A growing threat to the ozone layer from short-lived anthropogenic chlorocarbons (Oram et al.)

Supplementary material

1. Additional measurements

As mentioned in the main document, 21 air samples were also collected at the Hengchun station in southern Taiwan (22.0547N, 120.6995E) during March and early April 2013 (Figure S1). Unfortunately CH_2ClCH_2Cl was not analysed for in the 2013 samples, but the absolute concentrations and variability of CH_2Cl_2, $CHCl_3$ and C_2Cl_4 were very similar to those observed at Cape Fuguei in 2014 (see also Table 1).

2. Modelling

The Numerical Atmospheric-dispersion Modelling Environment (NAME, Jones et al. 2007) is a Lagrangian particle dispersion model, used here to understand the origin of the sampled air masses. For each air sample, NAME was used to calculate batches of 60000 inert backward trajectories. For the ground samples the trajectories started at the measurement site within an altitude range of 0-100 m and were started throughout a 3 hour period encompassing the sample time. For the aircraft samples the trajectories were started at the exact time, horizontal coordinates and altitude at which the sample was collected. The surface sample trajectories ran for 12 days and the aircraft sample trajectories for 20 days. Every 15 minutes the location of all trajectories within the lowest 100 m of the model atmosphere was recorded on a grid with a horizontal resolution of 0.5625° longitude by 0.375° latitude. From this information, and assuming a uniform surface air density consistent with a pressure of 1000 hPa and a temperature of 25°C, the sensitivity of the sampled air mass to surface emissions occurring in the previous 12 or 20 days within a particular grid cell can be derived (units sm^2g^{-1}).

The trajectories were calculated using three-dimensional meteorological fields produced by the UK Meteorological Office's Numerical Weather Prediction tool, the Unified Model (UM). These fields have a horizontal grid resolution of 0.35° longitude by 0.23° latitude and 59 vertical levels below ~30 km, and are available at 3 h intervals. Vertical velocities are obtained from the UM and available at grid nodes. The sub-grid-scale process of turbulence is parameterised in NAME (Morrison and Webster 2005). Another sub-grid scale process, convection, is not parameterised in our NAME calculations. However, past work (Heyes et al. 2009, Ashfold et al. 2012, Navarro et al. 2015) has shown atmospheric composition in the tropics can be interpreted using trajectories calculated with wind fields that, while not resolving individual up- and down-draughts, are consistent with large-scale convective activity.

2.1 Multi-year NAME calculations

By combining the emission sensitivities derived from NAME with a distribution of emissions it is possible to calculate a modelled mixing ratio of the emitted species, due only to emissions occurring within the timescale of the backward trajectories, at the measurement site (dimensionally, sm^2g^{-1} x $gm^{-2}s^{-1}$ = dimensionless mixing ratio). We have used an inventory of industrial and combustion carbon monoxide (CO) emissions (RCP8.5 for 2005; Granier et al. 2011, Riahi et al. 2011), which are likely to be similarly distributed to VSLS-Cl (e.g. regression in Figure 4b and Shao et al. 2011), to model anomalous CO volume mixing ratios (i.e. those due only to these industrial emissions north of 20ºN) at Bachok at 3-hourly resolution for six recent NH winters (Oct-Apr 2009/10-2014/15). Figure 4a in the main paper shows this modelled quantity over winter 2013/14, during which the Bachok observations were made, as

an example. The observed peak in VSLS-Cl is 1) captured well by the model, and 2) likely to be a regularly repeated event. In total during this winter there are ~57 days (i.e. 453 3-hour periods) with a modelled mixing ratio above a threshold of 25 ppb, and 19 days above 50 ppb. To demonstrate that winter 2013/14 was not unusual, the modelled CO anomalies for the other 5 winters examined are shown in Figure S2.

2.2 NAME animations

The two animations (Jan2014.mp4 and Feb2014.mp4) show 3-hourly NAME footprints of air arriving at Bachok in January and February 2014 and indicate where surface emissions have an influence on the composition of air arriving at the site. The animations give an indication of the frequency that air arriving at Bachok has been influenced by emissions from East Asia.

Supplementary References

Ashfold, M.J.; Harris, N.R.P.; Atlas, E.L.; Manning, A.J. & Pyle, J.A. Transport of short-lived species into the Tropical Tropopause Layer Atmospheric Chemistry And Physics, 12, 6309-6322, 2012.

Granier, C. et al., Evolution of anthropogenic and biomass burning emissions of air pollutants at global and regional scales during the 1980--2010 period, *Climatic Change*, **109**, 163-190, 2011.

Heyes, W. J.; Vaughan, G.; Allen, G.; Volz-Thomas, A.; Pätz, H.-W. & Busen, R. Composition of the TTL over Darwin: local mixing or long-range transport? Atmospheric Chemistry and Physics, 9, 7725-7736, 2009.

Jones, A., Thomson, D., Hort, M., and Devenish, B.: The U.K. Met Office's Next-Generation Atmospheric Dispersion Model, NAME III, in: *Air Pollution Modeling and Its Application XVII*, edited by Borrego, C. and Norman, A.-L., 580–589, Springer US, doi:10.1007/978-0-387-68854-1_62, 2007.

Morrison, N.L. and Webster, H.N.: An Assessment of Turbulence Profiles in Rural and Urban Environments Using Local Measurements and Numerical Weather Prediction Results, *Bound.-Lay. Meteorol.*, **115**, 223–239, doi:10.1007/s10546-004-4422-8, 2005.

Navarro, M.A.; Atlas, E.L.; Saiz-Lopez, A.; Rodriguez-Lloveras, X.; Kinnison, D.E.; Lamarque, J.-F.; Tilmes, S.; Filus, M.; Harris, N.R.P.; Meneguz, E.; Ashfold, M.J.; Manning, A.J.; Cuevas, C.A.; Schauffler, S.M. & Donets, V. Airborne measurements of organic bromine compounds in the Pacific tropical tropopause layer Proceedings of the National Academy of Sciences 112, 13789-13793, 2015.

Riahi, K. et al., RCP 8.5—A scenario of comparatively high greenhouse gas emissions. *Climatic Change*, **109**, 33-57, 2011.

Shao, M., Huang, D., Gu, D., Lu, S., Chang, C. and Wang, J. Estimate of anthropogenic halocarbon emission based on measured ratio relative to CO in the Pearl River Delta region, China. *Atmos. Chem. Phys.*, **11**, 5011-5025, 2011.
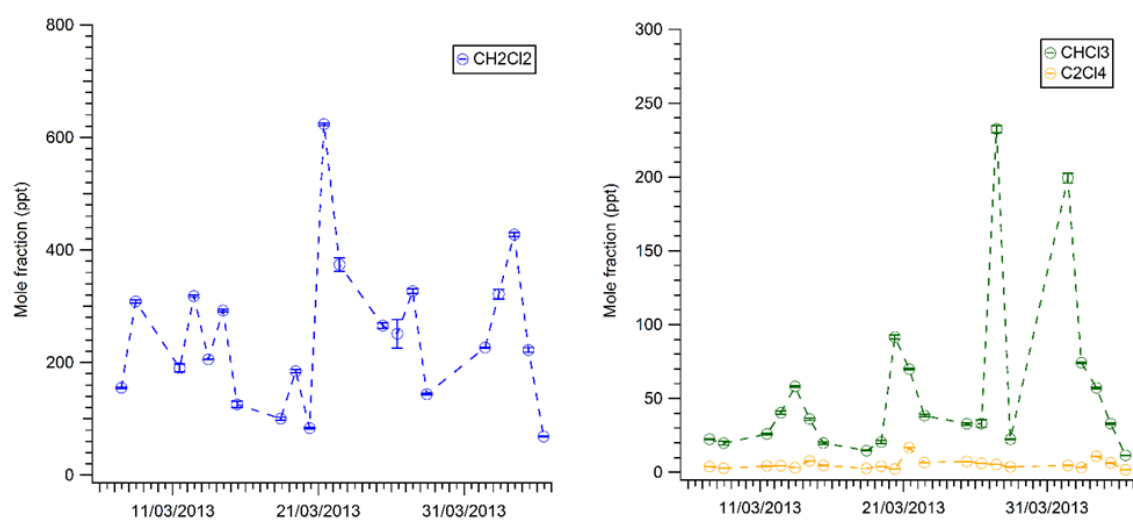
Figure S1: Mole fractions (ppt) of 3 chlorinated VSLS in air samples collected at Hengchun, Taiwan in March/April 2013. Note that CH_2ClCH_2Cl was not monitored in the 2013 samples. The error bars are ± 1 standard deviation.
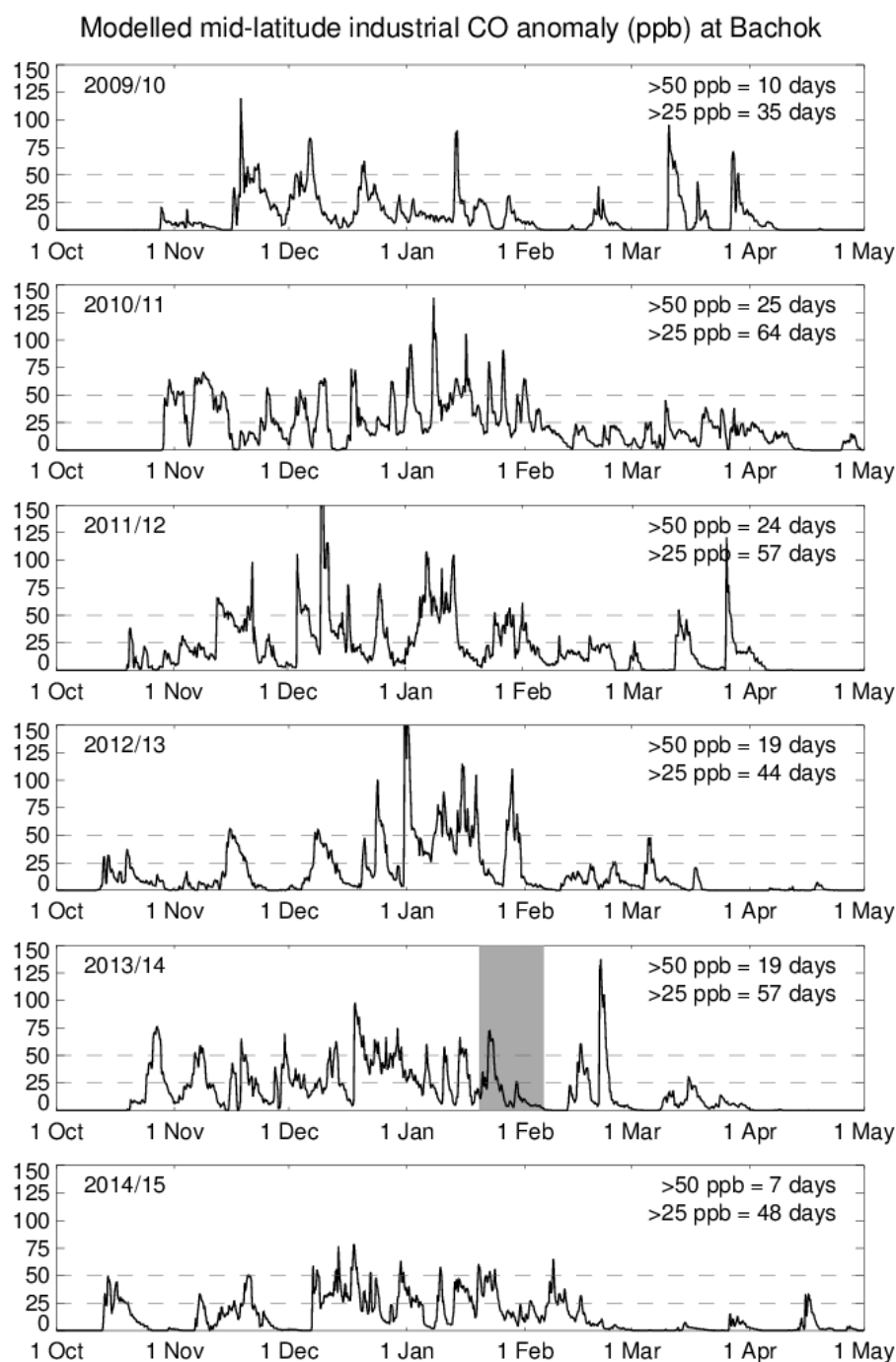
Figure S2: Time-series of the modelled carbon monoxide (CO) anomaly at Bachok, due only to industrial emissions from north of 20°N in the previous 12 days, for six winter seasons. The period of observations at Bachok during Jan and Feb 2014 is shaded in grey. Also shown are the number of days in each winter which exceed the 25 ppb and 50 ppb thresholds which, using the regression equation in Figure 4b, correspond to 176 ppt and 315 ppt of CH_2Cl_2.