Aircraft-Based Observations of Ozone-Depleting Substances in the Upper Troposphere and Lower Stratosphere in and Above the Asian Summer Monsoon

Karina E. Adcock, Paul J. Fraser, Brad D. Hall, Ray L. Langenfelds, Geoffrey Lee, Stephen A.Montzka, David E. Oram, Thomas Röckmann, Fred Stroh, William T. Sturges, Bärbel Vogel, and Johannes C. Laube

JGR Atmospheres

Research Article | Open Access

Volume 126, Issue 1
16 January 2021
e2020JD033137

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First published: 04 December 2020 | https://doi.org/10.1029/2020JD033137

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Metrics

Abstract

Recent studies show that the Asian summer monsoon anticyclone (ASMA) transports emissions from the rapidly industrializing nations in Asia into the tropical upper troposphere. Here, we present a unique set of measurements on over 100 air samples

Details

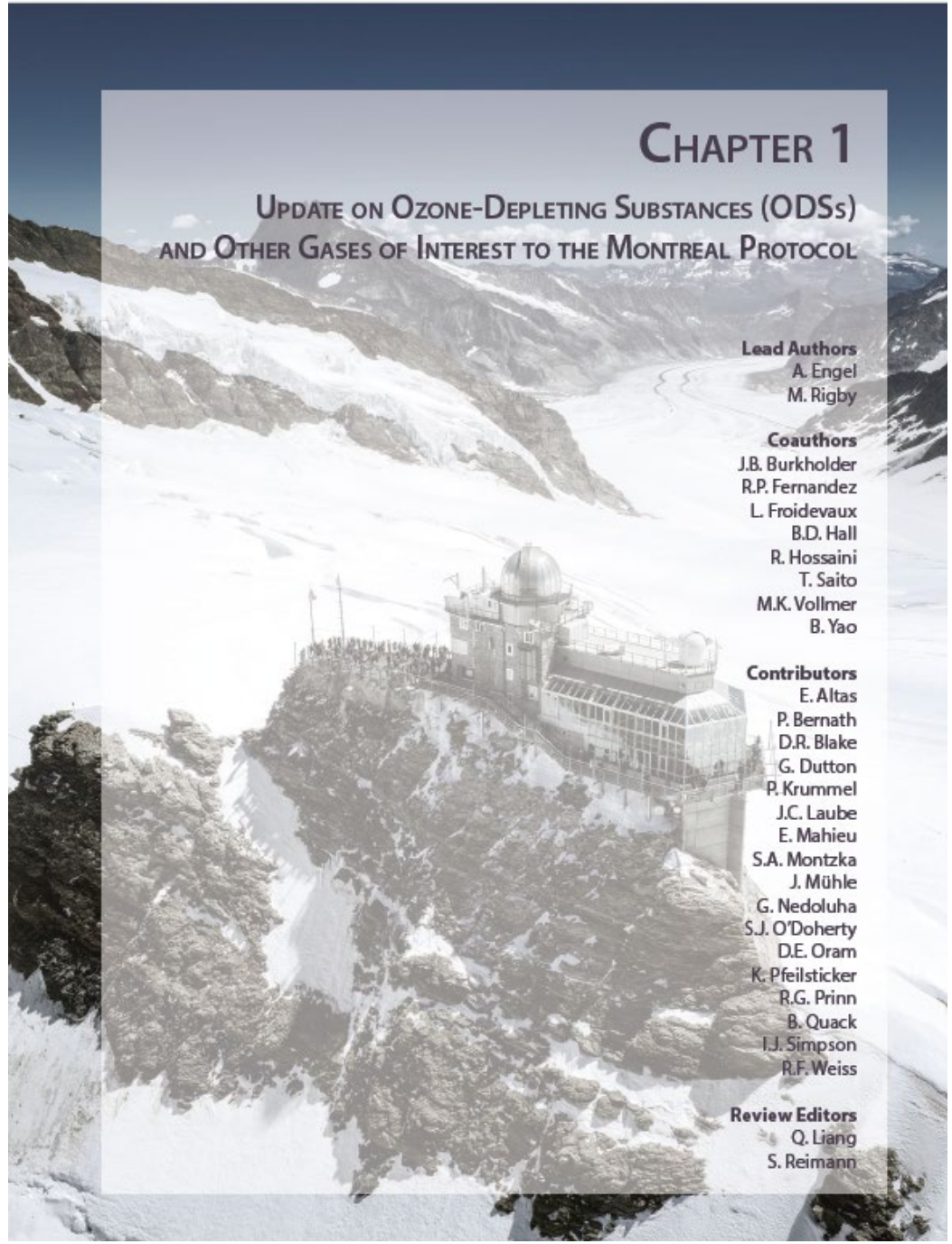
Paper Road Map

- Brief Background Information on VSLS and StratoClim
- StratoClim Long-Lived ODS
- StratoClim Short-Lived ODS
- Model Back-Trajectory Analysis
- Equivalent Chlorine (ECl)
- Equivalent Effective Stratospheric Chlorine (EESC)
- Wrap-up

Main Conclusions from Adcock et al. (2020)

Highlights the importance of the ASM as a fast transport mechanism in an important ODS region and the importance of Cl-VSLS in the northern extratropical lower stratosphere

- First set of in situ data for many ODS in lower stratosphere over ASM
- Cl-VSLS in ASM region higher than reported in 2018 WMO report. VSLS increase EESC estimate by 8-26% in NH extratropical lower stratosphere.
- The ECI and EESC for long-lived species is also higher than reported global averages recently.
  - The large emission sources and amount of input to the stratosphere during ASM are the reason



Chapter 1

Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol

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Review Editors
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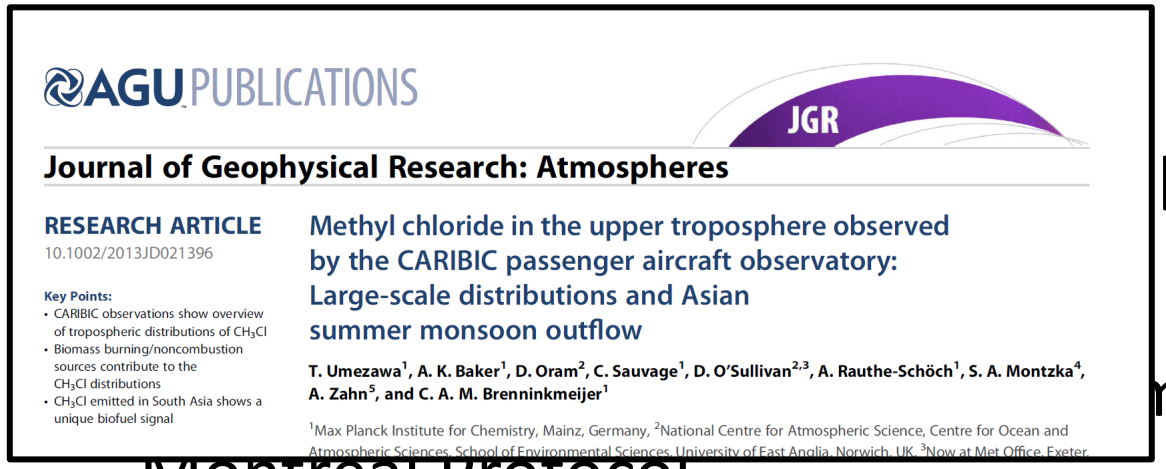
Very Short-Lived Substances (VSLS): Who Cares?

- Atmospheric lifetime less than 6 months and are not regulated by the Montreal Protocol

- ASM anticyclone is an efficient pathway to move air rapidly into the stratosphere – VSLS can reach stratosphere despite their short lifetime.

- Cl-VSLS emissions are on the rise, still a small portion of ODS but they are gaining attention

nces (VSLS): Who Cares?



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Journal of Geophysical Research: Atmospheres

RESEARCH ARTICLE

10.1002/2013JD021396

Key Points:
- CARIBIC observations show overview of tropospheric distributions of CH_3Cl
- Biomass burning/noncombustion sources contribute to the CH_3Cl distributions
- CH_3Cl emitted in South Asia shows a unique biofuel signal

Methyl chloride in the upper troposphere observed by the CARIBIC passenger aircraft observatory: Large-scale distributions and Asian summer monsoon outflow

T. Umezawa[1], A. K. Baker[1], D. Oram[2], C. Sauvage[1], D. O'Sullivan[2,3], A. Rauthe-Schöch[1], S. A. Montzka[4], A. Zahn[5], and C. A. M. Brenninkmeijer[1]

[1]Max Planck Institute for Chemistry, Mainz, Germany, [2]National Centre for Atmospheric Science, Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, UK, [3]Now at Met Office, Exeter

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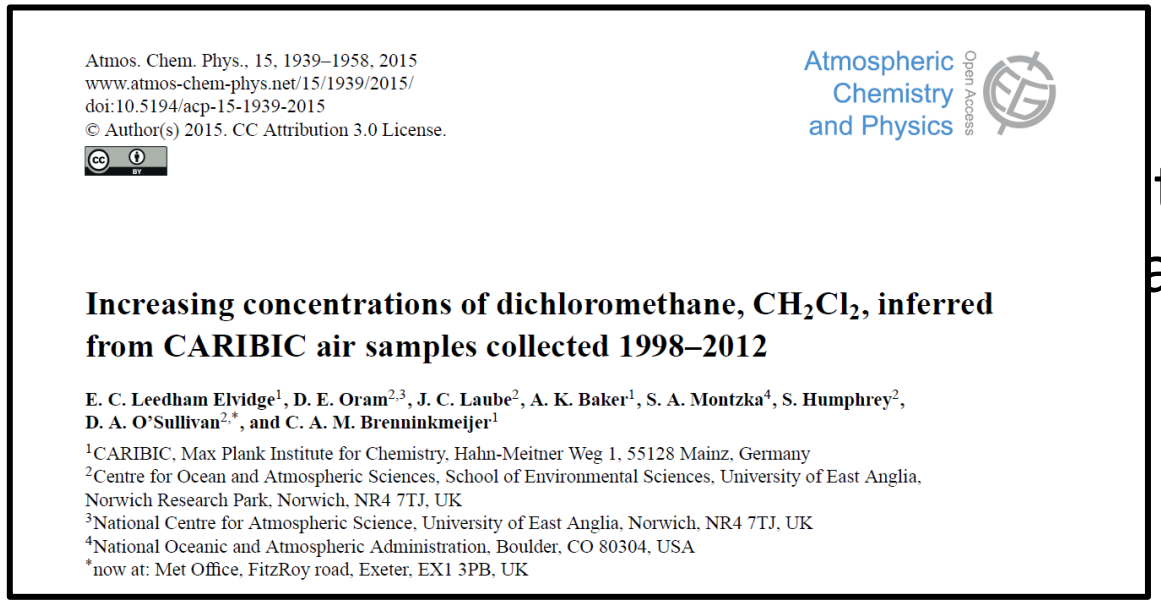

Atmos. Chem. Phys., 15, 1939–1958, 2015
www.atmos-chem-phys.net/15/1939/2015/
doi:10.5194/acp-15-1939-2015
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Atmospheric Chemistry and Physics Open Access

Increasing concentrations of dichloromethane, CH_2Cl_2, inferred from CARIBIC air samples collected 1998–2012

E. C. Leedham Elvidge[1], D. E. Oram[2,3], J. C. Laube[2], A. K. Baker[1], S. A. Montzka[4], S. Humphrey[2], D. A. O'Sullivan[2,*], and C. A. M. Brenninkmeijer[1]

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nature geoscience

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https://doi.org/10.1038/s41561-018-0278-2

Rapid increase in ozone-depleting chloroform emissions from China

Xuekun Fang[1*], Sunyoung Park[2], Takuya Saito[3], Rachel Tunnicliffe[4,5], Anita L. Ganesan[5*], Matthew Rigby[4*], Shanlan Li[2], Yoko Yokouchi[3], Paul J. Fraser[6], Christina M. Harth[7], Paul B. Krummel[6], Jens Mühle[7], Simon O'Doherty[4], Peter K. Salameh[6], Peter G. Simmonds[4], Ray F. Weiss[7], Dickon Young[4], Mark F. Lunt[4], Alistair J. Manning[8], Alicia Gressent[1] and Ronald G. Prinn[1]

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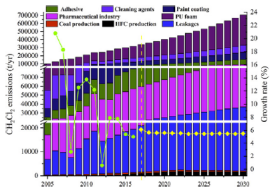
Bottom-up anthropogenic dichloromethane emission estimates from China for the period 2005–2016 and predictions of future emissions

Yanlin Feng, Pengju Bie, Ziyuan Wang, Lei Wang, Jianbo Zhang*

College of Environmental Sciences and Engineering, Peking University, China

GRAPHICAL ABSTRACT



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JGR Atmospheres

RESEARCH ARTICLE
10.1029/2018JD029400

Key Points:
- Stratospheric chlorine from very short-lived substances increased by 3.8 ppt/year over 2004–2017, with a growth slowdown in 2015–2017
- Chlorine from short-lived substances improves model representation of upper stratospheric HCl trends
- Short-lived chlorine offsets the 2004–2017 rate of upper stratospheric HCl decline by 15%

Supporting Information:
- Supporting Information S1

Recent Trends in Stratospheric Chlorine From Very Short-Lived Substances

Ryan Hossaini[1], Elliot Atlas[2], Sandip S. Dhomse[3], Martyn P. Chipperfield[3], Peter F. Bernath[4,5], Anton M. Fernando[6], Jens Mühle[7], Amber A. Leeson[1], Stephen A. Montzka[8], Wuhu Feng[3,9], Jeremy J. Harrison[10,11], Paul Krummel[12], Martin K. Vollmer[13], Stefan Reimann[13], Simon O'Doherty[14], Dickon Young[14], Michela Maione[15], Jgor Arduini[15], and Chris R. Lunder[16]

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and Physics

Geophysical Research Letters

RESEARCH LETTER
10.1029/2018GL081455

Key Points:
- Ozone depletion potentials of very short-lived substances ($CHCl_3$, CH_2Cl_2, C_2Cl_4, and $C_2H_4Cl_2$) were calculated using a chemical transport model
- Calculated ozone depletion potentials vary by a factor of 2-3 depending on emission location, larger ODPs for Asian emissions
- Efficient transport of very short-lived substances from continental East Asia to tropical lower stratosphere lead to larger Asian ODPs

Supporting Information:
- Supporting Information S1

On the Regional and Seasonal Ozone Depletion Potential of Chlorinated Very Short-Lived Substances

Tom Claxton[1], Ryan Hossaini[1], Oliver Wild[1], Martyn P. Chipperfield[2,3], and Chris Wilson[2,3]

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Abstract Chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), perchloroethylene (C_2Cl_4), and 1,2-dichloroethane ($C_2H_4Cl_2$) are chlorinated Very Short-Lived Substances (Cl-VSLS) with a range of commercial/industrial applications. Recent studies highlight the increasing influence of Cl-VSLS on the stratospheric chlorine budget and therefore their possible role in ozone depletion. Here we evaluate the ozone depletion potential (ODP) of these Cl-VSLS using a three-dimensional chemical transport model and investigate sensitivity to emission location/season. The seasonal dependence of the ODPs is small, but ODPs vary by a factor of 2–3 depending on the continent of emission: 0.0143–0.0264 ($CHCl_3$), 0.0097–0.0208 (CH_2Cl_2), 0.0057–0.0198 (C_2Cl_4), and 0.0029–0.0119 ($C_2H_4Cl_2$). Asian emissions produce the largest ODPs owing to proximity to the tropics and efficient troposphere-to-stratosphere transport of air originating from industrialized East Asia. The Cl-VSLS ODPs are generally small, but the upper ends of the $CHCl_3$ and

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https://doi.org/10.1038/s41561-018-0278-2

hloroform

nita L. Ganesan[5]*,
a M. Harth[7], Paul B. Krummel[6],
[4], Ray F. Weiss[7],
d Ronald G. Prinn[1]

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Bottom-up anthropogenic dichloromethane emission estimates from China for the period 2005–2016 and predictions of future emissions

Check for updates

StratoClim Project

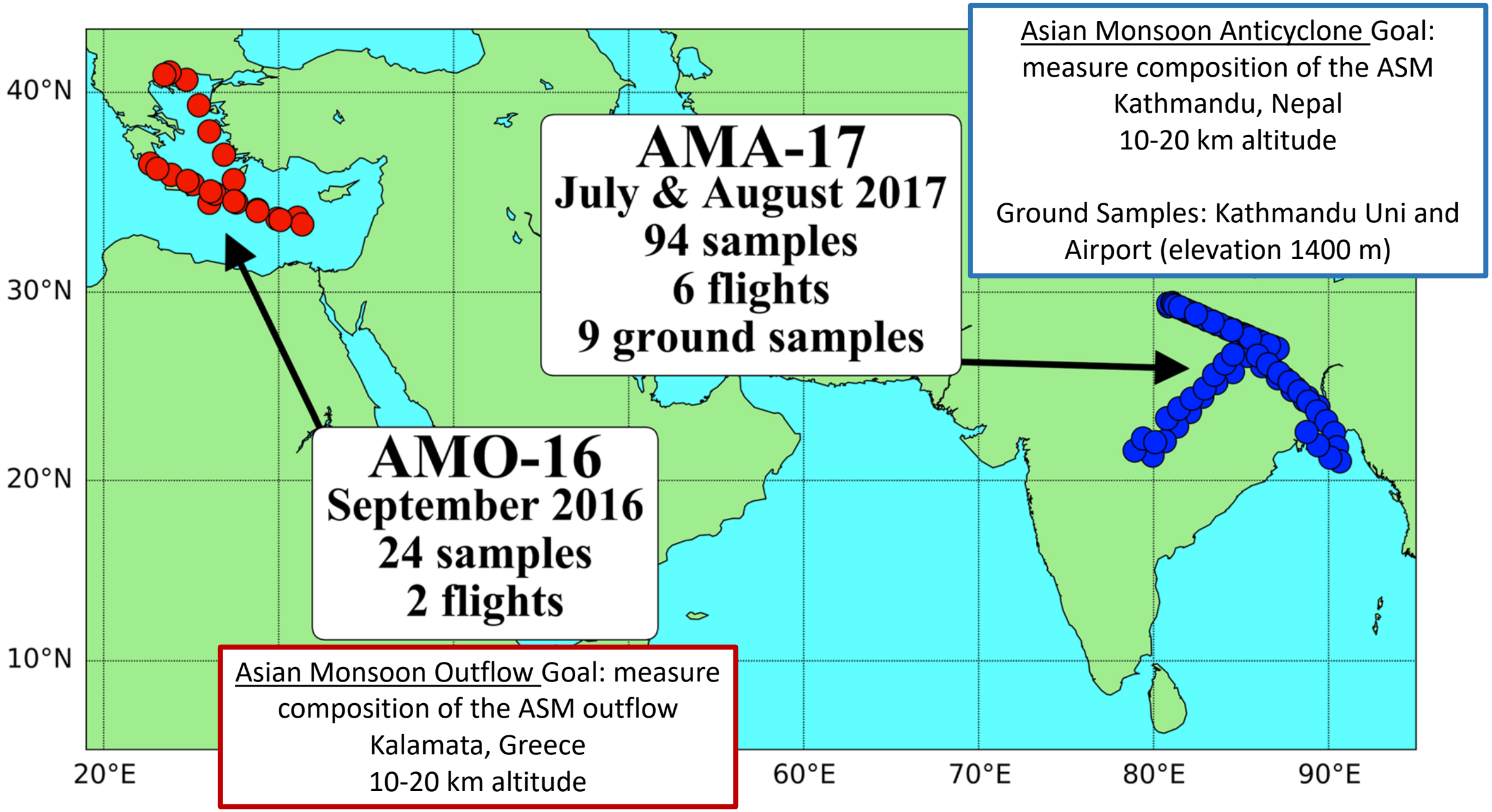
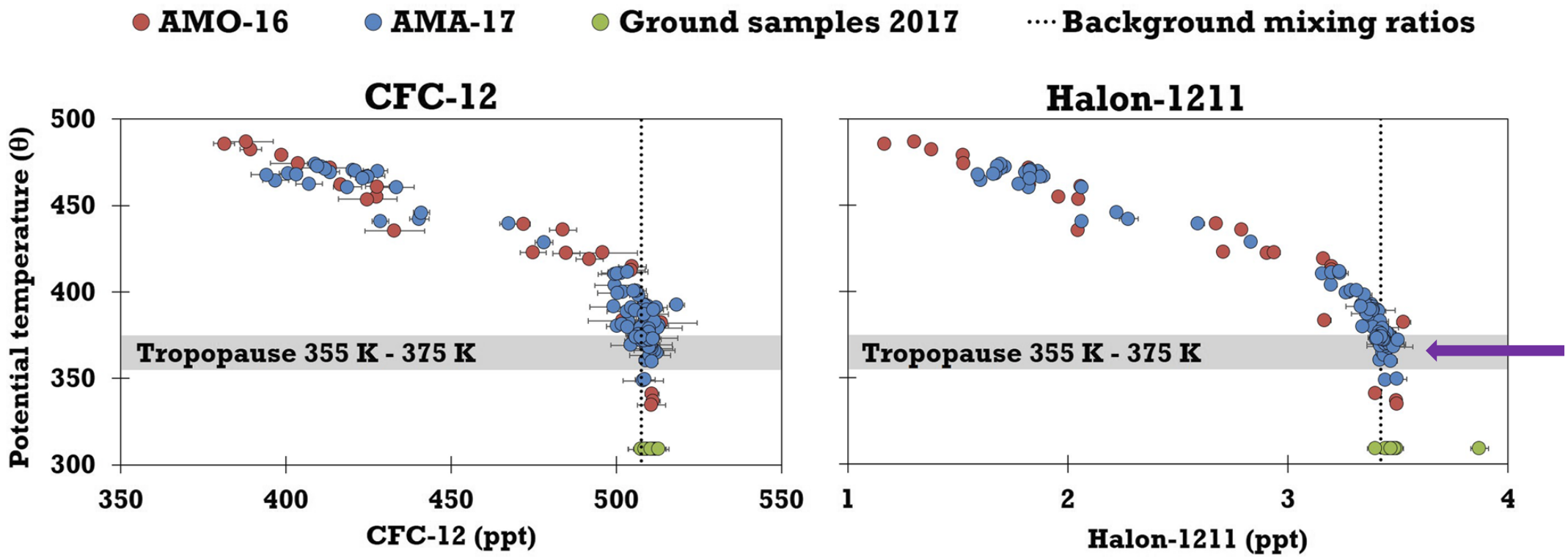


Figure 1: Whole air sample locations

Long-lived ODS phased out under Montreal Protocol



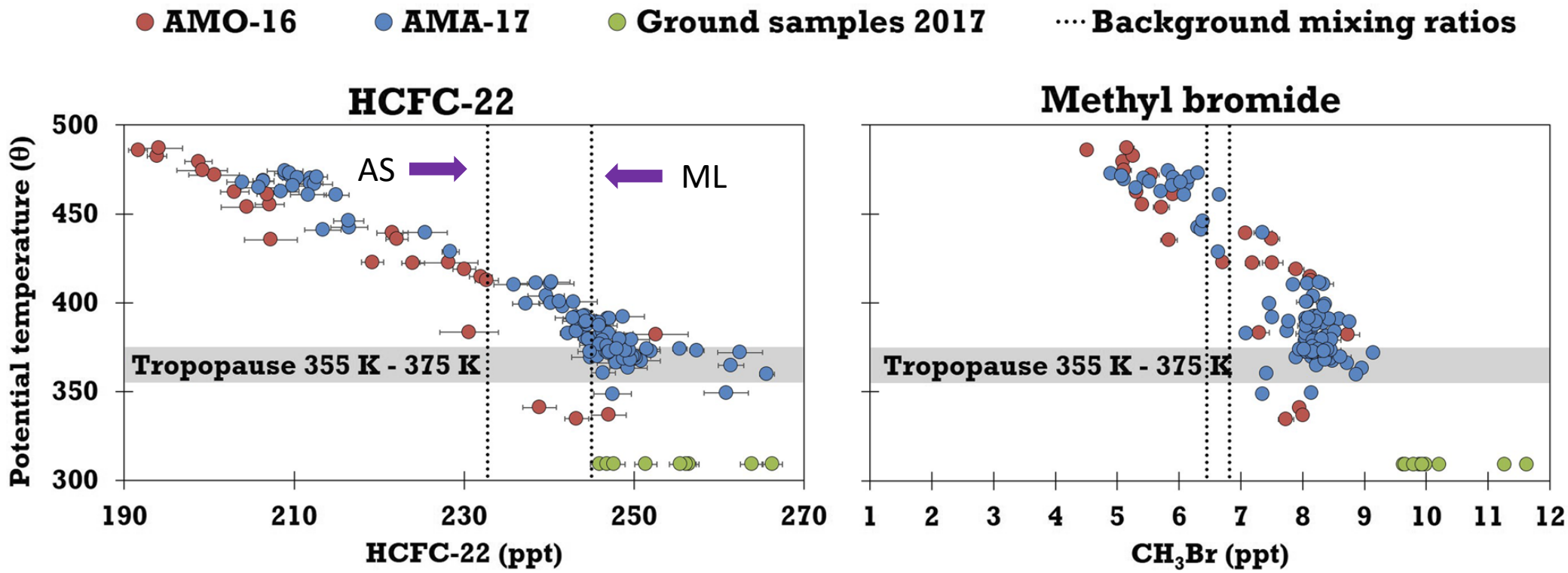
Similar mixing ratio, with little variation, to NOAA background average

Decrease in lower stratosphere, mixing and photochemical degradation

Halon-1211 and CFC-11 (not shown) decrease used to define stratosphere – gray band

Figure 2: Long-lived

Long-lived ODS phase out in progress under Montreal Protocol

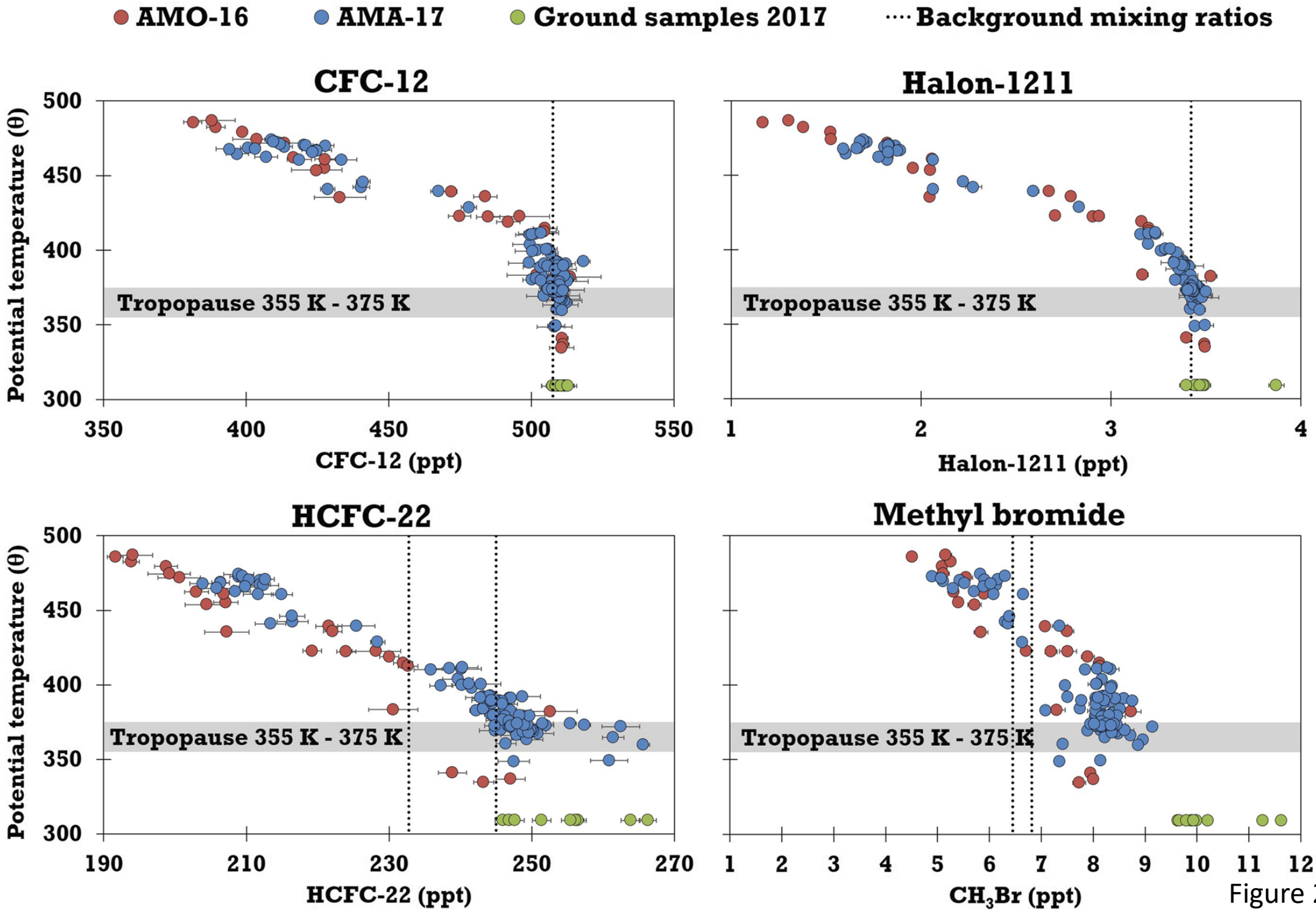


Two background sets: American Samoa lower line, Mauna Loa higher

Enhanced above background: 5% for HCFC-22 and 25% for CH_3Br
Similar for HCFC-141b (6%) and CH_3Cl (14%)

Large emissions in the monsoon region

Figure 2: Long-lived



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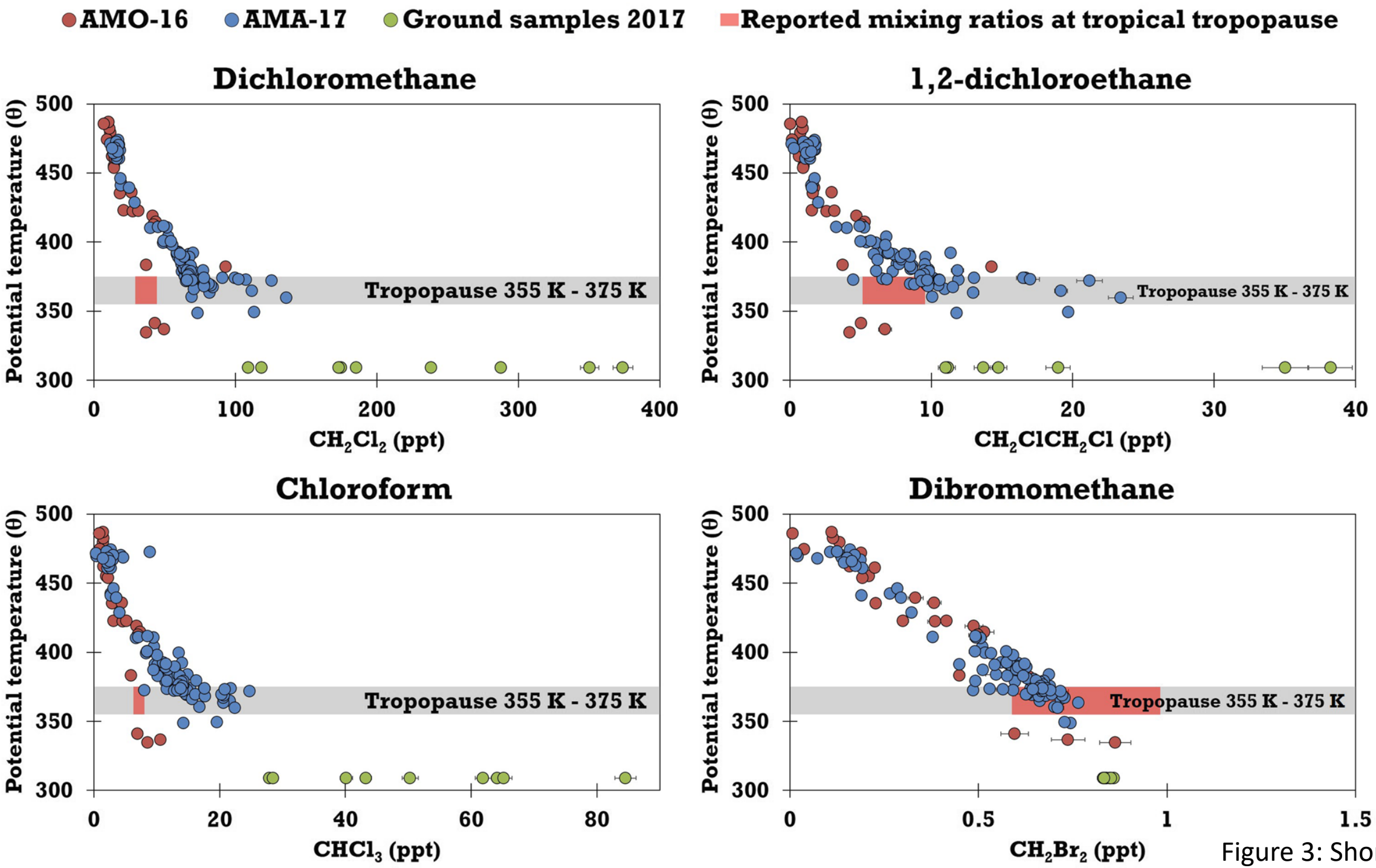
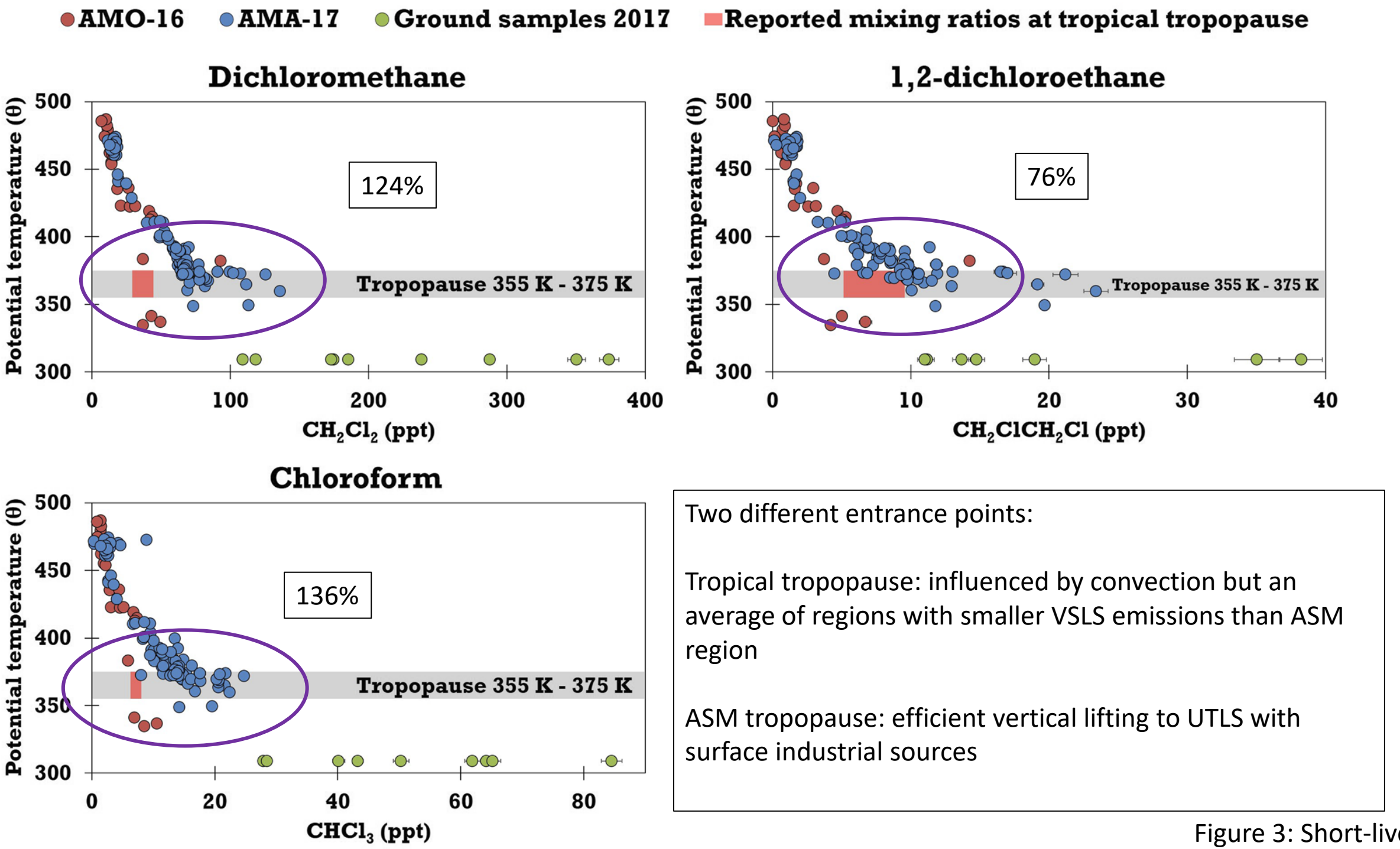


Figure 3: Short-lived

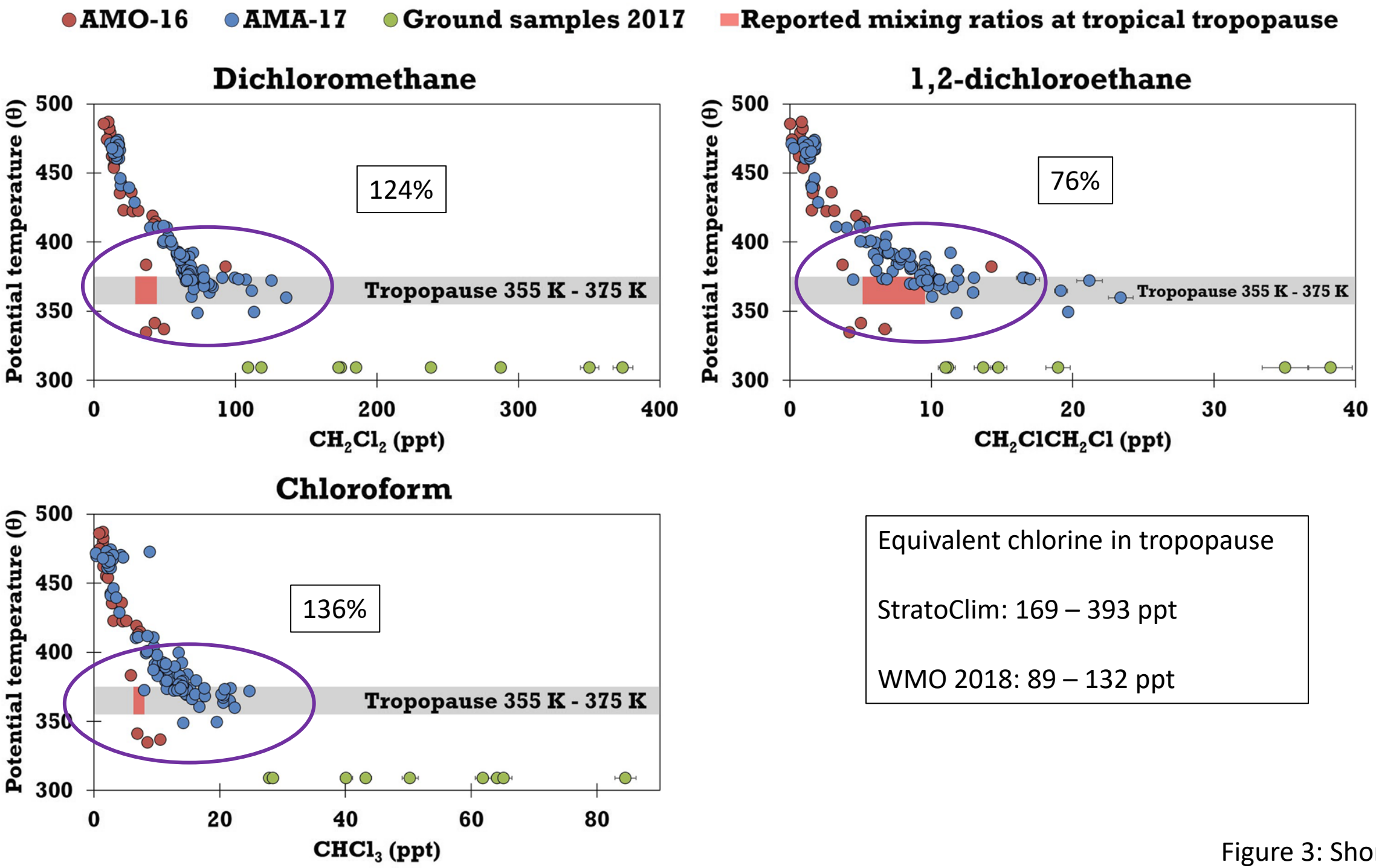


Two different entrance points:

Tropical tropopause: influenced by convection but an average of regions with smaller VSLS emissions than ASM region

ASM tropopause: efficient vertical lifting to UTLS with surface industrial sources

Figure 3: Short-lived



Equivalent chlorine in tropopause

StratoClim: 169 – 393 ppt

WMO 2018: 89 – 132 ppt

Figure 3: Short-lived

10-Day CLaMS Backward Trajectory end points in the model BL (9% of total)

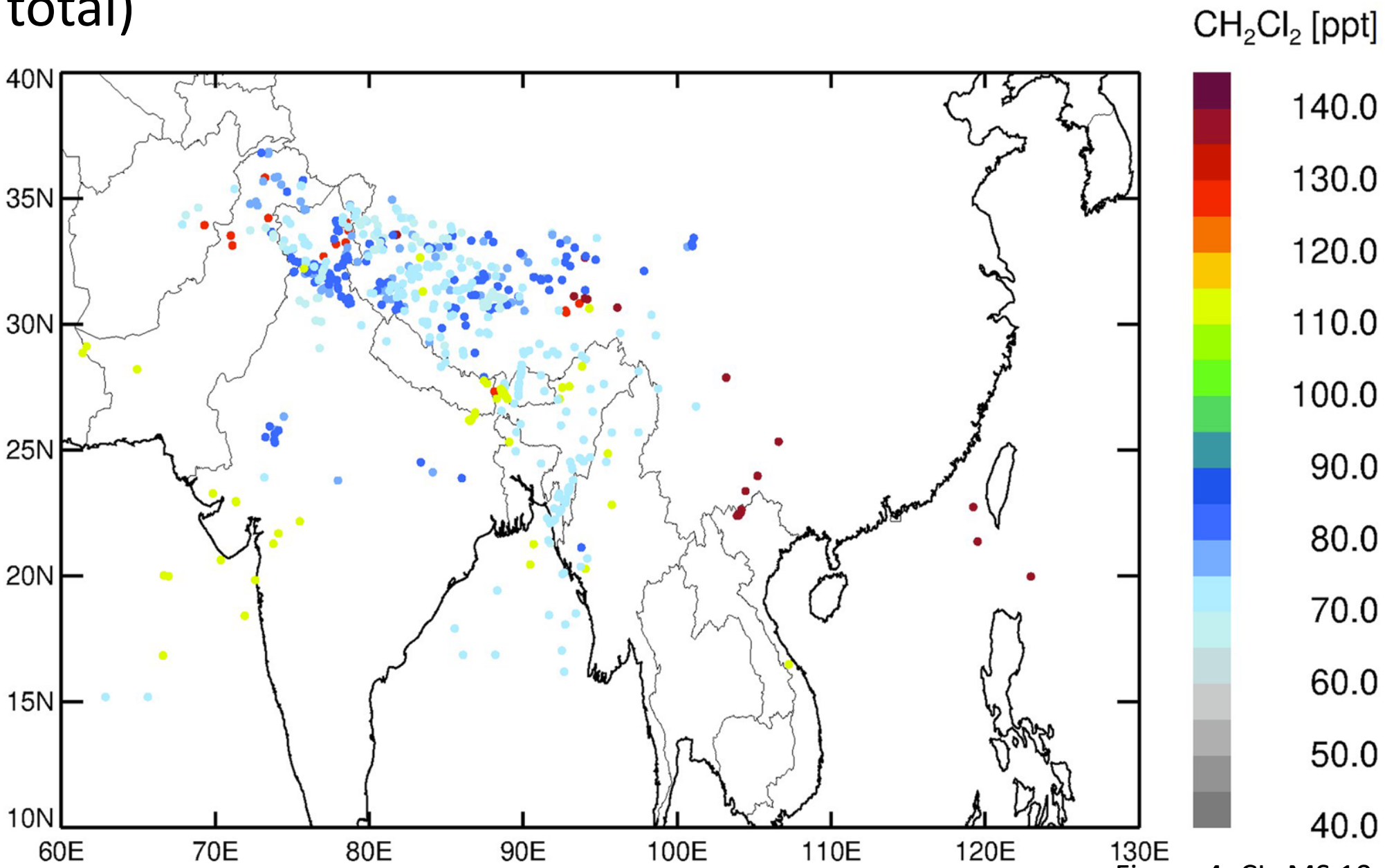


Figure 4: CLaMS 10 day end points

High DCM in east Asia/China and north-western flank of Tibetan Plateau (NW India and N Pakistan)

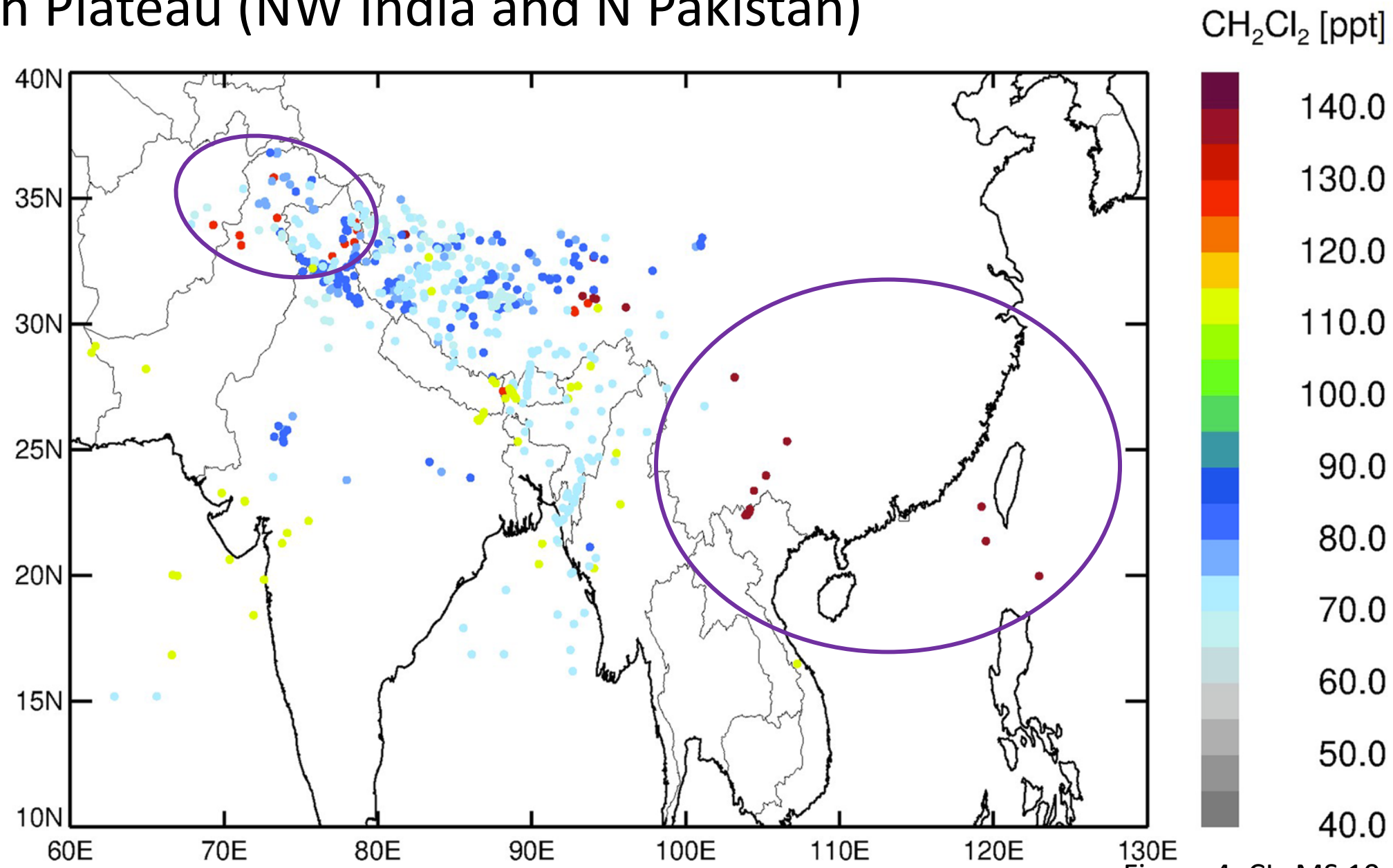


Figure 4: CLaMS 10 day end points

Low DCM along Tibetan Plateau and Bay of Bengal

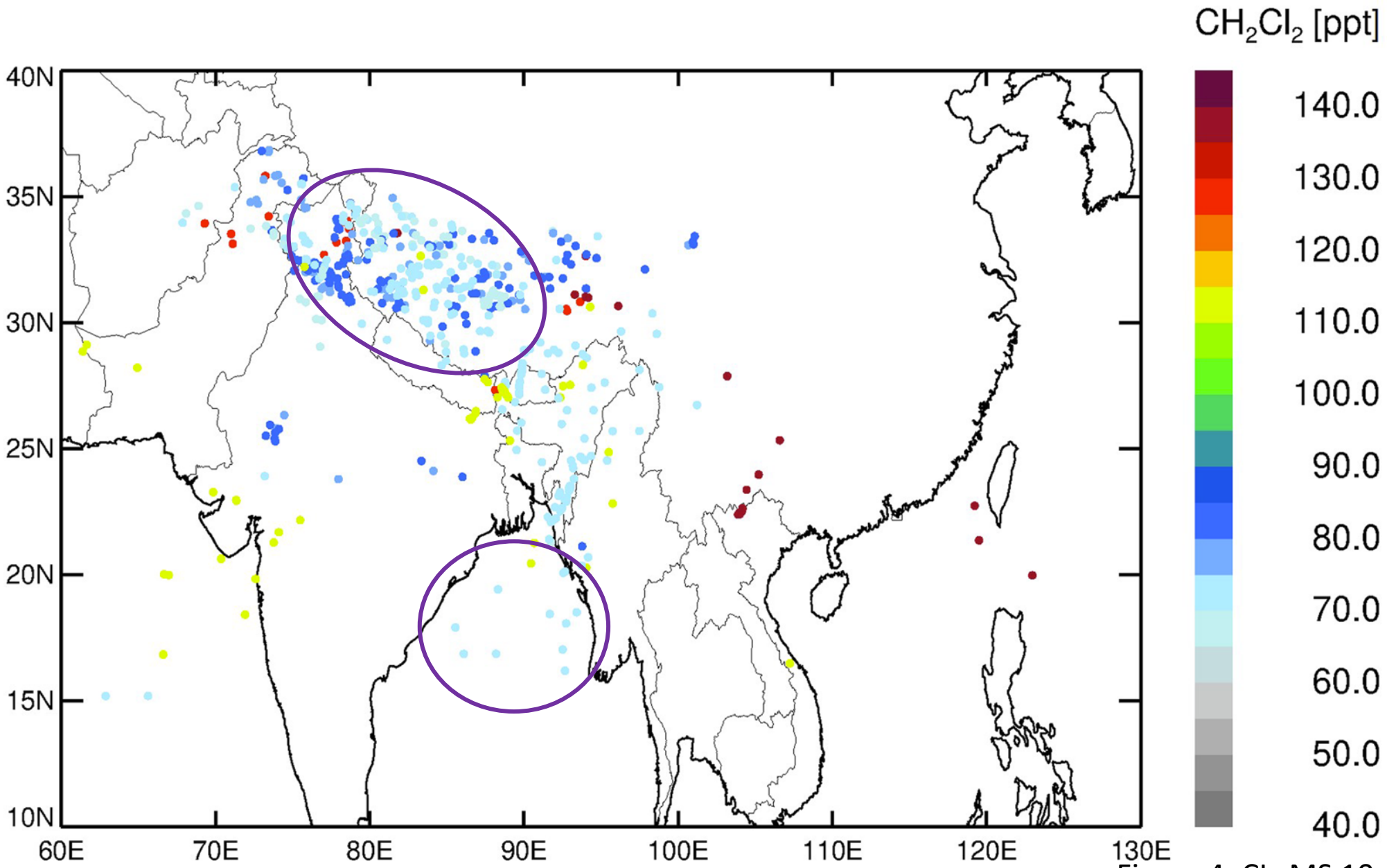


Figure 4: CLaMS 10 day end points

Equivalent Chlorine (ECl)

- Sum of Cl and Br mixing ratios from all halogen source gases. Br is multiplied by 60 to account for greater effectiveness (60-65x) at depleting ozone

- Two methods presented:
  - Global estimate for summer 2017 based on NOAA ground sites
  - AMA-17 estimate

Global Estimate

- Summer 2017 global monthly means from the NOAA/ESRL halocarbon program
- Cape Grim, Tasmania UEA measurements in early 2018
  - Shifted 6 months back, a good proxy for air entering the stratosphere from the UT in the tropics
- HCFCs and methyl halides data used from Mauna Loa and American Samoa (July-August 2017) since significant tropospheric sinks
- VSLS used WMO 2018 values at level of zero radiative heating (LZRH)
  - Based on campaigns in West Pacific from 2013-2014

AMA-17 Estimate

- Samples from 355 – 375 K to represent expanded LZRH region during ASM

- They did not consider the breakdown products of VSLS so this is a lower estimate

Global Estimate AMA-17 Estimate

Table 1
Comparison of the Global Estimate of Equivalent Chlorine (ECl) Based on Cape Grim, NOAA and WMO Mixing Ratios (See S1) and the Regional Estimate Based on the Air Samples From AMA-17

	Global estimate ECl (ppt) 355–365 K	AMA-17 ECl (ppt) 355–375 K
Chlorinated VSLSs	**89–132 (2%–3%)**	**163–393 (4%–8%)**
CH_2Cl_2	59–89	130–272
$CHCl_3$	19–24	24–74
CH_2ClCH_2Cl	10–19	9–47
Brominated VSLSs	**71–118**	**58–92**
CH_2Br_2	71–118	58–92
Long-lived chlorine	**3,159–3,186**	**3,188–3,356**
CFCs	1,960	1,939–1,997
HCFCs	310	317–343
CH_3CCl_3	6.5	4.8–6.0
CCl_4	321	321–338
CH_3Cl	558–586	603–669
Halon-1211	3.4	3.4–3.5
Long-lived bromine	**789–811**	**842–963**
Halons	402	398–414
CH_3Br	387–409	445–549
Estimated (not measured)[a]	**79–253**	**79–253**
Total equivalent chlorine (ECl)	**4,186–4499**	**4,331–5057**
	(4,107–4,246)[b]	**(4,252–4,804)**[b]

Abbreviation: VSLS, very short-lived substance.
[a]For the compounds that were not measured in this study the WMO 2018 reported values were used in both estimates.
[b]ECl excluding compounds that were not measured in this study.

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Higher but not unexpected for this region and time of year

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Total equivalent chlorine (ECl)	**4,186–4499**	**4,331–5057**
	(4,107–4,246)[b]	**(4,252–4,804)**[b]

Both estimates have big ranges that overlap

Abbreviation: VSLS, very short-lived substance.
[a]For the compounds that were not measured in this study the WMO 2018 reported values were used in both estimates.
[b]ECl excluding compounds that were not measured in this study.

Global Estimate AMA-17 Estimate

Table 1
Comparison of the Global Estimate of Equivalent Chlorine (ECl) Based on Cape Grim, NOAA and WMO Mixing Ratios (See S1) and the Regional Estimate Based on the Air Samples From AMA-17

	Global estimate ECl (ppt) 355–365 K	AMA-17 ECl (ppt) 355–375 K
Chlorinated VSLSs	**89–132 (2%–3%)**	**163–393 (4%–8%)**
CH_2Cl_2	59–89	130–272
$CHCl_3$	19–24	24–74
CH_2ClCH_2Cl	10–19	9–47
Brominated VSLSs	**71–118**	**58–92**
CH_2Br_2	71–118	58–92
Long-lived chlorine	**3,159–3,186**	**3,188–3,356**
CFCs	1,960	1,939–1,997
HCFCs	310	317–343
CH_3CCl_3	6.5	4.8–6.0
CCl_4	321	321–338
CH_3Cl	558–586	603–669
Halon-1211	3.4	3.4–3.5
Long-lived bromine	**789–811**	**842–963**
Halons		
CH_3Br		
Estimated (not measured)[a]	**79–253**	**79–253**
Total equivalent chlorine (ECl)	**4,186–4499**	**4,331–5057**
	(4,107–4,246)[b]	**(4,252–4,804)**[b]

Slightly higher for AMA-17 due to HCFCs and CH_3Cl

Abbreviation: VSLS, very short-lived substance.
[a]For the compounds that were not measured in this study the WMO 2018 reported values were used in both estimates.
[b]ECl excluding compounds that were not measured in this study.

Global Estimate AMA-17 Estimate

Table 1
Comparison of the Global Estimate of Equivalent Chlorine (ECl) Based on Cape Grim, NOAA and WMO Mixing Ratios (See S1) and the Regional Estimate Based on the Air Samples From AMA-17

	Global estimate ECl (ppt) 355–365 K	AMA-17 ECl (ppt) 355–375 K
Chlorinated VSLSs	**89–132 (2%–3%)**	**163–393 (4%–8%)**
CH_2Cl_2	59–89	130–272
$CHCl_3$	19–24	24–74
CH_2ClCH_2Cl	10–19	9–47
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CCl_4	321	321–338
CH_3Cl	558–586	603–669
Halon-1211	3.4	3.4–3.5
Long-lived bromine	**789–811**	**842–963**
Halons	402	398–414
CH_3Br	387–409	445–549
	(4,107–4,246)[b]	**(4,252–4,804)**[b]

CH_3Br higher for AMA-17 suggesting source in monsoon input region

Abbreviation: VSLS, very short-lived substance.
[a]For the compounds that were not measured in this study the WMO 2018 reported values were used in both estimates.
[b]ECl excluding compounds that were not measured in this study.

Global Estimate AMA-17 Estimate

Table 1
Comparison of the Global Estimate of Equivalent Chlorine (ECl) Based on Cape Grim, NOAA and WMO Mixing Ratios (See S1) and the Regional Estimate Based on the Air Samples From AMA-17

	Global estimate ECl (ppt) 355–365 K	AMA-17 ECl (ppt) 355–375 K
Chlorinated VSLSs	**89–132 (2%–3%)**	**163–393 (4%–8%)**
CH_2Cl_2	59–89	130–272
$CHCl_3$	19–24	24–74
CH_2ClCH_2Cl	10–19	9–47
Brominated VSLSs	**71–118**	**58–92**
CH_2Br_2	71–118	58–92

"If we assume that 5% of the additional ECl [estimated % in NH from ASM, Ploeger et al. (2017)] from the AMA-17 estimate ends up in the lower stratosphere of the Northern Hemisphere, this translates to an additional 0.3 – 34.9 ppt of ECl from all measured compounds, of which 1.6 – 15.2 ppt are from Cl-VSLS."

Further evidence that Cl-VSLS and methyl halides may be significant

Estimated (not measured)[a]	**79–253**	**79–253**
Total equivalent chlorine (ECl)	**4,186–4499**	**4,331–5057**
	(4,107–4,246)[b]	**(4,252–4,804)**[b]

Abbreviation: VSLS, very short-lived substance.
[a]For the compounds that were not measured in this study the WMO 2018 reported values were used in both estimates.
[b]ECl excluding compounds that were not measured in this study.

Equivalent Effective Stratospheric Chlorine (EESC)

- “EESC is a metric used to describe the combined impact of chlorine and bromine on stratospheric ozone and the temporal development of this effect due to tropospheric trends.” (Engel, Ribgy et al. 2018)

- Differs from Equivalent Chlorine because it factors in the effects of stratospheric transport and chemistry on releasing chlorine and bromine from long-lived ODS

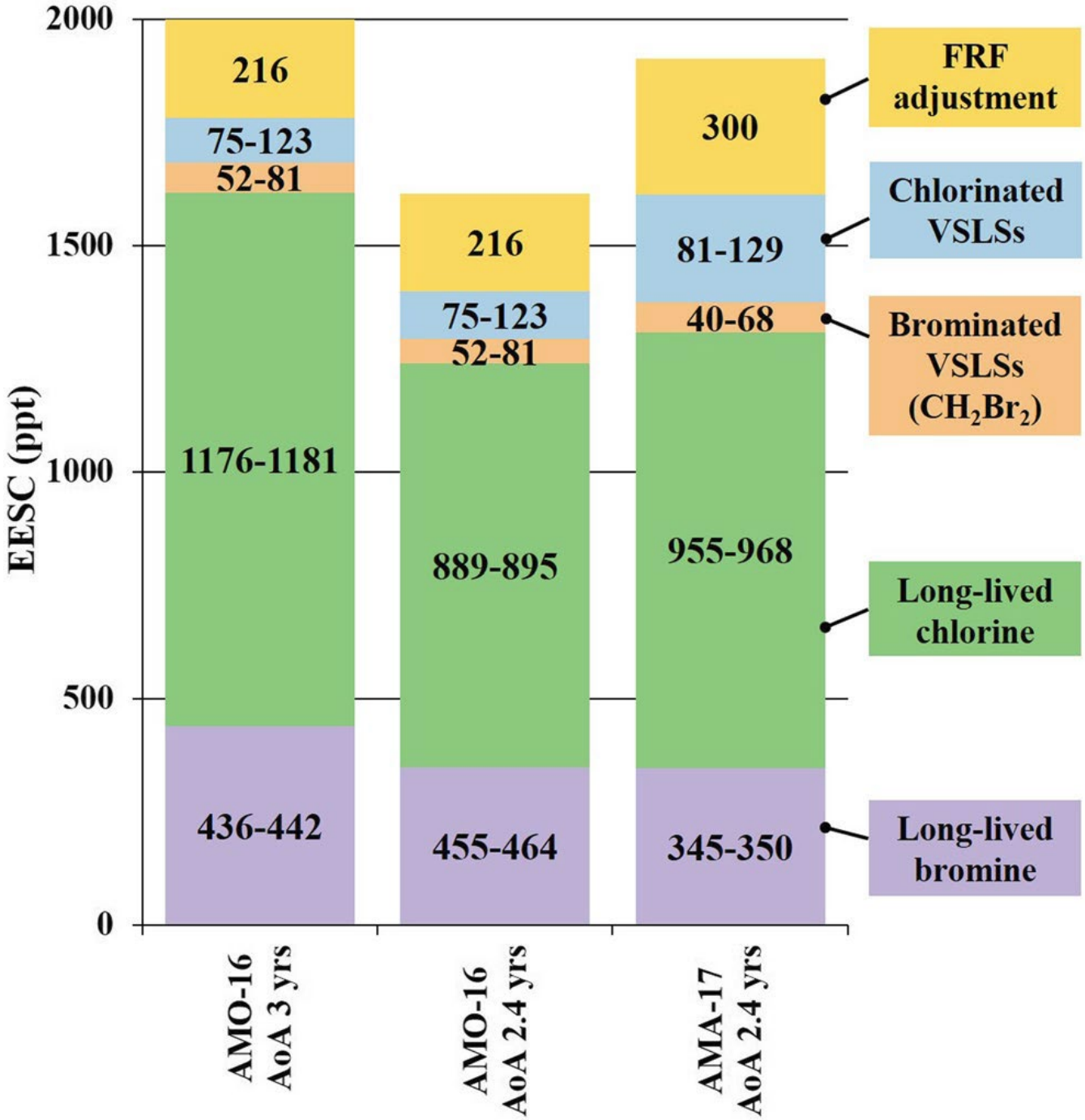
Equivalent Effective Stratospheric Chlorine (EESC) Calculations

- Used the NOAA and Cape Grim data as the tropospheric background (1978 – 2018)

- Used two mean age-of-air:
  - 3 years (literature value for midlatitudes and highest mean age-of-air in AMO-16)
  - 2.4 years (highest mean age-of-air calculated in AMA-17)

- Fractional Release Factor (FRF) for VSLS calculated by comparing highest and lowest mixing ratio in tropopause (355 – 375 K) to mixing ratio above 375 K

- If interested → used the newer method of age-of-air (Leedham Elvidge et al. (2018)) to compare and "improved" FRF calculation

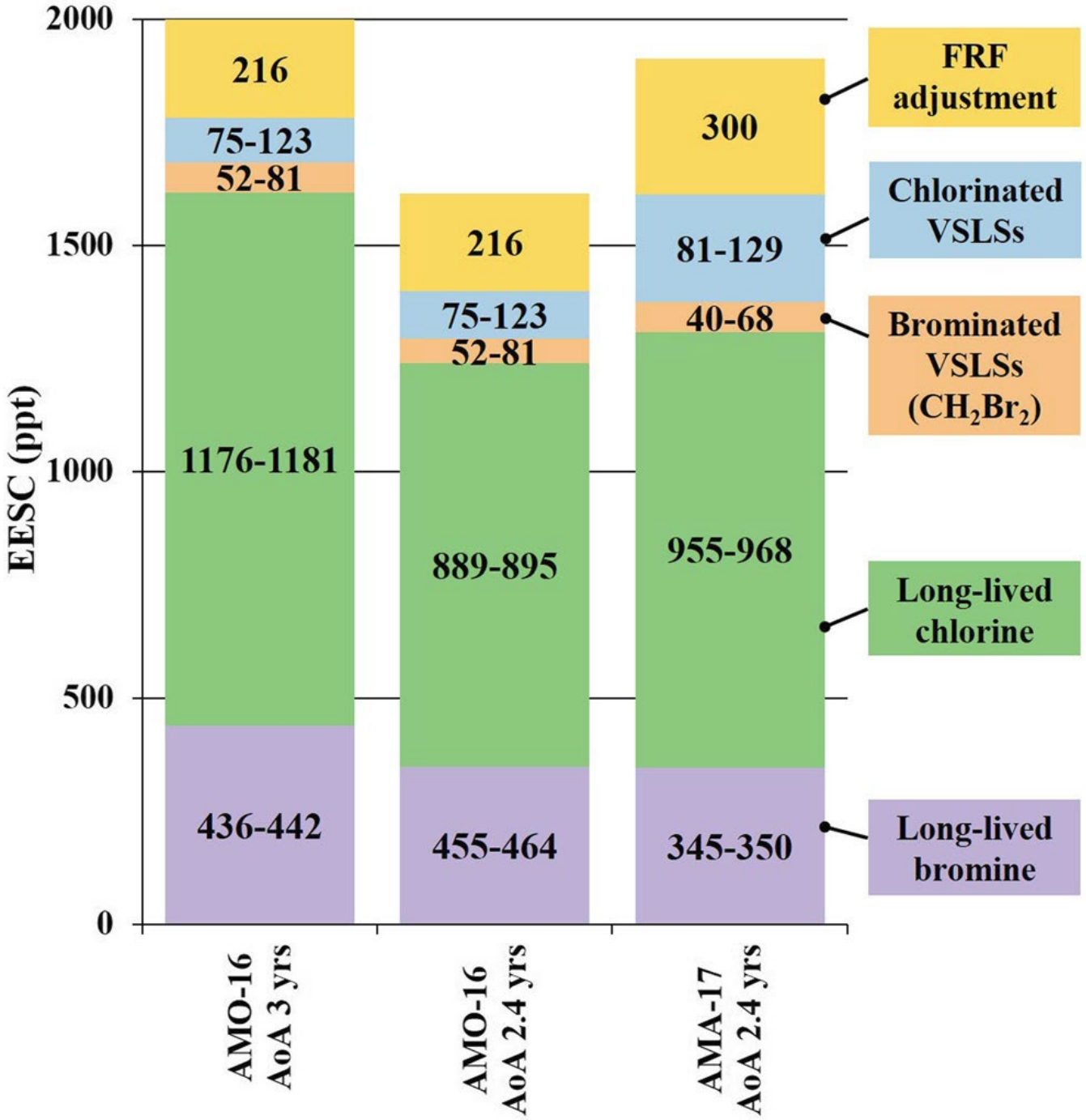


*Used “relevant age” EESC which takes into account interaction of chemical loss and transport time (based on Engel, Bönisch, et al 2018)

Figure 5: EESC

AMO-16 lower than AMA-17 by 135 ppt

AMO is a mix of ASM outflow and NH extratropical air



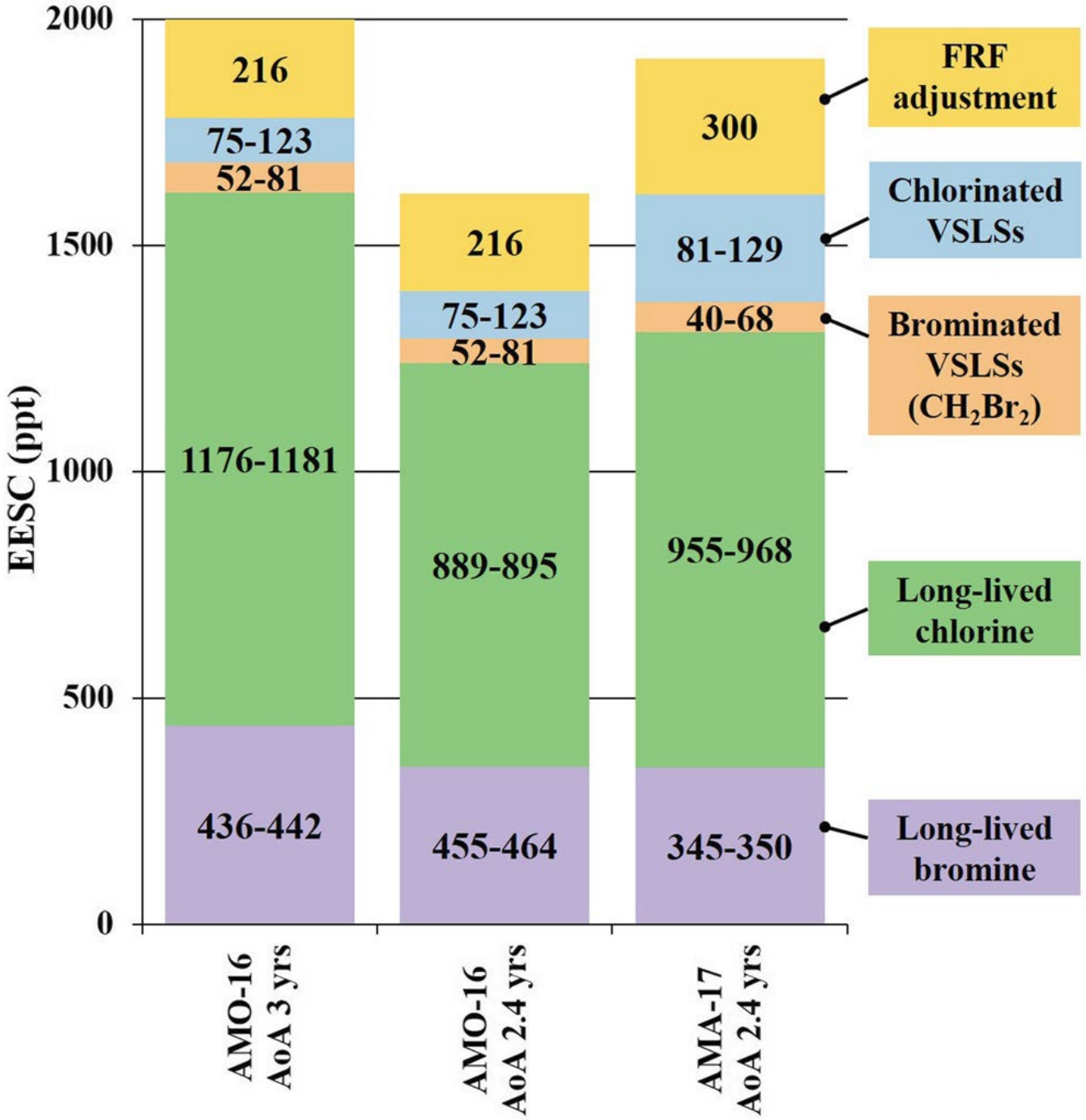
*Used “relevant age” EESC which takes into account interaction of chemical loss and transport time (Engel, Bönisch, et al 2018)

Figure 5: EESC

AMO-16 EESC is 12% higher than Engel, Bönisch, et al (2018)

**Excludes VSLS

Apples to Apples comparison with an age of air of 3 years



*Used "relevant age" EESC which takes into account interaction of chemical loss and transport time (Engel, Bönisch, et al 2018)

Figure 5: EESC

Including VSLS increases the EESC and the range.
VSLS contributions increase EESC estimate in NH extratropical lower stratosphere by 8-26%.

AMO-16 EESC is 12% higher than Engel, Bönisch, et al (2018)

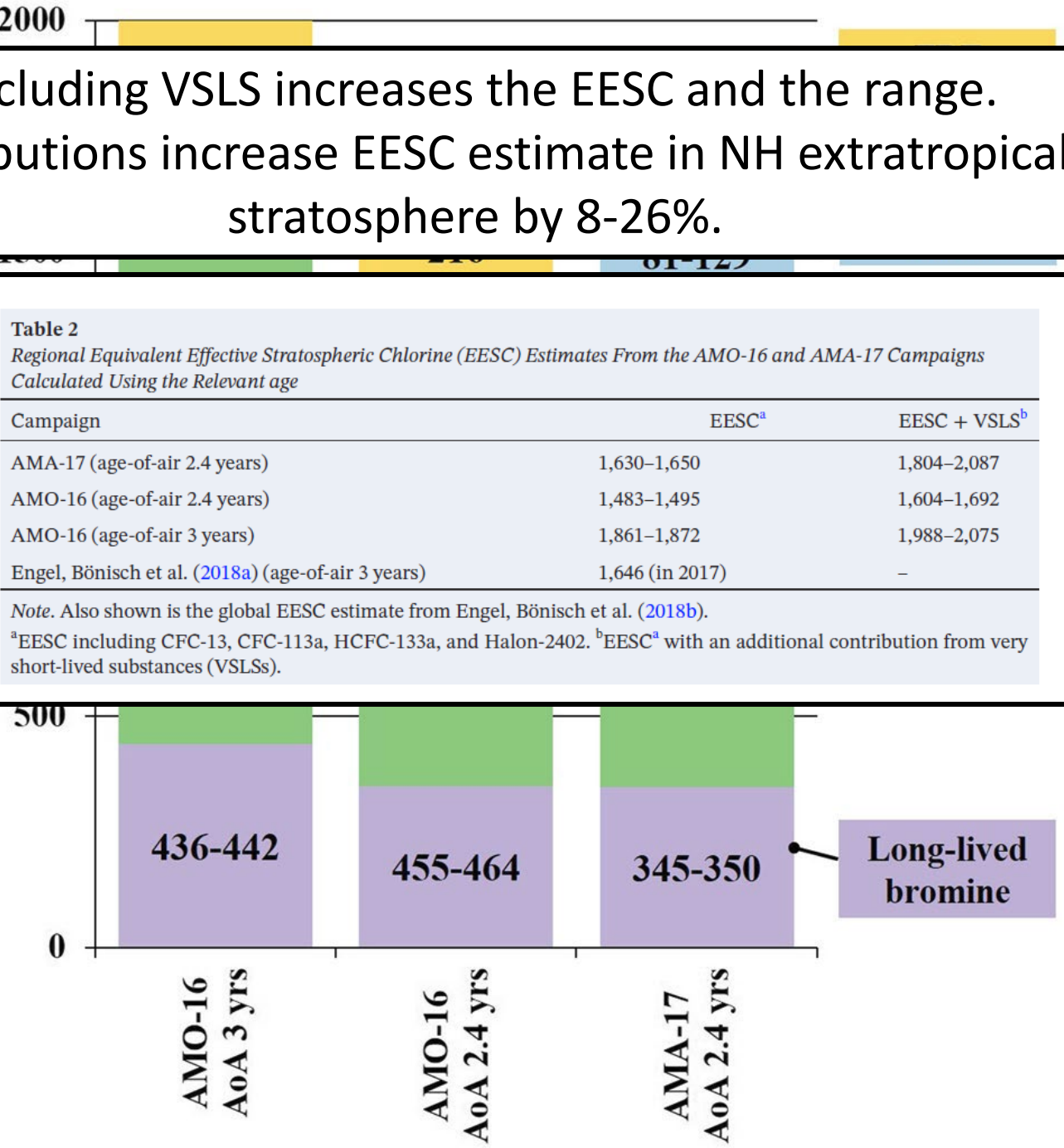
**Excludes VSLS

Apples to Apples comparison with an age of air of 3 years

Table 2
Regional Equivalent Effective Stratospheric Chlorine (EESC) Estimates From the AMO-16 and AMA-17 Campaigns Calculated Using the Relevant age

Campaign	EESC[a]	EESC + VSLS[b]
AMA-17 (age-of-air 2.4 years)	1,630–1,650	1,804–2,087
AMO-16 (age-of-air 2.4 years)	1,483–1,495	1,604–1,692
AMO-16 (age-of-air 3 years)	1,861–1,872	1,988–2,075
Engel, Bönisch et al. (2018a) (age-of-air 3 years)	1,646 (in 2017)	–

Note. Also shown is the global EESC estimate from Engel, Bönisch et al. (2018b).
[a]EESC including CFC-13, CFC-113a, HCFC-133a, and Halon-2402. [b]EESC[a] with an additional contribution from very short-lived substances (VSLSs).



relevant SC which to account interaction of chemical loss and transport time (Engel, Bönisch, et al 2018)

Figure 5: EESC

Main Conclusions from Adcock et al. (2020)

Highlights the importance of the ASM as a fast transport mechanism in an important ODS region and the importance of Cl-VSLS in the northern extratropical lower stratosphere

- First set of in situ data for many ODS in lower stratosphere over ASM
- Cl-VSLS in ASM region higher than reported in 2018 WMO report. VSLS increase EESC estimate by 8-26% in NH extratropical lower stratosphere.
- The ECI and EESC for long-lived species is also higher than reported global averages recently.
  - The large emission sources and amount of input to the stratosphere during ASM are the reason

Unexpected nascent atmospheric emissions of three ozone-depleting hydrochlorofluorocarbons

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Edited by Susan Solomon, Massachusetts Institute of Technology, Cambridge, MA, and approved December 7, 2020 (received for review Ma

Significance

We demonstrate the need to detect and track unexpected substances in the atmosphere and to locate their sources. Here, we report on three hydrochlorofluorocarbons (HCFCs) that have no known end-uses. HCFC-132b ($CH_2ClCClF_2$) is newly discovered in the global atmosphere. We identify East Asia as the dominant source region for global emissions of this compound and of HCFC-133a (CH_2ClCF_3). We also quantify global emissions of HCFC-31 (CH_2ClF). These compounds are most likely emitted as intermediate by-products of chemical production processes. The early discovery and identification of such unexpected emissions can identify the related industrial practices and help to develop and manage environmental policies to reduce unwanted and potentially harmful emissions before the scale of the problem becomes more costly to mitigate.

PNAS February 2, 2021
118 (5) e2010914118;
https://doi.org/10.1073/pnas.2010914118

Was also compared to the Newman et al. (2007) method

Fairly good agreement though mean-age was slightly higher.