Top-down validation of global and East Asian emissions of tetrafluoromethane (CF_4) and hexafluororethane (C_2F_6)

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Introduction

Importance of PFCs

Perfluorinated Carbon compounds (PFCs) are important in the atmosphere due to their long lifetimes and large global warming potentials (GWP), and thus regulated under the Kyoto Protocol.

- CF_4: lifetime of 50,000 yrs, $GWP_{100\text{-}CO2eqv}$ of 7,390
- C_2F_6: lifetime of 10,000 yrs, $GWP_{100\text{-}CO2eqv}$ of 12,200

Can the anthropogenic emissions of these PFCs be quantified and validated through measurement-based top-down emissions?

Anthropogenic Emission Sources of PFCs

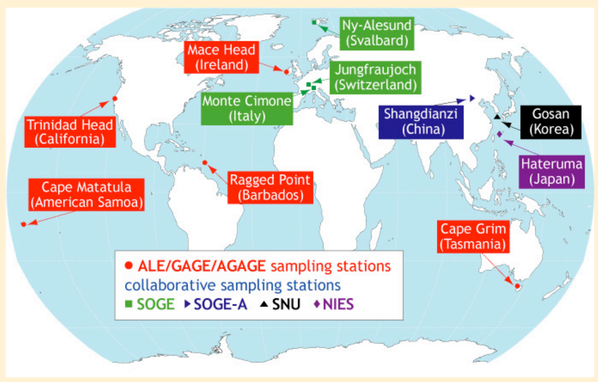
- Primary Aluminum Production (AL): PFC emissions occur during so-called “anode effects”, when concentrations of alumina (Al_2O_3) in the electrolytic cells become too low during the primary aluminum electrochemical smelting process. The AL industry has achieved significant reductions in PFC emissions by incorporating new technologies to reduce occurrence of anode effects, most notably the Point Fed Prebake (PFPB) technology widely used today.

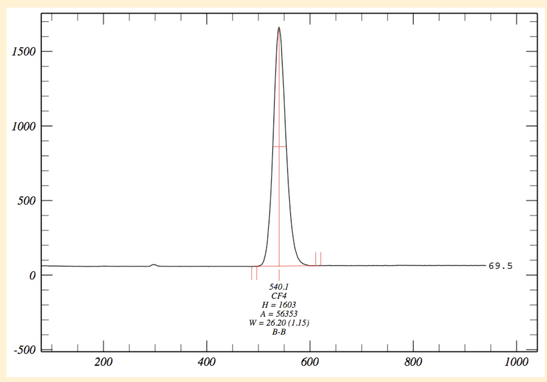
- Semiconductor Manufacture (SC): Emissions of PFCs from SC occur mainly during two processes - during usage of perfluorocompounds (including CF_4, C_2F_6, C_3F_8, c-C_4F_8, NF_3, SF_6, HFC-23) in plasma etching and cleaning of the chemical vapor deposition (CVD) chambers. C_2F_6 has traditionally been widely used in CVD chamber cleaning applications, however newer technologies with better abatement capabilities such as NF_3 are becoming more wide-spread in the industry. For the etching processes, finding a suitable replacement has turned out to be difficult, and thus the emissions of PFCs in etch are considered to be unavoidable for the foreseeable future.

Measurements

Medusa GC-MS and AGAGE

Data used in this study were collected from continuous *in situ* measurements using the Medusa GC-MS at Gosan (Jeju Island, Korea) and two stations in Australia (Cape Grim, Aspendale), as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) network. Measurement precisions of CF_4 and C_2F_6 on the Medusa GC-MS are below 1% of atmospheric concentrations.





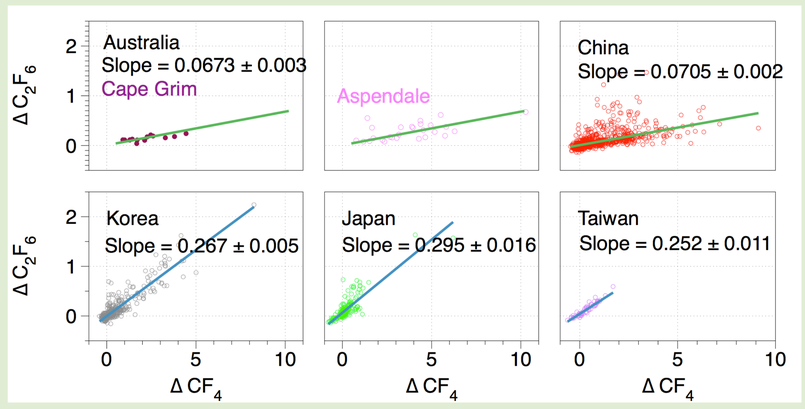
Industry Emissions History

PFC Emission Ratio in AL, SC

The C_2F_6/CF_4 emission ratio in AL were estimated from selected measurements in Cape Grim and Aspendale (Australia), when signals from aluminum smelting factories located in the east coast of Australia could be captured at the two stations.
The C_2F_6/CF_4 emission ratio in SC were estimated from selected measurements in Gosan, when air masses from Korea were determined to have arrived at the station. Aluminum smelters are not known to be present in Korea.

PFC Emission Ratios in East Asia

Despite at least one aluminum smelter known to be located in Japan, the C_2F_6/CF_4 emission ratio is very similar to Korea, and indicate strong emissions from SC related sources.
In addition, the C_2F_6/CF_4 emission ratio in Taiwan suggests emissions from SC sources, however detailed information regarding Taiwan’s industry structure is not known.
The dominant C_2F_6/CF_4 emission ratio found in China is very close to those of the Australian stations, and suggests strong emissions from AL sources. However, as evidenced by the outlier points in the ratio diagram, the emissions from SC in China should not be underestimated, and as such direct interpretation of China’s C_2F_6/CF_4 emission ratio is not trivial.

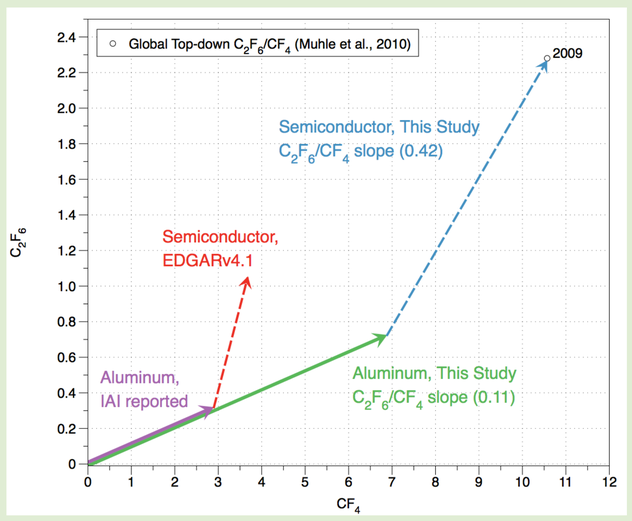


Vector-Analysis of Global Emissions

Industry-specific emissions of PFCs can be deduced from global total measurements by using the PFC emission ratio for AL and SC presented in this study, using the following formula:

$E_{CF4,global} = E_{CF4,AL} + E_{CF4,SC}$ (1)
$E_{C2F6,global} = (E_{CF4,AL})*R_{AL} + (E_{CF4,SC})*R_{EC}$ (2)

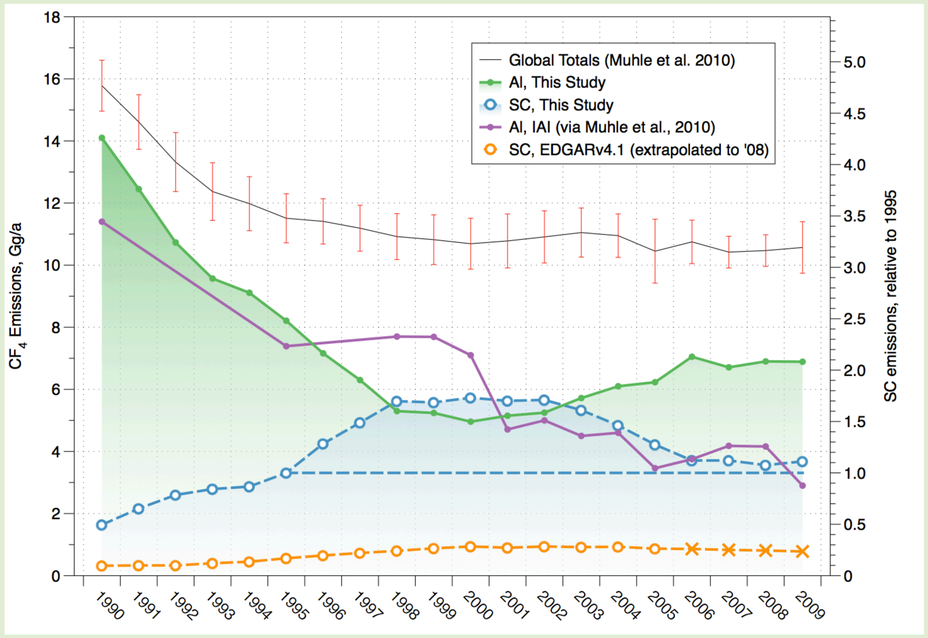
whereby $E_{CF4,global}$ and $E_{C2F6,global}$ are global emissions of CF_4 and C_2F_6 reported in Muhle et al. (2010), $E_{CF4,AL}$ and $E_{CF4,SC}$ are global CF_4 emissions from the aluminum industry (AL) and semiconductor industry (SC) respectively, and R_{AL} and R_{EC} are the emission ratios of C_2F_6 to CF_4 derived in this study. These formulas can be illustrated in a vector diagram form, as shown on the right.



Historical Analysis of Global Emissions

Using the vector analysis method described above, we estimate the historical changes in industry-specific emissions of PFCs from 1990 to present, and compare our results with reported (“bottom-up”) emissions from the International Aluminum Institute (IAI, for AL) and EDGARv4.1(for SC). Our findings show that the IAI emissions are generally well-matched with the AL emissions derived in this study until 2003, when the IAI emissions seem underestimated. The emissions in EDGARv4.1 for SC are found to be very low compared to the top-down emissions estimated in this study.

An important source of uncertainty in our study lies in assuming that the C_2F_6/CF_4 emission ratio of each industry has not changed significantly from 1990 to present. There are some evidence to suggest that this may be true for AL, but there’s much less confidence in SC due to lack of detailed data from industry.



PFC Emissions from East Asia: Global Perspective

The disagreement found between emissions reported by the IAI and AL emissions derived in this study may stem from underestimated emissions from China’s aluminum smelters. IAI estimates China’s 2009 emissions of CF_4 to be 1.29 Gg. Combining China’s C_2F_6/CF_4 emission ratio with C_2F_6 emissions reported by Saito et al. (2010; 0.499±0.038 Gg/yr), we can estimate China’s total emissions to be as large as 4.6 Gg/yr. Emissions calculated using HCFC-22 as reference (Kim et al., 2010) was reported to be 2.3 Gg/yr. While further work is needed in better quantifying the actual emission rates, it is likely that China’s emissions are currently underestimated. Even without factoring in the contributions from China, SC emissions from the rest of East Asia was 0.79 Gg/yr in 2008, equal to 22% of the global total SC emissions derived in this study.

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