

Appendix 1 (new) Possible Approaches for Estimating Fluorinated Compounds Emissions from Textile, Carpet, Leather and Paper Industries: Basis for Future Methodological Development

1a.1 Introduction

Fluorine-based treatment of textiles for waterproofing was introduced in the 1950s (Davies 2014). The first microporous membrane (polytetrafluoroethylene PTFE, also known as Teflon™) was created in 1969 and the first GORE-TEX™ materials appeared on the market in 1976 (Williams 2018). Since then, fluorochemical finishes have been widely used to functionalize fibres for water or oil repellence, soil and stain release, improving textile breathability, softening, dyeing ability, increasing mechanical strength, providing antibacterial and anti-odour finishes, and for fabricating wrinkle-free materials (Choudhury 2017). Such applications are widespread for the production of home textiles, upholstery furniture, protective clothing with signal colour, tent canvas, outdoor wear, medical textiles and work wear such as uniforms and shoes (Lacasse & Baumann 2004; Schindler & Hauser 2004; Singha 2012; Gulrajani 2013; Roshan 2014).

The conventional processes used for increasing the water repellence of fibres use perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSA), commonly referred to as 'C8' chemistry because the precursor molecules contain 8 carbon atoms. Such processes can lead to the formation of Perfluoroalkylated acid through oxidation, 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. As a result, the use of C8 fluorinated polymers in textiles, carpet, leather, and paper has been restricted in some regions, and the industry is moving towards shorter chained chemistry (from 'C8' to 'C6' and 'C4'). However, the C6 and C4 chemistries have been reported to perform more poorly than the conventional C8 chemistry (Davies 2014), and the C8 chemistry continues to be widely used in regions with large textile production capacities, particularly in developing countries (Fantke et al. 2015). Due to the lower performance of the shorter chained chemistry, alternate methods are being sought for the treatment of textile, carpet, leather and paper. In particular, plasma-based processes have shown promising performance (Davies 2014).

Fluorine-based plasma 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, in part due to the fact that plasma technologies provide excellent performance and that plasma processes can be tailored to achieve many desirable properties. 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. Several innovative treatment technologies and chemistries are now transitioning to industrial scale use, particularly plasma processing of textiles using gaseous fluorinated compounds (FC) such as CF₄, C₂F₆, C₃F₈, C₄F₈, C₅F₁₀, CHF₃, and SF₆ (Yip et al. 2002; Hochart et al. 2003; Raffaele-Addamo et al. 2003; Davis et al. 2011; Kwong et al. 2013; Ramamoorthy et al. 2013; Davies 2014; Zille et al. 2015; Saxena et al. 2017).

As in the case of the electronics sector, plasma-based processes using fluorinated compounds in the textile industry are expected to result in emissions of unreacted fluorinated compounds and by-products with high global warming potentials (GWPs). However, the extent to which plasma processes have been introduced in volume manufacturing is not clear. 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 (IPPC 2003; OECD 2004). A list of the most important fluorinated compounds used for plasma-based treatment processes is provided in Table 1A.1, 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 1A.2. While the magnitude of FC emissions from the textile industry as compared to other sources of fluorinated greenhouse gases (GHGs) is presently unknown, it is clear that the textile industry contributes to some degree to the total amount of fluorinated substances found in the environment (KEMI 2014).

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 emissions from such processes (EPA 1997; Schönberger & Schäfer 2003; MoEU 2012; DEPA 2013; UNIDO et al. 2017). Only one reference about emissions of hydro-fluorocarbons related to the textile industry in the United Kingdom has been found in the literature (Ricardo-AEA 2015). As a consequence,

the authors were not able – at the time of writing of this second 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 (i.e., product classes) treated and the sheer size and global nature of the industry.

1A.1.1 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 3,500 °C to 2,000 °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 textiles and polymers cannot withstand the high temperatures used in thermal plasmas, most applications for organic fibres' surface modification use cold plasmas. 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 (Sigurdsson & Shishoo 1997; Tenders et al. 2006; Morent et al. 2008; Sparavigna 2008; Jafari et al. 2013; Vietro et al. 2015; Zille et al. 2015; Gotoh et al. 2017).

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) (Saxena et al. 2017). 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 (Shishoo 2007; Muthu 2016).

Plasma processes used for the treatment of such materials can be divided into three process types: 1) plasma treatment, 2) plasma etching (or ablation), and 3) plasma polymerization (Roth 2001).

- 1) 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 (Tenders et al. 2006; Morent et al. 2008; Sparavigna 2008; Jafari et al. 2013; Yim et al. 2013; Vietro et al. 2015; Zille et al. 2015; Gotoh et al. 2017). Plasma treatments can be further separated into two processes sub-types: a) when 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); or b) when the fabric is first immersed in a fluid of hydrophobic fluorinated pre-polymer with added initiators followed by a plasma treatment leading to the grafting of the pre-polymer on the surface of the fabric.
- 2) Plasma etching is a process type where the substrate is bombarded with ions from the plasma. Three process sub-types may be defined within the etching process type, depending on whether plasma is used to a) clean, b) sterilize, or c) 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 (Sigurdsson & Shishoo 1997).
- 3) Plasma polymerization is a process type where a monomer in vapour phase such as CF₄, C₂F₆, C₃F₈, or larger fluorinated molecules such as fluorodecylacrylate is converted into reactive fragments to deposit a thin film onto the substrate. Plasma polymerization can be further separated into two process sub-types: a) plasma-induced polymerization is when the polymerization process is a surface-based reaction and, b) plasma-state polymerization is when fragments react in the gas phase to form larger molecules that are then deposited on the substrate (Morent et al. 2008).

For all process types and sub-types, it is highly improbable that all input chemicals are fully consumed in the process (IPCC 2006). Further, the plasma decomposition of input chemicals such as C₂F₆, C₃F₈, and larger chain fluorinated molecules is likely to result in the production of byproducts such as CF₄, C₂F₆, CHF₃ and other gases (Id.). Therefore, plasma-based fluorinated treatment of textile, carpet, leather, or paper is expected to lead to emissions of FC greenhouse gases. It should be noted that the potential for plasma-based polymerization processes to emit large amounts of FCs is likely lower than for the plasma treatment and plasma etching process types because, in the case of

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polymerization, the input FC chemicals are meant to react and form solid byproducts on the substrate as opposed to just treat or etch its surface. However, it should also be mentioned that plasma-based polymerization 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 Second Order Draft of the Guidelines, and comments are sought on this particular issue.

1A.1.2 WET TREATMENT PROCESSES

Wet treatment processes include several applications techniques but about 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 (Roshan 2014). Other techniques include vacuum extraction, spray applications, foam finishing, coating, and lamination.

Side-chain fluorinated polymers primarily based on fluorotelomer acrylates, fluorotelomer methacrylates or perfluoroalkane sulfonamidoethanols characterize the chemical structure of the fluorine-based surfactants and polymers used for the above-described applications. Unfortunately, the environmental and health characteristics of the new short-chain chemistry and associated processes are poorly described in the 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 (IPPC 2003; Ellis et al. 2004; OECD 2004; Dumoulin et al. 2005; Prevedouros et al. 2006; Barber et al. 2007; Jahnke et al. 2007; FOEN 2009; Young 2010; DEPA 2015; UNEP 2017). 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 (Heydebreck et al. 2016). 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 (European Commission 2003). 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 (Williams 2018). 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 when using fluorochemical deposition, but on the contrary no curing is required for some type of solvent soluble fluorinated soil release finishing agents for garments, upholstery and carpets (Goswami 2017). However, the latter kind of treatments has lower durability than water-based fluorochemicals because of the lack of fixation by crosslinking (Schindler & Hauser 2004). Generally, the higher the curing temperature, the shorter is the curing time in order to avoid 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 (Wang et al. 2017).

TABLE 1A.1
LIST OF MOST IMPORTANT INPUT CHEMICAL MONOMERS USED IN PLASMA TREATMENT OF TEXTILES

ATMOSPHERIC PLASMA ¹	LOW PRESSURE PLASMA ²
C ₁₁ H ₇ F ₁₃ O ₂	CF ₄ (PFC-14)
C ₁₃ H ₇ F ₁₇ O ₂ /C ₁₅ H ₇ F ₂₁ O ₂	C ₂ F ₄ (PFC-1114)
Unidyne TG-571 [®]	C ₃ F ₆ (Perfluorocyclopropane)
CF ₄ (PFC-14)	C ₂ F ₆ (PFC-116)
CHF ₂ CF ₃ (HFC-125)	C ₃ F ₈ (PFC-218)
CHF ₃ (HFC-23)	C ₄ F ₁₀ (PFC-31-10)
C ₃ F ₆ (Perfluorocyclopropane)	C ₆ F ₁₄ (PFC-51-14)
C ₂ F ₆ (PFC-116)	C ₄ F ₈ (PFC-318)
C ₈ F ₁₇ CH ₂ CH ₂ OCOCH=CH ₂	CHF ₂ CF ₃ (HFC-125)
C ₃ F ₈ (PFC-218)	SF ₆ (Sulfur hexafluoride)
C ₁₃ H ₇ F ₁₇ O ₂	CF ₃ SO ₃ H (co-monomer)
SF ₆ (Sulfur hexafluoride)	C ₂ ClF ₃ (co-monomer)
H ₂ C=CHCO ₂ CH ₂ CH ₂ (CF ₂) ₇ CF ₃	C ₆ F ₆ (co-monomer)
C ₆ H ₁₃ F ₃ O ₃ Si (FAS-3)	HC ₆ F ₅ (co-monomer)
C ₆ F ₅ Si(OC ₂ H ₅) ₃ (FAS-5)	CF ₃ (CF ₂) ₇ CH=CH ₂
C ₁₃ H ₁₃ F ₁₇ O ₃ Si (FAS-17)	1,1,2,2, tetrahydroperfluorodecyl acrylate (AC8)
<p>Note: Despite the fact that some chemicals have been defined using their common names, most of the listed chemicals represent chemical families, co-monomers or commercial products. Please refer to the IUPAC name for the other chemicals.</p> <p>Sources: ¹Yim et al. 2013; Gotoh et al. 2017; Tenders et al. 2006; Zille et al. 2015; Sparavigna 2008; Morent et al. 2008 ²Vietro et al. 2015; Zille et al. 2015; Sparavigna 2008; Morent et al. 2008; Jafari et al. 2013; Hochart et al. 2003; Hegemann 2006</p>	

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TABLE 1A.2 LIST OF MOST IMPORTANT INPUT CHEMICALS USED IN WET TREATMENT PROCESS, AND THEIR VAPOUR PRESSURE	
CHEMICAL NAME	VAPOUR PRESSURE (MM HG @ 25°C) ¹
Tetrafluoroethylene	24500
Chlorotrifluoroethylene	4590
Vinylidene fluoride	30000
Vinyl fluoride	19800
Hexafluoropropene	4900
Perfluoromethylvinyl ether	765
Perfluoropropylvinyl ether	534
Perfluorooctane sulfonic acid (PFOS)	0.002
Perfluorobutane sulfonic acid (PFBS)	0.027
n-methyl perfluorobutane sulfonamidoethanol (Me-FBSE)	0.05
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 isomers	1.26 - 2.04
Perfluorooctane sulfonyl fluoride (POSF)	5.75
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
Polyfluorinated fluorotelomer iodides (6:2 FTI)	2.9
C ₆ F ₁₄ (PFC-51-14)	232
C ₅ F ₁₁ NO	274
C ₈ F ₁₈	29
(perfluorooctyl)ethylene (PFOE) ¹	3.6
(Perfluorohexyl)ethylene	43.8
1H,1H,2H-Perfluoro-1-decene	6.36
Fluorotelomer alcohol 6:2 FTOH	6.6 - 0.1
C ₅ F ₁₂ (PFC-41-12)	610
C ₇ F ₁₆	79
Notes: - Please note that even though most of the PFOS and PFOA compounds have very low vapour pressure at 25 °C, they are cured during applications at temperatures of between 150 and 180 °C. - Despite the fact that some chemicals have been defined using their common names most of the listed chemicals represent chemical families. Please refer to the IUPAC name for the other chemicals. Sources: ¹ Schindler et al. 2013; National Institutes of Health; Nielsen 2012; Ruan et al. 2013; Harrad 2001	

1a.2 Methodological issues

1A.2.1 CHOICE OF METHOD

The choice of method will eventually depend on the availability of measured emission factors from which default factors might be derived. The bibliographic research conducted as of the date of this Second Order Draft does not indicate that representative FC emissions data can be obtained from the textile, carpet, leather, or paper industries to derive default emission factors for Tier 1 or Tier 2 methods. Nevertheless, the authors propose herewith a four-tiered methodological framework (Tier 1, Tier 2a, Tier 2b, and Tier 3) to account for emissions from this sector. At this point, because no Tier 1 or Tier 2 default factors are available, only the Tier 3 method is practicable, using equipment-specific, process-specific, or site-specific measured emission factors. Distinct methods are provided for plasma-based processes and for wet-based processes. This Appendix provides a basis for future methodological development rather than complete guidance.

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 FC 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 FC emitted per mass of FC 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) and/or class of products manufactured (textiles, leather, paper, etc.), while the Tier 2a method does not. A Tier 3 method would use the same equations as the Tier 2b method, but would use measured emission factors (equipment-specific, process-specific, substrate-specific, or site-specific) instead of default emission factors.

For wet-based processes, a Tier 1 approach is proposed as a framework to estimate FC emissions based on the mass of substrate treated, a method, which would therefore not require data on the consumption of input chemicals. Two Tier 2 methods (Tier 2a and 2b) are also proposed as frameworks to report emissions 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 processes is that the Tier 2b method would distinguish emission factors by process and/or substrate type (class of products) (see further discussion below), while the Tier 2a method would not. Finally, a Tier 3 method applicable to wet processes would use the same equations as the Tier 2b method, but would use measured emission factors (equipment-specific, process-specific, or site-specific) instead of default emission factors.

Generally, the higher tiered methods will be more accurate than the lowered tiered ones, and using equipment-specific, process-specific, or 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 the consumption of input chemicals, and in reporting the abatement efficiency and the uptime of emissions control systems. With respect to uncertainty, the confidence level of a particular emissions estimate will likely be principally driven by the uncertainty of the default emission factors.

1A.2.1.1 PLASMA TREATMENT PROCESSES

Table 1A.3 depicts the information sources necessary for completing the tiered methods for estimating emissions from plasma treatment processes. This information is preliminary and likely to evolve as the definitions of the various methods are refined. At the time of writing of this Second Order Draft, no information about emission factors could be obtained for plasma treatments from the textile, carpet, leather, or paper industries to derive default emission factors for the Tier 1, Tier 2a, or Tier 2b methods. Thus, currently, the only practicable means to estimate emissions from this sector is the use of the Tier 3 method. Nevertheless, when a statistically-significant number of representative experimental emission factors becomes available, preliminary recommendations are provided for estimating default emission factors and for choosing the most appropriate Tier 1, Tier 2a, or Tier 2b methods.

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. With respect to accounting for emissions control technologies, the approach provided here is analogous to the method provided for the electronics industry. For more information, please refer to Chapter 6 “Electronic Industry Emissions”.

While continuous (in-situ) emissions monitoring may be technically feasible, it is unclear whether such an approach could be an economically viable method to estimate emissions from the textile, carpet, leather, or paper industry. One alternate approach would be to measure emission factors during the development of new plasma processes when parameters such as input gas flows, chamber pressure, processing time, plasma power, etc. are adjusted for particular treatment needs or for manufacturing a particular product. Please see Box 1A.1 for guidance on the analytical methods that can be used for measuring emission factors.

Another approach would be for facilities to periodically (for short periods of time) install equipment to measure emissions from their stacks for purposes of developing facility-specific emission factors to estimate emissions over the long term (see, e.g., the Tier 3b method developed for Chapter 6 “Electronic Industry Emissions”). It is very important to note that emission factors (i.e. input gas utilization efficiencies and by-product formation rates) can be strongly affected by changes in process variables (e.g. type of textile substrate material, pressure, temperature, plasma power, FC gas flow, processing time, etc.) and by the design of the process reactors. Thus, emission factors can substantially fluctuate from one tool manufacturer to another and for a recipe ‘tuned’ for a particular purpose or product.

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TABLE 1A.3 INFORMATION SOURCES NECESSARY FOR COMPLETING THE TIERED EMISSIONS ESTIMATING METHODS FOR PLASMA TREATMENT OF TEXTILE, LEATHER, AND PAPER					
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. As envisioned, Tier 1 estimates would be made simultaneously for all (or for the most important) gases listed in Table 1A.1 and could only be used if reported as a complete set.

As proposed, 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. However, the members of the set would likely 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, would express average emissions per unit of substrate area (textile, carpet, leather, paper) produced during manufacture.

In using Tier 1, inventory compilers should not modify, in any way, the set of FCs assumed to represent average emissions. Further, as is common practice for IPCC methods, the Tier 1 method does not allow accounting for the use of emissions control technologies, and 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 CF₄ to estimate the emissions of CF₄ from textiles etching and combine it with the results of other FC gases from a Tier 2 or Tier 3 method. The formula used to calculate Tier 1 emissions is shown in Equation 1A.1.

EQUATION 1A.1**TIER 1 METHOD FOR ESTIMATION OF 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. 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)/m²

C_u = fraction of annual plant production capacity utilization, fraction

C_d = annual manufacturing design capacity, m² of substrate processed

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), the fraction of input chemicals i converted into FC by-products k during the process ($B_{k,i}$), and the fraction of FC destroyed by the emissions control technology (D_i). 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.¹

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

¹ For an example of how site-specific heel factors can be developed, please see Volume 3, Chapter 6 (Electronics Industry Guidelines).

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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 manufacturing site.

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 1A.2, and 1A.3 below.

EQUATION 1A.2**TIER 2A ESTIMATION OF EMISSIONS OF UNREACTED INPUT CHEMICALS**

$$E_i = (1 - h_i) \cdot FC_i \cdot (1 - U_i) \cdot (1 - D_i)$$

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 1A.4.

EQUATION 1A.3**TIER 2A ESTIMATION OF BY-PRODUCT EMISSIONS**

$$BPE_k = \sum_i (1 - h_i) \cdot B_{k,i} \cdot FC_i \cdot (1 - D_k)$$

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 1A.4 (replacing i by k indexes).

EQUATION 1A.4**EMISSIONS REDUCTION IMPACT OF EMISSIONS CONTROL TECHNOLOGY**

$$D_i = a_i \cdot d_i \cdot UT$$

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 1A.5

EQUATION 1A.5
UPTIME OF EMISSION CONTROL SYSTEM

$$UT = 1 - \frac{\sum_n Td_n}{\sum_n UT_n}$$

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. UT may be set to 1 if suitable backup abatement or interlocking with the process tool is implemented for each abatement system.²

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 and/or class of products (i.e. textile, carpet, leather, paper) used for production processes ' p '. 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 or classes of products 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. The Tier 2b method uses industry-wide default values for the fraction of input chemicals i used in plasma production 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 FC destroyed by the emissions control technology connected to tools using production process 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.³

Although the Tier 2b method is preferred over the Tier 2a method because process- or product-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 production process p . Thus, in the case where the consumption of input chemicals cannot directly be measured for each production process p , a gas consumption allocation model must be devised for applying the method,⁴ 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 1A.6, and 1A.7 below.

² 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.

³ For an example of how site-specific heel factors can be developed, please see Volume 3, Chapter 6 (Electronics Industry Guidelines).

⁴ For an example of how site-specific gas consumption allocation models can be developed, please see Volume 3, Chapter 6 (Electronics Industry Guidelines).

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EQUATION 1A.6**TIER 2B ESTIMATION OF EMISSIONS OF UNREACTED INPUT CHEMICALS**

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

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 production process p , kg. $U_{i,p}$ = use rate of input chemical i (fraction destroyed or transformed in production process p), fraction. $D_{i,p}$ = overall reduction of gas i emissions from tools using production process p , fraction, calculated per equation 1A.8.**EQUATION 1A.7****TIER 2B ESTIMATION OF BY-PRODUCT EMISSIONS**

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

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 production process p . $FC_{i,p}$ = consumption of input chemical i for production process p , kg. $D_{k,p}$ = overall reduction of gas k by-product emissions from tools using production process p , fraction, calculated per equation 1A.8 (replacing i by k indexes).**EQUATION 1A.8****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 production process p , fraction. $a_{i,p}$ = fraction of chemical i volume fed into production process p with emission control technologies (site-specific), fraction. $d_{i,p}$ = Destruction Removal Efficiency (DRE) for chemical i and production process p , fraction. UT_p = average uptime of all abatement systems connected to tools using production process p , fraction, calculated per Equation 1A.9.

EQUATION 1A.9
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 production process p , fraction.

$Td_{n,p}$ = The total time, in minutes, that abatement system n connected to process tool(s) running production process 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 production process p in operation. UT may be set to 1 if suitable backup abatement or interlocking with the process tool is implemented for each abatement system.⁵

n = abatement system.

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

The Tier 3 method uses the same set of equations (equations 1A.6 to 1A.9) as the Tier 2b method. However, when using the Tier 3 method, inventory compilers need to interpret ‘p’ in these equations as a specific production process using a specific ‘recipe’. A recipe corresponds to a particular combination of input gases under specific conditions of process duration, temperature, pressure, flow, plasma power, class or product, and other relevant process parameters adjusted to achieve a particular result (i.e. water or stain resistance, increased mechanical strength, etching medical polyamide, etc.) on a specific process reactor. 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 parameters (duration, temperature, pressure, flow, plasma power, reactor design, etc.).

When using the Tier 3 method, the (1-U) and BPE emission factors in Equations 1A.6 and 1A.7 should be measured for specific processes recipes. However, a centreline process recipe may be used to establish Tier 3 emission factors for sets of ‘similar’ recipes. Recipes can be deemed ‘similar’ when the centreline process can reasonably be deemed representative of facility-specific process conditions, of the potential variability of such process conditions around the centreline process during normal manufacturing operations, and when the process type (plasma treatment, plasma etching, and plasma polymerization), product, process tool, and input process gases are the same. When using the concept of ‘similarity’, inventory compilers should be able to reasonably demonstrate that emissions estimates are not biased (i.e. systematically over- or under-estimated) when using centreline process recipe(s) emission factors.

Once default Tier 2a or Tier 2b emission factors will be developed, the Tier 3 method should be used by manufacturing plants whose processes and recipes depart significantly from industry-wide patterns of use (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 or formation of byproducts. Further, if default 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 Tier 3 emission factors could be combined with Tier 2a or 2b default emission factors (once available) to use a hybrid method. A hybrid method would involve applying the Tier 2 defaults to processes and technologies that have not changed while applying Tier 3a, site-specific emission factors to processes and

⁵ 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.

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technologies that have changed. Indeed, higher accuracy might be achieved by using the Tier 3 method for specific input chemicals or site-specific processes. However, inventory compilers should not combine the Tier 1 method with any other method.

The Tier 3 method is not outlined further in this Appendix, but inventory compilers should refer to the Box 1A.1 on specific technologies for the measurement of FC emissions in order to develop facility- or country-specific emission factors as a resource for implementing the Tier 3 method. Also, measurement methods developed for the electronics industry could be used as a basis for measuring emission factors from plasma-based finishing processes in the textile, carpet, leather, and paper industries (Benaway et al. 2014).

BOX 1A.1**ANALYTICAL METHODS FOR MEASURING FC EMISSIONS**

Fourier transform infrared spectroscopy (FTIR) is the currently preferred option due to part per billion (ppb) sensitivity, portability, ability to enable near-real-time measurements, reprocess historical data, and provide multi-component analysis and resistance to magnetic fields. However, FTIRs are generally considered to be higher-cost systems, requiring significant upkeep during sampling campaigns. Depending on the absorptivity and concentration of the FC gases to be detected, FTIR gas cells with long path lengths (meters) might be required to reach suitable detection levels (Espinoza-Nava et al. 2016).

Gas chromatography followed by mass spectrometry (GC/MS) can provide a near real time measurement of FC, as well as several other gas sample components if desired. The instrument must be calibrated in place, prior to the start of FC monitoring. If GC/MS measurement is not possible on a continuous basis this technology allows for sample collection that can be transported to a laboratory for analysis, directly in sample bags or by desorbing components after time average sampling onto sorbent columns. Using samples in bags or metal canisters, detection limits of 0.05 ppmv and 0.04 ppmv for CF₄ and C₂F₆, respectively, can be achieved. Using the sorbent columns detection limits of 9 ppbv for CF₄ and 0.6 ppbv for C₂F₆ have been validated (EPA & IAI 2008). Detection limits can be improved with modification of desorption parameters if desired. Method Detection Limit (MDL) from 0.001 to 3.5 pg.m⁻³ were reported for indoor and outdoor determination of several volatile perfluorinated compounds with the use of high volume samples and efficient enrichment steps (Trojanowicz & Koc 2013).

1A.2.1.2 WET TREATMENT PROCESSES

Table 1A.4 depicts the information sources necessary for completing the tiered methods for estimating emissions from wet-based treatment of textiles, carpet, leather, and paper. This information is preliminary and likely to evolve, as the definitions of the various methods are refined. At the time of writing of this Second Order Draft, no information about emission factors could be obtained for wet-based treatments from the textile, carpet, leather, or paper industries to derive default emission factors for the Tier 1, Tier 2a, or Tier 2b methods. Thus, currently, the only practicable means to estimate emissions from this sector is the use of the Tier 3 method. Nevertheless, when a statistically-significant number of representative experimental emission factors become available, preliminary recommendations are provided for estimating default emission factors and for choosing the most appropriate Tier 1, Tier 2a, or Tier 2b methods.

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 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 (EV_i and B_{k,i} for the Tier 2a and EV_{i,p} and B_{k,i,p} for the Tier 2b and Tier 3 methods). Also, the equations for wet treatment processes do not include a heel factor (fraction of gas remaining

in the shipping container in the methods used for plasma-based processes). The emission factors for textile industry will be calculated for the emission potential of auxiliaries to the produced amount of textile in kg.⁶

While continuous (in-situ) emissions monitoring may be technically feasible, it is unclear whether such approach could be an economically viable method to estimate emissions from the textile, carpet, leather, or paper industry. One alternate approach would be to measure emission factors during the development of new wet-based processes when parameters such as coating velocity, liquid ratio, processing time, curing and drying temperatures, etc. are adjusted for particular treatment needs or for a particular product. Please see Box 1A.1 for guidance on the analytical methods that can be used for measuring emission factors.

Another approach would be for facilities to periodically (for short periods of time) install equipment to measure emissions from their stacks for purposes of developing facility-specific emission factors to estimate emissions over the long term. It is very important to note that emission factors (i.e. input liquid utilization efficiencies and by-product formation rates) can be strongly affected by changes in process variables (e.g. type of textile substrate material, curing temperature, liquid ratio, used chemical, processing time, etc.) and by the design of the process equipment. Thus, emission factors can substantially fluctuate from one tool manufacturer to another and for a recipe 'tuned' for a particular purpose or product.

⁶ Textile auxiliaries are defined as chemicals or formulated chemical products which enable a processing operation in preparation, dyeing, printing or finishing to be carried out more effectively or which is essential if a given effect is to be obtained.

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TABLE 1A.4 INFORMATION SOURCES NECESSARY FOR COMPLETING THE TIERED EMISSIONS ESTIMATING METHODS FOR WET-BASED TREATMENT OF TEXTILE, CARPET, LEATHER, AND PAPER					
Data		Tier 1	Tier 2		Tier 3
			2a	2b	
Consumption of liquid input chemicals	C_i = liquor concentration for input chemical i (fraction, kg of input chemical i per kg of liquor).		Me/Mo		
	LP_i = liquor pick-up for input chemical i (fraction, kg of liquor containing input chemical i per kg of textile substrate).		Me/Mo		
	$C_{i,p}$ = liquor concentration for input chemical i and process p , (fraction, kg of input chemical i per kg of liquor for process p).			Me/Mo	Me/Mo
	$LP_{i,p}$ = liquor pick-up for input chemical i and process p , (fraction, kg of input chemical i per kg of liquor for process p).			Me/Mo	Me/Mo
Formation of volatile by-products	$B_{k,i}$ = substance 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		
	$B_{k,i,p}$ = substance 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 kg of substrate produced)	D			
	C_u = fraction of annual plant production capacity utilization	Me			
	C_d = annual manufacturing design capacity (kg 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 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. As envisioned, Tier 1 estimates would be made simultaneously for all (or for the most important) gases listed in Tables 1A.1 and 1A.2 and can only be used if reported as a complete set.

As proposed, the Tier 1 calculation relies on a fixed set of generic emissions factors and does not account for differences among process and substrate types, individual processes or manufacturing tools. However, the members of the set would likely 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, would express 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 kg) 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 1A.10.

In using Tier 1, inventory compilers should not modify, in any way, the set of the FC assumed to represent average emissions. Further, as is common practice for IPCC methods, the Tier 1 method does not allow to account for the use of emissions control technologies, and 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 1,1,2,2-Tetrafluoroethyl methyl ether to estimate the emissions of 1,1,2,2-Tetrafluoroethyl methyl ether from pad-dry-cure textiles and combine it with the results of other FC gases from a Tier 2 or Tier 3 method. The formula used to calculate Tier 1 emissions is shown in Equation 1A.10.

EQUATION 1A.10
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 Tables 1A.1 and 1A.2) 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 mass of substrate for the product class (mass of volatile by-product k emitted, in kg/kg).

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

C_d = annual manufacturing design capacity, kg of substrate processed.

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

The Tier 2a method uses industry-wide default values for the ratio of the mass of chemical i evaporated divided by the mass of chemical i used (EV_i), the mass fraction of volatile by-product k formed from the use of liquid input chemical i ($B_{k,i}$), the liquor concentration (C_i), the liquor pick-up (L_i), the fraction of input chemical i used in the wet-based manufacturing process (D_i) and the fraction of FC by-products k destroyed by the emissions control technology (D_k). 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,

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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 evaporative losses of unreacted fluorinated chemicals i in the production process (E_i) plus emissions of all by-products k (BPE_k) resulting from the conversion of all input chemicals i used during production, as calculated using equations 1A.11, and 1A.12 below.

EQUATION 1A.11**TIER 2A ESTIMATION OF EMISSIONS OF UNREACTED INPUT CHEMICALS**

$$E_i = C_i \cdot LP_i \cdot EV_i \cdot (1 - D_i)$$

Where:

E_i = emissions of unreacted input chemical i through evaporative losses, kg.

C_i = liquor concentration, kg of input chemical i per kg of liquor.

LP_i = liquor pick-up, kg of liquor containing input chemical i per kg of textile substrate.

EV_i = ratio of the mass of chemical i evaporated divided by the mass of chemical i used.

D_i = overall reduction of chemical i , fraction, calculated per equation 1A.13 (replacing 'k' indices by 'i' indices).

EQUATION 1A.12**TIER 2A ESTIMATION OF BY-PRODUCT EMISSIONS**

$$BPE_k = \sum_i B_{k,i} \cdot C_i \cdot LP_i \cdot (1 - D_k)$$

Where:

BPE_k = textile-based emissions of volatile by-product k generated from the conversion of all input chemicals i per mass of textile substrate, kg/kg.

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

C_i = liquor concentration, kg of input chemical i per kg of liquor.

LP_i = liquor pick-up, kg of liquor containing input chemical i per kg of textile substrate.

D_k = overall reduction of by-product k emissions, fraction, calculated per equation 1A.13.

EQUATION 1A.13**EMISSIONS REDUCTION IMPACT OF EMISSIONS CONTROL TECHNOLOGY**

$$D_k = a_k \cdot d_k \cdot UT$$

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 1A.14.

EQUATION 1A.14
UPTIME OF EMISSION CONTROL SYSTEM

$$UT = 1 - \frac{\sum_n Td_n}{\sum_n UT_n}$$

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. UT may be set to 1 if suitable backup abatement or interlocking with the process tool is implemented for each abatement system.⁷

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 and/or classes of products. For the definition of ‘p’ compilers should refer to Box 1A.2. Thus, the Tier 2b approach is expected to be more accurate than the Tier 2a one because the Tier 2b method reflects the type of processes used or products made 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 or products manufactured. The Tier 2b method uses industry-wide default values for the ratio of the mass of chemical i evaporated divided by the mass of chemical i used during process type or product type p ($EV_{i,p}$), the for the mass fraction of volatile FC by-product k formed from the use of input chemical i per mass of substrate in process type or product type p ($B_{k,i,p}$), the liquor concentration ($C_{i,p}$) for substrate in process type or product type p , the liquor pick-up ($L_{i,p}$) for substrate in process type or for product type p , the fraction of input chemical i used in the wet-based manufacturing process using process type or product type p and the fraction of chemical i evaporated or FC by-products k destroyed by the emissions control technology connected to tools using process type or product type p ($D_{i,p}$ and $D_{k,p}$).

⁷ 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.

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BOX 1A.2**APPROACHES FOR DERIVING THE TIER 2B EMISSION FACTORS AND DEFINING 'P'**

Two approaches are proposed. A first approach would be to provide separate Tier 2b emission factors depending on the actual wet treatment method used in the process. In this case, default EFs would be provided for process types such as wet finishing (e.g. pad-dry-cure and exhaust applications), low wet pickup finish applications (e.g. vacuum extraction and kiss roll), spray application, foam finishing, coating, and lamination.

Another approach would be to provide separate Tier 2b emission factors based on the type of product manufactured. In this case, default EFs would be provided for substrate types such as cellulosic and regenerated cellulosic textiles (cotton, viscose, rayon, etc.), synthetic polymers for textile (polyamides, polyesters, polypropylenes, polyurethane), lignocellulosic (flax, jute, sisal, etc.), protein-based textiles (wool, silk), leather, paper and paperboard, and technical textile polymers.

The information currently available 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 product type (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 is preferred over the Tier 2a method because process-type-specific or product-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 or product type p . Thus, in the case where the consumption of input chemicals cannot directly be measured for each process type or product type p , a chemical consumption allocation model must be devised for applying the method,⁸ and inventory compilers should consider the trade-off of using more accurate process-specific or product-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 evaporative losses of unreacted fluorinated chemicals i used in all production processes p (E_i) plus emissions of all by-products k (BPE_k) resulting from the conversion of all input chemicals i used during the production of processes types or substrate types p , as calculated using equations 1A.15, and 1A.16 below.

EQUATION 1A.15**TIER 2B ESTIMATION OF EMISSIONS OF UNREACTED INPUT CHEMICALS**

$$E_i = \sum_p [C_{i,p} \cdot LP_{i,p} \cdot EV_{i,p} \cdot (1 - D_{i,p})]$$

Where:

E_i = emissions of unreacted input chemical i through evaporative losses, kg.

$C_{i,p}$ = liquor concentration, kg of input chemical i per kg of liquor for production process p .

$LP_{i,p}$ = liquor pick-up, kg of liquor containing input chemical i per kg of textile substrate for production process p .

$EV_{i,p}$ = ratio of the mass of chemical i evaporated divided by the mass of chemical i used.

$D_{i,p}$ = overall reduction of chemical i using production process p , fraction, calculated per equation 1A.17 (replacing 'k' indices by 'i' indices).

⁸ For an example of how site-specific gas consumption allocation models can be developed, please see Volume 3, Chapter 6 (Electronics Industry Guidelines).

EQUATION 1A.16**TIER 2B ESTIMATION OF BY-PRODUCT EMISSIONS**

$$BPE_k = \sum_{i,p} [B_{k,i,p} \cdot C_{i,p} \cdot LP_{i,p} \cdot (1 - D_{k,p})]$$

Where:

BPE_k = textile-based emissions of volatile by-product k generated from the conversion of all input chemicals i per mass of textile substrate used for all production processes p , kg/kg.

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

$C_{i,p}$ = liquor concentration, kg of input chemical i per kg of liquor for production process p

$LP_{i,p}$ = liquor pick-up, kg of liquor containing input chemical i per kg of textile substrate for production process p .

$D_{k,p}$ = overall reduction of volatile by-product k emissions from tools using production process p , fraction, calculated per Equation 1A.17.

EQUATION 1A.17**EMISSIONS REDUCTION IMPACT OF EMISSIONS CONTROL TECHNOLOGY**

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

Where:

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

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

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

UT_p = average uptime of all abatement systems connected to tools using production process p , fraction, calculated per Equation 1A.18.

EQUATION 1A.18**UPTIME OF EMISSION CONTROL SYSTEMS**

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

Where:

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

$Td_{n,p}$ = The total time, in minutes, that abatement system n connected to process tool(s) running production process 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 production process p in operation. UT may be set to 1 if suitable backup abatement or interlocking with the process tool is implemented for each abatement system.⁹

n = abatement system.

⁹ 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.

TIER 3 METHOD FOR WET PROCESSES – SITE-SPECIFIC PARAMETERS

The Tier 3 method uses the same set of equations (equations 1A.15 to 1A.18) as the Tier 2b method. However, when using the Tier 3 method, inventory compilers need to interpret ‘*p*’ in these equations as a specific production process using a specific ‘recipe’. A recipe corresponds to a particular combination of input liquids under specific conditions of process duration, temperature, type of substrate, and other relevant process parameters adjusted to achieve a particular result (e.g. water or stain resistance). It is very important to note that emission factors and by-product formation rates can be strongly affected by changes in process parameters (temperature, flows and nature of input chemicals, processing time, etc.).

When using the Tier 3 method, BPE emission factors in Equation 1A.16 should be measured for specific processes recipes. However, a centreline process recipe may be used to establish Tier 3 emission factors for sets of ‘similar’ recipes. Recipes can be deemed ‘similar’ when the centreline process can reasonably be deemed representative of facility-specific process conditions, of the potential variability of such process conditions around the centreline process during normal manufacturing operations, and when the substrate, process type, product, process tool, and input process gases are the same. When using the concept of ‘similarity’, inventory compilers should be able to reasonably demonstrate that emissions estimates are not biased (i.e. systematically over- or under-estimated) when using centreline process recipe(s) emission factors.

Once default Tier 2a or Tier 2b emission factors will be developed, the Tier 3 method should be used by manufacturing plants whose processes and recipes depart significantly from industry-wide patterns of use, or by manufacturing plants that may have developed specific processes whose characteristics may result in a significantly lower or higher utilization of input chemicals or formation of by-products. Further, if default 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 Tier 3 emission factors could be combined with Tier 2a or 2b default emission factors (once available) to use a hybrid method. A hybrid method would involve applying the Tier 2 defaults to processes and technologies that have not changed while applying Tier 3a, site-specific emission factors to processes and technologies that have changed. Indeed, higher accuracy might be achieved by using the Tier 3 method for specific input chemicals or site-specific processes. However, inventory compilers should not combine the Tier 1 method with any other method.

The Tier 3 method is not outlined further in this Appendix, but inventory compilers should refer to the Box 1.A.1 on specific technologies for the measurement of FC emissions in order to develop facility- or country-specific emission factors as a resource for implementing the Tier 3 method.

1a.3 Choice of emission factors

At the moment no representative FC emissions data can be obtained for textile, carpet, leather and paper industries to derive the Tier 1 or Tier 2 default emission factors. Thus, the Tier 3 methods is the only practical means to estimate emissions from this sector, where individual manufacturing sites will have to use measured emission factors (equipment-specific, process-specific, or site-specific). 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. Countries are encouraged to develop country-specific emission factors based on surveys of representative subsets of sources. Countries are also encouraged to work with equipment manufacturers and users of such equipment to measure equipment-specific, process-specific, or site-specific emission factors, with the aim of developing representative default emission factors that could eventually be used for site-specific, domestic, or industry-wide inventories. It is good practice to clearly and transparently document such emission factors. To support development of representative default emission factors, inventory compilers are encouraged to submit measurements of emission factors to the IPCC Emission Factor Database (EFDB).

1a.4 Choice of activity data

Activity data for the textile, carpet, leather and paper industries consist of data on gas or finishing agent sales/purchases and/or production figures (surface area or kg of substrate used during the textile treatments). For plasma and wet-based treatments the more data-intensive Tier 2 and Tier 3 methods, gas consumption and finishing agent data at the company or plant-level are necessary. The preferred methodologies for data collection are described in Box 1a.1. For Tiers 2 and 3, countries should create a national textile industry database with relevant data or information on textile companies, types of production/treatment, annual production data, consumption of

chemicals and other relevant parameters. For the Tier 1 methods, inventory compilers will need to determine the total surface area of textile substrates treated during the reporting year for plasma or the mass of textile substrates treated for wet-based processes in the reporting year. The best sources of either gas/finishing agent usage data or substrate area per kg data are the owners and operators of the textile manufacturing facilities in each country.

1A.8.2 REPORTING AND DOCUMENTATION

It is good practice to document and archive all information required to produce equipment-specific, process-specific or site-specific emission factors and national emissions inventory estimates as outlined in Volume 1, Section 6.11. The inventory should include summaries of methods used and references to source data such that the reported emissions estimates are transparent and steps in their calculation may be retraced. It is suggested that any inventory value outside the 95 percent confidence range of the data population variance be confirmed with the data source. Use of standard measurement methods improves the consistency of the resulting data and knowledge of the statistical properties of the data. Large differences should be explained and documented. In addition, the methods applied and references should be documented. It is good practice to conduct quality control checks and quality assurance procedures as outlined in Volume 1, Chapter 6. Inventory compilers are encouraged to use higher tier QA/QC for key categories as identified in Volume 1, Chapter 4. Transparent reporting of emissions factors will be required to ensure that representative default emission factors can be derived. Efforts to increase transparency should also take into account the protection of confidential business information related to specific gases or finishing agents used.

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