

**Interactive comment on “Atmospheric histories and emissions of chlorofluorocarbons CFC-13 (CClF<sub>3</sub>), CFC-114 (C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub>), and CFC-115 (C<sub>2</sub>ClF<sub>5</sub>)” by Martin K. Vollmer et al.**

Reply to : Anonymous Referee #1

Received and published: 10 November 2017

This paper describes the atmospheric histories of CFC-13, CFC-114, and CFC-115; substances controlled under the Montreal Protocol on Substances that Deplete the Ozone Layer. The authors present atmospheric measurements and measurements of air archived in cylinders and firn, and use these to estimate historical emissions. They also investigate regional emissions using high-frequency measurements at a site in Korea.

The results are significant in that they represent the first comprehensive study of atmospheric CFC-13. The results also complement a recent study of CFC-114. The Vollmer et al study includes new information on possible sources of these gases, including emission as impurities in other gases used in refrigeration. This study provides constraints on current emissions of gases controlled under the Montreal Protocol, and recent (possibly unexpected) increases in emissions.

Reply: We thank the referee for his/her thorough comments and have provided some answers below, which we have incorporated into a revised manuscript that would be ready to distribute in case the editor decides to proceed to the next review step with this manuscript.

**General Comments**

This paper is comprehensive, well-written, and based on well-established methods. I do not have any objections to publication. The overall body of work and technical information available in the Supplement will be of interest to others in this field.

**Specific Comments**

Table 1: Why not include GWP from WMO 2014 (CFC-114, CFC-115)? Also, the lifetime of CFC-13 was reported as 640 yr in WMO 2006 and WMO 2011, but is not listed in Table 1.

Reply: These suggestions are now added to the table.

Table 2: How do you define a “hot spot”? It looks like there could be “hot spot” emissions of CFC-114 also in 2013.

Reply: We have used the term “hot spot” in a loosely way of describing an area with enhanced emissions. We have now removed the wording in one place in the text and described it a bit more in detail in Table 2. It is true that there are also areas of enhanced emissions for CFC-114 but these are by far not as pronounced as for CFC-115, and for CFC-114 we do not have corresponding factory locations at hand (as the HFC-125 factory locations we have for CFC-115).

Pg. 8, Line 2: You use the term “primary calibration scale”. Consider using “interim calibration scale” instead since you refer to the “interim” scale on line 10.

Reply: done, this makes it more clear.

Pg 9, Line 28: Add “(See Supplement)” after “Extrapolation of the AFEAS data, as in Daniel and Velders (2007)”

Reply: Done

Pg. 9, Line 33: I don’t see emission scenarios from 1930-2100 in the 2006 Assessment Report. Do you mean atmospheric abundances from 1990-2040 (Fig 8-2) or 1955-2100 (Table 8-5)?

Reply: Emission scenarios were used to derive atmospheric abundances. To clarify this, we change the text to “*Some of these data were used in the Ozone Assessment Report 2006 to*

produce emission scenarios for 1930--2100 on which the atmospheric abundances for the same period were based (Daniels and Velders, 2007)".

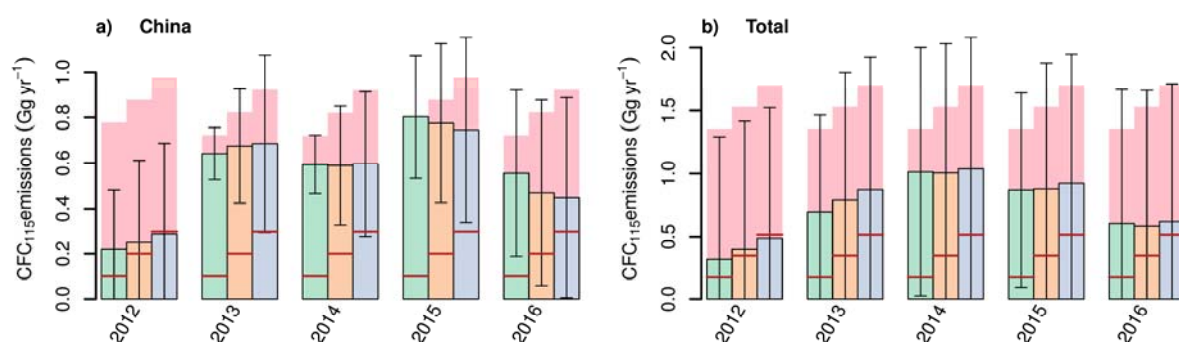
Pg 12, Line 11: What is meant by "regularization"? Do you simply mean "additional constraints"?

Reply: We have now removed that part and it now reads: *"The characteristics of these data necessitate the use of constraints on the inversion to avoid unrealistic oscillation in the reconstructed mole fractions or negative values of mole fraction or emissions."* In the Supplement we have described the regularization for the coefficient alpha in more detail.

Pg 13, Line 14: Can you comment on the sensitivity of posterior emissions to the magnitude of the priors?

Reply: We analyzed the sensitivity of our inversion results towards the magnitude of our prior. For differences of the prior of +/- 50 % we don't get a strong response in the a-posteriori emissions. For some years the a-posteriori emissions remain practically independent of the prior, whereas for other years the differences resulting from different priors are well within the uncertainty estimates of the a-posteriori (see figure below). We added the following sentence to the revised manuscript (in the Supplement):

*"The choice of the magnitude of the prior emission was tested by running additional sensitivity inversions with 50% higher and lower prior emissions. The influence on the a-posteriori emissions was small compared to the a-posteriori uncertainty estimate."*



Pg. 15, Line 33: "more unexpected" than what?

Reply: This is indeed poorly phrased: We have now rephrased this part (also following some suggestions of another reviewer), and the text now reads: *"For all three CFCs we find persistent lingering emissions in the past decades. While the emissions for CFC-13 and CFC-114 have remained stable within uncertainties, those for CFC-115 have increased in recent years."*

Pg. 17, Line 29: Suggest "projected by Velders and Daniel . . ." since 2016 emissions would have been a projection in 2014

Reply: Done

Pg. 18, Line 10: Do you mean that a "change" in the latitudinal gradient has not been detected? There is clearly a gradient (N-S).

Reply: This is indeed a wrong statement we have made. We suggest to change these sentences to: *"The observed latitudinal gradient in CFC-114 abundance suggests predominant NH emissions. Pollution events in the Asian region, as detected from our high-resolution in-situ measurements, and the absence thereof in other regions suggest that at least some of these emissions originate from Asia. Increased abundances of CFC-114a, compared to Cape Grim,*

from samples collected in Taiwan were reported on by Laube et al. (2016), partially supporting our findings.”

Pg 18, Line 19: Possibly re-phase. The use of “improvement/improved” in same sentence not entirely clear. Or refer to Supplement for model performance?

Reply: We agree and have revised the sentence. It now reads: *“The overall transport model performance and its improvement through the inversion (see Supplement) were considerably better as in the case of CFC-13, lending sufficient confidence in the inversion results.”*

Figure 2: I'm not sure how the blue line (SPO) adds to the story, being based on only one sample from the SPO firm. Since this paper does not focus heavily on firm results, it might be better to keep the SPO sample “point”, but delete the “line”.

Reply: We prefer to keep the line in there, leaving it out would make the reader wonder why it is not there. It also helps to put the SPO point into perspective.

Figure 6: Hard to tell the difference between orange and red lines.

Reply: Agreed, we have now changed the colors and hope that the two lines can now be distinguished more easily.

Figure S4: panels “b” and “c” look very similar. Perhaps draw a circle around green points in “c” to draw attention to what is different?

Reply: We agree, but we have decided to highlight the difference in a different way by changing colors and symbol sizes. We have now also modified the caption to clarify the purpose of this figure.

Pg S18, Line 11: Something still missing [Cathy to calculate this value]?

Reply: Thank you for spotting this, this is now fixed, it reads: *“The difference it makes to the CSIRO inversion, when we consider only zero mole fraction at 52 m DSSW20K, or with both the zero and non-zero value, is within the uncertainties in emissions.”*

Pg. 17, Line 4: Seems like a sentence is needed here to clarify that CFC-13 emissions were not reported by Fraser et al, 2013 (if that is what you are saying). I suggest: “CFC-13 was previously found in the emissions from aluminum plants (Penkett et al., 1981; Harnisch, 1997), but was not reported by Fraser et al (2013) from a similar study.” And then follow with: “On re-analysis of the Fraser et al samples, we found enhancements over background levels of 45 ppt – 130 ppt in the various smelter samples. “

Reply: In the Fraser et al. (2013) publication, CFC-13 emissions were reported as absent, which we discovered to be an erroneous statement. We have now rephrased this part, hoping that it is now clear that Fraser et al. (2013) reported zero CFC-13 emissions but that our re-analysis showed significant CFC-13 emissions.

#### Technical Corrections

Pg 7, Line 17: Add comma between “measurements” and “samples”

Reply: done

Pg 14, Line 5: delete “again”

Reply: done

Pg 15, line 11: Suggest: “Its growth rate then slowed during the mid-2000s to near zero, with . . .”

Reply: Changed according to the suggestion, but left the word “rate” out.

Pg 16, Line 3: Suggest substitute “removal rates” for “removal fluxes”

Reply: We prefer to keep the term “fluxes” as the term “rates” could here be confusing and e.g. mistaken for chemical reaction rates.

Pg. 18, Line 25: add “since 2010” after “steadily”

Reply: done

Pg. 19, Line 7: Suggest: “Large posterior emissions were detected for all analyzed years . . .”

Reply: We agree and changed the sentence accordingly.

Pg. 19, Line 13: I calculate a different number (0.63 kt) for the average Chinese emissions in the years 2013-2016 from values in Table 2 (0.68, 0.59, 0.78, 0.47).

Reply: This is an embarrassing mistake we made, it is now corrected --- thanks for spotting it.

Pg. 19, Line 13: Total Chinese emissions in 2012: (0.23±0.38 kt yr<sup>-1</sup>) does not match value shown in Table 2 for 2012.

Reply: Same as above, and we have now cross-checked other numbers as well to ensure that not more error of that kind are present.

Fig. 9 caption: change “derives from” to “was derived from”

Reply: We changed that phrase to: “... is the result from ...”

Fig. S4: “Laube et al 2017” should be “Laube et al 2016” (two places in figure, caption is correct)

Reply: Thank you for spotting this, it is now fixed.

Pg. S16, Line 8: Suggest replacing “emissions are rather faster” with “emissions occur earlier in the life-cycle”

Reply: We agree and have now changed to the suggested wording.

Pg. S17, Line 12: This sentence does not read well. “The very crude approach we have taken is still based on the above assumption of similarities to CFC-115 but are comparing production data, . . .”. Do you mean “ . . . but is based on a comparison of production data”?

Reply: Agreed. We changed the wording of several sentences in this paragraph to provide more clarity.

**Interactive comment on “Atmospheric histories and emissions of chlorofluorocarbons CFC-13 (CClF<sub>3</sub>), CFC-114 (C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub>), and CFC-115 (C<sub>2</sub>ClF<sub>5</sub>)” by Martin K. Vollmer et al.**

Reply to Anonymous Referee #2

Received and published: 15 November 2017

This is an impressive, comprehensive, thought-provoking, and very useful paper that describes the full atmospheric histories over eight decades for three CFCs that are present in the atmosphere at much lower concentrations than the primary CFCs. It documents continued emissions and, surprisingly, notable increases in global emissions of CFC-115 that are rightfully indicated as being difficult to explain given the global production phase-out for CFCs. New sources for emissions of these gases are identified and, using inverse analyses of high-frequency atmosphere data, continuing emissions of CFC-114 and -115 from East Asia (China) are inferred in amounts that account for a large portion of the ongoing global emissions.

Reply: We thank the referee for his/her thorough comments and have provided some answers below, which we have incorporated into a revised manuscript that would be ready to distribute in case the editor decides to proceed to the next review step with this manuscript.

The only substantive issue I have with the manuscript relates to two conclusions that I'm not convinced are defensible, given our uncertain knowledge of lifetimes. Once these are reconsidered, I think the paper is ready to publish.

Those issues:

1) on cumulative emission vs production comparisons (abstract and text), it seems necessary to express the influence of uncertain lifetimes on the differences argued for here for CFC-114. I pretty sure the lifetime uncertainty and hence uncertainty on derived global emissions is much larger than 10%, implying that one can't reliably conclude that there is a 10% discrepancy here or, by implication, evidence for significant unreported production. The authors might also consider if a discussion of bank magnitudes instead of cumulative emissions provides more insight (discussed below).

Reply: We agree with the reviewer that the uncertainties in the lifetimes are far too big to conclude on a significant discrepancy between cumulative emissions and production. We have now deleted the corresponding sentence from the abstract and will limit the discussion on this to the text. Then in the text, we change the wording. For CFC-114, we remove the word 'significantly' and add a comment, such that it now reads: *“Our cumulative emissions until 2016 (587 kt for the Bristol inversion and 586 kt for the CSIRO inversion) are higher than the cumulative emissions and productions derived by AFEAS from an inventory (521 kt) and those projected by Velders and Daniel (2014) (528 kt). However, despite this ~10% difference they agree within the large uncertainties, in particular those of the CFC-114 lifetime (Table 1).”* With regard to comparison of the cumulative emissions to those by Laube et al. (2016), see further below, where the reviewer has addressed this specifically. As for CFC-115, we write that our cumulative emissions agree with production within the large uncertainties of the lifetime.

2) the assertion that emissions of CFC-114 and CFC-13 have increased in recent years. It is not at all clear from the figures of mole fraction rate of change or derived global emissions that the authors are correct in stating that emissions of these gases have actually increased in recent years beyond the variability and uncertainty envelope of recent years.

Reply: We agree with the reviewer. We have previously assumed that the uncertainty envelope is dominated by lifetime uncertainties and primary calibration uncertainties, which both would need to be excluded for the assessment of a potential trend in the growth rates and emissions. However when excluding these systematic uncertainties in an additional analysis, stimulated by the reviewer's comment, the overall uncertainties do not get significantly smaller. We therefore



agree with the reviewer and removed all statements related to increase of growth rates and/or emissions for CFC-13 and CFC-114 in recent years. We now state that they have not declined (within the uncertainties).

While that abstract states that CFC-115 impurity in HFC-125 production cannot account for all of the ongoing CFC-115 emission, consider also stating that it isn't likely that this impurity source, given an average impurity content of  $10^{-3}$  to  $10^{-4}$  in HFC-125, is the cause of the identified CFC-115 emission increase in recent years (at least this is what I conclude looking at the numbers).

Reply: This is correct and we decided to include a statement about this in the abstract and in the text. This required some re-arranging of sentences, and it reads now: *"We find impurities of CFC-115 in the refrigerant HFC-125 (CHF<sub>2</sub>CF<sub>3</sub>) but if extrapolated to global emissions, they can neither account for the lingering global CFC-115 emissions determined from the atmospheric observations, nor for their recent increases."*

Consider mentioning 500-yr GWPs, given that this is the timeframe for atmospheric destruction for these gases so is certainly relevant... Along those lines, consider mentioning how CFC-115 impurities affect the 500-yr GWP of HFC-125 use (small effect it seems, on average).

Reply: This is a good point. We have now added the 500-yr GWPs to the Table 1 (Climate Metrics) and mention the large 500-yr GWP for CFC-13 in the introduction.

As for the second part (effect on 500-yr GWP of HFC-125), this is an interesting thought. However since this would be about the topic HFC-125, it would not add to the CFC stories, and given that this manuscript is already rather long, we decide to not elaborate on this topic. We agree that the effect would probably be small. It also raises the question on what compounds/life cycle effects should be added to the "process" HFC-125 use – if impurities should be added, then should e.g. emissions (e.g. CO<sub>2</sub>) of other parts of the life cycle (installation, maintenance) be added to that "HFC-125 use".

Discussion of bank sizes relative to the current emission rate as a fraction of peak emissions. CFC-12 recently has been ~10%, CFC-11 is higher... It mostly comes down to the size of banks and release rates from those banks.

Reply: Yes, we agree on this. Nevertheless, it is surprising that for CFC-13, it is >10% of the peak emission, or >15% if only the last few years are considered. And remaining high. Given the ban and assuming that the life-cycle of CFC-13 is similar to CFC-114 or CFC-115, this is not really expected. We do agree with the reviewer, a few years ago, CFC-12 has also been around 10% of the peak emissions, which is somewhat surprising also. CFC-11 cannot really be compared with these compounds because of its installment in foam – its life-cycle is much different, which is likely causing a less pronounced peak and a longer tail, which is still a large fraction (20%) of the peak. We don't see a need to change the text with regard to this comment.

The authors have done a good job of discussing the issue of CFC-114 and CFC-114a being measured as one chemical in this work and in most previous studies. The text is still confusing in places, however, as CFC-114 is used to indicate the sum of both and just the one isomer in studies in which separation was accomplished (in caption of Figure 5, to name one spot; in discussion of lifetime too, are lifetimes stated for 114 or is it 114+114a here? To clarify this I'd suggest not using CFC-114 to mean CFC-114 + CFC-114a; consider CFC-114\* or CFC-114s (where s=sym as in Supplement) or something else to refer to the sum. I presume the presence of 114a with 114 relates to unavoidable co-production during synthesis and an inability to separate these isomers before sales, so that the presence of both in perhaps changing source ratios relates to different production pathways. I didn't see this mentioned, or missed it if it was.

Reply: We agree that some of the terminology is still confusing. We have therefore adopted a new nomenclature for this article after intense discussions among co-authors, and we now refer to  $\Sigma$ CFC-114 as the combined (mainly Medusa GCMS) measurements of CFC-114 and CFC-114a. This comment by the reviewer, and an additional information, which became available on

the CFC-114/CFC-114a of the reference material used to produce the primary standards, have led us to completely re-write the Supplement S.3-4. The reviewer's comment on whether the lifetime statements apply to CFC-114 or CFC-114 + CFC-114a is very stimulating. In fact this question applies to the climate metrics (e.g. Table 1) in general. We have now investigated this further by consulting original literature of laboratory experiments, from which some of these climate metrics have been deduced. Interestingly even though these studies clearly target CFC-114 (CCIF2CCIF2) alone, there is no mentioning of potential CFC-114a impurities in their reference material, or any comment related to potential purification. Nevertheless it is well known that it is very difficult to produce pure CFC-114, and there are examples of impurities found at significant levels (5%). Such an impurity would have had an impact on the UV absorption spectra and ultimately the lifetime and other climate metrics. We have now added some comments on this in the introduction, and we extended Table 1 by stating that the values we cite from the literature should be for CFC-114, but could be biased.

Reconsider the discussion of banks and "cumulative emissions", as these seem different ways to express the outcome of essentially similar analyses. Yet it is difficult to ascertain the differences from the previous analyses (e.g., p. 9, line 28-31, bank determinations for 2016 are indicated to be v. small for 114 and 115 based on AFEAS emission histories and an analysis by Daniel and Velders (2007), that presumably considered atmospheric measurements in some way) and what the authors find here, which is expressed as "cumulative emissions" rather than an implied bank magnitude. This is relevant for 114, in particular, given the quite different history derived here compared to what has been considered in the past. I'm guessing that the new results suggest a negative bank for CFC-114 recently and a minimal bank for CFC-115 (i.e., <1 year's worth of emission). Typically, having an estimate of bank size is useful to consider for understanding current emission rates, and availing yourself of this would seem a useful addition. In the case of 114 and 115 it seems clear that any emission from banks are less likely to be the source of these ongoing emissions, since bank sizes estimated here are negligible (albeit their magnitude is not precisely known owing to lifetime uncertainty).

Reply: As the reviewer stated earlier, lifetime uncertainties are large and an assessment of implied bank size by comparing with the bottom-up emissions/banks is tagged with these uncertainties. From our descriptions of the banks in Section 2.7 it becomes obvious that those for AFEAS are negligibly small and those by Daniel and Velders are also not in line with the currently high emissions that we observe. As the reviewer states, the bank consideration is essentially a different way of expressing what we already state. We cannot state that the results suggest a negative bank for CFC-114 given the large uncertainties in the lifetime. The comparison of the cumulative emissions up to 2016 is, again within the lifetime uncertainties, a valuable approach to interpret the very different CFC-114 emission histories we find compared to the bottom-up approach. Nevertheless we add a sentence for each CFC-114 and CFC-115, where we compare our recent emissions with the banks of AFEAS and Velders and Daniel for 2016, to re-iterate in slightly different words, that the recent emissions we estimate are not in line with the model of bank and emissions by these bottom up approaches. The suggestion of the reviewer that "any emission from banks are less likely to be the source of these ongoing emissions" is a statement that we cannot support as such. We do not know if some shorter term banks have been built up in recent years, and hence we would need to launch a discussion on long-term and short-term banks, which does not seem appropriate here. For  $\Sigma$ CFC-114 the additional sentence now reads: *"Our estimates of the annual emissions for the recent years are large compared to the banks proposed by AFEAS (0.2 kt for 2016) and Velders and Daniel (2014) (6.4 kt for 2016) and are suggestive of additional recently-produced  $\Sigma$ CFC-114."* Similarly, the additional sentence we propose for CFC-115 is: *"Nevertheless, our annual emissions for the recent years are large compared to the banks proposed by AFEAS (<0.01 kt for 2016) and Velders and Daniel (2014) (8.6 kt for 2016) and are suggestive of additional, recently-produced CFC-115."*

What I find very curious is the peak emission derived for CFC-114 the 1970s (the first peak). This peak may generate the apparent negative bank today (assuming lifetimes are accurate). While a discussion is included to suggest it is a robust result, no discussion of its plausibility is presented. Given that this history is very different than the production-derived emission history, if it is accurate

does it suggest emissions from a process unrelated to reported production (byproduct emission)? Does the timing correspond to other chlorinated & fluorinated ethane production histories, such as CFC-113? HCFC-142b had unusually high concentrations in the early CCAA record. Is the timing of that similar or not? Is it possible that the CFC114&114a sum is causing trouble here (the Supplement indicates that the error created could be an offset in time), given that the true ratio is not known before 1975?

Reply: The referee is correct in saying that there is no plausibility discussion on the occurrence of two emission peaks over time. We would find any potential explanation as too speculative and hence prefer to not elaborate on these in the paper. It is not a-priori unrealistic that emissions had changed in that way from the main use of  $\Sigma$ CFC-114, perhaps there was better containment for a while, or excessive emissions (causing the first peak) or temporal changes in the productions and uses. While the idea of byproduct emissions at that time is interesting, we find it too speculative to be mentioned here. It is not possible that the CFC-114a/CFC-114 is causing trouble here, the potential errors involved with this are too small and are also gradual. Unlike the reviewer states, the true CFC-114a/CFC-114 ratio is somewhat known for before 1975, see firm air results by Laube et al., 2016 (also compare measured isomers in the firm (supplement) and modeled ratio in their main paper).

Figure 3. I don't understand why the "zero growth" line is included in the figure. This line has little meaning other than to indicate steady-state, which isn't emphasized in paper, and it's clearly evident which side of steady state emissions are on currently, given one look at Figure 4. It seems to me the important reference line to retain here is the one indicating growth for zero emission—this other line I find distracting.

Reply: The “zero growth” line serves both the purposes of providing a visual aid of where zero is in these plots (similar to the horizontal black lines for providing a zero line for the abundances), and to denote the steady-state balance between emissions and destructions. It is correct that some of this can be seen in Fig. 4, but we find it important to have this information in the same figure as the actual growth rates. Also Fig. 4 goes only back to 2004, so for example the “crossing over” for CFC-114 in about 1996 is not seen in Fig. 4. Further, the slow-down in the decline of CFC-114 abundances (or the increase in the growth rate) can be much better viewed in the presence of that “zero growth” reference line. Also for example for CFC-115, the “zero growth” line for the most recent years is outside the full uncertainty bands for the last few years, which is another information one would not get from Fig. 4. For these reasons we have decided to leave these “zero growth” lines in the figure, but we now change the plotting scheme (colors, lines) to avoid confusion and distraction, and we have modified the legend.

Figure 4 caption: the term "pollution filtered" isn't entirely clear. I presume you mean background atmospheric concentrations? Consider a different term.

Reply: We agree that this has not been termed clearly and we have now changed the text to read: *“Abundances of the chlorofluorocarbons CFC-13 (a),  $\Sigma$ CFC-114 (b), and CFC-115 (c) at selected stations of the AGAGE (Advanced Global Atmospheric Gases Experiment) network. These in situ data are binned into monthly means after applying a pollution filter to limit the records to samples under background conditions (O'Doherty et al., 2001; Cunnold et al., 2002). Vertical bars are standard deviations of the monthly means (1 sigma).”*

p. 2, line 2. Consider additions and changes: "larger than would be expected from zero emissions \*\*given currently estimated lifetimes\*\*\*". Also, "unaltered" is ambiguous meaning here. I think you mean "constant" or "unchanging".

Reply: We believe that the “given currently estimated lifetimes” is implicit. We have changed “unaltered” to “unchanging”.

p. 3, line 35. This isn't true a-priori. Be sure to comment on the lifetime difference for 114a and 114 to make clear to the reader if it is an important factor in affecting changes in the relative atmospheric abundance of these gases.



Reply: We agree that a comment on the lifetimes needs to be included to make this statement correct. We suggest a rephrasing to: *“These results showed for the first time an increasing ratio of CFC-114a/CFC-114 in the atmosphere, and, given a shorter lifetime of CFC-114a compared to CFC-114, pointing to an increasing CFC-114a/CFC-114 emission ratio over time”*.

p. 17, line 30, was the same lifetime used in Laube et al? Seems important to consider before discussing potential differences.

Reply: This is a good point. Regardless of what Laube et al 2016 have used for the (symmetric) CFC-114 lifetime (looks like they have used 189 yrs, same as we have used), they have used compound-dependent lifetimes (i.e. for CFC-114a they have used 102 yrs), while we have used the 189 yrs for the combined  $\Sigma$ CFC-114 measurements. Also, primary calibration scales are different for the two networks, which we deliberately do not correct for in our Fig. 6. Given these considerations, a quantitative comparison (as we had done in our first submission) of our (cumulative) emissions to those by Laube is questionable and hence we decided to delete that statement. Leaving it in there would have caused a lot of hand-waving and would have made the manuscript longer again.

p S18, line 11 (Supplement text) don't forget to add the missing value here.

Reply: done, it now reads *“The difference it makes to the CSIRO inversion, when we consider only zero mole fraction at 52 m DSSW20K, or with both the zero and non-zero values, is within the uncertainties in emissions.*

Regarding firn results, I didn't see the detection limit for instrumentation mentioned in the text or supplement, but would be useful to add.

Reply: Detection limits are given in the supplement Table S1. We now refer to that in the text by extending the sentence on flag values to “Further description of the flag values and the detection limits are given in Table S1. “.

# Atmospheric histories and emissions of chlorofluorocarbons CFC-13 (CClF<sub>3</sub>), $\Sigma$ CFC-114 (C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub>), and CFC-115 (C<sub>2</sub>ClF<sub>5</sub>)

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**Abstract.** Based on observations of ~~three chlorofluorocarbons~~, the chlorofluorocarbons CFC-13 (chlorotrifluoromethane),  $\Sigma$ CFC-114 (combined measurement of both isomers of dichlorotetrafluoroethane) and CFC-115 (chloropentafluoroethane) in atmospheric and firn samples, we reconstruct records of their tropospheric histories spanning nearly eight decades. These compounds were measured in polar firn air samples, in ambient air archived in canisters, and in-situ at the AGAGE (Advanced  
5 Global Atmospheric Gases Experiment) network and affiliated sites. Global emissions to the atmosphere are derived from these observations using an inversion based on a 12-box atmospheric transport model. For CFC-13, we provide the first comprehensive global analysis. This compound increased monotonically from its first appearance in the atmosphere in the late 1950s to a mean global abundance of 3.18 ppt (dry air mole fraction in parts-per-trillion, pmol mol<sup>-1</sup>) in 2016. Its growth rate has decreased since the mid 1980s but has remained at a surprisingly high level of 0.02 ppt yr<sup>-1</sup> since the late 2000s-, resulting  
10 in a continuing growth of CFC-13 in the atmosphere.  $\Sigma$ CFC-114 increased from its appearance in the 1950s to a maximum of

16.6 ppt in the early 2000s, and has since slightly declined to 16.3 ppt in 2016. CFC-115 increased monotonically from its first appearance in the 1960s and reached a global mean mole fraction of 8.52 ppt in 2016. Growth rates of all three compounds over the past years are significantly larger than would be expected from zero emissions. Under the assumption of ~~unaltered~~ unchanging lifetimes and atmospheric transport patterns, we derive global emissions from our measurements, which have remained unexpectedly high in recent years: Mean yearly emissions for the last decade (2007–2016) of CFC-13 are at  $0.48 \pm 0.15$  kt yr<sup>-1</sup> (>15% of past peak emissions), of ΣCFC-114 at  $1.90 \pm 0.84$  kt yr<sup>-1</sup> (~10% of peak emissions), and of CFC-115 at  $0.80 \pm 0.50$  kt yr<sup>-1</sup> (>5% of peak emissions). Mean yearly emissions of CFC-115 for ~~2014–2016 are 1.08~~ 2015–2016 are 1.14  $\pm 0.50$  kt yr<sup>-1</sup> and have more than doubled compared to ~~2009. Cumulative global emissions for CFC-114 derived from observations through 2016 exceed the global cumulative production derived from reported inventory data by >10% while those for CFC-115 agree well~~ the 2007–2010 minimum. We find CFC-13 emissions from aluminum smelters ~~and but if extrapolated to global emissions, they cannot account for the lingering global emissions determined from the atmospheric observations. We find~~ impurities of CFC-115 in the refrigerant HFC-125 (CHF<sub>2</sub>CF<sub>3</sub>) but if extrapolated to global emissions ~~neither of them can, they can neither~~ account for the lingering global CFC-115 emissions determined from the atmospheric observations, nor for their recent increases. We also conduct regional inversions for the years 2012–2016 for the north-east Asian area using observations from the Korean ~~Gosan AGAGE site~~ AGAGE site at Gosan, and find significant emissions for ΣCFC-114 and CFC-115, suggesting that a large fraction of their global emissions currently occur in north-eastern Asia and more specifically on the Chinese mainland.

## 1 Introduction

Chlorofluorocarbons (CFCs) are very stable man-made compounds known to destroy stratospheric ozone. For this reason they were regulated for phase-out under the Montreal Protocol on Substances that Deplete the Ozone Layer, and its subsequent amendments. The ban has been effective since the end of 1995 for developed countries and the end of 2010 for developing countries. The ban is put on production for emissive use and does not cover production for feedstock, or recycling of used CFCs for recharging of old equipment, the latter being applied particularly in the refrigeration sector. While the dominant CFCs in the atmosphere are CFC-12 (CCl<sub>2</sub>F<sub>2</sub>), CFC-11 (CCl<sub>3</sub>F), and CFC-113 (C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>), this article reports on CFC-13 (chlorotrifluoromethane, CClF<sub>3</sub>), ΣCFC-114, here defined as the combined ~~isomers~~ isomer 1,2-dichlorotetrafluoroethane (CClF<sub>2</sub>CClF<sub>2</sub>, CFC-114, CAS 76-14-2) and 1,1-dichlorotetrafluoroethane (CCl<sub>2</sub>FCF<sub>3</sub>, CFC-114a, CAS 374-07-2), and CFC-115 (chloropentafluoroethane, C<sub>2</sub>ClF<sub>5</sub>). The compounds were mainly used in specialized refrigeration, hence their abundances in the atmosphere are considerably smaller than those of the three major CFCs. However, their atmospheric lifetimes are significantly longer (see Table 1 for climate metrics). Ozone depletion potentials (ODPs) for the three compounds are high and their radiative efficiencies are high, thereby yielding high global warming potentials (GWPs), with ~~that those~~ for CFC-13 (13 900 ~~for~~ GWP-100yr and ~16 000 for GWP-500yr) only surpassed by very few other greenhouse gases.

Removal of these CFCs from the atmosphere occurs predominantly in the stratosphere through ultraviolet (UV) photolysis and reaction with excited atomic oxygen (O(<sup>1</sup>D)), and to a lesser extent by Lyman-α photolysis in the mesosphere. The

atmospheric lifetime for CFC-13 of 640 yr used in the present study is based on a study by Ravishankara et al. (1993) and is dominated (80%) by the removal through reaction with  $O(^1D)$ , see Table 1. The lifetimes for CFC-114 and CFC-115 have recently been revised as part of the SPARC (Stratosphere-troposphere Processes And their Role in Climate) lifetimes assessment (SPARC, 2013). In that study the lifetime of CFC-114 has been reported as 189 yr (153–247 yr) with 72% of the loss from UV-photolysis and 28% from reaction with  $O(^1D)$  (Burkholder and Mellouki, 2013). However, our closer inspection of the literature from laboratory studies, used to derive UV absorption spectra and  $O(^1D)$  reaction rates (Sander et al., 2011), suggests that no consideration was given in these older studies with regard to potential impurities of CFC-114a in CFC-114. Such impurities are likely present (Supplement, Laube et al. (2016)), in which case they could have biased the CFC-114 UV absorption spectra leading to an underestimate of its lifetime, as its absorption is significantly weaker compared to that of CFC-114a in the critical photolysis wavelength region (J. B. Burkholder, pers. comm., Nov. 2017, Davis et al. (2016)).  $O(^1D)$  kinetics for the two isomers are similar and hence would not have affected lifetime estimates as much, if such impurities were present (Baasandorj et al., 2011, 2013; Davis et al., 2016). For CFC-115 the lifetime has been significantly reduced from 1700 yr in earlier studies (Ravishankara et al., 1993) to 540 yr (404–813 yr) (SPARC, 2013) mainly due to significantly revised  $O(^1D)$  kinetics (Baasandorj et al., 2013). This revised lifetime gives 37% of the loss derived from UV-photolysis and 63% from reaction with  $O(^1D)$  and a minor contribution from Lyman- $\alpha$  photolysis (Burkholder and Mellouki, 2013).

CFC-13 and its R-503 blend with 40% by mass of HFC-23 ( $CHF_3$ ) have been used as special-application low-temperature refrigerants (Calm and Hourahan, 2011; IPCC/TEAP, 2005) but small enhancements in CFC-13 were also found in the emissions from aluminum plants (Penkett et al., 1981; Harnisch, 1997). CFC-13 could also be present as an impurity in CFC-12 ( $CCl_2F_2$ ) due to over-fluorination during production.

Reports on atmospheric CFC-13 in peer-reviewed articles are rare. Early measurements were reported on by Rasmussen and Khalil (1980), Penkett et al. (1981) and Fabian et al. (1981), who measured a first atmospheric vertical profile of this compound. CFC-13 measurements were made by Oram (1999) in the samples of the Southern Hemisphere Cape Grim Air Archive (CGAA) covering 1978 – 1995. He found increasing mole fractions from 1.2 pptv (therein reported in parts-per-trillion by volume) in 1978 to 3.5 pptv in 1995. Emissions deduced for this period peaked in 1987 at  $3.6 \text{ kt yr}^{-1}$ . Culbertson et al. (2004) published long records of CFC-13 measurements in background air from stations in the USA and Antarctica. For their longest record from Cape Meares (Oregon, USA), they reported on a near-constant growth of CFC-13 for the earlier part of the record with the tropospheric abundance leveling off in the late 1990s at  $\sim 3.5$  pptv.

$\Sigma$ CFC-114 was used as refrigerant, blowing agent, and aerosol propellant (Fisher and Midgley, 1993; IPCC/TEAP, 2005).  $\Sigma$ CFC-114 is listed as a refrigerant in blends R-400 with CFC-12 in various proportions, and in R-506 with 55% by mass HCFC-31 ( $CH_2ClF$ ) (Calm and Hourahan, 2011; IPCC/TEAP, 2005). It was also used unblended in specialized refrigeration e.g. in U.S. naval equipment from where it was phased out over the course of several decades following the Montreal Protocol ban (Toms et al., 2004; IPCC/TEAP, 2005). Uranium isotope effusion is a process that, at least in the past, involved significant amounts of  $\Sigma$ CFC-114 for cooling, but now PFCs are used as a substitute (IPCC/TEAP, 2005).

Some of the first  $\Sigma$ CFC-114 measurements were conducted at urban sites in the 1970s by Singh et al. (1977) who reported elevated mole fraction up to 170 ppt (parts-per-trillion or  $\text{picomol mol}^{-1}$ ). Measurements in background air followed

(Singh et al., 1979) and a transect across the equator in 1981 showed a global mole fraction of 14 ppt (Singh et al., 1983). In the early 1980s Fabian et al. (1981, 1985) measured vertical profiles of  $\Sigma$ CFC-114 in the atmosphere and found a decreasing mole fraction from 10.5 pptv at 10 km to 2.7 pptv at 35 km. Hov et al. (1984) measured  $\Sigma$ CFC-114 of 10.9 ppt in samples collected from Spitsbergen in spring ~~1983-1983~~ and Schauffler et al. (1993) reported on measurements of  $\Sigma$ CFC-114 near the tropical tropopause ~~and also~~. Chen et al. (1994) measured vertical profiles and a first multi-year record in both hemispheres showing increases of CFC-114 at Hokkaido from 10 pptv in 1986 to 15 pptv in 1993, and a first indication of a slow-down of the atmospheric growth. This was also the first group that separated CFC-114 from CFC-114a. Oram (1999) also separated the two isomers and measured records from the CGAA covering 1978 – 1995 showing increases from 8.5 pptv to 16.5 pptv for CFC-114 and from 0.55 pptv to 1.75 pptv for CFC-114a. These results showed for the first time an increasing ratio of CFC-114a/CFC-114 in the atmosphere, ~~pointing to a variable ratio of their emissions and, given a shorter lifetime of CFC-114a compared to CFC-114, pointing to an increasing CFC-114a/CFC-114 emission ratio~~ over time. The first high-frequency measurements of  $\Sigma$ CFC-114 from Cape Grim for 1998 and 1999 showed an abundance of 16.7 ppt, no pollution events in the footprint of the station and no detectable trend (Sturrock et al., 2001). A first atmospheric long-term record of  $\Sigma$ CFC-114 was published by Sturrock et al. (2002) based on firn air measurements from Antarctica and using the CGAA record from Oram (1999), revealing an onset of growth of this compound in the atmosphere in the early 1960s. Martinerie et al. (2009) modeled atmospheric  $\Sigma$ CFC-114 records based on several firn air profiles and found a much earlier atmospheric appearance and larger abundances up to approximately 1980 compared to Sturrock et al. (2002). In a recent study, Laube et al. (2016) reconstructed atmospheric CFC-114 and CFC-114a histories of abundances and emissions based on CGAA and firn air measurements. The study confirmed the temporally variable ratio of the two isomer abundances, ~~which translate into~~ and revealed a CFC-114a/CFC-114 emission ratio that increased sharply in the early 1990s, but gradually declined ~~since then~~ thereafter.

CFC-115 was used as refrigerant R-115 and occurred also in blends R-502 with 49% by mass HCFC-22 ( $\text{CHClF}_2$ ) and R-504 with 48% by mass HFC-32 ( $\text{CH}_2\text{F}_2$ ) (Calm and Hourahan, 2011; IPCC/TEAP, 2005; Fisher and Midgley, 1993). It has also been used as an aerosol propellant, and to a minor extent as a dielectric fluid (Fisher and Midgley, 1993). First measurements of CFC-115 were made by Penkett et al. (1981) and Fabian et al. (1981) who reported on an atmospheric vertical profile. These were later complemented by more vertical atmospheric profiles (Pollock et al., 1992; Schauffler et al., 1993; Fabian et al., 1996). Later temporal records of ground-based measurements based on flask samples were published by Oram (1999) for the CGAA and Culbertson et al. (2004) for both hemispheres. Sturrock et al. (2001) reported on the first in-situ measurements of CFC-115 at  $\sim 8$  ppt for Cape Grim for 1998/1999 with a small growth of  $\sim 5\% \text{ yr}^{-1}$ . The above-mentioned firn air analysis by Sturrock et al. (2002) produced a first long-term record of CFC-115, and showed significantly higher abundances for the 1980s compared with the CGAA record measured by Oram (1999). In contrast, CFC-115 reconstruction by Martinerie et al. (2009) were much in agreement with the early results from the CGAA record (Oram, 1999).

Here we report on measurements of CFC-13,  $\Sigma$ CFC-114 (~~combined  $\text{C}_2\text{Cl}_2\text{F}_4$  isomers~~), and CFC-115 from the Advanced Global Atmospheric Gases Experiment (AGAGE) and affiliated networks, and from measurements in archived air samples of the CGAA and the Northern Hemisphere. We further report on measurements from air samples collected from polar firn in both hemispheres, which we interpret using a firn air model. For each of the three compounds, all measurements are made



and reported against a single primary calibration scale. Our observations are used with the AGAGE 12-box model and two inversion systems to derive global emissions. We further apply an inversion system to estimate regional emissions of CFC-115 from north-eastern Asia for the years 2012 – 2016. For CFC-13, this is the first comprehensive study available on atmospheric abundances and emissions.

## 5 2 Methods

### 2.1 Stations and Data Records for in Situ and Flask Measurements

The present study includes in situ measurements at the stations of the AGAGE (Advanced Global Atmospheric Gases Experiment, URL: <https://www.agage.mit.edu>) and its affiliated networks (Fig. 1). Measurements reported here are mostly based on Medusa gas chromatography mass spectrometry (GCMS) techniques (Miller et al., 2008). In Europe, measurements are made at Zeppelin (Ny Ålesund, Spitsbergen), Mace Head (Ireland), Jungfraujoch (Switzerland), and Monte Cimone (Italy), the latter being equipped with different instrumentation (Maione et al., 2013). Measurements are further conducted at Trinidad Head (California, USA), Ragged Point (Barbados), Cape Matatula (American Samoa) and Cape Grim (Tasmania, Australia). The East Asian region is covered by stations at Gosan (Jeju Island, South Korea) and Shangdianzi (China). In addition to these in-situ measurements, we also include measurements of samples collected weekly since 2007 at the South Korean Antarctic station King Sejong, King George Island (South Shetland Islands) and analyzed at the Swiss Federal Laboratories for Materials Science and Technology (Empa) using Medusa-GCMS technologies (Vollmer et al., 2011). We also provide a qualitative description of measurements in urban areas from Tacolneston (Great Britain, 100 km northeast of London), Dübendorf (outskirts of Zurich, Switzerland), La Jolla (outskirts of San Diego, USA), and Aspendale (outskirts of Melbourne, Australia). At a few AGAGE stations, measurements of  $\Sigma$ CFC-114 and CFC-115 were previously made with different GCMS instrumentation (Adsorption-Desorption-System, Simmonds et al. (1995)), however the precisions and standards propagations of these early measurements are significantly poorer than those using Medusa-GCMS technology and hence these results are not included in the present analysis.

Most of the AGAGE network observations for the three CFCs are published here for the first time in a journal article. However some of the measurements have been previously used in Ozone Assessment Reports (e.g. Carpenter and Reimann, 2014), in modeling studies to derive global emissions (Rigby et al., 2014), and for Cape Grim, were reported in Baseline series starting 1997–1998 issue. ~~For CFC-114 and CFC-115 the~~ The in-situ data are available directly from the AGAGE website (<https://age.mit.edu/>) and data repositories mentioned therein.

### 2.2 Archived Air

Our analysis includes the results from Medusa-GCMS measurements of Cape Grim Air Archive (CGAA) samples collected for archival purposes since 1978 at the Cape Grim Baseline Air Pollution Station (Fig. 1). The CGAA includes >100 samples mostly collected into 34 L internally electropolished stainless steel canisters using cryogenic sampling techniques (Fraser et al.,

1991; Langenfelds et al., 1996, 2014; Fraser et al., 2016). Most samples were analyzed on the Medusa-9 instrument in 2006 at CSIRO (Aspendale, Australia) using Medusa-GCMS technology with a Medusa-standard PoraBOND Q chromatography column (Miller et al., 2008). In 2011 many samples were re-analyzed and newly-added samples were analyzed for CFC-13 and  $\Sigma$ CFC-114 on the same instrument but fitted with a GasPro chromatography column (Ivy et al., 2012). In 2016 all three compounds discussed here were reanalyzed and newly-added samples were analyzed on the same instrument fitted with a GasPro column and an additional GasPro pre-column (Vollmer et al., 2016). All samples collected since 2004 are also analyzed on the Cape Grim based Medusa-3 instrument. A comparison of the different analysis sets is provided in the Supplement and shows good agreement indicating stability of the three CFCs in the internally electropolished canisters. For the present analysis we use the mean of the measured mole fractions from these three analysis sets.

Archived air samples from the Northern Hemisphere (NH) are also included in this study. These >100 samples were collected at various sites and cover the period 1973 to ~~present-2016~~. The majority of the samples were provided by Scripps Institution of Oceanography (SIO) and collected at La Jolla and at Trinidad Head (California, USA). All samples were analyzed at SIO on Medusa-1. These NH archive air samples were not exclusively collected for archival purposes, and potentially ~~includes samples-include some~~ collected during non-background conditions (influenced by emission sources) or with non-conservative sampling techniques. Consequently a rigorous data processing was necessary to limit the record to results deemed representative of broad atmospheric regions far from emission sources (hereafter termed “background”). In particular, the earlier record of  $\Sigma$ CFC-114 proved not useful for the present analysis because there were too many anomalous sample measurement results. Numerical results for the NH and the CGAA measurements are given in the Supplement.

### 2.3 Air entrapped in Firn

Our data sets are complemented by measurements of the three CFCs in air entrapped in firn from samples collected in Antarctica and Greenland (Fig. 1). The Antarctic samples were collected in 1997–1998 at the DSSW20K site (66.77°S, 112.35°E, 1200 masl, ~20 km west of the deep DSS drill site near the summit of Law Dome, East Antarctica (Trudinger et al., 2002; Sturrock et al., 2002)), and one deep sample originates from the South Pole in 2001 (Butler et al., 2001). The Greenland firn air samples used in the present analysis were collected near the northwest Greenland ice drill site NEEM (North Greenland Eemian Ice Drilling) at 77.45°N, 51.06°W, 2484 m.a.s.l.) in 2008 (NEEM-2008, EU hole, Buizert et al. (2012)). Due to the remote locations of these sites, these samples are considered as representative of background air. More details on these samples and on their analysis are described by Vollmer et al. (2016) and Trudinger et al. (2016). Results for  $\Sigma$ CFC-114 and CFC-115 from the DSSW20K firn air profile based on older measurement technologies and interpreted with an old version of the CSIRO firn diffusion model were previously reported by Sturrock et al. (2002) and are compared to our measurements in the Supplement.

### 2.4 Measurement Techniques and Instrument Calibration

Almost all measurements reported here are conducted with Medusa-GCMS instruments (Miller et al., 2008). Typically a sample is preconcentrated on a first cold trap filled with HaySep D and held at ~−160°C before it is cryofocussed onto a second trap at similar temperature and in this process, remnants of oxygen and nitrogen and significant fractions of carbon dioxide and

some noble gases are removed. The sample is then injected onto the chromatographic column (CP-PoraBOND Q, 0.32 mm ID  $\times$  25 m, 5  $\mu$ m, Varian Chrompack, batch-made for AGAGE applications) of the GC (Agilent 6890), purged with helium (grade 6.0), which is further purified using a getter (HP2, VICI, USA). The sample is then detected in the quadrupole mass spectrometer in selected ion mode (initially Agilent model 5973 with upgrades to model 5975 over time for most stations).

5 In the Medusa-GCMS, ~~technology separation of the technology, separation of~~ CFC-114 (~~CClF<sub>2</sub>CClF<sub>2</sub>~~) isomer from CFC-114a (~~CCl<sub>2</sub>FCF<sub>3</sub>~~) is not possible hence the measurements include the cumulative abundances of the two ~~compounds. Throughout this paper we use the term “isomers ( $\Sigma$ CFC-114” for the combined measurement of the two isomers. Our inability to separate the two isomers can potentially lead to biases).~~ This leads to a potential bias compared to the numeric sum of ~~their individual measurements due to a combination of two facts; one being that the ratio~~ the separated, individually-measured isomers, due to  
10 ~~potentially differencing molar sensitivities of the mass spectrometer for the two isomers, and the fact that the ratios~~ of the two isomers ~~is likely to vary both~~ in the measured samples (~~Laube et al., 2016~~) and ~~are likely to differ from those~~ in the reference material used to propagate the primary calibration scales ~~and the other being that the molar responses of the mass spectrometer are potentially different for the two isomers~~ (Laube et al., 2016). We estimate a maximum potential bias, ~~which increases from ~0.3% for our modern record (2004–present) to ~3.1% for the oldest samples in our archived air records of <2% for our~~  
15 ~~measurements~~ (see Supplement).

For each of the three CFCs at least two fragments are routinely measured. While a target ion is used for the quantification of the peak size, the qualifying ions are mainly used for quality control by assessing the peak size ratio to the target ion, most importantly to check for potential coelution with compounds which share the target ion. CFC-13 is measured with the target ion C<sup>35</sup>ClF<sub>2</sub><sup>+</sup> (with a mass/charge,  $m/z$ , 85) and the qualifying ions CF<sub>3</sub><sup>+</sup> ( $m/z$  69) and C<sup>37</sup>ClF<sub>2</sub><sup>+</sup> ( $m/z$  87). On the PoraBOND Q  
20 column this compound elutes near HFC-32 (CH<sub>2</sub>F<sub>2</sub>) and precedes ethane by  $\sim$ 2 sec.  $\Sigma$ CFC-114 is measured with the target ion CF<sub>2</sub>C<sup>35</sup>ClF<sub>2</sub><sup>+</sup> ( $m/z$  135), and the ~~target-qualifying~~ ions CF<sub>2</sub>C<sup>37</sup>ClF<sub>2</sub><sup>+</sup> ( $m/z$  137) and C<sup>35</sup>ClF<sub>2</sub><sup>+</sup> ( $m/z$  85). It elutes a few seconds after H-1211 (CBrClF<sub>2</sub>) and ~~co-elutes co-elute~~ with n-butane. CFC-115 is measured with the target ion CF<sub>2</sub>CF<sub>3</sub><sup>+</sup> ( $m/z$  119) and the qualifying ions CF<sub>2</sub>C<sup>35</sup>ClF<sub>2</sub><sup>+</sup> ( $m/z$  135) and CF<sub>2</sub>C<sup>37</sup>ClF<sub>2</sub><sup>+</sup> ( $m/z$  137). It elutes  $\sim$ 12 sec after HFC-125 (CHF<sub>2</sub>CF<sub>3</sub>) and  $\sim$ 15 sec before HFC-134a (CH<sub>2</sub>FCF<sub>3</sub>). Some of the instruments are set to only acquire two fragments instead of three and for  
25 some, the sequences of target and qualifying ions are different from the above-mentioned orders.

$\Sigma$ CFC-114 measurements in strongly polluted air samples at some stations (mainly urban) have shown an analytical interference, which is believed to suppress the MS response to the quantities present in the sample. Although not fully understood, the interference is suspected to derive from large amounts of n-butane, which co-elutes with  $\Sigma$ CFC-114. A decrease of ~~in~~  $\Sigma$ CFC-114 of 0.20 ppt is estimated for ~~CFC-114 for an increase~~ ~~an increase in n-butane~~ of 1.0 ppb (parts-per-billion, nmol  
30 mol<sup>-1</sup>) ~~of n-butane~~. The measurements of  $\Sigma$ CFC-114 used in the present analysis derive from air samples not significantly polluted with n-butane where the suppression effect is estimated to be smaller than the precision of the measurement. More information is provided in the Supplement.

The sample preparation and analysis time is 60–65 min. For the in-situ measurements, samples are directed onto the first trap by means of a small membrane pump from a continuously-flushed sampling line. In general, each air sample measurement  
35 is bracketed by measurements of a quaternary working standard that allows tracking and correction of the MS sensitivity

change. The quaternary standards are whole-air samples compressed to 65 bar into 34 L internally electropolished stainless steel canisters (Essex Industries, Missouri, USA). These are collected by the individual groups within AGAGE at various sites during relatively clean air conditions using modified oil-less diving compressors (Rix Industries, USA) or cryogenic techniques. The repeated quaternary standard measurements are used to determine the measurement precisions. For CFC-13 they are  $\sim 1.5\%$  ( $1\sigma$ ) for the Agilent 5973 MSs and  $\sim 1\%$  for the newer Agilent 5975 MSs. For  $\Sigma$ CFC-114 the precisions range 0.2% – 0.3% and for CFC-115 0.4% – 0.8%, also showing some improvements with the change to the Agilent 5975 MSs.

As part of the network's calibration scheme and to assess for potential drift of the compounds in the canisters, the quaternary standards are compared once a week on-site against tertiary standards. These are provided by the central calibration facility at SIO and are also whole-air standards in Essex canisters filled under clean air conditions at Trinidad Head or La Jolla (California, USA). These tertiary standards are measured at SIO against secondary whole air standards before they are shipped to the sites and again after their return at the end of their usage times. They are also measured on-site against the previous and next tertiaries. The secondary standards and the synthetic primary standards at SIO provide the core of the AGAGE calibration scheme (Prinn et al., 2000; Miller et al., 2008).

## 2.5 Calibration Scales

AGAGE has been measuring CFC-13 for many years but so far none of these data have been published. This was, among other reasons, due to the use of a ~~primary-interim~~ calibration scale, which was not well defined as it was based on a dilution of a commercial reference gas. The present study prompted the creation of a primary calibration scale for CFC-13 in the ppt range by the Swiss Federal Institute of Metrology, METAS (Guillevis et al., in preparation). A suite of eleven primary standards was created using a technique that combines permeation tube substance loss determination by a magnetic suspension balance, dynamic dilution through mass flow controllers, and cryogenic collection in containers. These standards covered a range 2.7–4.3 ppt. Comparison between assigned mole fractions and measured relative mole fractions against one of these primary standards revealed an internal consistency of this METAS-2017 calibration scale of 0.6%. AGAGE adopted this calibration scale and all CFC-13 results reported here are on METAS-2017. ~~It replaced an interim calibration scheme, which was based on a diluted, commercially obtained (Linde) high concentration standard, and for which a~~ conversion factor of 1.05 ~~for this~~ METAS-2017 to the earlier interim calibration scale was determined.

Measurements of  $\Sigma$ CFC-114 and CFC-115 are reported on the SIO-05 primary calibration scales. They are defined through gravimetric preparations of 13 synthetic primary standards at ambient mole-fraction levels prepared at SIO in 2005 (Prinn et al., 2000). They cover mole fraction ranges of 16–20 ppt for  $\Sigma$ CFC-114 and 8–10 ppt for CFC-115. Internal consistencies for these sets of standards of 0.14% for  $\Sigma$ CFC-114 and 0.47% for CFC-115 were estimated based on their relative results from intercomparative measurements and their assigned relative mole fractions. Accuracies are initially estimated at 3% ( $1\sigma$ ) for each of the two CFCs and is a conservative estimate based on previous experience with other compounds (a strict statistical treatment of the known uncertainties such as impurities, balance etc would likely lead to a much smaller overall uncertainty). For  $\Sigma$ CFC-114, there is ~~potential for a considerable~~ a potential bias if our results of the combined isomer measurements were to be compared to the sum of their individual measurements (Supplement). ~~This bias is primarily caused by potentially~~

differing molar sensitivities for the two isomers, the magnitude of which we cannot easily assess on our MSs (see Supplement). Throughout this paper we report all our own measurements as dry air mole fraction (substance fraction) in ppt on these METAS and SIO calibration scales.

In some earlier articles (in particular Sturrock et al. (2001, 2002)),  $\Sigma$ CFC-114 and CFC-115 measurements were published on calibration scales that were based on diluted, commercially obtained (Linde) high-concentration standards and were referred to as “UB” or “SIO-interim” calibration scales. A later revision resulted in a renaming of these calibration scales to UB-98B for measurements conducted at CSIRO and Cape Grim. After the creation of the SIO-05 primary calibration scales, SIO-05/UB-98B conversion factors of 0.9565 for  $\Sigma$ CFC-114 and 1.0177 for CFC-115 were determined, with which UB-98B-based results need to be multiplied to determine their mole fraction on the SIO-05 calibration scales.

A comparison ~~between of~~ the SIO-05 primary calibration scale for  $\Sigma$ CFC-114 ~~and that of the~~ with the UEA-2014 calibration scales (University of East Anglia ~~(UEA)~~ UEA-2014 (Laube et al., 2016), Laube et al. (2016)) is of limited value and not straight forward because ~~in Medusa GCMS measurements the two isomers are not chromatographically separated. A detailed discussion on this is given in the Supplement with an intercomparison of the CGAA results measured on both calibration scales. The result of this separate analysis suggests that for near modern of the isomer issues addressed earlier. Nevertheless, for near-modern mole fractions~~ (starting about mid-1990s) ~~mole fractions~~ ( $\sim 16$  ppt), numerically summed CFC-114 and CFC-114a mole fractions reported on the UEA-2014 calibration scales can be converted to SIO-05 reported ~~combined  $\Sigma$ CFC-114 isomer results~~ by multiplication of 1.025 (see Supplement).

## 2.6 Uncertainty Assessment for Reported Measurements

To derive accuracies for the reported measurements we combine three independent uncertainties: uncertainties of the calibration scales mentioned in the previous subsection, a propagation uncertainty, and the instrumental precision of the measured sample, as listed in subsection 2.4. The propagation uncertainties derive from the hierarchical sequence of standards used to propagate assigned mole fraction in the primary standards to the quaternary standards on-site, by assuming measurement uncertainties for each of the steps, i.e. the secondary and tertiary standards. For this step, the measurement precisions are assumed the same as those of the quaternary standards on site. For  $\Sigma$ CFC-114 we add an “interference uncertainty”, which is based on the findings of a potentially suppressed MS signal in the presence of n-butane (see Supplement). We estimate a maximum depletion of  $\Sigma$ CFC-114 of 0.6 % in the presence of 0.5 ppb n-butane (which we consider an upper limit in unpolluted air) and add this value as an independent uncertainty. ~~As mentioned earlier (and discussed in the Supplement) there is a potential bias of our combined isomer measurement compared to the~~ For  $\Sigma$ CFC-114, there is also an earlier-mentioned potential isomer bias of  $\sim 2\%$  with respect to the numeric sum of individual isomer measurements. ~~However, because differentiation and thus quantification of the bias are not possible for us, it is not included in our uncertainty estimates, which we include in our calculations.~~ The resulting uncertainties ( $1\sigma$ ) for the three compounds are then 3.7% for CFC-13, ~~3.1% for~~ 3.7% for  $\Sigma$ CFC-114, and 3.2% for CFC-115. They are dominated by the calibration scale uncertainties. For direct comparisons of samples reported on the same calibration scale, the calibration scale uncertainties do not apply and the remaining uncertainties are ~~much considerably~~ smaller (2.2%, ~~0.72, 1%~~, and 1.2% for the three compounds, respectively).



## 2.7 Bottom-Up Inventory-Based and Other Emissions Estimates

Here we refer to bottom-up emissions as those derived from data related to production, distribution and usage of these compounds. For the CFCs discussed here such estimates have considerable uncertainties because of the large fraction of these CFCs installed in long-lasting equipment (banks) with unclear leakage rates. Nevertheless bottom-up emission estimates are useful for us as prior for our model analysis and to compare with our top-down observation-based results.

While bottom-up emissions are not available for CFC-13, they were published for  $\Sigma$ CFC-114 and CFC-115 from the refrigeration sector by Fisher and Midgley (1993). A more comprehensive set of emissions estimates for these two compounds was released by AFEAS (Alternative Fluorocarbon Environmental Acceptability Study) for 1934–2003. For  $\Sigma$ CFC-114, they show an early onset of emissions in the 1930s with significant released quantities in the late 1940s ( $\sim 7 \text{ kt yr}^{-1}$ ) and peak emissions ( $\sim 18 \text{ kt yr}^{-1}$ ) in 1986/1987. Extrapolation of the AFEAS data, as in Daniel and Velders (2007) (see Supplement), shows emissions of  $< 0.1 \text{ kt yr}^{-1}$  in the last few years and a remaining bank of 0.16 kt in 2016. On a similar basis, AFEAS CFC-115 bottom-up emissions started only in the mid 1960s and peaked in the early 1990s at  $\sim 13 \text{ kt yr}^{-1}$  before declining to  $< 0.1 \text{ kt yr}^{-1}$  from 2008 leaving a remaining bank of  $< 0.01 \text{ kt yr}^{-1}$  in 2016. Destruction of these two CFCs is considered insignificant in the AFEAS analysis hence the cumulative production matches the cumulative emissions. Some of these data were used in the Ozone Assessment Report 2006 to produce emission scenarios for 1930–2100 on which the atmospheric abundances for the same period were based (Daniel and Velders, 2007). Analogously, the AFEAS emission inventory for CFC-115 was also expanded into a scenario similar to  $\Sigma$ CFC-114, but these results were not graphically presented in the Assessment Report. To facilitate public access to both the AFEAS original numerical data and those expanded in the Assessment Report (“expanded AFEAS data”), we provide these in the Supplement, along with a description of how they were derived. These data are used in the present analysis as priors for the two global inversions.

We also compare our results with the data set derived by Velders and Daniel (2014), who reconstructed production, banks, and emissions for  $\Sigma$ CFC-114 and CFC-115, with projections into the future. Their reconstruction is a mix of bottom-up inventory-based and top-down observation based data. The earlier parts of their records are largely based on the AFEAS results and therefore do not provide significant additional information. Those from 1979–2008 are based on atmospheric observations. Their  $\Sigma$ CFC-114 emissions after 2008 are based on a bank of 15 kt for that year. This bank was derived as a remnant of a 60 kt bank for 1960, which was ‘back’-extrapolated from emissions based on atmospheric observations and using a yearly emission factor (Daniel and Velders (2011), G. J. M. Velders, pers. comm. ~~Velders~~, June 2017). For CFC-115 Velders and Daniel (2014) derived a bank of 15.9 kt from R-502 for 2008 (UNEP/TEAP (2009) and unpublished data). The Velders and Daniel (2014) bank and emissions after 2008 are significantly larger than those from AFEAS for both compounds.

## 2.8 Firn Model, Global Transport Model, and Inversions

Similar to the study by Vollmer et al. (2016) for halons, the present analysis uses a firn air model to characterize the age of the CFCs in the firn air samples (Trudinger et al., 2016), the AGAGE 12-box model to relate atmospheric mole fractions to surface

emissions (Rigby et al., 2013), two inversion approaches to estimate hemispheric emissions, and a Lagrangian transport model to study regional emissions of CFC-115 in north-eastern Asia.

### 2.8.1 Firn Model

The firn model used here was developed at CSIRO by Trudinger et al. (1997) and updated by Trudinger et al. (2013). It has previously been used for firn air measurement reconstructions of other greenhouse gases (Trudinger et al., 2002; Sturrock et al., 2002; Trudinger et al., 2016; Vollmer et al., 2016). Physical processes in the firn, foremost vertical diffusion, cause the air samples to represent age spectra rather than an individual discrete age as is found in e.g. tank samples like the CGAA. Green's functions are used to relate the measured mole fractions to the time-range of the corresponding atmospheric mole fractions. The update to the firn model described in Trudinger et al. (2013) included a process that had previously been neglected by Trudinger et al. (1997). This process was the upward flow of air due to compression of the pore space as new snow accumulates above, and it appears that this process is important. As discussed in Trudinger et al. (2013), including it in the model removed a discrepancy between DSSW20K firn and CGAA CFC-115 that was noted by Sturrock et al. (2002).

The diffusion coefficients used in this work for the three CFCs relative to CO<sub>2</sub> in air (for a temperature of 253 K) are 0.667 for CFC-13 (using le Bas molecular volumes as described by Fuller et al. (1966)), 0.495 for  $\Sigma$ CFC-114 (Matsunaga et al., 1993) and 0.532 for CFC-115 (Matsunaga et al., 1993). Measurement results and reconstructed firn air depth profiles are shown in Fig. 2. These modeled depth profiles are not based on the observations at the individual sites, but rather correspond to the optimized emissions history obtained using measurements from all firn sites as well as the atmospheric measurements used in this study. While  $\Sigma$ CFC-114 was present in all samples of the three sites, CFC-13 was absent within the detection limits in the South Pole sample and in one of the deepest duplicate samples at DSSW20K. CFC-115 was also absent in two of the three deepest DSSW20K duplicate samples.

### 2.8.2 AGAGE 12-box Model

The AGAGE box model was originally created by Cunnold et al. (1983) and has since been rewritten and modified (Cunnold et al., 1994, 1997; Rigby et al., 2013; Vollmer et al., 2016). In the current version of the model, the atmosphere is divided into four zonal bands, separated at the equator and at the 30° latitudes thereby creating boxes of similar air masses. Boxes are also separated at altitudes represented by 500 hPa and 200 hPa. Model transport parameters, and stratospheric photolytic loss vary seasonally and repeat interannually (Rigby et al., 2013). For the CFCs analyzed here, loss in the atmosphere is dominated by photolytic destruction in the stratosphere. Here our local stratospheric loss rates are tuned to reflect the current best estimates of the global lifetimes of these compounds from SPARC (2013) as shown in Table 1.

Monthly transport parameters in the 12-box model were tuned to match the simulation of a uniformly distributed passive tracer in the Model for Ozone and Related Tracers (MOZART, Emmons et al. (2010)), using Modern-Era Retrospective Analysis for Research and Application (MERRA) meteorology for the year 2000 (Rienecker et al., 2011). These transport parameters were repeated each year in our simulations. Whilst inter-annual variation in transport is known to impact the distribution of trace gases in the atmosphere, time-resolved atmospheric physical state estimates are not generally available throughout the entire

period of this investigation. Furthermore, we anticipate that variations in emissions dominate atmospheric trends, particularly over the longer (multi-annual) timescales, which are our primary focus.

### 2.8.3 Global Inversions

To estimate global emissions to the atmosphere we employ two different Bayesian inverse methods (“Bristol” and “CSIRO”). Both methods use the AGAGE 12-box model to relate observed tropospheric mole fractions to surface emissions of the CFCs. While past studies using the Bristol inversion have primarily targeted modern in-situ observations from the AGAGE network (Rigby et al., 2011; Vollmer et al., 2011; Rigby et al., 2014; O’Doherty et al., 2014; Vollmer et al., 2015b) the inversion method has also been extended to include firn air observations (Vollmer et al., 2016). Green’s functions from the CSIRO firn model are used in both global inversions to relate the firn air measurements to atmospheric mole fraction over the appropriate time range.

The Bristol approach is based on the methods outlined in Rigby et al. (2011) and extended in Rigby et al. (2014). Briefly, this method assumes a constraint (prior) on the rate of change of emissions, which is adjusted using the data in a Bayesian framework. The magnitude of the uncertainty in the prior year-to-year emissions growth rate is somewhat arbitrarily chosen to be 20% of the maximum emission rate for the entire period. In a minor modification to the approach in Rigby et al. (2014), we chose to solve for a change in absolute emissions (in  $\text{kt yr}^{-1}$ ), rather than a scaling of the prior emissions. This approach was found to lead to more consistent posterior emissions uncertainty estimates between the near-zero and relatively high emissions periods.

The random component of the model-measurement mismatch uncertainties in the Bristol inversion is composed of measurement ~~and calibration scale~~ uncertainties and those of the atmospheric and firn air models. The atmospheric model uncertainty is assumed to be equal to the variability of the estimated baseline within each monthly mean. These uncertainties are propagated through the model to provide a posterior emissions uncertainty estimate (Rigby et al., 2014). The posterior emissions uncertainty is then augmented with a term related to the calibration scale uncertainty, and the uncertainty due to the lifetime (Rigby et al., 2014). The observations that are compared with the 12-box model in the “Bristol” inversion (see following section) are from all the firn air (firn model output) and CGAA archived air samples described here, and the monthly mean background-filtered in-situ measurements from Mace Head, Trinidad Head, ~~Barbados, American Samoa~~ Ragged Point, Cape Matatula, and Cape Grim (Fig. 4).

The CSIRO inversion, also combined with the 12-box model and Green’s functions from the CSIRO firn model (Vollmer et al., 2016; Trudinger et al., 2016), was developed to focus on sparse observations from air archives, and firn air and ice core samples that are associated with age spectra. The characteristics of these data necessitate the use of ~~regularisation and~~ constraints on the inversion to avoid unrealistic oscillations in the reconstructed mole fractions or negative values of mole fraction or emissions. The CSIRO inversion therefore uses non-negativity constraints and favors relatively small changes to annual emissions in adjacent years rather than large, unrealistic fluctuations. A prior emissions history based on bottom up estimates is used as a starting point, then a non-linear constrained optimisation method is used to find the solution that minimises a cost function consisting of the model-data mismatch plus the sum of the year-to-year changes in emissions (Trudinger et al., 2016). The observations used in the CSIRO inversion are the firn measurements and annual values of mole fraction from a smoothing spline

fit to measurements at Cape Grim and the CGAA, and another spline fit to Mace Head and the NH air archive. Uncertainties are estimated using a bootstrap method that incorporates data uncertainties and uncertainties in the firm model through the use of an ensemble of firm Green's functions.

We use the expanded AFEAS bottom-up inventory based data for  $\Sigma$ CFC-114 and CFC-115 as prior in the inversions as these were produced without any input from atmospheric observations. For CFC-13, emission inventories do not exist to the best of our knowledge. As prior for this compound, we use the expanded CFC-115 AFEAS data, which we scale with a factor  $1/7$  based on an intercomparison of production estimates (see Supplement).

#### 2.8.4 Regional Scale Source Allocation and Atmospheric Inversion

Pollution events of the three compounds are absent, to within detection limits, from the measurements at all AGAGE field stations with the exception of Gosan (South Korea) and Shangdianzi (China). This has prompted a more detailed analysis of these compounds in north-eastern Asia to locate and quantify potential sources. Only observations from Gosan were used since these are less locally influenced, and therefore less subject to subgridscale model errors, than those from Shangdianzi, which are subject to pollution events originating in the nearby Beijing capital region.

We calculated qualitative emission distributions by combining model-derived source sensitivities with the above-baseline observations from Gosan. A smooth statistical baseline fit (Ruckstuhl et al., 2012) was subtracted from the observational data. Surface source sensitivities were computed with the Lagrangian Particle Dispersion Model (LPDM) FLEXPART (Stohl et al., 2005) driven by operational analysis/forecasts from the European Centre for Medium-Range Weather Forecasts (ECMWF) IFS modeling system. 50 000 model particles were released for each 3-hourly time interval and followed backward in time for 10 days. Surface source sensitivities (concentration footprints) were obtained by evaluating the residence times of the model particles along the backward trajectories (Seibert and Frank, 2004).

Qualitative emission distributions were then calculated as a spatially-distributed, weighted concentration average using the source sensitivities as weights. This method is based on the one described by Stohl (1996) for simple air mass trajectories, but was generalized for source sensitivities and applied to halocarbon observations previously (Stemmler et al., 2007; Vollmer et al., 2015a). The method provides a general first impression of potential source locations but cannot be used to quantify individual sources and their uncertainty (location and length).

In addition, we applied a spatially resolved, regional-scale emission inversion, using the same FLEXPART-derived source sensitivities and the Bayesian approach described in detail in Henne et al. (2016). In contrast to the above method, the Bayesian inversion provides a quantitative spatial distribution of posterior emissions and their uncertainties. Prior emissions were set proportional to the population density. The same emission factor per person was used for the entire inversion domain, which comprised most of China, North and South Korea, and the south-western part of Japan. This emission factor was set in such a way that total Chinese emissions were in line with China's share of the gross world product (GWP) of approximately 15% and the global emission estimates described in sections 3.2.1, 3.2.4, and 3.2.6.

Parameters describing the covariance uncertainty matrices were derived from a log-likelihood maximum search (Michalak et al., 2005; Henne et al., 2016). The prior emission uncertainties obtained from this optimization were relatively large and amounted

to 0.04, 0.4, and 0.6 kt yr<sup>-1</sup> for China for CFC-13,  $\Sigma$ CFC-114 and CFC-115, respectively (see Table 2). All analysis was done separately for each year from 2012 to 2016. More details on the applied method and additional results can be found in the Supplement.

### 3 Results and Discussion

#### 5 3.1 Atmospheric Histories and High Resolution Records

We combine our measurement results from firn air samples, archived air in canisters, and in-situ measurements to produce the full historic records for CFC-13,  $\Sigma$ CFC-114, and CFC-115 spanning nearly eight decades (Figs. 3–4). The modeled records discussed in this section derive from the Bristol and CSIRO inversions using these observations and the AGAGE 12-box model. The firn air depth profiles show a steady decline of all three CFCs with increasing depth (Fig. 2). All three compounds are at or below detection limits in the deepest samples of the Antarctic DSSW20K profile but clearly detectable in the deepest samples in the Greenland NEEM-2008 profile. These firn air results are plotted with the full historic record in Fig. 3 using dates based on the effective ages unless the mole fractions were near zero, when mean ages were used; note that these dates are used for graphical purposes only, and that the full Green’s functions (shown in the Supplement) were used in the inversions to represent the age of the compounds in firn air. On the temporal scale the firn air results overlap strongly with the results from the archived canisters. These canister samples span from the late 1970s to near-present and overlap with the high-resolution in-situ measurements shown in more detail in Fig. 4. The in situ data are binned into monthly means after applying a pollution filter to limit the records to samples under background conditions (O’Doherty et al., 2001; Cunnold et al., 2002).

##### 3.1.1 CFC-13

CFC-13 first appeared in the atmosphere in the late 1950s to early 1960s (Fig. 3). ~~Between the 1970s and 1980s its~~ Its growth rates were highest ~~before declining again in the late in the~~ 1980s with a significant decline thereafter, presumably as a consequence of reduced emissions due to restrictions on production and consumption by the Montreal Protocol in the non-Article 5 countries. Because of its very long lifetime, small emissions are sufficient to maintain the observed increase in its abundance and consequently CFC-13 continued to grow monotonically to a globally averaged mole fraction of 3.18 ppt in 2016. Its global growth rate leveled off at 0.01–0.03 ppt yr<sup>-1</sup> in the late 1990s. ~~There is, however, and there is~~ no indication of a further decline in the growth rate since then; ~~in contrast, our data suggest a slight increase during the last decade, which very likely indicates increasing emissions over this period.~~

Cape Matatula and Cape Grim, which are the two stations most influenced by SH air masses, have shown a small and consistent offset of 0.04 ppt compared to the NH stations (SH lower), which points to predominantly NH emissions (Fig. 4). For the overlapping period of 1978–1997, our CFC-13 abundances are significantly lower (~25%) compared to earlier published data (Oram, 1999; Culbertson et al., 2004) (Fig. 5).



For most of the AGAGE field stations the high-resolution records show an absence of CFC-13 pollution events indicating vanishing emission within the local footprints of these stations. However Gosan and Shangdianzi feature sporadic pollution events with abundances that reach up to  $\sim 6$  ppt. Measurements from the urban sites Tacolneston (England), Dübendorf (Switzerland), and Aspendale (Australia, after removal of a nearby CFC-13 source in early 2010) show no pollution events, while those at La Jolla (USA) exhibit occasional pollution events, which however are smaller and less frequent than those at the two Asian field sites. High-resolution records are shown in the Supplement.

### 3.1.2 $\Sigma$ CFC-114

$\Sigma$ CFC-114 appeared in the atmosphere in the late 1950s to early 1960s at similar times to CFC-13 (Fig. 3). Its growth rate was highest in the 1970s and 1980s ( $0.5\text{--}0.8$  ppt yr $^{-1}$ ) and declined strongly in the 1990s.  $\Sigma$ CFC-114 global mole fractions peaked in 1999–2002 at 16.6 ppt, ~~interhemispheric gradients have vanished since, and global atmospheric mole fractions and~~ have slightly declined since then to 16.3 ppt in 2016. Based on the data assimilated into the Bristol inversion framework, global growth rates have been negative since 2000 the early 2000s with a minimum at  $-0.035\text{--}0.04$  ppt yr $^{-1}$  but increased again since 2010 to  $-0.010$  ppt yr $^{-1}$  by 2016. Similar to CFC-13, this increase likely indicates increased emissions (mean 2004–2006) with no indication of a further decline since then. A small interhemispheric gradient has been persisting over the last decades as is shown by the lower mole fractions for Cape Matatula and Cape Grim compared to the NH sites (Fig.4).

Our SH  $\Sigma$ CFC-114 results exhibit lower mole fractions than those of Oram (1999), and those of Sturrock et al. (2002), who used a combination of the data from Oram (1999) and in-situ AGAGE Cape Grim data ~~based on from~~ older instrumentation (~~ADS, not used in the present study~~ Fig. 5). Also, our  $\Sigma$ CFC-114 abundances are significantly lower than those of Martinerie et al. (2009) for the records before 1980. In contrast, our CGAA mole fractions ~~match the summed agree closely with the sum of the~~ CFC-114 ~~isomers mole fractions recently published by and~~ CFC-114a mole fractions from Laube et al. (2016) in the older part of the record, but get progressively higher (up to 2.5%) for the modern part of the record compared to that reported by Laube et al. (2016).

The high-resolution records at the AGAGE field sites generally show no  $\Sigma$ CFC-114 pollution events indicating vanishing emissions in the airmass footprints of these stations (see Supplement). The single exception is Gosan, which shows frequent pollution events reaching mole fractions of up to  $\sim 20$  ppt (Shangdianzi data are hampered by an instrumental artifact and not further discussed here). The urban sites also exhibit a similar pattern as discussed for CFC-13 with Tacolneston, Dübendorf and Aspendale featuring minor and infrequent pollution events indicating that even in these urban areas emissions are small. However the record at La Jolla shows very frequent pollution events with magnitudes up to  $\sim 25$  ppt. This can be caused by either a rather local source or more widespread emissions in the airmass footprint of this station. A more detailed analysis is beyond the scope of this study.

### 3.1.3 CFC-115

CFC-115 appeared in the atmosphere with a delay of nearly a decade compared to CFC-13 and  $\Sigma$ CFC-114. Its growth peaked at similar times as CFC-13 and as the second maximum of  $\Sigma$ CFC-114, at rates of  $0.4\text{--}0.5$  ppt yr $^{-1}$ . ~~It~~ Its growth then slowed

during the mid 2000s to near-zero~~growth~~, with CFC-115 abundances leveling off at  $\sim 8.3$  ppt in the late 1990s. However, surprisingly, the CFC-115 growth rate has increased since its minimum ~~in 2008 ( $-0.005$  at  $0.007$  ppt yr $^{-1}$ )~~ (mean 2004–2009) to  ~~$\sim 0.02$ – $0.026$  ppt yr $^{-1}$  in 2015~~ (mean 2004–2009). This has caused an enhanced increase of the atmospheric abundances to 8.49 ppt in 2016, which is seen more clearly in the recent in-situ measurements from the stations, with increases led by northern hemisphere sites (Fig. 4).

Our CFC-115 abundances agree well with earlier-published results by Culbertson et al. (2004), Oram (1999), Martinerie et al. (2009), and the younger part of the record by Sturrock et al. (2002), as is shown in Fig. ??. The latter study found somewhat larger mole fractions in the 1970s and 1980s, but this was mainly due to a process neglected in the old version of the CSIRO firm model (upward flow of air due to compression, as mentioned above). There are currently no other published data records covering the past two decades, which we could compare to our results.

The high-resolution records at the AGAGE fields sites show, similar to CFC-13 and  $\Sigma$ CFC-114, no pollution events with the exception of a few rare and small excursions for some of the sites. Again, Gosan and Shangdianzi exhibit pollution events (typically up to 13 ppt), which have become more frequent since 2013 for Gosan, and evident in the Shangdianzi record only starting in 2016 because of missing data for 2013–2016. The urban sites La Jolla and Dubendorf exhibit pollution events, particularly the former with a more regular frequency. Aspendale showed CFC-115 pollution episodes mainly in 2006–2009 but to a much lesser degree in the most recent part of its record. CFC-115 pollution events are mostly absent from Tacolneston (see Supplement). These observations demonstrate that CFC-115 has not completely been removed from installed equipment in these urban areas.

### 3.2 Emissions

Global emissions of the three CFCs were calculated using the Bristol and CSIRO inversions covering nearly eight decades and are shown in Fig. 6 for 1950 to ~~the present. For 2016.~~ For  $\Sigma$ CFC-114 and CFC-115, industry-based bottom-up and other reported emissions are available for comparison. For all three CFCs we find persistent lingering emissions in the past decades, ~~which may be expected if release is continuing from banks. However, more unexpected is a recent increase in emissions for all three substances.~~ While the emissions for CFC-13 and CFC-114 have remained stable (within uncertainties), those for CFC-115 have increased in recent years. In our discussion of these recent emissions we assume that other effects are absent, which could artificially create these lingering emissions i.e. a slowdown of vertical air mass exchange between the troposphere and the stratosphere and/or reduced removal fluxes. The global emissions results are complemented with results for Asian regional emissions, and with emissions found from specific processes (CFC-13) and compound impurities (CFC-115).

#### 3.2.1 CFC-13 Global Emissions

Based on our inversions, CFC-13 emissions increased to a maximum of  $\sim 2.6 \pm 0.25$  kt yr $^{-1}$  (1 stdv) in the mid-1980s with a subsequent decline to relatively stable mean emissions of  $0.48 \pm 0.15$  kt yr $^{-1}$  during the last decade (2007–2016) Fig 6). Cumulative emissions until 2016 amount to 62 kt (both inversions) of which, due to its 640 yr lifetime (Table 1),  $\sim 90\%$  is still in the atmosphere. The persistent emissions over the past two decades are surprisingly high ( ~~$> 40$~~   $15\%$  of the peak emissions).

The absence of a clear downward trend over this long period ~~, even more so the recent increase in emissions, are~~ is inconsistent with a potential gradual replacement of CFC-13 in refrigeration units after the ban by the Montreal Protocol, which would lead to a decline of CFC-13 banks and emissions. Release functions for the other two CFCs used in the AFEAS vintage model (see Supplement) indicate that emissions of the whole charge of individual refrigeration equipment after installation take 20 years for ΣCFC-114 and 10 years for CFC-115. Assuming similar emission functions for CFC-13 in these applications could potentially explain the decline in the emissions in the 1990s but not the tailing emissions thereafter, about which we can only speculate. One explanation could be different release functions in the last two decades, for example a better containment for some time as a response to reduced availability of CFC-13 for refill, followed by a recent period of enhanced release perhaps due to intensified removal of old refrigeration equipment. Alternatively, CFC-13 could be emitted from sources other than refrigeration systems. It could be a by-product of fluorochemical manufacture and be released from the processes, or as an impurity of the end products. It is unlikely that CFC-13 is used as a process agent as it would need to be recorded and controlled under the regulations of the Montreal Protocol, which is, as far as we know, not the case. The many CFC-13 pollution events measured at Shangdianzi and Gosan, and the rare occurrence at other sites, point to emissions in the East Asian region (although emissions may also be taking place in regions not seen by our high-frequency network).

### 15 3.2.2 CFC-13 Emissions from Regional FLEXPART Inversion

The transport analysis of CFC-13 pollution peaks that were observed at Gosan did not reveal consistent and localised sources for the years 2012 to 2016. The strongest indication of sources were observed for 2013 and 2014 in China, whereas in 2015 and 2016 no specific source region could be identified (see Supplement). The Bayesian inversion showed relatively weak performance of the simulated prior time series (see Supplement) and the use of the posterior emission field did not improve these simulations to a large extent with the exception of the year 2013, for which a considerable improvement of the simulation was achieved through the emission inversion. Consequently, the posterior emissions of CFC-13 stayed relatively close to the prior estimates with the general tendency of lower posterior estimates for South Korea and Japan (Table 2, Figure 7). Chinese emissions remained very close to the prior estimates except for the year 2013. In summary, these results do not indicate an over-proportional share of CFC-13 emissions from north-eastern Asia, compared with the global estimate, and, considering the relatively weak model performance, are connected with a considerably large uncertainty.

### 3.2.3 CFC-13 Emissions from Aluminum Smelters

CFC-13 was previously found in the emissions from aluminum plants (Penkett et al., 1981; Harnisch, 1997). Our present CFC-13 study has prompted us to re-analyze emission measurements from an Australian aluminum smelter study (Fraser et al., 2013) (see Supplement), ~~and unlike~~ Unlike stated in Fraser et al. (2013), ~~we found that CFC-13 emissions were absent, our re-analysis revealed~~ significant enhancement of CFC-13 in the exhaust samples compared to ambient air, thereby qualitatively confirming the results from the ~~older~~ earlier studies. Enhancements over background levels of 45 ppt – 130 ppt were found in the various smelter samples. From these results an emission factor of  $0.025 \pm 0.017$  g CFC-13 per ton aluminum was calculated. A global extrapolation based on a yearly aluminum production of  $\sim 60$  Mt  $\text{yr}^{-1}$  for 2016 ([17](http://www.world-</a></p></div><div data-bbox=)

aluminium.org/statistics/#data, accessed June 2017) yields yearly CFC-13 emissions of  $0.0015 \pm 0.001 \text{ kt yr}^{-1}$ . Unless emission factors from other smelters were significantly higher, this is suggestive of a minor contribution of aluminum smelter emissions to the total global yearly emissions of CFC-13 derived from our atmospheric observations. Nevertheless from a chemical reaction standpoint, these CFC-13 emissions from aluminum production remain unexplained. Simplistically, since the carbon to produce  $\text{CF}_4$  in ~~aluminium~~-aluminum smelters comes from the carbon in the smelter graphite anodes, chlorine impurities in the carbon anodes could be the source of chlorine to produce CFC-13 in the smelters.

### 3.2.4 $\Sigma\text{CFC-114}$ Global Emissions

Based on our global inversions,  $\Sigma\text{CFC-114}$  emissions started in the 1950s–1960s and reached a maximum in the mid 1970s at  $21 \pm 0.28 \text{ kt yr}^{-1}$  followed by a second maximum in 1988 at  $22 \pm 0.19 \text{ kt yr}^{-1}$  (Fig. 6). Using the CSIRO inversion we have conducted a sensitivity analysis to investigate the robustness of this double peak. This has shown that the feature remains present when excluding each data set one at a time from the inversion, hence it is not an artifact of the contribution from an individual data set (see Supplement). Global emissions have declined strongly in the 1990s but remained at a surprisingly stable and high level at  $1.9 \pm 0.84 \text{ kt yr}^{-1}$  (mean of last decade, 2007–2016, see Fig. 6). Our global emissions differ significantly from the AFEAS bottom-up emissions for the first part of the record until about 1980. Bottom-up emissions are significantly elevated compared to our results until 1965 and lower after that. Also, while we derive continuing emissions in the last decade, those from expanded AFEAS data sets were predicted to decline gradually to  $<0.1 \text{ kt yr}^{-1}$  after 2014. Emissions of the last decade reported by Velders and Daniel (2014), which are derived in a bottom-up approach from assumed remaining banks, are higher than those from AFEAS but considerably smaller than the emissions we derived from our observations. Our estimates of the annual emissions for the recent years are large compared to the banks proposed by AFEAS (0.2 kt for 2016) and Velders and Daniel (2014) (6.4 kt for 2016) and are suggestive of additional, recently-produced  $\Sigma\text{CFC-114}$ . Our cumulative emissions until 2016 (587 kt for the Bristol inversion and 586 kt for the CSIRO inversion) are ~~significantly~~ higher than the cumulative emissions and productions derived by AFEAS from an inventory (521 kt) and those ~~reported-projected~~ by Velders and Daniel (2014) (528 kt). However, despite this  $\sim 10\%$  difference they agree within the large uncertainties, in particular those in the  $\Sigma\text{CFC-114}$  lifetime (Table 1). Emissions derived by Laube et al. (2016) from atmospheric observations agree well with our emissions after 1980 but with some potential discrepancies in the earlier record (see Laube et al. (2016) for their full emissions record). ~~The cumulative emissions reported by Laube et al. (2016) up to 2014 are 553 kt and agree better with our results than the inventory-based estimates compare with our results.~~

We can only speculate on these relatively high lingering ~~-, and recently increasing emissions of~~  $\Sigma\text{CFC-114}$ . One possible explanation is a change in release functions as was outlined for CFC-13. Alternatively,  $\Sigma\text{CFC-114}$  could be fugitively emitted during synthesis of HFC-134a, where it is an intermediate compound in some synthesis pathways (Rao, 1994; Banks and Sharratt, 1996; McCulloch and Lindley, 2003). We have analyzed a diluted sample of HFC-134a from a container of the high-purity substance and found  $\Sigma\text{CFC-114}$  present at  $2.8 \times 10^{-5} \text{ mol per mol of HFC-134a}$ . If extrapolated to global HFC-134a emissions of  $180 \text{ kt yr}^{-1}$  (Rigby et al., 2014) this would correspond to global emissions of  $0.084 \text{ kt yr}^{-1}$

of  $\Sigma\text{CFC-114}$ , which is a minor fraction of the current  $1.9 \text{ kt yr}^{-1}$ . A more comprehensive analysis would be necessary to get an understanding of the variability of such an impurity.

The observed latitudinal gradient in  $\Sigma\text{CFC-114}$  abundance suggests predominant NH emissions. Pollution events in the Asian region, as detected from our high-resolution in-situ measurements, and the absence thereof in other regions suggest predominant emissions that at least some of these emissions originate from Asia. However, there is no clear latitudinal gradient in CFC-114 abundance detected from our observations. Nevertheless, increased  $\Sigma\text{CFC-114}$  abundances of CFC-114a<sub>6</sub> compared to Cape Grim, from samples collected in Taiwan were reported on by Laube et al. (2016), partially supporting our findings.

### 3.2.5 $\Sigma\text{CFC-114}$ Emissions from Regional FLEXPART Inversion

In contrast to CFC-13, potential emission sources of  $\Sigma\text{CFC-114}$  derived from our observations at Gosan could be identified on the Chinese mainland for the years after 2013 through the atmospheric transport analysis (see Supplement). The Bayesian regional inversion corroborates this finding, yielding largely increased posterior emissions for China for the years 2014 onwards, with a peak of  $1.0 \pm 0.2 \text{ kt yr}^{-1}$  in 2013 (Table 2, Figure 7). South Korean and Japanese emissions remained around or below the prior values. Posterior emissions were mostly localised in two areas in China, in the Shanghai and its neighboring provinces Zhejiang and Jiangsu, and in the Shandong province (Fig. 8). The overall transport model performance and its improvement through the inversion was largely improved as compared with that for CFC-13 (see Supplement) were considerably better as in the case of CFC-13, lending sufficient confidence in the inversion results.

### 3.2.6 CFC-115 Global Emissions

Based on our inversions, CFC-115 emissions started in the mid-1960s and increased to a maximum of  $12.8 \pm 1.3 \text{ kt yr}^{-1}$  in the late 1980s. Emissions declined strongly thereafter to a minimum of  $0.59 \pm 0.51 \text{ kt yr}^{-1}$  (mean 2007–2010). Surprisingly the emissions have since increased steadily increased steadily since 2010 to  $1.14 \pm 0.50 \text{ kt yr}^{-1}$  (mean 2015–2016), and the mean yearly emissions for the decade 2007–2016 were  $0.80 \pm 0.50 \text{ kt yr}^{-1}$ . Our observations agree very well with the bottom-up emissions by AFEAS except for an earlier maximum in our emissions, by a few years, compared to that by AFEAS, and for our lingering and increasing emissions over the past years, compared to vanishing emissions in the AFEAS record. Consequently, our cumulative emissions until 2016 of 243–245 kt (both inversions) agree well with the cumulative emissions and productions in the expanded AFEAS data of 237 kt and with those by Velders and Daniel (2014) of 228 kt, all within the large uncertainties of the CFC-115 lifetime (Table 1). Nevertheless, our annual emissions for the recent years are large compared to the banks proposed by AFEAS ( $<0.01 \text{ kt}$  for 2016) and Velders and Daniel (2014) (8.6 kt for 2016) and are suggestive of additional, recently-produced CFC-115.

### 3.2.7 CFC-115 Emissions from Regional FLEXPART Inversion

The transport analysis of CFC-115 pollution peaks that were observed at Gosan indicated potential emission sources to be mainly located on the Chinese mainland (see Supplement). For the year 2012, no strong sources were located in the domain.



Thereafter, potential source locations were identified in the larger Shanghai area (years 2013–2015) and more diffusely from a broad area along the eastern Chinese coast (year 2016). Similarly, the Bayesian inversion yielded increases in posterior emissions mostly located within two areas in Eastern China (Fig. 9), the larger Shanghai area (including the Zhejiang and Jiangsu provinces) and the northern part of the Shandong province. ~~Emissions in these areas showed large posterior emissions~~

5 Large posterior emissions were detected for all analyzed years with the most prominent ~~emission hot spots emissions~~ in 2013 and 2014 and smaller posterior emissions in 2012. The locations of increased posterior emissions largely agree with the location of HFC-125 factories (B. Yao, pers. comm. 2017), which we speculate are sources of CFC-115 emissions, see below, and which were not used in the prior. Large posterior emissions in other parts of the domain were not robust, varied from year to year and were also connected with large posterior uncertainties. Total Chinese CFC-115 emissions were estimated to

10 average ~~0.54~~0.63 $\pm$ ~~0.34~~0.32 kt yr<sup>-1</sup> for the years 2013 to 2016 (Table 2, Fig. 7), whereas they remained relatively close to the prior value in 2012 (~~0.230.25~~ $\pm$ ~~0.38~~0.36 kt yr<sup>-1</sup>). The contribution of those grid cells containing the HFC-125 factories to the total Chinese emissions was considerably increased in the posterior estimates and reached between 12% and 41%, whereas they only contributed 9% in the prior. Posterior estimates for Japan and South Korea did not increase compared to the prior emission estimates.

### 15 3.2.8 CFC-115 Emissions from HFC-125 Production and Use

We hypothesize that the increased CFC-115 emissions derive, at least in part, from the production of hydrofluorocarbons (HFCs), which have been produced in large quantities during the last two decades. Similar hypotheses were recently put forward for emissions of other CFCs and HCFCs. HCFC-133a (Laube et al., 2014; Vollmer et al., 2015c) and CFC-114a (Laube et al., 2016) emissions were speculated to derive, at least in part, from the production of HFC-134a, and HCFC-31

20 from the production of HFC-32 (Schoenenberger et al., 2015). The most likely candidate, in the case of CFC-115, is the synthesis of the refrigerant HFC-125. CFC-115 is a known byproduct in one possible pathway to synthesize HFC-125, where tetrachloroethylene is treated with hydrogen fluoride (Rao, 1994; Shanthan Rao et al., 2015) followed by fluorine/chlorine exchanges. Although this pathway is not expected to be widely applied (pers. comm A. McCulloch) there are nevertheless four out of twelve production facilities in China using this route (Chinese Chemical Investment Network, 2017). A possible source is

25 the leakage of CFC-115 to the atmosphere as an intermediate product at factory level, similarly to the speculations put forward in the above studies. However, this hypothesis is difficult to test without factory-level measurements because uncertainties in the localization of “hot spot” emissions, such as the one identified with our regional modeling, exceed the narrow geographical location of a factory potentially present in the area. Nevertheless our analysis of regional emissions agrees with this hypothesis.

In addition to potential CFC-115 emissions at the HFC-125 factory level, we tested the hypothesis of CFC-115 impurities in

30 HFC-125, which would then be emitted to the atmosphere during leakage of HFC-125 in installed refrigeration equipment. In contrast to the cases of HCFC-133a/HFC-134a and HCFC-31/HFC-32, HFC-125 and CFC-115 have similar physico-chemical properties making it technically difficult to separate the two compounds (Corbin and Reutter, 1997; Kohno and Shibnuma, 2001; Brandstater et al., 2003; Cuzzato and Peron, 2003; Azzali and Basile, 2004; Piepho et al., 2006). We have detected CFC-115 in dilutions of high-purity HFC-125 (Fig. 4). We have also found excess (above ambient) CFC-115 in laboratory air at

AGAGE sites at times of air conditioner leakage (Fig. 4). Excess CFC-115 correlated strongly with the main constituents of the air conditioners (R-410, 50–55% by mass HFC-125, rest HFC-32), but ratios varied depending on site and recharge batch of the air conditioner fluid. These measurements have enabled us to demonstrate impurities ranging from  $0.7 - 11 \times 10^{-4}$  mol CFC-115 / mol HFC-125. We extrapolate these to global CFC-115 emissions based on this range, and using estimates of global HFC-125 emissions (40 kt yr<sup>-1</sup>, Rigby et al. (2014)), we conclude that this “impurity” source accounts only for 0.0036 – 0.057 kt yr<sup>-1</sup>. These impurity-based emissions are significantly below the last decade’s (2007–2016) mean yearly emissions of 0.80 kt yr<sup>-1</sup> derived from our inversions and they are also much lower than the recent growth in the CFC-115 global emissions. Note that HFC-125 in polluted air advected to the sites is generally too low to detect a corresponding CFC-115 enhancement, hence we cannot extend this CFC-115/HFC-125 analysis to the regular air measurements. The CFC-115/HFC-125 ratios in the CFC-115 pollution events observed at Gosan largely exceed the ratios found from air conditioner leakage thereby indicating sources other than HFC-125 impurities.

## 4 Conclusions

Based on a wealth of new observations, we reconstruct the atmospheric histories of CFC-13,  $\Sigma$ CFC-114, and CFC-115 from their first appearance in the atmosphere to 2016. This is the first comprehensive study of the very long lived CFC-13 in the atmosphere. ~~Our global model results suggest that over the last decade the global growth rate for~~ We show that growth rates for CFC-13 (> zero) and  $\Sigma$ CFC-114 has not declined and those of (< zero) have not declined for at least the last decade. For CFC-115, model results are suggestive of an increase in the growth rates in recent years. These observations make CFC-13 and CFC-115 ~~have increased, thereby making them~~ two of the few CFCs left with increasing global atmospheric abundances. Under the assumptions of no significant change in global atmospheric transport patterns or sink processes, these growth rates correspond to ongoing emissions, which have remained stable or even increased (in the case of CFC-115) over the past decade. This contrasts with the expectations of declining emissions due to the phase-out of these compounds under the regulations of the Montreal Protocol. We provide evidence for small emissions of  $\Sigma$ CFC-114 and CFC-115 as impurities in HFCs and speculate on the possibility of fugitive emissions at the process level. We also find evidence of small emissions of CFC-13 from ~~aluminium~~ aluminum smelting, but the chemistry that leads to CFC-13 production is not obvious. Impurities and fugitive emissions are not regulated by the Montreal Protocol, however even if these are small emissions, they can potentially lead to an increasing atmospheric abundance, particularly for the long-lived CFC-13. For  $\Sigma$ CFC-114 and CFC-115, we find significant emissions from the Asian region but the processes responsible remain largely unknown.

Data used in this study are available from the Supplement, from <https://agage.mit.edu/>, and from data repositories referenced therein.

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**Table 1.** Evolution of Atmospheric Metrics of CFC-13 ( $\text{CClF}_3$ ), CFC-114 ( ~~$\text{C}_2\text{Cl}_2\text{F}_4$~~  $\text{C}_2\text{Cl}_2\text{F}_4$ ), CFC-114a ( $\text{CCl}_2\text{FCF}_3$ ) and CFC-115 ( $\text{C}_2\text{ClF}_5$ ).

	CFC-13	CFC-114 <sup>a</sup>	<u>CFC-114a</u>	CFC-115
Ozone Depletion Potential (ODP)				
<del>ODP</del> in Montreal Protocol <sup>a</sup> <sup>b</sup>	1.0	1.0	~	0.6
<del>ODP</del> , semiempirical, WMO <del>2011</del> <sup>b</sup> <u>Ozone Assessment 2010</u> <sup>c</sup>	–	0.58	~	0.57
<del>ODP</del> , semiempirical, WMO <u>Ozone Assessment 2014</u> <sup>c</sup> <sup>d</sup>	–	0.50	~	0.26
ODP uncertainties, Velders and Daniel (2014) <sup>d</sup> <sup>e</sup>	–	37%/30%	~	34%/32%
Global Warming Potential (GWP): 100 yr [ <u>500 yr</u> ]				
<del>GWP</del> , WMO <del>2011</del> <sup>b</sup> <u>WMO Ozone Assessment 2010</u> <sup>c</sup>	14400 [ <u>16400</u> ]	9180 [ <u>6330</u> ]	~	7230 [ <u>9120</u> ]
IPCC 2013 <sup>e</sup> <sup>f</sup>	13900	8590	~	<u>7670</u>
<u>WMO Ozone Assessment 2014</u> <sup>g</sup>	<u>13900</u>	<u>8590</u>	~	7670
Velders and Daniel (2014) <sup>f</sup> <sup>h</sup>	–	9170 (28%) [ <u>6310 (36%)</u> ]	~	6930 (27%) [ <u>7520 (34%)</u> ]
<u>Davis et al. (2016)</u>	~	~	<u>6510</u>	~
Atmospheric lifetime [yr]				
Ravishankara et al. (1993) <sup>d</sup> <sup>i</sup>	640	300	~	1700
WMO Ozone Assessment 2006 <sup>h</sup> <sup>j</sup>	<del>640</del>	300	~	1700
WMO Ozone Assessment <del>2011</del> <sup>k</sup> <u>2010</u> <sup>k</sup>	<del>640</del>	190	~	1020
Baasandorj et al. (2013)	–	214 (210–217)	~	574 (528–625)
SPARC (2013) <sup>i</sup> <sup>l</sup>	–	189 (153–247)	~	540 (404–813)
WMO Ozone Assessment 2014 <sup>k</sup> <sup>m</sup>	640	189 (153–247)	~	540 (404–813)
<u>Davis et al. (2016)</u> <sup>n</sup>	~	~	<u>105 (103–107)</u>	~
<u>Laube et al. (2016)</u> <sup>o</sup>	~	~	<u>102 (82–133)</u>	~

a) Literature suggests that CFC-114 climate metrics were derived from laboratory studies for the CFC-114 ( $\text{CClF}_2\text{CClF}_2$ ) isomer alone (Sander et al. (2011) and references therein). However, in these studies there is no indication of removal of potential CFC-114a ( $\text{CCl}_2\text{FCF}_3$ ) impurities, which could have caused biases in the results, e.g. leading to an underestimate of the CFC-114 lifetime due to larger UV photolysis rates for the CFC-114a (lifetime 105 years, Davis et al. (2016)).

b) Handbook for the Montreal Protocol (UNEP, 2017).

c) WMO Ozone Assessment ~~2011~~<sup>b</sup> 2010 (Daniel and Velders, 2011).

d) WMO Ozone Assessment 2014 (Harris and Wuebbles, 2014) using the lifetimes from SPARC (2013) and the fractional release values from Montzka and Reimann (2011).

e) Absolute values as in WMO Ozone Assessment 2014. Uncertainties are  $\pm$  for “possible”/“most likely” (on a 95% confidence interval).

f) ICPP (Intergovernmental Panel on Climate Change) 2013 (Myhre et al., 2013) based on Hodnebrog et al. (2013).

g) WMO Ozone Assessment 2014 (Harris and Wuebbles, 2014).

h) Updates of WMO Ozone Assessment ~~2011~~<sup>b</sup> 2010 with lifetimes from SPARC (2013), and “possible” uncertainty ranges ( $\pm$ , 95% confidence interval).

i) Ravishankara et al. (1993) give a lower limit value of 380 yr for CFC-13 based on the assumption of a faster vertical mesospheric mixing.

j) WMO Ozone Assessment 2006 (Clerbaux and Cunnold, 2007).

k) WMO Ozone Assessment ~~2011~~<sup>k</sup> 2010 (Montzka and Reimann, 2011).

l) Stratosphere-troposphere Processes And their Role in Climate (SPARC), SPARC (2013).

m) WMO Ozone Assessment 2014 (Carpenter and Reimann, 2014).

n) Ranges in parentheses are due to the  $2\sigma$  uncertainty in the UV absorption spectra and  $\text{O}(^1\text{D})$  rate coefficients included in the model calculations.

o) Laube et al. (2016) adopted an uncertainty range of 83–133 years in analogy to the range for CFC-114 from SPARC (2013).

**Table 2.** By-country emissions of CFC-13,  $\Sigma$ CFC-114, and CFC-115, estimated by the regional inversion: Prior and posterior ~~estimate~~estimates. Emissions from areas with HFC-125 factories are termed “hot spot”. All values are given in units of kt yr<sup>-1</sup>; uncertainties represent 1- $\sigma$  range.

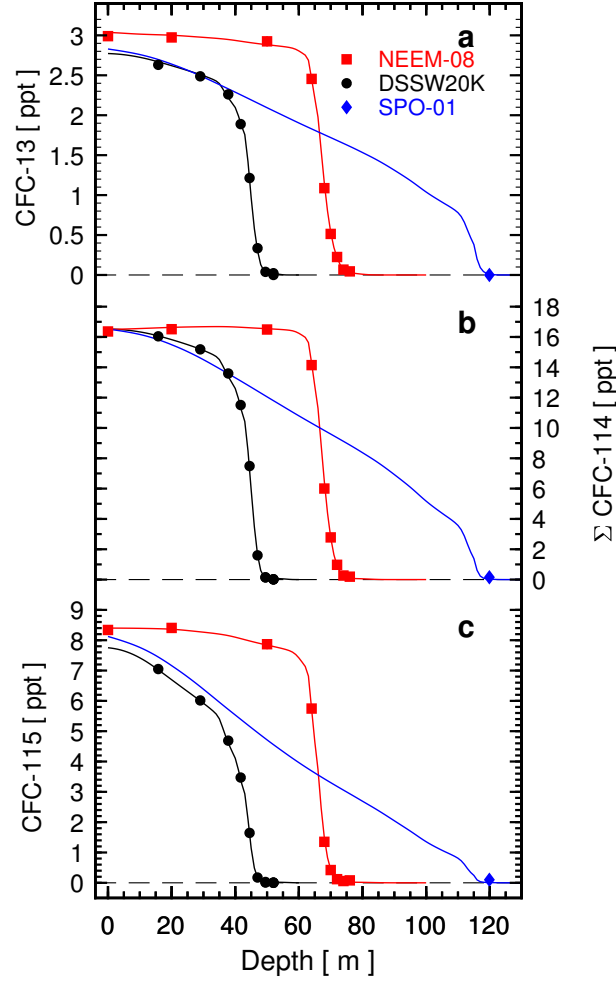
Compound	Year	China		Hot spot		South Korea		Japan	
		Prior	Posterior	Prior	Posterior	Prior	Posterior	Prior	Posterior
CFC-13	2012	0.1±0.045	0.14±0.03	—	—	0.004±0.004	0.001±0.002	0.01±0.008	0.007±0.006
CFC-13	2013	0.1±0.043	0.20±0.03	—	—	0.004±0.004	0.001±0.002	0.01±0.008	0.007±0.005
CFC-13	2014	0.1±0.043	0.15±0.03	—	—	0.004±0.004	0.003±0.002	0.01±0.008	0.007±0.006
CFC-13	2015	0.1±0.045	0.10±0.03	—	—	0.004±0.004	0.002±0.002	0.01±0.008	0.004±0.006
CFC-13	2016	0.1±0.045	0.10±0.03	—	—	0.004±0.004	0.001±0.002	0.01±0.008	0.004±0.005
$\Sigma$ CFC-114	2012	0.4±0.37	0.66±0.23	—	—	0.015±0.033	0.007±0.008	0.04±0.065	0.019±0.026
$\Sigma$ CFC-114	2013	0.4±0.35	1.00±0.24	—	—	0.015±0.034	0.005±0.005	0.04±0.068	0.033±0.029
$\Sigma$ CFC-114	2014	0.4±0.35	0.64±0.21	—	—	0.015±0.034	0.003±0.006	0.04±0.067	0.017±0.027
$\Sigma$ CFC-114	2015	0.4±0.37	0.61±0.17	—	—	0.015±0.033	0.004±0.007	0.04±0.065	0.034±0.036
$\Sigma$ CFC-114	2016	0.4±0.37	0.79±0.23	—	—	0.015±0.033	0.003±0.008	0.04±0.065	0.019±0.034
CFC-115	2012	0.2±0.68	0.25±0.36	0.018±0.13	0.046±0.039	0.007±0.051	0.004±0.008	0.02±0.13	0.020±0.066
CFC-115	2013	0.2±0.62	0.68±0.25	0.018±0.13	0.28 ±0.03	0.007±0.053	0.002±0.005	0.02±0.12	0.029±0.035
CFC-115	2014	0.2±0.62	0.59±0.26	0.016±0.13	0.18 ±0.04	0.007±0.053	0.002±0.006	0.02±0.12	0.048±0.038
CFC-115	2015	0.2±0.68	0.78±0.35	0.018±0.13	0.080±0.041	0.007±0.051	0.002±0.009	0.02±0.12	0.015±0.032
CFC-115	2016	0.2±0.62	0.47±0.41	0.018±0.13	0.12 ±0.06	0.007±0.053	0.005±0.008	0.02±0.12	0.009±0.029

~~Emissions of CFC-115 from north-eastern Asia as estimated by inverse modeling using the CFC-115 observations at Gosan (marked with a blue cross). a) common prior distribution, b-f) posterior distribution for the years 2012 to 2016. Red plus signs mark the location of known HFC-125 factories, which are hypothesized to be potential sources of CFC-115.~~

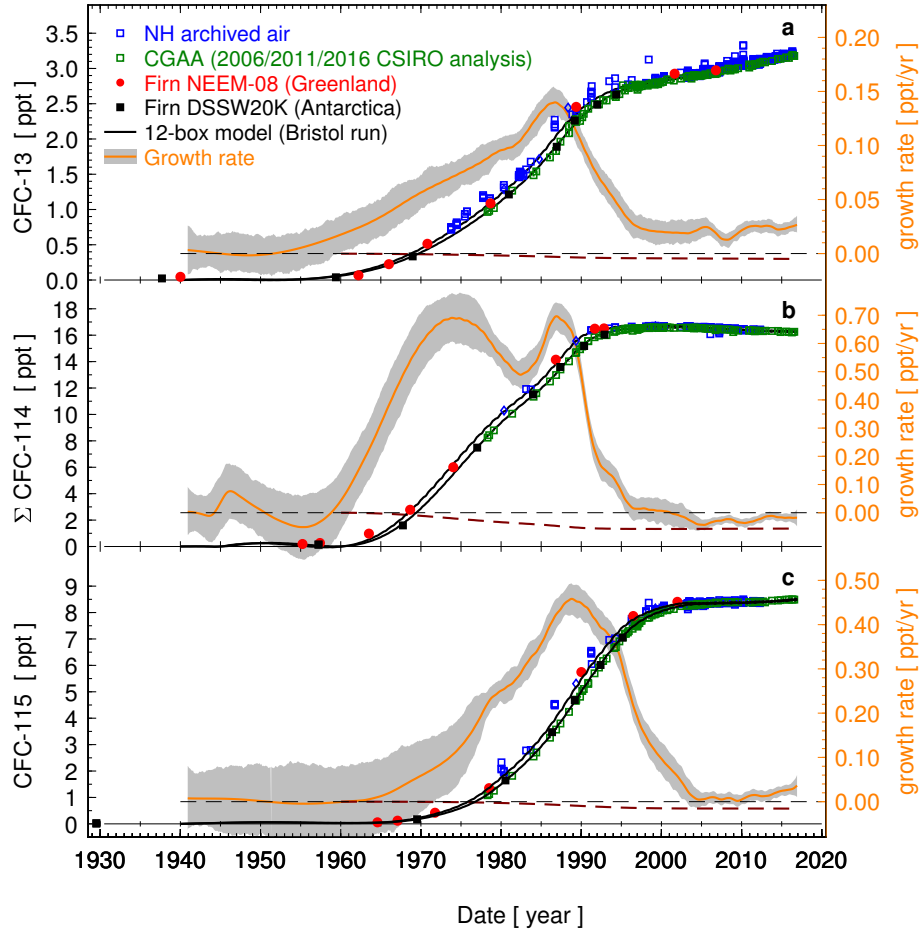




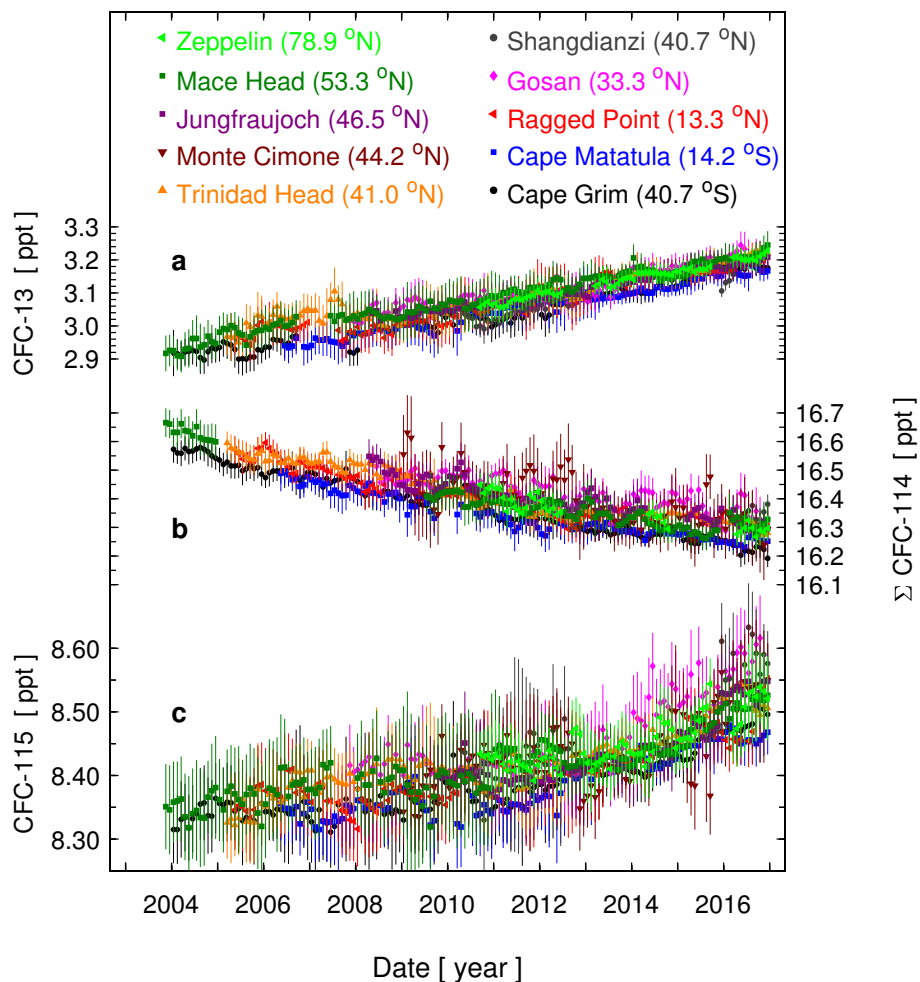
**Figure 1.** Sampling locations for the chlorofluorocarbons CFC-13,  $\Sigma$ CFC-114, and CFC-115 used in this analysis. Filled red diamonds are field sites of AGAGE (Advanced Global Atmospheric Gases Experiment) and related networks, green filled squares are urban sites, the cyan triangles denote the sampling stations for the firn air samples and the yellow filled circle is for the flask sampling site King Sejong, Antarctica.



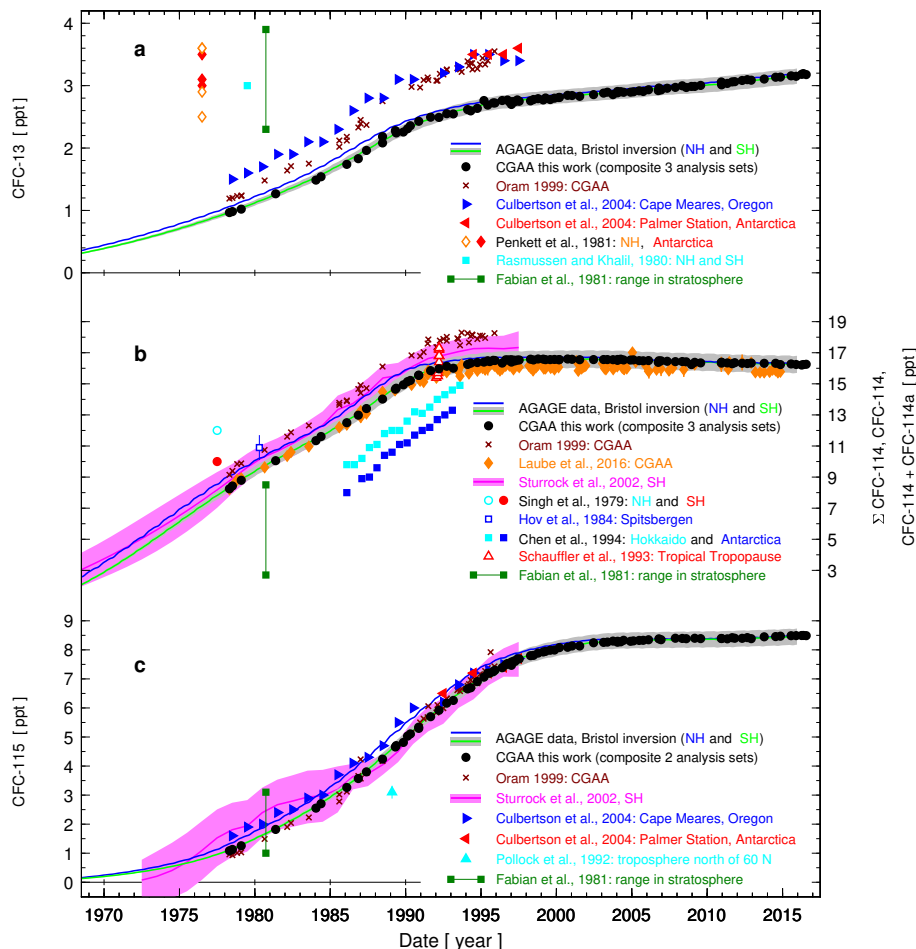
**Figure 2.** Depth profiles for the three chlorofluorocarbons CFC-13 (a),  $\Sigma$ CFC-114 (b), and CFC-115 (c) in polar firn. Measured dry-air mole fractions are shown for the Greenland site NEEM-08 (red squares), and the Antarctic sites Law Dome (DSSW20K, black circles) and South Pole (SPO-01, blue diamond). Generally the measurement precisions ( $1\sigma$ ) are smaller than the plotting symbols. The modeled mole fraction depth profiles (solid lines) correspond to the optimized emissions history from the CSIRO inversion, derived from the combined observations of all three firn sites, archived air and in-situ measurements.



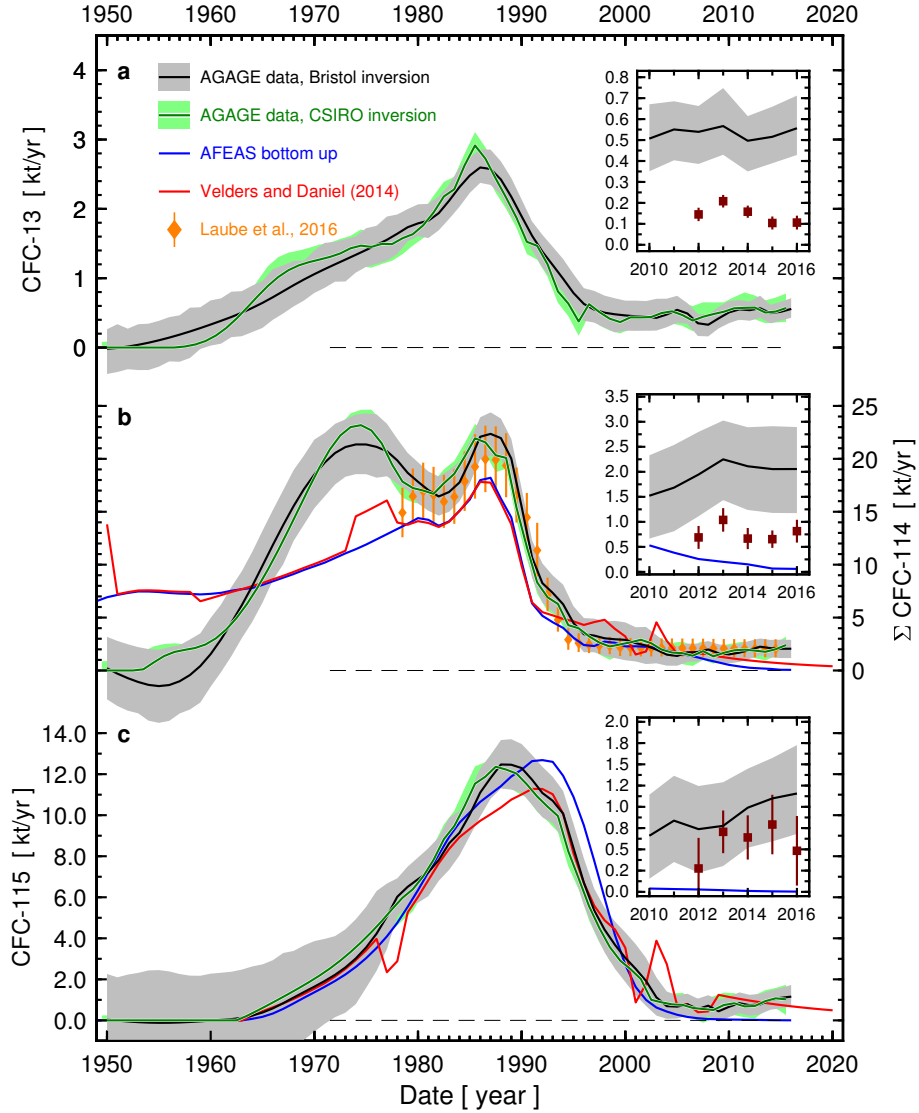
**Figure 3.** Measurements of the chlorofluorocarbons CFC-13 (a),  $\Sigma$ CFC-114 (b), and CFC-115 (c) from archived air samples and firn. Firn measurements are plotted against either effective or mean ages of the samples (see text). In-situ measurement results from the AGAGE stations are not plotted for clarity. The inversion results are given for the northern hemisphere (upper solid lines) and southern hemisphere (lower solid lines). Growth rates (shown in orange using the right axes) are globally averaged from model results. Note that zero growth, shown as dashed ~~orange~~ ~~black~~ lines, is offset relative to the left axes. With focus to the recent part of the record ~~these the~~ growth rates deviate significantly from the growth rates that would be obtained if zero emissions were assumed (shown as maroon dashed lines, calculated by dividing the global mole fraction by the lifetime).



**Figure 4.** ~~Monthly mean abundances~~ Abundances of the chlorofluorocarbons CFC-13 (a),  $\Sigma$ CFC-114 (b), and CFC-115 (c) at ~~selected~~ stations of the AGAGE (Advanced Global Atmospheric Gases Experiment) network. These in situ data are binned into monthly means after applying a pollution filter to limit the records to samples under background conditions (O'Doherty et al., 2001; Cunnold et al., 2002). Vertical bars are standard deviations of the monthly means ( $1\sigma$ ) ~~of pollution-filtered observations~~. Occasional deviations of the Monte Cimone measurements from the other sites for  $\Sigma$ CFC-114 and CFC-115 (CFC-13 not measured at this site) are explained by the significantly larger propagation uncertainties (partially caused by larger precisions) for this site compared to the other site.

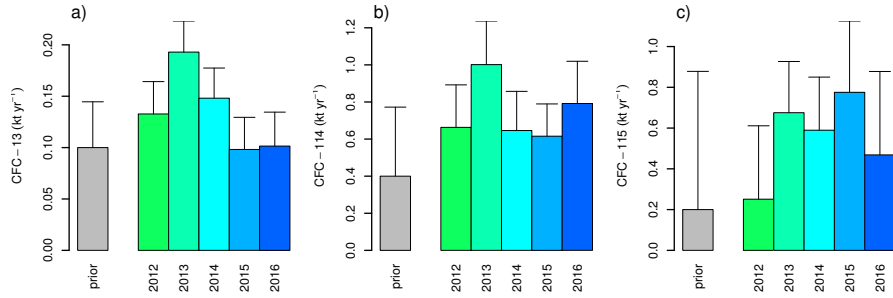


**Figure 5.** Comparison of the atmospheric records of CFC-13 (a),  $\Sigma$ CFC-114 (b), and CFC-115 (c) from this study with previous results. Cape Grim Air Archive (CGAA) samples and subsamples have been analyzed multiple times — here we show analysis results published by Oram (1999), Laube et al. (2016) and the present study (three separate analysis sets are averaged, see Supplement). Light grey bands denote the uncertainty on our SH model results including calibration uncertainty. Uncertainty bands for the NH, which are similar to the SH, are omitted from this plot for clarity. Results for  $\Sigma$ CFC-114 are from combined measurements of the two analytically unseparated  $\text{CFC-114-C}_2\text{Cl}_2\text{F}_4$  isomers. Exceptions to this are the studies by Oram (1999) and Laube et al. (2016) where the numerical sums of the two individual isomer measurements are shown. Also, results by Chen et al. (1994) (values approximated only from their graphical display) are of the  $\text{CClF}_2\text{CClF}_2$  isomer-CFC-114 only. Assuming a 5%–6% contribution of CFC-114a in  $\Sigma$ CFC-114, these results are still significantly lower compared to our study. All results are left on the calibration scales of the published data.

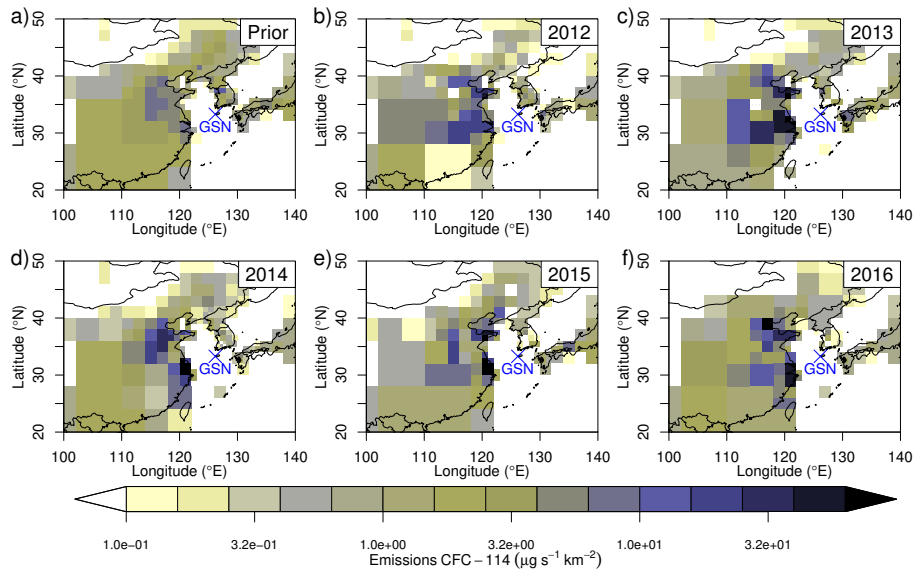


**Figure 6.** Global emissions of the chlorofluorocarbons CFC-13 (a),  $\Sigma$ CFC-114 (both isomers combined) (b), and CFC-115 (c) from atmospheric observations. Black lines and grey shaded areas are for the 'Bristol' inversion and green lines and green shaded areas for the 'CSIRO' inversion (see text). ~~CFC-114 emissions~~ Emissions from Laube et al. (2016) are the sum of the emissions of both  $\text{C}_2\text{Cl}_2\text{F}_4$  isomers. In the insets, our observation-based global emissions and the expanded AFEAS bottom-up emissions are compared to the East Asian emissions (maroon diamonds).

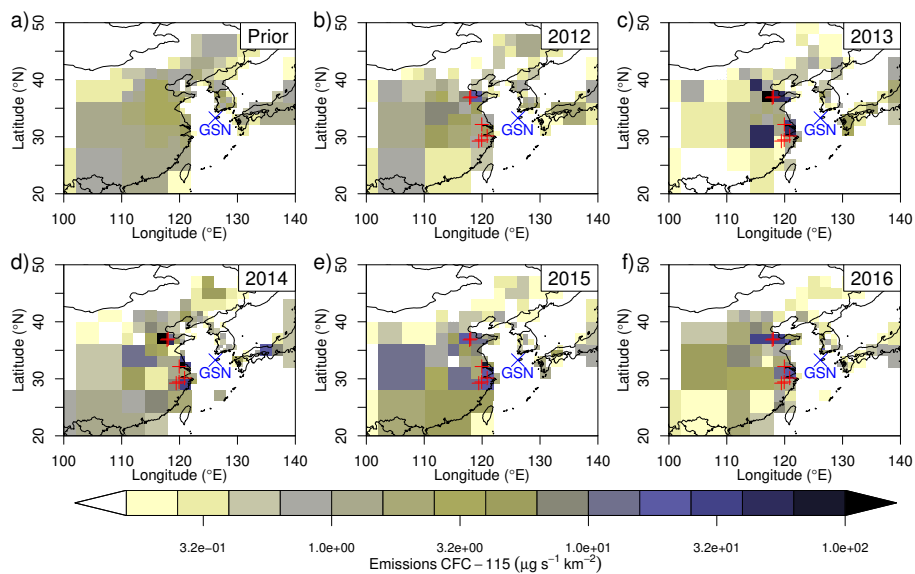




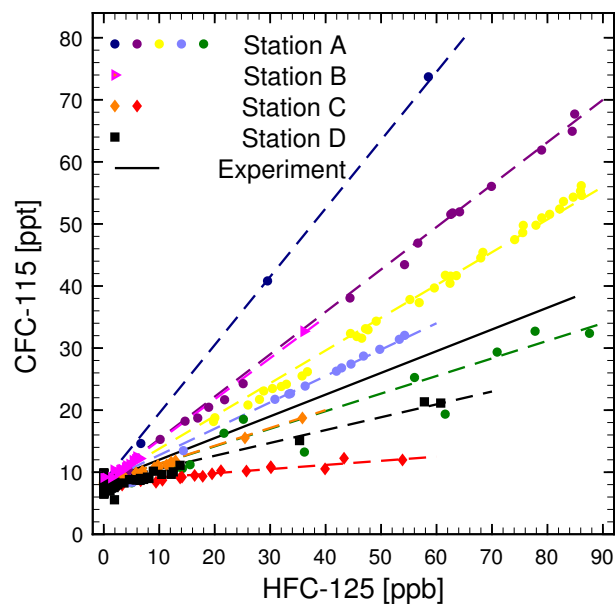
**Figure 7.** Total Chinese emissions of CFC-13 (a),  $\Sigma\text{CFC-114}$  (b), and CFC-115 (c), estimated by the regional inversion. Uncertainties represent  $1-\sigma$  range.



**Figure 8.** Emissions of  $\Sigma\text{CFC-114}$  from north-eastern Asia as estimated by inverse modeling using the  $\Sigma\text{CFC-114}$  observations at Gosan (marked with a blue cross). a) common prior distribution, b-f) posterior distribution for the years 2012 to 2016.



**Figure 9.** Emissions of CFC-115 from north-eastern Asia as estimated by inverse modeling using the CFC-115 observations at Gosan (marked with a blue cross). a) common prior distribution, b-f) posterior distribution for the years 2012 to 2016. Red plus signs mark the location of known HFC-125 factories, which are hypothesized to be potential sources of CFC-115.



**Figure 10.** CFC-115 contamination in HFC-125 as found in contaminated laboratory air samples at AGAGE stations. Measurements are shown for four stations (A–D) during times of air conditioner leakages (R-410, 50–55% by mass HFC-125, rest is HFC-32). They are plotted for a HFC-125 range 0 – 90 ppb (parts per billion,  $10^{-9}$ ). Differently-colored episodes are separated by times of air conditioner maintenance and refilling demonstrating the variable fraction of CFC-115 in differing batches of the refrigerant. Based on these observations we find a range from  $0.7 - 11 \times 10^{-4}$  mol CFC-115 / mol HFC-125. The solid line ( $3.5 \times 10^{-4}$  mol CFC-115 / mol HFC-125) ~~derives~~ is the result from a direct measurement of CFC-115 in a dilution of an independently-obtained sample of pure HFC-125. Dashed lines are approximated only and serve as visual support of the data.