

1 **Meteorological constraints on oceanic halocarbons above the Peruvian**  
2 **Upwelling**

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9

10 **Abstract**

11 Halogenated very short lived substances (VSLS) are naturally produced in the ocean and  
12 emitted to the atmosphere. Recently, oceanic upwelling regions in the tropical East Atlantic  
13 were identified as strong sources of brominated halocarbons to the atmosphere. During a  
14 cruise of R/V METEOR in December 2012 the oceanic sources and emissions of various  
15 halogenated trace gases and their mixing ratios in the marine atmospheric boundary layer  
16 (MABL) were investigated above the Peruvian Upwelling for the first time. This study  
17 presents novel observations of the three VSLS bromoform, dibromomethane and methyl  
18 iodide together with high resolution meteorological measurements and Lagrangian transport  
19 modelling. Although relatively low oceanic emissions were observed, except for methyl  
20 iodide, surface atmospheric abundances were elevated. Radiosonde launches during the  
21 cruise revealed a low, stable MABL and a distinct trade inversion above acting both as strong  
22 barriers for convection and trace gas transport in this region. Significant correlations between  
23 observed atmospheric VSLS abundances, sea surface temperature, relative humidity and  
24 MABL height were found. We used a simple source-loss estimate to identify the contribution  
25 of oceanic emissions to observed atmospheric concentrations which revealed that the  
26 observed marine VSLS abundances were dominated by horizontal advection below the trade  
27 inversion. The observed VSLS variations can be explained by the low emissions and their  
28 accumulation under different MABL and trade inversion conditions. This study confirms the  
29 importance of oceanic upwelling and trade wind systems on creating effective transport

30 barriers in the lower atmosphere controlling the distribution of VSLs abundances above  
31 ocean upwelling regions.

32

### 33 **1. Introduction**

34 Short-lived halocarbons from the oceans contribute to reactive atmospheric halogens, which  
35 are involved in tropospheric and stratospheric ozone depletion, aerosol formation, and other  
36 chemical cycles, influencing the fate of pollutants and climate (McGivern et al., 2000;Saiz-  
37 Lopez and von Glasow, 2012;Simpson et al., 2015). Recent studies have identified open  
38 ocean upwelling areas in the Atlantic as large source regions for a number of brominated and  
39 iodinated oceanic trace gases (Quack et al., 2004;Quack et al., 2007;O'Brien et al.,  
40 2009;Raimund et al., 2011;Hepach et al., 2015a). Their sources are related to biological and  
41 chemical processes in the productive waters of the upwelling. The compounds are emitted  
42 from the ocean and are horizontally transported and vertically mixed in the marine  
43 atmospheric boundary layer (MABL) (Carpenter et al., 2010). In the Mauritanian upwelling,  
44 it was found that besides oceanic sources meteorological conditions strongly influenced the  
45 atmospheric mixing ratio of the marine compounds bromoform ( $\text{CHBr}_3$ ), dibromomethane  
46 ( $\text{CH}_2\text{Br}_2$ ) and also methyl iodide ( $\text{CH}_3\text{I}$ ) (Hepach et al., 2014). Especially the combination of  
47 a pronounced low MABL above cold upwelling waters with high concentrations and  
48 emissions of the compounds caused elevated atmospheric mixing ratios. In return, these  
49 atmospheric mixing ratios also reduce the marine emissions through a decrease of the sea-air  
50 concentration gradient (Fuhlbrügge et al., 2013). Similar relationships would be expected for  
51 other oceanic upwelling areas, where not only the oceanic emissions, but also meteorological  
52 conditions in the lowermost atmosphere, i.e., the height, type and structure of the boundary  
53 layer and trade inversion, determine the VSLs contribution to atmospheric chemical  
54 processes. The intense oceanic upwelling in the Southeast Pacific off the coast of Peru  
55 transports large amounts of subsurface waters to the ocean surface and creates one of the  
56 highest productive oceanic regions worldwide (Codispoti et al., 1982). The Peruvian  
57 Upwelling is therefore a potentially intense source region for halogenated VSLs, e.g.  
58 bromoform, dibromomethane and methyl iodide (Yokouchi et al., 1999;Butler et al.,  
59 2007;Carpenter et al., 2009). Indeed, Schönhardt et al. (2008) detected elevated IO columns  
60 during September and November 2005 along the Peruvian coast with the SCIAMACHY  
61 satellite instrument and implied elevated iodine source gases from the Peruvian Upwelling.

62 Although, recent studies investigated halocarbons in the East Pacific (Yokouchi et al.,  
63 2008;Mahajan et al., 2012;Saiz-Lopez et al., 2012;Gómez Martin et al., 2013;Liu et al., 2013)  
64 few studies concentrated on the Peruvian Upwelling in the Southeast Pacific. Only  
65 measurements of methyl iodide exist in this region, revealing atmospheric abundances of 7  
66 ppt (Rasmussen et al., 1982). Observations of bromocarbons above the Peruvian Upwelling  
67 are lacking.

68 In this study we present a high resolution dataset of meteorological parameters, oceanic  
69 concentrations, emissions and atmospheric abundances of VSLS along the Peruvian coast and  
70 in the Upwelling. Not much is known of the oceanic source strength of the VSLS and the  
71 meteorological influence on the marine trace gas distribution and abundances in this region.  
72 The goal of this study is to assess the influence of oceanic upwelling and meteorological  
73 conditions on the atmospheric VSLS abundances above the Peruvian Upwelling, and the  
74 contribution of the local oceanic emissions to MABL and free tropospheric VSLS  
75 concentrations.

76 The paper is structured as following. Chapter 2 gives an overview of the data and methods we  
77 use in this study. Chapter 3 presents the results from our atmospheric and oceanic  
78 observations and analyses the contribution from oceanic VSLS emissions to the MABL, as  
79 well as meteorological constrains on the observations. Chapter 4 discusses the results, before  
80 the study is summarized in Chapter 5.

81

## 82 **2. Data and Methods**

83 The cruise M91 on R/V METEOR from December 01 to 26, 2012 started and ended in Lima,  
84 Peru. The ship reached the most northern position during the cruise on December 03, 2012 at  
85 5° S. In the following three weeks the ship headed southward and reached its southern most  
86 position at 16° S on December 21, 2012. During this time the track alternated between open  
87 ocean sections and sections very close to the Peruvian coast in the cold upwelling waters to  
88 collect coastal as well as open ocean data. Diurnal variations were observed during 6 stations  
89 along the cruise track.

90

### 91 **2.1 Meteorological observations**

92 Meteorological measurements of surface air temperature (SAT), sea surface temperature  
93 (SST), relative humidity, air pressure, wind speed and direction were taken every second at  
94 about 25 m height on R/V METEOR and averaged to 10 minute intervals for our  
95 investigations. Atmospheric profiles of temperature, wind and humidity were obtained by 98

96 radiosonde launches at standard UTC time (0, 6, 12, 18 UTC) and additionally 3 hourly  
97 during the diurnal stations along the cruise track, using Vaisala RS92 radiosondes. Due to  
98 permission limitations, radiosondes could not be launched within 12 nautical miles of the  
99 Peruvian coast. The collected radiosonde data was integrated in near real time into the Global  
100 Telecommunication System (GTS) to improve meteorological reanalysis (e.g. ERA-Interim)  
101 and operational European Centre for Medium Range Weather Forecast models (opECMWF).

102

## 103 **2.2 MABL height**

104 The radiosonde data are used to identify the height of the MABL, which is the atmospheric  
105 surface layer above the ocean in which trace gas emissions are mixed horizontally on a short  
106 time scale of an hour or less by convection and turbulence (Stull, 1988). Two different kinds  
107 of MABL can be distinguished, the convective and the stable MABL, which can be  
108 characterized by the gradient of the virtual potential temperature  $\theta_v$ . A negative or neutral  
109 gradient reveals an unstable convective layer, while a positive gradient reveals a stable  
110 atmospheric layer. In case of an increase of the virtual potential temperature near the surface,  
111 mixing in the MABL is suppressed. The upper limit of the convective MABL is set by a  
112 *stable layer*, e.g., a temperature inversion or a significant reduction in air moisture and is  
113 typically found above open ocean regions between 100 m and 3 km height (Stull,  
114 1988;Seibert et al., 2000). For the determination of this *stable layer* above the convective  
115 MABL, we use the practical approach described in Seibert et al. (2000) and compute the  
116 virtual potential temperature during the radiosonde ascent whose increase with altitude  
117 indicates the base of a *stable layer*. In this study the base of this *stable layer* increased by half  
118 of this *stable layer* depth is the definition for the MABL height. Over oceanic upwelling  
119 regions this stable layer can even descend to the ocean surface (e.g. Höflich et al., 1972 and  
120 Fuhlbrügge et al., 2013).

121

### 122 **2.2.1 Relative humidity**

123 Estimates for atmospheric surface stability and MABL conditions in oceanic upwelling  
124 region can also be obtained from variations of the surface humidity. While the absolute  
125 humidity determines the amount of water in a specific volume of air, the relative humidity is  
126 the ratio of the partial pressure of water vapour to the equilibrium vapour pressure at the  
127 observed temperature. Variations of the SAT therefore directly influence the relative  
128 humidity at the surface. A decrease of the SAT due to cold upwelling water leads to an  
129 increase of the relative humidity, while the absolute humidity stays constant or even

130 decreases due to condensation of water vapour once the relative humidity reaches 100 % and  
131 the air is saturated with water vapour. An elevated relative humidity in this oceanic region  
132 therefore points to stable layers with suppressed mixing of surface air and to a low and stable  
133 MABL height.

134

### 135 **2.2.2 Estimation of MABL height above the upwelling**

136 To estimate the MABL height above upwelling areas close to the coast, where radiosonde  
137 launches were permitted (Section 2.1) a multiple linear regression was applied. Using  
138 observed meteorological parameters revealing significant correlations (see Section 3.5) with  
139 the observed MABL height, relative humidity ( $x_1$ ), SAT ( $x_2$ ), SST ( $x_3$ ) and wind speed ( $x_4$ ),  
140 along the cruise we obtained the following Eq. 1:

141

$$114 \text{ MABL height} = b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 \quad (\text{Eq. 1})$$

with  $b_1 = -0.0117$ ;  $b_2 = 0.0202$ ;  $b_3 = 0.0467$ ;  $b_4 = 0.0089$

142

### 143 **2.3 Atmospheric VSLs measurements**

144 A total of 198 air samples were collected 3 hourly during the cruise at about 20 m height on  
145 the 5<sup>th</sup> superstructure deck of R/V METEOR using a portside jib of 5 – 6 m. The air samples  
146 were pressurized to 2 atm in pre-cleaned stainless steel canisters with a metal bellows pump  
147 and were analysed at the Rosenstiel School for Marine and Atmospheric Sciences (RSMAS,  
148 Miami, Florida) within 6 months after the cruise. Details about the analysis, the instrumental  
149 precision and the preparation of the samples are described in Schaffler et al. (1999) and  
150 Fuhlbrügge et al. (2013). The atmospheric mixing ratios were calculated with a NOAA  
151 standard (SX3573) from GEOMAR.

152

### 153 **2.4 Oceanic concentrations and sea – air flux**

154 102 water samples were taken 3 hourly at a depth of 6.8 m from a continuously working  
155 water pump in the hydrographic shaft, an opening in the base of the ship hull of R/V Meteor,  
156 after December 9, 2012. The samples were then analysed for bromoform, dibromomethane  
157 and methyl iodide and other halogenated trace gases by a purge and trap system, attached to a  
158 gas chromatograph combined with an ECD (electron capture detector) with a precision of 10  
159 % determined from duplicates. The approach is described in detail by Hepach et al. (2014).

160

161 **2.4.1 Sea – air flux**

162 The sea – air flux ( $F$ ) of bromoform, dibromomethane and methyl iodide is calculated with  $k_w$   
163 as transfer coefficient and  $\Delta c$  as concentration gradient between the water and equilibrium  
164 water concentration determined from the atmospheric concentrations (Eq. 2). The transfer  
165 coefficient was determined by the air – sea gas exchange parameterization of Nightingale et  
166 al. (2000) after a Schmidt number ( $Sc$ ) correction for the three gases (Eq. 3).

$$F = k_w \cdot \Delta c \quad (\text{Eq. 2})$$

$$k_w = k_{CO_2} \cdot \frac{Sc^{-\frac{1}{2}}}{600} \quad (\text{Eq. 3})$$

169  
170 Details on deriving the air – sea concentration gradient and emissions are further described in  
171 Hepach et al. (2014) and references therein.

172  
173 **2.5 Trajectory calculations**

174 The Lagrangian Particle Dispersion Model FLEXPART of the Norwegian Institute for Air  
175 Research in the Department of Atmospheric and Climate Research (Stohl et al., 2005) was  
176 used to analyse the air mass origins and the transport of surface air masses along the cruise  
177 track to the free troposphere (Stohl et al., 1998;Stohl and Trickl, 1999). The model includes  
178 moist convection and turbulence parameterizations in the atmospheric boundary layer and  
179 free troposphere (Stohl and Thomson, 1999;Forster et al., 2007). We use the ECMWF  
180 (European Centre for Medium-Range Weather Forecasts) reanalysis product ERA-Interim  
181 (Dee et al., 2011) with a horizontal resolution of  $1^\circ \times 1^\circ$  and 60 vertical model levels as  
182 meteorological input fields, providing air temperature, horizontal and vertical winds,  
183 boundary layer height, specific humidity, as well as convective and large scale precipitation  
184 with a 6 hourly temporal resolution. Due to the spatial resolution of ERA-Interim data along  
185 the Peruvian coast defining the land-sea mask of our trajectory calculations, 98 out of 140  
186 release points for the forward and backward trajectory calculations were analysed along the  
187 cruise track. At each these release points 10,000 forward and 50 backward trajectories were  
188 launched from the ocean surface within  $\pm 30$  minutes and  $\sim 20$  m distance to the ship position.  
189 Time and position of the release events are synchronized with air samples taken on R/V  
190 METEOR (Section 2.3).

191

## 192 **2.6 Oceanic contribution to MABL VSLS abundances**

193 To obtain an estimate of the contribution of local oceanic sources to the atmospheric mixing  
194 ratios in the lowermost atmosphere above the Peruvian upwelling we apply a mass balance  
195 concept to the oceanic emissions, to the time scales of air mass transport and to the chemical  
196 loss (Fuhlbrügge et al., 2015). First we define a box above each release event with a size of  
197  $\sim 400 \text{ m}^2$  around the measurement location and the height of the MABL and assume a steady-  
198 state observed VSLS mixing ratio within the box (Figure 1). During each trajectory release  
199 event we assume the specific sea-air flux to be constant and the emissions to be  
200 homogeneously mixed within the box. Then the contribution of the sea-air flux is computed  
201 as the ratio of the VSLS flux from the ocean into the MABL (in mol per day) and the total  
202 amount of VSLS in the box (in mol) and is defined as the Oceanic Delivery (OD) and OD is  
203 given in percentage per day. In addition to the delivery of oceanic VSLS to the box, the loss  
204 of VSLS out of the box into the free troposphere is defined as the CONvective Loss (COL)  
205 and is derived from the mean residence time derived from the FLEXPART trajectories in the  
206 box during each release event. Since this process is a loss process, COL is given as a negative  
207 quantity and in percentage per day. The chemical degradation of VSLS by OH and photolysis  
208 in the MABL is considered by the chemical lifetime of each compound in the MABL. We use  
209 lifetimes of 16 days for bromoform and 60 days for dibromomethane (Hossaini et al., 2010)  
210 and 3 days for methyl iodide (R. Hossaini, personal communication), representative for the  
211 tropical boundary layer. The Chemical Loss (CL) acts as loss process as well and is given as  
212 a negative quantity in percentage per day. We further assume a steady state in the box. OD,  
213 COL and CL must therefore be balanced by an advective transport of air masses in and out of  
214 the box. The change of the VSLS through advective transport is defined as Advective  
215 Delivery (AD) and given in percentage per day.

216 By ratioing OD to COL, we estimate an Oceanic Delivery Ratio (ODR) (Eq. 4):

217

$$ODR = \frac{OD [\%d^{-1}]}{-COL [\%d^{-1}]} = \frac{Sea-Air \text{ flux contribution } [\%d^{-1}]}{Loss \text{ of box air to the FT } [\%d^{-1}]} \quad (\text{Eq. 4})$$

218

219 Similarly, the Chemical Loss in the box (CL) and the change in VSLS due to advection (AD)  
220 are related to COL to get the Chemical Loss Ratio (CLR) and the Advective Delivery Ratio  
221 (ADR) with  $ADR = 1 - CLR - ODR$ . Since CL, OD and AD are divided by  $-COL$ , ratios for  
222 source processes are positive and negative for loss processes (Fuhlbrügge et al., 2015).

223

### 224 **3. Observations on R/V METEOR**

#### 225 **3.1. Meteorological observations**

226 The Peruvian coast is dominated by the southern hemisphere trade wind regime with  
227 predominantly southeast winds (Figure 2). The Andes, which are known to act as a barrier to  
228 zonal wind in this region, affect the horizontal air mass transport along the coast (Figure 2b-  
229 d). The steeply sloping mountains at the coast form strong winds parallel to the South  
230 American coastline (Garreaud and Munoz, 2005), leading to distinct wind-driven oceanic  
231 upwelling of cold water along the coast. The 10-day backward trajectories reveal  
232 predominantly near-shore air masses with coastal influence and marine air masses (Figure 2).  
233 The average wind direction observed on R/V Meteor during the cruise is  $160^\circ \pm 34^\circ$  (mean  
234  $\pm \sigma$ ) with a moderate average wind speed of  $6.2 \pm 2.2 \text{ ms}^{-1}$  (Figure 3b). ERA-Interim reveals  
235 similar winds along the cruise track with a mean wind speed of  $5.6 \pm 1.8 \text{ ms}^{-1}$  and a mean  
236 wind direction of  $168^\circ \pm 21^\circ$  (not shown here). The divergence of the wind driven Ekman  
237 transport along the Peruvian coast leads to the observed oceanic upwelling of cold waters.  
238 The most intense upwelling is observed for several times near the coast where both, SST and  
239 SAT rapidly drop from  $19 - 22^\circ \text{C}$  to less than  $18^\circ \text{C}$  (Figure 3a). The impact of the cold  
240 upwelling water on the observed air masses is also visible in the observed humidity fields  
241 (Figure 3c). Here, the decreasing SAT reduces the amount of water vapour that the surface air  
242 is able to contain, leading to an increase of the relative humidity. The decreasing SAT and  
243 increasing relative humidity above the oceanic upwelling indicate a stable atmospheric  
244 surface layer with suppressed vertical mixing. The absolute humidity stays constant or even  
245 decreases above the oceanic upwelling due to condensation of water vapour when surface air  
246 cools and becomes saturated, which coincides with fog observations on the ship above the  
247 upwelling regions. A decrease of the absolute humidity outside the upwelling points to a  
248 change in advected air masses for example between December 9 and 11, but also on  
249 December 19, 2012 (Figure 3c).

250

#### 251 **3.2. VLSL observations and oceanic emissions**

252 Surface bromoform concentrations in the Peruvian upwelling are generally lower during the  
253 cruise compared to the Mauritanian upwelling while dibromomethane surface water  
254 concentrations are comparable. However methyl iodide concentrations are almost 8 times  
255 higher than in the Mauritanian upwelling (Figure 3d, Table 1, Hepach et al., 2014). Samples  
256 taken in the upwelling areas show elevated concentrations compared to the open ocean for all

257 compounds. For further discussion on the distribution of the oceanic halocarbons, see Hepach  
258 et al. (2016, submitted to ACPD).

259 Atmospheric mixing ratios of bromoform are on average  $2.91 \pm 0.68$  ppt (Table 1).  
260 Dibromomethane mixing ratios of  $1.25 \pm 0.26$  ppt ppt are low and show a similar temporal  
261 pattern with bromoform (Table 3). Mixing ratios of both compounds are significantly lower  
262 above the Peruvian upwelling compared to observations above the Mauritanian upwelling,  
263 while methyl iodide mixing ratios are comparable (Fuhlbrügge et al., 2013). Elevated mixing  
264 ratios for all three compounds are generally found above intense cold oceanic upwelling  
265 regions close to the Peruvian coast (Figure 3e). While the bromocarbons double above the  
266 upwelling, methyl iodide mixing ratios increase up to 5-fold, showing its stronger  
267 accumulation in the low boundary layer.

268 The concentration ratio of dibromomethane and bromoform can be used as an indicator of  
269 fresh bromocarbon sources along coastal areas. Low ratios of about 0.1 have been observed at  
270 coastal source regions and are interpreted as the emission ratios of macro algae (Yokouchi et  
271 al., 2005; Carpenter et al., 2003). The applied shorter mean lifetime of bromoform (15 days)  
272 in contrast to dibromomethane (94 days) in the boundary layer after Carpenter et al. (2014)  
273 leads to an increase of the ratio during transport as long as the air mass is not enriched with  
274 fresh bromoform. A general decrease of the concentration ratio is found from the North to the  
275 South during the cruise (Figure 3f), implying relatively remote air masses in the North and an  
276 intensification of fresh sources towards the south, which is also reflected by the elevated  
277 water concentrations. Atmospheric methyl iodide measurements along the cruise track reveal  
278 a mean mixing ratio of  $1.54 \pm 0.49$  ppt, which, similar to the two bromocarbons, maximizes  
279 over the coastal upwelling regions (Figure 3e).

280 Oceanic emissions during the cruise were calculated from the synchronized measurements of  
281 sea water concentrations and atmospheric mixing ratios, sea surface temperatures and wind  
282 speeds, measured on R/V METEOR (Section 2.4.1). Oceanic concentrations and atmospheric  
283 mixing ratios of each compound are weakly or not at all correlated ( $R_{\text{bromoform}} = 0.00$ ,  
284  $R_{\text{dibromomethane}} = 0.29$  and  $R_{\text{methyl iodide}} = 0.34$ ). Mean sea-air fluxes of the bromocarbons during  
285 the cruise are very low with  $117 \pm 492$  pmol m<sup>-2</sup> hr<sup>-1</sup> for bromoform and  $245 \pm 299$  pmol m<sup>-2</sup>  
286 hr<sup>-1</sup> for dibromomethane, but for methyl iodide the fluxes are elevated with  $856 \pm 623$  pmol  
287 m<sup>-2</sup> h<sup>-1</sup> (Figure 3g, Table 1). Further investigations of the distributions and sources of  
288 iodinated compounds during this cruise are carried out by Hepach et al. (2015b).

289

### 290 **3.3. Lower atmosphere conditions**

291 The relative humidity shows a strong vertical gradient from over 75 % to less than 50 % at ~1  
292 km height (Figure 4a) which indicates an increase of the atmospheric stability with height due  
293 to suppressed mixing. This convective barrier, known as the trade inversion (Riehl, 1954,  
294 1979;Höflich, 1972), is also reflected in the meridional wind (Figure 4b). Below ~1 km  
295 altitude the Southeast trade winds create a strong positive meridional wind component, also  
296 visible in the forward trajectories (Figure 2c-d). The flow of air masses in the Hadley Cell  
297 back to the subtropics causes a predominantly northerly wind above ~1 km height. The  
298 intense increase of  $\theta_v$  in combination with the relative humidity decrease and the wind shear  
299 at ~1 km height identifies this level as a strong vertical transport barrier (Figure 4c). Above  
300 the cold upwelling water, temperature inversions create additional stable layers above the  
301 surface, leading to very low MABL heights of < 100 m, e.g., on December 03, 08 or 17, 2012  
302 and to a reduced vertical transport of surface air. The mean MABL height from the  
303 radiosonde observations is  $370 \pm 170$  m (ERA-Interim  $376 \pm 169$  m). The relative humidity,  
304 SAT, SST and wind speed are good indicators for the MABL conditions in this oceanic  
305 region and these meteorological parameters show significant correlations with the observed  
306 MABL height (Table 3). Thus, we use a multiple linear regression based on these parameters  
307 to estimate the MABL height above the coastal upwelling (Section 2.2.2). The regressed  
308 MABL heights above the cold upwelling regions are  $158 \pm 79$  m and go down to even 10 m  
309 as was previously observed above the Mauritanian Upwelling (Fuhlbrügge et al., 2013). With  
310 the regressed MABL heights, the mean MABL height during the cruise decreases to  $307 \pm$   
311  $177$  m. The stable atmospheric conditions from the surface to the trade inversion lead to  
312 strong transport barriers and to a suppressed transport of surface and MABL air into the free  
313 troposphere (Figure 4d).

314 We interpret the observations as the following. In the region of the Peruvian Upwelling,  
315 compounds emitted from the ocean and observed at the marine surface are first  
316 homogeneously distributed within the MABL during a couple of hours, before advection  
317 transport them further within the second transport barrier of the lowermost atmosphere the  
318 trade wind inversion. For air masses above or close to oceanic upwelling regions, the MABL  
319 height is the first weak transport barrier on short time scales (hours), while the trade  
320 inversions acts as the second more pronounced barrier for vertical transport on long time  
321 scales (days).

322

### 323 **3.4. Contribution of oceanic emissions to observed VSLS abundances in the** 324 **MABL**

325 We estimate the contribution of oceanic emissions to mixing ratios within the MABL and  
326 below the trade inversion with a VSLS source-loss estimate (Table 2). The loss of VSLS out  
327 of the MABL box is  $-351.0 \text{ \% d}^{-1}$  and equal for all compounds, since it is computed from the  
328 loss of trajectories out of the box. The loss is based on a mean residence time of the  
329 FLEXPART trajectories of 7 hours in the observed MABL height during the cruise. The ratio  
330 of the OD of each compound and the COL results in the particular ODR. The ODR reveals  
331 that on average only 3 % of the observed atmospheric bromoform in the MABL origins from  
332 nearby oceanic emissions and that 99 % are advected. Local oceanic emissions of  
333 dibromomethane contribute about 10 % of the observed abundances in the MABL, while  
334 methyl iodide emissions contribute with 28 %, which is far less compared to observations in  
335 other source regions with high convection as in the South China and Sulu Seas (Fuhlbrügge  
336 et al., 2015). Generally, the low ODRs along the cruise track are caused by the relatively low  
337 oceanic emissions. Since the observed atmospheric concentrations cannot be explained by the  
338 local oceanic emissions advection leads to the background concentrations of bromoform and  
339 methyl iodide. According to the backward trajectories, potential source regions may be found  
340 closer to the coast and to the South. The elevations of the atmospheric mixing ratios above  
341 the cold coastal upwelling can partly be explained by accumulation of local oceanic  
342 emissions in the stable low MABL. However, as the emissions appear generally not strong  
343 enough, except for methyl iodide, to explain the mixing ratios, the contribution of coastal  
344 sources is very likely (Figure 2b). While the surface air masses can leave the MABL within  
345 hours, they are suppressed from entering the free troposphere through the trade inversion  
346 barrier. Adapting an average trade inversion height of 1.1 km as the transport barrier for  
347 surface air masses into the free troposphere reveals an average residence time of the  
348 FLEXPART trajectories of 48 hrs below this trade inversion height. The atmospheric VSLS  
349 below the trade inversion originate to 11 % from oceanic emissions (ODR) for bromoform, to  
350 33 % for dibromomethane and to 92 % for methyl iodide. The increased residence time of air  
351 masses below the trade inversion, reflected by the FLEXPART trajectories, leads to a  
352 stronger enrichment of air masses with VSLS from the oceanic emissions, reflected by OD,  
353 compared to the MABL box. However, the low sea-air fluxes of bromoform and  
354 dibromomethane are by far not strong enough to lead to the observed mixing ratios. These  
355 numbers imply that observed VSLS concentrations are advected below the trade inversion in  
356 the more open ocean regions during the cruise. An overall discussion is given in Section 4.

357

### 358 **3.5. Meteorological constrains on atmospheric VSLS in the MABL**

359 Fuhlbrügge et al. (2013) identified the influence of meteorological conditions, in particular of  
360 MABL height variations on VSLS abundances in the tropical Northeast Atlantic above the  
361 Mauritanian Upwelling, and suggested a general correlation of MABL conditions and VSLS  
362 abundances over oceanic upwelling regions. Indeed, we also find significant high correlations  
363 between meteorological parameters and the abundances of bromoform, dibromomethane and  
364 methyl iodide (Table 3) along the Peruvian coast. The predominantly moderate winds during  
365 the cruise are negatively correlated with the atmospheric VSLS and positively correlated with  
366 the MABL height. This shows that VSLS abundances tend to be elevated during periods of  
367 lower wind speeds which occur also lead to reduced mixing of surface air and therefore to  
368 lower MABL heights, in particular above the coastal upwelling events on December 11, 15-  
369 17 and 24, 2012, where local sources could accumulate even more. SAT and SST both are  
370 negatively correlated with atmospheric VSLS, since elevated atmospheric VSLS mixing  
371 ratios are generally found close to the oceanic upwelling regions with low SATs and SSTs. In  
372 these regions the decrease of the SATs leads to an increase of the relative humidity (section  
373 3.1), resulting in a significantly high correlation between the surface relative humidity and  
374 the VSLS. Since SAT and SST impact the MABL, which affects the relative humidity, these  
375 correlation coefficients are co-correlated with each other. Correlation coefficients between  
376 the MABL height and the VSLS are slightly lower (Table 3). A principle component analysis  
377 of the parameters in Table 3 furthermore underlined a strong connection between SAT, SST,  
378 MABL height, relative humidity and atmospheric mixing ratios of bromoform and  
379 dibromomethane (not shown here).

380 The results reveal that the MABL properties (height and stability) during M91 influence the  
381 VSLS abundances at the marine surface, although not as distinct as above the Mauritanian  
382 Upwelling during the DRIVE campaign (Fuhlbrügge et al., 2013). A comparison between the  
383 observations from this campaign and DRIVE (Figure 5) shows that the lower variance of  
384 observations during M91 may explain the lower correlation. Generally higher emissions and  
385 occasional lower and even more stable MABL-heights during DRIVE can explain up to  
386 100% of the atmospheric abundances (Fuhlbrügge et al., 2013; Hepach et al., 2014), while  
387 during M91 the observed elevations could only partly be explained by the local oceanic  
388 emissions.

389

## 390 **4. Discussion**

391 The observations reveal a significant correlation between the MABL height and atmospheric  
392 VSLs abundances above the Peruvian Upwelling. However, the correlation coefficients  
393 between the determined MABL height and the atmospheric VSLs are not as high as above  
394 the Mauritanian Upwelling during the DRIVE campaign (Fuhlbrügge et al., 2013). Reasons  
395 might be the large area of the investigated region in the Northeast Atlantic Ocean during the  
396 DRIVE campaign ( $25^\circ$  latitude x  $10^\circ$  longitude) in contrast to this study along the Peruvian  
397 coast ( $12^\circ$  latitude x  $2^\circ$  longitude). M91 observations therefore involve less variability of  
398 covered oceanic regimes of open ocean and coastal upwelling, VSLs concentrations and  
399 meteorological parameters, in particular of the MABL height, than the DRIVE observations.  
400 The Andes along South America lead to predominantly Southerly winds along the West coast  
401 line with minor continental influence, while the Mauritanian Upwelling is influenced by both,  
402 maritime and continental air masses. The latter can lead to strong surface inversions above  
403 the Mauritanian Upwelling and strongly suppressed mixing of surface air. Although our  
404 investigations revealed low MABL heights close to the Peruvian coast, the distinct surface  
405 inversions as observed above the Mauritanian Upwelling are not present in the available  
406 radiosonde data for this Peruvian Upwelling region. In addition, the relatively low sea-air  
407 fluxes of bromoform and dibromomethane, caused by moderate winds and small  
408 concentration gradients between the surface ocean and the surface atmosphere, as well as the  
409 short lifetime of methyl iodide lead to an insufficient enrichment of VSLs in the atmosphere.  
410 The observed air masses therefore contain VSLs mixing ratios which are predominantly  
411 advected. This is confirmed by our computed ADR (Section 3.4). The backward trajectories  
412 reveal air masses originating from the open ocean, which are transported along the coast for  
413 about 5 days until they reach the ship. In combination with the distinct trade inversion acting  
414 as strong barrier to the vertical mixing of trace gases, air-masses along the coast travel close  
415 to the surface where they can be enriched with local emissions before they are observed on-  
416 board. In addition, the in-situ observed oceanic emissions along the cruise track of R/V  
417 METEOR therefore cause small variations to the accumulated background mixing ratios of  
418 the advected air masses. This leads to lower correlation coefficients between the MABL  
419 height and the VSLs abundances compared to the Mauritanian Upwelling.  
420 Although the oceanic emissions are already well mixed within days below the trade  
421 inversion, methyl iodide mixing ratios indicate a positive correlation with the trade inversion  
422 height, which is unexpected. The correlation coefficient might be artificial, as we observe  
423 elevated methyl iodide above the upwelling, where trade wind inversion heights are missing  
424 but can be assumed to be low (Riehl, 1954), which is also indicated by the correlation

425 coefficients with SAT and SST. Nevertheless, this circumstance should be taken into account  
426 in future studies.

427 The contribution of oceanic emissions to the atmospheric mixing ratios in the MABL of the  
428 Peruvian upwelling reveals to be rather low in its more open ocean area under the given  
429 meteorological conditions. While the cruise track covered a representative area of the  
430 Peruvian upwelling elevated oceanic VSLs emissions that could explain the generally high  
431 atmospheric VSLs were only observed for methyl iodide. Bromocarbon emissions would  
432 have to be two magnitudes larger to explain the observed VMR in the more open ocean  
433 regions and a magnitude larger in the direct coastal upwelling regions with low MABL  
434 heights. These observations of the brominated compounds need to include upwind advection  
435 of elevated sources from the South, and higher elevated coastal emissions not measured  
436 during the cruise, while dynamical fluctuations in emissions scenarios close to the cruise time  
437 and place may also have to be considered.

438 Uncertainties may result from the applied method, which accounts for a 400 m<sup>2</sup> box around a  
439 measurement point assuming steady state. The cruise track covered a significantly large area  
440 of the Peruvian Upwelling between 5° S and 16° S and higher elevated seas surface  
441 concentrations and emissions are not to be expected during these rather stable meteorological  
442 conditions. Additional uncertainties in our source-loss estimate may arise from deficiencies in  
443 the meteorological input fields from ERA-Interim reanalysis as well as from the air mass  
444 transport simulated by FLEXPART. Both could lead to either a shorter or longer residence  
445 time of the surface air masses within the MABL or below the trade inversion and thus  
446 influence the COL term. In particular very close to the coast, where the source-loss estimate  
447 could not be applied due to the trajectory analysis gaps (Section 2.5), the ODRs of the  
448 compounds might be different. Here potential high coastal emissions in combination with  
449 stable atmospheric stratification leading to slow vertical transport into the free troposphere,  
450 could significantly increase the oceanic contribution to the MABL and to the atmosphere  
451 below the trade inversion and explain the elevated atmospheric mixing ratios. In addition,  
452 different parameterizations for the wind-based transfer coefficient  $k_w$ , as discussed in  
453 Lennartz et al. (2015) and Fuhlbrügge et al (2015) in more detail, can impact the air-sea gas  
454 exchange and thus the ODRs. Applying the  $k_w$  parameterizations of Liss and Merlivat  
455 (1986) as well as Wanninkhof and McGillis (1999) lead both to mean ODRs in the MABL of  
456 0.02 (bromoform), 0.07 (dibromomethane) and 0.21 (methyl iodide) and below the trade  
457 inversion of 0.08 / 0.08 (bromoform), 0.25 / 0.26 (dibromomethane) and 0.69 / 0.75 (methyl  
458 iodide) and thus an even lower oceanic contribution to the atmosphere in this region. Further

459 uncertainties may arise from variations of the MABL VSLs lifetimes and thus the chemical  
460 degradation of the compounds we use in this study. This would affect the computed  
461 advection (ADR) and not the oceanic contribution. After the air masses are observed on R/V  
462 METEOR, the 10 day FLEXPART forward trajectories reveal a near-surface transport  
463 towards the equator (Figure 2c-d). These trajectories predominantly stay below 1 km altitude  
464 due to the horizontal extent of the trade inversion. The contribution of oceanic VSLs  
465 emissions from the Peruvian Upwelling to the free troposphere above this region is therefore  
466 strongly suppressed by the trade inversion (Figure 4d). A contribution of oceanic emissions  
467 from the Peruvian Upwelling to the free troposphere is only achieved in the inner tropics after  
468 a transport time of 5 – 8 days, where the VSLs abundances are transported into higher  
469 altitudes. Since the lifetime of methyl iodide is only 4 days in the MABL a significant  
470 contribution of methyl iodide from the Peruvian upwelling to observations made by  
471 Yokouchi et al. (2008) at San Cristobal, Galapagos is not to be expected. However, it can  
472 partly explain the elevated IO observed above the Peruvian upwelling (Hepach et al., 2016, to  
473 be submitted; Schönhardt et al., 2008). The elevated mixing ratios of methyl iodide is further  
474 investigated by Hepach et al. (2015b). It has to be noted that the determined low contribution  
475 of oceanic emissions and boundary layer air to the free troposphere in this region is only  
476 representative for normal El Niño Southern Oscillation conditions as it was observed in  
477 December 2012  
478 ([http://www.cpc.ncep.noaa.gov/products/analysis\\_monitoring/enso\\_disc\\_nov2012/ensodisc.p](http://www.cpc.ncep.noaa.gov/products/analysis_monitoring/enso_disc_nov2012/ensodisc.pdf)  
479 [df](http://www.cpc.ncep.noaa.gov/products/analysis_monitoring/enso_disc_nov2012/ensodisc.pdf)). Since the Walker Circulation is reversed during El Niño, upwelling along the Peruvian  
480 coast is known to be suppressed and convective activity enhanced (Philander, 1989).

481

## 482 **5. Summary**

483 This study investigated the contribution of oceanic emissions to VSLs abundances in the  
484 lowermost atmosphere as well as meteorological constraints on this contribution above both,  
485 coastal upwelling and open ocean along the Peruvian coast during December 2012.  
486 Meteorological data were obtained on R/V METEOR near the ocean surface and by  
487 radiosondes up to the stratosphere. Oceanic VSLs emissions along the cruise track were  
488 determined from air and surface water data. The transport of air masses was determined with  
489 FLEXPART trajectories.

490 Oceanic upwelling was observed close to the Peruvian coast. On average a low, stable MABL  
491 height of  $307 \pm 177$  m was encountered during the cruise, decreasing to on average 100 m  
492 above the upwelling. A distinct trade inversion at  $1.1 \pm 0.3$  km height evolved as the

493 dominant transport barrier for MABL air into the free troposphere during the cruise. The  
494 halogenated VSLS bromoform and dibromomethane showed low oceanic emissions of  $117 \pm$   
495  $492 \text{ pmol m}^{-2} \text{ hr}^{-1}$  for bromoform and  $245 \pm 299 \text{ pmol m}^{-2} \text{ hr}^{-1}$  for dibromomethane, while  
496 methyl iodide emissions were elevated with  $856 \pm 623 \text{ pmol m}^{-2} \text{ hr}^{-1}$ . The atmospheric  
497 mixing ratios of the compounds were elevated with  $2.9 \pm 0.7$  ppt (bromoform),  $1.3 \pm 0.3$  ppt  
498 (dibromomethane) and  $1.5 \pm 0.5$  ppt (methyl iodide). The oceanic emissions along the cruise  
499 track explained on average only 3 % (-8 to 33 %) of bromoform, 10 % (-5 to 45 %) of  
500 dibromomethane, and 28 % (3 to 80 %) of methyl iodide abundances in the MABL. Thus, the  
501 expected significant contribution of local oceanic VSLS emissions from the Peruvian  
502 upwelling to the overlying atmosphere was not captured during the time and location of the  
503 cruise. The elevated atmospheric VSLS mixing ratios above the Peruvian upwelling therefore  
504 appear largely advected and enriched along the Peruvian coast before reaching the ship.  
505 Additional potential source regions must exist closer to the coast and also further South of the  
506 cruise track along the coast line. Nevertheless, significant correlations between the MABL  
507 height and marine atmospheric abundances of the VSLS reveal an impact of the oceanic  
508 emissions on the atmospheric VSLS mixing ratio variations.

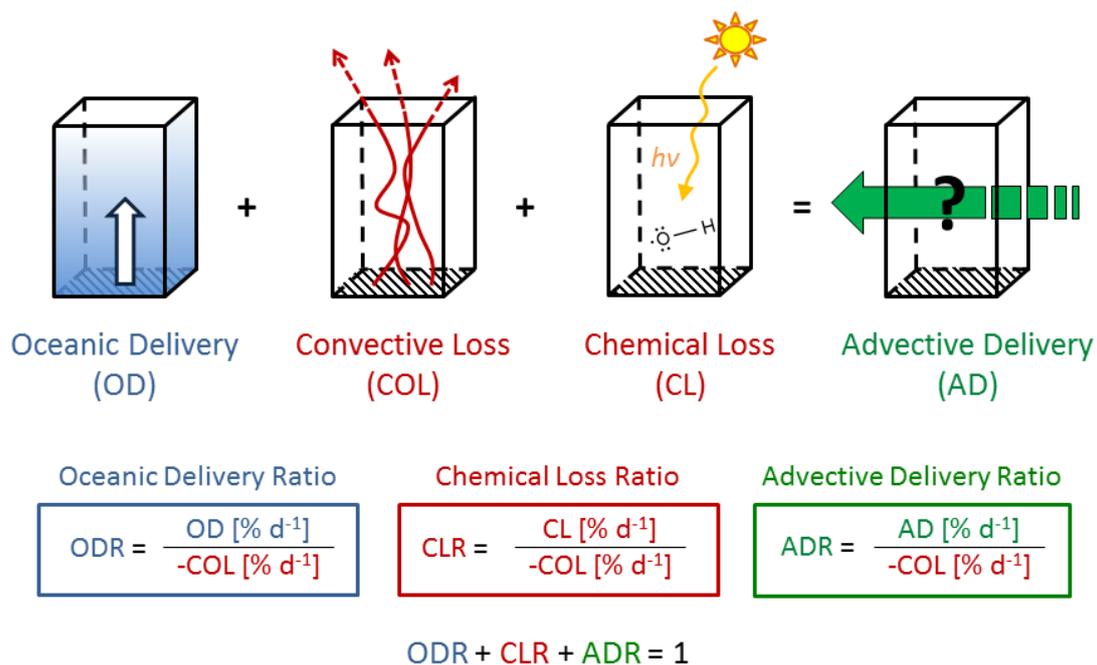
509 Our study confirms that MABL height and stability are generally related with atmospheric  
510 VSLS abundances above oceanic upwelling regions. Additionally, a widespread trade  
511 inversion can lead to a near-surface accumulation of the VSLS and thus also impact oceanic  
512 emissions. Despite the observed elevated atmospheric concentrations during the cruise, a  
513 significant contribution of oceanic emissions to the atmosphere, in particular of the  
514 bromocarbons bromoform and dibromomethane, was not identified in the observed area  
515 during the time of the cruise. Further studies are necessary to clearly uncover the source  
516 regions of the elevated atmospheric VSLS in the Peruvian upwelling. Also the double  
517 transport barrier phenomena should be investigated in future studies of other oceanic  
518 upwelling regions as well.

519

520       **Acknowledgements**

521       This study was supported by the BMBF grant SOPRAN II FKZ 03F0611A. We acknowledge  
522       the authorities of Peru for the permissions to work in their territorial waters. We thank the  
523       European Centre for medium range weather forecast (ECMWF) for the provision of ERA-  
524       Interim reanalysis data and the Lagrangian particle dispersion model FLEXPART used in this  
525       publication. We also like to thank the captain and crew of R/V METEOR, and the Deutscher  
526       Wetterdienst (DWD) for the support.

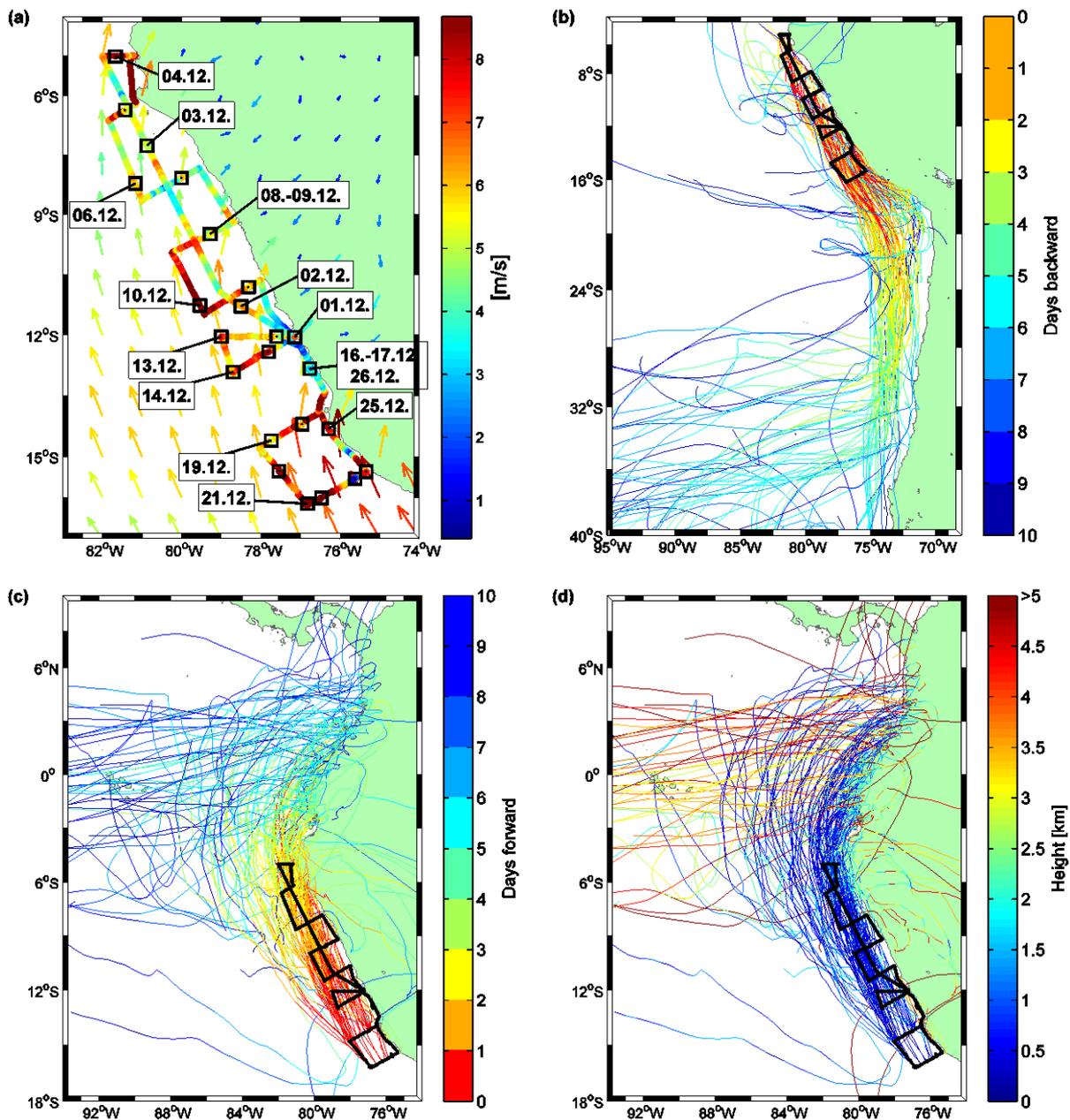
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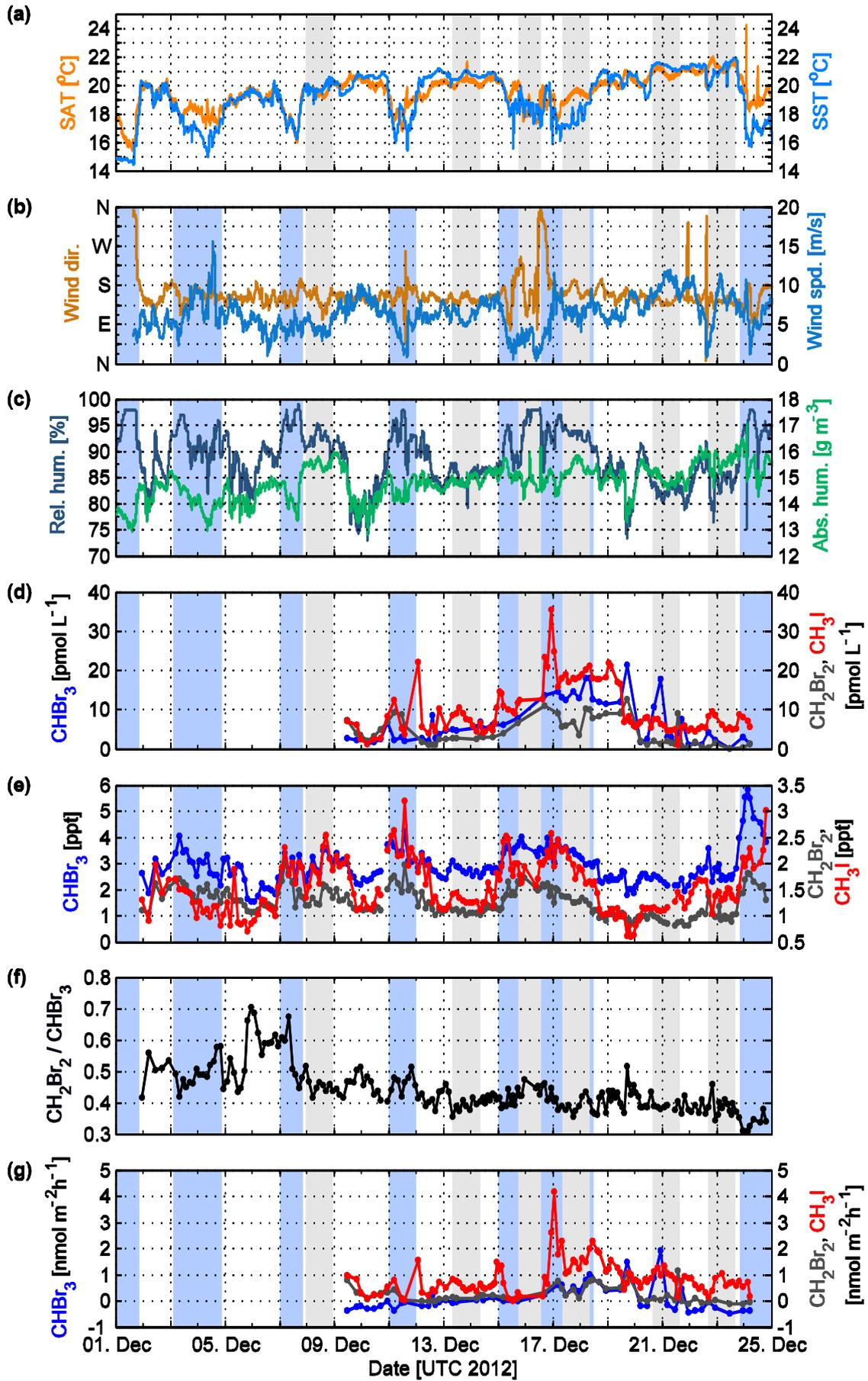
530 Figure 1: Schematic summary of the components of the applied mass-balance concept from  
 531 Fuhlbrügge et al. (2015): Oceanic Delivery (OD), the Convective Loss (COL), the Chemical  
 532 Loss (CL), the Advective Delivery (AD), the Oceanic Delivery Ratio (ODR), the Chemical  
 533 Loss Ratio (CLR) and the Advective Delivery Ratio (ADR). The shaded area reflects an area  
 534 of 400 m<sup>2</sup>.

535



536

537 Figure 2a-d: (a) 10 minute mean of wind speed observed on R/V METEOR displayed along  
 538 the cruise track; monthly mean (December 2012) of 10 m wind speed and direction from  
 539 ERA-Interim displayed as arrows. (b) Extract from 10-day FLEXPART backward trajectories  
 540 coloured according to the time until they reach the specific ship position on the cruise track of  
 541 R/V METEOR (black). (c) Extract from 10-day FLEXPART forward trajectories coloured  
 542 according to the time since they were released. (d) same as c) coloured according to the  
 543 height (km) of the trajectories.

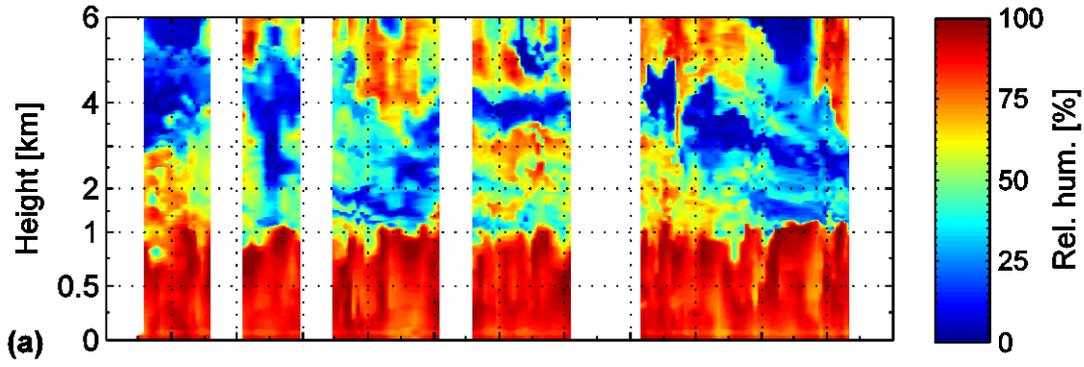


545 Figure 3a-e: Observations during December 1 – 25, 2012 on R/V METEOR. Diurnal stations  
546 are indicated by grey background shades. (a) 10 minute mean of the SAT (orange) and the  
547 SST (blue) in °C. According to SST decrease, upwelling regions are marked with a light blue  
548 background shade in Figure 3b-e. (b) 10 minute mean of wind direction in cardinal directions  
549 (ocher) and wind speed in m/s (blue). (c) 10 minute mean of relative humidity in % (dark  
550 blue) and absolute humidity in  $\text{gm}^{-3}$  (green). (d) Oceanic surface concentrations of  
551 bromoform ( $\text{CHBr}_3$ , blue), dibromomethane ( $\text{CH}_2\text{Br}_2$ , dark grey) and methyl iodide ( $\text{CH}_3\text{I}$ ,  
552 red) in  $\text{pmol L}^{-1}$ . (e) Atmospheric mixing ratios of bromoform, dibromomethane and methyl  
553 iodide in ppt. (f) Concentration ratio of dibromomethane and bromoform. (g) Sea-air flux for  
554 bromoform, dibromomethane and methyl iodide in  $\text{pmol m}^{-2} \text{h}^{-1}$ .

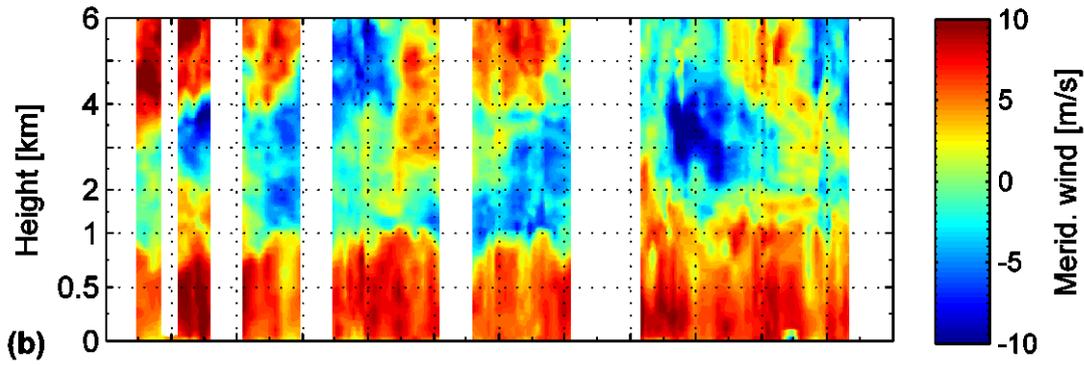
555 Table 1: Oceanic concentrations, atmospheric mixing ratios and sea-air fluxes of bromoform  
 556 ( $\text{CHBr}_3$ ), dibromomethane ( $\text{CH}_2\text{Br}_2$ ), the concentration ratio of bromoform and  
 557 dibromomethane and methyl iodide ( $\text{CH}_3\text{I}$ ) observed during the cruise. Values are given in  
 558 mean  $\pm 1\sigma$  [range].

	$\text{CHBr}_3$	$\text{CH}_2\text{Br}_2$	$\text{CH}_2\text{Br}_2 / \text{CHBr}_3$	$\text{CH}_3\text{I}$
Oceanic concentration [ $\text{pmol L}^{-1}$ ]	$6.6 \pm 5.5$ [0.2 – 21.5]	$4.3 \pm 3.4$ [0.2 – 12.7]	$0.9 \pm 0.8$ [0.1 – 4.2]	$9.8 \pm 6.3$ [1.1 – 35.4]
Atmospheric mixing ratio [ppt]	$2.9 \pm 0.7$ [1.5 – 5.9]	$1.3 \pm 0.3$ [0.8 – 2.0]	$0.4 \pm 0.1$ [0.3 – 0.7]	$1.5 \pm 0.5$ [0.6 – 3.2]
Sea-air flux [ $\text{pmol m}^{-2} \text{hr}^{-1}$ ]	$117 \pm 492$ [-477 – 1916]	$245 \pm 299$ [-112 – 1169]	$0.4 \pm 8.6$ [-24.5 – 48.9]	$856 \pm 623$ [18 - 4179]

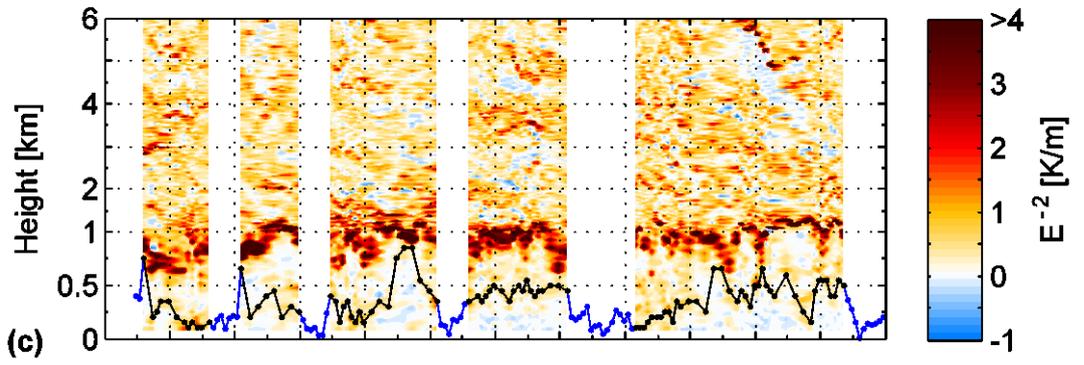
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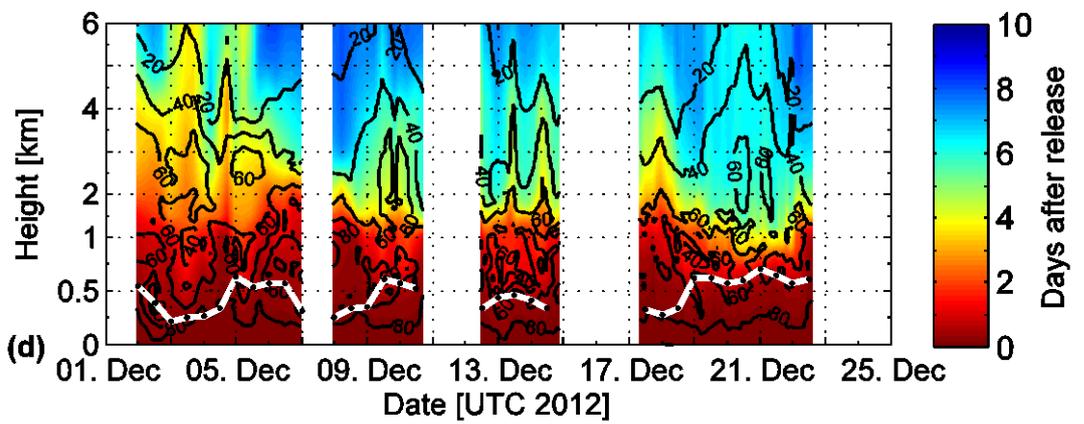
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563

564 Figure 4: (a-c) Radiosonde observations of the lower 6 km of the atmosphere between  
565 December 2 and 24, 2012 on R/V Meteor. Shown are (a) the relative humidity in %, (b) the  
566 meridional wind in m/s and (c) the gradient of the virtual potential temperature in  $E^{-2}$  K/m in  
567 combination with the determined MABL height (black) and the complimented MABL height  
568 above the oceanic upwelling from the multiple linear regressions (blue). (d) Distribution of  
569 10-day FLEXPART forward trajectories. The black contour lines give the amount of  
570 trajectories in percentage that reach a specific altitude within the 10 days. The elapsed time in  
571 days until these trajectories reach this height is reflected by the colour shading. The white line  
572 shows the ERA-Interim MABL height at the ship position. Trajectory analyses gaps close to  
573 the coast are whitened (Section 2.5). The y-axes are non-linear.

574 Table 2: Mean  $\pm 1\sigma$  of Oceanic Delivery (OD), Advective Delivery (AD), Chemical Loss  
 575 (CL), Convective Loss (COL), Oceanic Delivery Ratio (ODR), Advective Delivery Ratio  
 576 (ADR) and Chemical Loss Ratio (CLR) of bromoform ( $\text{CHBr}_3$ ), dibromomethane ( $\text{CH}_2\text{Br}_2$ )  
 577 and methyl iodide ( $\text{CH}_3\text{I}$ ). Parameters have been computed for a box with the vertical  
 578 extension of the MABL height (MABLH) and a mean trade inversion height of 1.1 km (TIH).

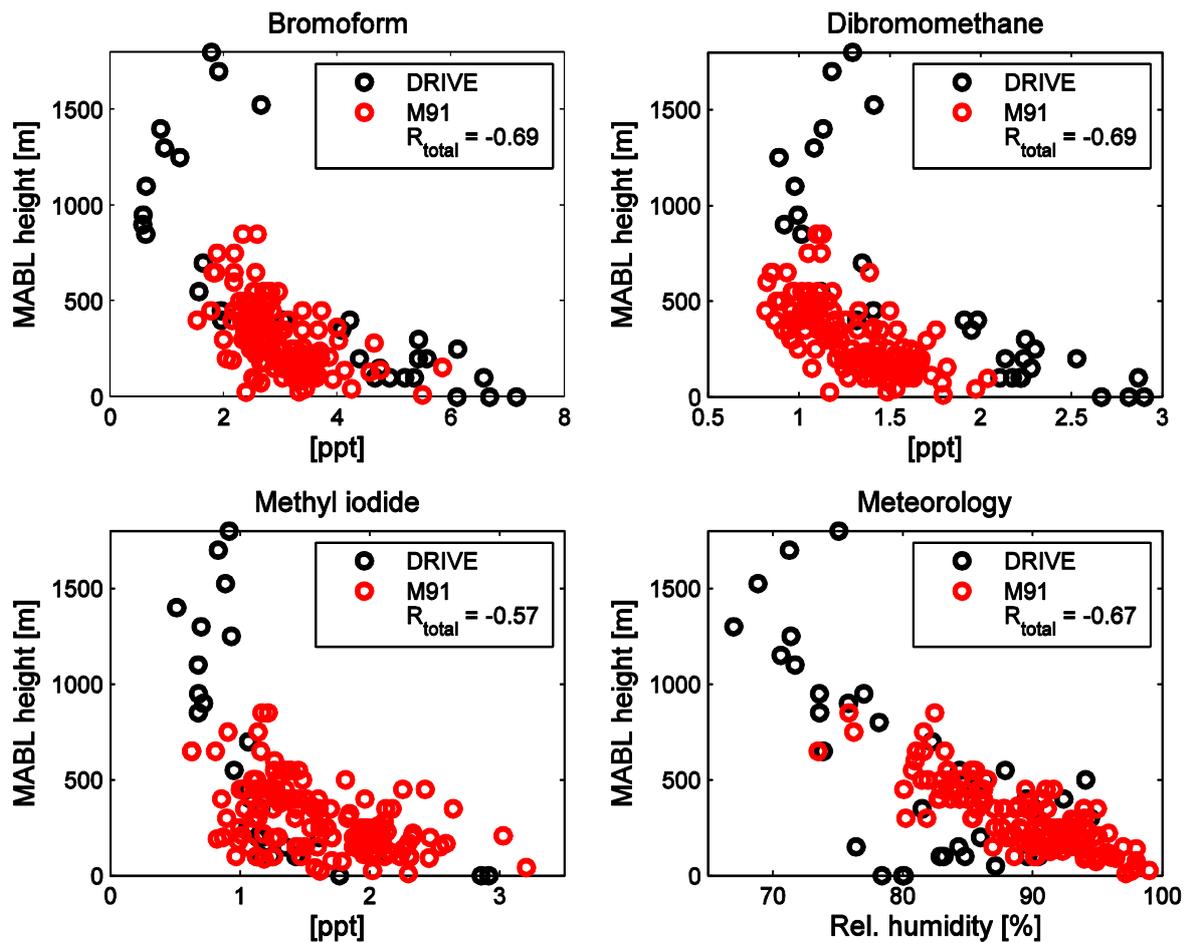
		OD [% d <sup>-1</sup> ]	AD [% d <sup>-1</sup> ]	CL [% d <sup>-1</sup> ]	COL [% d <sup>-1</sup> ]	ODR	ADR	CLR
$\text{CHBr}_3$	MABLH	9.1 $\pm 28.0$	349.0 $\pm 113.4$	-7.1	-351.0 $\pm 109.4$	0.03 $\pm 0.08$	0.99 $\pm 0.08$	-0.02 $\pm 0.01$
	TIH	3.9 $\pm 12.0$	53.2 $\pm 23.2$	-7.1	-50.0 $\pm 18.4$	0.11 $\pm 0.4$	1.06 $\pm 0.39$	-0.17 $\pm 0.07$
$\text{CH}_2\text{Br}_2$	MABLH	32.1 $\pm 38.7$	320.1 $\pm 115.6$	-1.2	-351.0 $\pm 109.4$	0.10 $\pm 0.11$	0.90 $\pm 0.11$	-0.00 $\pm 0.00$
	TIH	13.8 $\pm 16.5$	37.4 $\pm 25.9$	-1.2	-50.0 $\pm 18.4$	0.33 $\pm 0.54$	0.7 $\pm 0.54$	-0.03 $\pm 0.01$
$\text{CH}_3\text{I}$	MABLH	88.9 $\pm 48.1$	286.1 $\pm 119.7$	-24.0	-351.0 $\pm 109.4$	0.28 $\pm 0.17$	0.80 $\pm 0.16$	-0.08 $\pm 0.03$
	TIH	36.8 $\pm 20.5$	37.2 $\pm 32.1$	-24.0	-50.0 $\pm 18.4$	0.92 $\pm 0.69$	0.64 $\pm 0.55$	-0.56 $\pm 0.24$

579

580 Table 3: Spearman correlation coefficients (R) of meteorological parameters, MABL height  
 581 and trade inversion height correlated with atmospheric bromoform (CHBr<sub>3</sub>), dibromomethane  
 582 (CH<sub>2</sub>Br<sub>2</sub>) and methyl iodide (CH<sub>3</sub>I). MABL height\* is the determined MABL height from the  
 583 radiosonde launches, complimented by the regressed MABL height (Section 3.3). Bold  
 584 coefficients have a p-value of < 0.05.

	MABL height	MABL height*	Trade inversion	CHBr <sub>3</sub>	CH <sub>2</sub> Br <sub>2</sub>	CH <sub>3</sub> I
Wind speed	<b>0.35</b>	<b>0.44</b>	-0.06	<b>-0.38</b>	<b>-0.53</b>	<b>-0.33</b>
SAT	<b>0.65</b>	<b>0.79</b>	<b>0.24</b>	<b>-0.50</b>	<b>-0.78</b>	<b>-0.37</b>
SST	<b>0.66</b>	<b>0.80</b>	<b>0.23</b>	<b>-0.57</b>	<b>-0.81</b>	<b>-0.42</b>
SAT – SST	<b>-0.39</b>	<b>-0.47</b>	-0.11	<b>0.38</b>	<b>0.48</b>	<b>0.30</b>
Rel. humidity	<b>-0.77</b>	<b>-0.81</b>	-0.06	<b>0.74</b>	<b>0.77</b>	<b>0.67</b>
MABL height*	-	-	0.08	<b>-0.55</b>	<b>-0.61</b>	<b>-0.45</b>
CHBr <sub>3</sub>	<b>-0.55</b>	<b>-0.60</b>	-0.03	-	<b>0.79</b>	<b>0.79</b>
CH <sub>2</sub> Br <sub>2</sub>	<b>-0.61</b>	<b>-0.72</b>	-0.02	<b>0.79</b>	-	<b>0.66</b>
CH <sub>3</sub> I	<b>-0.45</b>	<b>-0.50</b>	<b>0.30</b>	<b>0.79</b>	<b>0.66</b>	-

585



586

587 Figure 5: Scatter plots of atmospheric mixing ratios of bromoform, dibromomethane, methyl  
 588 iodide and relative humidity vs. MABL height. Black circles reflect observations from the  
 589 DRIVE campaign in the Mauritanian Upwelling (Fuhlbrügge et al., 2013) and red circles  
 590 from this study (M91).  $R_{total}$  gives the Spearman correlation coefficients for both data sets  
 591 together.

592

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