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 3b and Shao et al. 2011), to model anomalous CO volume mixing ratios 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.

3. CH_2Cl_2 emission calculations

China does not report production or emission figures for CH_2Cl_2. However emissions of CH_2Cl_2 can be estimated from known Chinese production of HCFC-22 ($CHClF_2$). This is possible because the production of HCFC-22 requires $CHCl_3$ as feedstock (1 kg HCFC-22 requires 1.5 kg $CHCl_3$) and because $CHCl_3$ is produced almost entirely (>99%) for HCFC-22 production. Production of chloromethanes by any manufacturing process leads to the inevitable co-production of CH_2Cl_2 and $CHCl_3$, with smaller (3-5%) co-production of carbon tetrachloride (CCl_4). The production ratios vary by individual plant but are within the range 30:70-70:30 (% CH_2Cl_2:$CHCl_3$). Chinese chloromethanes plants, which together represent some 60% of global capacity and production, are generally built to a 40:60 - 60:40 flexibility ratio. With falling CFM demand due to diminished feedstock demand for HCFC-22 production, and based on regular discussions with the individual large producers, ratios in China have been switching in recent years from the traditional 40:60 towards 50:50 (CH_2Cl_2:$CHCl_3$; Nolan Sherry 2016).

It can be calculated that in 2015 China produced approximately 600 kt of HCFC-22 for all uses (Nolan Sherry 2016), which would require 900 kt of $CHCl_3$ as feedstock. By subtracting Chinese imports of $CHCl_3$ (40 kt; Comtrade 2016) and allowing for some limited emissive solvent use (15 kt) suggests that China produced around 875 kt of $CHCl_3$ in 2015. As noted above, in the chlorocarbon industry CH_2Cl_2 and $CHCl_3$ are produced in the same manufacturing process and in China this is currently moving from a historic production ratio of around 40:60 towards 50:50. Using this range of production ratios it can therefore be estimated that China produced between 700 and 875 kt CH_2Cl_2 in 2015. Approximately 90 kt of this was exported (Comtrade 2016) and another 170 kt was used for the production of HFC-32 (CH_2F_2), which is a non-emissive application (Nolan Sherry 2016). This leaves an estimated 440-615 kt of CH_2Cl_2 which is used almost exclusively in emissive applications such as paint stripping, foam blowing, pharmaceuticals, solvent use, etc. Although there is no specific industry-based aggregation of these numbers, they have been verified in discussion with Chinese and other industry sources. A similar method has recently been used to assess emissions of CCl_4 (SPARC 2016).

Supplementary References

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Nolan Sherry Associates (NSA) proprietary information: some of the data used in these calculations is proprietary in nature, being based on direct information from discussions with the producers and have been aggregated for reasons of confidentiality. In the case of the HCFC-22 production data this is also because there are two uses of HCFC22; as a chemical intermediate, and as a refrigerant and a foam blowing agent. The latter uses are "emissive" and are controlled by the Montreal Protocol (http://ozone.unep.org) and are in the public domain. Information on the controlled uses of HCFC-22 may be found on this website, or by access to the Multilateral Fund of the Montreal Protocol (http://www.multilateralfund.org), and, in the case of China, by private subscription to the industry magazine China Fluoride Materials (www.cnchemicals.com).

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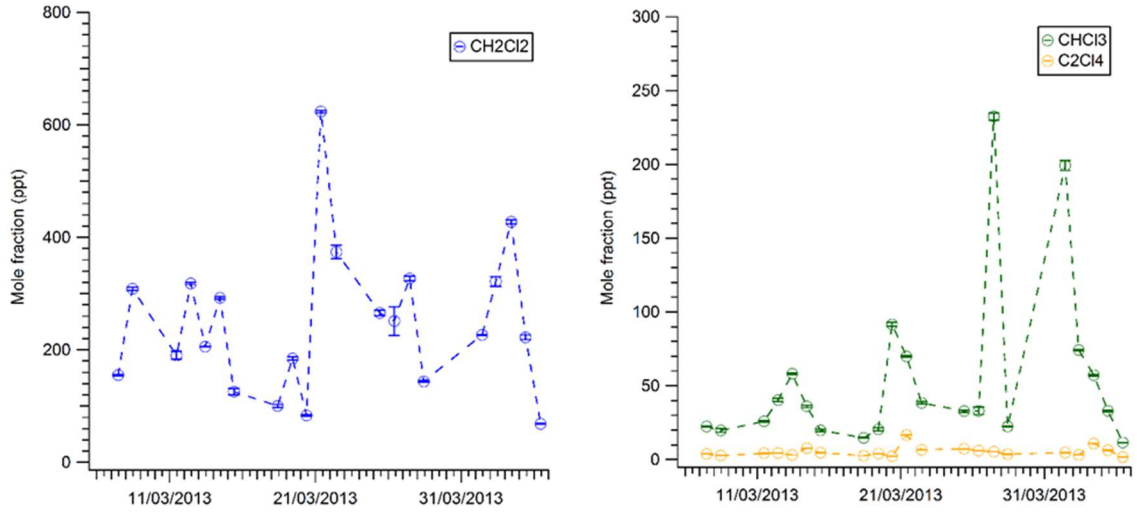

Figure S1: Mole fractions (ppt) of 3 chlorinated VSLS in air samples collected at Hengchun, Taiwan in March/April 2013. Note that CH_2ClCH_2Cl was not monitored in the 2013 samples. The error bars are ± 1 standard deviation.

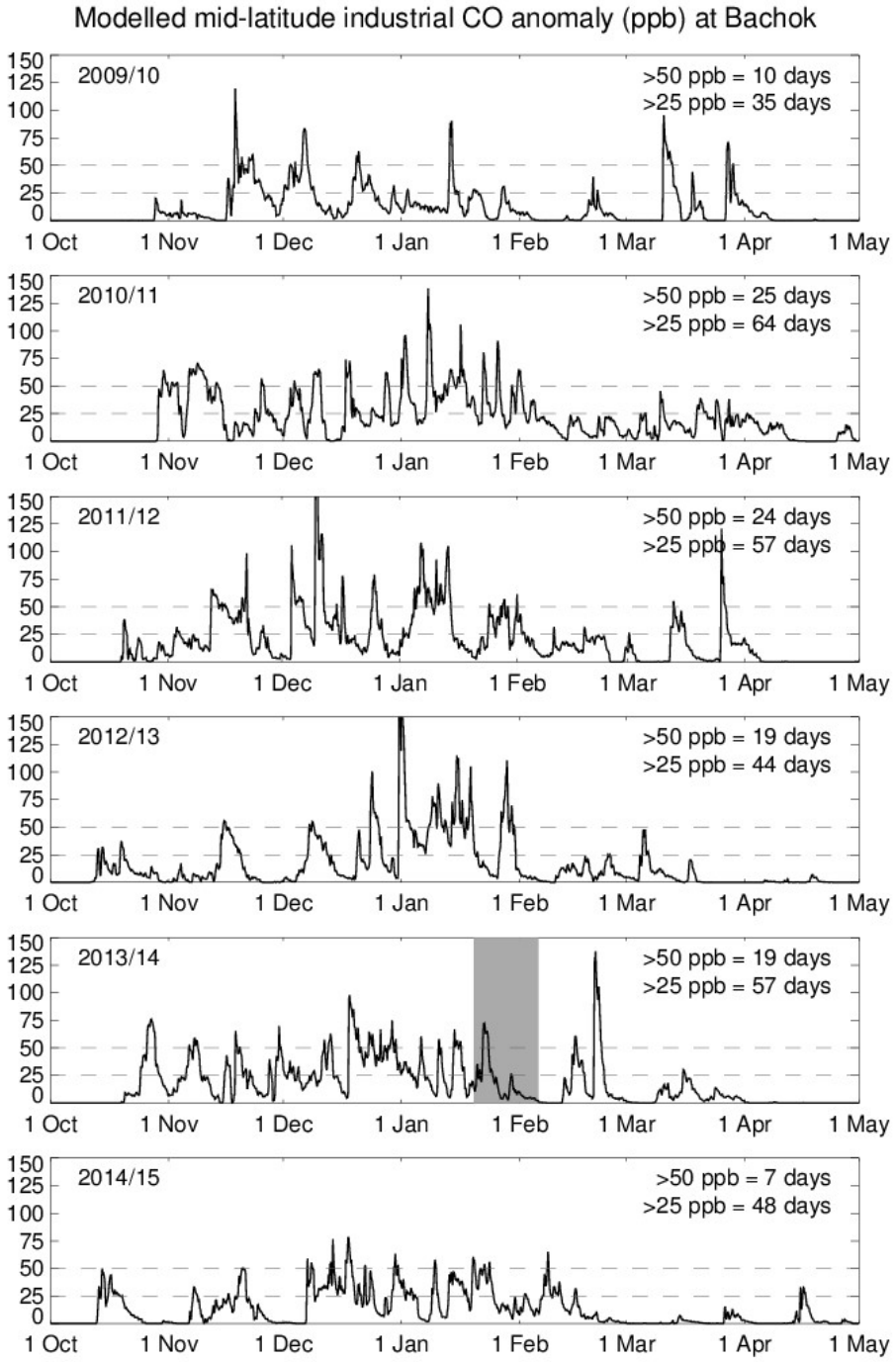

Figure S2: Time-series of the modelled carbon monoxide (CO) anomaly at Bachok, due only to industrial emissions from north of 20°N in the previous 12 days, for six winter seasons. The period of observations at Bachok during Jan and Feb 2014 is shaded in grey. Also shown are the number of days in each 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.