

# 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 ( $\text{CH}_2\text{Cl}_2$ ), which has increased by around 60% over the past  
27 decade. Here we report dramatic enhancements of several chlorine-containing VSLS (Cl-  
28 VSLS), including  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_2\text{ClCH}_2\text{Cl}$  (1,2-dichloroethane), observed in surface and  
29 upper tropospheric air in East and South East Asia. Surface observations were, **on occasion**,  
30 an order of magnitude higher than previously reported in the marine boundary layer, whilst  
31 upper tropospheric data were up to 3 times higher than expected. In addition we provide  
32 further evidence of an atmospheric transport mechanism whereby substantial amounts of  
33 industrial pollution from East Asia, including these chlorinated VSLS, can rapidly, and  
34 regularly, be transported to tropical regions of the western Pacific and subsequently uplifted  
35 to the tropical upper troposphere. This latter region is a major provider for air entering the  
36 stratosphere and so this mechanism, in conjunction with increasing emissions of Cl-VSLS  
37 from East Asia, could 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 ( $\text{CH}_2\text{Cl}_2$ ), 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 CH<sub>2</sub>Cl<sub>2</sub> 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  $1.3 \pm 0.2$  ppt Cl yr<sup>-1</sup>, the majority of this increase being due to CH<sub>2</sub>Cl<sub>2</sub>, 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<sup>-1</sup>) 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 (CH<sub>3</sub>CCl<sub>3</sub>) and carbon  
71 tetrachloride (CCl<sub>4</sub>). 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 CH<sub>3</sub>CCl<sub>3</sub>. However, most CH<sub>3</sub>CCl<sub>3</sub>  
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) (see Box  
96 1-3, Figure 1 in Carpenter and Reimann et al., 2015). The vertical flux into the TTL is thought  
97 to be dominated by two main regional pathways, (1) ascent above the western Pacific during  
98 Northern Hemispheric (NH) winter and (2) the circulation of the Asian (Indian) Monsoon during  
99 NH summer (Fueglistaler et al., 2009). The latter has been suggested as the most important  
100 region for transport of anthropogenic pollution (Randel et al., 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 in the western Pacific  
126 region. Indeed, trajectory calculations show that it can take less than 10 days for air masses  
127 to travel from the East Asian boundary layer (>35°N) to the upper tropical troposphere  
128 (altitudes > 200 hPa), thereby providing a fast route by which VSLS (and many other  
129 pollutants) may enter the lower stratosphere, despite their relatively short atmospheric  
130 lifetimes (Ashfold et 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 CH<sub>2</sub>Cl<sub>2</sub>, 1,2-  
136 dichloroethane (CH<sub>2</sub>ClCH<sub>2</sub>Cl), trichloromethane (CHCl<sub>3</sub>) and tetrachloroethene (C<sub>2</sub>Cl<sub>4</sub>).  
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 CH<sub>2</sub>Cl<sub>2</sub>

142 emissions from East Asia and use these to estimate the likely emissions of CH<sub>2</sub>ClCH<sub>2</sub>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 IAGOS-CARIBIC aircraft between Germany  
151 and Thailand/Malaysia. IAGOS-CARIBIC is a European project making regular measurements  
152 from an in-service passenger aircraft operated by Lufthansa (Airbus A340-600;  
153 Brenninkmeijer et al., 2007; <http://www.caribic-atmospheric.com/>).

154

155 A total of 21 samples were collected at Hengchun between 7 March and 5 April 2013 with a  
156 further 22 samples taken at Cape Fuguei between 11 March and 4 April 2014. 28 samples  
157 were collected at Bachok between 20 January and 5 February 2014, during the period of the  
158 NE winter monsoon. The approximate location of each surface site is shown in Figure 1. The  
159 CARIBIC aircraft samples were collected during seven return flights between (i) Frankfurt  
160 (Germany) and Bangkok (Thailand), and (ii) Bangkok and Kuala Lumpur (Malaysia) during the  
161 periods December 2012 - March 2013 (4 flights) and November 2013 - January 2014 (3  
162 flights). All CARIBIC flights in this region between December 2012 and January 2014 have  
163 been included in this analysis. With the exception of 3 samples that were taken at altitudes  
164 between 8.5 and 9.8 km, the CARIBIC samples were all (n=179) collected at altitudes between  
165 10 and 12.3 km.

166

### 167 **2.1 Sample collection**

168 Air samples from Taiwan and Malaysia were collected in 3.2 litre silco-treated stainless steel  
169 canisters (Restek) at a pressure of approximately 2 bar using a battery-powered diaphragm  
170 pump (Air Dimensions, B series). In Taiwan the samples were collected from the surface via  
171 a 1 m x ¼" OD Dekabon sampling line, whilst in Bachok the samples were collected from the  
172 top of an 18 m tower via a 5 m x ¼" OD Dekabon sampling line. In both cases the tubing was  
173 flushed for at least 5 minutes prior to sampling. The sampling integrity was confirmed by  
174 sampling high purity air (BTCA-178, BOC) through the inlet tubing and pump. Samples were  
175 collected within 50 m of the sea and only when the prevailing winds were from the sea,  
176 minimising the impact of any local emissions. The CARIBIC aircraft samples were collected in  
177 2.7 litre glass flasks at a pressure of 4.5 bar using a two-stage metal bellows pumping system  
178 (Brenninkmeijer et al., 2007; Baker et al., 2010).

179

### 180 **2.2 Sample analysis**

181 The collected air samples were shipped to UEA and analysed for their halocarbon content by  
182 gas chromatography – mass spectrometry (GC-MS) following trace gas enrichment using  
183 previously published methods. All samples (i.e. Taiwan, Bachok and CARIBIC) were analysed  
184 for CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and C<sub>2</sub>Cl<sub>4</sub> using an Entech-Agilent GC-MS system operating in electron  
185 ionisation (EI) mode, as described in Leedham-Elvidge et al., (2015). 1 litre samples were  
186 dried and pre-concentrated before injection onto a 30 m x 0.32 mm GS Gas Pro capillary  
187 column (Agilent), temperature ramped from -10°C to 200°C. Samples were interspersed with  
188 repeated analyses of a working standard (SX-706070), a high pressure air sample contained  
189 in a 34 litre electropolished stainless steel cylinder (Essex Industries) provided by the Earth

190 System Research Laboratory of the National Oceanic and Atmospheric Administration  
191 (NOAA-ESRL, Boulder, CO, USA).  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{C}_2\text{Cl}_4$  were quantified on ions with a  
192 mass-to-charge ratio of 84 ( $\text{CH}_2^{35}\text{Cl}_2^+$ ), 83 ( $\text{CH}^{35}\text{Cl}_2^+$  and  $\text{C}_2^{35}\text{Cl}_3^{37}\text{Cl}^+$ ) respectively. Mean  
193 analytical precisions were  $\pm 2\%$  for  $\text{CH}_2\text{Cl}_2$  and  $\text{C}_2\text{Cl}_4$ , and  $\pm 3\%$  for  $\text{CHCl}_3$ . Instrument blanks,  
194 determined by analysing 1 litre aliquots of high purity nitrogen (BOC, Research grade), were  
195 always below the detection limit of the instrument.

196

197 Some of the ground-based samples and a subset of the CARIBIC samples were also analysed  
198 for a range of halocarbons, including the newly-identified  $\text{CH}_2\text{ClCH}_2\text{Cl}$ , using a pre-  
199 concentration/GC system coupled to a Waters AutoSpec magnetic sector MS instrument, also  
200 operating in EI mode, but run at a mass resolution of 1000 at 5 % peak height. Samples (using  
201 between 200 and 250 ml of air) were analysed on an identical GS GasPro column following a  
202 previously described method (Laube et al., 2010; Laube et al., 2012; Leedham-Elvidge et al.,  
203 2015).  $\text{CH}_2\text{ClCH}_2\text{Cl}$  was monitored on the ions with mass-to-charge ratios of 61.99 ( $\text{C}_2\text{H}_3^{35}\text{Cl}^+$ ,  
204 qualifier) and 63.99 ( $\text{C}_2\text{H}_3^{37}\text{Cl}^+$ , quantifier). Mean analytical precision was 1.4 % for  
205  $\text{CH}_2\text{ClCH}_2\text{Cl}$  and the average blank signal was 0.07 ppt (as quantified using regular  
206 measurements of research-grade helium) and was corrected for on a daily basis.

207

### 208 **2.3 Calibration and quality assurance**

209  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{C}_2\text{Cl}_4$  data are reported on the latest (2003) calibration scales provided by  
210 NOAA-ESRL. As was shown in Leedham-Elvidge et al., (2015) our  $\text{CH}_2\text{Cl}_2$  measurements  
211 compare very well with those of NOAA-ESRL at our mutual long-term sampling site at Cape  
212 Grim, Tasmania over more than 6 years. As a recognised international calibration scale for  
213  $\text{CH}_2\text{ClCH}_2\text{Cl}$  is not yet available this compound was calibrated at UEA using the established  
214 static dilution technique recently described (Laube et al., 2012).  $\text{CH}_2\text{ClCH}_2\text{Cl}$  was obtained  
215 from Sigma Aldrich with a stated purity of 99.8 %. Three dilutions were prepared at 7.1, 11.9  
216 and 15.8 ppt. The mixing ratio assigned to our working standard from these dilutions was 5.67  
217 ppt with a 1  $\sigma$  standard deviation of 1.8 %. CFC-11 was added to the dilutions as an internal  
218 reference compound and the CFC-11 mixing ratios assigned to the working standard through  
219 these dilutions agreed with the value assigned by NOAA-ESRL within 4.3 %. This is well within  
220 the estimated uncertainty of the calibration system of 7 % (Laube et al., 2012). In addition the  
221 mixing ratios of  $\text{CH}_2\text{ClCH}_2\text{Cl}$  in the working standard were compared with those in three other  
222 high-pressure canisters (internal surface was either electropolished stainless steel or  
223 passivated aluminium) over the whole measurement period. The ratios between standards did  
224 not change within the 2  $\sigma$  standard deviation of the measurements for any of the canisters  
225 analysed indicating very good long-term stability for  $\text{CH}_2\text{ClCH}_2\text{Cl}$ . This was also the case for  
226  $\text{CHCl}_3$  and  $\text{C}_2\text{Cl}_4$ . As noted in Leedham-Elvidge et al., (2015) mixing ratios of  $\text{CH}_2\text{Cl}_2$  were  
227 found to change over longer timescales in some of our standard canisters, but this drift has  
228 been successfully quantified and corrected for as indicated by the very good comparability  
229 with NOAA-ESRL measurements at the Cape Grim site noted above.

230

### 231 **3. Results**

232

233 Figure 1 shows the location of the three surface observation stations as well as the location of  
234 the CARIBIC samples. The aircraft sampling points have been coloured by their  $\text{CH}_2\text{Cl}_2$   
235 concentration (see later discussion). Data from the surface stations and from the CARIBIC  
236 aircraft flights are summarised in Table 1, together with a summary of published observations  
237 as reported in the most recent Scientific Assessment of Stratospheric Ozone Depletion

238 (Carpenter and Reimann et al., 2015). It should be noted that  $\text{CH}_2\text{ClCH}_2\text{Cl}$  was only analysed  
239 for in selected samples and no data is available from Hengchun 2013 or from CARIBIC flights  
240 between Bangkok and Kuala Lumpur. In addition, only 16 Bachok samples were analysed for  
241  $\text{CH}_2\text{ClCH}_2\text{Cl}$ .

242  
243 The highest concentrations of chlorinated VSLs were measured in samples collected in  
244 Taiwan, suggesting that Taiwan is located relatively close to major emission regions. Figure 2  
245 shows the March/April 2014 data from Cape Fuguei. The Numerical Atmospheric-dispersion  
246 Modelling Environment model (NAME, see supplementary material) can be used to infer the  
247 recent transport history of this pollution. Our NAME analysis (Fig. 2 b-d) indicates that most of  
248 the samples that contained high concentrations of Cl-VSLs had originated from regions to the  
249 north of Taiwan, primarily the East Asian mainland. The median sum of chlorine from the 4  
250 VSLs listed above ( $\Sigma\text{Cl}_{\text{VSLs}}$ ) in 22 samples collected at Cape Fuguei in March/April 2014 was  
251 756 ppt (range 232-2178 ppt). Similarly high concentrations and variation were seen in the 21  
252 samples collected at Hengchun in March/April 2013 (Fig. S1 in the supplementary material).  
253 To put these concentrations in a global context, the total organic chlorine derived from all  
254 known source gases in the background troposphere (including CFCs, HCFCs, and longer-  
255 lived chlorocarbons) is currently around 3300 ppt, with a typical Cl-VSLs contribution in the  
256 remote marine boundary layer of approximately 3 % (Carpenter and Reimann et al., 2015).  
257 Of the four VSLs measured, the two largest contributors to  $\Sigma\text{Cl}_{\text{VSLs}}$  in Taiwan were  $\text{CH}_2\text{Cl}_2$   
258 (55-76 %) and  $\text{CH}_2\text{ClCH}_2\text{Cl}$  (14-30 %).

259  
260 Figure 3 shows the Cl-VSLs data from 28 samples collected at Bachok, Malaysia during the  
261 winter monsoon season in late January/ early February 2014. During this phase of the East  
262 Asian monsoon the prevailing winds are from the northeast and, as described earlier, are often  
263 impacted by emissions further to the north, including from mainland China. As can be seen in  
264 Figure 3, there was a 7 day period between 19 and 26 January when significantly enhanced  
265 concentrations of Cl-VSLs were observed. During this period NAME back trajectories show  
266 air travelling from continental East Asia and across the South China Sea before arriving at  
267 Bachok. Three examples during this cold surge event are shown in Fig. 3 (b-d). These  
268 trajectories often pass over Taiwan and, in some instances, also over parts of Indochina where  
269 additional emissions could have been picked up. As in the Taiwan samples,  $\text{CH}_2\text{Cl}_2$  is the  
270 largest contributor to  $\Sigma\text{Cl}_{\text{VSLs}}$  (59-66 %), having a mean concentration of  $179.9 \pm 71.9$  ppt  
271 (range 94.0 – 354.9 ppt, 9 samples) during the 7-day period of the pollution event. The mean  
272 concentration of  $\text{CH}_2\text{ClCH}_2\text{Cl}$  was  $64.4 \pm 23.9$  ppt (range 30.2 – 119.5 ppt), accounting for 19-  
273 23 % of  $\Sigma\text{Cl}_{\text{VSLs}}$ . These abundances are substantially higher than those typically found in the  
274 marine boundary layer. For example, the range of  $\Sigma\text{Cl}_{\text{VSLs}}$  from the 4 compounds listed above  
275 in the tropical marine boundary layer reported in WMO (2014) is 70-134 ppt. The range  
276 observed at Bachok over the entire sampling period was 207-1078 ppt, with medians of 546  
277 ppt and 243 ppt during the polluted (20-26 Jan) and less-polluted (27 Jan – 5 Feb) periods  
278 respectively (see Table 1). It is interesting to note that even in the period after the cold surge  
279 event (Fig.3 e,f), the levels of Cl-VSLs are still significantly higher than would be expected,  
280 suggesting that this region of the South China Sea is widely impacted by emissions from E  
281 Asia.

282  
283 The pollution or “cold surge” event observed at Bachok lasted for 6-7 days and the back  
284 trajectories shown in Figure 3 are typical of those arriving at Bachok during the winter  
285 monsoon period (see NAME animations in supplement). To further investigate the frequency



286 and typical duration of these events a NAME trajectory analysis using carbon monoxide (CO)  
287 as a tracer of industrial emissions from regions north of 20°N was conducted for the entire  
288 winter season (see supplementary information for details). Figure 4(a) shows a time series of  
289 this industrial CO tracer for winter 2013/2014 and suggests that the observed event in January,  
290 during which there was a strong correlation between the industrial CO tracer and CH<sub>2</sub>Cl<sub>2</sub> (Fig.  
291 4b), is likely to be repeated regularly throughout the winter. An analysis of a further 5 winters  
292 (Fig. 4c) demonstrates that 2013/14 was not unusual and that the events depicted in Figure  
293 3a occur repeatedly every year (Fig. S2 in the supplementary material).

294  
295 The Bachok measurements clearly demonstrate the rapid long-range transport of highly  
296 elevated concentrations of Cl-VSLS for several thousand kilometres across the South China  
297 Sea, as predicted by Ashfold et al., (2015). However, to have an impact on stratospheric ozone  
298 it is necessary to demonstrate that these high concentrations of Cl-VSLS can be rapidly lifted  
299 to the upper tropical troposphere (lower TTL) or above. Such evidence can be found in  
300 samples from several recent CARIBIC aircraft flights in the Southeast Asia region. Figure 1  
301 shows significant enhancements of CH<sub>2</sub>Cl<sub>2</sub> during flights over northern India and the Bay of  
302 Bengal, and also between Bangkok and Kuala Lumpur. The same data is plotted against  
303 longitude in Figure 5(a) which shows that elevated concentrations were observed in the seven  
304 CARIBIC flights in the region during the periods Dec 2012 - Mar 2013 and Nov 2013 - Jan  
305 2014. The samples were collected in the altitude range 10-12.3 km, showing that recent  
306 industrial emissions can regularly reach the lower boundary of the TTL. Although CH<sub>2</sub>CICH<sub>2</sub>Cl  
307 was only analysed for in a selection of samples during the flights from Germany to Bangkok,  
308 elevated mixing ratios coinciding with the high levels of CH<sub>2</sub>Cl<sub>2</sub> were clearly observed (Fig.  
309 5b). CHCl<sub>3</sub> and C<sub>2</sub>Cl<sub>4</sub> were also enhanced during these flights (Table 1), with ΣCl<sub>VSLs</sub> being in  
310 the range 48-330 ppt (Fig. 5c). This is up to 3.2 times higher than that previously found in the  
311 lower TTL (36-103 ppt; Carpenter and Reimann et al., 2015). The highest abundances of Cl-  
312 VSLS were seen in samples collected over the Bay of Bengal, and on flights between Bangkok  
313 and Kuala Lumpur (Fig. 5a). NAME back trajectories (Fig. 5d) indicate that in these cases the  
314 sampled air had almost always been transported from the east, and had often been impacted  
315 by emissions from East Asia, with possible contributions from other countries including the  
316 Philippines, Malaysia and Indochina.

317

#### 318 **4. Discussion**

319

320 The high mixing ratios of CH<sub>2</sub>Cl<sub>2</sub> observed in the Taiwan samples are not entirely unexpected.  
321 Previous studies have found very high levels (> 1 ppb) of CH<sub>2</sub>Cl<sub>2</sub> in various Chinese cities  
322 (Barletta et al., 2006) and in the Pearl River Delta region (Shao et al., 2011). Elevated levels  
323 (several hundred ppt) were also observed in aircraft measurements in polluted air emanating  
324 from China during the TRACE-P campaign in 2001 (Barletta et al., 2006). These studies took  
325 place in the early 2000s and emissions may be expected to have grown significantly since.  
326 CH<sub>2</sub>Cl<sub>2</sub> is predominantly (~90%) anthropogenic in origin, and is widely used as a chemical  
327 solvent, a paint stripper and as a degreasing agent (McCulloch and Midgeley, 1996; Montzka  
328 et al., 2011). Other uses include foam blowing and agricultural fumigation. A growing use of  
329 CH<sub>2</sub>Cl<sub>2</sub> is in the production of HFC-32 (CH<sub>2</sub>F<sub>2</sub>), an ozone friendly replacement for HCFC-22  
330 (CHF<sub>2</sub>Cl) in refrigeration applications. Around 10% of global CH<sub>2</sub>Cl<sub>2</sub> emissions come from  
331 natural marine and biomass burning sources (Simmonds et al., 2006; Montzka and Reimann  
332 et al., 2011).

333

334 Whilst the strong enhancements of  $\text{CH}_2\text{Cl}_2$  are not entirely unexpected, the presence of high  
335 concentrations of  $\text{CH}_2\text{ClCH}_2\text{Cl}$  most certainly are. There are very few previously reported  
336 measurements of  $\text{CH}_2\text{ClCH}_2\text{Cl}$ , particularly in recent years. Elevated levels have been  
337 observed in urban environments close to known emission sources (Singh et al., 1981) and,  
338 more recently, Xue et al., (2011) reported elevated levels ( $91 \pm 79$  ppt) in air samples collected  
339 in the boundary layer over north-eastern China in 2007. The few reported measurements of  
340  $\text{CH}_2\text{ClCH}_2\text{Cl}$  in the remote marine boundary layer are typically in the low ppt range (see Table  
341 1) but these were mostly made well over a decade ago. No long-term atmospheric  
342 measurements of  $\text{CH}_2\text{ClCH}_2\text{Cl}$  have been reported, and  $\text{CH}_2\text{ClCH}_2\text{Cl}$  is not reported by the  
343 main surface monitoring networks (AGAGE and NOAA), so current background  
344 concentrations and longer term trends are unknown.  $\text{CH}_2\text{ClCH}_2\text{Cl}$  is **predominantly**  
345 anthropogenic in origin, its primary use being in the manufacture of vinyl chloride, the  
346 precursor to polyvinyl chloride (PVC), and a number of chlorinated solvents.  $\text{CH}_2\text{ClCH}_2\text{Cl}$  also  
347 finds use as a solvent, dispersant and has historically been added to leaded petrol as a lead  
348 scavenger (EPA, 1984). In common with  $\text{CH}_2\text{Cl}_2$  it has also used as a cleaning/degreasing  
349 agent and as a fumigant. China is the world's largest producer of PVC accounting for 27% of  
350 global production in 2009 (DCE, 2017). Production has increased rapidly in recent years (14%  
351 per year over the period 2000-2009; DCE, 2017), which could potentially have led to increased  
352 atmospheric emissions of  $\text{CH}_2\text{ClCH}_2\text{Cl}$ . **Simpson et al. (2011) observed a small enhancement**  
353 **in  $\text{CH}_2\text{ClCH}_2\text{Cl}$  in Canadian boreal forest fire plumes (background average, June-July 2008,**  
354  **$9.9 \pm 0.3$  ppt, plume average  $10.6 \pm 0.3$  ppt) and estimated a global boreal fire source of  $0.23$**   
355  **$\pm 0.19$  kilotonnes (kt)  $\text{yr}^{-1}$ .**

356  
357 The other CI-VSLS presented here are  $\text{C}_2\text{Cl}_4$  and  $\text{CHCl}_3$ . In contrast to  $\text{CH}_2\text{ClCH}_2\text{Cl}$ , long-term  
358 atmospheric data records are available for these compounds, although there are few data  
359 from the SE Asia region. Current trends show that  $\text{C}_2\text{Cl}_4$  is declining in the background  
360 troposphere ( $\sim 6\% \text{ yr}^{-1}$ ), whilst  $\text{CHCl}_3$  is approximately constant (Carpenter and Reimann et  
361 al., 2015). However, both compounds were elevated in the samples containing high  
362 concentrations of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_2\text{ClCH}_2\text{Cl}$ , suggesting that significant, co-located sources  
363 remain. Like  $\text{CH}_2\text{ClCH}_2\text{Cl}$ ,  $\text{C}_2\text{Cl}_4$  is **almost** exclusively anthropogenic in origin, used primarily  
364 as a solvent in the dry cleaning industry, as a metal degreasing agent and as a chemical  
365 intermediate, for example in the manufacture of the hydrofluorocarbons HFC-134a and HFC-  
366 125.  $\text{CHCl}_3$  is believed to be largely natural in origin (seawater, soils, macroalgae), but  
367 potential anthropogenic sources include the pulp and paper industry, water treatment facilities  
368 and HFC production (McCulloch, 2003; Worton et al., 2006; Montzka et al., 2011).

#### 369 370 *4.1 Regional emissions of $\text{CH}_2\text{Cl}_2$ and $\text{CH}_2\text{ClCH}_2\text{Cl}$*

371  
372 China does not report production or emission figures for  $\text{CH}_2\text{Cl}_2$ . However emissions of  $\text{CH}_2\text{Cl}_2$   
373 can be estimated from known Chinese production of HCFC-22 ( $\text{CHClF}_2$ ). This is possible  
374 because the production of HCFC-22 requires  $\text{CHCl}_3$  as feedstock (1 kg HCFC-22 requires 1.5  
375 kg  $\text{CHCl}_3$ ) and because  $\text{CHCl}_3$  is produced almost entirely (>99%) for HCFC-22 production.  
376 Production of chloromethanes by any manufacturing process leads to the inevitable co-  
377 production of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , with smaller (3-5%) co-production of carbon tetrachloride  
378 ( $\text{CCl}_4$ ). The production ratios vary by individual plant but are within the range 30:70-70:30 (%  
379  $\text{CH}_2\text{Cl}_2$ : $\text{CHCl}_3$ ). Chinese chloromethanes plants, which together represent some 60% of global  
380 capacity and production, are generally built to a 40:60 - 60:40 flexibility ratio. With falling CFM  
381 demand due to diminished feedstock demand for HCFC-22 production, and based on regular



382 discussions with the individual large producers, ratios in China have been switching in recent  
383 years from the traditional 40:60 towards 50:50 (CH<sub>2</sub>Cl<sub>2</sub>:CHCl<sub>3</sub>; Nolan Sherry 2016).

384

385 It can be calculated that in 2015 China produced approximately 600 kt of HCFC-22 for all uses  
386 (Nolan Sherry 2016), which would require 900 kt of CHCl<sub>3</sub> as feedstock. By subtracting  
387 Chinese imports of CHCl<sub>3</sub> (40 kt; Comtrade 2016) and allowing for some limited emissive  
388 solvent use (15 kt) suggests that China produced around 875 kt of CHCl<sub>3</sub> in 2015. As noted  
389 above, in the chlorocarbon industry CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> are produced in the same  
390 manufacturing process and in China this is currently moving from a historic production ratio of  
391 around 40:60 towards 50:50. Using a production ratio of 45:55 it can therefore be estimated  
392 that China produced around 715 kt of CH<sub>2</sub>Cl<sub>2</sub> in 2015. Approximately 90 kt of this was exported  
393 (Comtrade 2016) and another 170 kt was used for the production of HFC-32 (CH<sub>2</sub>F<sub>2</sub>), which  
394 is a non-emissive application (Nolan Sherry 2016). This leaves an estimated 455 kt (± 10%)  
395 of CH<sub>2</sub>Cl<sub>2</sub> which is used almost exclusively in emissive applications such as paint stripping,  
396 foam blowing, pharmaceuticals, solvent use, etc. Although there is no specific industry-based  
397 aggregation of these numbers, they have been verified in discussion with Chinese and other  
398 industry sources. A similar method has recently been used to assess emissions of CCl<sub>4</sub>  
399 (SPARC 2016).

400

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

410

## 411 **5. Concluding remarks**

412

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

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

432

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

440

441 Unlike the bromine-containing VSLS which are largely natural in origin, the CI-VSLS reported  
442 here are mainly anthropogenic and consequently it would be possible to control their  
443 production and/or release to the atmosphere. Of particular concern are the rapidly growing  
444 emissions of CH<sub>2</sub>Cl<sub>2</sub>, and potentially CH<sub>2</sub>CICH<sub>2</sub>Cl, especially when considering the  
445 geographical location of these emissions, close to the major uplift regions of the western  
446 Pacific (winter) and the Indian sub-continent (summer). Without a change in industrial  
447 practices the contribution of CI-VSLS to stratospheric chlorine loading is likely to increase  
448 substantially in the coming years, thereby endangering some of the hard-won gains achieved,  
449 and anticipated, under the Montreal Protocol.

450

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595

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597

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607 Taiwan EPA and MOST. J.L and L.G. were funded through a NERC fellowship  
608 (NE/1021918/1) and studentship (NE/1210143) respectively. We acknowledge use of the  
609 NAME atmospheric dispersion model and associated NWP meteorological data sets made  
610 available to us by the UK Met Office. We also acknowledge the significant storage resources  
611 and analysis facilities made available to us on JASMIN by STFC CEDA along with the  
612 corresponding support teams.

613

614

615

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

620

621 **Figure 1:** Map of the region showing the location of each CARIBIC sample. The markers have  
622 been coloured according to their CH<sub>2</sub>Cl<sub>2</sub> concentration to highlight the regions where  
623 enhanced levels of VSLS were observed. Also shown are the approximate locations of the 3  
624 surface stations (orange crosses).

625

626 **Figure 2:**

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

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

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

636

637 **Figure 3:**

638 *Upper panel (a):* Mole fractions (ppt) of the 4 chlorinated VSLS in air samples collected at  
639 Bachok in Jan/Feb 2014. Strongly enhanced levels of all 4 compounds were seen for a 7-  
640 day period at the beginning of the campaign (20-26 Jan). Also shown (dashed line) are the  
641 approximate median background concentrations in the remote marine boundary layer in  
642 2012 (from Carpenter and Reimann et al., 2015).

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

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

651 **Figure 4:**

652 (a) Time-series of the modelled carbon monoxide (CO) anomaly at Bachok (i.e. that due only  
653 to industrial emissions from north of 20°N in the previous 12 days) for winter 2013/14. The  
654 CH<sub>2</sub>Cl<sub>2</sub> data (grey squares) from the Bachok sampling period are overlaid. The dashed lines  
655 show the 25 ppb and 50 ppb thresholds referred to in 3c (see supplement for further details).

656 (b) Correlation of the modelled CO anomaly with the observed CH<sub>2</sub>Cl<sub>2</sub>.

657 (c) Average number of days each month, averaged over six consecutive winters (2009/10 –  
658 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<sub>2</sub>Cl<sub>2</sub>). 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<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>ClCH<sub>2</sub>Cl in selected CARIBIC samples (note: CH<sub>2</sub>ClCH<sub>2</sub>Cl 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<sub>2</sub>Cl<sub>2</sub> (90<sup>th</sup> percentile, [CH<sub>2</sub>Cl<sub>2</sub>] >75.6 ppt), with the  
677 composite footprint from the remaining samples ([CH<sub>2</sub>Cl<sub>2</sub>] < 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.

681 **Table 1**

682

|   | Taiwan 2013 |            | Taiwan 2014 |            | Bachok 2014                |                 |                           | MBL (WMO 2014) <sup>(b)</sup> |                                 |
|---|-------------|------------|-------------|------------|----------------------------|-----------------|---------------------------|-------------------------------|---------------------------------|
|   | Median      | Range      | Median      | Range      | Median (CS) <sup>(a)</sup> | Median (non-CS) | Range                     | Median                        | Range                           |
| <b>CH<sub>2</sub>Cl<sub>2</sub></b>     | 226.6       | 68 - 624   | 227.4       | 70 - 639   | 170.4                      | 81.9            | 64.8 - 355                | <b>28.4</b>                   | <b>21.8 - 34.4</b>              |
| <b>CH<sub>2</sub>CICH<sub>2</sub>Cl</b> | -           | -          | 85.4        | 16.7 - 309 | 62.2                       | 21.7            | 16.4 - 120 <sup>(c)</sup> | <b>3.7</b>                    | <b>0.7 - 14.5<sup>(d)</sup></b> |
| <b>CHCl<sub>3</sub></b>                 | 33.0        | 11.6 - 232 | 35.1        | 13.8 - 103 | 22.8                       | 14.7            | 12.8 - 30.5               | <b>7.5</b>                    | <b>7.3 - 7.8</b>                |
| <b>C<sub>2</sub>Cl<sub>4</sub></b>      | 4.4         | 1.7 - 16.6 | 5.5         | 1.7 - 18.6 | 4.5                        | 1.9             | 1.5 - 9.5                 | <b>1.3</b>                    | <b>0.8 - 1.7</b>                |
| <b>Σ Cl<sub>VLSL</sub></b>              | -           | -          | 755.8       | 232 - 2178 | 546.0                      | 243.1           | 207 - 1078 <sup>(c)</sup> | <b>93.4</b>                   | <b>70 - 134</b>                 |

683

684

|   | CARIBIC (FRA-BKK, 65-97°E)<br>10-12 km |             |                   | CARIBIC (BKK-KUL, 100-105°E)<br>10-12 km |        |            | Lower TTL (WMO 2014) <sup>(b)</sup><br>12-14 km |                   |
|---|--|-------------|-------------------|--|--------|------------|---|-------------------|
|   | Mean                                   | Median      | Range             | Mean                                     | Median | Range      | Mean  | Range             |
| <b>CH<sub>2</sub>Cl<sub>2</sub></b>                   | 43.2                                   | 31.6        | 14.6 - 121        | 50.4                                     | 46.5   | 22.5 - 100 | <b>17.1</b>                                     | <b>7.8 - 38.1</b> |
| <b>CH<sub>2</sub>CICH<sub>2</sub>Cl<sup>(e)</sup></b> | 9.9                                    | 6.1         | 0.4 - 29.1        | -  | -      | -          | <b>3.6</b>                                      | <b>0.8 - 7.0</b>  |
| <b>CHCl<sub>3</sub></b>                               | 7.0                                    | 6.0         | 2.0 - 15.6        | 9.3                                      | 8.7    | 3.7 - 46.6 | <b>6.8</b>                                      | <b>5.3 - 8.2</b>  |
| <b>C<sub>2</sub>Cl<sub>4</sub></b>                    | 0.87                                   | 0.65        | 0.1 - 4.4         | 1.6                                      | 1.5    | 0.2 - 5.9  | <b>1.1</b>                                      | <b>0.7 - 1.3</b>  |
| <b>Σ Cl<sub>VLSL</sub><sup>(e)</sup></b>              | 153.7                                  | 119.3       | 48.4 - 330        |  |        |            | <b>67</b>                                       | <b>36 - 103</b>   |
| <b>Σ Cl<sub>VLSL</sub>*<sup>(f)</sup></b>             | <b>110.9</b>                           | <b>81.4</b> | <b>35.2 - 301</b> | 134.8                                    | 127.8  | 56.6 - 251 | -   | -                 |

685

686

687 <sup>(a)</sup> CS and non-CS refer to the cold surge (polluted) and non-cold surge periods at Bachok

688 <sup>(b)</sup> The WMO data is a compilation of all reported global measurements up to, and including, the year 2012. The  
689 range represents the smallest mean minus one standard deviation and the largest mean plus one standard  
690 deviation of all considered datasets. **Data from the TTL was derived from various aircraft and balloon**  
691 **campaigns.**

692 <sup>(c)</sup> CH<sub>2</sub>CICH<sub>2</sub>Cl was only analysed for in 16 of the 28 samples collected at Bachok693 <sup>(d)</sup> Note that the CH<sub>2</sub>CICH<sub>2</sub>Cl MBL data actually date back to the early 2000s. No recent data was reported.

694 <sup>(e)</sup> CH<sub>2</sub>CICH<sub>2</sub>Cl was only analysed for in selected samples from the Frankfurt-Bangkok flights and in no samples  
695 collected during the Bangkok-Kuala Lumpur flights. **These statistics are therefore based on a reduced number**  
696 **of samples on the FRA-BKK route (24 out of 98).**

697 <sup>(f)</sup> Σ Cl<sub>VLSL</sub>\* is defined as the sum of Cl-VLSL excluding the contribution from CH<sub>2</sub>CICH<sub>2</sub>Cl. **Statistics derived from**  
698 **all samples (98 FRA-BKK; 81 BKK-KUL).**

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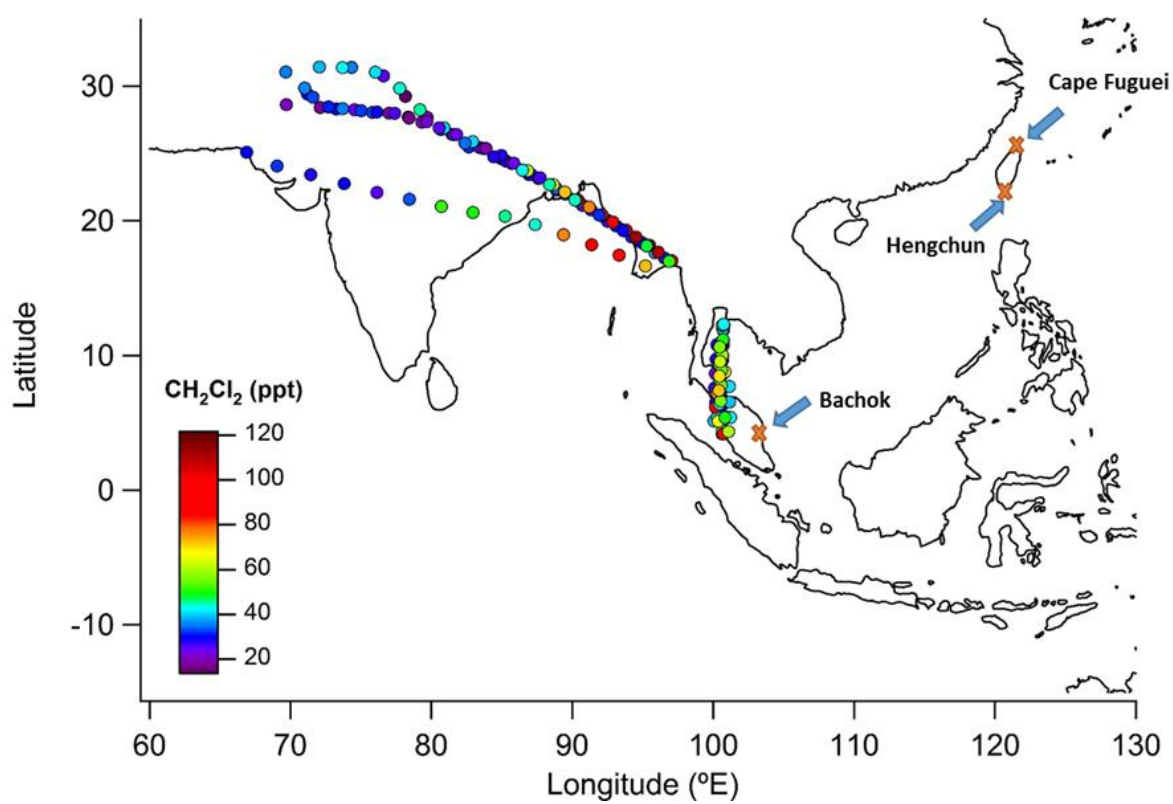
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702 **Figure 1**

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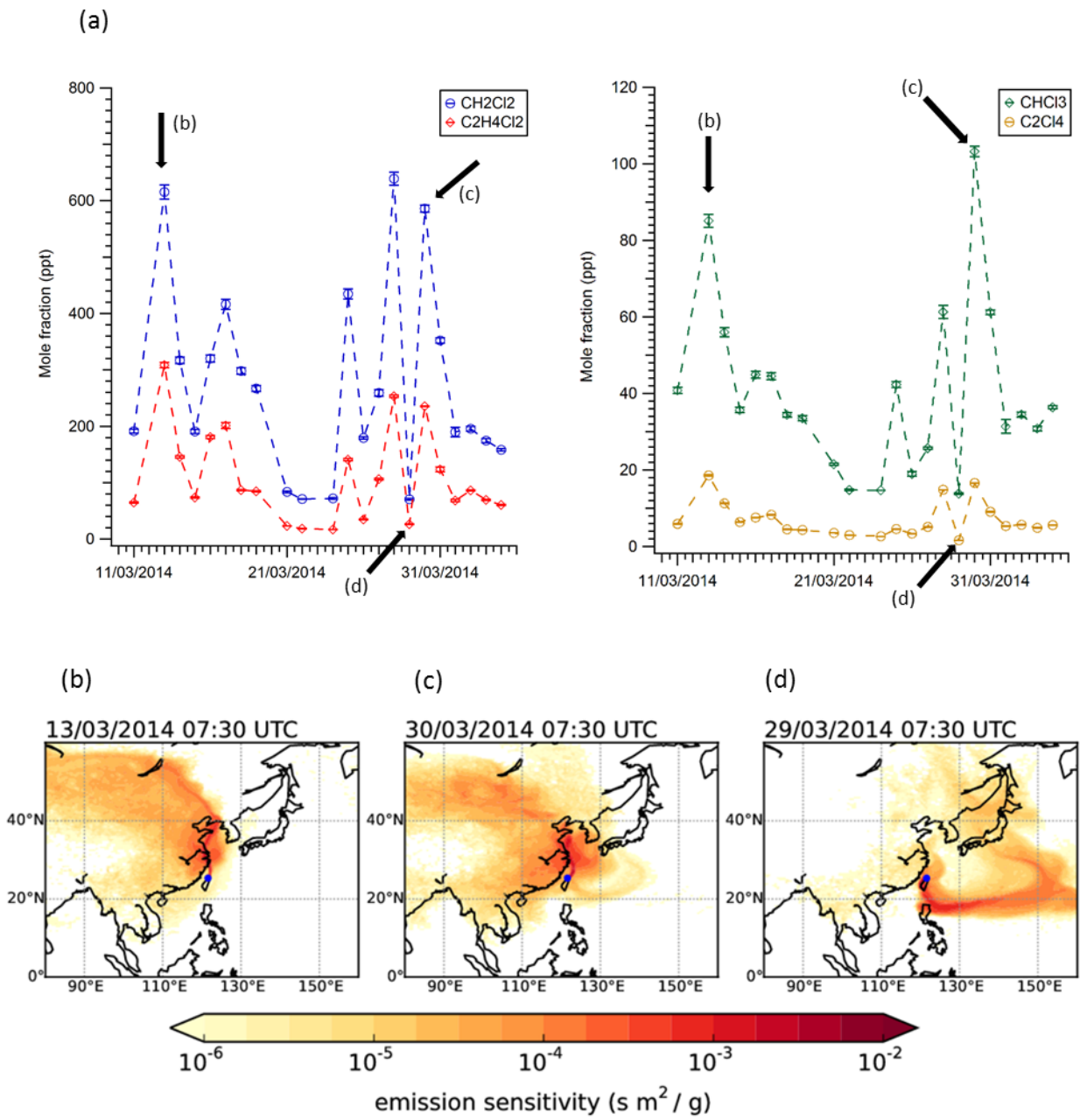
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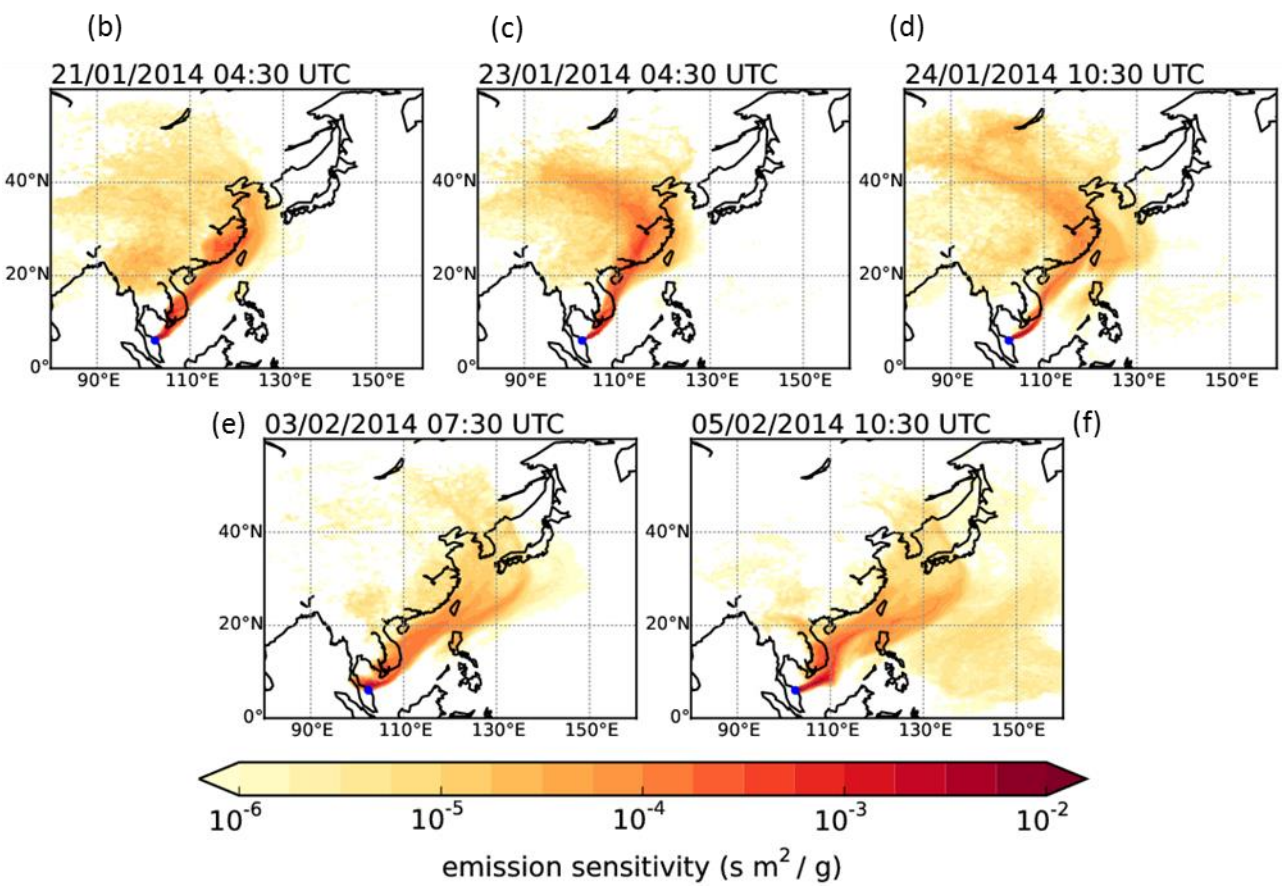
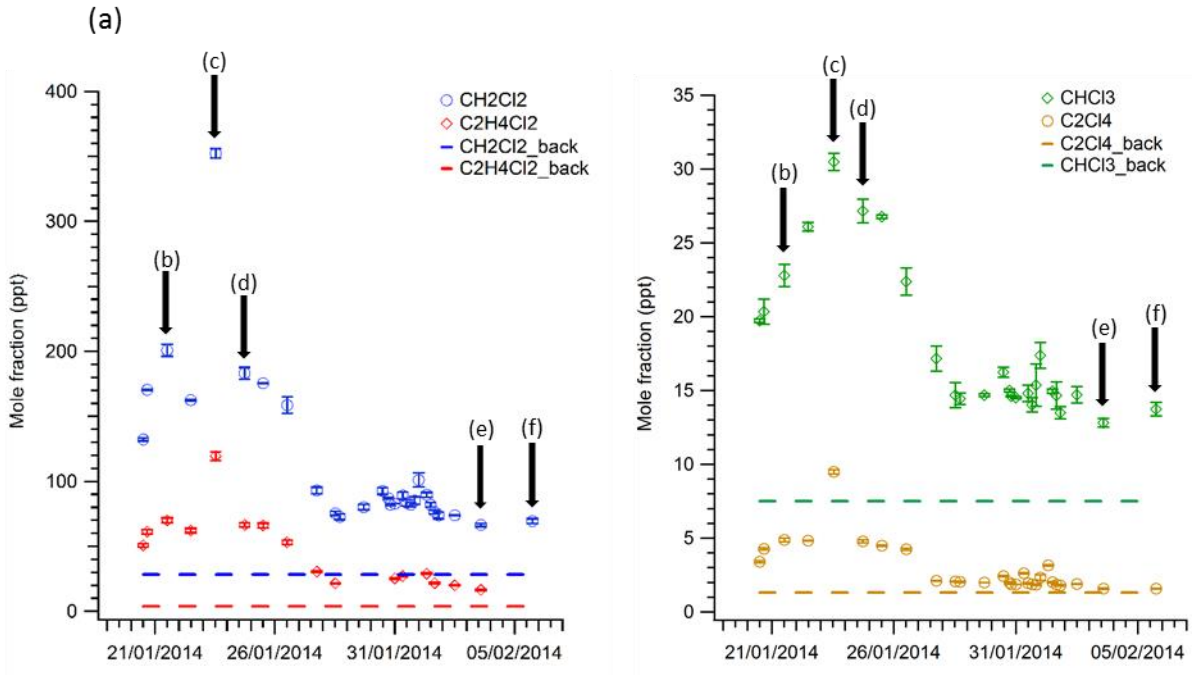
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713 **Figure 2**  
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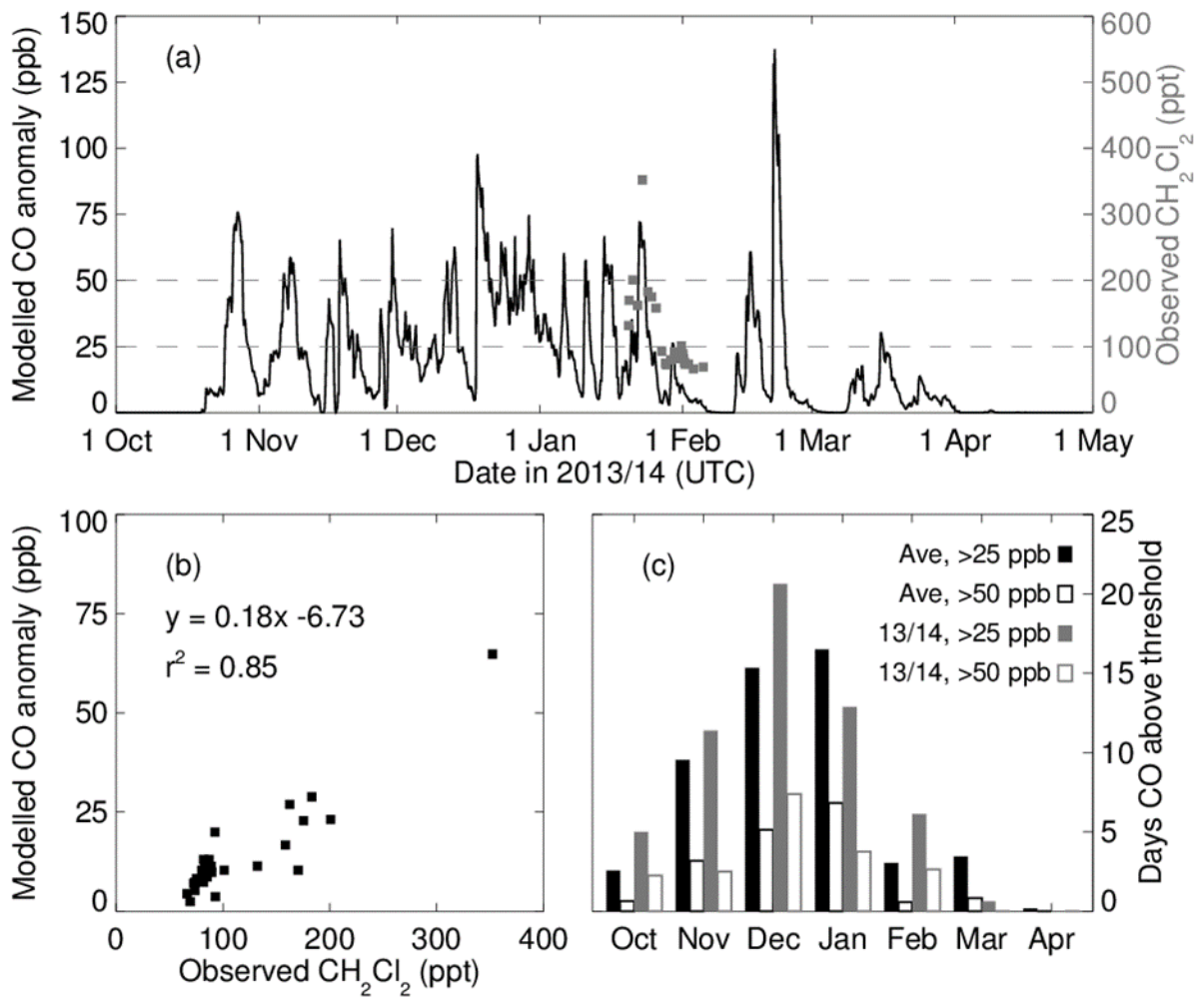
718 **Figure 3**  
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724 **Figure 4**

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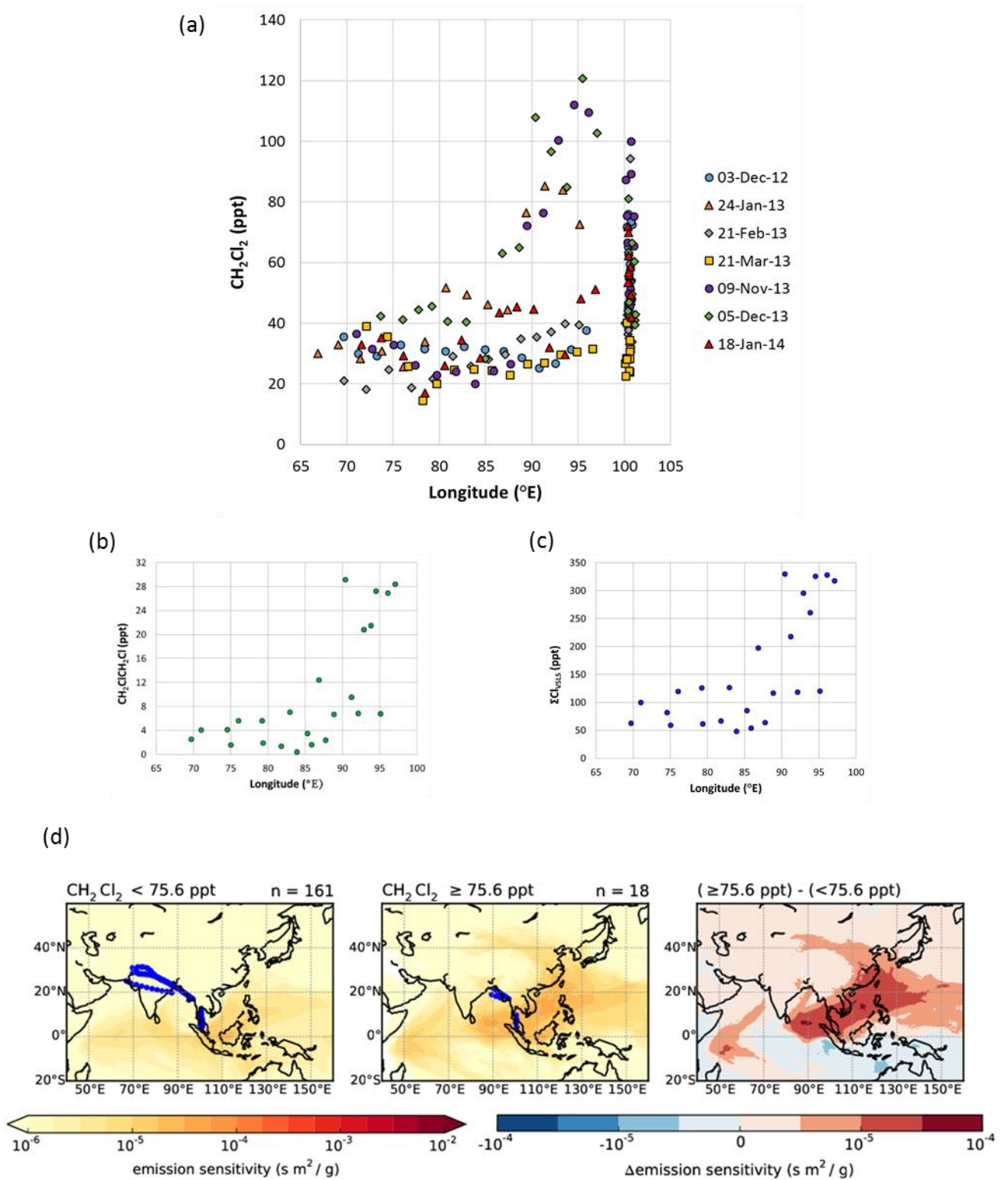
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733 **Figure 5**

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# 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  $\text{CH}_2\text{ClCH}_2\text{Cl}$  was not analysed for in the 2013 samples, but the absolute concentrations and variability of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{C}_2\text{Cl}_4$  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  $0.5625^\circ$  longitude by  $0.375^\circ$  latitude. From this information, and assuming a uniform surface air density consistent with a pressure of 1000 hPa and a temperature of  $25^\circ\text{C}$ , 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  $\text{sm}^2\text{g}^{-1}$ ).

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  $0.35^\circ$  longitude by  $0.23^\circ$  latitude and 59 vertical levels below  $\sim 30$  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,  $\text{sm}^2\text{g}^{-1} \times \text{gm}^{-2}\text{s}^{-1} = \text{dimensionless mixing ratio}$ ). We have used an inventory of industrial and combustion carbon monoxide (CO) emissions (RCP8.5 for 2005; Granier et al. 2011, Riahi et al. 2011), which are likely to be similarly distributed to VSLs-Cl (e.g. regression in Figure 4b and Shao et al. 2011), to model anomalous CO volume mixing ratios (i.e. those due only to these industrial emissions north of  $20^\circ\text{N}$ ) 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

789 be a regularly repeated event. In total during this winter there are ~57 days (i.e. 453 3-hour  
790 periods) with a modelled mixing ratio above a threshold of 25 ppb, and 19 days above 50 ppb.  
791 To demonstrate that winter 2013/14 was not unusual, the modelled CO anomalies for the other  
792 5 winters examined are shown in Figure S2.

793

## 794 **2.2 NAME animations**

795

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

800

801

## 802 **Supplementary References**

803

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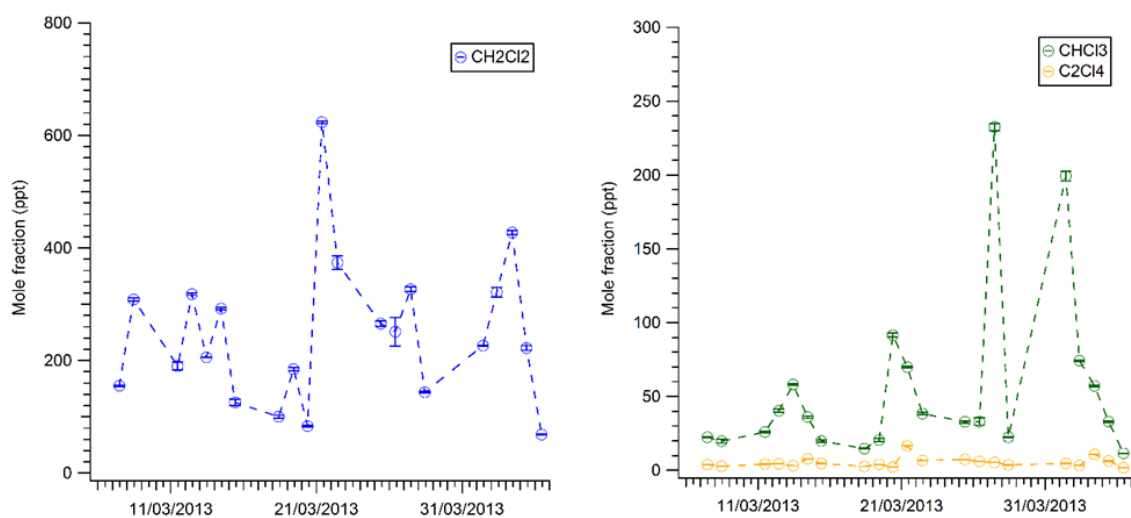
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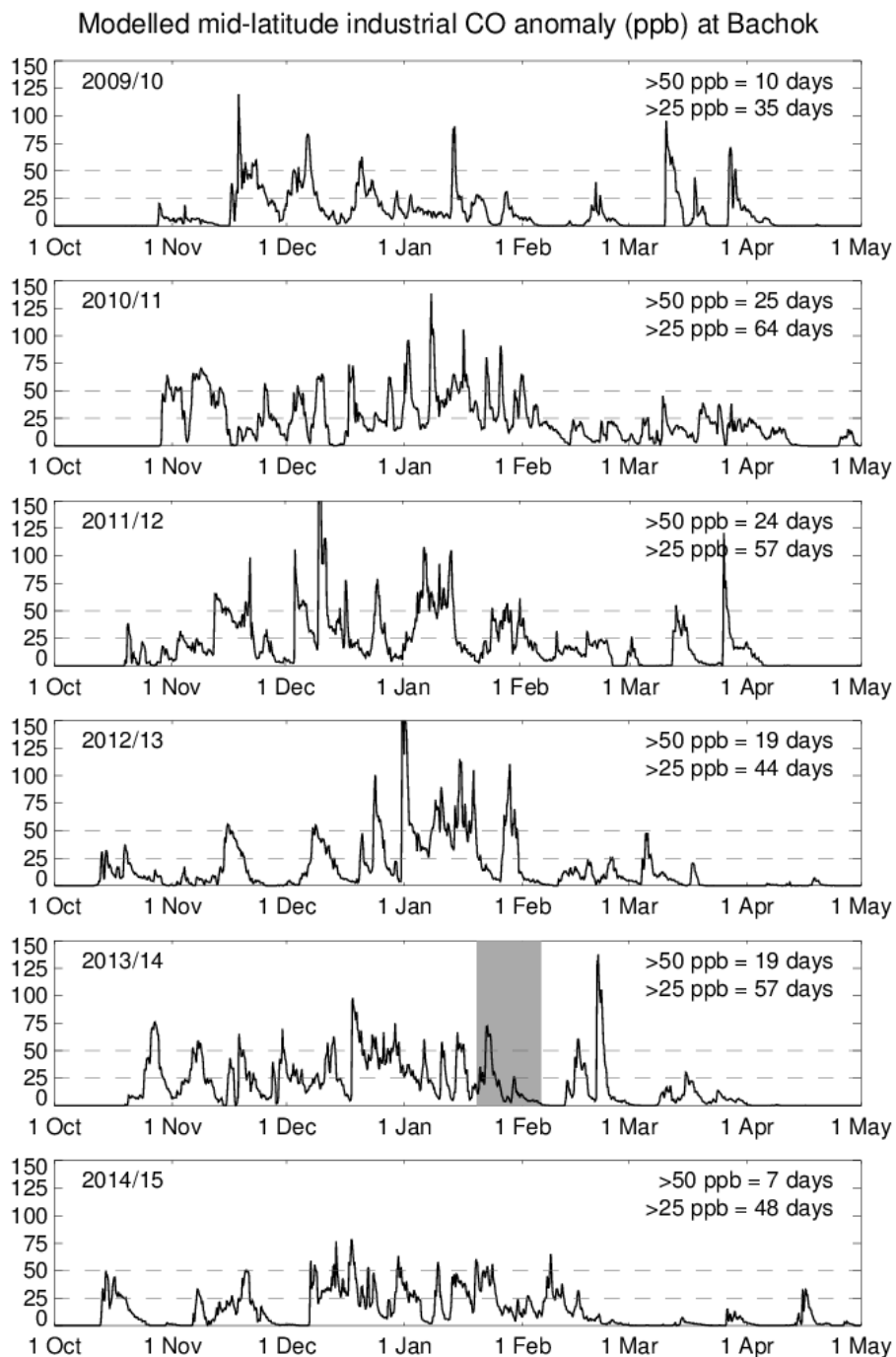
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833

834 **Figure S1:** Mole fractions (ppt) of 3 chlorinated VSLs in air samples collected at Hengchun,  
835 Taiwan in March/April 2013. Note that CH<sub>2</sub>ClCH<sub>2</sub>Cl was not monitored in the 2013 samples.  
836 The error bars are ± 1 standard deviation.



838

839

840 **Figure S2:** Time-series of the modelled carbon monoxide (CO) anomaly at Bachok, due only  
 841 to industrial emissions from north of 20°N in the previous 12 days, for six winter seasons. The  
 842 period of observations at Bachok during Jan and Feb 2014 is shaded in grey. Also shown are  
 843 the number of days in each winter which exceed the 25 ppb and 50 ppb thresholds which,  
 844 using the regression equation in Figure 4b, correspond to 176 ppt and 315 ppt of CH<sub>2</sub>Cl<sub>2</sub>.

845

846

## Response to Reviewers

847 We would like to thank the reviewers for their very helpful comments and we have  
848 addressed these as follows (reviewer's comment in bold):

849 **Reviewer 1** (Sinnhuber)

850 **As one general comment I feel that the presentation of CH<sub>2</sub>Cl<sub>2</sub> emission estimates**  
851 **and the correlation with CH<sub>2</sub>CICH<sub>2</sub>Cl to infer new CH<sub>2</sub>CICH<sub>2</sub>Cl emission estimates**  
852 **(lines 337 - 343) deserves (and requires) more detail, given its importance. Part of the**  
853 **information on estimating the CH<sub>2</sub>Cl<sub>2</sub> emissions given in the supplementary material**  
854 **should be included in the main text and a bit more explanation on the "simple**  
855 **correlation" should be included.**

856 We have moved the discussion about the emission estimates from the supplement into the  
857 manuscript as suggested. We have also made a slight modification to our analysis and  
858 rather than giving the extreme range of potential CH<sub>2</sub>Cl<sub>2</sub> emissions as before (based on the  
859 40:60 and 50:50 production ratios) we have opted to give an estimate based on the more  
860 likely ratio of 45:55. This leads us to production and emission figures of 715 kt and 455 kt  
861 respectively, with an approximate uncertainty of ± 10%.

862 We have also expanded the section on the correlation between the two compounds to  
863 include the following text

864 *"There is a strong linear correlation between the observed CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>2</sub>CICH<sub>2</sub>Cl data at*  
865 *both Bachok (R<sup>2</sup> = 0.9799) and Cape Fuguei (R<sup>2</sup> = 0.9189). Combining the datasets yields a*  
866 *slope of 0.4456 ± 0.0194 (R<sup>2</sup> = 0.9228). Using the emissions for CH<sub>2</sub>Cl<sub>2</sub> derived above (455*  
867 *kt) and making the assumptions that (1) all emissions originate in China and (2) there are no*  
868 *significant relative losses of the two compounds since emission (lifetimes are 144 days for*  
869 *CH<sub>2</sub>Cl<sub>2</sub> and 65 days for CH<sub>2</sub>CICH<sub>2</sub>Cl) we can estimate Chinese emissions of CH<sub>2</sub>CICH<sub>2</sub>Cl to*  
870 *be of the order of 203 ± 9 kt yr<sup>-1</sup>. If accurate, the scale of these emissions is a major surprise*  
871 *as CH<sub>2</sub>CICH<sub>2</sub>Cl is highly toxic (suggesting that local emissions would be minimised) and*  
872 *believed to be used almost exclusively in non-emissive applications."*

873 **Abstract, I.31: "higher than expected": what is this expectation based upon? Based**  
874 **on previously reported measurements? On line 360 and following it is discussed that**  
875 **many of the previous measurements have been made over a decade ago and in**  
876 **different regions ("... not the 2 key regions ..."). I believe it would be good to make a**  
877 **bit clearer from the start if the enhancements seen in this study are likely because of**  
878 **recent increases in emissions, regional differences, or both.**

879 By "higher than expected" we do indeed mean higher than previously reported data. This  
880 was stated earlier in the sentence and refers to both our surface and aircraft measurements.  
881 We compare our data with the most recent review (WMO, 2015) as we describe in the text  
882 (Section 3, line 236-238) and in Table 1. The enhancements we observe are likely to result  
883 from a combination of increasing emissions and the location of the measurements, although  
884 based on our measurements alone, which are over a relatively short period of time, we have  
885 no evidence that emissions are increasing. We do know from previous work that  
886 atmospheric levels of CH<sub>2</sub>Cl<sub>2</sub> have increased, which implies increasing emissions of this  
887 compound. The long term trend of CH<sub>2</sub>CICH<sub>2</sub>Cl is unknown.

888 **I.36: define "CI-VSLS" when first used. Moreover better use this consistently**  
889 **throughout (e.g. Table 1 uses VSLS-CL, which I suppose means the same)**

890 Done



891 **I.45: you may want to cite also the recent study by Hossaini et al., The increasing**  
892 **threat to stratospheric ozone from dichloromethane, Nature communications, 2017,**  
893 **that was published after submission of the present manuscript.**

894 As our paper was published in ACPD before the Hossaini et al paper it does not seem  
895 appropriate to include it in our reference list at this stage.

896 **I.104: I suggest to break the sentence in two: “... in the TTL. Surface measurements**  
897 **...”**

898 Done

899 **I. 126: I don’t understand the meaning of “globally” here.**

900 We have removed the word “globally”.

901 **I.129: “shorter lifetimes” could be misleading here, as it may imply lifetimes shorter**  
902 **than the 10 days for air masses to travel from East Asia to the TTL, which is probably**  
903 **not what is meant?**

904 Text changed to “*despite their relatively short atmospheric lifetimes*”

905 **I.150: “the CARIBIC aircraft”: better include a sentence or two on the CARIBIC project,**  
906 **describing that these are measurements from in-service aircrafts, ideally including a**  
907 **reference paper (in addition to the http link).**

908 Done

909 **I.328: “CH<sub>2</sub>CICH<sub>2</sub>Cl is exclusively anthropogenic in origin ...”: WMO (2014) lists also**  
910 **biomass burning as a source of CH<sub>2</sub>CICH<sub>2</sub>Cl. Can you include references on**  
911 **additional sources?**

912 We have added the following text: “*Simpson et al. (2011) observed a small enhancement in*  
913 *CH<sub>2</sub>CICH<sub>2</sub>Cl in Canadian boreal forest fire plumes (background average, June-July 2008,*  
914 *9.9 ± 0.3 ppt, plume average 10.6 ± 0.3 ppt) and estimated a global boreal fire source of*  
915 *0.23 ± 0.19 kilotonnes (kt) yr<sup>-1</sup>.*” Of the references given in WMO 2014 (Chapter 1, page  
916 1.38), this is the only one that reported CH<sub>2</sub>CICH<sub>2</sub>Cl.

917 We have also changed the word “*exclusively*” to “*predominantly*” when referring to  
918 anthropogenic sources of CH<sub>2</sub>CICH<sub>2</sub>Cl.

919 **I.334: “Production has increased rapidly ...”: Can you give a reference for this**  
920 **increase in production?**

921 Reference added (same as in the next sentence)

922 **I. 362: Does the superscript “1” have any meaning? Footnote?**

923 The superscript was actually a missing reference, which has now been added (Carpenter  
924 and Reimann et al. 2015).

925 **I. 367: “2”-> “two”**

926 Done

927 **Table 1: Why not use the IATA code “FRA” for Frankfurt (rather than “FFT”, which is**  
928 **the IATA code for Frankfort, Kentucky)?**

929 Done

930 **Table 1: Why is the sum of VLSL-CL excluding CH<sub>2</sub>ClCH<sub>2</sub>Cl not given for the other**  
931 **data for comparison?**

932 The sum of Cl-VLSL excluding CH<sub>2</sub>ClCH<sub>2</sub>Cl is not a widely used number so it was not  
933 included in the Table apart from where necessary. There is no equivalent number reported in  
934 WMO. However, we have added the information for the CARIBIC flights between Frankfurt  
935 and Bangkok for comparison as suggested.

936 **Reviewer 2**

937 **In general, all the information on the samples: time, locations for all the data, number**  
938 **of flights for CARIBIC data, number of sampling at the ground-based stations should**  
939 **be added in this section. For instance, the 7 IAGOS-CARIBIC flights time should be**  
940 **mentioned. Days and months of samples should be specified in this section as well. It**  
941 **will help the reader to get the general feature of the sampling.**

942 **The altitude of CARIBIC needs to be shown. Have you filtered IAGOS-CARIBIC data to**  
943 **analyze data between 10 and 12 km only? The statistics of the sampling in this layer is**  
944 **needed.**

945 We have added more detail at the beginning of the methods section:

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

957 The full CARIBIC flight dates have also been added to Figure 5.

958 **In the text it is mentioned that 10-12km over East Asia is the lower boundary of the**  
959 **TTL. It would be very helpful to show a map of TTL or a figure of TTL and aircraft**  
960 **altitudes together with respect of the flight tracks (latitude). It would be also useful to**  
961 **directly refer to Box 1-3, Figure 1 of Carpenter and Reimann et al. (2015) that shows**  
962 **the altitude range of the TTL.**

963 We have added a reference to the Figure from Carpenter and Reimann et al. (2015). We do  
964 not think it is necessary to reproduce a similar Figure here.

965 **About the results shown in Figure 3, a sentence explaining that three days have been**  
966 **chosen out of the seven days of the cold surge event would be helpful. The term “cold**  
967 **surge” should be mentioned.**

968 New text added: *“Three examples during this cold surge event are shown in Fig. 3 (b-d).”*

969 **In general, “see in supplement” is largely used in the manuscript but I would suggest**  
970 **to refer to figure number and section names of the supplement materials to help the**  
971 **reader.**

972 Done

973 **Results from Carpenter and Reimann et al., 2015 are cited as reference for CI-VSLS**  
974 **last information. For results at the lower TTL, it would be useful to recall the type of**  
975 **observations used in the assessment report: aircraft campaigns and balloons.**

976 We have added the following sentence to Table 1: *“Data from the TTL was derived from*  
977 *various aircraft and balloon campaigns.”*

978 **Table: Units need to be added in Table 1 and its caption**

979 Done

980 **In general, the way to write CI-VSLS should be consistent along the captions and the**  
981 **text (sometimes chlorinated VSLS or VSLS-CI).**

982 Done

983 **Figure 1: “(red crosses)” for surface sites on the map need to be added in the caption**  
984 **to guide the reader.**

985 Done

986 **Figure 2: We don’t see the blue circle on the map.**

987 We apologise that the incorrect Figure was included in the original submission. The blue  
988 circles have now been added.

989 **Figures 2,3,5: Helpful to have a recall of ground-based stations location.**

990 Blue circles have been added to Figures 2 and 3 showing the location of the surface  
991 sampling sites.

992 **Figure 2 and 3: I would rather use letter to name the panels in the caption and I would**  
993 **rather use numbers to link plots in upper panel with maps of the bottom panels.**

994 We use letters to label the arrows which refer to the individual NAME plots underneath.  
995 Mixing letters and numbers would, in our opinion, be more confusing.

996 **Figure 3: Use arrows as for Figure 2 to help the reader to find the days that are**  
997 **chosen for air masses origin (map below). In the caption it is mentioned “true**  
998 **background levels”, how these levels are estimated? Figure 3 a) is not specified, “a)”**  
999 **should be added on the figure.**

1000 Arrows have been added to Figure 3 as requested. The baseline levels are taken from WMO  
1001 2015, based on tropical mean background levels. The actual expected background is difficult  
1002 to define for VSLS as they would be expected to vary substantially across the globe (i.e. with  
1003 latitude and with distance from source). We have added a reference to WMO in the Figure  
1004 caption.

1005 The missing (a) has been added to Figure 3.

1006 **Figure 4 and S2: What does CO anomaly mean? What is the reference value?**

1007 By the term “CO anomaly” we mean the fraction of CO observed at Bachok from industrial  
1008 emissions from regions north of 20N. This is explained in Section 3 (lines 285-288) and in  
1009 the supplement. We have added a sentence in the caption for Figure 4 to remind readers.

1010 **Line 126: “Both in the western Pacific region and globally”. It is not clear what**  
1011 **globally means.**

1012 We have removed the word “globally”.

1013 **Line 147: “Various time” needs to be specified (see general comments).**

1014 More sampling information has been added (see earlier response to reviewer 2))

1015 **Line 150: Change “CARIBIC aircraft” to “IAGOS-CARIBIC aircraft” as CARIBIC is part**  
1016 **of the IAGOS program.**

1017 Done

1018 **Line 230: Change “shows the 2014 data ...” to “shows data from CAPE Fuguei in the**  
1019 **end of March, beginning of April 2014”.**

1020 Text has been changed to “*shows the March/April 2014 data...*”. In addition the sampling  
1021 dates have been defined more clearly in the text (see earlier comment of reviewer 2). The  
1022 dates are also evident in the Figures.

1023 **Line 237: Change “March/April 2013” to “mid of March/beginning of April 2013”.**

1024 To be consistent with the text in the previous comment we have not made this change but  
1025 note that the sampling dates have been defined more clearly in the text (see above). The  
1026 dates are also evident on the Figures.

1027 **Line 246: “January/February”: the entire months are not shown so “end of**  
1028 **January/beginning of February” would be more appropriate. “During this phase of the**  
1029 **monsoon”: A recall about the Asian Monsoon phases and references would be useful,**  
1030 **maybe recall that it is the East Asian winter monsoon circulation as mentioned in the**  
1031 **introduction.**

1032 Text has been changed to “*late January/ early February 2014*”. Sampling dates have been  
1033 clarified in methods section.

1034 We have added the words “*East Asian*” when referring to the monsoon and reminded  
1035 readers that this was described earlier.

1036 **Line 252: change “often” to “most of the case studies we are analyzing here” or “for N**  
1037 **days out of Ntotal days of observations” or give the information in Line 277:**

1038 We would prefer to keep the word “often”. This was deliberately vague as we have not done  
1039 any specific analysis to determine how many times the air may have picked up emissions  
1040 from Taiwan. The observation was also based on the NAME animations which are referred  
1041 to in line 285.

1042 **Change “(see supplement for further details)” to “(Fig. S2 in the supplement**  
1043 **material)”.**

1044 Done

1045 **Line 287: Change “in all CARIBIC flights” to “in the seven CARIBIC flights” and**  
1046 **remove “(7)”.**

1047 Done

1048 **Line 334: Need a reference.**

1049 Reference added

1050 **Line 362: Need a reference.**

1051 Reference added

1052 **Line 383: Examples of other chemical pollutants would be useful.**

1053 The pollution we were referring to are chemicals that are routinely found in industrialised  
1054 countries. These include CO, O<sub>3</sub>, CH<sub>4</sub>, volatile organic compounds (VOCs) including  
1055 hydrocarbons, oxygenated hydrocarbons and certain halocarbons. These measurements are  
1056 likely to feature in a future publications.

1057 **Line 384: Remove “etc”.**

1058 Done

1059