Challenges in Estimating Global CF_4 and C_2F_6 Emissions

Eleni Michalopoulou

Abstract

CF_4 and C_2F_6 are very long-lived greenhouse gases (GHG) 50,000 and 10,000 years respectively with a global warming potential (GWP100) of 7390 and 9200. These two perfluorocarbons (PFCs) are almost entirely anthropogenic. Three main sources have been identified: (a) Aluminium Industry (AI), (b) Semiconductor Industry (SCI) and (c) Rare Earth Smelting (RES). Estimating global emissions over time and compiling a bottom-up inventory, are both challenging tasks as there are several limitations related to them. Identifying and addressing those challenges in order to produce an updated and inclusive bottom-up inventory could result in a better understanding of previous CF_4 and C_2F_6 emissions and improved future estimates of these potent greenhouse gasses.

Keywords

PFC • Aluminium • Semiconductor • Rare earth

Introduction

CF_4 (tetrafluoromethane, PFC-14) and C_2F_6 (hexafluoroethane, PFC-116) are very long-lived perfluorocarbons (PFCs) with atmospheric lifetimes of about 50,000 and 10,000 years respectively and a global warming potential (GWP100) of 7390 and 9200 [1–8]. CF_4 and C_2F_6 are not ozone depleting substances [9]. According to Ralph and Weston [10], CF_4 and C_2F_6 emissions are almost entirely anthropogenic, with very few natural sources [11–16]. Three main sources of CF_4 and C_2F_6 have been identified so far: The Aluminium Industry (AI), the Semiconductor Industry (SCI, c) Rare Earth Smelting (RES). There is currently no bottom-up inventory that includes all three industries in a consistent, comprehensive and replicable manner, and more importantly, one that represents the current state of all the PFC emitting industries. Our inventory predominately focuses on the following information: coordinates of each facility, kg of PFCs produced per year per facility and emission factors. In the first instance, the first version of the inventory will only include the three industries mentioned above (Al, SC, RES) and the information that it provides will be limited to the years 2015–2017. At a later stage, we plan on adding information that will include the flat panel and photovoltaic industry and expand the inventory to cover years prior to 2015. This paper sets out to describe the challenges and limitations involved in making a bottom-up inventory and estimating global CF_4 and C_2F_6 emissions.

CF_4, C_2F_6 Emissions from the Industries

Aluminium Industry

PFC emissions occur during primary aluminium smelting processes, through events referred to as anode effects (AE [17]). AEs are events where, during the Hall-Heroult process, an insufficient amount of alumina is dissolved in the electrolyte bath [17]. This causes the voltage in the pot to be elevated above the normal operating range, the normal reactions that produce aluminium are interrupted and other electrochemical reactions take place with the formations of gases such as CO, CF_4 and C_2F_6. Anode effects are further sub-divided into high voltage (HVAE) or low voltage (LVAE). HVAE events are the result of the average cell voltage exceeding some defined trigger voltage (e.g. when the cell voltage exceeds 8 V for more than 3 s, [17, 18]. The trigger voltage used to declare an HVAE can vary between smelters and different countries from 6 to 10 V and from 1 to 90 s [18–20] while LVAE events can occur without the cell

E. Michalopoulou (✉)
Department of Chemistry, University of Bristol, Bristol, UK
e-mail: em15151@bristol.ac.uk

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reaching the defined trigger voltage. Broadly speaking, emissions of PFCs can be estimated by combining total aluminium production with estimates of the overall amount of PFCs that is released to the atmosphere through these processes per tonne of production. In 1990, the International Aluminium Institute (IAI) introduced an annual voluntary monitoring program in the form of a survey. The facilities that participate monitor and report the annual primary aluminium metal production, anode effect frequency, anode effect duration, and anode effect overvoltage. These definitions form the basis for AE performance statistics used in the global aluminium smelting industry to estimate total PFC emissions. It should be noted that LVAEs are typically not detectable by current process control systems and are not accounted for by IAI survey participants. Therefore, the IAI surveys collect only HVAE data and the surveys do not include LVAE emissions. The Intergovernmental Panel on Climate Change (IPCC) suggests three methods to calculate PFC emissions: Tier 1 (Eq. 1), Tier 2 (Eq. 2) and Tier 3 (Eq. 3).

$$E_{CF_4} = \sum_i (EF_{CF_4,i} \times MP_i) \tag{1}$$

$$E_{CF_4} = S_{CF_4} \times AEM \times MP \tag{2}$$

$$E_{CF_4} = OVC \times \frac{AEO}{CE/100} \times MP \tag{3}$$

Tier 1 methodology is presented in Eq. (1) in which ECF_4 is CF_4 emissions (kg), EFCF4, i is the emission factor for a given cell technology type, i (kg CF_4/tonne Al) and MP_i is the aluminium production by a given cell type, i (tonnes). And methods tier 2 and 3 use smelter specific data, where ECF_4 is CF_4 emissions (kg), SCF_4 is the slope coefficient for CF_4 [(kg CF_4/tonne Al)/anode event minutes per cell day)], AEM is the anode effect minutes per cell day, OVC is the overvoltage coefficient for CF_4 [(kg CF_4/tonne Al)/mV], AEO is the anode effect overvoltage (mV), CE is the process current efficiency (%) and MP is aluminium production (tonne).

The IAI derives the CF_4 emissions by using the Intergovernmental Panel on Climate Change (IPCC) Guidelines for National Greenhouse Gas Inventories and the methods Tier 2 (Eq. 2) and Tier 3 (IPCC Guidelines 2006). There are several entities that do not participate in the IAI survey, especially in China. The lack of reporting makes it more challenging to estimate CF_4 emissions per unit of production for these facilities. Recent (2008–2013) CF_4 emissions measurements made at 27 PFPB facilities in China have yielded a median emission factor of 0.100 kg of CF_4/t Al (IAI anode effect survey 2017). These measured values, that included HAVE and LVAE, are considerably higher than those reported by PFPB facilities (which have a median value of 0.021 kg of CF_4/t Al). Over the period 1990–2015, aluminium production rose from 20,000 kt (or Gg) to approximately 60,000 kt (IAI 2015), notably, over the same period the Aluminium Industry managed to significantly reduce their PFC emissions from 86.1 to 35.2 million of tonne equivalents of CO_2. Several events that took place during this period, most importantly the significant shift of the geographical distribution of the production, that may have influence PFC emissions. In 1990, USA and Russia accounted for more than 60% of global production. Since this time, production in these countries has dropped, whilst it grew dramatically in China, such that Chinese production accounted for over 55% of the global total in 2016 (IAI 2016). Changes in the geographical distribution of the primary aluminium production are often associated with uses of different smelting technologies, and therefore changes in PFC emissions factors (Fig. 1).

As summarised in Table 1, the IAI use different emission factors (emissions of CF_4 per tonne of production) to calculate emissions from different technologies (IAI 2015).

The alumina reduction cells, and in general, the aluminium smelters, can be divided into two categories depending on how their anodic system is arranged: pre-bake cell and the Soderberg cell. The quality of the baked Soderberg anode is lower than the quality of the prebaked one, hence the Soderberg cells are always characterized by a lower current efficiency and a higher pot voltage, needed also to produce the extra heat necessary for the anode baking [21]. Each of the five technologies used corresponds to a different PFC emission factor. It should also be noted that some factories do not use the same technology for every potline, so there could be different technologies within the same smelters.

Semiconductor Industry

The semiconductor industry is a subset of the broader electronics industry category which includes LCD (flat panel display) and PV (photovoltaic market). In the semiconductor industry, CF_4 is mainly used for chamber cleaning (a process that removes surface deposits from the interior of a chemical vapor deposition chamber (CVD) and etching. “Dry” (plasma) etching is used for circuit-defining steps, while “wet” etching (using chemical baths) is used mainly to clean wafers. Dry etching is a frequently used process in semiconductor manufacturing. Before etching begins, a wafer is coated with photoresist or a hard mask and exposed to a circuit pattern during photolithography. Etching removes material only from the pattern traces. This sequence of patterning and etching is repeated multiple times during the chip making process (Applied Materials 2016). The semiconductor industry was heavily impacted a lot by events like

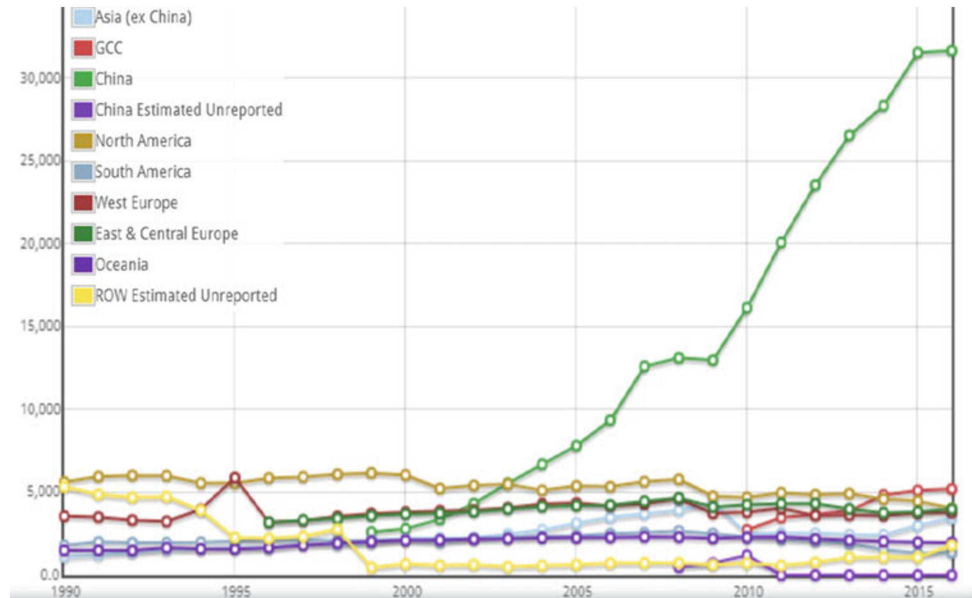

Fig. 1 Total for 1990–2017: 845,744 thousand metric tonnes of aluminium *Source* http://www.world-aluminium.org/statistics/#linegraph

Table 1 Emission factors from the 2015 anode effect survey

Technology type	Emission factor by technology type/kg CF_4 emitted per tonne Al
CWPB	0.02
PFPB	0.025
SWPB	0.278
VSS	0.127
HSS	0.187

Technology types: *Bar Broken Centre Worked Prebake* (CWPB), *Point Feed Prebake* (PFPB), *Side Worked Prebake* (SWPB), *Vertical Stud Søderberg* (VSS) and *Horizontal Stud Søderberg* (HSS)

the burst of the internet bubble in 2002 and the financial crisis in 2009. Notably, those events also had an impact on the global production of semiconductors and therefor may have impacted the PFC emissions from this industry (Fig. 2).

Prior to the late 1990s, CF_4 was mainly used as a chamber cleaning gas (more than 70% of the gas used by the SC industry went into this use), but recently it has been largely replaced by NF_3 for this purpose [22]. The main source of semiconductor production and CF_4, C_2F_6 emission data for this industry is the World Semiconductor Council (WSC), which is comprised of the Semiconductor Industry Associations (SIAs) in the United States, Europe, Japan, Korea, China and Chinese Taipei. The WSC annually release a Joint Statement, in which they estimate PFC emissions in tonnes of CO_2 equivalent. The Joint Statement of the 20th Meeting of WSC reports that in 2015, PFC emissions from participating organisations decreased by 4.5% when compared to the 2013 report. The IPCC 2006 Guidelines provide a set of methods for estimating electronics industry emissions, Tier 1 (Eq. 4), Tier 2a (Eq. 5) and Tier 2b (Eq. 6):

$$E_i = EF_i \times C_d \times C_u \tag{4}$$

$$E_i = (1 - h) \times FC_i \times (1 - U_i) \times (1 - a_i d_i) \tag{5}$$

$$\begin{aligned} E_i = \{(1 - h) \times FC_{i,etch} \times \left(1 - U_{i,etch}\right) \times \left(1 - a_{i,etch} d_{i,etch}\right)\}_{etch} + \{(1 - h) \\ \times 0.9 \times FC_{i,CVD}\left(1 - U_{i,CVD}\right) \times \left(1 - a_{i,CVD} d_{i,CVD}\right)\}_{CVD} \end{aligned} \tag{6}$$

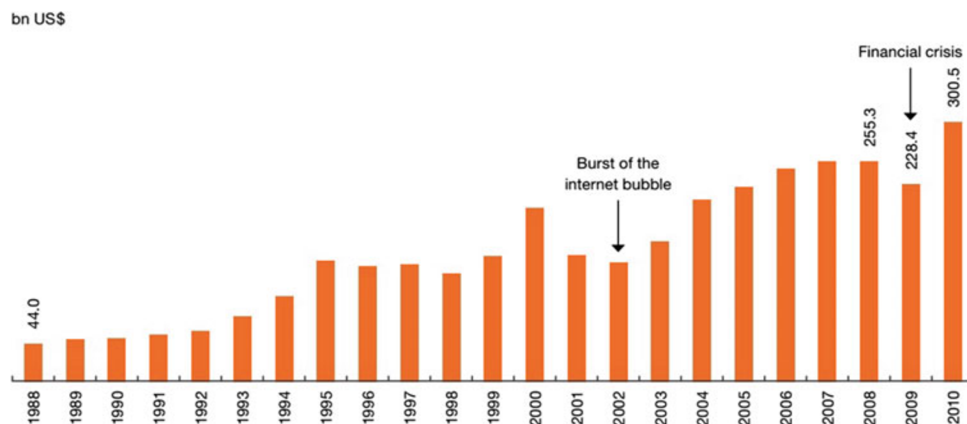

Fig. 2 Historical development of global semiconductor sales and identifies several influential economic factors. (*Source* Faster, greener, smarter—reaching beyond the horizon in the world of semiconductors Published by PricewaterhouseCoopers AG Wirtschaftsprüfungsgesellschaft By Werner Ballhaus, Dr.-Ing. Alessandro Pagella, Constantin Vogel and Christoph Wilmsmeier January 2012, 62 pages, 25 figures)

where, for Tier 1, E_i is the emissions of gas i (kg), EF_i is the emissions factor for gas i (mass of gas i produced per year per square meter of substrate, kg m^{-2} y^{-1}), C_d is the annual capacity of substrate processed (m^2) and C_u is the fraction of this production capacity that is utilised, on average, h is the fraction of the gas obtained by a facility that is not used, FC_i is the consumption of gas i (kg), U_i is the fraction of the gas that is used up in the process, a_i is the fraction of gas i that is used in processes with abatement technologies and d_i is the fraction of the gas i that is destroyed by the abatement process. FC_i, etch is the total consumption of gas i multiplied by the fraction that is used in etching processes. Similarly, FCi, CVD is the total consumption of gas i multiplied by the fraction that is used for CVD processes. In general, the Tier 1 method is based on activity data such as wafers produced per year and aggregate industry-wide emissions factors but the methods Tier 2a and Tier 2b use facility specific information as the ones described above. Semiconductor manufacturers who are members of the World Semiconductor Council have used IPCC Tier 2 or higher methods to estimate annual emissions since the late 1990s. There are also IPCC Guidelines that try to account for PFC emissions as by-products.

Rare Earth Smelting

During industrial neodymium electrolysis, an electrolyte composed of about 85 wt% NdF3 and 15 wt% Li is used to dissolve Nd_2O_3. On a vertical tungsten cathode, the metal is deposited in liquid form at about 1050 °C. The high melting dysprosium can be electrolytically won by using an iron cathode which forms a low melting alloy. The liquid metal drops in an inert crucible and is periodically tapped out of the cell. The ring-shaped graphite anode surrounds the cathode vertically and reacts with the oxygen containing ion to CO and CO_2. Because the electrode distance is not variable in this cell design, the voltage cannot be manipulated which is the key controller within the aluminium electrolysis ([23] EMC). The small cell runs at high energy input. The voltage in combination with the current density and oxide concentration in the electrolyte is crucial for the anodic reaction. At too high voltage and too low oxide concentration fluorides are oxidized and CF_4 with some C_2F_6 are created. The forming mechanism is like the aluminium system. Experiments show, that the process of rare earth electrolysis in contrast to the aluminium electrolysis is likely to run continuously with a PFC emission. In the aluminium electrolysis with a low superheat and horizontal electrodes the anodes tend to passivate with the development of PFCs and the cell voltage rises very high. Estimates for the world production of rare earths are based on oxides and account for about 130,000 t in 2013 [24]. The rare earth industry is predominantly based in China and some small capacities exist in Vietnam and Laos close to the border of China. The biggest production site is in Baotao, Inner Mongolia, many places in southern China and in the Sichuan region. Currently there is no inventory of the emission and no documentation of the smelting capacity, technology level and location of the smelters. So far, no model includes the emission coming from the rare earth smelting. The overall estimation of rare earth metal production is about 30,000 t in 2014 with a high uncertainty due to an estimated 40% illegal mining and black market [25].

Challenges and limitations in Estimating PFC Emissions

It is very important to understand how the industries have evolved and changed over time to understand how their emissions have changed and estimate the global CF_4 and

C_2F_6 emissions overtime. There are several factors that play a very important role in this, and are connected to the making of an inventory or the estimation of global emissions, such as changes in technologies, global and/or local financial crises and geographical shifts of the industries. Some challenges and limitations could be resolved, some could not, and some have the potential to be resolved in the future.

Additionally, and on an industry specific level:

Aluminium Industry

(a) **Accounting for LVAE**: Marks and Bayliss [26] report a median 22% contribution of the LVAEs for potlines outside China and a 70% median contribution of LVAEs for the Chinese facilities [26] and that is because the Chinese industry has larger cells, poor alumina distribution and higher amperage (all identified as factors that can have an impact on LVAE). Chinese production accounts for 55% of global production and as such, the majority of PFC emissions from the aluminium industry and the IAI estimates do include Chinese LVAE contributions. LVAE emissions are not currently accounted for in the data reported by IAI survey participants. The Chinese emissions, while including both HVAE and LVAE emissions, have a high associated uncertainty because a single factor is applied to the entire Chinese production and there is considerable variation in emission factors from facility to facility there.

(b) **Different technologies and different PFC emissions over time**: Not all types of technology used by the aluminium smelters emit the same amounts of PFCs. Technologies can differ from smelter to smelter and sometimes they can differ even within a specific smelter as different potlines can be using different technologies. In order to address this challenge, we did an extensive online search to find which technologies are used by every smelter (or potline), additionally we tried to find records for when each smelter switched from one technology to another. That was possible mainly for potlines outside of China.

(c) **Methodology and data**: There are 3 methodologies for estimating PFC emissions suggested by the IPCC. Tier 1, Tier 2 and Tier 3 as described above. The IAI uses the methods Tier 2 and Tier 3 as these are more accurate and based on smelter specific information. The data and information required for methods Tier 2 and Tier 3 are not publicly available so Eq. 1 was used that comes however with great uncertainty as shown in Table 2. Additionally, the activity data available on the internet and/or from several other sources can be conflicting. It should also be noted that when looking for activity data from online sources the difference between "production" and "capacity" when referring to the tonnes of aluminium produced by each smelter is quite unclear. This was a challenge that we could not overcome as we were constrained by the IPCC Guidelines and the information available.

(d) **Locations**: One of the biggest challenges we faced when compiling our bottom-up inventory was the fact that we did not know the locations for many of the Chinese smelters. We did extensive online research in an attempt to locate the missing factories and in some cases, especially outside of China, proved quite successful. Another way we are trying to address this challenge is by developing a reliable automated smelter detection system using satellite imagery, in collaboration with the university of Rochester and Scripps Oceanography Institute.

Semiconductor Industry

(a) **By-product CF_4 and C_2F_6**: In the semiconductor industry, chemical vapor deposition (CVD) chambers were traditionally cleaned using PFC gases such as C_2F_6 and CF_4. These gases decomposed in a plasma within the process chamber, yielding highly reactive fluorine radicals that reacted with process deposits on the chamber walls and furniture. The volatile fluorinated

Table 2 Emission factors from the 2015 anode effect survey

Technology type	Emission factor by technology type/kg CF_4 emitted per tonne Al	Emission factor by technology type/kg C_2F_6 emitted per tonne Al	Uncertainty in emission factor/%
CWPB	0.02	0.002	−99/+380
PFPB	0.025	0.003	−99/+380
SWPB	0.278	0.074	−40/+150
VSS	0.127	0.007	−70/+260
HSS	0.187	0.016	−80/+180

Technology types: *Bar Broken Centre Worked Prebake* (CWPB), *Point Feed Prebake* (PFPB), *Side Worked Prebake* (SWPB), *Vertical Stud Søderberg* (VSS) and *Horizontal Stud Søderberg* (HSS)
Emission factor uncertainties from the 2006 IPCC Guidelines for National Greenhouse Gas Inventories

gases thus formed (e.g., SiF_4) could then be pumped away. A relatively small fraction (typically ~30%) of the cleaning gas took part in the chamber cleaning reactions; the remainder passed through into the exhaust and the atmosphere [22]. Semiconductor manufacturing uses vacuum and abatement technologies to remove and neutralize process wastes and by-products. To that end several gas abatement systems are used depending on which process will be used and/or which gasses are produced by the process. There are two main categories of exhaust gas abatement systems: open flame combustion and inward fired combustor. As described by Czerniak et al. [22] despite the efforts the SC industry made to replace the previously used volatile C_2F_6 and CF_4 gases to NF_3 (a gas which decomposes very efficiently into fluorine and nitrogen in a plasma, either in or near the process chamber) there is indication that NF_3 converts to CF_4 [27].

(b) **Methodological**: In the case of the semiconductor industry we were not constrained by the IPCC guidelines in using only the Tier 1 approach as we acquired a combination of databases that allowed us to use methods Tier 2a and Tier 2b as well. However, we had to make several assumptions based on expert knowledge of the subject. For Tiers 2a and 2b (and as per Eqs. 5 and 6) it was assumed that all the gas obtained by a facility was used, hence h = 0. The values of U_i and d_i given in the IPCC guidelines of 0.1 and 0.9, respectively, were used. The value of a_i was estimated to be 0.7 for the Tier 2a method. Abatement systems only became widely used from 2003 onwards, so for 1990–2002 it was assumed that no abatement took place, so $a_i d_i = 0$. As with the Tier 1 method, the increase to 90% efficient abatement by 2010 was considered to be gradual between 2003 and 2010, so the percentage efficiencies shown in Table 3 were used as d_i for this period. Finally, the Tier 2b method was used to calculate CF_4 emissions. The Tier 2b method differs from the Tier 2a method in that it involves the use of process specific parameters. Equation 6 was used to calculate the CF_4 emissions using this method. The terms in Eq. 6 have the same meaning as those described for Eq. 5, the only difference being that in Eq. 6 we have two separate terms for etching (etch) and Chemical Vapour Deposition chamber cleaning (CVD) processes. The gas consumption term is also split by process type, $FC_{i,\ etch}$ is the total consumption of gas i multiplied by the fraction that is used in etching processes. Similarly, $FC_{i,\ CVD}$ is the total consumption of gas i multiplied by the fraction that is used in etching processes. Similarly, $FC_{i,\ CVD}$ is the total consumption of gas i multiplied by the fraction that is used for CVD processes. As with the Tier 2a method, it was assumed that all the gas consumed by a facility was used (i.e. h = 0). The CF_4 consumption data was provided by the industrial source, as was the estimate that approximately 10% of CF_4 consumption is used in etching processes and 90% in CVD processes, except for facilities producing 300 mm wafers, where 100% of CF_4 consumption is used in etching processes. The values of U_i used were 0.7 for etch processes and 0.9 for CVD processed, as suggested in the 2006 IPCC guidelines. The value of d_i used for both processes was 0.9, also estimated in the 2006 IPCC guidelines. The values of $a_{i,\ etch}$ and $a_{i,\ CVD}$ were assumed to be 1 and 0.85, respectively. As with the Tier 2a method, it was assumed that no abatement took place before 2003, so $a_i d_i = 0$ and the increase to 90% efficient abatement by 2010 was considered to be gradual between 2003 and 2010, so the percentage efficiencies shown in Table 3 were used as d_i for this period.

Table 3 Percentage abatements applied to Tier 1 CF_4 emissions from the semiconductor industry

Year	CF_4 abatement efficiency/%
1990–2002	0
2003	11.25
2004	22.5
2005	33.75
2006	45
2007	56.25
2008	67.5
2009	78.75
2010–2016	90

Rare earth Smelting Industry

(a) **Uncertainty**: The biggest challenge when estimating PFC emissions from the rare earth smelting is the uncertainty related to the production numbers of rare earth oxides per year and accounting for the illegal smelting (Vogel 2017—in preparation). The conversion rate of RE oxides to metal by electrolysis is similarly uncertain. The biggest uncertainty comes from the assumption of the specific PFC emission per kilogram or tonne RE metal. There are currently three emission scenarios suggested by Vogel et al. (2017—in preparation) (worst, medium and best case) based on different estimates (Vogel 2017—in preparation).

Discussion—Conclusion—Future work

There are several challenges related to the making of a bottom-up inventory and the estimate of global PFC emissions. However, having an updated and inclusive bottom-up inventory could prove to be extremely valuable for a number of reasons: (a) the inventory could (and will) be used as our prior information for atmospheric dispersion model runs, (b) we will be able to compare our results with model runs that have been based on other/different priors (c) the industries can monitor the results of their efforts to decrease PFC emissions over time, (d) the inventory has the potential to be updated every year so it always represents the current state of the PFC emissions, (e) this inventory could serve as a platform where industry experts and academics collaborate and exchange expertise in order to produce PFC estimates that are as accurate as possible. Our future work will be focused on adding more sources of PFCs such as the electronics industry, fugitive emissions, exploring potential new sources of PFCs such as silica gel and siloxane production and on modelling the emissions on a local and global scale.

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