions = (Number of university and research particle accelerators in the country) • (SF₆ Use Factor) • (SF₆ Charge Factor, kg) • (SF₆ university and research particle accelerator Emission Factor)

Where:

Number of university and research particle accelerators in the country = The total number of university and research particle accelerators in the country. This rough method does not require countries to determine the number of accelerators that use SF₆. To determine if a country has a particle accelerator, go to http://www-elsa.physik.uni-bonn.de/Informationen/accelerator_list.html

SF₆ Use Factor = 0.33 Approximately one third of university and research particle accelerators use SF₆ as an insulator.

SF₆ Charge Factor = 2400 kg, SF₆, the average SF₆ charge in a university and research particle accelerator.

SF₆ university and research particle accelerator Emission Factor = 0.07, the average annual university and research particle accelerator emission rate as a fraction of the total charge.

Tier 2 method – accelerator-level emission-factor approach

If data on the quantity of SF₆ contained within each university and research accelerator are available, a default emission factor of 7 percent may be multiplied by the total SF₆ charge contained in university and research accelerators in the country. The total country SF₆ emission rate from university and research accelerators is therefore calculated from Equation 8.15.

EQUATION 8.15

UNIVERSITY AND RESEARCH PARTICLE ACCELERATOR EMISSIONS (ACCELERATOR-LEVEL EMISSION FACTOR)

$$\text{Total Emissions} = \text{SF}_6 \text{ university and research particle accelerator Emission Factor} \bullet \sum \text{Individual Accelerator Charges}$$

Where:

SF₆ university and research particle accelerator Emission Factor = 0.07, the average annual university and research particle accelerator emission rate as a fraction of the total charge.

Individual User Accelerator Charges = SF₆ contained within each university and research accelerator.

Tier 3 method –accelerator-level mass-balance method

SF₆ emissions from university and research facilities operating particle accelerators may be most accurately determined at the user level on an accelerator-by-accelerator basis. Emission calculations are estimated by tracking accelerator charge as well as SF₆ consumption and disposal. As detailed in Equation 8.16, the total emissions are equal to the sum of the individual users' emissions. Note, under this method, as the overall SF₆ emission rate from particle accelerators is small compared to other SF₆ uses, the associated SF₆ lost in manufacturing is considered negligible and is not included in the calculation.

EQUATION 8.16

TOTAL RESEARCH ACCELERATOR EMISSIONS

$$\text{Total Emissions} = \sum \text{Individual Accelerator Emissions}$$

Each particle accelerator's emissions can be calculated as follows:

EQUATION 8.17

RESEARCH ACCELERATOR EMISSIONS (ACCELERATOR-LEVEL MASS-BALANCE)

$$\text{Accelerator Emissions} = \text{Decrease in SF}_6 \text{ Inventory} + \text{Acquisitions of SF}_6 - \text{Disbursements of SF}_6 - \text{Net Increase in Accelerator Charge}$$

Where:

Decrease in SF₆ Inventory = SF₆ stored in containers at the beginning of the year – SF₆ stored in containers at the end of the year

Acquisitions of SF₆ = SF₆ purchased from chemical producers or distributors in bulk + SF₆ purchased from accelerator manufacturers or distributors with or inside of new accelerator components + SF₆ returned to site after off-site recycling

Disbursements of SF₆ = SF₆ contained in components transferred to other entities + SF₆ returned to suppliers + SF₆ sent off-site for recycling + SF₆ destroyed

Net Increase in Accelerator Charge = SF₆ Charge of New Components – SF₆ Charge of Retiring Components

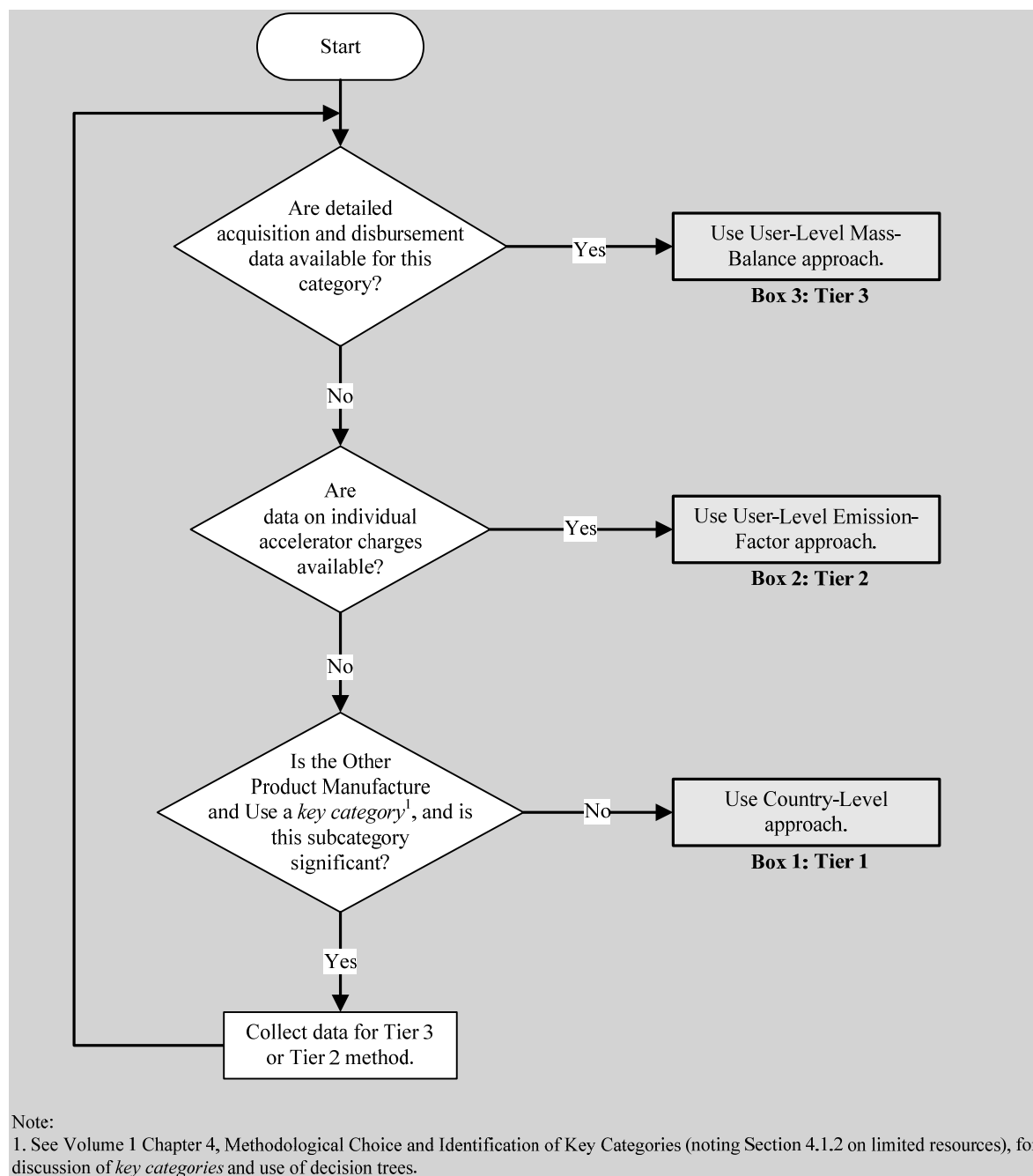
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SF₆ EMISSIONS FROM INDUSTRIAL AND MEDICAL PARTICLE ACCELERATORS

SF₆ is used as an insulating gas in two types of industrial particle accelerators (low and high voltage) and also in medical (cancer therapy) particle accelerators, as is the case for university and research particle accelerators. However, the emission and charge factors for industrial and medical particle accelerators are different from those of university and research accelerators, as discussed below.

Global banked capacity for industrial particle accelerators is roughly estimated to be 500 tonnes with annual SF₆ emissions of 35 tonnes. Global banked capacity for medical (radiotherapy) particle accelerators is roughly estimated to be less than 5 tonnes with annual SF₆ emissions of less than 5 tonnes. (Schwarz, 2005).

Figure 8.4 Decision tree for industrial and medical particle accelerators



Tier 1 method – country-level method

In cases where individual user accelerator charge data is unavailable, one extremely rough method involves determining the total number of particle accelerators by process description in the country and using factors to determine the country level annual emission rate as noted in Equation 8.18. For this Tier 1 method, the only data

that requires collection is the total number of particle accelerators which contain SF₆ by process description in the given country.

EQUATION 8.18**INDUSTRIAL/MEDICAL ACCELERATOR EMISSIONS (COUNTRY-LEVEL)**

$$\text{Emissions} = (\text{Number of particle accelerators that use SF}_6 \text{ by process description in the country}) \bullet (\text{SF}_6 \text{ Charge Factor, kg}) \bullet (\text{SF}_6 \text{ applicable particle accelerator Emission Factor})$$

Where:

Number of particle accelerators by type in the country = The total number of particle accelerators by type (industrial high voltage, industrial low voltage and radiotherapy) that use SF₆ in the country, 1, 2, etc. (Only count particle accelerators that use SF₆. This differs for the Tier 1 calculation for university and research particle accelerators)

SF₆ Charge Factor = The average SF₆ charge in a particle accelerator by process description as noted below.

SF₆ particle accelerator Emission Factor = The average annual SF₆ particle accelerator emission rate as a fraction of the total charge by process description.

TABLE 8.9**AVERAGE SF₆ CHARGE IN A PARTICLE ACCELERATOR BY PROCESS DESCRIPTION**

Process Description	SF ₆ Charge Factor, kg
Industrial Particle Accelerators – high voltage (0.3-23 MV)	1300
Industrial Particle Accelerators – low voltage (<0.3 MV)	115
Medical (Radiotherapy)	0.5 ^a

^a This is the average of values ranging from 0.05 kg to over 0.8 kg, depending on model and manufacturer.
Source: Schwarz (2005)

Tier 2 method – user-level emission-factor approach

If data on the quantity of SF₆ contained within each industry and medical accelerator are available, use the Tier 2 method for university and research facilities; however, multiply the emission factor for each process description provided below by the total, country-specific SF₆ charge for that process description.

TABLE 8.10**EMISSION FACTOR FOR EACH PROCESS DESCRIPTION,
(SF₆ EMISSIONS FROM INDUSTRIAL AND MEDICAL PARTICLE ACCELERATORS)**

Process Description	Emission Factor, kg /kg SF ₆ charge
Industrial Particle Accelerators – high voltage (0.3-23 MV)	0.07
Industrial Particle Accelerators – low voltage (<0.3 MV)	0.013
Medical (Radiotherapy)	2.0 ^a

^a This emission factor is the average of values ranging from 1 kg to 10 kg per kg charge, depending on model, manufacturer, and service intervals.
Source: Schwarz (2005)

Tier 3 method – user-level mass-balance method

To calculate SF₆ emissions from industrial and medical particle accelerators, use the same Tier 3 method as the university and research facilities. The customer service organisations for manufacturers and distributors of the equipment are likely to have information on equipment stocks, imports, and exports, and on the quantities of SF₆ used to fill and refill the equipment.

EMISSIONS FROM OTHER APPLICATIONS OF SF₆ AND PFCs

It is good practice to contact all gas producers/distributors to identify SF₆ and PFC users and to investigate the gas consumption of source categories other than those mentioned above. The key difference among the applications

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discussed below is the typical delay between the purchase of the SF₆ or PFC and the release of the chemical. In some cases (e.g., SF₆ used in sound-proof glazing, PFCs used as heat transfer fluids), the chemical is fairly well contained during the life of the equipment or product, and most emissions are associated with the manufacture and disposal of the product. In these cases, the delay between the purchase of the chemical and its final emission depends on the lifetime of the product, ranging from three years for tyres and sport-shoes to 25 years for sound-proof glazing. In other cases (e.g., use of SF₆ and PFCs as tracers or in medical applications), the chemical is fully emitted within a year of its purchase. If, as a result of an initial survey, applications with distinctive delayed emissions appear significant, then *good practice* is to use a source category-specific emission calculation, taking into account the delay in emissions.

Adiabatic uses

Adiabatic uses of SF₆ and some PFCs exploit the low permeability of these gases through rubber. Historically, SF₆ has been the dominant gas in these applications; however, PFCs with similar molecular weights (such as C₃F₈) have recently been used as well. Applications with a delay period of 3 years include car tyres, sport shoe soles and tennis balls (Schwarz *et al.*, 1996). For applications with emissions that are delayed by three years, the following formula can be used.

EQUATION 8.19**ADIABATIC PROPERTY APPLICATIONS**

$$\text{Emissions in year } t = \text{Sales in year } (t - 3)$$
Sound-proof glazing

Double-glazed sound-proof windows: Approximately one-third of the total amount of SF₆ purchased is released during assembly (i.e., filling of the double glass window) (Schwarz/Leisewitz, 1999). For the stock of gas remaining inside the window (capacity), an annual leakage rate of 1 percent is assumed (including glass breakage). Thus, about 75 percent of initial stock remains at the end of its 25-year lifetime. The application of SF₆ in windows began in 1975, so disposal is only beginning to occur. Emissions from this source sub-category should be calculated using Equations 8.20 to 8.22:

EQUATION 8.20**DOUBLE-GLAZED WINDOWS: ASSEMBLY**

$$\text{Assembly Emissions in year } t = 0.33 \bullet \text{SF}_6 \text{ purchased to fill windows assembled in year } t$$
EQUATION 8.21**DOUBLE-GLAZED WINDOWS: USE**

$$\text{Leakage Emissions in year } t = 0.01 \bullet \text{Capacity of Existing Windows in year } t$$
EQUATION 8.22**DOUBLE-GLAZED WINDOWS: DISPOSAL**

$$\text{Disposal Emissions in year } t = \text{Amount Left in Window at End of Lifetime in year } t \bullet (1 - \text{Recovery Factor})$$

Unless country-specific data are available, a default recovery factor value of zero should be assumed in Equation 8.22. If no specific information is available for these sub-source categories, *good practice* is to treat them as prompt emissions.

Fluorochemicals used to waterproof electronic circuits

[This section is still under development. The draft guidance below groups gases as high-GWP (CF₄, C₂F₆ and CHF₃) and low-GWP (CH₄, C₃F₆, COF₂, C₂H₄) to protect sensitive process information for the company that provided the data. The authors are investigating whether the emission factors, which are currently expressed in terms of emissions of CO₂e/week/chamber, can be provided in terms of emissions of one or more of the dominant gases/unit area of the material water-proofed, similar to the Tier 1 method for electronics (See Volume 3, Chapter 6).]

There are two basic approaches to adding waterproofing layers onto assembled electronic circuits:

1. Liquid-based PFOS or PFOA-containing films, applied by aerosol spray or immersion, or
2. Long-chain perfluorocarbon polymers applied by gas-phase reaction in a plasma.

The second category can result in emissions of fluorochemicals (FCs) and is therefore the focus of this guidance.

The deposition step involves the introduction of a variety of hydrocarbon gases where the hydrogen atoms are replaced by fluorine supplied from an FC gas source.

Periodically, the process chamber is also cleaned using FC gases in a way similar to the way that CVD chambers are cleaned in the semiconductor industry. (See the 2006 IPCC Guidelines, Volume 3, Chapter 6 and the 2019 Refinement, Volume 3, Chapter 6.)

The emission factors in Tables 8.11 and 8.12 represent weekly process chamber emissions from a typical process chamber in a high-volume manufacturing environment (HVM). The process exhaust gases have been split into 2 groups (the members of which are identified) with their combined emissions, in grams CO₂ equivalent. These were measured by FTIR on a working fab installation.

TABLE 8.11
EMISSION FACTOR FOR HIGH-GWP GASES FROM WATERPROOFING OF ELECTRONIC CIRCUITS

High-GWP emissions (gCO ₂ eq/week/chamber)	Gas emitted
8,453,881	CF ₄
	C ₂ F ₆
	CHF ₃

TABLE 8.12
EMISSION FACTOR FOR LOW-GWP GASES FROM WATERPROOFING OF ELECTRONIC CIRCUITS

Low-GWP emissions (gCO ₂ eq/week/chamber)	Gas emitted
830	CH ₄
	C ₃ F ₆
	COF ₂

EQUATION 8.22A
WATERPROOFING OF ELECTRONIC CIRCUITS

$$\text{Emissions}_{\text{HGWP}} = \text{EF}_{\text{HGWP}} * C * W$$

$$\text{Emissions}_{\text{LGWP}} = \text{EF}_{\text{LGWP}} * C * W$$

Where

Emissions_{HGWP} = Emissions of CF₄, C₂F₆, CHF₃ in CO₂e

EF_{HGWP} = Emission factor for CF₄, C₂F₆, CHF₃ in Table 8.11

Emissions_{LGWP} = Emissions of CH₄, C₃F₆, and COF₂ in CO₂e

EF_{LGWP} = Emission factor for CH₄, C₃F₆, and COF₂ in Table 8.11

C = Number of process chambers in the manufacturing facility

W = Average number of weeks the process chambers are in operation during the year

PFCs used as heat transfer fluids in consumer and commercial applications

PFCs are used as heat transfer fluids in a number of high-power-density commercial and consumer electronic applications. Commercial applications include cooling for supercomputer, telecommunication, and airport radar systems, as well as drive units (rectifiers) on high-speed trains (Burton, 2006). These applications consume much smaller volumes of liquid PFCs than electronics manufacturing, but are believed to be significant among ‘niche’ applications. Consumer applications include cooling kits for desktop computers that are operated at high voltages to increase their processing speed. The specific PFCs used in these applications are believed to be similar to those identified as heat transfer fluids in electronics manufacturing in Chapter 6. In all of these applications, the liquid PFCs are used in closed modules, indicating that most emissions occur during the manufacture, maintenance, and disposal of the product or equipment. Thus, if inventory compilers can acquire information on emission rates during the manufacture, maintenance, and disposal of the equipment, along with the quantities of equipment manufactured, used, and disposed each year, they can use the Tier 2 or Tier 3 method for electrical equipment to estimate emissions. For applications with different emissions profiles (e.g., prompt emissions), the appropriate equation from Section 8.2 may be used.

PFCs used in cosmetic and medical applications

PFCs with relatively large molecular weights (e.g., C₁₀F₁₈) are used in cosmetic and medical applications, exploiting their ability to carry oxygen to living tissue (May, 2006). Cosmetic applications include anti-wrinkle creams and are estimated to consume fairly small amounts. Current and potential medical applications include storage of pancreatic tissue for transplants (using the ‘two-layer method’), eye surgery (to repair retinal tears), pneumonectomy (lung therapy and diagnosis), use as a contrast agent in ultrasonic and MRI examinations, blood extension, wound healing, and treatment of diseases of the middle ear. All but the first two medical applications involve only small quantities and/or are at the research stage. Storage of pancreatic tissue is a small but growing application. Emissions from medical uses are uncertain but are believed to be small.

In all of these applications, the PFC is believed to be emitted into the atmosphere within one year of its purchase. Thus, emissions from these sources can be estimated using Equation 8.23 for prompt emissions.

Any other uses of SF₆ and PFCs

Other applications for SF₆ and PFCs that are not specifically addressed above include their use as tracers (in leak detection, indoor and outdoor tracking of air-masses, and oil recovery²) and use of SF₆ in the production of optical cables (for fluorodoping of glass fibres³). Often the gases or liquids are emitted within one year of purchase. In this case, *good practice* in calculating SF₆ and PFC emissions from these ‘prompt’ emissive applications is to use the following formula:

EQUATION 8.23
PROMPT EMISSIONS

$$\text{Emissions in year } t = (0.5 \bullet \text{Amount Sold in year } t) + (0.5 \bullet \text{Amount Sold in year } t - 1)$$

This equation is similar to the equation for prompt ODS Substitute applications (e.g., aerosols and solvents) addressed in Chapter 7 of this volume. The equation covers more than one year because both sales and emissions are assumed to be continuous over the year; that is, chemical sold in the middle of year $t-1$ is not fully emitted until the middle of year t .

8.3.2.2 CHOICE OF EMISSION FACTORS

For ‘other’ source categories of SF₆ and PFCs that contribute substantially to a country’s SF₆ and PFCs emissions, countries are encouraged to develop country-specific emission factors based on occasional surveys of representative subsets of sources. It is good practice to clearly document such emission factors. Default emission

² D. Vlachogiannis *et al.* (2005). This paper indicated that some fraction of injected PFCs and SF₆ was destroyed during fuel combustion, but the magnitude of this fraction (compared to the fraction of injected chemical that escaped before combustion) was unclear.

³ See further information on this application in Schwarz (2005).

factors are provided above for AWACS, accelerators, waterproofing of electronic circuits, prompt emissive applications and adiabatic applications, including windows.

8.3.2.3 CHOICE OF ACTIVITY DATA

No refinement

8.3.2.4 COMPLETENESS

No refinement

8.3.2.5 DEVELOPING A CONSISTENT TIME SERIES

No refinement

8.3.3 Uncertainty assessment

No refinement

8.3.4 Quality Assurance/Quality Control (QA/QC), Reporting and Documentation

No refinement

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474 **8.4 N₂O FROM PRODUCT USES**

475 No refinement

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8.5 TEXTILE, CARPET, LEATHER AND PAPER FLUORINATED TREATMENT EMISSIONS

[This section, 8.5 is a new section in the Chapter 8 Volume 3 of the 2019 Refinement, it should be placed after section 8.4 Chapter 8 Volume 3 of the 2006 IPCC Guidelines; the place of the section will be considered further].

8.5.1 Introduction

Fluorine-based treatment of textile, carpet, leather, and paper has received increased interest and has been a fertile subject for research and development (R&D) since the early 2000s. An increasing number of peer-reviewed papers have been published since 2006, and a growing number of patents have been filed worldwide in the last 5 to 8 years, indicating that technological and industrial developments are occurring rapidly in this emerging field.^{4,5}

Several innovative treatment technologies and chemistries are now transitioning to industrial scale use, particularly plasma processing of textiles using gaseous fluorinated compounds (FCs) such as CF₄, C₂F₆, C₃F₈, C₄F₈, C₅F₁₀, CHF₃, and SF₆.^{6,7,8,9,10,11,12,13} As in the case of the electronics sector, plasma-based processes using FCs in the textile industry are expected to result in emissions of unreacted fluorinated compounds and by-products with high global warming potentials (GWPs). Also, the wet application of fluorinated surfactants and fluorine-based polymers commonly used to treat textile, carpet, leather, and paper fibres can result in emissions of volatile fluorinated compounds through evaporative losses and cracking.^{14,15} A list of the most important fluorinated compounds used for plasma-based treatment processes is provided in Table 8.3, and a list of the most important fluorotelomers, fluorocarbons, and fluorosurfactants used for wet applications, as well as their vapour pressures, is provided in Table 8.7. These treatment technologies are used, inter alia, to control the surface properties of textile, carpet, leather, or paper fibres, and enhance their hydrophobicity or hydrophilicity, increase their stain resistance, dyeing ability, or mechanical strength, and for producing wrinkle-free materials.

The increased interest in fluorine-based treatment of fibres can in part be attributed to the fact that the technologies provide excellent performance and that they can be tailored to reach many desirable properties. Also, the search for alternate water-proofing processes for fabrics, leather, and paper treatment – currently based on wet processes using long-chain ‘C8’ fluorinated compounds that can lead to the formation of persistent and bio-accumulative by-products,¹⁶ has led to the emerging utilization of shorter-chain fluorine chemistries that have however seldom been characterized from a climate impact standpoint.

⁴ Communication from S. Raoux to the IPCC Working Group on Unidentified Sources of PFCs Emissions, August 15, 2016.

⁵ See file entitled “V3_Ch8_References on Fluorinated Plasmas & Textiles.xlsx” downloaded the IPCC TFI Sharepoint account in the folder entitled “Chapter 8. Other Product Manufacture and Use”, incorporated to this draft by reference.

⁶ A. Zille, Fr. Oliveira, A.P. Souto. Plasma treatment in the textile industry. *Plasma Processes and Polymers*. 10, 98-131, 2015.

⁷ A. Davies. Durable water repellency – Study phase 1, De Montfort University, 2014.

⁸ A. Ramamoorthy, A. El-Shafei, P. Hauser. Plasma induced graft polymerization of C6 fluorocarbons on cotton fabrics for sustainable finishing applications. *Plasma Processes and Polymers*. 10, 430-443, 2013.

⁹ C.H. Kwong, S.P. Ng, C.W. Kan, R. Molina. Parametric study of CF₄ plasma on the hydrophobicity of polyester synthetic leather. *Fibres and Polymers*. 14 (10), 1608-1613, 2013.

¹⁰ R. Davies, A. El-Shafei, P. Hauser. Use of atmospheric pressure plasma to confer durable water repellent functionality and antimicrobial functionality on cotton/polyester blend. *Surface and Coatings Technology*, 205, 4791-4797, 2011.

¹¹ A. Raffaele-Addamo, et al. Characterization of plasma processing for polymers. *Surface and Coatings Technology*, 174-175, 2003.

¹² F. Hochart, R. De Jaeger, J. Levalois-Grützmacher. Graft polymerization of as hydrophobic monomer onto PAN textile by low-pressure plasma treatments. *Surface and Coatings Technology*, 165, 201-210, 2003.

¹³ J. Yip, K. Chan, K.M. Sin, K.S. Lau. Study of physico-chemical surface treatment on dyeing properties of polyamides. Part 1: Effect of tetrafluoromethane low temperature plasma. *Coloration Technol.*, 118, 2002.

¹⁴ OECD Emission Scenario Document (ESD) provides information on the sources, use patterns and release pathways of chemicals used in textile finishing industry and to assist in the estimation of releases of chemicals to the environment (ENV/JM/MONO(2004)12)

¹⁵ Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for the Textiles Industry (2003)

¹⁶ The conventional processes used for increasing the water repellency of fibers use perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs). Such processes can lead to the formation of perfluoroalkyl acids (PFAAs)

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Although several international and national reports refer to the possible off-gas emissions of fluorinated compounds into the atmosphere due to textile treatment, no emission factors appear to be available in the open literature to estimate greenhouse gas (GHG) emissions from such processes.^{11,12,17,18,19,20,21,25} Also, the extent to which plasma-based textile treatment processes have penetrated volume production is unclear, and the authors were not able – at the time of writing of this first order draft – to estimate the volume of fluorinated compounds that are used or emitted by the textile, carpet, leather, and paper industries. Nevertheless, FC emissions in this sector could represent a significant new source, due to the large volume of substrates treated and the sheer size and global nature of the industry.

Plasma treatment processes

Plasmas are frequently subdivided into thermal (hot) and non-thermal (cold) plasmas. For thermal plasmas, the temperature of electrons, ions, neutrals and excited species in the plasma state is in equilibrium, ranging from 3500 °C to 20000 °C. Non-equilibrium (cold) plasmas have electron temperatures that are much higher than the temperature of the ions and neutrals, where the temperature of the plasma is typically in the range of 40 to 250 °C. Because textile and polymers cannot withstand the high temperatures used in thermal plasmas, most applications for organic fibres' surface modification use cold plasmas. The types of plasma processes used for the treatment of such materials can be divided into three categories: 1) plasma treatment, 2) plasma etching (or ablation), and 3) plasma polymerization.²²

Plasma treatment uses inert gases such as Ar, He, N₂, and chemically active molecules such as O₂ or NH₃, as well as fluorinated gases such as CF₄, C₂F₆, C₃F₈, C₄F₈, C₅F₁₀, CHF₃, SF₆, and other (larger size) fluorine-containing molecules such as perfluoroalkyl acrylates.^{3,23,24,25,26,27,28,29,30} The plasma-activated gases introduce chemical functionalities or create and deposit free radicals onto the target surface that can be subsequently used to cross-link or surface-graft other molecules to attain specific surface properties (very often more hydrophilic surfaces). Another method consists in the immersion of the fabric in a fluid of hydrophobic fluorinated pre-polymer with added initiators followed by a plasma treatment leading to the grafting on the surface of the fabric.

Plasma etching occurs when the substrate is bombarded with ions from the plasma to clean, sterilize, or enhance surface adhesion of the fabrics. For example, dry plasma etching can be accomplished by using CF₄ in a plasma discharge to create active species capable of reacting chemically with the layer to be etched.³¹ Plasma polymerization is a process where a monomer in vapour phase such as CF₄, C₂F₆, C₃F₈, or larger fluorinated molecules such as fluorodecylacrylate is converted into reactive fragments, which polymerize at the surface (plasma-induced polymerization) or combine

residues, and in particular to the environmental release of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), two chemicals of concern due their persistent and bio-accumulative nature. While some of these conventional processes have been banned or are being phased out in several developed countries, the long-chain 'C8' chemistry remains in use in many developing countries with less stringent environmental controls.

¹⁷ UNIDO, UNITAR, UNEP. Guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on Persistent Organic Pollutants, 2012.

¹⁸ U.S. Environmental Protection Agency. Profile of the Textile Industry, 1997

¹⁹ Gontek J. et al. BAT Guide for textile industry, Project TR-2008-IB-EN-03, MoEU Turkey and IPPC E.U., 2008

²⁰ Schönberger H & Schäfer T, German Federal Environmental Agency, Best Available Techniques in Textile Industry, Research Report 200 94 329, UBA-FB 000325/e, 2003

²¹ Lassen C. et al. Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances, The Danish Environmental Protection Agency, 2013

²² [Roth, J. Reece. Industrial Plasma Engineering: Volume 2-Applications to Nonthermal Plasma Processing. Vol. 2. CRC press, 2001.](#)

²³ <http://www.sciencedirect.com/science/article/pii/S0257897213002910>

²⁴ <http://journals.sagepub.com/doi/abs/10.1177/0040517517698988>

²⁵ http://file.scirp.org/pdf/JSEMAT_2015060115003244.pdf

²⁶ <http://www.sciencedirect.com/science/article/pii/S0584854705002843>

²⁷ <http://onlinelibrary.wiley.com/doi/10.1002/ppap.201400052/full>

²⁸ <https://arxiv.org/abs/0801.3727>

²⁹ <http://www.sciencedirect.com/science/article/pii/S025789720701270>

³⁰ <https://link.springer.com/article/10.1007/s11090-012-9413-9>

³¹ DOI: 10.1002/(SICI)1097-4628(19971121)66:8<1591::AID-APP21>3.0.CO;2-5

with polymers in the gas phase (plasma-state polymerization) to be deposited on the substrate. The deposition can occur while the plasma is excited or in a two-step process: (i) creation of radicals on the fibre surface by plasma in inert gas (e.g. argon) and, (ii) reaction of these radicals with unsaturated monomers.³² The main difference between these mechanisms is that in the case of plasma-state polymerization, gaseous phase by-products are formed, whereas no by-products should be formed in plasma-induced polymerization. However, even if no by-products are formed in the case of plasma-state polymerization, it is highly improbable that all the input chemicals are consumed in either plasma-induced polymerization or plasma-state polymerization.

The majority of plasma-based textile treatment processes for the production of hydrophobic and oleophobic surfaces (but also for some polymer coating, flame retardant and medical antimicrobial fabrics) reported in the technical literature are based on non-thermal plasmas generated at low pressure (between 1 mTorr and 1 Torr) and in few cases at atmospheric pressure. Plasma source designs based on corona discharges, glow discharges, dielectric barrier discharges (DBDs), plasma jet, capacitively or inductively coupled discharges, and RF- or microwave-induced discharges have been studied.^{2,21-30}

Although most plasma processing technologies for textile treatments are still at an emerging stage, several manufacturers have developed pilot- to commercial-scale machinery, and applications for specialized textiles have been or are currently being implemented at industrial scale. Indeed, plasma treatment proves particularly effective for the production of specialty textiles for the medical industry (gowns, masks, protective clothing), the automotive industry (seats, trim, headliners, airbags), the apparel industry (outer and under garments), the filtration industry (air, water filtration) and the flooring industry (carpet fibres).³³ However, the high capital and operational costs of plasma treatment (in particular for low-pressure plasma technologies requiring a closed vacuum system) currently limits the commercial viability of the technique for treating conventional (non-specialized) fabrics. Polymerization of textiles using plasma at atmospheric pressure offers a low-cost and environmentally-friendly alternative, but the technology is still under development.^{34, 35}

As mentioned earlier, plasma-based processes using fluorinated compounds in the textile industry are expected to result in emissions of high GWP gases. In addition to the limited utilization efficiency of the input gases, emissions of by-products such as CF₄, C₂F₆, CHF₃, and other FC gases can also be expected, due to the decomposition and chemical reaction of the FC input gas(es) during plasma treatment. Moreover, even though the potential for plasma-based polymerization processes to emit large amounts of FCs is likely lower than for processes directly using FC gases as input chemicals, high-GWP emissions from plasma-based polymerization can be expected from either chemical reactions or evaporative losses. It should also be mentioned that the deposition of a polymer onto the fabric surface directly in the plasma reactor is more effective than many conventional wet-based chemistries, and that such characteristics may contribute to shifting emissions towards high-GWP gases. Finally, the extent to which reactor cleaning processes (to remove the deposits that build on the chamber walls after multiple depositions) may contribute to GHG emissions is unclear at the time of writing of this FOD.

Wet treatment processes

Wet treatment processes include several applications techniques but 80% of the processes use the pad-dry-cure method, where the dry fabric is immersed in the finishing liquor and then squeezed between rollers before being dried and finally cured, usually at a temperature of between 150 and 180 °C.^{12,1} Other techniques include vacuum extraction, spray applications, foam finishing, coating, and lamination. These processes are widely used to functionalize fibres with fluorine-based chemicals for water repellence and soil and stain release, improving textile breathability, softening, antibacterial and anti-odour finishing for the treatment of home textiles, upholstery furniture, protective clothing with signal colour, tent canvas, outdoor wear, medical textiles and work wear such as uniforms and shoes.^{36, 37, 38, 39, 40}

³² <https://doi.org/10.1016/j.surfcoat.2007.12.027>

³³ 10.1007/978-981-10-2185-5_2

³⁴ Shishoo, Roshan, ed. *Plasma technologies for textiles*. Elsevier, 2007.

³⁵ Muthu, Subramanian Senthilkannan. *Textiles and Clothing Sustainability*. Springer Verlag, Singapor, 2016.

³⁶ Gulrajani, Mohan L., ed. *Advances in the dyeing and finishing of technical textiles*. Elsevier, 2013.

³⁷ Paul, Roshan, ed. *Functional finishes for textiles: improving comfort, performance and protection*. Elsevier, 2014.

³⁸ Singha, Kunal. "A review on coating & lamination in textiles: processes and applications." *American Journal of Polymer Science* 2, no. 3 (2012): 39-49.

³⁹ Lacasse, Katia, and Werner Baumann. *Textile Chemicals: Environmental data and facts*. Springer Science & Business Media, 2004.

⁴⁰ Schindler, Wolfgang D., and Peter J. Hauser. *Chemical finishing of textiles*. Elsevier, 2004.

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The chemical structure of the fluorine-based surfactants and polymers used for the above-described applications is characterized by side-chain fluorinated polymers primarily based on fluorotelomer acrylates, fluorotelomer methacrylates or per-fluoroalkane sulfonamidoethanols. Unfortunately, the environmental and health characteristics of the new short-chain chemistry and associated processes are poorly described in recent scientific literature. Although some reports refer to possible emissions of fluorocarbon in the atmosphere due to textile wet coating, no data or estimations of emissions are provided.^{11,12,41,42,43,44,45,46,47,48,49,50} Data on the volatile PFASs that are emitted immediately after the production of textiles, the type of PFASs that can be formed by hydrolysis of the perfluorinated polymer side chains during use, washing and degradation of the fabrics is also seemingly missing.

Importantly, it must be considered that fluorochemical products are likely to be released to the air during their industrial application to fibres, particularly during the curing phase of the treatment. It has been shown that, during the drying and curing phases, off-gas emissions can be produced by the volatility of the active substances themselves as well as by their constituents, which can contain on average 1% of unreacted and unbound residuals such as monomers, fluorotelomer alcohols (sometimes up to 6-8% of the dry weight) and perfluoroalkyl carboxylic acids.⁵¹ Overall, it can be expected that the magnitude of emissions will depend on the drying or curing temperature, the substrate material, and the reagents' volatility, concentrations and reactivity.⁵² To complicate the matter, there is a wide range of different application methods (e.g. padding, spray, foaming, coating, lamination, etc.), different vapour pressure of input chemicals, and different temperature and time of drying and curing steps of the treated substrates. For example, some leather stain resistant finishing agents are applied by spray and dried at room temperature while most of the textile finishing require a drying (110-130°C) and curing (150-180 °C) steps.⁵³ Carpet products may be cured at a lower temperature of 110 °C while other products may be treated for 2 minutes at 170°C or for 30 seconds at 190°C (e.g. cotton). Moreover, some carpet treatments require a curing step for water and oil repellence fluorochemical deposition but on the contrary no curing is required for some type of fluorinated soil release finishing agents.⁵⁴ Generally, the higher the curing temperature, the shorter the curing time to avoid the yellowing of the fabric. Residuals and impurities may also be released directly from the products into the environment through volatilization, and FC emissions may result from the cracking of input chemicals. Thus, presumptively, emissions of high-GWP gases from wet-based fluorinated treatment of textile, leather, and paper fibres may represent a substantial source. However, the potential climate impact of such processes and substances does not appear to have been characterized in the literature, which typically focuses on formaldehyde, total organic carbon release and on a very limited selection of well-known long-chain PFASs such as perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA) and their precursors.⁵⁵

⁴¹ UNEP Guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on Persistent Organic Pollutants (UNEP-POPS-GUID-NIP-2012)

⁴² Lassen C. Polyfluoroalkyl substances (PFASs) in textiles for children. The Danish Environmental Protection Agency, 2015.

⁴³ https://www.bafu.admin.ch/dam/bafu/en/dokumente/chemikalien/uw-umwelt-wissen/substance_flow_analysisforswitzerland.pdf.download.pdf/substance_flow_analysisforswitzerland.pdf

⁴⁴ Young, Cora Jean Louise. Atmospheric Chemistry of Polyfluorinated Compounds: Long-lived Greenhouse Gases and Sources of Perfluorinated Acids. 2010. PhD Thesis.

⁴⁵ <https://www.meetings.copernicus.org/www.cosis.net/abstracts/EGU05/10257/EGU05-J-10257.pdf>

⁴⁶ Jahnke, A.; Huber, S.; Temme, C.; Kylin, H.; Berger, U. Development and application of a simplified sampling method for volatile polyfluorinated alkyl substances in indoor and environmental air. *Journal of Chromatography A* 2007, 1164, 1-9

⁴⁷ Barber, J.L.; Berger, U.; Chaemfa, C.; Huber, S.; Jahnke, A.; Temme, C.; Jones, K.C. Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *Journal of Environmental Monitoring* 2007, 9, 530-541

⁴⁸ 10.1021/es0512475

⁴⁹ 10.1021/es0512475

⁵⁰ 10.1021/es049860w

⁵¹ DOI: 10.1021/acs.est.6b03213

⁵² http://eippcb.jrc.ec.europa.eu/reference/BREF/txt_bref_0703.pdf

⁵³ Williams J., *Waterproof and Water Repellent Textiles and Clothing*, Woodhead Publishing, 2017

⁵⁴ Goswami K.K., *Advances in Carpet Manufacture*, Woodhead Publishing, 2009

⁵⁵ Wang, Zhanyun, Jamie C. DeWitt, Christopher P. Higgins, and Ian T. Cousins. "A never-ending story of per- and polyfluoroalkyl substances (PFASs)?" (2017): 2508-2518.

8.5.2 Methodological issues

8.5.2.1 CHOICE OF METHOD

[The choice of method will depend on the availability of measured emission factors from which default factors might be derived. Although it is unclear at this point whether representative FC emissions data can be obtained from the textile, carpet, leather, or paper industries, the authors propose herewith a methodological framework to account for emissions from this sector. Distinct methods are provided for plasma-based processes in section 8.5.2.2 and for wet-based processes in section 8.5.2.3. Please note however that the equations proposed for plasma- and wet-based processes can likely be consolidated. This will be addressed as part of the Second Order Draft (SOD).]

The inventory methods proposed for plasma-based processes are analogous to those used in the electronics industry due to the similarity of the processes, and include four tiered methods (Tier 1, 2a, 2b, 3). The Tier 1 method does not require gas consumption data and provides an estimate of emissions based on default (industry average) emission factors expressed in mass of FCs emitted per unit area of substrate treated. The Tier 2a and 2b methods require FC consumption data at the site or national level and are based on process gas-specific default emission factors expressed in terms of mass of FCs emitted per mass of FCs consumed (including both emissions of unreacted FC and emissions of all FC by-products formed during the process). For plasma processes, the difference between the Tier 2a and 2b methods is that the Tier 2b method differentiates emission factors by type of plasma process (plasma treatment, plasma etching, and plasma polymerization), while the Tier 2a method does not. For wet-based processes, the difference between the Tier 2a and 2b methods is that the Tier 2b method would distinguish emission factors [by process and/or substrate type (see further discussion below)]. The Tier 3 method uses the same equations as the Tier 2b method, but is based on emission factors measured for site-specific processes.

For wet-based processes, a Tier 1 approach is proposed to estimate FC emissions based on the surface area of substrate treated, a method, which would therefore not require data on the consumption of input chemicals. Two Tier 2 methods are proposed (Tier 2a and 2b) based on default FC emission factors allowing to correlate the mass of wet input chemicals consumed to the mass of volatile by-products formed during the processes. The difference between the Tier 2a and 2b methods for wet-based processes is that the Tier 2b method would distinguish emission factors [by process and/or substrate type (see further discussion below)]. Finally, a Tier 3 method would use the same equations as the Tier 2 method, but would use measured (site-specific) emission factors instead of default ones.

Generally, the higher tiered methods will be more accurate than the lowered tiered ones, and using site-specific emission factors will improve accuracy and greatly reduce the uncertainty of emissions estimates. The accuracy of the methods using default emission factors depends, inter alia, on the differences between the emission factors of the processes actually used in production and the averaged (default) emission factors of a particular method, as well as on potential errors in allocating gas consumption, and in reporting abatement efficiency and uptime. With respect to uncertainty, the confidence level of a particular estimate is principally driven by the uncertainty of the default emission factors [see Table 8.24]. Thus, the use of higher tiered methods is strongly encouraged.

[Please note that if no representative FC emissions data can be obtained for industry to derive the Tier 1 or Tier 2 default emission factors, the Tier 3 methods will become the only practical means to estimate emissions from the sector, where individual manufacturing sites will have to measure their own emission factors. In this case, applying the Tier 3 methods and reporting emission factors across representative manufacturing sites will become essential in building a database of emission factors that can later be used to derive the Tier 1 and Tier 2 emission factors.]

[Note: a decision tree for selecting the different methods for the estimation of GHG emissions from the sector will be devised.]

8.5.2.2 PLASMA TREATMENT PROCESSES

Table 8.13 depicts the information sources necessary for completing the tiered methods for estimating emissions from plasma treatment processes. Depending on the method used, data based on production capacity (Tier 1), or data about input chemicals consumption, use rate, by-products formation rates, and the effectiveness of emissions control measures (Tier 2a, 2b, 3) will be required for the calculation of emissions. For each variable, depending on the tiered method, an industry default value (D) may be used, measured (Me), or modelled (Mo) to account for site-specific values. [Additional guidance will be provided in subsequent drafts for measuring or modelling specific values for the heel, gas consumption, site-specific emission factors, the fraction of gas abated, and the destruction removal efficiency (DRE) of the gases.]

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TABLE 8.13					
INFORMATION SOURCES NECESSARY FOR COMPLETING THE TIERED EMISSIONS ESTIMATING METHODS FOR PLASMA TREATMENT OF TEXTILE, LEATHER, AND PAPER					
[The information provided in this table is preliminary and likely to evolve as the definition of the various methods is refined]					
Data		Tier 1	Tier 2		Tier 3
			2a	2b	
Process Gas Entering Tools	FC _i = consumption of gas <i>i</i>		Me/Mo		
	FC _{i,p} = consumption of gas <i>i</i> for process <i>p</i> . ^a			Me/Mo	Me/Mo
	h _i = Fraction of gas remaining in shipping container after use (heel) for gas <i>i</i> .		D/Me	D/Me	Me
Process Gas Reactions and Conversion in Tools	U _i = Use rate (fraction destroyed or transformed) for each gas <i>i</i> .		D		
	U _{i,p} = Use rate (fraction destroyed or transformed) for each gas <i>i</i> and process <i>p</i> . ^a			D	Me
	B _{k,i} = Emission factor for by-product <i>k</i> for input gas <i>i</i> .		D		
	B _{k,i,p} = Emission factor for by-product <i>k</i> for input gas <i>i</i> and process <i>p</i> . ^a			D	Me
Downstream FC Emission Control	a _i = Fraction of gas <i>i</i> volume used in processes with certified FC emission control technology		Me		
	a _{i,p} = Fraction of gas <i>i</i> volume fed into processes <i>p</i> with certified FC emission control technology			Me ^a	Me ^a
	d _i = Destruction Removal Efficiency (DRE) for gas <i>i</i>		D/Me		
	d _{i,p} = Destruction Removal Efficiency (DRE) for gas <i>i</i> for process <i>p</i>			D/Me ^a	D/Me ^a
	UT = Average uptime factor of all abatement systems connected to process tools		Me		
	UT _p = Average uptime factor of all abatement systems connected to process tools running process type <i>p</i>			Me ^a	Me ^a
Annual Production Capacity	EF _i = emission factor for FC gas <i>i</i>	D			
	C _u = fraction of annual plant production capacity utilization	Me			
	C _d = annual manufacturing design capacity	Me			

Me = measurement; Mo = model {modelling criteria TBD}; D = Use default factors from guidance.

^a Depending on the method used, 'p' is to be interpreted as a particular plasma process type (Tier 2b) or a site-specific process (Tier 3).

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TIER 1 METHOD FOR PLASMA TREATMENT PROCESSES – DEFAULT

The Tier 1 method is the least accurate estimation method and should be used only in cases where site-specific data on the consumption of input chemicals are not available. The Tier 1 method, unlike the Tier 2a, 2b or Tier 3 methods, is designed to give an aggregated estimate of FC emissions although its methodology appears to produce gas-specific emissions. Estimates are made simultaneously for all gases as listed in [Table 8.15] and can only be used if reported as a complete set.

The Tier 1 calculation relies on a fixed set of generic emissions factors and does not account for differences among process types (plasma treatment, etching, or polymerization), individual processes or manufacturing tools. The members of the set differ depending on the surface area of textile, carpet, leather, or paper products being manufactured. Each member of a set, which is a gas-specific emission factor, expresses average emissions per unit of substrate area (textile, carpet, leather, paper) produced during manufacture. For any class of product, the factors (members of the set) are multiplied by the annual capacity utilization (C_u , a fraction) and the annual manufacturing design capacity (C_d , in square meters (m^2)) of substrate processes. The product ($C_u \cdot C_d$) is an estimate of the quantity of substrate produced during the manufacture of textile, leather, or paper. The result is a set of annual emissions expressed in kg of the gases that comprise the set for each class of products. The Tier 1 formula is shown in Equation 8.25.

EQUATION 8.25**TIER 1 METHOD FOR ESTIMATING THE SET OF FC EMISSIONS**

$$\{FC_i\}_n = \{EF_i \cdot C_u \cdot C_d\}_n \quad (i = 1, \dots, n)$$

Where:

$\{FC_i\}_n$ = emissions of FC gas i , mass of gas i

Note: $\{ \}_n$ denotes the set for each class of products (e.g. textile, carpet, leather, or paper) and n denotes the number of gases included in each set [See Table 8.4]. The estimates are only valid if made and reported for all members of the set using this Tier 1 methodology.

EF_i = FC emission factor for gas i expressed as annual mass of emissions per square meters of substrate surface area for the product class, (mass of gas i)/ m^2

C_u = fraction of annual plant production capacity utilization, fraction

C_d = annual manufacturing design capacity, m^2 of substrate processed

In using Tier 1, inventory compilers should not modify, in any way, the set of the FCs assumed in [Table 8.15]. Further, the Tier 1 method does not allow to account for the use of emissions control technologies. Inventory compilers should not combine emissions estimated using Tier 1 method with emissions estimated using the Tier 2 or 3 methods. Neither may inventory compilers use, for example, the Tier 1 factor for CF_4 to estimate the emissions of CF_4 from textiles etching and combine it with the results of other FC gases from a Tier 2 or Tier 3 method.

TIER 2A METHOD FOR PLASMA TREATMENT PROCESSES – PROCESS CHEMICAL-SPECIFIC PARAMETERS

The Tier 2a method uses industry-wide default values for the fraction of input chemicals used in the plasma manufacturing process (U_i) [see Table 8.17], the fraction of input chemicals i converted into FC by-products k during the process ($B_{k,i}$) [see Table 8.17], and the fraction of FCs destroyed by the emissions control technology (D_i) [see Table 8.23]. The Tier 2a method also calculates emissions for each input chemical used on the basis of site-specific data on chemicals consumption and emissions control technologies. Thus, to use the Tier 2a method, inventory compilers must have direct communication with industry (e.g., annual emissions reporting) to gather consumption data and ensure that emission control technologies are installed and used in accordance with the guidelines provided in this document. For the ‘heel’ or fraction of the purchased gas remaining in the shipping container after use (h_i), facilities may use default or site-specific values {guidance will be provided to calculate site-specific h_i values}.

Unlike the Tier 2b and Tier 3 methods that are explained later in this section, the Tier 2a method does not distinguish between process types (treatment, etching, or polymerization) or site-specific processes. However, the Tier 2a default emission factors are formed separately for each input chemical, which, unlike the Tier 1 method, allows to account for the actual mix of input chemicals used at a particular site.

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Total Tier 2a emissions are equal to the sum of emissions from all unreacted fluorinated chemicals i used in the production process (E_i) plus emissions of all by-products k (BPE_k) resulting from the conversion of all input chemicals used during production, as calculated using equations 8.26, and 8.27 below.

EQUATION 8.26**TIER 2A ESTIMATION OF EMISSIONS OF UNREACTED INPUT CHEMICALS**

$$E_i = (1 - h_i) * FC_i * (1 - U_i) * (1 - D_i)$$

Where:

E_i = emissions of unreacted input chemical i , kg.

h_i = fraction of input gas i remaining in shipping container (heel) after use, fraction.

FC_i = consumption of input chemical i , kg.

U_i = use rate of input chemical i (fraction destroyed or transformed in process), fraction.

D_i = Overall reduction of gas i emissions, fraction, calculated per equation 8.28.

EQUATION 8.27**TIER 2A ESTIMATION OF BY-PRODUCT EMISSIONS**

$$BPE_k = \sum (1 - h_i) * B_{k,i} * FC_i * (1 - D_i)$$

Where:

BPE_k = emissions of by-product k generated from the conversion of all input chemicals i , kg.

h_i = fraction of input gas i remaining in shipping container (heel) after use, fraction.

FC_i = consumption of input chemical i , kg.

$B_{k,i}$ = emission factor, kg of by-product k created per kg of input chemical i used.

D_k = overall reduction of gas k by-product emissions, fraction, calculated per equation 8.28 (replacing i by k indexes).

EQUATION 8.28**EMISSIONS REDUCTION IMPACT OF EMISSIONS CONTROL TECHNOLOGY**

$$D_i = a_i * d_i * UT$$

Where:

D_i = overall reduction of chemical i emissions, fraction.

a_i = fraction of chemical i volume used in processes with emission control technologies (site-specific), fraction.

d_i = Destruction Removal Efficiency (DRE) for chemical i , fraction.

UT = average uptime of all abatement systems, fraction, calculated per Equation 8.29

EQUATION 8.29**UPTIME OF EMISSION CONTROL SYSTEM**

$$UT = 1 - \frac{\sum_n T d_n}{\sum_n UT_n}$$

Where:

UT = average uptime factor of all abatement systems connected to process tools, fraction.

Td_n = The total time, in minutes, that abatement system n connected to process tool(s) in the plant, is not in operational mode when at least one of the manufacturing tools connected to abatement system n is in operation.

UT_n = total time, in minutes per year, in which abatement system n has at least one associated manufacturing tool in operation. For determining the amount of tool operating time, you may assume that tools that were installed for the whole of the year were operated for 525,600 minutes per year. For tools that were installed or uninstalled during the year, you should prorate the operating time to account for the days in which the tool was not installed; treat any partial day that a tool was installed as a full day (1,440 minutes) of tool operation. For an abatement system that has more than one connected tool, the tool operating time is 525,600 minutes per year if at least one tool was installed at all times throughout the year. If you have tools that are idle with no gas flow through the tool for part of the year, you may calculate total tool time using the actual time that gas is flowing through the tool. *Nota bene*: UT may be set to 1 if suitable backup abatement or interlocking with the process tool is implemented for each abatement system.

n = abatement system.

TIER 2B METHOD FOR PLASMA TREATMENT PROCESSES – PROCESS TYPE-SPECIFIC PARAMETERS

The Tier 2b method is similar to the Tier 2a approach in the sense that it is based on chemical-specific default emission factors, but the Tier 2b factors also account for the type of plasma process ' p ' used in manufacturing (p = plasma treatment, plasma etching, and plasma polymerization). Thus, the Tier 2b approach is expected to be more accurate than the Tier 2a one because the Tier 2b method reflects the mix of processes used in a particular manufacturing facility. Also, the Tier 2b method allows to account for the trend where some chemicals tend to be used predominantly in particular process types and class of products manufactured (textile, carpet, leather, paper). The Tier 2b method uses industry-wide default values for the fraction of input chemicals i used in plasma manufacturing process p ($U_{i,p}$), the fraction of input chemicals i converted into FC by-products k during process p ($B_{k,i,p}$), and the fraction of FCs destroyed by the emissions control technology connected to tools using process type p ($D_{i,p}$). For the 'heel' or fraction of the purchased gas remaining in the shipping container after use (h_i), facilities may use default or site-specific values {guidance will be provided to calculate site-specific h_i values}.

Although the Tier 2b method is preferred over the Tier 2a method because process-type-specific emission factors are more accurate, it should be noted that the Tier 2b method presents increased complexity because the consumption of input chemicals must be allocated to each process type p . Thus, in the case where the consumption of input chemicals cannot directly be measured for each process p , a gas consumption allocation model must be devised for applying the method {guidance will be provided to model the allocation of gas consumption}, and inventory compilers should consider the trade-off of using more accurate process-specific emission factors versus introducing errors in the Tier 2b estimate, due to uncertainties in the allocation model.

Total Tier 2b emissions are equal to the sum of emissions from all unreacted fluorinated chemicals i used in all production processes p (E_i) plus emissions of all by-products k resulting from the conversion of all input chemicals used during all production processes p (BPE_k), as calculated using equations 8.30, and 8.31 below.

EQUATION 8.30 TIER 2B ESTIMATION OF EMISSIONS OF UNREACTED INPUT CHEMICALS

$$E_i = (1 - h_i) \sum [FC_{i,p} * (1 - U_{i,p}) * (1 - D_{i,p})]$$

Where:

E_i = emissions of unreacted input chemical i , kg.

h_i = fraction of input gas i remaining in shipping container (heel) after use, fraction.

$FC_{i,p}$ = consumption of input chemical i for process type p , kg.

$U_{i,p}$ = use rate of input chemical i (fraction destroyed or transformed in process type p), fraction.

$D_{i,p}$ = overall reduction of gas i emissions from tools using process type p , fraction, calculated per equation 8.32.

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EQUATION 8.31**TIER 2B ESTIMATION OF BY-PRODUCT EMISSIONS**

$$BPE_k = \sum_i \left[(1 - h_i) \cdot \sum_p [B_{k,i,p} \cdot FC_{i,p} \cdot (1 - D_{k,p})] \right]$$

Where:

BPE_k = emissions of by-product k generated from the conversion of all input chemicals i used for all process types p , kg.

h_i = fraction of input gas i remaining in shipping container (heel) after use, fraction.

$B_{k,i,p}$ = emission factor, kg of by-product k created per kg of input chemical i used for process p .

$FC_{i,p}$ = consumption of input chemical i for process type p , kg.

$D_{k,p}$ = overall reduction of gas k by-product emissions from tools using process type p , fraction, calculated per equation 8.32 (replacing i by k indexes).

EQUATION 8.32**EMISSIONS REDUCTION IMPACT OF EMISSIONS CONTROL TECHNOLOGY**

$$D_{i,p} = a_{i,p} \cdot d_{i,p} \cdot UT_p$$

Where:

$D_{i,p}$ = overall reduction of chemical i emissions from process type p , fraction.

$a_{i,p}$ = fraction of chemical i volume fed into process type p with emission control technologies (site-specific), fraction.

$d_{i,p}$ = Destruction Removal Efficiency (DRE) for chemical i and process type p , fraction.

UT_p = average uptime of all abatement systems connected to tools using process type p , fraction, calculated per Equation 8.33.

EQUATION 8.33**UPTIME OF EMISSION CONTROL SYSTEMS**

$$UT_p = 1 - \frac{\sum_n Td_{n,p}}{\sum_n UT_{n,p}}$$

Where:

UT_p = average uptime factor of all abatement systems connected to process tools running process type p , fraction.

$Td_{n,p}$ = The total time, in minutes, that abatement system n connected to process tool(s) running process type p in the plant, is not in operational mode when at least one of the manufacturing tools connected to abatement system n is in operation.

$UT_{n,p}$ = total time, in minutes per year, in which abatement system n has at least one associated manufacturing tool running process type p in operation. For determining the amount of tool operating time, you may assume that tools that were installed for the whole of the year were operated for 525,600 minutes per year. For tools that were installed or uninstalled during the year, you should prorate the operating time to account for the days in which the tool was not installed; treat any partial day that a tool was installed as a full day (1,440 minutes) of tool operation. For an abatement system that has more than one connected tool, the tool operating time is 525,600 minutes per year if at least one tool

was installed at all times throughout the year. If you have tools that are idle with no gas flow through the tool for part of the year, you may calculate total tool time using the actual time that gas is flowing through the tool. *Nota bene*: UT may be set to 1 if suitable backup abatement or interlocking with the process tool is implemented for each abatement system.

n = abatement system.

TIER 3 METHOD FOR PLASMA TREATMENT PROCESSES – SITE-SPECIFIC PARAMETERS

The Tier 3 method uses the same set of equations as the Tier 2b method. However, the Tier 3 method can use site-specific values for the parameters used in equations 8.30 to 8.33. Notably, ‘*p*’ in these equations can represent a site-specific process, having a more refined definition than the three process types defined in the Tier 2b method. In the Tier 3 method, a process *p* can be defined as a centreline process (or a small set of centreline processes) for which site-specific emission factors have been measured. For example, a site-specific centreline process could be defined as a low-pressure plasma process for etching medical polyamide, or for the polymerization of CF₄ for anti-stain fabric. Centreline conditions refer to specific process conditions for which a manufacturer may have tuned a process for achieving a particular result, or specific process conditions (i.e. a ‘recipe’) that may have been provided by a tool manufacturer who standardized its equipment for sale.

It is very important to note that emission factors such as input gas utilisation efficiencies and by-product formation rates can be strongly affected by changes in process conditions (e.g. pressure, temperature, plasma power, flows of input chemicals, processing time, etc.), and that emission factors for a recipe tuned for a particular purpose or product can differ from those of the centreline process recipe that may have been used for measuring emission factors. Further, emission factors are affected by the design of the plasma process reactors and can substantially fluctuate from one tool manufacturer to another, even when the process function is similar. Thus, compilers using the Tier 3 method should bear in mind that using a single emission factor for multiple distinct processes *p* (i.e. using a single emission factor for a small set of processes *p*) should only be done when the processes are similar. [A definition of ‘similarity’ will be developed based on the principle that a single emission factor could be used for multiple similar processes so long as the emission factors does not change by more than +/- [XX]%. For example, ‘similarity’ would require that the input chemicals are the same, and that the process temperature, plasma power, or flows of input chemicals do not vary by more than a certain percentage point].

The Tier 3 method should be used by manufacturing plants whose processes depart significantly from industry-wide patterns of usage (e.g. for facilities using an input chemical primarily in plasma etching while others primarily use it in plasma polymerization), or by manufacturing plants that may have developed specific processes whose characteristics may result in a significantly lower or higher utilization of input chemicals. Further, if default Tier 1 or Tier 2 emission factors are not available for a particular process or input chemical, manufacturing facilities should measure their site-specific emission factors and use the Tier 3 method.

It should also be noted that the Tier 3 method may be combined with the Tier 2a or 2b method. Indeed, higher accuracy might be achieved by using the Tier 3 method for a specific input chemicals and site-specific processes, and these estimates may be combined with estimates based on Tier 2a or 2b default emission factors for other gases and processes instead of using only the Tier 2a or 2b methods. However, reporters should not combine the Tier 1 method with any other method.

8.5.2.3 WET TREATMENT PROCESSES

Table 8.14 depicts the information sources necessary for completing the tiered methods for estimating emissions from wet-based treatment of textiles, carpet, leather, and paper. Depending on the method used, data based on production capacity (Tier 1), or data about input chemicals consumption, use rate, by-products formation rates, and the effectiveness of emissions control measures (Tier 2a, 2b, 3) will be required for the calculation of emissions. For each variable, depending on the method, an industry default value (D) may be used, modelled (Mo), or measured (Me) to account for site-specific values. As mentioned earlier, emissions of greenhouse gases from wet treatment processes may result from evaporative losses of the input liquid chemicals and from the formation of volatile fluorinated compounds through chemical reactions during the processes, all of which can be considered as volatile by-product emissions resulting from the use of the liquid input chemicals. Thus, unlike for plasma-based processes, the equations for the Tier 2a, 2b and Tier 3 methods for wet treatment processes do not take into account the utilization efficiency of the input liquid chemicals – most of which remain on the substrate as a coating (in a solid state), and only volatile by-product emission factors are necessary to account for all emissions ($B_{k,i}$ for the Tier 2a and $B_{k,i,p}$ for the Tier 2b and Tier 3 methods). Also, the equations for wet treatment processes do not

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include a heel factor (fraction of gas remaining in the shipping container in the methods for plasma-based processes). [Additional guidance will be provided in subsequent drafts for measuring site-specific emission factors, the fraction of gas abated, and the destruction removal efficiency (DRE) of the gases.]

TABLE 8.14 INFORMATION SOURCES NECESSARY FOR COMPLETING THE TIERED EMISSIONS ESTIMATING METHODS FOR WET TREATMENT OF TEXTILE, CARPET, LEATHER, AND PAPER [The information provided in this table is preliminary and is likely to evolve as the definition of the various methods is refined]					
Data		Tier 1	Tier 2		Tier 3
			2a	2b	
Consumption of liquid input chemicals	$FC_{i,}$ = consumption of input chemical i (kg)		Me/Mo		
	$FC_{i,p}$ = consumption of input chemical i for process p (kg) ^a			Me/Mo	Me/Mo
Formation of volatile by-products	$B_{k,i}$ = emission factor for volatile by-product k for input chemical i (fraction, kg of volatile by-product formed per kg of input chemical consumed)		D		
	$B_{k,i,p}$ = emission factor for volatile by-product k for input chemical i and process p (fraction, kg of volatile by-product formed per kg of input chemical consumed for process p)			D ^a	Me ^a
Downstream FC Emission Control	a_k = fraction of by-product k produced in processes with certified FC emission control technology		Me		
	$a_{k,p}$ = fraction of by-product k produced from processes p with certified FC emission control technology			Me ^a	Me ^a
	d_k = Destruction Removal Efficiency (DRE) for by-product k (%)		D/Me		
	$d_{k,p}$ = Destruction Removal Efficiency (DRE) for by-product k for process p (%)			D/Me ^a	D/Me ^a
	UT = Average uptime factor of all abatement systems connected to process tools		Me		
	UT _p = Average uptime factor of all abatement systems connected to process tools running process type p			Me ^a	Me ^a
Annual Production Capacity	EF _k = emission factor for volatile by-product k (kg of volatile by-product formed per m ² of substrate produced)	D			
	C _u = fraction of annual plant production capacity utilization	Me			
	C _d = annual manufacturing design capacity (m ² of substrate processed)	Me			

Me = measurement; Mo = model {modelling criteria TBD}; D = Use default factors from guidance.

^a {For the Tier 2b method 'p' is to be interpreted as a wet process type and/or a substrate type (see further discussion below)}. For the Tier 3 'p' is to be interpreted as a site-specific process.

TIER 1 METHOD FOR WET PROCESSES – DEFAULT

The Tier 1 method is the least accurate estimation method and should be used only in cases where site-specific data on the consumption of input chemicals are not available. The Tier 1 method, unlike the Tier 2 or Tier 3 methods, is designed to give an aggregated estimate of FC emissions although its methodology appears to produce by-product-specific emissions. Estimates are made simultaneously for all volatile by-products as listed in [Table 8.19] and can only be used if reported as a complete set.

The Tier 1 calculation relies on a fixed set of generic emissions factors and does not account for differences among process types, individual processes, or manufacturing tools. The members of the set differ depending on the surface area of textile, carpet, leather, or paper products being manufactured. Each member of a set, which is a gas-specific emission factor, expresses average emissions per unit of substrate area (textile, carpet, leather, paper) produced during manufacture. For any class of product, the factors (members of the set) are multiplied by the annual capacity utilization (C_u , a fraction) and the annual manufacturing design capacity (C_d , in square meters (m^2)) of substrate processes. The product ($C_u \cdot C_d$) is an estimate of the quantity of substrate produced during the manufacture of textile, carpet, leather, or paper. The result is a set of annual emissions expressed in kg of the volatile by-products that comprise the set for each class of products. The Tier 1 formula is shown in Equation 8.34.

EQUATION 8.34 TIER 1 METHOD FOR ESTIMATION OF THE SET OF FC EMISSIONS

$$\{FC_k\}_n = \{EF_k \cdot C_u \cdot C_d\}_n \quad (k = 1, \dots, n)$$

Where:

$\{FC_k\}_n$ = emissions of FC volatile by-product k (kg)

Note: $\{ \}_n$ denotes the set for each class of products (e.g. textile, carpet, leather, or paper) and n denotes the number of volatile by-products included in each set [See Table 8.19]. The estimates are only valid if made and reported for all members of the set using this Tier 1 methodology.

EF_k = FC emission factor for volatile by-product k expressed as annual mass of emissions per square meters of substrate surface area for the product class, (mass of volatile by-product k emitted, in kg/m^2).

C_u = fraction of annual plant production capacity utilization, fraction.

C_d = annual manufacturing design capacity, m^2 of substrate processed.

In using Tier 1, inventory compilers should not modify, in any way, the set of FCs k assumed in [Table 8.19]. Inventory compilers should not combine emissions estimated using Tier 1 method with emissions estimated using the Tier 2 or 3 methods.

TIER 2a METHOD FOR WET TREATMENT PROCESSES – PROCESS CHEMICAL-SPECIFIC PARAMETERS

The Tier 2a method uses industry-wide default values for the mass fraction of volatile by-product k formed from the use of liquid input chemical i ($B_{k,i}$) and the fraction of FCs by-products k destroyed by the emissions control technology (d_k) [see Table 8.21]. The Tier 2a method also calculates emissions for each input chemical used on the basis of site-specific data on chemicals consumption and emissions control technologies. Thus, to use the Tier 2a method, inventory compilers must have direct communication with industry (e.g., annual emissions reporting) to gather consumption data and ensure that emission control technologies are installed and used in accordance with the guidelines provided in this document.

Unlike the Tier 2b and Tier 3 methods that are explained later in this section, the Tier 2a method does not distinguish between process or substrate types, or site-specific processes. However, the Tier 2a default emission factors are formed separately for each input chemical, which, unlike the Tier 1 method, allows to account for the actual mix of input chemicals used at a particular site.

Total Tier 2a emissions are equal to the sum of emissions from all volatile by-products k (BPE_k) resulting from the conversion of all input chemicals used during production, as calculated using equations 8.35 below.

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EQUATION 8.35
TIER 2A ESTIMATION OF BY-PRODUCT EMISSIONS

$$\text{BPE}_k = \sum \text{B}_{k,i} * \text{FC}_i * (1 - \text{D}_k)$$

Where:

BPE_k = emissions of by-product k generated from the conversion of all input chemicals i , kg.

$\text{B}_{k,i}$ = emission factor, kg of volatile by-product k created per kg of input chemical i consumed.

FC_i = consumption of input chemical i , kg.

D_k = overall reduction of by-product k emissions, fraction, calculated per equation 8.36.

EQUATION 8.36
EMISSIONS REDUCTION IMPACT OF EMISSIONS CONTROL TECHNOLOGY

$$\text{D}_k = \text{a}_k * \text{d}_k * \text{UT}$$

Where:

D_k = overall reduction of volatile by-product k emissions, fraction.

a_k = fraction of by-product k produced from processes with emission control technologies (site-specific), fraction.

d_k = Destruction Removal Efficiency (DRE) for by-product k , fraction.

UT = average uptime of all abatement systems, fraction, calculated per Equation 8.37.

EQUATION 8.37
UPTIME OF EMISSION CONTROL SYSTEM

$$\text{UT} = 1 - \frac{\sum_n \text{Td}_n}{\sum_n \text{UT}_n}$$

Where:

UT = average uptime factor of all abatement systems connected to process tools, fraction.

Td_n = The total time, in minutes, that abatement system n connected to process tool(s) in the plant, is not in operational mode when at least one of the manufacturing tools connected to abatement system n is in operation.

UT_n = total time, in minutes per year, in which abatement system n has at least one associated manufacturing tool in operation. For determining the amount of tool operating time, you may assume that tools that were installed for the whole of the year were operated for 525,600 minutes per year. For tools that were installed or uninstalled during the year, you should prorate the operating time to account for the days in which the tool was not installed; treat any partial day that a tool was installed as a full day (1,440 minutes) of tool operation. For an abatement system that has more than one connected tool, the tool operating time is 525,600 minutes per year if at least one tool was installed at all times throughout the year. If you have tools that are idle with no gas flow through the tool for part of the year, you may calculate total tool time using the actual time that gas is flowing through the tool. *Nota bene:* UT may be set to 1 if suitable backup abatement or interlocking with the process tool is implemented for each abatement system.

n = abatement system.

TIER 2b METHOD FOR WET PROCESSES – PROCESS / SUBSTRATE SPECIFIC PARAMETERS

The Tier 2b method is similar to the Tier 2a approach in the sense that it is based on chemical-specific default emission factors, but the Tier 2b factors also account for the types of wet processes ‘*p*’ used in manufacturing. Thus, the Tier 2b approach is expected to be more accurate than the Tier 2a one because the Tier 2b method reflects the mix of processes and/or substrates used in a particular manufacturing facility. Also, the Tier 2b method allows to account for the trend where some chemicals tend to be used predominantly in particular process types and class of products manufactured (textile, carpet, leather, paper). The Tier 2b method uses industry-wide default values for the mass fraction of volatile by-product *k* formed from the use of liquid input chemical *i* in process type or for substrate type *p* ($B_{k,i,o}$) and the fraction of FCs by-products *k* destroyed by the emissions control technology connected to tools using process type or substrate type *p* ($d_{k,p}$) [see Table 8.22 and Table 8.23]

[At the time of writing of this first order draft, the authors propose two approaches for deriving the Tier 2b emission factors and defining ‘*p*’. A first approach would be to provide separate Tier 2b emission factors depending on the actual wet treatment method used in production. In this case, default EFs would be provided for process types such as 1) wet finishing (e.g. pad-dry-cure and exhaust applications), 2) low wet pickup finish applications (e.g. vacuum extraction and kiss roll), 3) spray application, 4) foam finishing, 5) coating, and 6) lamination. Another approach would be to provide separate Tier 2b emission factors based on the type of substrate produced. In this case, default EFs would be provided for substrate types such as 1) cellulosic, cellulosic blends and cellulose regenerated (cotton, viscose, rayon, etc.), 2) synthetic polymers for textile (polyamides, polyesters, polypropylenes, polyurethane), 3) lignocellulosic (flax, jute, sisal, etc.) 4) protein-based textiles (wool, silk), 5) leather, 6) paper and paperboard, and 7) technical textile polymers. The information currently available to the authors is insufficient to determine which of the two approaches above (or a combination thereof) might be most suitable, or if separate methods should be provided to distinguish EFs by process type (a separate Tier 2b method) and by substrate (an additional Tier 2c method). Further discussion is required on this point, and an analysis of how emission factors may be grouped based on different treatment process conditions (temperature, timing, type of chemicals used, etc.) should be conducted. Nevertheless, the Tier 2b methodological framework proposed here could be adapted to the (to be determined) best approach.]

Although the Tier 2b method would be preferred over the Tier 2a method because process-type-specific or substrate-type-specific emission factors will be more accurate, it should be noted that the Tier 2b method presents increased complexity because the consumption of input chemicals must be allocated to each process type *p*. Thus, in the case where the consumption of input chemicals cannot directly be measured for each process *p*, a chemical consumption allocation model must be devised for applying the method {guidance will be provided to model the allocation of chemical consumption}, and inventory compilers should consider the trade-off of using more accurate process-specific emission factors versus introducing errors in the Tier 2b estimate, due to uncertainties in the allocation model.

Total Tier 2b emissions are equal to the sum of emissions from all volatile by-products *k* resulting from the conversion of all input chemicals used during all production processes *p* (BPE_k), as calculated using equations 8.38 below.

EQUATION 8.38
TIER 2B ESTIMATION OF BY-PRODUCT EMISSIONS

$$BPE_k = \sum_{i,p} B_{k,i,p} \cdot FC_{i,p} \cdot (1 - D_{k,p})$$

Where:

BPE_k = emissions of volatile by-product *k* generated from the conversion of all input chemicals *i* used for all process types *p*, kg.

$B_{k,i,p}$ = emission factor, kg of volatile by-product *k* created per kg of input chemical *i* used for process *p*.

$FC_{i,p}$ = consumption of input chemical *i* for process type *p*, kg.

$D_{k,p}$ = overall reduction of volatile by-product *k* emissions from tools using process type *p*, fraction, calculated per equation 8.39.

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EQUATION 8.39
EMISSIONS REDUCTION IMPACT OF EMISSIONS CONTROL TECHNOLOGY

$$D_{k,p} = a_{k,p} * d_{k,p} * UT_p$$

Where:

$D_{k,p}$ = overall reduction of volatile by-product k emissions produced from process type p , fraction.

$a_{k,p}$ = fraction of by-product k volume produced from process type p with emission control technologies (site-specific), fraction.

$d_{i,p}$ = Destruction Removal Efficiency (DRE) for by-product k and process type p , fraction.

UT_p = average uptime of all abatement systems connected to tools using process type p , fraction, calculated per Equation 8.40.

EQUATION 8.40
UPTIME OF EMISSION CONTROL SYSTEMS

$$UT_p = 1 - \frac{\sum_n Td_{n,p}}{\sum_n UT_{n,p}}$$

Where:

UT_p = average uptime factor of all abatement systems connected to process tools running process type p , fraction.

$Td_{n,p}$ = The total time, in minutes, that abatement system n connected to process tool(s) running process type p in the plant, is not in operational mode when at least one of the manufacturing tools connected to abatement system n is in operation.

$UT_{n,p}$ = total time, in minutes per year, in which abatement system n has at least one associated manufacturing tool running process type p in operation. For determining the amount of tool operating time, you may assume that tools that were installed for the whole of the year were operated for 525,600 minutes per year. For tools that were installed or uninstalled during the year, you should prorate the operating time to account for the days in which the tool was not installed; treat any partial day that a tool was installed as a full day (1,440 minutes) of tool operation. For an abatement system that has more than one connected tool, the tool operating time is 525,600 minutes per year if at least one tool was installed at all times throughout the year. If you have tools that are idle with no gas flow through the tool for part of the year, you may calculate total tool time using the actual time that gas is flowing through the tool. *Nota bene*: UT may be set to 1 if suitable backup abatement or interlocking with the process tool is implemented for each abatement system.

n = abatement system.

TIER 3 METHOD FOR WET PROCESSES – SITE-SPECIFIC PARAMETERS

[Note: most of the discussion for the Tier 3 method for wet processes is the same as for the Tier 3 method for plasma processes and could be consolidated into a single section; this will be considered for the subsequent draft.]

The Tier 3 method for wet processes uses the same set of equations as the Tier 2b method for wet processes. However, the Tier 3 method can use site-specific values for the parameters used in equations 8.14 to 8.16. Notably, ‘ p ’ in these equations can represent a site-specific process, having a more refined definition than the process types and/or substrate types defined in the Tier 2b method. In the Tier 3 method, a process p can be defined as a centreline process (or a small set of centreline processes) for which site-specific emission factors have been measured. For example, a site-specific centreline process could be defined as a process to treat carpet with application of a specific fluorochemical product by the spray method, or a process to treat textile for water and oil repellency using a specific fluoropolymer and the pad-dry-cure method. Centreline conditions refer to specific process conditions for which a manufacturer may have tuned a process for achieving a particular result, or specific process conditions (i.e. a ‘recipe’) that may have been provided by a tool manufacturer who standardized its equipment for sale.

It is very important to note that emission factors can be strongly affected by changes in process conditions (e.g. temperature, flows and nature of input chemicals, processing time, etc.), and that emission factors for a recipe tuned

for a particular purpose or product can differ from those of the centreline process recipe that may have been used for measuring emission factors. Further, emission factors are affected by the design of the processing tools and can substantially fluctuate from one tool manufacturer to another, even when the process function is similar. Thus, compilers using the Tier 3 method should bear in mind that using a single emission factor for multiple distinct processes p (i.e. using a single emission factor for a small set of processes p) should only be done when the processes are similar. [A definition of ‘similarity’ will be developed based on the principle that a single emission factor could be used for multiple similar processes so long as the emission factors does not change by more than +/- [XX]%. For example, ‘similarity’ would require that the input chemicals are the same, and that the process temperature or flows of input chemicals do not vary by more than a certain percentage point].

The Tier 3 method should be used by manufacturing plants whose processes depart significantly from industry-wide patterns of usage, or by manufacturing plants that may have developed a particular process whose characteristics may result in a significantly lower or higher utilization of input chemicals. Further, if default Tier 1 or Tier 2 emission factors are not available for a particular process or input chemical, manufacturing facilities should measure their site-specific emission factors and use the Tier 3 method.

It should also be noted that the Tier 3 method may be combined with the Tier 2a or 2b method. Indeed, higher accuracy might be achieved by using the Tier 3 method for a specific input chemicals and site-specific processes, and these estimates may be combined with estimates based on Tier 2a or 2b default emission factors for other input chemicals and processes instead of using only the Tier 2a or 2b methods. However, reporters should not combine the Tier 1 method with any other method.

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8.5.3 Choice of emission factors

[work in progress – see discussion above]

8.5.3.1 PLASMA TREATMENT PROCESS

TABLE 8.15 LIST OF MOST IMPORTANT INPUT CHEMICALS USED IN PLASMA TREATMENT OF TEXTILES	
Atmospheric plasma	Low pressure plasma
Monomer	Monomer
C ₁₁ H ₇ F ₁₃ O ₂	CF ₄
C ₁₃ H ₇ F ₁₇ O ₂ /C ₁₅ H ₇ F ₂₁ O ₂	C ₂ F ₄
Unidyne TG-571®	C ₃ F ₆
CF ₄	C ₂ F ₆
CF ₃ CHF ₂	C ₃ F ₈
CHF ₃	C ₄ F ₁₀
C ₃ F ₆	C ₆ F ₁₄
C ₂ F ₆	C ₄ F ₈
C ₈ F ₁₇ CH ₂ CH ₂ OCOCH=CH ₂	CF ₃ CHF ₂
Dynasylan F 8815® (H ₂ O)	SF ₆
C ₃ F ₈	CF ₃ SO ₃ H (co-monomer)
C ₁₃ H ₇ F ₁₇ O ₂	C ₂ ClF ₃ (co-monomer)
SF ₆	C ₆ F ₆ (co-monomer)
H ₂ C=CHCO ₂ CH ₂ CH ₂ (CF ₂) ₇ CF ₃	HC ₆ F ₅ (co-monomer)
C ₆ H ₁₃ F ₃ O ₃ Si (FAS-3)	CF ₃ (CF ₂) ₇ CH=CH ₂
C ₆ F ₅ Si(OC ₂ H ₅) ₃ (FAS-5)	
C ₁₃ H ₁₃ F ₁₇ O ₃ Si (FAS-17)	
Sources: http://www.sciencedirect.com/science/article/pii/S0257897213002910 http://journals.sagepub.com/doi/abs/10.1177/0040517517698988 http://file.scirp.org/pdf/JSEMAT_2015060115003244.pdf http://www.sciencedirect.com/science/article/pii/S0584854705002843 http://onlinelibrary.wiley.com/doi/10.1002/ppap.201400052/full https://arxiv.org/abs/0801.3727 http://www.sciencedirect.com/science/article/pii/S0257897207012704 https://link.springer.com/article/10.1007/s11090-012-9413-9	

TIER 1

[Table 8.16 – Tier 1 emission factors for FC emissions from textile, leather, and paper plasma treatment processes]

TIER 2A

[Table 8.17 – Tier 2a emission factors for FC emissions from textile, leather, and paper plasma treatment processes]

TIER 2B

[Table 8.18 – Tier 2b emission factors for FC emissions from textile, leather, and paper plasma treatment processes]

TIER 3

[work in progress – see discussion above]

8.5.3.2 WET TREATMENT PROCESS

TABLE 8.19 LIST OF MOST IMPORTANT INPUT CHEMICALS USED IN WET TREATMENT PROCESS, AND THEIR VAPOUR PRESSURE	
Chemical name	Vapor pressure (mm Hg @ 25°C)
Tetrafluoroethylene	24500
Chlorotrifluoroethylene	4590
Vinylidene fluoride	30000
Vinyl fluoride	19800
Hexafluoropropene	27 (20°C)
Perfluoromethylvinyl ether	765
Perfluoropropylvinylether	534
Perfluorooctane sulfonic acid (PFOS)	0.002
Perfluorobutane sulfonic acid (PFBS)	0.027
n-methyl perfluorobutane sulfonamidoethanol (Me-FBSE)	0.05
perfluorohexanoic acid (PFHxA)	0.52
3-(Perfluorobutyl)propanol (PFBP)	0.7
Ethyl perfluorooctanoate (EPFO)	0.97-1
Perfluoro-3,6-dioxahexanoic acid (PDHA)	1.06
Fluorotelomer alcohol 10:2 FTOH	1.1 - 0.001
PFOA isomer 2,2,3,4,4,5,6,6-nonafluoro- 3,5-bis(trifluoromethyl)-hexanoic acid	1.26
PFOA isomer 2,2,3,3,5,5,6,6-nonafluoro- 4,4-bis(trifluoromethyl)-hexanoic acid	1.37
Perfluorooctane sulfonyl fluoride (POSF)	1.66 (20°)
Fluorotelomer alcohol 8:2 FTOH	1.9 - 0.03
Perfluorohexanoic acid (PFHxA)	1.98
Heptafluorobutyric acid - C ₄ HF ₇ O (PFBA)	10
Perfluorobutanoic acid (PFBA)	10 (20°C)
Fluorotelomer alcohol 4:2 FTOH	12.5 - 1.6
1,1,2,2-Tetrafluoroethyl methyl ether	1280
Perfluorobutyl iodide	158
PFOA isomer 2,2,3,3,4,4,6,6-nonafluoro- 5,5-bis(trifluoromethyl)-hexanoic acid	2.04
PFOA isomer 2,3,3,4,4,5,5,6,6- decafluoro-2-(1,1,2,2,2-pentafluoroethyl)-hexanoic acid	2.04
Polyfluorinated fluorotelomer iodides (6:2 FTI)	2.9

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TABLE 8.19 (CONT.) LIST OF MOST IMPORTANT INPUT CHEMICALS USED IN WET TREATMENT PROCESS, AND THEIR VAPOUR PRESSURE	
Chemical name	Vapor pressure (mm Hg @ 25°C)
C6F14	232
C5F11NO	274
C8F18	29
(perfluorooctyl)ethylene (PFOE)	3.6
(Perfluorohexyl)ethylene	43.8
1H,1H,2H-Perfluoro-1-decene	6.36
Fluorotelomer alcohol 6:2 FTOH	6.6 - 0.1
C5F12	610
C7F16	79
Note: Please note that even though most of the PFOS and PFOA compounds have very low vapor pressure at 25 °C, they are cured during applications at temperatures of between 150 and 180 °C Sources: DOI: 10.1021/je400205g http://eu.wiley.com/WileyCDA/WileyTitle/productCd-1405169303.html http://pubs.acs.org/doi/abs/10.1021/es4018128 http://www.miljodirektoratet.no/old/klif/publikasjoner/2944/ta2944.pdf https://kitairu.net/ru/chemicals/basic-chemicals https://pubchem.ncbi.nlm.nih.gov	

TIER 1

[Table 8.20 – Tier 1 emission factors for FC emissions from wet treatment processes for textile, carpet, leather, and paper]

TIER 2A

[Table 8.21 – Tier 2a emission factors for FC emissions from wet treatment processes for textile, carpet, leather, and paper]

TIER 2B

[Table 8.22 – Tier 2b emission factors for FC emissions from wet treatment processes for textile, carpet, leather, and paper]

TIER 3

[work in progress – see discussion above]

8.5.3.3 EMISSION CONTROL FACTORS

[Table 8.23 – Default efficiency parameters for emission reduction technologies]

8.5.4 Choice of activity data

[work in progress]

8.5.5 Completeness

[work in progress]

8.5.6 Developing a consistent time series

[work in progress]

8.5.7 Uncertainty assessment

[work in progress]

8.5.7.1 EMISSION FACTOR UNCERTAINTIES

[work in progress]

[Table 8.24 – Default estimates of relative errors (%) for emission factors, 95% confidence intervals]

8.5.7.2 ACTIVITY DATA UNCERTAINTY

[work in progress]

8.5.8 Quality assurance / quality control (QA/QC), reporting and documentation

[work in progress]

8.5.8.1 QUALITY ASSURANCE / QUALITY CONTROL (QA/QC)

[work in progress]

8.5.9 Reporting and documentation

[work in progress]

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1245 [see Section 8.5]