A growing threat to the ozone layer from short-lived anthropogenic chlorocarbons

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Abstract

Large and effective reductions in emissions of long-lived ozone-depleting substance (ODS) are being achieved through the Montreal Protocol, the effectiveness of which can be seen in the declining atmospheric abundances of many ODS. An important remaining uncertainty concerns the role of very short lived substances (VSLS) which, owing to their relatively short atmospheric lifetimes (less than 6 months), are not regulated under the Montreal Protocol. Recent studies have found an unexplained increase in the global tropospheric abundance of one VSLS, dichloromethane (CH_2Cl_2), which has increased by around 60% over the past decade. Here we report dramatic enhancements of several chlorine-containing VSLS (Cl-VSLS), including CH_2Cl_2 and CH_2ClCH_2Cl (1,2-dichloroethane), observed in surface and upper tropospheric air in East and South East Asia. Surface observations were, on occasion, an order of magnitude higher than previously reported in the marine boundary layer, whilst upper tropospheric data were up to 3 times higher than expected. In addition we provide further evidence of an atmospheric transport mechanism whereby substantial amounts of industrial pollution from East Asia, including these chlorinated VSLS, can rapidly, and regularly, be transported to tropical regions of the western Pacific and subsequently uplifted to the tropical upper troposphere. This latter region is a major provider for air entering the stratosphere and so this mechanism, in conjunction with increasing emissions of Cl-VSLS from East Asia, could potentially slow the expected recovery of stratospheric ozone.

1. Introduction

Large-scale ozone depletion in the stratosphere is a persisting global environmental problem. It is predominantly caused by the release of reactive chlorine and bromine species from halogenated organic compounds. Although the basic science is well established, there remains significant uncertainty surrounding the long-term recovery of the ozone layer (Hegglin et al., 2015). One important issue is the recent, unexplained increase in the global tropospheric abundance of dichloromethane (CH_2Cl_2), which has increased by ~60% over the past decade (Leedham-Elvidge et al., 2015; Hossaini et al., 2015a; Carpenter and Reimann et al., 2015).

CH_2Cl_2 is one of a large group of halogenated compounds known as VSLS (very short-lived substances). Owing to their relatively short atmospheric lifetimes (typically less than 6 months) and their correspondingly low Ozone Depletion Potentials (ODPs), VSLS are not currently regulated by the Montreal Protocol. It is however estimated that a significant fraction of VSLS and their atmospheric degradation products reach the stratosphere (>80% in the case of chlorinated VSLS; Carpenter and Reimann et al., 2015) and, furthermore, halogenated VSLS have been shown to have a disproportionately large impact on radiative forcing and climate due to their atmospheric breakdown, and the subsequent depletion of ozone, occurring at lower, climate sensitive altitudes (Hossaini et al., 2015b). According to the most recent Scientific Assessment of Stratospheric Ozone Depletion (Carpenter and Reimann et al., 2015) over the period 2008-2012 the total chlorine from VSLS increased at a rate of approximately 1.3 ± 0.2 ppt Cl yr^{-1}, the majority of this increase being due to CH_2Cl_2, and this has already begun to offset the decline in total tropospheric chlorine loading over the same period (13.4 ± 0.9 ppt Cl yr^{-1}) caused by the reduced emissions of substances controlled by the Montreal Protocol.

In recent years much attention has been focussed on the potential of bromine-containing VSLS to contribute to stratospheric ozone depletion (Law and Sturges, 2007; Montzka and Reimann, 2011). This is primarily due to the large observed discrepancy between the measured inorganic bromine in the stratosphere and the amount of bromine available from known, longer lived source gases, namely the halons and methyl bromide (Dorf et al., 2006). In contrast, the role of very short-lived chlorine compounds (Cl-VSLS) in ozone depletion has been considered relatively minor because they are believed to contribute only a few percent to the total chlorine input to the stratosphere, the majority of which is supplied by long-lived compounds such as the chlorofluorocarbons (CFCs), methyl chloroform (CH_3CCl_3) and carbon tetrachloride (CCl_4). Since 1987 the consumption of these long-lived anthropogenic compounds has been controlled by the Montreal Protocol and the sum of total organic chlorine in the troposphere has been falling since its peak of around 3660 parts per trillion (ppt) in 1993/94 to ~3300 ppt in 2012 (Carpenter and Reimann et al., 2015). Because of its relatively short atmospheric lifetime (~5 years) and its high chlorine content (3 chlorine atoms per molecule), the main contributor to this decline has been CH_3CCl_3. However, most CH_3CCl_3 has now been removed from the atmosphere with a present day abundance of less than 5 ppt. Consequently the rate of decline in total organic chlorine has fallen to 13.4 ppt/year (2008-2012), which is around 50% smaller than the maximum seen in the late 1990s (Carpenter and Reimann et al., 2015).

Owing to their short atmospheric lifetimes and their hitherto low background concentrations, chlorinated VSLS have not been considered of major importance for ozone depletion. Indeed the contribution of VSLS to the total chlorine entering the stratosphere is estimated to be only 55 (38–95) ppt (Carpenter and Reimann et al., 2015), which is between 1% and 3% of the present day (2012) total (3300 ppt). However, because of their short lifetimes, the potential impact of VSLS on stratospheric ozone is highly dependent on the location of their sources, with emissions close to the major stratospheric input regions being of far greater significance for ozone depletion.

The transport of trace gases and aerosols from the troposphere into the stratosphere occurs primarily in the tropics, where convective activity and vertical uplift are most intense. In order to get to the stratosphere an air parcel has to pass through the tropical tropopause layer (TTL),

the region of the atmosphere between the level of maximum convective outflow (~12 km altitude, 345K potential temperature) and the cold-point tropopause (~17 km, 380K) (see Box 1-3, Figure 1 in Carpenter and Reimann et al., 2015). The vertical flux into the TTL is thought to be dominated by two main regional pathways, (1) ascent above the western Pacific during Northern Hemispheric (NH) winter and (2) the circulation of the Asian (Indian) Monsoon during NH summer (Fueglistaler et al., 2009). The latter has been suggested as the most important region for transport of anthropogenic pollution (Randel et al., 2010).

Because of their short lifetimes, to be able to accurately determine the VSLS contribution to total organic halogen loading in the stratosphere it is highly desirable to collect data in the TTL. Surface measurements alone, particularly in regions outside the tropics where most long-term surface stations are sited, are not sufficient. Furthermore, because of the distribution and seasonality of stratospheric entry points it is also essential to measure in specific locations and at specific times of year, i.e. in the Indian summer monsoon and over the winter western Pacific. Unfortunately there are very few available measurements of VSLS in the TTL generally as it is above the maximum altitude of most research aircraft, and, furthermore, there is a paucity of both ground and aircraft data available in these two key regions of interest. Where recent TTL data is available it is primarily from different regions and focussed on brominated VSLS (e.g. Sala et al., 2014; Navarro et al., 2015).

The focus of the present study is the western Pacific and, in particular, the region of the South China Sea. During NH winter the region is heavily influenced by the large anticyclone that forms over Siberia each year which gives rise to strong north-easterly winds that impact deep into the tropics as far south as Malaysia, Singapore and Indonesia. These north-easterly winds typically prevail for 4-5 months (November-March) and form part of the East Asian winter monsoon circulation. Superimposed on this seasonal synoptic flow are transient disturbances known as cold surges, which are triggered by a southward shift of the anticyclone and lead to sudden drops in surface air temperatures and increased wind speeds (Zhang et al., 1997; Garreaud, 2001). It has been proposed that during these events significant amounts of pollution from continental East Asia (>35°N) can be transported rapidly to the tropics (Ashfold et al., 2015). Furthermore, these events, which can last for many days, occur regularly each winter and are associated with some of the strongest convective activity in the western Pacific region. Indeed, trajectory calculations show that it can take less than 10 days for air masses to travel from the East Asian boundary layer (>35°N) to the upper tropical troposphere (altitudes > 200 hPa), thereby providing a fast route by which VSLS (and many other pollutants) may enter the lower stratosphere, despite their relatively short atmospheric lifetimes (Ashfold et al., 2015).

Here we provide strong evidence to support this proposed transport mechanism based on new atmospheric observations in the East and SE Asia region. We will present new Cl-VSLS measurements from recent ground-based and aircraft campaigns in the region during which we have observed dramatic enhancements in a number of Cl-VSLS, including CH_2Cl_2, 1,2-dichloroethane (CH_2ClCH_2Cl), trichloromethane ($CHCl_3$) and tetrachloroethene (C_2Cl_4). Furthermore we will demonstrate how pollution from China and the surrounding region can rapidly, and regularly, be transported across the South China Sea and subsequently uplifted to altitudes of 11-12 km, the region close to the lower TTL. Using the NAME particle dispersion model we will also investigate the origin of the observed Cl-VSLS and examine the frequency and duration of cold surge events. Finally we present some new estimates of CH_2Cl_2

emissions from East Asia and use these to estimate the likely emissions of CH_2ClCH_2Cl, for which there is little information in the recent literature.

2. Methods

Between 2012 and 2014, air samples were collected at various times at (1) two coastal sites in Taiwan, Hengchun (22.0547°N, 120.6995°E) and Fuguei Cape (25.297°N, 121.538°E); (2) the Bachok Marine Research Station on the Northeast coast of Peninsular Malaysia (6.009°N, 102.425°E); and (3) during several flights of the IAGOS-CARIBIC aircraft between Germany and Thailand/Malaysia. IAGOS-CARIBIC is a European project making regular measurements from an in-service passenger aircraft operated by Lufthansa (Airbus A340-600; Brenninkmeijer et al., 2007; http://www.caribic-atmospheric.com/).

A total of 21 samples were collected at Hengchun between 7 March and 5 April 2013 with a further 22 samples taken at Cape Fuguei between 11 March and 4 April 2014. 28 samples were collected at Bachok between 20 January and 5 February 2014, during the period of the NE winter monsoon. The approximate location of each surface site is shown in Figure 1. The CARIBIC aircraft samples were collected during seven return flights between (i) Frankfurt (Germany) and Bangkok (Thailand), and (ii) Bangkok and Kuala Lumpur (Malaysia) during the periods December 2012 - March 2013 (4 flights) and November 2013 - January 2014 (3 flights). All CARIBIC flights in this region between December 2012 and January 2014 have been included in this analysis. With the exception of 3 samples that were taken at altitudes between 8.5 and 9.8 km, the CARIBIC samples were all (n=179) collected at altitudes between 10 and 12.3 km.

2.1 Sample collection

Air samples from Taiwan and Malaysia were collected in 3.2 litre silco-treated stainless steel canisters (Restek) at a pressure of approximately 2 bar using a battery-powered diaphragm pump (Air Dimensions, B series). In Taiwan the samples were collected from the surface via a 1m x ¼" OD Dekabon sampling line, whilst in Bachok the samples were collected from the top of an 18 m tower via a 5 m x ¼" OD Dekabon sampling line. In both cases the tubing was flushed for at least 5 minutes prior to sampling. The sampling integrity was confirmed by sampling high purity air (BTCA-178, BOC) through the inlet tubing and pump. Samples were collected within 50 m of the sea and only when the prevailing winds were from the sea, minimising the impact of any local emissions. The CARIBIC aircraft samples were collected in 2.7 litre glass flasks at a pressure of 4.5 bar using a two-stage metal bellows pumping system (Brenninkmeijer et al., 2007; Baker et al., 2010).

2.2 Sample analysis

The collected air samples were shipped to UEA and analysed for their halocarbon content by gas chromatography – mass spectrometry (GC-MS) following trace gas enrichment using previously published methods. All samples (i.e. Taiwan, Bachok and CARIBIC) were analysed for CH_2Cl_2, $CHCl_3$ and C_2Cl_4 using an Entech-Agilent GC-MS system operating in electron ionisation (EI) mode, as described in Leedham-Elvidge et al., (2015). 1 litre samples were dried and pre-concentrated before injection onto a 30 m x 0.32 mm GS Gas Pro capillary column (Agilent), temperature ramped from -10°C to 200°C. Samples were interspersed with repeated analyses of a working standard (SX-706070), a high pressure air sample contained in a 34 litre electropolished stainless steel cylinder (Essex Industries) provided by the Earth

System Research Laboratory of the National Oceanic and Atmospheric Administration (NOAA-ESRL, Boulder, CO, USA). CH_2Cl_2, $CHCl_3$ and C_2Cl_4 were quantified on ions with a mass-to-charge ratio of 84 ($CH_2{}^{35}Cl_2{}^+$), 83 ($CH^{35}Cl_2{}^+$ and 166 ($C_2{}^{35}Cl_3{}^{37}Cl^+$) respectively. Mean analytical precisions were ± 2% for CH_2Cl_2 and C_2Cl_4, and ± 3% for $CHCl_3$. Instrument blanks, determined by analysing 1 litre aliquots of high purity nitrogen (BOC, Research grade), were always below the detection limit of the instrument.

Some of the ground-based samples and a subset of the CARIBIC samples were also analysed for a range of halocarbons, including the newly-identified CH_2ClCH_2Cl, using a pre-concentration/GC system coupled to a Waters AutoSpec magnetic sector MS instrument, also operating in EI mode, but run at a mass resolution of 1000 at 5 % peak height. Samples (using between 200 and 250 ml of air) were analysed on an identical GS GasPro column following a previously described method (Laube et al., 2010; Laube et al., 2012; Leedham-Elvidge et al., 2015). CH_2ClCH_2Cl was monitored on the ions with mass-to-charge ratios of 61.99 ($C_2H_3{}^{35}Cl^+$, qualifier) and 63.99 ($C_2H_3{}^{37}Cl^+$, quantifier). Mean analytical precision was 1.4 % for CH_2ClCH_2Cl and the average blank signal was 0.07 ppt (as quantified using regular measurements of research-grade helium) and was corrected for on a daily basis.

2.3 Calibration and quality assurance

CH_2Cl_2, $CHCl_3$ and C_2Cl_4 data are reported on the latest (2003) calibration scales provided by NOAA-ESRL. As was shown in Leedham-Elvidge et al., (2015) our CH_2Cl_2 measurements compare very well with those of NOAA-ESRL at our mutual long-term sampling site at Cape Grim, Tasmania over more than 6 years. As a recognised international calibration scale for CH_2ClCH_2Cl is not yet available this compound was calibrated at UEA using the established static dilution technique recently described (Laube et al., 2012). CH_2ClCH_2Cl was obtained from Sigma Aldrich with a stated purity of 99.8 %.Three dilutions were prepared at 7.1, 11.9 and 15.8 ppt. The mixing ratio assigned to our working standard from these dilutions was 5.67 ppt with a 1 σ standard deviation of 1.8 %. CFC-11 was added to the dilutions as an internal reference compound and the CFC-11 mixing ratios assigned to the working standard through these dilutions agreed with the value assigned by NOAA-ESRL within 4.3 %. This is well within the estimated uncertainty of the calibration system of 7 % (Laube et al., 2012). In addition the mixing ratios of CH_2ClCH_2Cl in the working standard were compared with those in three other high-pressure canisters (internal surface was either electropolished stainless steel or passivated aluminium) over the whole measurement period. The ratios between standards did not change within the 2 σ standard deviation of the measurements for any of the canisters analysed indicating very good long-term stability for CH_2ClCH_2Cl. This was also the case for $CHCl_3$ and C_2Cl_4. As noted in Leedham-Elvidge et al., (2015) mixing ratios of CH_2Cl_2 were found to change over longer timescales in some of our standard canisters, but this drift has been successfully quantified and corrected for as indicated by the very good comparability with NOAA-ESRL measurements at the Cape Grim site noted above.

3. Results

Figure 1 shows the location of the three surface observation stations as well as the location of the CARIBIC samples. The aircraft sampling points have been coloured by their CH_2Cl_2 concentration (see later discussion). Data from the surface stations and from the CARIBIC aircraft flights are summarised in Table 1, together with a summary of published observations as reported in the most recent Scientific Assessment of Stratospheric Ozone Depletion

(Carpenter and Reimann et al., 2015). It should be noted that CH_2ClCH_2Cl was only analysed for in selected samples and no data is available from Hengchun 2013 or from CARIBIC flights between Bangkok and Kuala Lumpur. In addition, only 16 Bachok samples were analysed for CH_2ClCH_2Cl.

The highest concentrations of chlorinated VSLS were measured in samples collected in Taiwan, suggesting that Taiwan is located relatively close to major emission regions. Figure 2 shows the March/April 2014 data from Cape Fuguei. The Numerical Atmospheric-dispersion Modelling Environment model (NAME, see supplementary material) can be used to infer the recent transport history of this pollution. Our NAME analysis (Fig. 2 b-d) indicates that most of the samples that contained high concentrations of Cl-VSLS had originated from regions to the north of Taiwan, primarily the East Asian mainland. The median sum of chlorine from the 4 VSLS listed above (ΣCl_{VSLS}) in 22 samples collected at Cape Fuguei in March/April 2014 was 756 ppt (range 232-2178 ppt). Similarly high concentrations and variation were seen in the 21 samples collected at Hengchun in March/April 2013 (Fig. S1 in the supplementary material). To put these concentrations in a global context, the total organic chlorine derived from all known source gases in the background troposphere (including CFCs, HCFCs, and longer-lived chlorocarbons) is currently around 3300 ppt, with a typical Cl-VSLS contribution in the remote marine boundary layer of approximately 3 % (Carpenter and Reimann et al., 2015). Of the four VSLS measured, the two largest contributors to ΣCl_{VSLS} in Taiwan were CH_2Cl_2 (55-76 %) and CH_2ClCH_2Cl (14-30 %).

Figure 3 shows the Cl-VSLS data from 28 samples collected at Bachok, Malaysia during the winter monsoon season in late January/ early February 2014. During this phase of the East Asian monsoon the prevailing winds are from the northeast and, as described earlier, are often impacted by emissions further to the north, including from mainland China. As can be seen in Figure 3, there was a 7 day period between 19 and 26 January when significantly enhanced concentrations of Cl-VSLS were observed. During this period NAME back trajectories show air travelling from continental East Asia and across the South China Sea before arriving at Bachok. Three examples during this cold surge event are shown in Fig. 3 (b-d). These trajectories often pass over Taiwan and, in some instances, also over parts of Indochina where additional emissions could have been picked up. As in the Taiwan samples, CH_2Cl_2 is the largest contributor to ΣCl_{VSLS} (59-66 %), having a mean concentration of 179.9 ± 71.9 ppt (range 94.0 – 354.9 ppt, 9 samples) during the 7-day period of the pollution event. The mean concentration of CH_2ClCH_2Cl was 64.4 ± 23.9 ppt (range 30.2 – 119.5 ppt), accounting for 19-23 % of ΣCl_{VSLS}. These abundances are substantially higher than those typically found in the marine boundary layer. For example, the range of ΣCl_{VSLS} from the 4 compounds listed above in the tropical marine boundary layer reported in WMO (2014) is 70-134 ppt. The range observed at Bachok over the entire sampling period was 207-1078 ppt, with medians of 546 ppt and 243 ppt during the polluted (20-26 Jan) and less-polluted (27 Jan – 5 Feb) periods respectively (see Table 1). It is interesting to note that even in the period after the cold surge event (Fig.3 e,f), the levels of Cl-VSLS are still significantly higher than would be expected, suggesting that this region of the South China Sea is widely impacted by emissions from E Asia.

The pollution or “cold surge” event observed at Bachok lasted for 6-7 days and the back trajectories shown in Figure 3 are typical of those arriving at Bachok during the winter monsoon period (see NAME animations in supplement). To further investigate the frequency

and typical duration of these events a NAME trajectory analysis using carbon monoxide (CO) as a tracer of industrial emissions from regions north of 20°N was conducted for the entire winter season (see supplementary information for details). Figure 4(a) shows a time series of this industrial CO tracer for winter 2013/2014 and suggests that the observed event in January, during which there was a strong correlation between the industrial CO tracer and CH_2Cl_2 (Fig. 4b), is likely to be repeated regularly throughout the winter. An analysis of a further 5 winters (Fig. 4c) demonstrates that 2013/14 was not unusual and that the events depicted in Figure 3a occur repeatedly every year (Fig. S2 in the supplementary material).

The Bachok measurements clearly demonstrate the rapid long-range transport of highly elevated concentrations of Cl-VSLS for several thousand kilometres across the South China Sea, as predicted by Ashfold et al., (2015). However, to have an impact on stratospheric ozone it is necessary to demonstrate that these high concentrations of Cl-VSLS can be rapidly lifted to the upper tropical troposphere (lower TTL) or above. Such evidence can be found in samples from several recent CARIBIC aircraft flights in the Southeast Asia region. Figure 1 shows significant enhancements of CH_2Cl_2 during flights over northern India and the Bay of Bengal, and also between Bangkok and Kuala Lumpur. The same data is plotted against longitude in Figure 5(a) which shows that elevated concentrations were observed in the seven CARIBIC flights in the region during the periods Dec 2012 - Mar 2013 and Nov 2013 - Jan 2014. The samples were collected in the altitude range 10-12.3 km, showing that recent industrial emissions can regularly reach the lower boundary of the TTL. Although CH_2ClCH_2Cl was only analysed for in a selection of samples during the flights from Germany to Bangkok, elevated mixing ratios coinciding with the high levels of CH_2Cl_2 were clearly observed (Fig. 5b). $CHCl_3$ and C_2Cl_4 were also enhanced during these flights (Table 1), with ΣCl_{VSLS} being in the range 48-330 ppt (Fig. 5c). This is up to 3.2 times higher than that previously found in the lower TTL (36-103 ppt; Carpenter and Reimann et al., 2015). The highest abundances of Cl-VSLS were seen in samples collected over the Bay of Bengal, and on flights between Bangkok and Kuala Lumpur (Fig. 5a). NAME back trajectories (Fig. 5d) indicate that in these cases the sampled air had almost always been transported from the east, and had often been impacted by emissions from East Asia, with possible contributions from other countries including the Philippines, Malaysia and Indochina.

4. Discussion

The high mixing ratios of CH_2Cl_2 observed in the Taiwan samples are not entirely unexpected. Previous studies have found very high levels (> 1 ppb) of CH_2Cl_2 in various Chinese cities (Barletta et al., 2006) and in the Pearl River Delta region (Shao et al., 2011). Elevated levels (several hundred ppt) were also observed in aircraft measurements in polluted air emanating from China during the TRACE-P campaign in 2001 (Barletta et al., 2006). These studies took place in the early 2000s and emissions may be expected to have grown significantly since. CH_2Cl_2 is predominantly (~90%) anthropogenic in origin, and is widely used as a chemical solvent, a paint stripper and as a degreasing agent (McCulloch and Midgely, 1996; Montzka et al., 2011). Other uses include foam blowing and agricultural fumigation. A growing use of CH_2CL_2 is in the production of HFC-32 (CH_2F_2), an ozone friendly replacement for HCFC-22 (CHF_2Cl) in refrigeration applications. Around 10% of global CH_2Cl_2 emissions come from natural marine and biomass burning sources (Simmonds et al., 2006; Montzka and Reimann et al., 2011).

Whilst the strong enhancements of CH_2Cl_2 are not entirely unexpected, the presence of high concentrations of CH_2ClCH_2Cl most certainly are. There are very few previously reported measurements of CH_2ClCH_2Cl, particularly in recent years. Elevated levels have been observed in urban environments close to known emission sources (Singh et al., 1981) and, more recently, Xue et al., (2011) reported elevated levels (91 ± 79 ppt) in air samples collected in the boundary layer over north-eastern China in 2007. The few reported measurements of CH_2ClCH_2Cl in the remote marine boundary layer are typically in the low ppt range (see Table 1) but these were mostly made well over a decade ago. No long-term atmospheric measurements of CH_2ClCH_2Cl have been reported, and CH_2ClCH_2Cl is not reported by the main surface monitoring networks (AGAGE and NOAA), so current background concentrations and longer term trends are unknown. CH_2ClCH_2Cl is predominantly anthropogenic in origin, its primary use being in the manufacture of vinyl chloride, the precursor to polyvinyl chloride (PVC), and a number of chlorinated solvents. CH_2ClCH_2Cl also finds use as a solvent, dispersant and has historically been added to leaded petrol as a lead scavenger (EPA, 1984). In common with CH_2Cl_2 it has also used as a cleaning/degreasing agent and as a fumigant. China is the world's largest producer of PVC accounting for 27% of global production in 2009 (DCE, 2017). Production has increased rapidly in recent years (14% per year over the period 2000-2009; DCE, 2017), which could potentially have led to increased atmospheric emissions of CH_2ClCH_2Cl. Simpson et al. (2011) observed a small enhancement in CH_2ClCH_2Cl in Canadian boreal forest fire plumes (background average, June-July 2008, 9.9 ± 0.3 ppt, plume average 10.6 ± 0.3 ppt) and estimated a global boreal fire source of 0.23 ± 0.19 kilotonnes (kt) yr^{-1}.

The other Cl-VSLS presented here are C_2Cl_4 and $CHCl_3$. In contrast to CH_2ClCH_2Cl, long-term atmospheric data records are available for these compounds, although there are few data from the SE Asia region. Current trends show that C_2Cl_4 is declining in the background troposphere (~6 % yr^{-1}), whilst $CHCl_3$ is approximately constant (Carpenter and Reimann et al., 2015). However, both compounds were elevated in the samples containing high concentrations of CH_2Cl_2 and CH_2ClCH_2Cl, suggesting that significant, co-located sources remain. Like CH_2ClCH_2Cl, C_2Cl_4 is almost exclusively anthropogenic in origin, used primarily as a solvent in the dry cleaning industry, as a metal degreasing agent and as a chemical intermediate, for example in the manufacture of the hydrofluorocarbons HFC-134a and HFC-125. $CHCl_3$ is believed to be largely natural in origin (seawater, soils, macroalgae), but potential anthropogenic sources include the pulp and paper industry, water treatment facilities and HFC production (McCulloch, 2003; Worton et al., 2006; Montzka et al., 2011).

4.1 Regional emissions of CH_2Cl_2 and CH_2ClCH_2Cl

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 a production ratio of 45:55 it can therefore be estimated that China produced around 715 kt of 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 455 kt (± 10%) 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).

There is a strong linear correlation between the observed CH_2Cl_2 and CH_2ClCH_2Cl data at both Bachok (R^2 = 0.9799) and Cape Fuguei (R^2 = 0.9189). Combining the datasets yields a slope of 0.4456 ± 0.0194 (R^2 =0.9228). Using the emissions for CH_2Cl_2 derived above (455 kt) and making the assumptions that (1) all emissions originate in China and (2) there are no significant relative losses of the two compounds since emission (lifetimes are 144 days for CH_2Cl_2 and 65 days for CH_2ClCH_2Cl) we can estimate Chinese emissions of CH_2ClCH_2Cl to be of the order of 203 ± 9 kt yr^{-1}. If accurate, the scale of these emissions is a major surprise as CH_2ClCH_2Cl is highly toxic (suggesting that local emissions would be minimised) and believed to be used almost exclusively in non-emissive applications.

5. Concluding remarks

When calculating the VSLS contribution to stratospheric chlorine, it is usual to assume an average concentration in the region of the TTL known as the level of zero radiative heating (LZRH). The LZRH is located at the transition between clear-sky radiative cooling and clear-sky radiative heating. This occurs at an approximate altitude of 15 km and it is believed that air masses above this level will go on to enter the stratosphere (Carpenter and Reimann et al., 2015). As noted above there are very few measurements in this region and, furthermore, many of the available measurements were made over a decade ago and assumptions based on surface temporal trends have to be made in order to estimate present day values (Carpenter and Reimann et al., 2015: Hossaini et al., 2015). Another key deficiency in this estimation of VSLS concentrations entering the stratosphere is that most of the reported measurements have not been made in the two key regions where the strongest troposphere to stratosphere transport occurs. Although we have no data from the region of the LZRH, the CARIBIC data over northern India and SE Asia suggests that the contribution of VSLS to stratospheric chlorine loading may be significantly higher than is currently estimated (50-95 ppt, Carpenter and Reimann et al., 2015). It is also interesting to note that the much-discussed contribution of VSLS-Br compounds to stratospheric bromine is approximately 5 ppt, which is equivalent to 300 ppt of chlorine (1 ppt of bromine is roughly equivalent to 60 ppt chlorine,

Sinnhuber et al., 2009). The CARIBIC measurements suggest that Cl-VSLS could currently, on occasion, contribute a similar amount.

These new measurements of Cl-VSLS in Taiwan, Malaysia and from an aircraft flying above South-East Asia show that there are substantial regional emissions of these compounds; that these emissions can be rapidly transported long distances into the deep tropics; and that an equally rapid vertical transport to the upper tropical troposphere is a regular occurrence. Although the focus of this paper is short-lived chlorinated gases, there are many other chemical pollutants contained in these air masses which will have a large impact on such things as regional air quality.

Unlike the bromine-containing VSLS which are largely natural in origin, the Cl-VSLS reported here are mainly anthropogenic and consequently it would be possible to control their production and/or release to the atmosphere. Of particular concern are the rapidly growing emissions of CH_2Cl_2, and potentially CH_2ClCH_2Cl, especially when considering the geographical location of these emissions, close to the major uplift regions of the western Pacific (winter) and the Indian sub-continent (summer). Without a change in industrial practices the contribution of Cl-VSLS to stratospheric chlorine loading is likely to increase substantially in the coming years, thereby endangering some of the hard-won gains achieved, and anticipated, under the Montreal Protocol.

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544 Nolan Sherry Associates (NSA) proprietary information: some of the data used in these
545 calculations is proprietary in nature, being based on direct information from discussions
546 with the producers and have been aggregated for reasons of confidentiality. In the case of
547 the HCFC-22 production data this is also because there are two uses of HCFC22; as a
548 chemical intermediate, and as a refrigerant and a foam blowing agent. The latter uses are
549 "emissive" and are controlled by the Montreal Protocol (http://ozone.unep.org) and are in
550 the public domain. Information on the controlled uses of HCFC-22 may be found on this
551 website, or by access to the Multilateral Fund of the Montreal Protocol
552 (http://www.multilateralfund.org), and, in the case of China, by private subscription to the
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Table 1: Summary of Cl-VSLS data from the 3 surface stations and the 7 CARIBIC flights. For comparison, the ranges reported in the most recent WMO Ozone Assessment (Carpenter and Reimann et al., 2015) for the marine boundary layer (MBL) and lower Tropical Tropopause Layer (TTL, 12-14 km altitude) are also shown. All data are reported as mole fractions (ppt).

Figure 1: Map of the region showing the location of each CARIBIC sample. The markers have been coloured according to their CH_2Cl_2 concentration to highlight the regions where enhanced levels of VSLS were observed. Also shown are the approximate locations of the 3 surface stations (orange crosses).

Figure 2:

Upper panel (a): Mole fractions (ppt) of the 4 chlorinated VSLS in air samples collected at Cape Fuguei, Taiwan in March/April 2014. The error bars are ± 1 standard deviation. The black arrows show the dates of the footprint maps shown below.

Lower panel (b-d): NAME footprint maps indicating the likely origin of the air sampled at Cape Fuguei. Figures (b, 13 March) and (c, 30 March) show examples where the observed VSLS levels are very high and suggest a strong influence from continental East Asia. Figure (d) is from 29 March where the influence of the mainland is much lower and the VSLS mole fractions are much closer to the expected background level.

The location of Cape Fuguei is indicated with a blue circle (see also Figure 1).

Figure 3:

Upper panel (a): Mole fractions (ppt) of the 4 chlorinated VSLS in air samples collected at Bachok in Jan/Feb 2014. Strongly enhanced levels of all 4 compounds were seen for a 7-day period at the beginning of the campaign (20-26 Jan). Also shown (dashed line) are the approximate median background concentrations in the remote marine boundary layer in 2012 (from Carpenter and Reimann et al., 2015).

Lower panels (b-f): NAME footprint maps indicating the likely origin of the air sampled at Bachok. During the pollution episode (b = 21 Jan; c = 23 Jan; d = 24 Jan) the samples would have been heavily impacted by emissions from the East Asian mainland, whilst this influence is much reduced during the cleaner, non-polluted periods (e = 3 Feb; f = 5 Feb). Note that even after the main pollution event, the abundance of the VSLS remain significantly above true background levels for much of the time, suggesting a widespread influence from industrial emissions on a regional scale.

The location of Bachok is indicated with a blue circle (see also Figure 1).

Figure 4:

(a) Time-series of the modelled carbon monoxide (CO) anomaly at Bachok (i.e. that due only to industrial emissions from north of 20°N in the previous 12 days) for winter 2013/14. The CH_2Cl_2 data (grey squares) from the Bachok sampling period are overlaid. The dashed lines show the 25 ppb and 50 ppb thresholds referred to in 3c (see supplement for further details).

(b) Correlation of the modelled CO anomaly with the observed CH_2Cl_2.

(c) Average number of days each month, averaged over six consecutive winters (2009/10 – 2014/15) where the modelled carbon monoxide anomaly at Bachok is above a particular

659 threshold (25 ppb and 50 ppb which, from the regression in 3b, correspond to 176 ppt and
660 315 ppt of CH_2Cl_2). The 2013/14 winter is shown separately for comparison with the 6-year
661 average.

662 **Figure 5**

663 (a) Mole fractions (ppt) of CH_2Cl_2 in CARIBIC air samples collected at 10-12km altitude over
664 Northern India, the Bay of Bengal and SE Asia. The samples are plotted against longitude
665 and have been coloured by date.

666 (b) Mole fraction (ppt) of CH_2ClCH_2Cl in selected CARIBIC samples (note: CH_2ClCH_2Cl was
667 not monitored in the samples collected between Bangkok to Kuala Lumpur, and only in a
668 selection of samples on the Frankfurt-Bangkok route).

669 (c) Total Cl-VSLS derived from the 4 compounds of interest in the CARIBIC samples (note:
670 total Cl-VSLS could only be calculated for the samples shown in Fig 5b above).

671 (d) NAME footprint maps indicating the likely origin of the air sampled by the CARIBIC
672 aircraft. NAME footprints at this altitude, and particularly in regions of strong sub-grid-scale
673 convection not captured fully in the gridded meteorological input data, may be less reliable
674 than those at the surface sites. This makes pinpointing particular emission regions more
675 difficult. The central panel therefore shows a composite footprint derived from the samples
676 that contained the highest levels of CH_2Cl_2 (90^{th} percentile, $[CH_2Cl_2]$ >75.6 ppt), with the
677 composite footprint from the remaining samples ($[CH_2Cl_2]$ < 75.6 ppt) shown in the left hand
678 panel. To emphasise the likely source regions the right hand panel shows the difference
679 between the middle and left hand panels. The geographical location of each sample
680 included in the composite analysis are shown in blue circles.

Table 1

	Taiwan 2013		Taiwan 2014		Bachok 2014			MBL (WMO 2014) [b]	
	Median	*Range*	*Median*	*Range*	*Median (CS)* [a]	*Median (non-CS)*	*Range*	*Median*	*Range*
CH_2Cl_2	226.6	68 - 624	227.4	70 - 639	170.4	81.9	64.8 – 355	**28.4**	**21.8 – 34.4**
CH_2ClCH_2Cl	-	-	85.4	16.7 – 309	62.2	21.7	16.4 – 120 [c]	**3.7**	**0.7 - 14.5** [d]
$CHCl_3$	33.0	11.6 – 232	35.1	13.8 - 103	22.8	14.7	12.8 – 30.5	**7.5**	**7.3 – 7.8**
C_2Cl_4	4.4	1.7 – 16.6	5.5	1.7 – 18.6	4.5	1.9	1.5 – 9.5	**1.3**	**0.8 – 1.7**
ΣCl_{VSLS}	-	-	755.8	232 -2178	546.0	243.1	207 – 1078 [c]	**93.4**	**70 - 134**

	CARIBIC (FRA-BKK, 65-97°E) 10-12 km			CARIBIC (BKK-KUL, 100-105°E) 10-12 km			Lower TTL (WMO 2014) [b] 12-14 km	
	Mean	*Median*	*Range*	*Mean*	*Median*	*Range*	*Mean*	*Range*
CH_2Cl_2	43.2	31.6	14.6 - 121	50.4	46.5	22.5 - 100	**17.1**	**7.8 – 38.1**
CH_2ClCH_2Cl [e]	9.9	6.1	0.4 – 29.1	-	-	-	**3.6**	**0.8 – 7.0**
$CHCl_3$	7.0	6.0	2.0 – 15.6	9.3	8.7	3.7 - 46.6	**6.8**	**5.3 – 8.2**
C_2Cl_4	0.87	0.65	0.1 – 4.4	1.6	1.5	0.2 - 5.9	**1.1**	**0.7 – 1.3**
ΣCl_{VSLS} [e]	153.7	119.3	48.4 - 330				**67**	**36 - 103**
*ΣCl_{VSLS}** [f]	*110.9*	*81.4*	*35.2 - 301*	*134.8*	*127.8*	*56.6 – 251*	**-**	**-**

[a] CS and non-CS refer to the cold surge (polluted) and non-cold surge periods at Bachok

[b] The WMO data is a compilation of all reported global measurements up to, and including, the year 2012. The range represents the smallest mean minus one standard deviation and the largest mean plus one standard deviation of all considered datasets. Data from the TTL was derived from various aircraft and balloon campaigns.

[c] CH_2ClCH_2Cl was only analysed for in 16 of the 28 samples collected at Bachok

[d] Note that the CH_2ClCH_2Cl MBL data actually date back to the early 2000s. No recent data was reported.

[e] CH_2ClCH_2Cl was only analysed for in selected samples from the Frankfurt-Bangkok flights and in no samples collected during the Bangkok-Kuala Lumpur flights. These statistics are therefore based on a reduced number of samples on the FRA-BKK route (24 out of 98).

[f] ΣCl_{VSLS}* is defined as the sum of Cl-VSLS excluding the contribution from CH_2ClCH_2Cl. Statistics derived from all samples (98 FRA-BKK; 81 BKK-KUL).

Figure 1

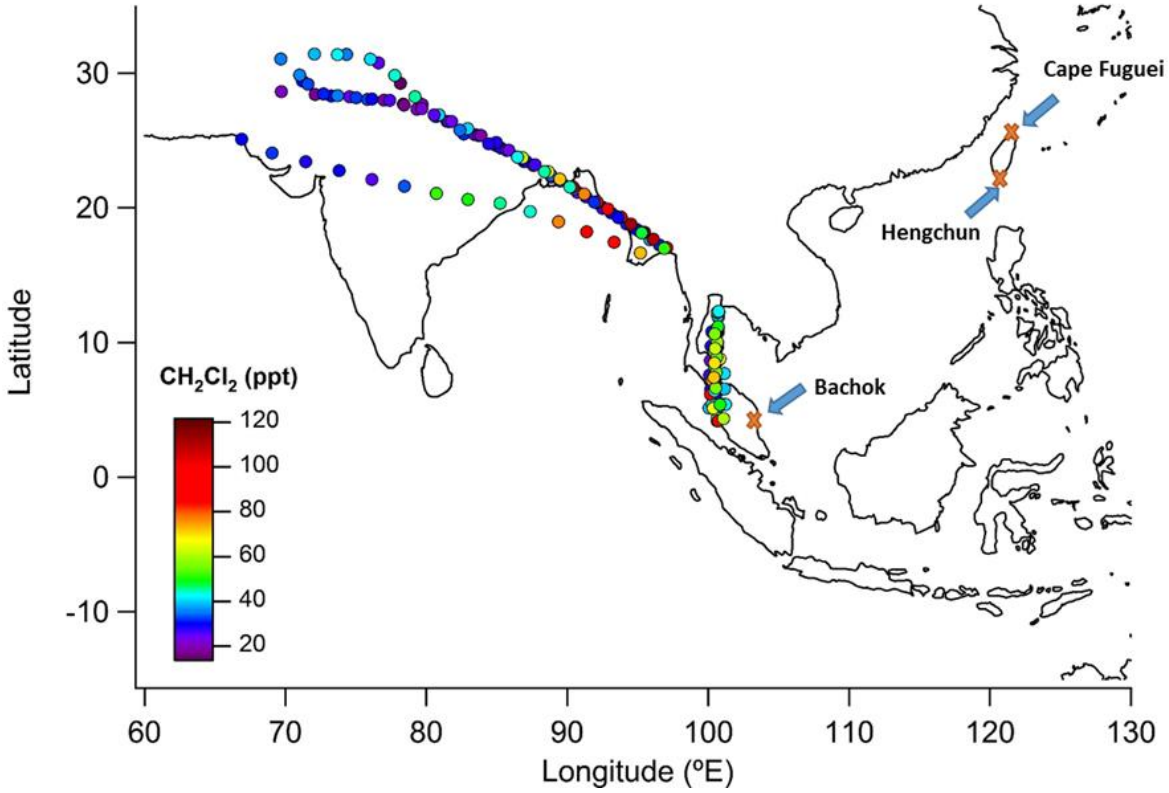
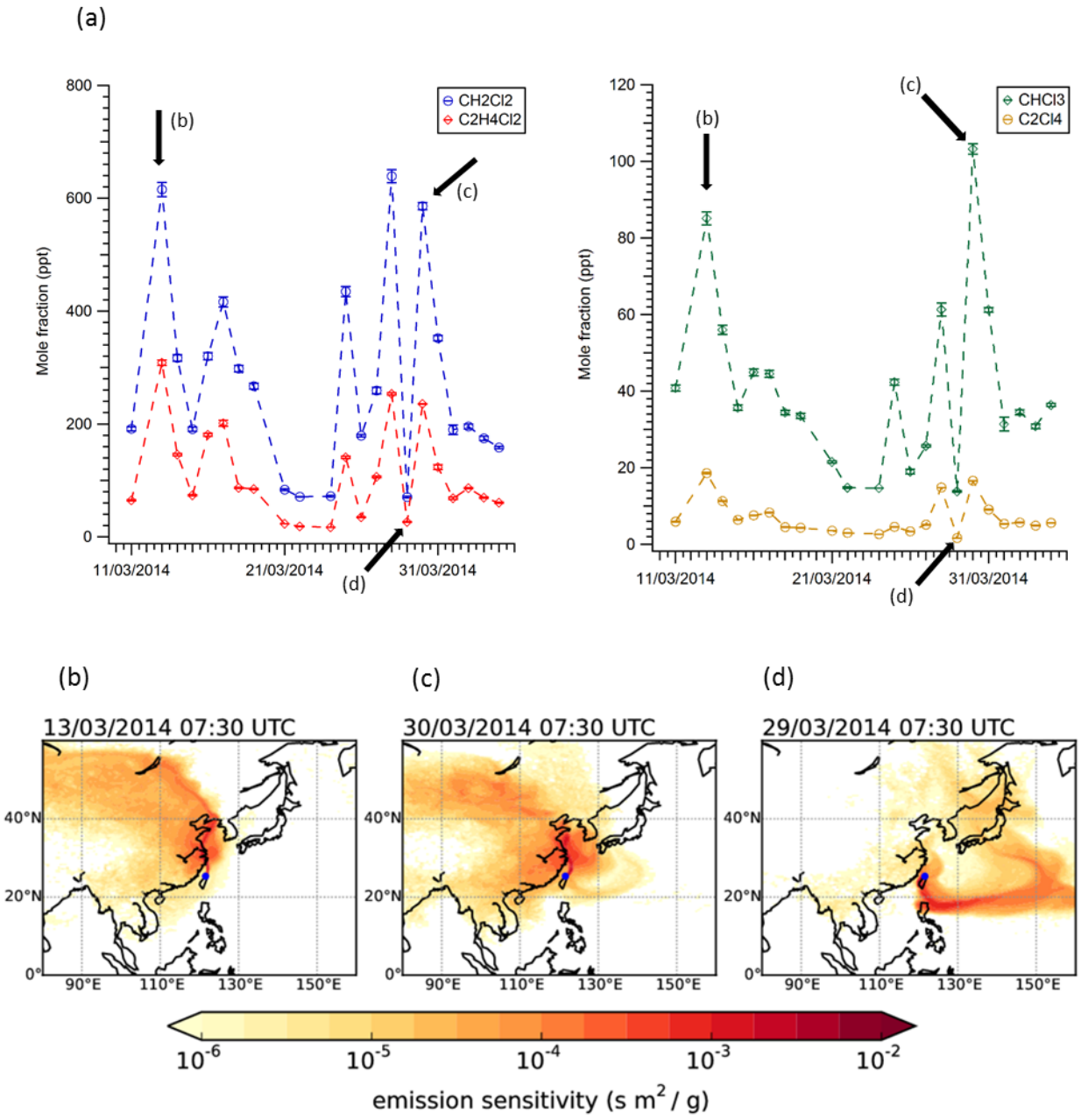
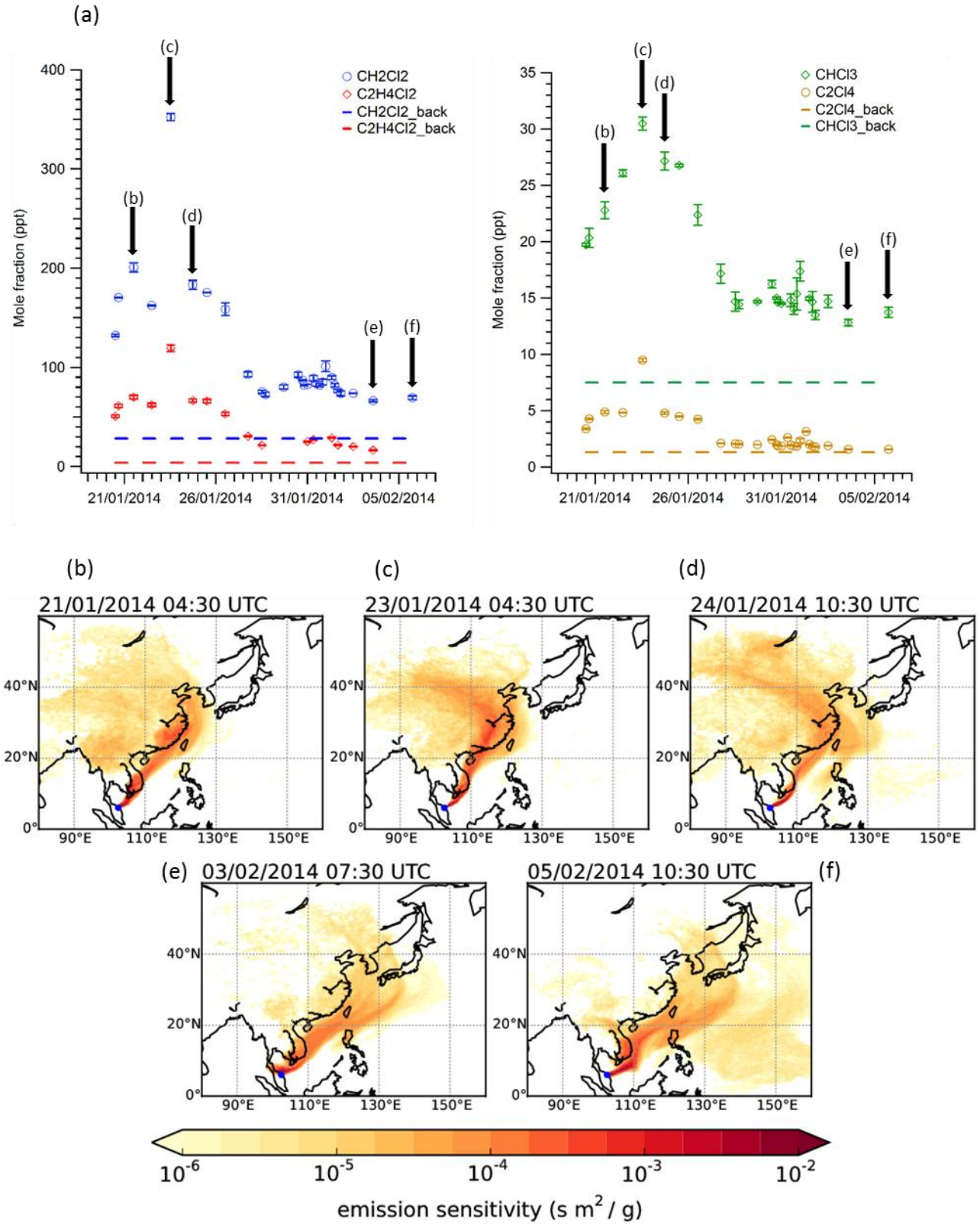

Cape Fuguei
Hengchun
Bachok
CH_2Cl_2 (ppt)
120
100
80
60
40
20
30
20
10
0
-10
Latitude
60
70
80
90
100
110
120
130
Longitude (ºE)

Figure 2


(a)
CH2Cl2
C2H4Cl2
Mole fraction (ppt)
(b)
(c)
(d)
11/03/2014
21/03/2014
31/03/2014
CHCl3
C2Cl4
(b)
13/03/2014 07:30 UTC
(c)
30/03/2014 07:30 UTC
(d)
29/03/2014 07:30 UTC
40°N
20°N
0°
90°E
110°E
130°E
150°E
10-6
10-5
10-4
10-3
10-2
emission sensitivity (s m2 / g)

718 **Figure 3**

719



720

721

722

723

Figure 4

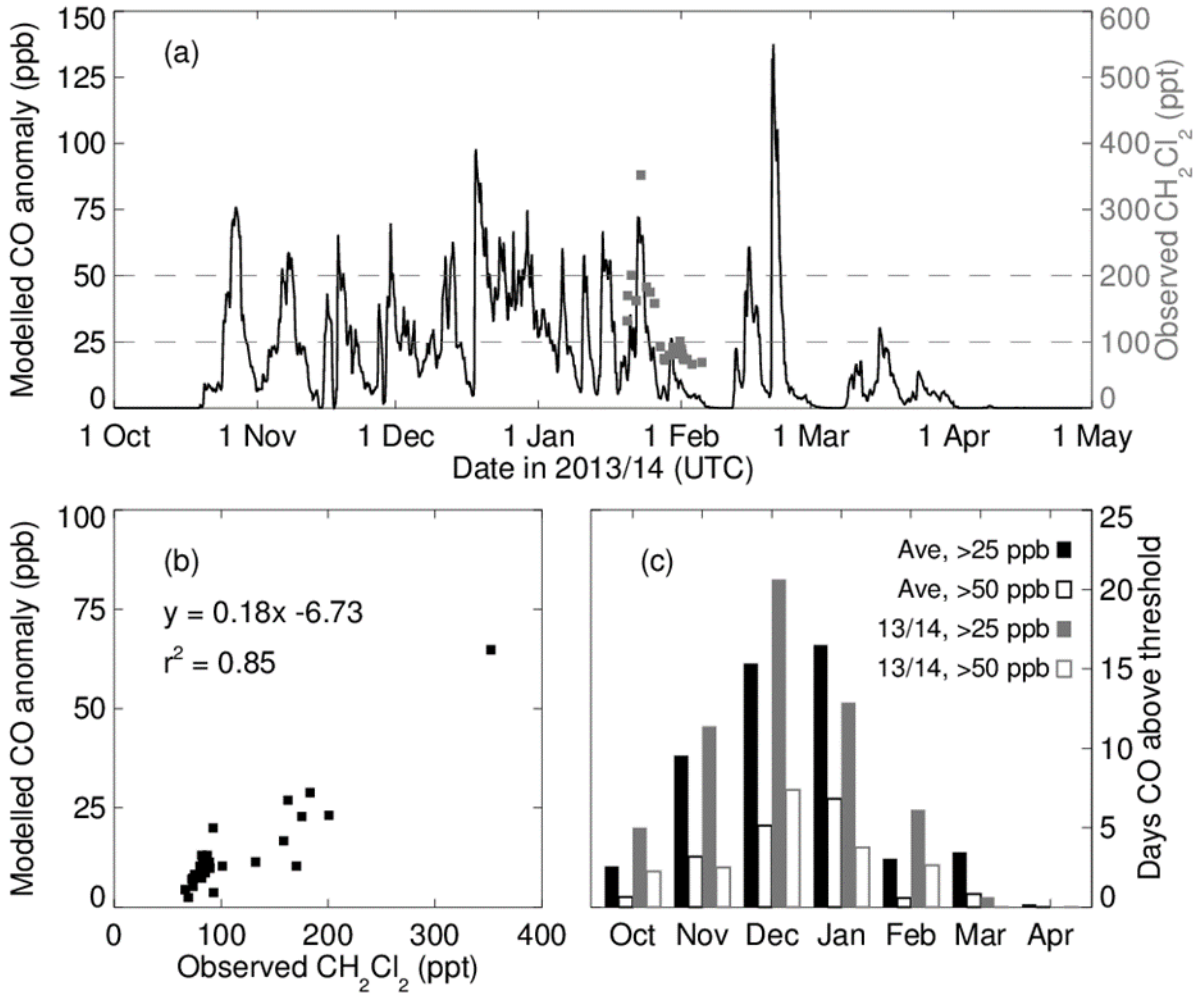
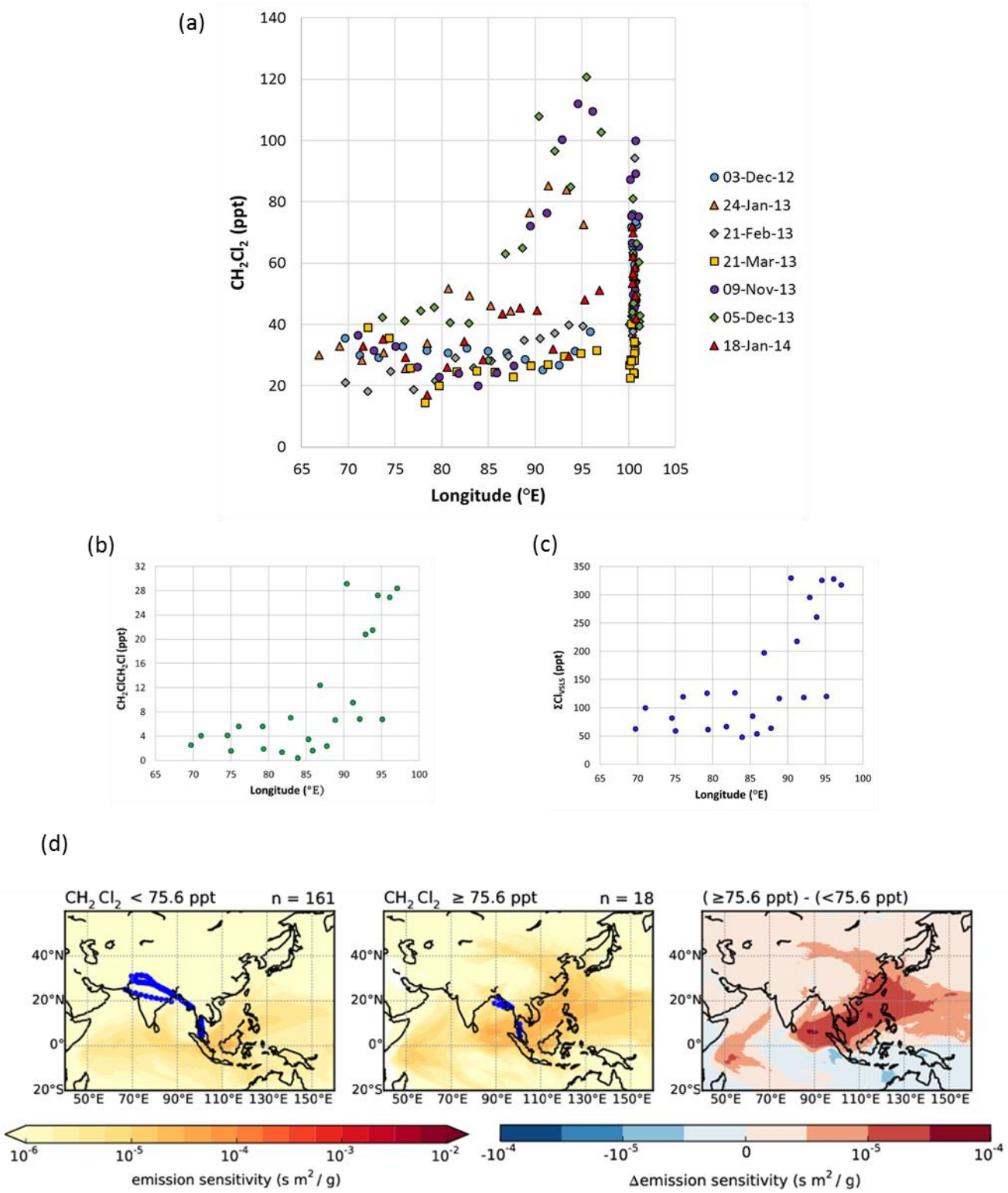

(a)
Modelled CO anomaly (ppb)
Observed CH_2Cl_2 (ppt)
1 Oct
1 Nov
1 Dec
1 Jan
1 Feb
1 Mar
1 Apr
1 May
Date in 2013/14 (UTC)
(b)
y = 0.18x -6.73
r^2 = 0.85
Modelled CO anomaly (ppb)
Observed CH_2Cl_2 (ppt)
(c)
Ave, >25 ppb
Ave, >50 ppb
13/14, >25 ppb
13/14, >50 ppb
Days CO above threshold
Oct
Nov
Dec
Jan
Feb
Mar
Apr

Figure 5


(a)
CH_2Cl_2 (ppt)
Longitude (°E)
03-Dec-12
24-Jan-13
21-Feb-13
21-Mar-13
09-Nov-13
05-Dec-13
18-Jan-14
(b)
CH_2ClCH_2Cl (ppt)
Longitude (°E)
(c)
ΣCl_{VSLS} (ppt)
Longitude (°E)
(d)
CH_2Cl_2 < 75.6 ppt n = 161
CH_2Cl_2 ≥ 75.6 ppt n = 18
(≥75.6 ppt) - (<75.6 ppt)
emission sensitivity (s m² / g)
Δemission sensitivity (s m² / g)