



1 **A growing threat to the ozone layer from short-lived anthropogenic** 2 **chlorocarbons**

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19 **Abstract**

20 Large and effective reductions in emissions of long-lived ozone-depleting substance (ODS)
21 are being achieved through the Montreal Protocol, the effectiveness of which can be seen in
22 the declining atmospheric abundances of many ODS. An important remaining uncertainty
23 concerns the role of very short lived substances (VSLS) which, owing to their relatively short
24 atmospheric lifetimes (less than 6 months), are not regulated under the Montreal Protocol.
25 Recent studies have found an unexplained increase in the global tropospheric abundance of
26 one VSLS, dichloromethane (CH_2Cl_2), which has increased by around 60% over the past
27 decade. Here we report dramatic enhancements of several chlorine-containing VSLS,
28 including CH_2Cl_2 and $\text{CH}_2\text{ClCH}_2\text{Cl}$ (1,2-dichloroethane), observed in surface and upper
29 tropospheric air in East and South East Asia. Surface observations were an order of
30 magnitude higher than previously reported in the marine boundary layer, whilst upper
31 tropospheric data were up to 3 times higher than expected. In addition we provide further
32 evidence of an atmospheric transport mechanism whereby substantial amounts of industrial
33 pollution from East Asia, including these chlorinated VSLS, can rapidly, and regularly, be
34 transported to tropical regions of the western Pacific and subsequently uplifted to the tropical
35 upper troposphere. This latter region is a major provider for air entering the stratosphere and
36 so this mechanism, in conjunction with increasing emissions of Cl-VSLS from East Asia, could
37 potentially slow the expected recovery of stratospheric ozone.

38 **1. Introduction**

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



46 CH₂Cl₂ is one of a large group of halogenated compounds known as VSLS (very short-lived
47 substances). Owing to their relatively short atmospheric lifetimes (typically less than 6 months)
48 and their correspondingly low Ozone Depletion Potentials (ODPs), VSLS are not currently
49 regulated by the Montreal Protocol. It is however estimated that a significant fraction of VSLS
50 and their atmospheric degradation products reach the stratosphere (>80% in the case of
51 chlorinated VSLS; Carpenter and Reimann et al., 2015) and, furthermore, halogenated VSLS
52 have been shown to have a disproportionately large impact on radiative forcing and climate
53 due to their atmospheric breakdown, and the subsequent depletion of ozone, occurring at
54 lower, climate sensitive altitudes (Hossaini et al., 2015b). According to the most recent
55 Scientific Assessment of Stratospheric Ozone Depletion (Carpenter and Reimann et al., 2015)
56 over the period 2008-2012 the total chlorine from VSLS increased at a rate of approximately
57 1.3 ± 0.2 ppt Cl yr⁻¹, the majority of this increase being due to CH₂Cl₂, and this has already
58 begun to offset the decline in total tropospheric chlorine loading over the same period ($13.4 \pm$
59 0.9 ppt Cl yr⁻¹) caused by the reduced emissions of substances controlled by the Montreal
60 Protocol.

61

62 In recent years much attention has been focussed on the potential of bromine-containing
63 VSLS to contribute to stratospheric ozone depletion (Law and Sturges, 2007; Montzka and
64 Reimann, 2011). This is primarily due to the large observed discrepancy between the
65 measured inorganic bromine in the stratosphere and the amount of bromine available from
66 known, longer lived source gases, namely the halons and methyl bromide (Dorf et al., 2006).
67 In contrast, the role of very short-lived chlorine compounds (Cl-VSLS) in ozone depletion has
68 been considered relatively minor because they are believed to contribute only a few percent
69 to the total chlorine input to the stratosphere, the majority of which is supplied by long-lived
70 compounds such as the chlorofluorocarbons (CFCs), methyl chloroform (CH₃CCl₃) and carbon
71 tetrachloride (CCl₄). Since 1987 the consumption of these long-lived anthropogenic
72 compounds has been controlled by the Montreal Protocol and the sum of total organic chlorine
73 in the troposphere has been falling since its peak of around 3660 parts per trillion (ppt) in
74 1993/94 to ~3300 ppt in 2012 (Carpenter and Reimann et al., 2015). Because of its relatively
75 short atmospheric lifetime (~5 years) and its high chlorine content (3 chlorine atoms per
76 molecule), the main contributor to this decline has been CH₃CCl₃. However, most CH₃CCl₃
77 has now been removed from the atmosphere with a present day abundance of less than 5 ppt.
78 Consequently the rate of decline in total organic chlorine has fallen to 13.4 ppt/year (2008-
79 2012), which is around 50% smaller than the maximum seen in the late 1990s (Carpenter and
80 Reimann et al., 2015).

81

82 Owing to their short atmospheric lifetimes and their hitherto low background concentrations,
83 chlorinated VSLS have not been considered of major importance for ozone depletion. Indeed
84 the contribution of VSLS to the total chlorine entering the stratosphere is estimated to be only
85 55 (38–95) ppt (Carpenter and Reimann et al., 2015), which is between 1% and 3% of the
86 present day (2012) total (3300 ppt). However, because of their short lifetimes, the potential
87 impact of VSLS on stratospheric ozone is highly dependent on the location of their sources,
88 with emissions close to the major stratospheric input regions being of far greater significance
89 for ozone depletion.

90

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



94 the region of the atmosphere between the level of maximum convective outflow (~12 km
95 altitude, 345K potential temperature) and the cold-point tropopause (~17 km, 380K). The
96 vertical flux into the TTL is thought to be dominated by two main regional pathways, (1) ascent
97 above the western Pacific during Northern Hemispheric (NH) winter and (2) the circulation of
98 the Asian (Indian) Monsoon during NH summer (Fueglistaler et al., 2009). The latter has been
99 suggested as the most important region for transport of anthropogenic pollution (Randel et al.,
100 2010).

101

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

113

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

131

132 Here we provide strong evidence to support this proposed transport mechanism based on new
133 atmospheric observations in the East and SE Asia region. We will present new Cl-VSLs
134 measurements from recent ground-based and aircraft campaigns in the region during which
135 we have observed dramatic enhancements in a number of Cl-VSLs, including CH₂Cl₂, 1,2-
136 dichloroethane (CH₂ClCH₂Cl), trichloromethane (CHCl₃) and tetrachloroethene (C₂Cl₄).
137 Furthermore we will demonstrate how pollution from China and the surrounding region can
138 rapidly, and regularly, be transported across the South China Sea and subsequently uplifted
139 to altitudes of 11-12 km, the region close to the lower TTL. Using the NAME particle dispersion
140 model we will also investigate the origin of the observed Cl-VSLs and examine the frequency
141 and duration of cold surge events. Finally we present some new estimates of CH₂Cl₂



142 emissions from East Asia and use these to estimate the likely emissions of $\text{CH}_2\text{ClCH}_2\text{Cl}$, for
143 which there is little information in the recent literature.

144

145 **2. Methods**

146

147 Between 2012 and 2014, air samples were collected at various times at (1) two coastal sites
148 in Taiwan, Hengchun (22.0547°N, 120.6995°E) and Fuguei Cape (25.297°N, 121.538°E); (2)
149 the Bachok Marine Research Station on the Northeast coast of Peninsular Malaysia (6.009°N,
150 102.425°E); and (3) during several flights of the CARIBIC aircraft between Germany and
151 Thailand/Malaysia (<http://www.caribic-atmospheric.com/>).

152

153 **2.1 Sample collection**

154 Air samples from Taiwan and Malaysia were collected in 3.2 litre silco-treated stainless steel
155 canisters (Restek) at a pressure of approximately 2 bar using a battery-powered diaphragm
156 pump (Air Dimensions, B series). In Taiwan the samples were collected from the surface via
157 a 1 m x 1/4" OD Dekabon sampling line, whilst in Bachok the samples were collected from the
158 top of an 18 m tower via a 5 m x 1/4" OD Dekabon sampling line. In both cases the tubing was
159 flushed for at least 5 minutes prior to sampling. The sampling integrity was confirmed by
160 sampling high purity air (BTCA-178, BOC) through the inlet tubing and pump. Samples were
161 collected within 50 m of the sea and only when the prevailing winds were from the sea,
162 minimising the impact of any local emissions. The CARIBIC aircraft samples were collected in
163 2.7 litre glass flasks at a pressure of 4.5 bar using a two-stage metal bellows pumping system
164 (Brennkmeijer et al., 2007; Baker et al., 2010) during flights between (i) Frankfurt (Germany)
165 and Bangkok (Thailand), and (ii) Bangkok and Kuala Lumpur (Malaysia). Samples were
166 generally collected at altitudes between 10 and 12 km.

167

168 **2.2 Sample analysis**

169 The collected air samples were shipped to UEA and analysed for their halocarbon content by
170 gas chromatography – mass spectrometry (GC-MS) following trace gas enrichment using
171 previously published methods. All samples (i.e. Taiwan, Bachok and CARIBIC) were analysed
172 for CH_2Cl_2 , CHCl_3 and C_2Cl_4 using an Entech-Agilent GC-MS system operating in electron
173 ionisation (EI) mode, as described in Leedham-Elvidge et al., (2015). 1 litre samples were
174 dried and pre-concentrated before injection onto a 30 m x 0.32 mm GS Gas Pro capillary
175 column (Agilent), temperature ramped from -10°C to 200°C. Samples were interspersed with
176 repeated analyses of a working standard (SX-706070), a high pressure air sample contained
177 in a 34 litre electropolished stainless steel cylinder (Essex Industries) provided by the Earth
178 System Research Laboratory of the National Oceanic and Atmospheric Administration
179 (NOAA-ESRL, Boulder, CO, USA). CH_2Cl_2 , CHCl_3 and C_2Cl_4 were quantified on ions with a
180 mass-to-charge ratio of 84 ($\text{CH}_2^{35}\text{Cl}_2^+$), 83 ($\text{CH}^{35}\text{Cl}_2^+$ and $166 (\text{C}_2^{35}\text{Cl}_3^{37}\text{Cl}^+)$ respectively. Mean
181 analytical precisions were $\pm 2\%$ for CH_2Cl_2 and C_2Cl_4 , and $\pm 3\%$ for CHCl_3 . Instrument blanks,
182 determined by analysing 1 litre aliquots of high purity nitrogen (BOC, Research grade), were
183 always below the detection limit of the instrument.

184

185 Some of the ground-based samples and a subset of the CARIBIC samples were also analysed
186 for a range of halocarbons, including the newly-identified $\text{CH}_2\text{ClCH}_2\text{Cl}$, using a pre-
187 concentration/GC system coupled to a Waters AutoSpec magnetic sector MS instrument, also
188 operating in EI mode, but run at a mass resolution of 1000 at 5 % peak height. Samples (using
189 between 200 and 250 ml of air) were analysed on an identical GS GasPro column following a



190 previously described method (Laube et al., 2010; Laube et al., 2012; Leedham-Elvidge et al.,
191 2015). $\text{CH}_2\text{ClCH}_2\text{Cl}$ was monitored on the ions with mass-to-charge ratios of 61.99 ($\text{C}_2\text{H}_3^{35}\text{Cl}^+$,
192 qualifier) and 63.99 ($\text{C}_2\text{H}_3^{37}\text{Cl}^+$, quantifier). Mean analytical precision was 1.4 % for
193 $\text{CH}_2\text{ClCH}_2\text{Cl}$ and the average blank signal was 0.07 ppt (as quantified using regular
194 measurements of research-grade helium) and was corrected for on a daily basis.

195

196 **2.3 Calibration and quality assurance**

197 CH_2Cl_2 , CHCl_3 and C_2Cl_4 data are reported on the latest (2003) calibration scales provided by
198 NOAA-ESRL. As was shown in Leedham-Elvidge et al., (2015) our CH_2Cl_2 measurements
199 compare very well with those of NOAA-ESRL at our mutual long-term sampling site at Cape
200 Grim, Tasmania over more than 6 years. As a recognised international calibration scale for
201 $\text{CH}_2\text{ClCH}_2\text{Cl}$ is not yet available this compound was calibrated at UEA using the established
202 static dilution technique recently described (Laube et al., 2012). $\text{CH}_2\text{ClCH}_2\text{Cl}$ was obtained
203 from Sigma Aldrich with a stated purity of 99.8 %. Three dilutions were prepared at 7.1, 11.9
204 and 15.8 ppt. The mixing ratio assigned to our working standard from these dilutions was 5.67
205 ppt with a 1 σ standard deviation of 1.8 %. CFC-11 was added to the dilutions as an internal
206 reference compound and the CFC-11 mixing ratios assigned to the working standard through
207 these dilutions agreed with the value assigned by NOAA-ESRL within 4.3 %. This is well within
208 the estimated uncertainty of the calibration system of 7 % (Laube et al., 2012). In addition the
209 mixing ratios of $\text{CH}_2\text{ClCH}_2\text{Cl}$ in the working standard were compared with those in three other
210 high-pressure canisters (internal surface was either electropolished stainless steel or
211 passivated aluminium) over the whole measurement period. The ratios between standards did
212 not change within the 2 σ standard deviation of the measurements for any of the canisters
213 analysed indicating very good long-term stability for $\text{CH}_2\text{ClCH}_2\text{Cl}$. This was also the case for
214 CHCl_3 and C_2Cl_4 . As noted in Leedham-Elvidge et al., (2015) mixing ratios of CH_2Cl_2 were
215 found to change over longer timescales in some of our standard canisters, but this drift has
216 been successfully quantified and corrected for as indicated by the very good comparability
217 with NOAA-ESRL measurements at the Cape Grim site noted above.

218

219 **3. Results**

220

221 Figure 1 shows the location of the three surface observation stations as well as the location of
222 the CARIBIC samples. The aircraft sampling points have been coloured by their CH_2Cl_2
223 concentration (see later discussion). Data from the surface stations and from the CARIBIC
224 aircraft flights are summarised in Table 1, together with a summary of published observations
225 as reported in the most recent Scientific Assessment of Stratospheric Ozone Depletion
226 (Carpenter and Reimann et al., 2015).

227

228 The highest concentrations of chlorinated VSLs were measured in samples collected in
229 Taiwan, suggesting that Taiwan is located relatively close to major emission regions. Figure 2
230 shows the 2014 data from Cape Fuguei. The Numerical Atmospheric-dispersion Modelling
231 Environment model (NAME, see supplementary material) can be used to infer the recent
232 transport history of this pollution. Our NAME analysis (Fig. 2 b-d) indicates that most of the
233 samples that contained high concentrations of Cl-VSLs had originated from regions to the
234 north of Taiwan, primarily the East Asian mainland. The median sum of chlorine from the 4
235 VSLs listed above ($\sum\text{Cl}_{\text{VSLs}}$) in 22 samples collected at Cape Fuguei in March/April 2014 was
236 756 ppt (range 232-2178 ppt). Similarly high concentrations and variation were seen in the 21
237 samples collected at Hengchun in March/April 2013 (see supplementary material). To put



238 these concentrations in a global context, the total organic chlorine derived from all known
239 source gases in the background troposphere (including CFCs, HCFCs, and longer-lived
240 chlorocarbons) is currently around 3300 ppt, with a typical Cl-VSLS contribution in the remote
241 marine boundary layer of approximately 3 % (Carpenter and Reimann et al., 2015). Of the
242 four VSLS measured, the two largest contributors to $\Sigma\text{Cl}_{\text{VSLS}}$ in Taiwan were CH_2Cl_2 (55-76 %) and
243 $\text{CH}_2\text{ClCH}_2\text{Cl}$ (14-30 %).

244
245 Figure 3 shows the Cl-VSLS data from 25 samples collected at Bachok, Malaysia during the
246 winter monsoon season in January/February 2014. During this phase of the monsoon the
247 prevailing winds are from the northeast and, as described earlier, are often impacted by
248 emissions further to the north, including from mainland China. As can be seen in Figure 3,
249 there was a 7 day period between 19 and 26 January when significantly enhanced
250 concentrations of Cl-VSLS were observed. During this period NAME back trajectories (Fig. 3
251 b-d) show air travelling from continental East Asia and across the South China Sea before
252 arriving at Bachok. These trajectories often pass over Taiwan and, in some instances, also
253 over parts of Indochina where additional emissions could have been picked up. As in the
254 Taiwan samples, CH_2Cl_2 is the largest contributor to $\Sigma\text{Cl}_{\text{VSLS}}$ (59-66 %), having a mean
255 concentration of 179.9 ± 71.9 ppt (range 94.0 – 354.9 ppt, 9 samples) during the 7-day period
256 of the pollution event. The mean concentration of $\text{CH}_2\text{ClCH}_2\text{Cl}$ was 64.4 ± 23.9 ppt (range
257 30.2 – 119.5 ppt), accounting for 19-23 % of $\Sigma\text{Cl}_{\text{VSLS}}$. These abundances are substantially
258 higher than those typically found in the marine boundary layer. For example, the range of
259 $\Sigma\text{Cl}_{\text{VSLS}}$ from the 4 compounds listed above in the tropical marine boundary layer reported in
260 WMO (2014) is 70-134 ppt. The range observed at Bachok over the entire sampling period
261 was 207-1078 ppt, with medians of 546 ppt and 243 ppt during the polluted (20-26 Jan) and
262 less-polluted (27 Jan – 6 Feb) periods respectively (see Table 1). It is interesting to note that
263 even in the period after the cold surge event (Fig.3 e,f), the levels of Cl-VSLS are still
264 significantly higher than would be expected, suggesting that this region of the South China
265 Sea is widely impacted by emissions from E Asia.

266
267 The pollution or “cold surge” event observed at Bachok lasted for 6-7 days and the back
268 trajectories shown in Figure 3 are typical of those arriving at Bachok during the winter
269 monsoon period (see NAME animations in supplement). To further investigate the frequency
270 and typical duration of these events a NAME trajectory analysis using carbon monoxide (CO)
271 as a tracer of industrial emissions from regions north of 20°N was conducted for the entire
272 winter season (see supplementary information for details). Figure 4(a) shows a time series of
273 this industrial CO tracer for winter 2013/2014 and suggests that the observed event in January,
274 during which there was a strong correlation between the industrial CO tracer and CH_2Cl_2 (Fig.
275 4b), is likely to be repeated regularly throughout the winter. An analysis of a further 5 winters
276 (Fig. 4c) demonstrates that 2013/14 was not unusual and that the events depicted in Figure
277 3a occur repeatedly every year (see supplement for further details).

278
279 The Bachok measurements clearly demonstrate the rapid long-range transport of highly
280 elevated concentrations of Cl-VSLS for several thousand kilometres across the South China
281 Sea, as predicted by Ashfold et al., (2015). However, to have an impact on stratospheric ozone
282 it is necessary to demonstrate that these high concentrations of Cl-VSLS can be rapidly lifted
283 to the upper tropical troposphere (lower TTL) or above. Such evidence can be found in
284 samples from several recent CARIBIC aircraft flights in the Southeast Asia region. Figure 1
285 shows significant enhancements of CH_2Cl_2 during flights over northern India and the Bay of



286 Bengal, and also between Bangkok and Kuala Lumpur. The same data is plotted against
287 longitude in Figure 5(a) which shows that elevated concentrations were observed in all
288 CARIBIC flights in the region (7) during the periods Dec 2012 - Mar 2013 and Nov 2013 - Jan
289 2014. The samples were collected in the altitude range 10-12 km, showing that recent
290 industrial emissions can regularly reach the lower boundary of the TTL. Although $\text{CH}_2\text{ClCH}_2\text{Cl}$
291 was only analysed for in a selection of samples during the flights from Germany to Bangkok,
292 elevated mixing ratios coinciding with the high levels of CH_2Cl_2 were clearly observed (Fig.
293 5b). CHCl_3 and C_2Cl_4 were also enhanced during these flights (Table 1), with $\Sigma\text{Cl}_{\text{VSLs}}$ being in
294 the range 48-330 ppt (Fig. 5c). This is up to 3.2 times higher than that previously found in the
295 lower TTL (36-103 ppt; Carpenter and Reimann et al., 2015). The highest abundances of Cl-
296 VSLs were seen in samples collected over the Bay of Bengal, and on flights between Bangkok
297 and Kuala Lumpur (Fig. 5a). NAME back trajectories (Fig. 5d) indicate that in these cases the
298 sampled air had almost always been transported from the east, and had often been impacted
299 by emissions from East Asia, with possible contributions from other countries including the
300 Philippines, Malaysia and Indochina.

301

302 **4. Discussion**

303

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

317

318 Whilst the strong enhancements of CH_2Cl_2 are not entirely unexpected, the presence of high
319 concentrations of $\text{CH}_2\text{ClCH}_2\text{Cl}$ most certainly are. There are very few previously reported
320 measurements of $\text{CH}_2\text{ClCH}_2\text{Cl}$, particularly in recent years. Elevated levels have been
321 observed in urban environments close to known emission sources (Singh et al., 1981) and,
322 more recently, Xue et al., (2011) reported elevated levels (91 ± 79 ppt) in air samples collected
323 in the boundary layer over north-eastern China in 2007. The few reported measurements of
324 $\text{CH}_2\text{ClCH}_2\text{Cl}$ in the remote marine boundary layer are typically in the low ppt range (see Table
325 1) but these were made well over a decade ago. No long-term atmospheric measurements of
326 $\text{CH}_2\text{ClCH}_2\text{Cl}$ have been reported, and $\text{CH}_2\text{ClCH}_2\text{Cl}$ is not reported by the main surface
327 monitoring networks (AGAGE and NOAA), so current background concentrations and longer
328 term trends are unknown. $\text{CH}_2\text{ClCH}_2\text{Cl}$ is exclusively anthropogenic in origin, its primary use
329 being in the manufacture of vinyl chloride, the precursor to polyvinyl chloride (PVC), and a
330 number of chlorinated solvents. $\text{CH}_2\text{ClCH}_2\text{Cl}$ also finds use as a solvent, dispersant and has
331 historically been added to leaded petrol as a lead scavenger (EPA, 1984). In common with
332 CH_2Cl_2 it has also used as a cleaning/degreasing agent and as a fumigant. China is the world's
333 largest producer of PVC accounting for 27% of global production in 2009 (DCE, 2017).



334 Production has increased rapidly in recent years (14% per year over the period 2000-2009),
335 which could potentially have led to increased atmospheric emissions of $\text{CH}_2\text{CICH}_2\text{Cl}$.

336

337 Based on an analysis of chlorocarbon production, sales and import/export figures, we have
338 estimated annual CH_2Cl_2 emissions from China to be of the order of 440-615 kilotonnes (kt)
339 yr^{-1} (see supplementary material for methods). A simple correlation of CH_2Cl_2 and $\text{CH}_2\text{CICH}_2\text{Cl}$
340 mixing ratios from the 2014 Bachok data ($R^2 = 0.9799$) would then imply Chinese $\text{CH}_2\text{CICH}_2\text{Cl}$
341 emissions of 163-227 kt yr^{-1} . If true, the scale of these emissions is a major surprise as
342 $\text{CH}_2\text{CICH}_2\text{Cl}$ is highly toxic and believed to be used almost exclusively in non-emissive
343 applications.

344

345 The other CI-VSLS presented here are C_2Cl_4 and CHCl_3 . In contrast to $\text{CH}_2\text{CICH}_2\text{Cl}$, long-term
346 atmospheric data records are available for these compounds, although there are few data
347 from the SE Asia region. Current trends show that C_2Cl_4 is declining in the background
348 troposphere ($\sim 6\% \text{ yr}^{-1}$), whilst CHCl_3 is approximately constant (Carpenter and Reimann et
349 al., 2015). However, both compounds were elevated in the samples containing high
350 concentrations of CH_2Cl_2 and $\text{CH}_2\text{CICH}_2\text{Cl}$, suggesting that significant, co-located sources
351 remain. Like $\text{CH}_2\text{CICH}_2\text{Cl}$, C_2Cl_4 is exclusively anthropogenic in origin, used primarily as a
352 solvent in the dry cleaning industry, as a metal degreasing agent and as a chemical
353 intermediate, for example in the manufacture of the hydrofluorocarbons HFC-134a and HFC-
354 125. CHCl_3 is believed to be largely natural in origin (seawater, soils, macroalgae), but
355 potential anthropogenic sources include the pulp and paper industry, water treatment facilities
356 and HFC production (McCulloch, 2003; Worton et al., 2006; Montzka et al., 2011).

357

358 When calculating the VSLS contribution to stratospheric chlorine, it is usual to assume an
359 average concentration in the region of the TTL known as the level of zero radiative heating
360 (LZRH). The LZRH is located at the transition between clear-sky radiative cooling and clear-
361 sky radiative heating. This occurs at an approximate altitude of 15 km and it is believed that
362 air masses above this level will go on to enter the stratosphere¹. As noted above there are
363 very few measurements in this region and, furthermore, many of the available measurements
364 were made over a decade ago and assumptions based on surface temporal trends have to be
365 made in order to estimate present day values (Carpenter and Reimann et al., 2015; Hossaini
366 et al., 2015). Another key deficiency in this estimation of VSLS concentrations entering the
367 stratosphere is that most of the reported measurements have not been made in the 2 key
368 regions where the strongest troposphere to stratosphere transport occurs. Although we have
369 no data from the region of the LZRH, the CARIBIC data over northern India and SE Asia
370 suggests that the contribution of VSLS to stratospheric chlorine loading may be significantly
371 higher than is currently estimated (50-95 ppt, Carpenter and Reimann et al., 2015). It is also
372 interesting to note that the much-discussed contribution of VSLS-Br compounds to
373 stratospheric bromine is approximately 5 ppt, which is equivalent to 300 ppt of chlorine (1 ppt
374 of bromine is roughly equivalent to 60 ppt chlorine, Sinnhuber et al., 2009). The CARIBIC
375 measurements suggest that CI-VSLS could currently, on occasion, contribute a similar
376 amount.

377

378 These new measurements of CI-VSLS in Taiwan, Malaysia and from an aircraft flying above
379 South-East Asia show that there are substantial regional emissions of these compounds; that
380 these emissions can be rapidly transported long distances into the deep tropics; and that an
381 equally rapid vertical transport to the upper tropical troposphere is a regular occurrence.



382 Although the focus of this paper is short-lived chlorinated gases, there are many other
383 chemical pollutants contained in these air masses which will have a large impact on regional
384 air quality, etc.

385
386 Unlike the bromine-containing VSLS which are largely natural in origin, the Cl-VSLS reported
387 here are mainly anthropogenic and consequently it would be possible to control their
388 production and/or release to the atmosphere. Of particular concern are the rapidly growing
389 emissions of CH_2Cl_2 , and potentially $\text{CH}_2\text{ClCH}_2\text{Cl}$, especially when considering the
390 geographical location of these emissions, close to the major uplift regions of the western
391 Pacific (winter) and the Indian sub-continent (summer). Without a change in industrial
392 practices the contribution of Cl-VSLS to stratospheric chlorine loading is likely to increase
393 substantially in the coming years, thereby endangering some of the hard-won gains achieved,
394 and anticipated, under the Montreal Protocol.

395

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- 521



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523

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540

541 **Table 1:** Summary of VSLS-Cl data from the 3 surface stations and the 7 CARIBIC flights. For
542 comparison, the ranges reported in the most recent WMO Ozone Assessment (Carpenter and
543 Reimann et al., 2015) for the marine boundary layer (MBL) and lower Tropical Tropopause
544 Layer (TTL, 12-14 km altitude) are also shown.

545

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

550

551 **Figure 2:**

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

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

560 The location of Cape Fuguei is indicated with a blue circle (see also Figure 4)

561

562 **Figure 3:**

563 *Upper panel (a):* Mole fractions (ppt) of the 4 chlorinated VSLS in air samples collected at
564 Bachok in Jan/Feb 2014. Strongly enhanced levels of all 4 compounds were seen for a 7-
565 day period at the beginning of the campaign (20-26 Jan). Also shown (dashed line) are the
566 reported median background concentrations in the remote marine boundary layer in 2012¹.

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

574 The location of Bachok is indicated with a blue circle (see also Figure 4)

575 **Figure 4:**

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

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

581 (c) Average number of days each month, averaged over six consecutive winters (2009/10 –
582 2014/15) where the modelled carbon monoxide anomaly at Bachok is above a particular
583 threshold (25 ppb and 50 ppb which, from the regression in 3b, correspond to 176 ppt and



584 315 ppt of CH_2Cl_2). The 2013/14 winter is shown separately for comparison with the 6-year
585 average.

586 **Figure 5**

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

590 (b) Mole fraction (ppt) of $\text{CH}_2\text{ClCH}_2\text{Cl}$ in selected CARIBIC samples (note: $\text{CH}_2\text{ClCH}_2\text{Cl}$ was
591 not monitored in the samples collected between Bangkok to Kuala Lumpur, and only in a
592 selection of samples on the Frankfurt-Bangkok route).

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

595 (d) NAME footprint maps indicating the likely origin of the air sampled by the CARIBIC
596 aircraft. NAME footprints at this altitude, and particularly in regions of strong sub-grid-scale
597 convection not captured fully in the gridded meteorological input data, may be less reliable
598 than those at the surface sites. This makes pinpointing particular emission regions more
599 difficult. The central panel therefore shows a composite footprint derived from the samples
600 that contained the highest levels of CH_2Cl_2 (90th percentile, $[\text{CH}_2\text{Cl}_2] > 75.6$ ppt), with the
601 composite footprint from the remaining samples ($[\text{CH}_2\text{Cl}_2] < 75.6$ ppt) shown in the left hand
602 panel. To emphasise the likely source regions the right hand panel shows the difference
603 between the middle and left hand panels. The geographical location of each sample
604 included in the composite analysis are shown in blue circles.

605 **Table 1**

606

	Taiwan 2013		Taiwan 2014		Bachok 2014			MBL (WMO 2014) ^(b)	
	Median	Range	Median	Range	Median (CS) ^(a)	Median (non-CS)	Range	Median	Range
CH ₂ Cl ₂	226.6	68 - 624	227.4	70 - 639	170.4	81.9	64.8 - 355	28.4	21.8 - 34.4
CH ₂ ClCH ₂ Cl	-	-	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 ₂ Cl 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
Σ Cl _{VSLs}	-	-	755.8	232 - 2178	546.0	243.1	207 - 1078 ^(c)	93.4	70 - 134

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	CARIBIC (FFT-BKK, 65-97°E)			CARIBIC (BKK-KUL, 100-105°E)			Lower TTL (WMO 2014) ^(b)	
	10-12 km			10-12 km			12-14 km	
	Mean	Median	Range	Mean	Median	Range	Mean	Range
CH ₂ Cl ₂	43.2	31.6	14.6 - 121	50.4	46.5	22.5 - 100	17.1	7.8 - 38.1
CH ₂ ClCH ₂ Cl ^(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 ₂ Cl ₄	0.87	0.65	0.1 - 4.4	1.6	1.5	0.2 - 5.9	1.1	0.7 - 1.3
Σ Cl _{VSLs} ^(e)	153.7	119.3	48.4 - 330	-	-	-	67	36 - 103
Σ Cl _{VSLs} * ^(f)	-	-	-	134.8	127.8	56.6 - 251	-	-

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610

611 ^(a) CS and non-CS refer to the cold surge (polluted) and non-cold surge periods at Bachok612 ^(b) The WMO data is a compilation of all reported global measurements up to, and including, the year 2012. The
613 range represents the smallest mean minus one standard deviation and the largest mean plus one standard
614 deviation of all considered datasets.615 ^(c) CH₂ClCH₂Cl was only analysed for in 16 of the 28 samples collected at Bachok616 ^(d) Note that the CH₂ClCH₂Cl MBL data actually date back to the early 2000s. No recent data was reported.617 ^(e) CH₂ClCH₂Cl was only analysed for in selected samples from the Frankfurt-Bangkok flights and in no samples
618 collected during the Bangkok-Kuala Lumpur flights619 ^(f) Σ Cl_{VSLs}* is defined as the sum of VSLs-Cl excluding the contribution from CH₂ClCH₂Cl.

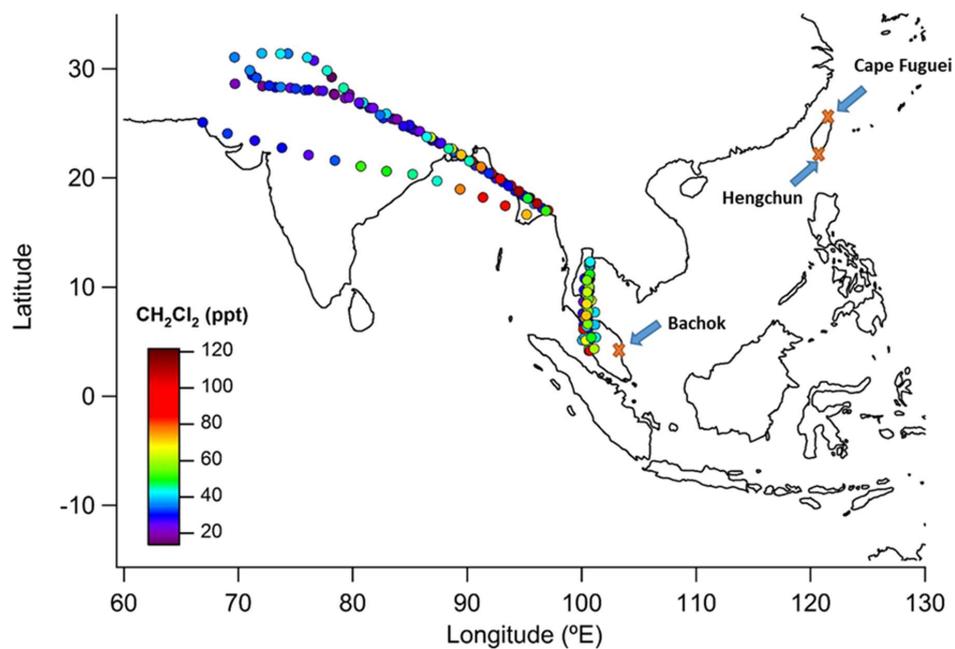
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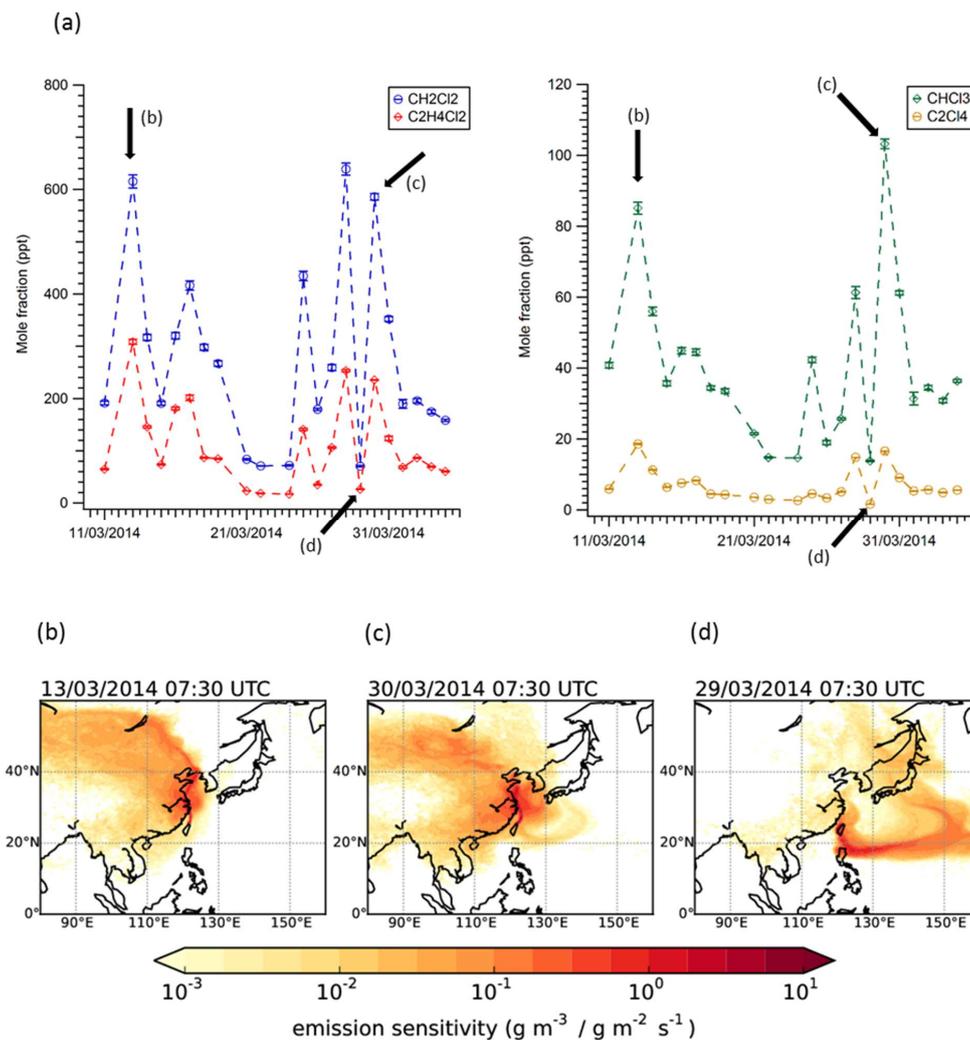
623 **Figure 1**
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634 **Figure 2**
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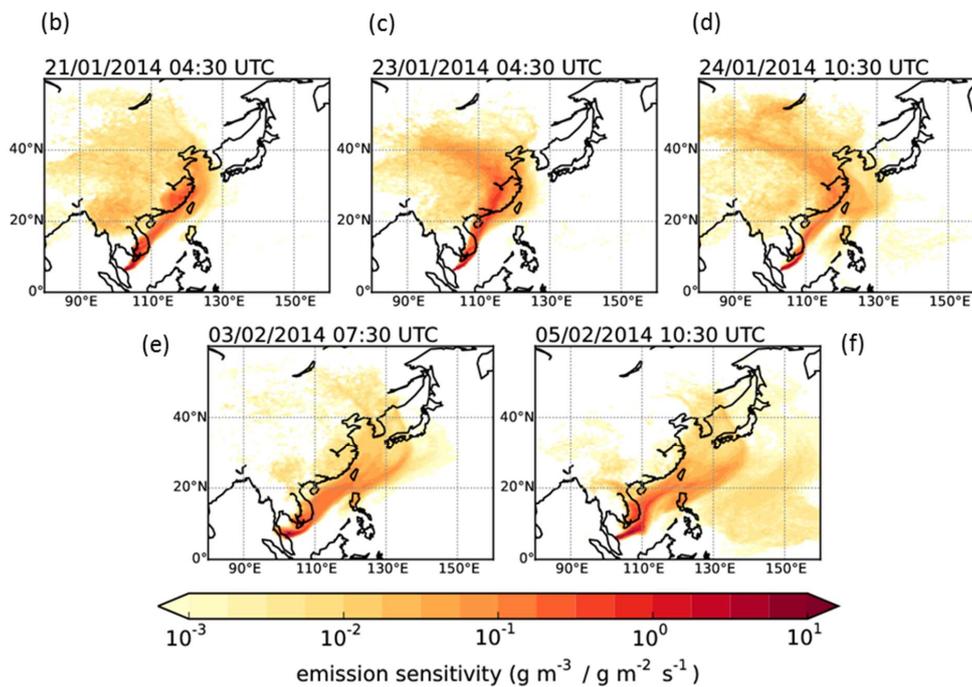
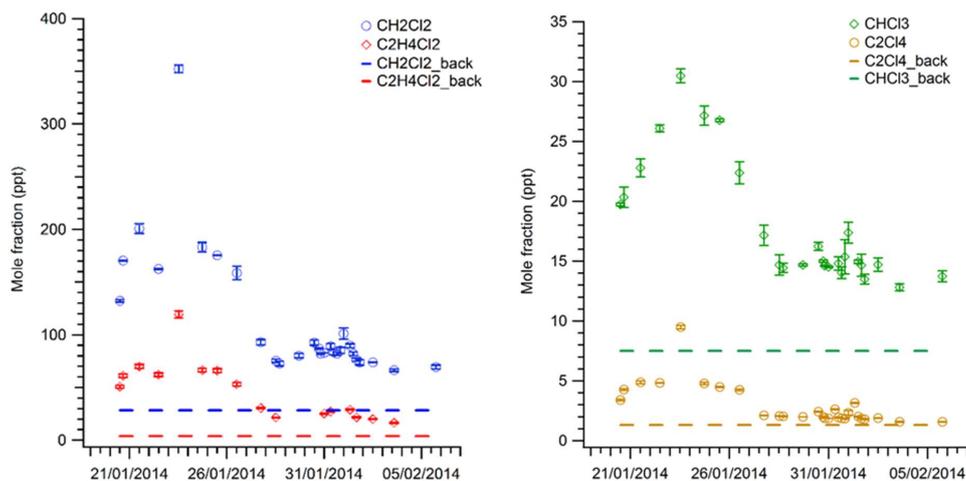


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643 **Figure 3**

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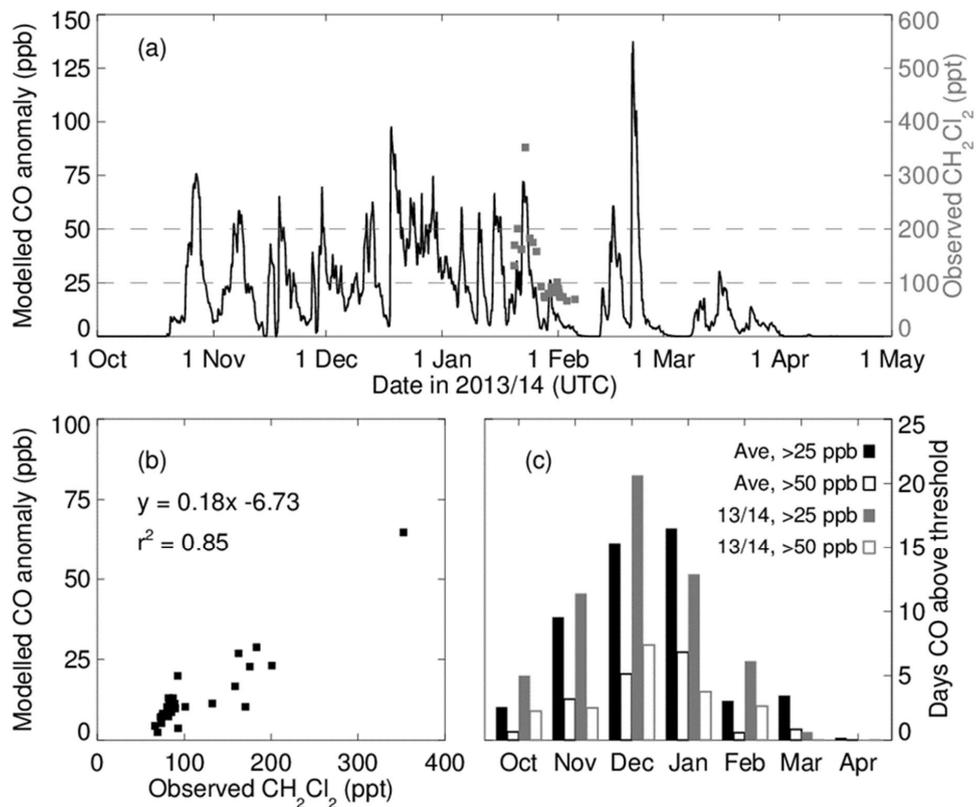


649 **Figure 4**

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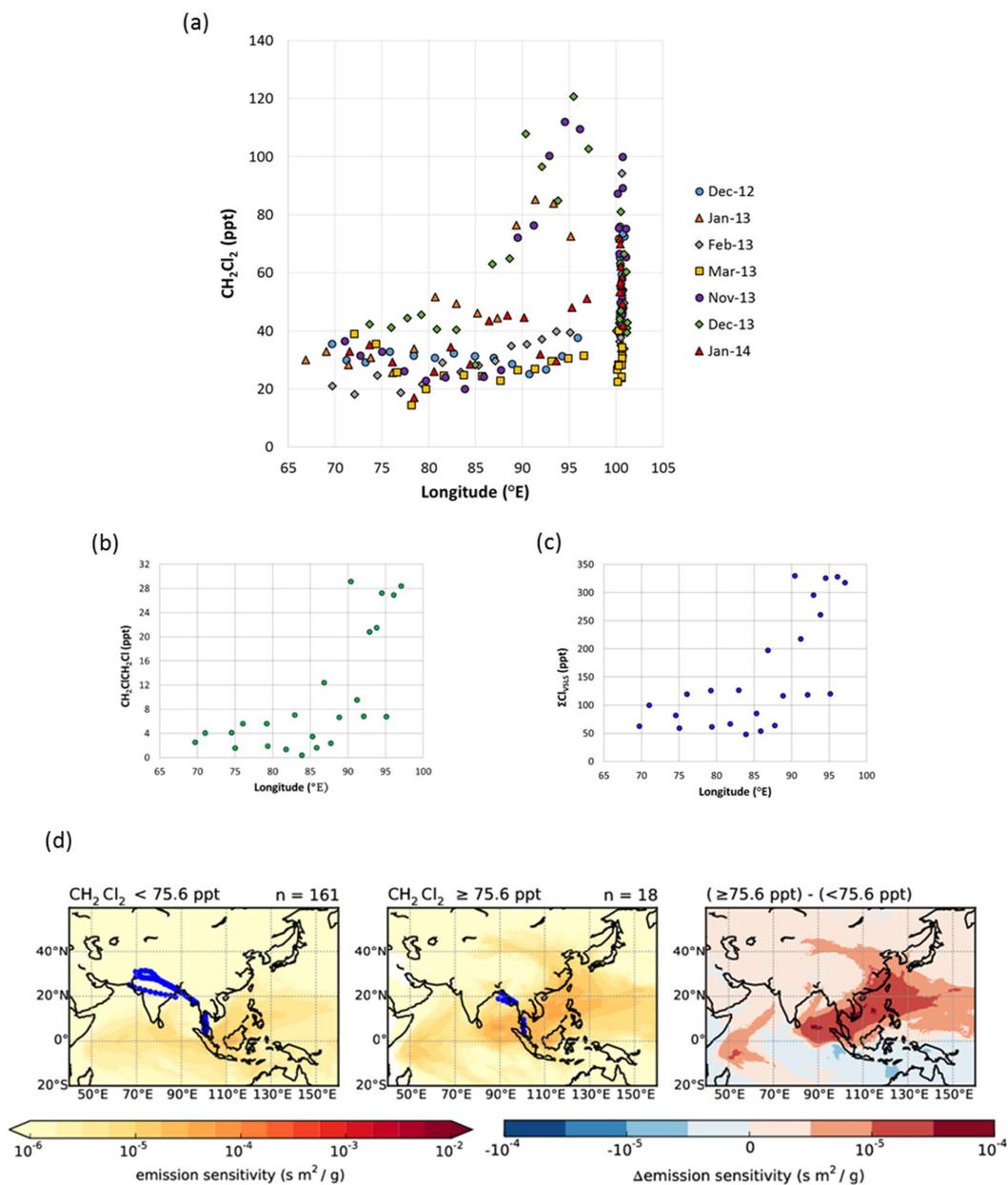
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658 **Figure 5**

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