Supporting Information

Investigation of East Asian emissions of CFC-11 using atmospheric observations in Taiwan

Karina E. Adcock[*†], Matthew J. Ashfold[°], Charles C-K Chou[⊥], Lauren J. Gooch[†], Norfazrin Mohd Hanif[†,‡], Johannes C. Laube[†,§], David E. Oram[†,|], Chang-Feng Ou-Yang[#], Marios Panagi[∇], William T. Sturges[†] and Claire E. Reeves[†]*

[†]Centre for Oceanography and Atmospheric Science, School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

[°]School of Environmental and Geographical Sciences, University of Nottingham Malaysia, 43500 Semenyih, Malaysia

[⊥]Research Center for Environmental Changes, Academia Sinica, Taipei 11529, Taiwan

[‡]Now at School of Environmental and Natural Resource Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

[§]Now at Institute of Energy and Climate Research – Stratosphere (IEK-7), Forschungszentrum Jülich GmbH, Jülich, Germany

[|]National Centre for Atmospheric Science, University of East Anglia, Norwich NR4 7TJ, U.K.

[#]Department of Atmospheric Sciences, National Central University, Taoyuan 320, Taiwan

[∇] National Centre for Atmospheric Science, Department of Chemistry, University of Leicester, Leicester LE1 7RH UK

*Corresponding author: Karina.Adcock@uea.ac.uk

The Supporting Information consist of a total of 10 pages and includes text, 6 supplementary figures (S1-S6) and 3 supplementary tables.

Analytical technique

Air samples were collected in 3-litre silco-treated stainless-steel canisters (Restek) using a small 12 VDC diaphragm pump (Air Dimensions, model B161). Prior to sampling the canisters were repeatedly evacuated to < 0.01 mbar and pressurised with ultra-pure nitrogen (BOC research grade) whilst being heated to 130 ºC. During sampling they were filled and vented at least 3 times before filling to a final pressure of ~2 bar which takes a few minutes. The samples were collected on the coast, well away from any local sources of pollution, when the wind direction was from the sea. The lowest mixing ratios reported here are in good agreement with NOAA background measurements in this region.

The samples were then transported to the University of East Anglia (UEA) and analysed for about 50 trace gases including CFC-11. The samples were analysed on an Agilent 6890 gas chromatograph coupled to a high-sensitivity Waters AutoSpec magnetic sector mass spectrometer (GC-MS) using an Agilent GS-GasPro column (length ~50 m; ID: 0.32mm). The instrument set up is the same as in Laube et al.[1] and Laube et al.[2] Samples were dried by passing them through a magnesium perchlorate ($Mg(ClO_4)_2$) drying tube. Condensable trace gases were then cryogenically pre-concentrated from about 300 ml of air at −78 ºC in a sample loop filled with an adsorbent (Hayesep D, 80/100 mesh) which was heated to 100 ºC immediately after injection. The mass spectrometer typically has a detection limit of < 0.1 femtomole per mole of air (10^{-16}) and was operated in electron impact selected ion recording (EI-SIR) mode, using a mass resolution of ~1000. The ionization was carried out at 70 eV and a source temperature of 240 °C. Hexadecane is used as an internal reference compound and helium is used as a carrier gas. CFC-11 was measured using the mass fragment $CF^{35}Cl^{37}Cl^{+}$ (m/z 102.9332). The average precision of the CFC-11 measurements was 1.4%. Every day a 'blank' sample of

research-grade helium was measured to ensure there was no system contamination. The linearity of the detector response was evaluated using a static dilution series of a background air sample with pure nitrogen. The system has a proven linear response behaviour over the observed concentration range which is underlined by the good comparability of trace gas time series with those derived by the internationally recognized NOAA-GMD group over several decades.[3]

References

(1) Laube, J. C.; Martinerie, P.; Witrant, E.; Blunier, T.; Schwander, J.; Brenninkmeijer, C. A. M.; Schuck, T. J.; Bolder, M.; Röckmann, T.; Van Der Veen, C.; Bönisch, H.; Engel, A.; Mills, G. P.; Newland, M. J.; Oram, D. E.; Reeves, C. E.; Sturges, W. T., Accelerating growth of HFC-227ea (1,1,1,2,3,3,3- heptafluoropropane) in the atmosphere. *Atmospheric Chemistry and Physics* **2010,** *10*, 5903-5910.

(2) Laube, J. C.; Mohd Hanif, N.; Martinerie, P.; Gallacher, E.; Fraser, P. J.; Langenfelds, R.; Brenninkmeijer, C. A. M.; Schwander, J.; Witrant, E.; Wang, J.-L.; Ou-Yang, C.-F.; Gooch, L. J.; Reeves, C. E.; Sturges, W. T.; Oram, D. E., Tropospheric observations of CFC-114 and CFC-114a with a focus on long-term trends and emissions. *Atmospheric Chemistry and Physics* **2016,** *16*, (23), 15347-15358.

(3) Laube, J. C.; Keil, A.; Bönisch, H.; Engel, A.; Röckmann, T.; Volk, C. M.; Sturges, W. T., Observation-based assessment of stratospheric fractional release, lifetimes, and ozone depletion potentials of ten important source gases. *Atmos. Chem. Phys.* **2013,** *13*, 2779-2791.

Table S1. The sampling sites in Taiwan, the dates of the campaign period, the number of samples collected, the average and range of CFC-11 mixing ratios and the NOAA mixing ratios for each year of the campaign.

Site	**Year**	**Campaign period**		**No. of samples**	**Mean (ppt)**	**Median (ppt)**	**Range (ppt)**	**Manua Loa range (ppt)**
		start	**end**					
Cape Fuguei	2014	11-Mar-14	04-Apr-14	23	236	236	228-248	232-236
Hengchun	2015	12-Mar-15	25-Apr-15	20	241	241	234-253	228-238
Cape Fuguei	2016	16-Mar-16	29-Apr-16	33	241	238	228-272	229-232
Cape Fuguei	2017	17-Apr-17	18-May-17	31	238	236	226-260	229-231
Cape Fuguei	2018	05-Apr-18	01-Jun-18	28	238	236	230-254	228-231

Table S2. CFC-11 emission estimates from previous studies for China or eastern China; the years the estimates are for; the uncertainties in the estimates; and comments on the methods used.

Reference	Year	Best estimate (Gg yr $^{-1}$)	Lower uncertainty (Gg yr $^{-1}$)	Upper uncertainty (Gg yr $^{-1}$)	Method
Earlier period					
Wan et al. (2009)	2008	14.259			Bottom-up method based on reported production and estimated emission rates
Wan et al. (2009)	2009	12.858			
Wan et al. (2009)	2010	11.541			
Wan et al. (2009)	2011	9.638			
Fang et al. (2018)	2008	13.0			Bottom-up method based on reported production and estimated emission rates
Fang et al. (2018)	2009	12.3			
Fang et al. (2018)	2010	11.6			
Fang et al. (2018)	2011	10.9			
Kim et al. (2010)	2008	12	9.4	17	Measurements at Gosan, Jeju Island, Korea and atmospheric inversion modeling using FLEXPART
An et al. (2012)	2009	15.8	8.6	23	Measurements at Shangdianzi Global Atmosphere Watch (GAW) Regional Station (SDZ) which is 120 km North East of Beijing and atmospheric inversion modeling using FLEXPART. Limited coverage in South and Central China
Fang et al. (2012)	2009	7.8	4	11.6	Measurements in 2009/10 at Peking University Station (PKU) in Beijing using correlations with CO mixing ratios and CO emission estimates
Fang et al. (2012)	2009	10	8.4	11.7	Measurements in 2009/10 at PKU in Beijing using correlations with HCFC-22 mixing ratios and HCFC-22 emission estimates
Wang et al. (2014)	2011	10.5	2.4	18.6	CO correlations based on measurements in Shangdong Peninsula, 2010-2011. Uncertainty +/-8.1 kt/y
Rigby et al. (2019)	2008-2012	6.4	5.2	7.6	Measurements at Gosan, Jeju Island, Korea and Hateruma, Japan and NAME and FLEXPART atmospheric inversions
Combined estimates of earlier period					
Mean of earlier estimates (excluding Rigby et al., 2019)	2008-2011	11.7	9.6	13.8	Standard deviation of the estimates
Mean of earlier estimates (including Rigby et al., 2019)	2008-2012	10.3	7.4	13.2	Standard deviation of the estimates

Later period					
Current study (CH_2Cl_2, Feng)	2014-2018	11.7	9.2	14.2	Taiwan interspecies correlation with CH_2Cl_2 emission estimate from Feng et al., (2018)
Current study (CH_2Cl_2, Oram)	2014-2018	16.7	14.7	18.7	Taiwan interspecies correlation with CH_2Cl_2 emission estimate from Oram et al., (2017)
Current study (CH_3Cl, FLEXPART)	2014-2018	19.4	17.4	21.3	Taiwan interspecies correlation with CH_3Cl emission estimate from Fang et al., (2019) using FLEXPART inversion model
Current study (CH_3Cl, NAME)	2014-2018	18.1	15.3	22.4	Taiwan interspecies correlation with CH_3Cl emission estimate from Fang et al., (2019) using NAME inversion model
Current study (CCl_4, FLEXPART)	2014-2018	17.0	9.1	24.9	Taiwan interspecies correlation with CCl_4 emission estimate from Lunt et al., (2018) using FLEXPART inversion model
Current study (CCl_4, NAME)	2014-2018	22.2	14.3	31.5	Taiwan interspecies correlation with CCl_4 emission estimate from Lunt et al., (2018) using NAME inversion model
Current study (HCFC-22)	2014-2018	26.5	19.6	33.4	Taiwan interspecies correlation with HCFC-22 emission estimate from Li et al., (2016)
Rigby et al. (2019)	2014-2017	13.4	11.7	15.1	Measurements at Gosan, Jeju Island, Korea and Hateruma, Japan and NAME and FLEXPART atmospheric inversions
Combined estimates of later period					
Mean of current study	2014-2018	18.8	14.2	23.5	Uncertainties are standard deviation of the estimates
Mean of current study and Rigby et al. (2019)	2014-2018	17.1	12.7	21.5	Uncertainties are standard deviation of the estimates
Increase					
Average increase from 2008-2011 to 2014-2018 (excluding Rigby et al., 2019)	2014-2018	7.1	2.0	12.2	The uncertainties are the square root of the sum of the uncertainties for each time period squared
Average increase from 2008-2011 to 2014-2018 (including Rigby et al., 2019)	2014-2018	6.7	1.5	12.0	The uncertainties are the square root of the sum of the uncertainties for each time period squared
Other estimates					
EIA (2018)	2012-2017		10.3	12.2	Bottom-up method based on interviews with members of the foam industry in China
Wan et al. (2009)	2014	6.038			Bottom-up method based on reported production and estimates of emission rates
Wan et al. (2009)	2015	4.941			
Wan et al. (2009)	2016	3.982			
Wan et al. (2009)	2017	3.088			

Wan et al. (2009)	2018	2.256			
Fang et al. (2018)	2014	8.3			Bottom-up method based on reported production and estimates of emission rates
Fang et al. (2018)	2015	7.2			
Fang et al. (2018)	2016	5.9			
Fang et al. (2018)	2017	5.2			
Fang et al. (2018)	2018	4.5			
Average of Wan et al. (2009) and Fang et al. (2018)	2014-2018	5.1	3.3	6.9	Uncertainties are standard deviation of the estimates
Mean of current study minus average of Wan et al. (2009) and Fang et al. (2018)	2014-2018	13.7	8.7	18.7	The uncertainties are the square root of the sum of the uncertainties for the estimates

Table S3: Emission estimates based on the correlation slopes with $CHCl_3$, CH_2Cl_2, CCl_4 and HCFC-22. The molecular weight used for CFC-11 was 137.36 g mol^{-1}.

Compound	Molecular Weight	Spearman's R	Trendline (total linear least squares regression)	Emissions (Gg yr^{-1})	Location of Emissions	Years of Emissions	Reference	CFC-11 emissions (Gg yr^{-1})
CH_2Cl_2	84.93	0.622	y = 0.023x + 2.436	318 (254-384)	China	2016	Feng et al., 2018	11.7 (9.2-14.2)
CH_2Cl_2	84.93	0.622	y = 0.023x + 2.436	455(410-501)	China	2015	Oram et al., 2017	16.7 (14.7-18.7)
$CHCl_3$	119.37	0.720	y = 0.192x + 1.635	88 (80-95)	East China	2015	Fang et al., 2019 (FLEXPART)	19.4 (17.4-21.3)
$CHCl_3$	119.37	0.720	y = 0.192x + 1.635	82 (70-101)	East China	2015	Fang et al., 2019 (NAME)	18.1 (15.3-22.4)
CCl_4	153.82	0.713	y = 1.466x + 0.573	13 (7-19)	East China	2009-2016	Lunt et al., 2018 (FLEXPART)	17.0 (9.1-24.9)
CCl_4	153.82	0.713	y = 1.466x + 0.573	17 (11-24)	East China	2009-2016	Lunt et al., 2018 (NAME)	22.2 (14.3-31.5)
HCFC-22	86.47	0.593	y = 0.125x + 2.718	134 (100-167)	China	2016	Li et al., 2016	26.5 (19.6-33.4)

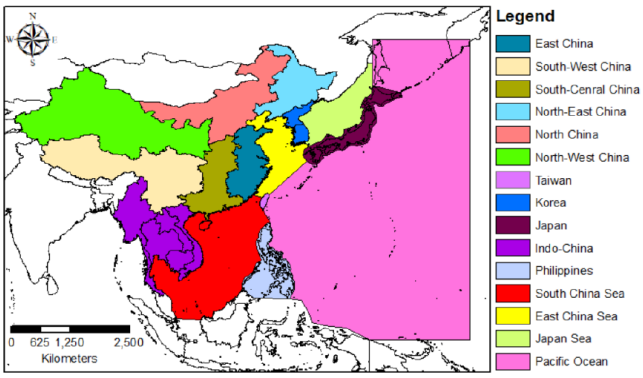

Figure S1: Regions for which the contribution to the footprint simulated by the NAME model is quantified.

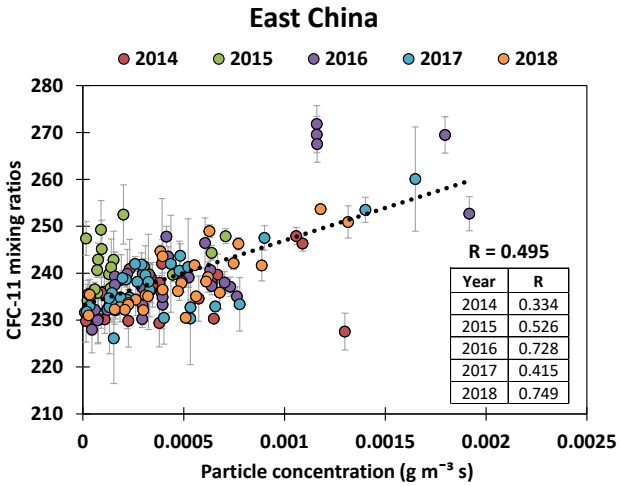

Figure S2: CFC-11 mixing ratios (ppt) against particle concentration from the East China source region arriving at Taiwan at the time the analysed samples were collected as simulated by the NAME particle dispersion model. The dashed line is the trend line calculated using ordinary least squares regression.

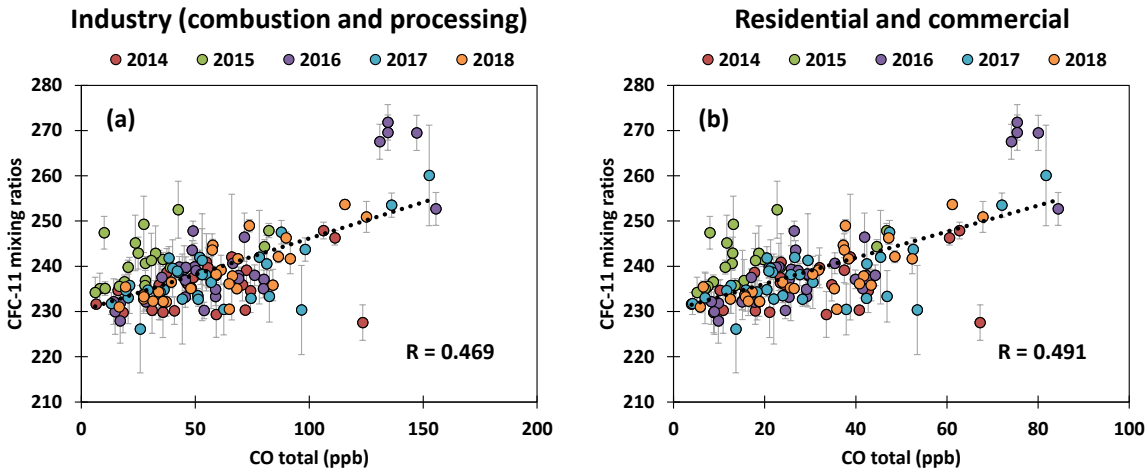

Figure S3: CFC-11 mixing ratios against simulated CO total from (a) Industry and (b) Residential and commercial. The dashed line is the trend line calculated using ordinary least squares regression.

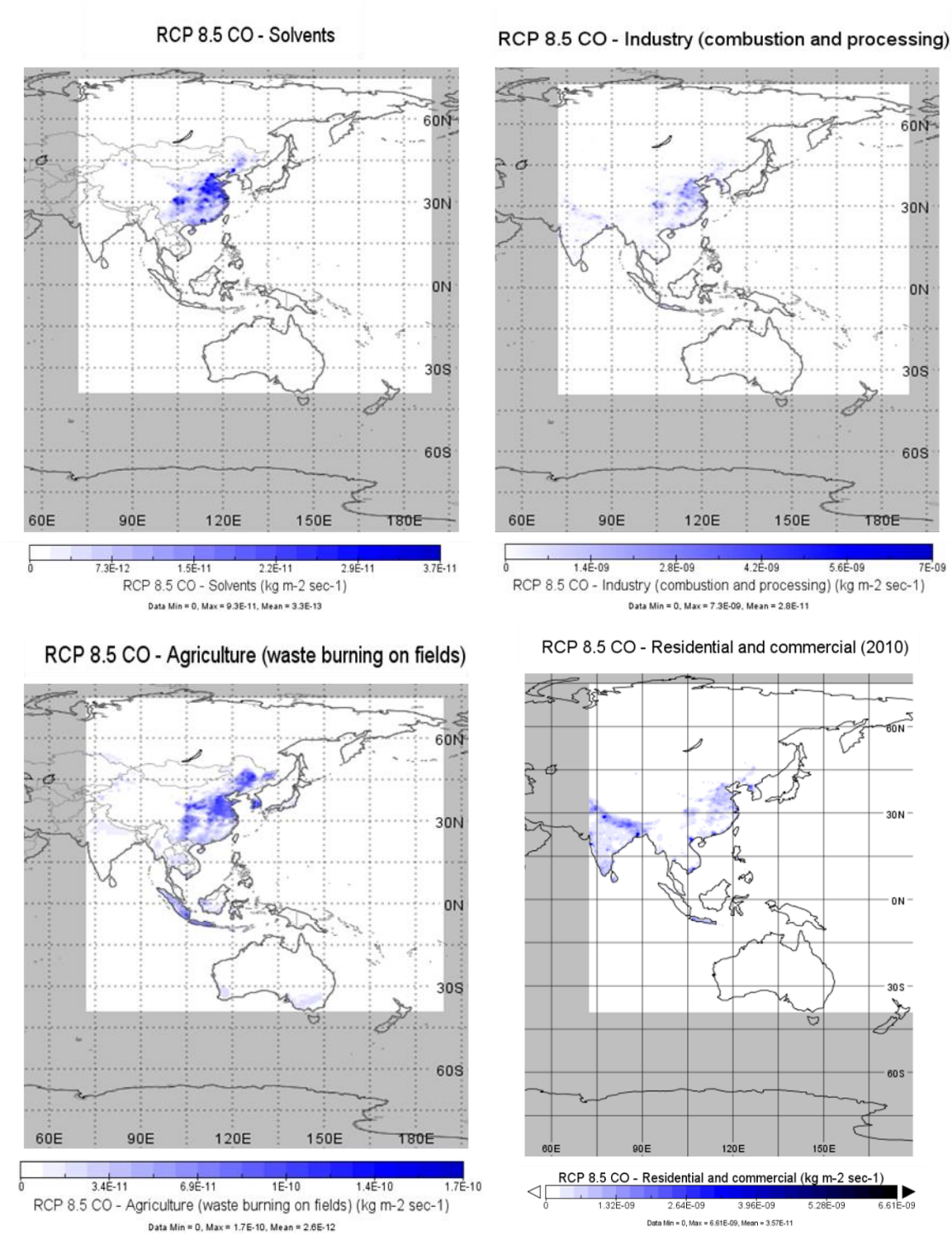

Figure S4. The distribution of carbon monoxide (CO) emissions ($kgm^{-2}s^{-1}$) taken from the Representative Concentration Pathway 8.5 (2010) inventories of CO for four emission sectors: industry, residential and commercial, solvents and agriculture waste burning.

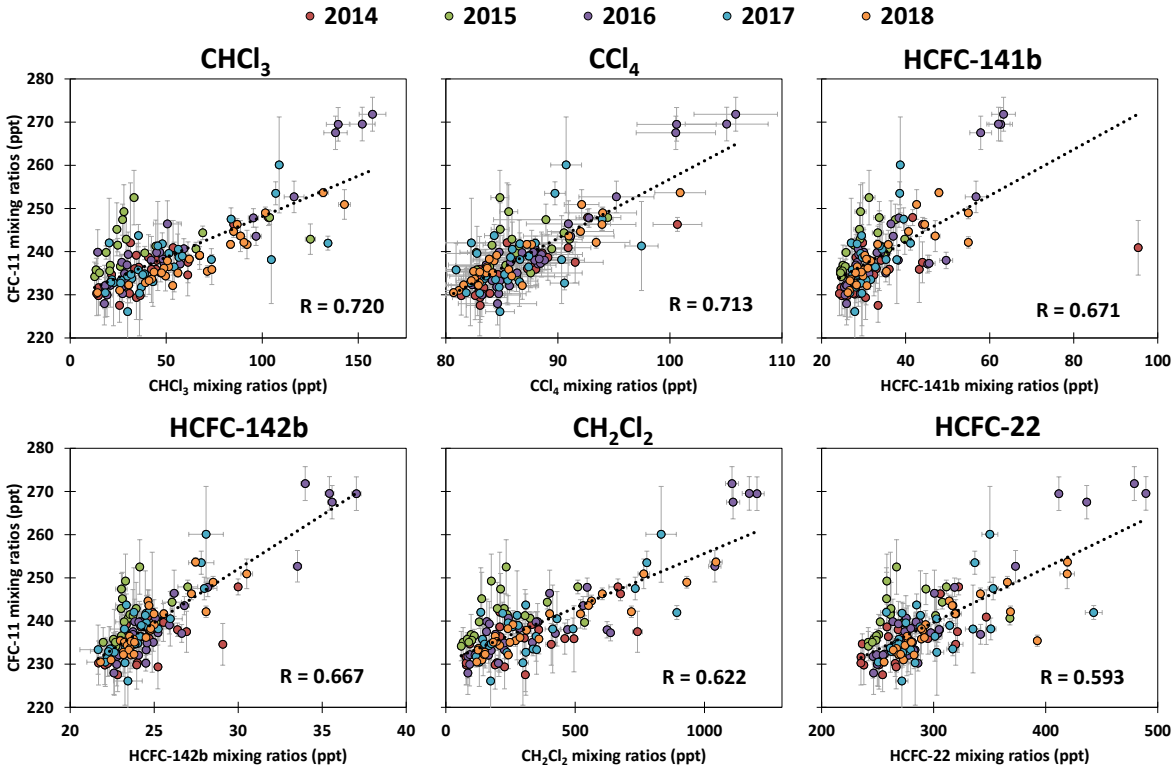

Figure S5: Interspecies correlations of CFC-11 mixing ratios with those of other halogenated trace gases. The dashed line is the trend line calculated by total least squares regression using the York-Williamson method.

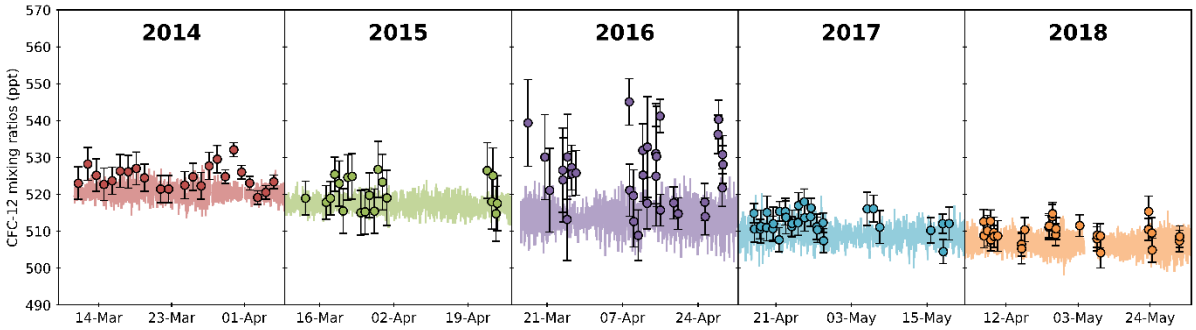

Figure S6. CFC-12 mixing ratios in Taiwan 2014-2018. The measurement campaigns lasted for 1-3 months each year. Uncertainties represented by the error bars are described in the text. Hourly in situ measurements of CFC-12 mixing ratios at Mauna Loa, Hawaii from the NOAA/ESRL Global Monitoring Division are included for comparison (ftp://ftp.cmdl.noaa.gov/hats/cfcs/cfc12/insituGCs/CATS/hourly/). The standard deviation error bars of the Mauna Loa measurements are plotted in the same color as the data.