The urgency of measuring fluorinated greenhouse gas emission factors from the treatment of textile and other substrates

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The fashion industry is responsible for up to 10% of global CO_2 emissions, and according to the United Nations Framework Convention on Climate Change (UNFCCC), the sector's emissions are expected to rise by more than 60% by 2030 (*1-5*). While the vast majority of the sector's carbon footprint results from CO_2 emissions, an additional source – still unaccounted for and growing – likely results from emissions of fluorinated greenhouse gases (F-GHGs) during the treatment of textile and leather. Indeed, fluorine-based treatment of fibers and other substrates (paper, metals, plastics, etc.) is increasingly performed using wet- or plasma-based methods to functionalize surfaces for water and oil repellence, soil and stain release, improved textile breathability, softening, dyeing ability, increased mechanical strength, reduced adherence, antibacterial and anti-odor properties, and to fabricate wrinkle-free materials (*6*).

Although F-GHG emissions only represent 2.6% of global greenhouse gas emissions, F-GHGs have long atmospheric life (up to 50,000 years for CF_4) and high global warming potential (GWP, up to 23,500 for SF_6) (*7*). Thus, it is concerning that the atmospheric concentration of some of these gases is higher than what is predicted through bottom-up analyses (*8*). During the 2015-2016 Technical Assessment of the 2006 IPCC Guidelines for National GHG Inventories, potential emissions from the textile industry were accounted, among others, as a possible reason for the gap between top-down and bottom-up estimates of F-GHG emissions (*9*). Surprisingly, although several international and national reports refer to possible atmospheric emissions of F-GHGs during finishing of textile, carpet, leather, and paper, no corresponding emission factors were found to have been measured and published in the open literature (*6*).

Fluorinated wet treatment processes include several application techniques but about 80% of the processes use the pad-dry-cure method, where the dry fabric is immersed in a F-based finishing liquor and then squeezed between rollers before being dried and finally cured, usually at temperatures up to 180 ºC. Chemicals used for wet treatment processes include fluorotelomer alcohols, and perfluoroalkyl carboxylic acids. Although such

chemicals may not be GHGs by themselves, it is unclear whether fluorinated ethers, unreacted monomers or by-products formed during the deposition processes, and in the atmosphere, can produce relevant F-GHGs (*10*). Notwithstanding, it has been proved that during the drying and curing phases, F-based off-gas emissions can be produced by the volatility of the active substances themselves as well as by their constituents through evaporative losses and cracking (*11*). Moreover, high-GWP perfluoropolyethers were identified as being used in a number of commercial applications, including for textile treatment, increasing the concerns about the atmospheric release of these compounds (*11, 12*).

Recently, due to the persistent and bio-accumulative nature of the chemicals used in wet processes, several manufacturers have developed alternate plasma-based treatments for specialized fibers and substrates (*6, 13*). Plasma technology can be tailored to achieve many desirable properties and may provide equal or even better performance than wet methods.[5] Plasma processes can be divided into three process types: 1) plasma treatment, 2) plasma polymerization and 3) plasma etching. Plasma treatment and polymerization are the main processes of concern because they can use large quantities of F-GHG feedstocks such as CF_4, C_2F_6, C_3F_8, C_4F_8, C_5F_{10}, CHF_3, SF_6, and other larger molecules such as perfluoroalkyl acrylates to deposit thin films on a substrate. Because the application of high plasma power densities could damage fragile substrates, it is highly probable that feedstock molecules are not fully disassociated by the plasma. Further, the plasma disassociation of F-GHGs is well known to result in the formation of other F-GHG byproducts (e.g. of CF_4 from C_2F_6) (*8, 14*). Therefore, plasma-based fluorinated treatment of textile, carpet, leather, paper, and other substrates is expected to lead to higher F-GHG emissions than wet chemistry methods.

The authors of the 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories have proposed four distinct tiered methods (Tier 1, Tier 2a, Tier 2b, and Tier 3) to account for emissions from wet- and plasma-based fluorinated treatment of textile, leather, carpet, and paper (*6*). However, because no Tier 1 or Tier 2 default (industry average) factors are available, only the Tier 3 method is practicable, using equipment-specific, process-specific, or site-specific measured emission factors. Measurements should preferentially be performed by Fourier transform infrared spectroscopy (FTIR) due to part per billion (ppb) sensitivity and portability or by gas chromatography followed by mass spectrometry (GC/MS), allowing near real time measurements.

Emissions of F-GHGs from wet- and plasma-based fluorinated treatment of textile, leather, paper fibers, and other substrates may be substantial due to the large volume of materials treated and the sheer size and global nature of these industrial sectors. It is therefore urgent to measure the corresponding emissions factors and to create a comprehensive international database of such factors in order to estimate emissions from these sources.

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Acknowledgments: The authors would like to thank you the Intergovernmental Panel on Climate Change (IPCC) for the invitation as Lead author to contribute in the 2019 Refinement to the 2006 Intergovernmental Panel on Climate Change (IPCC) Guidelines for National Greenhouse Gas Inventories (Volume 3, Chapter 8: Textile, carpet, leather and paper fluorinated treatment emissions).

Funding: Andrea Zille acknowledges the Centro de Ciência e Tecnologia Têxtil (2C2T) of the Universidade do Minho for the travel expenses reimbursement through the project UID/CTM/00264/2019 of the Portuguese Fundação para a Ciência e Tecnologia (FCT).

Author contributions: The authors have equally contributed to the work development.

Competing interests: Andrea Zille declare no financial conflict of interest but as Senior Researcher at the University of Minho, He have co-authored the 2019 Refinement to the 2006 Intergovernmental Panel on Climate Change (IPCC) Guidelines for National Greenhouse Gas Inventories (Volume 3, Chapter 8: Textile, carpet, leather and paper fluorinated treatment emissions) which are directly connected to the opinions expressed in the proposed manuscript. More information is disclosed in the submitted Conflict of Interest form.