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Supplement of

Increasing concentrations of dichloromethane, CH_2Cl_2, inferred from CARIBIC air samples collected 1998–2012

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Supplementary Information

Increasing concentrations of dichloromethane, CH_2Cl_2, inferred from CARIBIC air samples collected 1998-2012

Leedham Elvidge et al. (2014)

In Section 3.1 of the manuscript CARIBIC data collected over Europe, analysed at the University of East Anglia (UEA), is compared to data collected at Mace Head by NOAA. Fig. 2 (main manuscript) and the associated discussion (main manuscript Section 3.1) show that the same trend is observed by both UEA and NOAA, although mean values for each year are slightly higher for NOAA. This is likely to be due to the fact that the NOAA samples are taken within the boundary layer, whereas the majority of CARIBIC samples are collected at altitudes of 10-12 km. To provide an additional quality measure Fig. S1 shows a comparison between UEA and NOAA samples collected in boundary layer air at Cape Grim, Tasmania. Samples were collected and analysed independently though the calibration of UEA (including CARIBIC) data is derived directly from NOAA standards. Good agreement is observed between the two datasets, with no significant offset or changes in the relationship over time, suggesting consistent maintenance of the calibration scales over time.

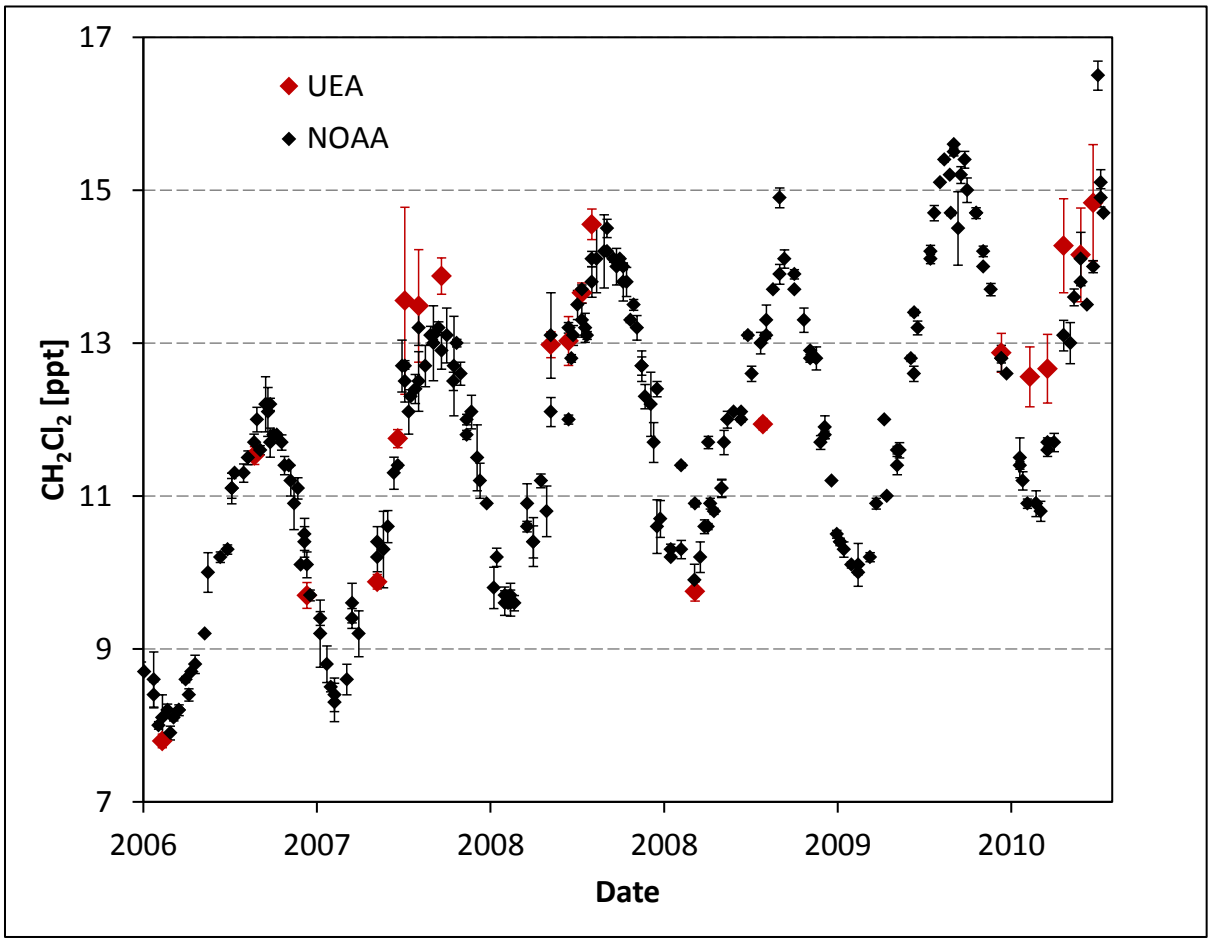

Figure S1. Time series of CH_2Cl2_2 concentrations (ppt) observed in whole air samples collected at Cape Grim, Tasmania and analysed independently by UEA and NOAA (see inset legend).

In addition, we provide here further details on the internal propagation of calibration scales. On all three GCMS systems used for this work mixing ratios were assigned through adjacent measurements of working standard tanks. These working standards were calibrated, high-pressure whole samples of clean air representative of northern hemispheric background concentrations which were collected at Niwot Ridge, Colorado (near Boulder) and supplied and initially calibrated by NOAA-ESRL-GMD. Table S1 lists the standards used as well as the measurement periods for the three instruments. Notably from 2006 onwards we purchased a series of electro-polished stainless steel canisters (Essex Industries), which are known to have better stability for the long-term storage of certain halocarbons, including CH_2Cl_2 (Hall et al., 2014). All aluminium-based working standards were found to show long-term concentration increases. These were corrected for by using a) originally supplied NOAA dry air mole fractions and b) a number of internal working standard intercomparison experiments. As an example Figure S2 shows the changes observed in the ALM-64957 standard over time as well as the polynomial fit function used for correction.

Two further calibrated stainless steel canisters (in addition to the three listed in Table S1) were purchased from NOAA in 2009 and 2013. The originally assigned NOAA mixing ratios of all five SX tanks were used to assess the stability of CH_2Cl_2 in this type of canister between 2009 and 2014. Within the 1 σ measurement uncertainties no significant changes in CH_2Cl_2 mixing ratios were observed within five years of filling (2 σ for longer periods).

Table S1. Overview of NOAA-filled and calibrated cylinders used as working standards

Instrument	Working standard (period, cylinder material)
V. G. AutoSpec (CARIBIC1)	ALM-39753 (1998-2008, Aculife-treated aluminium)
Entech system	ALM-64957 (1999-2006, Aculife-treated aluminium)
	SX-3546 (2006-2011, electro-polished stainless steel)
	SX-0706070 (2011-2012, electro-polished stainless steel)
AutoSpec 2 (CARIBIC2)	AAL-071170 (2008-2012, Aculife-treated aluminium)

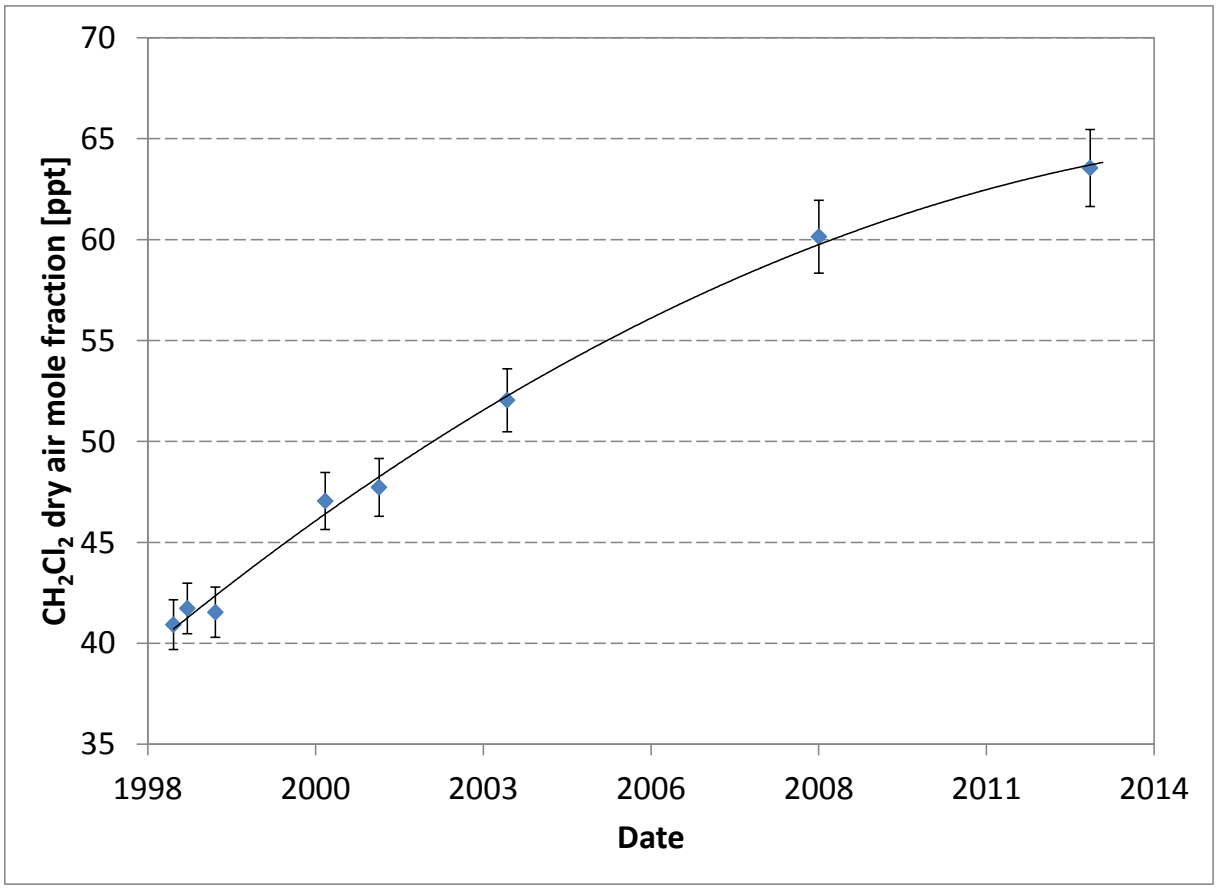

Figure S2. Temporal changes in mixing ratios (◆) of the aluminium-based ALM-64957 working standard compared against other calibrated NOAA standards. The fit is a second order polynomial fit function used to correct for the observed changes.

References:

Hall, B. D., Engel, A., Mühle, J., Elkins, J. W., Artuso, F., Atlas, E., Aydin, M., Blake, D., Brunke, E.-G., Chiavarini, S., Fraser, P. J., Happell, J., Krummel, P. B., Levin, I., Loewenstein, M., Maione, M., Montzka, S. A., O'Doherty, S., Reimann, S., Rhoderick, G., Saltzman, E. S., Scheel, H. E., Steele, L. P., Vollmer, M. K., Weiss, R. F., Worthy, D. and Yokouchi, Y.: Results from the International Halocarbons in Air Comparison Experiment (IHALACE), Atmos. Meas. Tech., 7, 469-490, doi:10.5194/amt-7-469-2014, 2014.