Continuing emissions of methyl chloroform from Europe

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The consumption of methyl chloroform (1,1,1-trichloroethane), an industrial solvent, has been banned by the 1987 Montreal Protocol because of its ozone-depleting potential. During the 1990s, global emissions have decreased substantially and, since 1999, near-zero emissions have been estimated for Europe and the United States. Here we present measurements of methyl chloroform that are inconsistent with the assumption of small emissions. Using a tracer transport model, we estimate that European emissions were greater than 20 Gg in 2000. Although these emissions are not significant for stratospheric ozone depletion, they have important implications for estimates of global tropospheric hydroxyl radical (OH) concentrations, deduced from measurements of methyl chloroform. Ongoing emissions therefore cast doubt upon recent reports of a strong and unexpected negative trend in OH during the 1990s and a previously calculated higher OH abundance in the Southern Hemisphere compared to the Northern Hemisphere.

The principal uses of methyl chloroform (MCF) have been the degreasing of precision engineered components (31%) and cold cleaning (18%)[1]. Its low toxicity compared to other non-flammable halogenated solvents favoured its use in many other applications such as dry cleaning, inks and coatings. The ultimate fate of MCF is evaporation into the atmosphere where its principal loss mechanism is oxidation by hydroxyl radicals (OH). The lifetime of MCF towards OH oxidation in the troposphere is relatively long (5–6 yr) and a significant MCF fraction is transported to the stratosphere where it releases chlorine through photolysis. For this reason, MCF was included in the Montreal Protocol (1987) and its amendments with a final phase-out in 1996 in developed countries, and 2015 in developing countries.

Compliance with the Montreal Protocol resulted in a rapid decrease of emissions and hence in the atmospheric MCF burden, beginning in the early 1990s (ref. 2). Currently, mean tropospheric concentrations are less than 40 $\mathrm{pmol\,mol^{-1}}$, close to the levels that were observed before 1975, when the emissions were increasing rapidly. The highest atmospheric concentrations were measured around 1992, with background levels up to 160 $\mathrm{pmol\,mol^{-1}}$. Until 1995, historical emissions of MCF were proficiently quantified because it is likely that all material produced finally ended up in the atmosphere. A detailed study using audited production data supplied by the chemical manufacturers showed that about 75% was released in the year of production and 25% in the following year[1]. In the early 1990s some stockpiling took place and the total banked quantities were estimated to be around 5 Gg for 1997–2000 (ref. 3). From 1995 onwards the emission estimates have been based on the non-audited consumption and production data supplied by the parties under the Montreal Protocol[3,4].

Long-term measurements of MCF in the atmosphere have been combined with the emission estimates provided by industry and inverse modelling procedures to derive the mean MCF lifetime in the troposphere[5–10] and thereby the average atmospheric OH concentration. The temporal evolution of the average atmospheric OH concentration has been calculated using the 1978–2000 data obtained from the ALE/GAGE/AGAGE programme at remote stations[6–8]. From these analyses, using the most recent estimates of MCF emissions, it has been inferred that global OH levels increased by 5% or more during the 1980s (refs 8–10). However, the recent decrease in the atmospheric MCF concentrations is less rapid than was anticipated from the phase-out of MCF production and use in the 1990s, assuming constant OH levels. These observations have been explained by a substantial and unexpected drop in tropospheric OH since 1990 (ref. 8).

Prinn *et al.*[8] attributed the inferred tropospheric mean OH reduction mainly to changes in the Northern Hemisphere, for which they found that OH levels are on average 14% lower than in the Southern Hemisphere. Higher OH levels south of the intertropical convergence zone (ITCZ) have also been inferred from NOAA flask samples combined with a budget analysis[11]. The asymmetry in OH distribution inferred from the MCF measurement programmes is a contentious result, with some global chemistry/transport models predicting more OH in the Northern Hemisphere compared to the Southern Hemisphere[12–14]. These

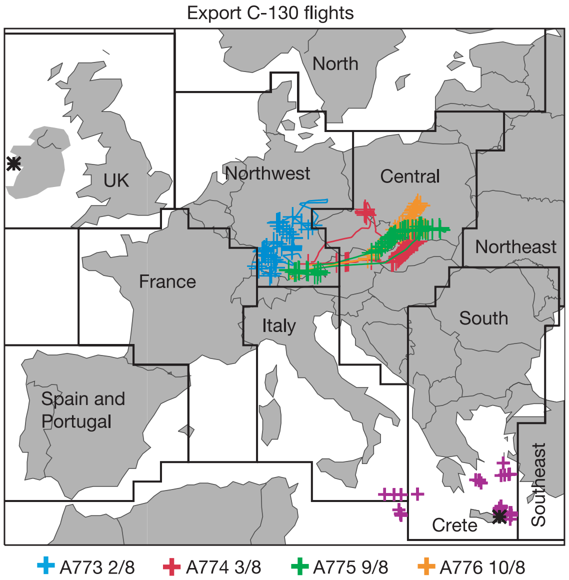

Figure 1 Flight tracks of the British C-130 aircraft. Coloured crosses indicate the locations at which the air samples were taken. The asterisk on Ireland shows the location of Mace Head. In sensitivity simulations, 4 Gg MCF $\mathrm{yr^{-1}}$ has been added to ten regions within Europe (northeastern and southeastern Europe extend further eastwards). The asterisk on Crete and the purple crosses around Crete refer to the MINOS campaign.

model results may be flawed by wrongly simulated OH precursor distributions. Calculated hemispheric OH concentrations become about equal if observed OH precursor fields are used[15], although appreciable uncertainties remain.

All methods that use MCF to estimate OH levels, trends, and hemispheric distributions critically rely on the accuracy of the MCF emission estimates and the accuracy of the MCF absolute calibration. The observed decline in atmospheric concentrations at remote sites is indeed consistent with a significant drop in emissions. Not only have the measured concentrations declined rapidly, but the observed atmospheric variability has also decreased dramatically, indicating that emissions no longer occur, at least not in the regions where the measurement stations are located.

Evidence for methyl chloroform emissions

We present MCF measurements taken in the free troposphere and the boundary layer over central Europe during the EXPORT (European export of precursors and ozone by long-range transport) experiment involving the UK Met Office C-130 aircraft (see Methods). The MCF measurements have been interpreted using tracer-transport model simulations (see 'Model description' section). The accuracy of the modelled transport has been verified using CO observations that were taken during the EXPORT flights and at Mace Head (Ireland, see Fig. 1)[2]. To locate potential MCF emission regions, several model 'experiments' have been carried out that include additional European emissions. In each experiment, the European emissions were enhanced by 4 Gg yr^{-1} over one of the regions depicted in Fig. 1. In an additional simulation, the emissions were enhanced with 4 Gg yr^{-1} over eastern North America.

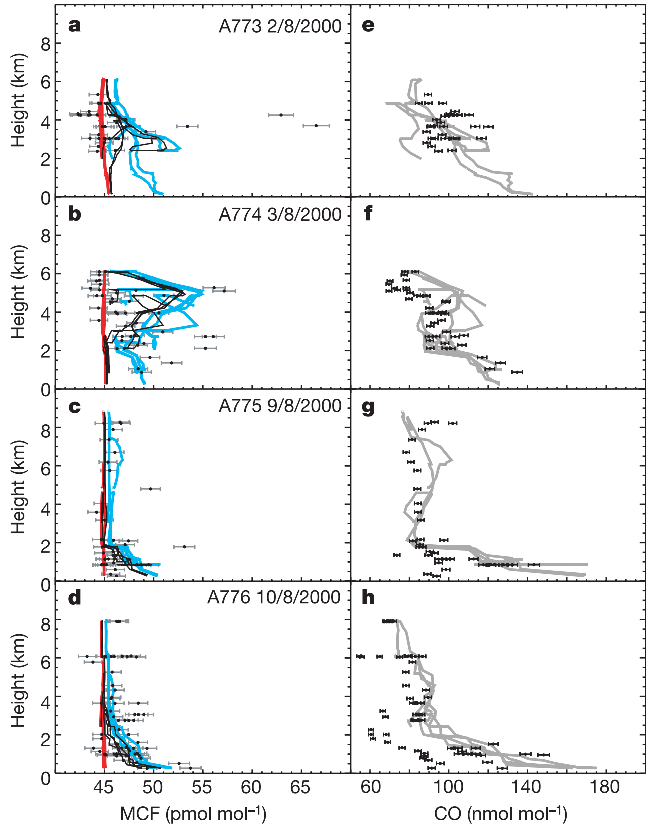

Figure 2 Analysis of the EXPORT flights as a function of height. The number and date of each flight is given. The black dots indicate the measured methyl chloroform (MCF) (pmol mol^{-1}) and CO (nmol mol^{-1}) concentrations and the bars represent the measurement errors. **a**–**d**, The red lines show the modelled MCF concentrations along the flight tracks in the reference simulation (1 Gg yr^{-1} European emissions). The blue lines represent the concentrations in a simulation with enhanced emissions in the regions Spain and Portugal (6 Gg yr^{-1}), Italy (9 Gg yr^{-1}), central Europe (3 Gg yr^{-1}), northwestern Europe (3 Gg yr^{-1}) and France (2 Gg yr^{-1}). The thin black lines refer to enhanced emissions only in Spain and Portugal (A773), Italy (A774), and central Europe (A775 and A776). **e**–**h**, The grey lines show the simulated CO concentrations along the EXPORT flight tracks corresponding to **a**–**d**.

Figure 2 shows the simulated MCF (Fig. 2a–d) and CO (Fig. 2e–h) concentrations as a function of height during four flights of the EXPORT measurement campaign. The reference simulation (1 Gg yr^{-1} MCF emissions over Europe, red line in Fig. 2a–d) shows negligible concentration variations. This indicates that the much higher and more variable concentrations observed are the result of unexpected MCF emissions. On the basis of the sensitivity simulations described below, possible source regions have been located in Spain and Portugal ($\sim$6 Gg yr^{-1}), Italy ($\sim$9 Gg yr^{-1}), central Europe ($\sim$3 Gg yr^{-1}), northwestern Europe ($\sim$3 Gg yr^{-1}), and France ($\sim$2 Gg yr^{-1}). Although the estimated emissions and their geographic locations (broadly outlined in Fig. 1) are rather uncertain, the simulated concentrations (with 24 Gg yr^{-1} emissions over Europe; blue line in Fig. 2a–d) are in much better agreement with the measurements.

The 2 August 2000 flight (A773) over Germany (in Fig. 2a) shows increased concentrations in the free troposphere around 4 km altitude. From the sensitivity simulations, it can be inferred that the probable source of these high concentrations is in Spain (black line in Fig. 2a), although contributions from France cannot be ruled out. A trajectory analysis indicates that stagnant air over northern Spain was lifted over the Pyrenees by frontal thunderstorms before being advected in the free troposphere to Germany.

Similar observations were made on 3 August 2000 (A774) when the front moved towards the Alps. The model simulations and trajectory analysis indicate that, in this case, the source of the increased concentrations is located in Italy (black line in Fig. 2b). Again, stagnant and polluted air parcels were lifted over the Alps, followed by advection in the free troposphere to central Europe. The last part of the flight was at altitudes below 2,000 m and indicates possible sources over northwestern Europe, France and central Europe.

The 9 August 2000 flight (A775) was performed mostly in the boundary layer over central Europe. The increased MCF concentrations observed are probably caused by emissions in central Europe (black line in Fig. 2c) and northwestern Europe. Finally, the boundary layer concentrations during the 10 August 2000 flight (A776) are most probably explained by emissions from central Europe (black line in Fig. 2d) and from northwestern Europe.

Although the simulations with enhanced European emissions are closer to the observations, the agreement is qualitative and individual peaks are not resolved. This is only to be expected, because the exact locations of the emissions are unknown. The model resolution is also limited and model errors that are associated with, for example, vertical transport may be appreciable. The simulation of the CO distribution during the EXPORT flights (Fig. 2e–h) nevertheless shows that the model reproduces the observed CO enhancements in the free troposphere and in the boundary layer. Only the remarkably low CO concentrations during flight A776 were not resolved by the model. For the rest, the observed vertical CO distribution of all flights is simulated adequately, which indicates that the modelled vertical transport is realistic. The simulations furthermore indicate that European MCF emissions of more than 20 Gg yr^{-1} are needed to explain the large range of observed concentrations. With no or very small additional emissions, the calculated MCF variability is absent or unrealistically small. Hence there is little doubt that the emissions are substantially higher than the $<$1.0 Gg yr^{-1} estimate for Europe[3].

Ground-based measurements

Routine monitoring of MCF in Europe has historically been limited to the background station Mace Head in Ireland (Fig. 1). To investigate the extent to which the additional emissions in Europe would influence the concentrations at Mace Head during the summer of 2000, Fig. 3a and b compare the model calculated CO and MCF time series to the observations from mid-May to late August 2000. The reference MCF simulation (1 Gg yr^{-1} emissions over Europe, red lines in Fig. 3b and c) appears quite consistent with the observations. The observed and modelled MCF fluctuations are associated with meteorological variability. Air masses originating from the subtropics (southerly winds) are generally more strongly depleted in MCF, which is caused by the higher OH levels in these regions. The model captures these fluctuations quite well. These findings are supported by the CO simulation, which shows generally good agreement with the CO variability observed at Mace Head.

The temporal MCF decline is largely caused by OH oxidation, which reaches a maximum in summer. The calculated decline in the simulation with enhanced MCF emissions (24 Gg yr^{-1} emissions over Europe, blue lines) is about 13% smaller than in the reference simulation. Owing to the prevailing westerly winds, European MCF emissions normally reach Mace Head only after hemispheric transport, so that European emissions cannot be detected directly at Mace Head. Some pollution events are evident from the CO measurements and simulation. To facilitate comparison with the MCF sensitivity simulations (Fig. 3d), Fig. 3c shows the MCF series with the trends removed.

The perturbation simulation with the additional 23 Gg yr^{-1} of MCF emissions from Europe (blue line in Fig. 3c) reveals that some observed concentration enhancements are now captured better by the model. On some days, however, the modelled enhancements are not measured at Mace Head. This is not unexpected, because the emissions have been applied over relatively large regions, weighted with the population density. A number of point sources would probably be more realistic, but the unknown nature of the MCF sources precludes such an approach.

The sensitivity calculations shown in Fig. 3d indicate that during the summer of 2000 the following occurred: (1) air masses from the regions labelled Italy and central Europe (and southern, northeastern and southeastern Europe—not shown) reach Mace Head only in hemispherically diluted form; (2) substantial eastern USA sources (>4 Gg yr^{-1}) do not seem to be consistent with the observations at Mace Head; and (3) some remaining discrepancies between model and measurements can be explained by small emissions from the regions labelled UK and North in Fig. 1. Most importantly, the additional European MCF emissions required to explain the EXPORT measurements are not in conflict with the Mace Head observations.

Previous attempts to estimate European source strengths from the Mace Head MCF observations indicated that MCF emissions dropped from about 30 Gg yr^{-1} in 1995 to about 2 Gg yr^{-1} in 1998 (ref. 16). We note, however, that this study[16] confirms that sources from Italy, Spain, central and eastern Europe do not significantly contribute to the measured concentrations at Mace Head.

Additional evidence

The unexpected large MCF variability, as observed during EXPORT, is also confirmed by MCF measurements by aircraft over the eastern Mediterranean and at a background station on Crete, performed during the Mediterranean intensive oxidant study (MINOS)[17] in August 2001 (see Figs 1 and 4). Boundary layer concentrations well above the background were regularly observed in air masses transported from southern and eastern Europe. Back-trajectory analysis suggests that the peak value of about 50 pmol mol^{-1} observed north of Crete (Fig. 4a) was caused by eastern European sources with a possible contribution from Greece. This peak coincided with the second peak measured at the surface (13–14 August, Fig. 4b).

Figure 4c shows MCF measurements from samples collected

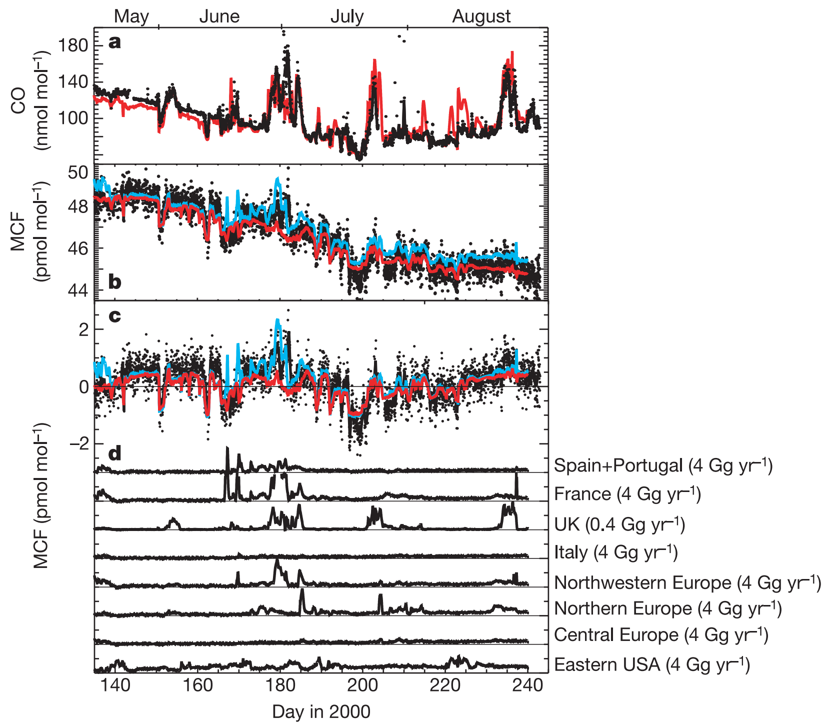

Figure 3 MCF and CO simulations compared to Mace Head observations. **a**, CO measurements (dots, the black line represents 6-hourly means) and corresponding model calculations (red). **b**, MCF measurements (dots; the black lines represent 6-hourly means) and model calculations (red and blue). **c**, The data from **b** normalized to zero and the trend removed (about 3 pmol mol^{-1} over this period). The red lines represent the reference simulation with 1 Gg yr^{-1} European MCF emissions, and the blue lines the simulation with 23 Gg yr^{-1} additional emissions (see legend of Fig. 2). **d**, Calculated concentration perturbations (relative to the reference simulation and on the same scale) with 4 Gg yr^{-1} additional emissions in the regions defined in Fig. 1 and in the eastern USA. Considering the large effect on the MCF concentration at Mace Head, the additional emissions in the UK region have been assumed to be 0.4 Gg yr^{-1} only.

during upper tropospheric aircraft measurements in the CARIBIC project (civil aircraft for the regular investigation of the atmosphere based on an instrument container)[18]. The MCF trend between 1998 and 2001 is consistent with that observed from background stations at the surface[8,11]. The observed concentrations at flight altitude (200–300 hPa) are rather variable. The highest concentration of nearly 75 pmol mol^{-1} was observed in August 1999 near India, associated with rapid upward transport of polluted air in monsoon convection. These MCF enhancements in the upper troposphere indicate that significant emissions may also occur outside Europe.

Possible sources of methyl chloroform

The MCF concentrations measured during EXPORT are strongly correlated with tetrachloromethane (CCl_4) observations ($R^2 = 0.6$). Production of CCl_4, largely used as an intermediate in the production of chlorofluorocarbons (CFCs), is also regulated under the Montreal Protocol, and the high concentration fluctuations point to considerable emissions of this compound as well. Moreover, the high correlation suggests that both compounds have a very similar source signature. It is unlikely that this result is associated with similar loss processes in the atmosphere because the removal of CCl_4 is controlled by stratospheric photolysis, whereas MCF is predominantly removed by tropospheric OH.

A natural origin for the MCF emissions can also be excluded, considering the near absence of MCF in pre-industrial air retrieved from polar firn[19]. If the consumption data of the European countries are reliable, current use of MCF in the traditional applications can be ruled out. However, the MCF surface concentrations measured during MINOS were highly correlated with CFC-113 observations ($R^2 = 0.5$). Because the applications of CFC-113 are similar to those of MCF, this may indicate active use of both compounds, at least in southern and eastern parts of Europe. MCF is produced for non-dispersive uses, but widespread losses during production are not expected. Alternatively, the banking of MCF in consumer goods may have been underestimated. MCF in coatings, inks and textiles represents a considerable fraction of its total use before 1996 (ref. 1) and the distribution and use of these products is rather uncertain. They may have ended up in waste and landfills from which MCF slowly diffuses into the atmosphere. The fact that MCF sources are probably located in southern and central Europe, where waste dumping is more common than waste burning, gives some credence to this explanation. Moreover, diffusion from landfills would be more efficient in summer owing to the higher temperatures. An alternative explanation involves (chemical) waste burning of MCF-containing material. There is some evidence that this compound is still present in the exhaust gases after high-temperature burning of MCF-containing mixtures[20].

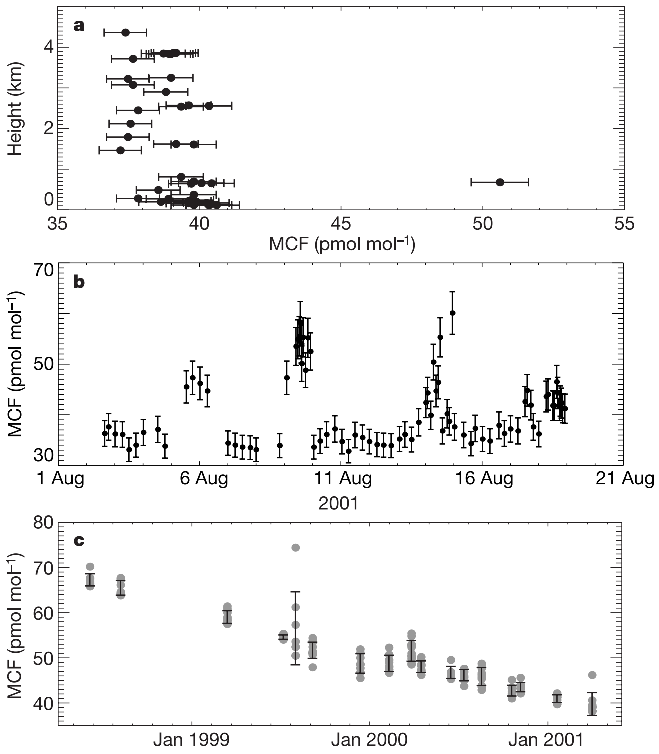

Figure 4 Methyl chloroform measurements performed in the MINOS and CARIBIC projects, showing substantial variability up to 2001. **a**, The black dots represent MCF measurements (and uncertainty bars) from 15 flights over the eastern Mediterranean Sea in August 2001 (see purple crosses in Fig. 1). **b**, Ground-based MCF measurements from Crete (35° N, 26° E). **c**, MCF measurements (~120 grey dots), including flight mean and 1σ standard deviation, from samples taken in the upper troposphere during 16 flights between the Maldives/Sri Lanka and Germany.

Implications for OH trends

The unexpected remaining MCF emissions are small compared to the amounts that were emitted in the early 1990s. Given the low ozone depletion potential of MCF compared to CFCs[4], the effect of these emissions on stratospheric ozone depletion will be relatively insignificant. However, the continuing emissions strongly influence analyses of global OH concentrations as well as the inferred hemispheric OH ratio. Montzka *et al.*[11] performed a hemispheric budget analysis based on the MCF burden, sources and sinks. They showed that 1998–99 emissions of about 40 Gg yr^{-1} in the Northern Hemisphere would lead to a south-to-north hemispheric OH ratio of about 1. On the other hand, if MCF emissions in the Northern Hemisphere were very small, about 15% more OH in the Southern Hemisphere compared to the Northern Hemisphere would explain the MCF measurements. Our analysis, however, suggests that in Europe alone, emissions of more than 20 Gg yr^{-1} would be consistent with the MCF measurements reported here, thus rendering a strong interhemispheric OH asymmetry, with higher OH in the Southern Hemisphere, unlikely.

A similar argument applies to MCF-derived OH trends since the late 1970s. Prinn *et al.*[8] estimated the MCF sources that would correspond to a time-invariant global tropospheric OH abundance. For the years 1996–2000, the required additional MCF sources would have to be 17, 41, 29, 16 and 14 Gg yr^{-1}, respectively. Again, even by considering the European MCF emissions alone, a strong negative OH trend during the 1990s seems unlikely. Finally, if the emissions did not cease as expected in recent years, and the gross MCF production has been estimated correctly, more MCF should have been attributed to the 'slow use' category. If the additional emissions during the 1990s would in fact represent delayed release into the atmosphere, not only would the presumed negative trend in this period vanish, but the positive OH trend in the preceding decade would also be much smaller than previously inferred[8,9]. We estimated that the large OH anomaly around 1990 that is calculated with the emission estimates used by ref. 8 disappears if MCF emissions of about 65 Gg were delayed from the early to the late 1990s[10]. The implication is that tropospheric OH has been relatively constant in time over the past decades, being more consistent with observed methane growth rates and with atmospheric chemistry modelling[21,22].

Definite conclusions about the global OH distribution and trend cannot be drawn before the emissions and distribution of MCF are better quantified. Additional measurements are required to locate possible sources. ☐

Methods

Experimental method

During EXPORT, whole-air samples (not dried) were collected in 3-litre, silica-lined, stainless steel canisters (Restek Corporation) pressurized to 2–3 atm using a stainless steel, double-headed bellows pump (Metal Bellows) to draw air from the aircraft air sample inlet. The samples were analysed for a large number of halocarbons, including MCF, as soon as possible (1–20 days after each flight) using a fully automated gas chromatograph/mass spectrometer (Agilent 6890/5973 GC-MSD) in select ion monitoring mode. An 800-ml sample from each flask was processed using an Entech 7100 pre-concentrator system (Entech Instruments Inc.) by sampling at 100 ml min^{-1} onto an 1/8-inch (outer diameter) stainless steel trap (trap 1) packed with glass beads and held at −150 °C. To facilitate the removal of water and carbon dioxide from the enriched sample, the contents of trap 1 were swept onto a second trap (same size and material as trap 1) packed with Tenax at −40 °C. Any water in the original sample remained on trap 1, whereas CO_2 passed through trap 2 without significant retention. A final trapping stage involved cryo-focusing on fused silica-lined stainless steel tubing (1/32-inch) before transfer onto the gas chromatography column. A DB-5 capillary column (J&W Scientific, 105 m × 0.32 mm inner diameter, 1.5 μm film thickness) with helium carrier gas (UHP) was used for temperature-programmed separation before detection. Analytical precision was typically ±2%. Samples of MCF-free, zero air were analysed to ensure there was no contamination from either the analytical system or the aircraft sampling manifold. All air samples were analysed against one of a series of secondary whole-air samples stored in 3.2-litre, electropolished, stainless steel flasks. These working standards were calibrated against a high-pressure whole-air sample stored in an Aculife-treated, aluminium cylinder supplied by NOAA-Climate Monitoring and Diagnostics Laboratory (CMDL). The MCF measurements are reported on the most recent NOAA-CMDL calibration scale (CMDL-2002). Overall uncertainty in the measurements, which includes uncertainties in the NOAA standard, propagation of working standards and experimental precision, was approximately 5%. The CARIBIC MCF measurements were obtained using a combination of the system described above and a second GC-MS technique described elsewhere[23,24].

The CO measurements were made with a fast-response, vacuum-ultraviolet resonance fluorescence instrument[25]. It has a 1-s time resolution, a detection limit of 3 nmol mol^{-1} and a precision of ±1.5 nmol mol^{-1} at an atmospheric mixing ratio of 100 nmol mol^{-1}. In-flight calibrations were performed approximately every 30 min using a British Oxygen Company (BOC) alpha standard (±1%). The high-frequency CO measurements were aggregated to reproduce the sampling intervals of the MCF measurements.

The MINOS flight canisters were analysed using a gas chromatograph equipped with an electron capture detector at Utrecht University[26]. The canisters collected at the ground station were analysed at the Max Planck Institute, Mainz, with a GC-MS (Agilent 6890/5973) similar to that described above.

Model description

The MCF distribution over Europe at the time of the EXPORT experiment (August 2000) was simulated using the global Tracer Model, version 5 (TM5), that zooms in over Europe. The global and regional simulations were coupled by means of two-way nesting[27,28]. The European simulations were initialized by monthly averaged MCF distributions. The initial MCF field was taken from a long-term global simulation (1951–2000) with a coarse-grid model version. Monthly averaged OH fields were used to oxidize MCF. These fields have been scaled such that the observed decline in MCF in the summer of 2000 was reproduced[10]. The initial MCF concentration field at the start of the simulations (1 May 2000) was scaled to match the Mace Head observations. The simulations accounted for removal by OH oxidation, oceanic uptake and MCF destruction by photolysis in the stratosphere[9,29].

Carbon monoxide (CO) distributions have been simulated to verify the modelled transport. Initial fields were taken from a full chemistry simulation[22] and CO was oxidized by the same OH fields that were used for MCF. Anthropogenic CO emissions are based on the EDGAR3.2 database[30] for the year 1995. Emissions from fossil fuel amount to 296 Tg CO yr^{-1}; from biofuel to 235 Tg CO yr^{-1}; from biomass burning to 256 Tg CO yr^{-1}; and from temperate fires to 58 Tg CO yr^{-1}. The highly uncertain natural emissions from vegetation, soils and oceans are taken as 115 Tg CO yr^{-1}. Apart from surface emissions, an additional CO source from methane oxidation has been accounted for, assuming constant methane levels of 1.8 μmol mol^{-1}.

Transport is performed using 6-hourly fields from the European Centre for Medium range Weather Forecasts (ECMWF). All physical parameterizations in the zoom model are identical to the global model as used in previous studies[31,32] and the boundary layer representation is based on 3-hourly surface fields to resolve better the diurnal cycle of near-surface mixing[33]. The modelled concentrations are evaluated every 15 min, which corresponds to the integration time step within the European model domain. The global resolution of the model is 6° latitude by 9° longitude, and the European region is resolved at a higher horizontal resolution of 1° × 1°. In the vertical direction, 25 of the 60 layers used by the parent ECMWF model are retained, mostly in the boundary layer and the free troposphere. Concentrations are interpolated to the C-130 aircraft EXPORT flight tracks. In addition, the MCF and CO concentrations are evaluated at the AGAGE station Mace Head in western Ireland (53° N, 10° W).

From 1980 onward, the estimated annual global MCF emissions were divided over seven distinct regions[1,3]. Within these regions emissions were distributed according to the population density. The global total MCF source applied in the reference model simulation for the year 2000 amounts to 19.7 Gg[3], mostly emitted outside North America and Europe. European and North American emissions for the year 2000 were assumed to be 1 and 5 Gg, respectively. These amounts are already somewhat higher than the most recent emission compilation, which reports that consumption in Europe and North America had already dropped to zero in 1999 (ref. 3).

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