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# The global $SF_6$ source inferred from long-term high precision atmospheric measurements and its comparison with emission inventories

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**Abstract.** Emissions of sulphur hexafluoride ($SF_6$), one of the strongest greenhouse gases on a per molecule basis, are targeted to be collectively reduced under the Kyoto Protocol. Because of its long atmospheric lifetime (estimated as 800 to 3200 years), the accumulation of $SF_6$ in the atmosphere is a direct measure of its global emissions. Examination of our extended data set of globally distributed high-precision $SF_6$ observations shows an increase in $SF_6$ abundance from near zero in the 1970s to a global mean of 6.7 ppt by the end of 2008. In-depth evaluation of our long-term data records shows that the global source of $SF_6$ decreased after 1995, most likely due to $SF_6$ emission reductions in industrialised countries, but increased again after 1998. By subtracting those emissions reported by Annex I countries to the United Nations Framework Convention of Climatic Change (UNFCCC) from our observation-inferred $SF_6$ source leaves a surprisingly large gap of more than 70–80% of non-reported $SF_6$ emissions in the last decade. This suggests a strong under-estimation of emissions in Annex I countries and underlines the urgent need for independent atmospheric verification of greenhouse gases emissions accounting.

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## 1 Introduction

$SF_6$ is an extremely stable mainly anthropogenic gas, having a very high global warming potential of 23 900 (Forster et al., 2007). Traces of $SF_6$ have been shown to be produced in the Earth' crust (Harnisch and Eisenhauer, 1998), but natural fluxes into the atmosphere are negligible in the context of the present study (Busenberg and Plummer, 2000). The industrial production of $SF_6$ began in 1953 for use as an insulation gas in high voltage installations (Ko et al., 1993; Maiss and Brenninkmeijer, 1998). Emissions from the electricity sector (through leakage and venting) continue to form the largest source of $SF_6$ to the atmosphere, with additional contributions from magnesium production, semiconductor manufacturing as well as other minor sources (Olivier et al., 2005). $SF_6$ is primarily destroyed in the mesosphere; its atmospheric lifetime is estimated to range from 800 to 3200 years (Ravishankara et al., 1993; Morris et al., 1995) with the latter number being adopted by IPCC (Forster et al., 2007). Therefore, more than 96–99% of all $SF_6$ emitted to the atmosphere accumulates there, allowing us to directly infer its global emissions from the observed atmospheric concentration increase (Maiss and Levin, 1994). Assuming that the distribution of emissions is well known (e.g. from inventories such as EDGAR, 2009), $SF_6$ has been widely used as

**Table 1.** Characteristics of $SF_6$ measurement stations; the column "type" distinguishes between long-term background stations (LTB), regular aircraft sampling (RAS) and balloon sites (B). For the balloon sites, the figure in brackets after the "B" denotes the number of vertical $SF_6$ profiles taken.

| Station | latitude | longitude | altitude (m a.s.l.) | Type | Sample type | Period |
|---|---|---|---|---|---|---|
| Alert (Canada) | 82°27′ N | 62°31′ W | 50 | LTB | High pressure cylinder | Apr 1993–Dec 2003 |
| Alert (Canada) | 82°27′ N | 62°31′ W | 50 | LTB | Glass flask | Oct 2004–June 2009 |
| Cherskii (Siberia, Russia) | 68°44′ N | 161°19′ E | 150–3050 | RAS | Glass flask | Sep 2003–Sep 2005 |
| Kiruna (Sweden) | 67°51′ N | 20°13′ E | 9500–30 400 | B (6) | Cryosampler | Feb 1997–Jun 2003 |
| Syktyvkar (Russia) | 61°24′ N | 52°18′ E | 200–3300 | RAS | Glass flask | Jun 1998–Aug 2005 |
| Rhine Valley (Germany) | 47°55′ N | 7°55′ E | 270–3200 | RAS | Glass flask | Nov 2001–Jun 2005 |
| Aire sur l'Adour (France) | 42°42′ N | 0°16′ W | 10 500–32 400 | B (5) | Cryosampler | Dec 1994–Oct 2002 |
| Izaña (Tenerife, Spain) | 28°18′ N | 16°29′ W | 2400 | LTB | High pressure cylinder | Jun 1991–Apr 1999 |
| Teresina (Brazil) | 5°05′ S | 42°47′ W | 15 200–34 300 | B (2) | Cryosampler | Jun 2005 |
| Cape Grim (Tasmania, Australia) | 40°41′ S | 144°41′ E | 104 | LTB | High pressure cylinder archive | Apr 1978–Oct 1994 |
| Cape Grim (Tasmania, Australia) | 40°41′ S | 144°41′ E | 164 | LTB | Stainless steel flask | Jan 1996–June 2009 |
| Cape Grim (Tasmania, Australia) | 40°41′ S | 144°41′ E | 300–7600 | RAS | Glass flask | Feb 1997–Dec 1999 |
| Neumayer (Antarctica) | 70°39′ S | 8°15′ E | 30 | LTB | High pressure cylinder | Aug 1986–Jan 2008 |
| Neumayer (Antarctica) | 70°39′ S | 8°15′ E | 30 | LTB | Glass flask | Mar 1994–Jan 2009 |

a tracer to compare and validate atmospheric transport models (e.g., Levin and Hesshaimer, 1996; Denning et al., 1999; Kjellström et al., 2000; Waugh and Hall, 2002; Peters et al., 2004; Gloor et al., 2007; Bönisch et al, 2008; Patra et al., 2009).

In this study, global $SF_6$ emissions from 1978 to 2008 are estimated using its accumulation rate in the atmosphere based on new observational data. These top-down source estimates, hereafter called *inferred emissions*, are compared to *global* annual emissions published in the most recent compilation (V4.0) of the EDGAR data base (EDGAR, 2009) which uses a so-called bottom-up approach, based on statistical information on the sources and their global distribution. Both, top-down inferred and bottom-up estimates are further compared to $SF_6$ emissions reported by Annex I countries to UNFCCC (2009). Annex I countries include all major industrial countries of Western Europe, Canada, the United States, Japan, Australia, and New Zealand, as well as Eastern European countries, the Russian Federation and Turkey. At least until the mid 1990s, emissions from Annex I countries should comprise the major share of global $SF_6$ emissions. After 2000 emissions from newly industrialised countries also significantly contribute to the increasing global atmospheric $SF_6$ burden (EDGAR, 2009). The difficulties to validate, on the regional scale, reported bottom-up emissions with spatially distributed observations and atmospheric transport modelling will also be discussed.

## 2 The 30-year atmospheric $SF_6$ record

Our $SF_6$ observational network data comprise: (1) long-term data records from Alert (Arctic), Izaña (sub-tropics, Tenerife Island), Cape Grim (Tasmania, Australia), and Neumayer (Antarctica), (2) two meridional profiles collected in November 1990 and November 1993 over the Atlantic Ocean (50° N to 68° S), (3) regular vertical aircraft profiles over the Rhine Valley (Germany), Syktyvkar (Russia), Cherskii (Siberia), and over Tasmania (Australia), and (4) stratospheric profiles collected between 1997 and 2005 at Kiruna (Sweden), Aire sur l'Adour (France) and Teresina (Brazil). Details of the sampling techniques and site locations can be found in Maiss and Levin (1994), Langenfelds et al. (1996), Levin et al. (2001; 2002), Engel et al. (2002), Schmitgen et al. (2004), and Weller et al. (2007); they are summarized in Table 1. All samples have been analysed at the Institut für Umweltphysik, Universität Heidelberg. A description of the analysis technique and the development of the Heidelberg $SF_6$ calibration scale is described by Maiss et al. (1996) as well as in the Supplementary Material Sects. 1 and 2 http://www.atmos-chem-phys.net/10/2655/2010/acp-10-2655-2010-supplement.pdf.

The tropospheric $SF_6$ records from Neumayer, Cape Grim, Izaña, Alert and the aircraft sites (altitude $>2500$ m) are displayed in Fig. 1. From 1998 to 2006 an almost constant increase rate (solid lines) is observed, suggesting near constant global $SF_6$ emissions; only in the last four years emissions are increasing again. The measurement records from Izaña and Alert, starting in 1991 and 1993 respectively, show that mixing ratios from the Northern Hemisphere are about 0.3 to 0.4 ppt higher than the Southern Hemispheric data from Cape Grim and Neumayer. The observed inter-hemispheric difference is due to the uneven distribution of sources (more than 95% of $SF_6$ emissions originate in the Northern Hemisphere; Olivier et al., 2005; EDGAR, 2009), combined with the ca. 1 year inter-hemispheric exchange time of air masses.

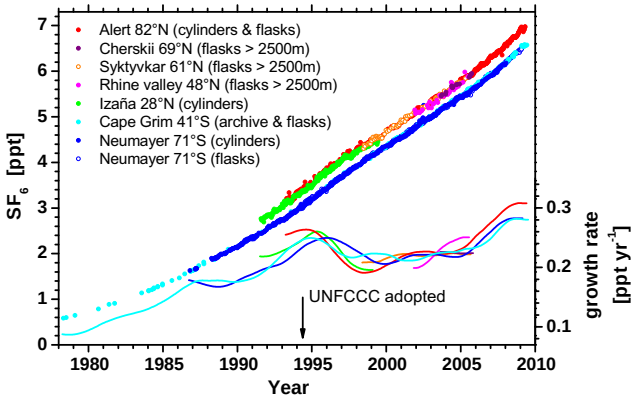


**Fig. 1.** Global observations of tropospheric $SF_6$: Symbols and left axis: Atmospheric $SF_6$ mixing ratios (given in ppt = parts per trillion, i.e. pico moles of $SF_6$ per mole of dry air) observed in the Northern and Southern Hemispheres. The overlapping flask and cylinder data from Neumayer are virtually indistinguishable (note that 12 data points in total have been rejected as outliers from the figure). Lines and right axis: $SF_6$ growth rates calculated for individual stations from de-seasonalized measurements using a fit routine from Nakazawa et al. (1997) (colour codes: same as original data).

## 3 A new top-down estimate of global $SF_6$ emissions

Observations at the four globally distributed stations and along meridional transects over the Atlantic Ocean show relatively uniform $SF_6$ mixing ratios north of 30° N, and south of about 15° S. A nearly linear north-to-south decrease is observed in the tropics (Maiss et al., 1996; Geller et al., 1997). If we assume that observations from these background stations and the Syktyvkar aircraft location represent the zonal mean tropospheric $SF_6$ mixing ratios in their respective latitudinal bands, it is possible to reconstruct the temporal evolution of the tropospheric $SF_6$ distribution from this network. Further, combination with observed stratospheric $SF_6$ profiles (Supplementary Fig. A2, http://www.atmos-chem-phys.net/10/2655/2010/acp-10-2655-2010-supplement.pdf) yields an estimate of the temporal development of the global $SF_6$ distribution on a latitude – altitude grid, which – when integrated over the entire atmosphere – gives the temporal development of the global atmospheric $SF_6$ inventory (see Supplementary Material Sect. 3, http://www.atmos-chem-phys.net/10/2655/2010/acp-10-2655-2010-supplement.pdf).

With an atmospheric lifetime of 800–3200 years (Ravishankara et al., 1993; Morris et al., 1995), the total atmospheric $SF_6$ sink in 2005 was 0.04–0.17 Gg (1 Gg = $10^9$ g), i.e. approximately 1–4% of the observed annual atmospheric increase of ca. 5–6 Gg. Considering that the oceanic sink is one order of magnitude smaller than the atmospheric sink (Ko et al., 1993), the total $SF_6$ sink can be neglected. Therefore, we claim that the first temporal derivative of the global atmospheric $SF_6$ inventory provides a direct observation-based estimate of global $SF_6$ emissions which are presented in Fig. 2a. Inferred global $SF_6$ emissions increase from ca. 2.1±0.13 Gg/a in 1978 to 6.4±0.4 Gg/a in 1995 (Table 2). In 1996, just two years after the UNFCCC agreement went into force, global emissions start to drop and reach a minimum of 5.4±0.3 Gg/a in 1998; but they increased again to 7.2±0.4 Gg/a in 2008. Our inferred annual emissions up to 2005 compare rather well (within a 2$\sigma$ error margin of our estimates) with independent estimates from other observational studies (see Supplementary Fig. A3 and respective references in the Supplementary Material, http://www.atmos-chem-phys.net/10/2655/2010/acp-10-2655-2010-supplement.pdf). Also the

**Table 2.** Observed global atmospheric $SF_6$ inventory and inferred annual $SF_6$ source. The 1$\sigma$ uncertainties of the inventory are ±3-4Gg, while the uncertainties of the annual emissions are ±6%, neglecting oceanic and atmospheric sinks. A total atmospheric mass of $5.1\times10^{21}$ g of air was used for the source estimates. Note that the inventory refers to the middle of each year, whereas the source refers to the period 1 January–31 December

| Year | Global inventory [Gg] | Global annual source [Gg] |
|---|---|---|
| 1978 | 15.93 | 2.07 |
| 1979 | 17.81 | 2.25 |
| 1980 | 20.17 | 2.52 |
| 1981 | 22.85 | 2.84 |
| 1982 | 25.79 | 3.05 |
| 1983 | 28.92 | 3.21 |
| 1984 | 32.24 | 3.48 |
| 1985 | 35.91 | 3.89 |
| 1986 | 40.00 | 4.28 |
| 1987 | 44.36 | 4.39 |
| 1988 | 48.70 | 4.30 |
| 1989 | 53.00 | 4.32 |
| 1990 | 57.52 | 4.77 |
| 1991 | 62.45 | 5.14 |
| 1992 | 67.79 | 5.57 |
| 1993 | 73.57 | 6.00 |
| 1994 | 79.75 | 6.36 |
| 1995 | 86.17 | 6.41 |
| 1996 | 92.44 | 6.04 |
| 1997 | 98.24 | 5.56 |
| 1998 | 103.68 | 5.35 |
| 1999 | 109.01 | 5.42 |
| 2000 | 114.53 | 5.53 |
| 2001 | 120.04 | 5.51 |
| 2002 | 125.59 | 5.63 |
| 2003 | 131.31 | 5.79 |
| 2004 | 137.12 | 5.84 |
| 2005 | 143.01 | 5.98 |
| 2006 | 149.12 | 6.29 |
| 2007 | 155.63 | 6.79 |
| 2008 | 162.63 | 7.16 |

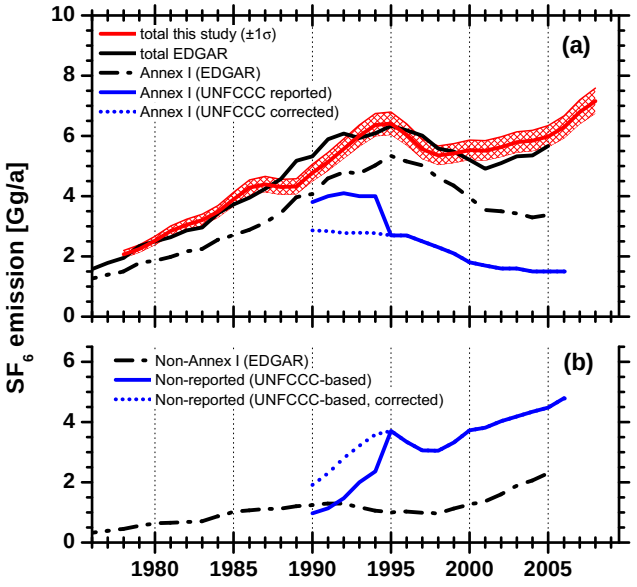


**Fig. 2.** **(a)** Comparison of annual observation-inferred global $SF_6$ emissions (red line with $\pm 1\sigma$ uncertainty range) with global emissions estimated by EDGAR (2009). Also included are the (Japan-corrected and original, see main text) emissions reported by Annex I countries to UNFCCC in 2009 (dashed resp. solid blue line) as well as estimated Annex I emissions from the EDGAR data base. **(b)** $SF_6$ emissions for Non-Annex I countries from the EDGAR data base (dashed dotted line) as well as Non-reported emissions, calculated as residual from the total inferred source in (a) and UNFCCC-reported Annex I emissions (blue lines).

total global emissions estimated by EDGAR (2009) (Fig. 2a, solid black line) compare well with our data within ±20%, which global estimates of annual emissions were compiled largely independently from atmospheric observations (J. G. J. Olivier, personal communication, 2010).

## 4 Comparison with data reported to UNFCCC

Figure 2a also shows the total share of annual $SF_6$ emissions which Annex I countries officially reported to UNFCCC (2009) from 1990 to 2006 (solid blue line). We applied a downward correction to the figure Japan reported to UNFCCC before 1994 (dashed blue line) because they probably overestimated pre-1994 emissions due to an inadequate methodology used (Jigme, UNFCCC, pers, comm., see Supplementary Material Sect. 4.2, http://www.atmos-chem-phys.net/10/2655/2010/acp-10-2655-2010-supplement.pdf). While in 1990 total reported emissions by Annex I countries still correspond to 80% of the global inferred emissions, they decrease in 1995 to 43%, and to less than 24% in 2005. The EDGAR (2009) data base not only provides global emissions but also emissions per country. The annual sum of all Annex I emissions as estimated by EDGAR for 1976 to 2005 is also plotted in Fig. 2a (dashed-dotted black line). These emissions are higher by more than 90% compared to what was officially reported to UNFCCC for 1995, and by more than a factor of two from 1997 until 2005.

Newly industrialized countries not included in Annex I of the UNFCCC, such as China, India, Brazil, and others, are not required to report $SF_6$ emissions to UNFCCC. Their $SF_6$ emissions as estimated by EDGAR are displayed in Fig. 2b (dashed-dotted black line). These data are compared here with the residual emissions as calculated from the difference between the total observation-inferred $SF_6$ source and Annex I reported $SF_6$ emissions. These so-called Non-reported emissions are also plotted in Fig. 2b, either based on originally reported or Japan-corrected emissions. We call these "scenarios" of $SF_6$ emissions "UNFCCC-based". From 1995 to 2000 Non-reported emissions in the UNFCCC-based scenario are more than three times higher than EDGAR estimates for Non-Annex I countries, and in 2000 they already account for about 2/3 of the global $SF_6$ source. Both, the *increase* of Non-reported emissions and their respective *share* in the global emissions are surprisingly large, in particular if all these Non-reported emissions would have to be assigned to emissions from Non-Annex I countries. The dominant sector for $SF_6$ use and emission is electricity production (Olivier and Berdowski, 2001). Interestingly, the share of Non-Annex I countries in global electricity production was only 1/3 in 2000 (BP, 2009). Assuming that the UNFCCC-based $SF_6$ emission scenario is correct therefore implies that the annual $SF_6$ emissions per GWh electricity production would be two to more than three times larger in Non-Annex I countries than in Annex I countries. The large discrepancies between the two emission scenarios, EDGAR and UNFCCC-based are further investigated in the next section.

## 5 Comparison of observed mixing ratios with model simulations

A comparison of observed mixing ratios with atmospheric transport model estimates that are based on different emission scenarios may help to decide which of these scenarios is more likely correct. Here we have deployed the two emission distribution estimates, EDGAR and the corrected UNFCCC-based in a coarse-resolution two-dimensional atmospheric box model GRACE (Levin et al., 2010). Thereby, simulated tropospheric $SF_6$ mixing ratios were compared with observations at Alert (82° N), Cape Grim (41° S) and Neumayer (71° S). The core of the GRACE model consists of an atmospheric module with 28 boxes, representing zonal mean tracer mixing ratios in six zonal, and either four (tropics) or five (extra-tropics) vertical subdivisions. Air mass (and tracer) exchange between the atmospheric boxes is controlled by three processes: (1) (turbulent) diffusive exchange between neighbouring boxes, (2) the Brewer-Dobson circulation, and (3) seasonal lifting and lowering of the

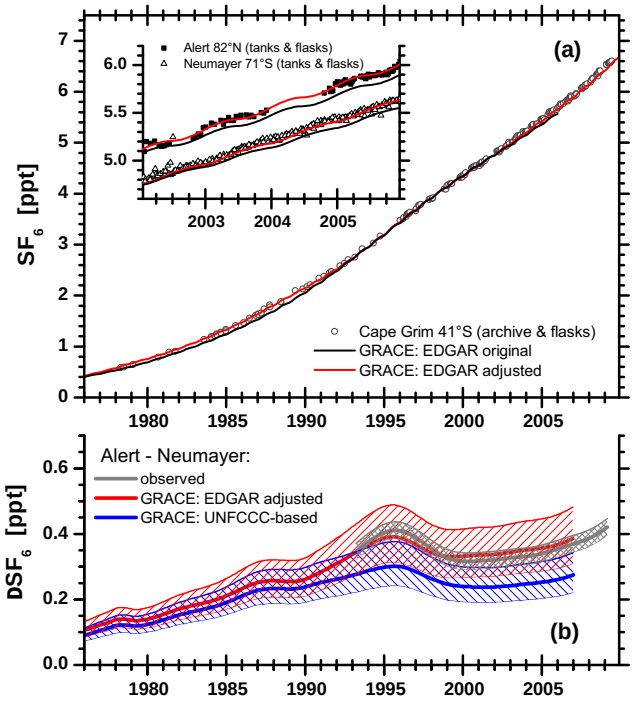


**Fig. 3.** Comparison of observed and simulated $SF_6$ mixing ratios and north-south differences: **(a)** $SF_6$ observations from Cape Grim (41° S), Alert (82° N) and Neumayer (71° S) (inlay) in comparison with GRACE simulations for the respective model box, based on the original EDGAR (2009) emissions (black lines) as well as simulations obtained when total EDGAR emissions were adjusted to the inferred emissions from Figure 2a (red line). **(b)** $SF_6$ differences between Alert and Neumayer (taken from the fitted curves through the data and $1\sigma$ error estimates, grey line and hatched area) in comparison with GRACE simulations. Hatched areas show model results when inter-hemispheric transport is varied by ±25%.

extra-tropical tropopause. While the meridional distribution of $SF_6$ emissions for the EDGAR scenario can be directly taken from the data base (EDGAR, 2009), we used for the source distribution of the UNFCCC-based scenario for Annex I countries the officially reported emissions corrected for Japan (UNFCCC, 2009). For Non-Annex I countries the residual from the global inferred $SF_6$ source (dotted blue line in Fig. 2b) was distributed according to the electrical power production of these countries (see Supplementary Material Sect. 4.3 and Fig. A4, http://www.atmos-chem-phys.net/10/2655/2010/acp-10-2655-2010-supplement.pdf).

Simulated $SF_6$ mixing ratios from 1976 to 2009 for the mid latitude box of GRACE in the southern hemisphere are displayed in Fig. 3a, together with the observations at Cape Grim (41° S) starting in 1978. There is generally good agreement of the long-term trends between EDGAR-based simulations and the observations, with model results being slightly lower than observations up to 1992 and again from about 2003 onwards. When using the relative latitudinal distribution of $SF_6$ emissions from EDGAR adjusted to our observation-inferred annual totals, we obtain almost perfect agreement with observations for the whole period from 1978 until present. This confirms our top-down method, but also shows how sensitively global tropospheric $SF_6$ mixing ratio trends can reflect the underlying source strengths.

With the adjusted EDGAR distribution, the mixing ratios at Alert (82° N) and Neumayer (71° S) (inlay in Fig. 3a) as well as the north-south gradient (Fig. 3b, thick red line) are also correctly reproduced. However, model simulations using the UNFCCC-based emission scenario slightly underestimate the observed north-south gradient for the period of 1995 to the present (Fig. 3b, thick blue line). This could be an indication that in the UNFCCC-based scenario the distribution of sources is not correct, i.e. that emissions are overestimated in the southern hemisphere or in the tropics and underestimated in mid latitudes of the northern hemisphere. Except for Australia and New Zealand, inhabited regions of all Annex I countries are located in northern mid-latitudes (30° N–60° N), while large areas of Non-Annex I countries (i.e. Southern China, India and Brazil) are located in subtropical and tropical regions of the Northern and Southern Hemispheres. Consequently, a shift of $SF_6$ emissions from Annex I to Non-Annex I countries (e.g. after the beginning of the 1990s) would imply a southward redistribution of the global $SF_6$ source. This in turn should result in a smaller $SF_6$ mixing ratio difference between the north and the south, as simulated with the UNFCCC-based emission scenario after about 1992 (Fig. 3b).

Besides incorrect distribution of sources, model-data mismatch can, however, also be caused by several other factors: Meridional mixing in the model may be over-estimated, resulting in under-estimation of inter-hemispheric $SF_6$ differences or vice versa. Also, the observations at Alert and Neumayer may not necessarily be representative for the large GRACE model boxes. Atmospheric transport between the different boxes in GRACE, which was kept constant from year to year, has been optimized using bomb $^{14}CO_2$, $^{10}Be/^{7}Be$, but also $SF_6$ with estimates of the total $SF_6$ source taken from Levin and Hesshaimer (1996), assumed to be spatially distributed according to electricity production (Prather et al., 1987). However, this transport optimization still allows for an uncertainty of hemispheric residence times on the order of ±25%. Indeed, increasing hemispheric residence times by 25% would bring model simulations with the UNFCCC-based scenario almost into agreement with the observations (upper boundary of the blue hatched area in Fig. 3b; the mean inter-hemispheric exchange time was increased here from 0.95 to 1.19 years); in this case the EDGAR distribution would over-estimate the north-south difference (upper boundary of the red hatched area in Fig. 3b). At this stage, using the observed north-south difference of $SF_6$ we thus cannot firmly reject one of the two $SF_6$ emission scenarios. This is mainly because of the lack of really independent validation of transport properties in our model, i.e. independent from any prior calibration with $SF_6$

or other tracers, whose emissions also have source distributions similar to that of electricity production, such as fluorocarbons (Prather et al., 1987). A possible tracer for transport validation may be $^{85}$Krypton (Jacob et al., 1987; Levin and Hesshaimer, 1996) which is mainly emitted from nuclear fuel reprocessing plants. However, these $^{85}$Krypton emissions are essentially confined to a few large point sources (Winger et al., 2005), a distribution not suitable for transport validation of our coarse resolution GRACE model.

## 6 Conclusions

Rigorously assessing the reliability of the EDGAR or the UNFCCC-based emission *distribution*, and validation of reported emissions by Annex I countries may be possible with a high resolution atmospheric transport model; however, such a model needs to be very well validated to correctly simulate atmospheric transport and mixing, i.e. with different tracers that have different but well-known source characteristics and distribution. Also, this would require a denser observational network. At present we are thus left with only the evidence from total Non-reported $SF_6$ emissions as well as from specific $SF_6$ emissions per electricity production, which suggests, that Annex I reported UNFCCC emissions during the 1990s (and possibly until today) are too low. This suggestion is confirmed by the EDGAR (2009) data base which assumes much lower emission factors for leakage and maintenance for Annex I than for Non-Annex I countries, but which results in similar emission intensities of $SF_6$ per GWh electricity produced (J. G. J. Olivier, personal communication, 2010). Annex I reported emissions may be too low because of intrinsic uncertainties of estimated $SF_6$ stored in end-use applications in the US and Europe (Maiss and Brenninkmeijer, 1998), and possibly due to underestimated emissions from economies in transition. The accelerating increase of *global* $SF_6$ emissions since the end of the 1990s may be linked to rising emissions from Non-Annex I countries, which *qualitatively* agree with their economic growth (e.g. China) (RHGDP, 2008). However, as long as these countries are not obliged to report their emissions to UNFCCC, there will remain large inaccuracies in related bottom-up emission estimates.

Our study clearly shows that top-down verification of reported emissions is without alternative for greenhouse gases budgeting. On a country level, such validation can, however, only be achieved with a dense network of high-precision atmospheric observations in combination with adequately calibrated atmospheric transport models. Verification of *total global* $SF_6$ emissions by atmospheric measurement is accurately possible *without* a sophisticated transport model, even with only one or a few globally distributed background stations. This mechanism should, therefore, be included as an additional measure in the Kyoto reporting process, as it provides the only ultimate proof of total reported emissions (changes), at least for gases with well-defined sinks such as $SF_6$, and other fluorinated and chlorinated compounds.

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