Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights

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Abstract. Nonmethane hydrocarbons and halocarbons were measured during two Lagrangian experiments conducted in the lower troposphere of the North Atlantic as part of the June 1992 Atlantic Stratosphere Transition Experiment/Marine Aerosol and Gas Exchange (ASTEX/MAGE) expedition. The first experiment was performed in very clean marine air. Meteorological observations indicate that the height of the marine boundary layer rose rapidly, entraining free tropospheric air. However, the free tropospheric and marine boundary layer halocarbon concentrations were too similar to allow this entrainment to be quantified by these measurements. The second Lagrangian experiment took place along the concentration gradient of an aged continental air mass advecting from Europe. The trace gas measurements confirm that the National Center for Atmospheric Research (NCAR) Electra aircraft successfully intercepted the same air mass on consecutive days. Two layers, a surface layer and a mixed layer with chemically distinct compositions, were present within the marine boundary layer. The composition of the free troposphere was very different from that of the mixed layer, making entrainment from the free troposphere evident. Concentrations of the nonmethane hydrocarbons in the Lagrangian surface layer were observed to become depleted relative to the longer-lived tetracloroethene. A best fit to the observations was calculated using various combinations of the three parameters, loss by reaction with hydroxyl, loss by reaction with chlorine, and/or dilution from the mixed layer. These calculations provided estimated average concentrations in the surface layer for a 5-hour period from dawn to 11 UT of 0.3 ± 0.5 x 10^6 molecules cm^-3 for HO, and 3.3 ± 1.1 x 10^4 molecules cm^-3 for Cl. Noontime concentration estimates were 2.6 ± 0.7 x 10^6 molecules cm^-3 for HO and 6.5 ± 1.4 x 10^4 molecules cm^-3 for Cl.

Introduction

Despite their low atmospheric abundance, hydroxyl radicals (HO) play a crucial role in the oxidation of many important trace atmospheric gases including hydrocarbons, hydrogen-containing halocarbons, and dimethyl sulfide. Direct measurements of HO have been made by various techniques. Recently, good agreement has been reported between measured and modeled HO levels [Poppe et al., 1994; Eisele et al., 1994]. However, HO has been directly characterized for a very limited range of field situations. Average concentrations of HO have been calculated indirectly from the atmospheric distribution of species such as methyl chloroform [Singh et al., 1979; Prinn et al., 1995]. In addition, hydroxyl has been indirectly determined from temporal changes in nonmethane hydrocarbon (NMHC) concentrations in well-defined air masses such as urban plumes [Blake et al., 1993] and in rural air masses [Roberts et al., 1984]. However, observations of NMHCs with different reactivities have been observed to give a wide range of estimates for HO [Calvert, 1976; Singh et al., 1981; Roberts et al., 1984; Blake et al., 1993]. This variation has been attributed to atmospheric dilution effects [McKeen et al., 1990; Parrish et al., 1992; McKeen and Liu, 1993; Jobson et al., 1994a] or the influence of chlorine chemistry [Finlayson-Pitts, 1993a].

Recently, there has been considerable interest regarding the impact of chlorine atoms on the oxidative capacity of the lower troposphere [Singh and Kastiging, 1988; Finlayson-Piits, 1993a,b; Parrish et al., 1993; McKeen and Liu, 1993; Graedel and Keene, 1995; Singh et al., 1995]. Reactions that yield atomic chlorine (Cl) can be grouped into several types, including those with a diurnal variation similar to HO as in reaction (1),

\[ \text{HCl} + \text{HO} \rightarrow \text{Cl} + \text{HOH} \]  

and those that build up photochemically active chlorine species overnight to yield Cl shortly after sunrise, such as in 2(a) and 2(b),

\[ \text{NO}_2 \text{(gas)} + \text{NaCl(aq)} \rightarrow \text{XCl(gas)} + \text{products} \]  
\[ \text{XCl} + h\nu \rightarrow \text{Cl} + \text{products} \]  

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The HCl in (1) is thought to be degassed more efficiently from marine aerosol under polluted conditions, when sulfuri and nitric acids have raised the aerosol acidity [Clegg and Brimblecombe, 1985; Singh and Kasting, 1988]. Reaction (2a) requires nitrate or another NO, species such as NO, NO₂, N₂O₃, or NO₂⁺ to react with NaCl associated with marine aerosol [Green, 1972; Finlayson-Pitts, 1983; Zetzsch et al., 1988; Finlayson-Pitts et al., 1989; Lax et al., 1994]. In the subsequent reaction (2b), XCl is an easily photolyzed Cl species such as Cl₂, NOCl, ClONO₂, or HOCl, all of which dissociate within about 1 hour after sunrise. Another proposed mechanism for the production of Cl atoms involves the reaction of ozone with sea-salt aerosol in the presence of sunlight [Behnke and Zetzsch, 1989, 1995; Keene et al., 1990] and is consistent with the measurements of Keene et al. [1990] and Pechen et al. [1993]. The NMHC measurements made during the Polar Sunrise 1992 Experiment [Jobson et al., 1994b] show strong evidence of Cl chemistry in the Arctic boundary layer during spring.

In this paper we present aircraft measurements of selected anthropogenic halocarbons and C₂-C₅ NMHCs obtained during two Lagrangian experiments performed in the North Atlantic as part of the June 1992 Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange (ASTEX/MAGE) project. The main objective of these experiments was to observe, in a Lagrangian reference frame, the in situ time evolution of the marine boundary layer (MBL) structure, and the formation of clouds from their precursors. A Lagrangian reference frame is one in which the observer moves with the object under investigation such that there is no relative motion between them. The NMHC and halocarbon measurements were used in three main ways. First, as dynamical tracers to establish those sections of the experiments which successfully conformed to the Lagrangian reference frame. The availability of such a large suite of trace gases from various source types, and each with different loss rates, made it possible to identify individual air masses by their chemical signature [Blake et al., this issue]. Second, in many cases it was possible to use the measurements to quantify the extent of entrainment or other mixing processes, allowing the integrity of the sampled air mass to be determined. After fulfilling the first two criteria, it was then possible to estimate the amount and type of photo-oxidation taking place in the air mass. This information is required in the calculation of two important terms, the permeability of the Lagrangian air parcel and the photo-oxidative loss terms used in budget calculations.

Experiment

Whole air samples were collected onboard the National Center for Atmospheric Research (NCAR) Electra aircraft. This paper deals with the lower tropospheric measurements of two anthurupgenic halocarbons and five C₂-C₅ NMHCs made during the seven flights comprising the two ASTEX/MAGE Lagrangian experiments. These flights took place during the periods, June 12-13 and June 18-20, 1992, in the North Atlantic east of the Azores from 30° to 41°N, and 20° to 26°W. Eight additional flights, as well as several more NMHCs and 13 halocarbons assayed during the project, are discussed by Blake et al. [this issue]. For an overview of the project, see also Huebert et al. [this issue].

Two-liter stainless steel canisters were pressurized to 40 psig onboard the Electra aircraft using a dual metal bellows pump. Each whole air sample was assayed for NMHCs and halocarbons using complementary three-column gas chromatography with electron capture and flame ionization detection. Three different chromatography columns were contained in two independently programmed Hewlett-Packard 5890 Series II Gas Chromatographs (GCs). A 60 m x 0.25 mm, 0.25-μm film thickness DB-1 column (J & W Scientific) was installed in the first GC. The effluent separated by the DB-1 column was split. A portion of the flow was directed to an electron capture detector (ECD), which measured the halocarbons, and the remainder of the flow went to a flame ionization detector (FID) for C₁-C₅ NMHC detection. In the second GC a 30 m x 0.53 mm Al₂O₃/KCl PLOT column (J & W Scientific) was coupled to an FID to quantify the C₆-C₇ NMHCs. The C₆-C₁₁ NMHCs were separated on a 30 m x 0.25 mm, 0.25-μm film thickness CD-B/Cyclolex column (J & W Scientific) and detected with an FID. Compounds which had similar retention times on one column were resolved completely on one of the other columns [see also Blake et al., 1992, 1994, 1995, this issue].

A 600.0-μg aliquot of each sample (1520 cm³ at STP) was cryogenically preconcentrated in about 5 min on a glass bead filled loop immersed in liquid nitrogen. After trapping, the loop was isolated, then quickly warmed, and the sample directed to the separating columns by a stream of hydrogen carrier gas. Forty-five percent of the total carrier flow was directed to the PLOT column; 21%, 17%, and 17% was directed onto the DB-1/ECD, DB-1/FID, and Cyclolex columns, respectively. A 40 L x 2000 psig whole air sample collected at Niwot Ridge, Colorado, was used as the working standard. It was assayed between each set of four samples in the same manner used to analyze the canister samples [Blake et al., this issue]. Two other pressurized whole air standards were periodically assayed to ascertain the integrity of the working standard over time. They revealed no statistically significant (less than 1 sigma) changes in the reported gases over the 379 working standard analyses made during the entire project. The absolute calibration of these standards and further analytical details are described by Blake et al. [1992, 1994].

The measurement precision for the gases quantified during the Lagrangian experiments can be estimated from four samples collected during a 6-min period in a well mixed air mass encountered at low altitude during the first hour of flight 11. The mean mixing ratios, along with the corresponding 1-sigma standard deviations were (in ppbv) ethane, 1112±5, propane 144.0±1.9, n-butane 69.1±1.9, i-butane 53.5±1.6, i-pentane 23.1±0.7, tetrachloroethene 26.3±0.2, and methyl chloroform 182.2±0.5. The measurement precisions for these gases are consistent over a wide range of concentrations which is illustrated by the following mean and standard deviation values for six samples collected in the ML during flight 4: Ethane 1115±5, propane 89.3±1.7, n-butane 7.6±1.4, i-butane 3.8±0.8, tetrachloroethene 15.9±0.2 and methyl chloroform 150.0±1.0. Except for ethane, which had the same mixing ratio in both sets, the flight 4 samples exhibited lower concentrations than those of flight 11, yet had similar measurement precision. During the Lagrangian portion of the flights described in this paper, all reported gases were at levels well above their detection limits.

Results and Discussion

Implicit in a Lagrangian strategy is the need to intercept the same air mass at different times. To assist in this task, before each Lagrangian experiment the National Oceanic and
Atmospheric Administration (NOAA) R/V Oceana released a series of constant-volume balloons (tetroons) equipped with Global Position System transmitters [Businger et al., this issue]. The tetroons were to "tag" the air mass and be advected with it while relaying their satellite-derived positions back to the research aircraft.

In addition to balloons, chemical species can be used as tracers to follow the motion of an air mass advecting relative to the ground or other air masses. Ideally, a conservative tracer is used that moves passively with the air mass and has no additive or removal processes that are significant over the timescale of the experiment. Changes in the concentration of this tracer then will indicate where the observation was made relative to any spatial gradients present. Tetrachloroethylene (C\textsubscript{2}Cl\textsubscript{4}) is a particularly good chemical tracer because its emissions are solely anthropogenic and is used exclusively in urban areas. With an average atmospheric lifetime against HO attack of approximately 5 months, C\textsubscript{2}Cl\textsubscript{4} has low background concentrations [Koppmann et al., 1993; Wang et al., 1995]. Therefore adjacent air masses can have substantially different concentrations.

All samples were collected over the ocean. None of the halocarbon or NMHC gases discussed in this paper are water soluble but they do react with HO and Cl radicals at various rates. Some of the hydrocarbons have oceanic sources. The majority of C\textsubscript{2}-C\textsubscript{4} NMHCs emitted from the North Atlantic are in the form of short-lived akenes, with ethene comprising an average of 40% of these NMHCs [Plass-Dülmer et al., 1995]. Based on fluxes reported by Singh and Zimmerman [1992] and Plass-Dülmer et al. [1995], we estimate that emissions into a 500-m-deep surface layer during the longest experimental period would contribute less than 1 ppv of ethene and less than 0.3 pptv of propane. Therefore such emissions are not large enough to significantly perturb the ethene and propane concentrations encountered during this project.

The first Lagrangian experiment took place in very uniform clean marine air. In addition, frequent drizzle added sufficient weight to the tetroons to force them into the ocean early in this experiment. Another very important parameter is the amount of dilution of the Lagrangian air parcel during the course of the experiment. No statistically significant difference between the free troposphere and the marine boundary layer was observed for any of the assayed halocarbons, negating the use of these species as chemical tracers to indicate how much mixing may have occurred during this experiment.

The second Lagrangian experiment, which examined the change with time of a polluted continental/marine air mass, provided a unique opportunity to study the atmospheric oxidation processes and chemical budgets of several NMHCs and halocarbons in the MBL. Therefore this paper will discuss results from the second experiment only.

**Second Lagrangian Experiment**

The second Lagrangian experiment was made up of flights 11 through 14 which were flown June 18 to 20. During flight 11, 53 samples were collected, while 48 canisters were filled on each of flights 12-14. Of the several tracking balloons released before flight 11, only one tetroon survived the duration of the experiment. The flights were based on the path of this balloon as well as on the wind speeds and directions measured onboard the various research aircraft. For a complete logistical overview of all ASTEX/MAGE balloon, ship, and aircraft operations, see Huebert et al. [this issue].

The detailed meteorology for this experiment can be found in the work by Bretherton and Pincus [1995] and Bretherton et al. [1995]. In summary, the MBL over the ocean was generally stratified into a surface layer (SL) below about 500 m, and a mixed layer (ML) (between about 650 and 1700 m). The boundary region, typically between 500 and 650 m, was frequently marked by scud or broken cumulus (the surface cloud layer). The SL was usually unstable or conditionally stable. The ML was conditionally stable, indicating that significant convective turbulence could only be observed in the ML when the air was at its saturation point, or associated with cloud dynamics. The boundary between the ML and the free troposphere (FT) was usually marked by thick sheets of stratuscumulus clouds. At the beginning of flight 11 the wind in the FT was from the NW, while the ML wind was predominately out of the north, producing wind shear between the two layers. Surface layer winds were initially from the NE but were out of the north by the beginning of flight 12, minimizing any wind shear between the mixed and surface layers.

During flight 11, there were 12 samples collected in the SL (below 500 m), 18 in the ML (between 750 and 1700 m), and 14 in the FT (above 1850 m). All were collected between 2242 UT on June 18, and 0219 UT on June 19: local clock time and UT were the same. The C\textsubscript{2}Cl\textsubscript{4} concentrations in these samples are plotted versus longitude in Figure 1. Their positions have been normalized or corrected to midnight using backward and forward trajectories based on the measured wind speeds and directions. Little longitude correction was required, as the winds were predominantly out of the north. The largest longitudinal correction was 0.22°, with an average ±1 sigma correction of ±0.04°.

Figure 1 shows that the ML between 21.6° and 21.8°W longitude had low concentrations of C\textsubscript{2}Cl\textsubscript{4} relative to the SL. This feature was also present for all other assayed gases. Because the FT exhibited considerably lower concentrations of all assayed gases, these observations suggest that the air in this region of the ML had undergone recent entrainment from the FT. The seven ML samples most resembling the slightly higher SL C\textsubscript{2}Cl\textsubscript{4} concentrations are plotted versus corrected longitude in Figure 2. The values of concentration versus corrected longitude given by the linear regression through
Figure 2. C$_2$Cl$_4$ versus longitude (corrected for wind drift) in the surface layer and mixed layer for Flight 11 with recently entrained points removed.

Figure 3a. Mixed layer C$_2$Cl$_4$ deficit versus longitude (corrected for wind drift) for flight 11.

Figure 3b. Mixed layer CH$_3$CCl$_3$ deficit versus longitude (corrected for wind drift) for flight 11.

facilitated comparison between flights at different points along the advecting concentration gradient. The fact that flight 11 was made in a region with a characteristic concentration gradient for so many chemical species made it relatively easy to identify the same air mass when it was reacquired during flight 12.

Figure 4 shows the C$_2$Cl$_4$ concentration gradient for the 16 SL samples collected during flight 12. A longitudinal gradient with a slope of 13 pptv C$_2$Cl$_4$/deg longitude is present west of 21.9° W longitude, with a much shallower slope of about 2 pptv C$_2$Cl$_4$/deg longitude to the east. Comparison of the flight 11 SL C$_2$Cl$_4$ concentrations in Figure 1 with the flight 12 SL samples in Figure 4 shows that the C$_2$Cl$_4$ concentrations for both flights were in the 20 to 27 pptv range, indicating that the same portion of the gradient was sampled. The similarities in the gradient features, together with nearly identical concentration ranges sampled throughout this gradient, strongly suggest that the SL samples collected during flight 12 came from the same air mass encountered in flight 11. A similar comparison of CH$_3$CCl$_3$ concentrations from flights 11 and 12 supports this conclusion.

Entrainment analysis similar to that performed for flight 11 indicates that over the period from the end of flight 11 through
flight 12, the ML was losing its original homogeneity as a result of entrainment from the FT. Thus, by the end of flight 12, many isolated pockets of FT air were being sampled in the ML, significantly changing the composition of this layer compared to flight 11.

Flights 13 and 14 were conducted in a very similar air mass. However, for flight 13, C$_2$Cl$_4$ exhibited lower concentrations in the SL and very little gradient. CH$_3$CCl$_3$ retained some of its original horizontal gradient with patches of inhomogeneity. Higher concentrations of ethane and propane to the southwest suggest influence from natural gas emissions [Blake et al., this issue]. Thus the characteristic signature created by the outflow gradient of the northern European continental air mass had been lost. This made it more difficult to employ the analysis methods discussed above. Therefore the next sections focus on the changes between certain portions of flight 11 and flight 12 only and are used to calculate hydroxyl and chlorine radical concentrations in the SL and to quantify mixing between the ML and SL.

Calculation of [HO], [Cl], and Mixing From Hydrocarbon Concentration Changes

Two time periods were employed for the detailed study of the NMHC (and CH$_3$CCl$_3$) concentration changes relative to C$_2$Cl$_4$ in the Lagrangian SL. The first results are derived from changes over the approximately 11 hours between around midnight during flight 11 (from 2246 to 0215, with a median time ± 1 sigma of 2231 ± 28 min) and the first part of flight 12 (from 1030 to 1131, median time 1106 ± 16 min). Even though the initial collection period was relatively long (3.5 hours), the samples could be considered together because little photochemistry is expected to occur at night. The lack of nighttime photochemistry also meant that the HO and Cl concentrations calculated for this time period were scaled to the 5 hours of daylight, i.e., from sunrise at 0606 to 1106. The second set of results was derived from changes over a daytime period of 2 hours and 19 min between the first part of flight 12 (from 1050 to 1131, 1106 ± 16 min) and the second part of flight 12 (1322 to 1332, 1325 ± 3 min). Local solar noon was 1324.

Model description. The theoretical model used to fit the NMHC losses assumed that the SL and ML were vertically well mixed within their respective layers. After removal of samples contaminated by exhaust and ML samples recently affected by entrainment from the FT, the measurements were consistent with this assumption. The vertical column above the ocean did not remain intact; i.e., between flights 11 and 12, the ML moved about 35° more to the west than did the SL, thus, only mixing into the SL from the initial or final observed ML could be accounted for. As shown in Table 1, the ML was highly stratified with respect to the SL during flight 11. However, by 1100, when the Electra returned to sample the air mass for flight 12, most of the stratification between the SL and ML had been removed. This could have been the result either of advection of the ML over a more similar portion of the SL and/or mixing between the layers. The ML and the SL were similar in composition as compared to the FT; thus the ML acted as a buffer to separate the SL from the very different FT.

The surface and mixed layers were compared vertically for mixing and temporally for chemical loss, using C$_2$Cl$_4$ as the principal tracer. The latitudinal gradient of C$_2$Cl$_4$ and its good correlation with the NMHCs and CH$_3$CCl$_3$ ($R^2 > 0.9$) allowed the Cartesian coordinate system of latitude and longitude to be transformed to a Lagrangian or chemical coordinate system via C$_2$Cl$_4$. The mixing ratio of C$_2$Cl$_4$ was then used to refer to a

![Figure 3c. Mixed layer CH$_3$CCl$_3$ deficit versus C$_2$Cl$_4$ deficit for flight 11.](image)

![Figure 4. Surface layer C$_2$Cl$_4$ versus longitude for flight 12.](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Surface Layer $^a$</th>
<th>Mixed Layer $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C$_{SL}$</td>
<td>C$_{ML}$</td>
</tr>
<tr>
<td>Ethane</td>
<td>1037.0 ± 6.6</td>
<td>1020.0 ± 15.8</td>
</tr>
<tr>
<td>Propane</td>
<td>132.1 ± 2.8</td>
<td>125.1 ± 4.1</td>
</tr>
<tr>
<td>n-Butane</td>
<td>62.8 ± 0.9</td>
<td>67.3 ± 1.9</td>
</tr>
<tr>
<td>i-Butane</td>
<td>48.2 ± 0.5</td>
<td>49.4 ± 1.3</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>73.3 ± 0.5</td>
<td>22.0 ± 0.8</td>
</tr>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>178.6 ± 0.3</td>
<td>170.4 ± 1.0</td>
</tr>
</tbody>
</table>

Values are in ppbv.

$^a$ Concentrations taken from the appropriate linear regression plot of each species with C$_2$Cl$_4$ at a C$_2$Cl$_4$ concentration of 24.5 ppbv. The 1 sigma confidence intervals are calculated from the scatter about the linear regression.

$^b$ Concentrations taken from the appropriate linear regression plot of each species with C$_2$Cl$_4$ in the ML directly above the corresponding SL. The 1 sigma confidence intervals are calculated from the scatter about the linear regression.
Table 2. HO and Cl Rate Constants

<table>
<thead>
<tr>
<th>Compound</th>
<th>HO Reaction Rate ( (k_{HO}) ) cm(^3) molecule(^{-1}) s(^{-1})</th>
<th>Reference</th>
<th>CI Reaction Rate ( (k_{CI}) ) cm(^3) molecule(^{-1}) s(^{-1})</th>
<th>Reference</th>
<th>Ratio ( k_{CI}/k_{HO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-Pentane</td>
<td>3.94 x 10(^{-12})</td>
<td>Atkinson [1994]</td>
<td>2.03 x 10(^{-10})</td>
<td>Atkinson and Aschmann [1985]</td>
<td>52</td>
</tr>
<tr>
<td>n-Butane</td>
<td>2.54 x 10(^{-12})</td>
<td>Atkinson [1994]</td>
<td>1.97 x 10(^{-10})</td>
<td>Atkinson and Aschmann [1985]</td>
<td>78</td>
</tr>
<tr>
<td>i-Butane</td>
<td>2.34 x 10(^{-12})</td>
<td>Atkinson [1994]</td>
<td>1.37 x 10(^{-10})</td>
<td>Atkinson and Aschmann [1985]</td>
<td>59</td>
</tr>
<tr>
<td>Propane</td>
<td>1.14 x 10(^{-12})</td>
<td>Atkinson et al. [1992]</td>
<td>1.4 x 10(^{-10})</td>
<td>Atkinson et al. [1992]</td>
<td>123</td>
</tr>
<tr>
<td>Ethane</td>
<td>2.5 x 10(^{-13})</td>
<td>Atkinson et al. [1992]</td>
<td>5.9 x 10(^{-11})</td>
<td>Atkinson et al. [1992]</td>
<td>236</td>
</tr>
<tr>
<td>(C_2Cl_4)</td>
<td>1.7 x 10(^{-13})</td>
<td>Atkinson et al. [1992]; DeMore et al. [1992]</td>
<td>4.1 x 10(^{-11})</td>
<td>Atkinson and Aschmann [1987]</td>
<td>243</td>
</tr>
<tr>
<td>(CH_2CCl_3)</td>
<td>1.0 x 10(^{-14})</td>
<td>DeMore et al. [1992]</td>
<td>4.0 x 10(^{-14}) (^*)</td>
<td>DeMore et al. [1992]</td>
<td>4</td>
</tr>
</tbody>
</table>

\(^*\)The reference recommends a rate of < 4.0 x 10\(^{-14}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\).

particular position on the concentration gradient, rather than referring to spatially fixed coordinates.

Model calculations. The laboratory determined rate constants used in the calculations below [Atkinson, 1994; Atkinson and Aschmann, 1985, 1987; Atkinson et al., 1992; DeMore et al., 1992] are shown in Table 2. The average temperature at 500 m for both flights 11 and 12 was 287±2 K. When available, rate constants at 287 K were used; otherwise the 298 K rate constant was substituted. This is expected to introduce very little error (less than 5%), as the rates do not change much over this narrow temperature range.

The residual of the linear best fit to the weighted ethane, propane, n-butane, i-butane, i-pentane, and \(CH_2CCl_3\) losses was minimized using the following scenarios: HO only chemistry, CI only chemistry, and mixing between the ML and SL only. The losses were also fitted to combined HO chemistry and mixing; CI chemistry and mixing; HO and CI chemistry; and HO, CI and mixing. These linear regressions were calculated based on the York method [York, 1966], which takes into account error in both coordinates. Examples for n-butane are shown in Figures 5 and 6. The confidence intervals were calculated based on the scatter about the linear regression, and are thought mainly to be the result of slight inhomogeneities in the mixing of the two air masses along the chemical gradient. The Student's t factor was also used in the calculation of the confidence intervals.

Equation (3) calculates a concentration at time \(t\) for each compound using the initial hydrocarbon and \(CH_2CCl_3\) values taken from their linear relationships with \(C_2Cl_4\) in the SL and ML (\(C_{SL}(0)\) and \(C_{ML}(0)\), respectively).

\[
C_{SL}^{calc}(t) = (1-f)C_{SL}(0) + fC_{ML}(0)\exp[-t(k_{HO}[HO] + k_{CI}[Cl])] \tag{3}
\]

where \(C_{SL}^{calc}(t)\) is the calculated mixing ratio of a compound at time \(t\) and \(f\) is the fraction of SL air being replaced by the ML. The terms \(k_{HO}\) and \(k_{CI}\) are second-order rate constants taken from Table 2, and [HO] and [CI] represent the time-averaged concentrations of HO and CI. This method assumes that the air mixing into the SL from the ML underwent similar chemistry as did the SL.

Dividing both sides of equation (3) by \(C_{SL}(0)\) yields equation (4),

\[
R_{SL}^{calc}(t) = (1-f)R_{ML}(0)\exp[-t(k_{HO}[HO] + k_{CI}[Cl])] \tag{4}
\]

Figure 5. Surface layer n-butane versus \(C_2Cl_4\) for the first half of flight 12. Confidence intervals and error arcs are 1 sigma.
Figure 6. Surface layer n-butane versus C₂Cl₄ for the second half of flight 12. Confidence intervals and error bars are 1 sigma.

where $R_{SL}^{\text{calc}}(t)$ is the ratio of the SL concentration at time $t$ divided by the initial SL concentration and $R_{ML}(0)$ is the initial ML concentration divided by the initial SL concentration. Self-consistent with the above iteration (with respect to the amount of mixing, HO and/or CI loss), the C₂Cl₄ concentration at time $t$ is calculated. The program recalculates equation (4) to minimize $S$ ($\chi^2$) in equation (5) until it obtains the best fit for the parameters used:

$$S = \sum w_i (R_{SL}^{\text{obs}}(t) - R_{SL}^{\text{calc}}(t))^2$$

where $w_i$ is the statistical weight based on a linear least squares fit of the hydrocarbon or CH₂CCL₃ and is defined in (6),

$$w_i = 1 + (\frac{\text{RSL}^{\text{obs}}(t)}{\text{RSL}^{\text{calc}}(t)})^2$$

where $\sigma$ is the estimated error for the corresponding ratio.

The initial C₂Cl₄ concentration calculated by the program is obtained by minimizing $S$ for all of the correlations for the NMHCs and methyl chloroform with C₂Cl₄. For example, the initial concentration of C₂Cl₄ for the first part of flight 12 is 24.5±0.1 pptv, which corresponds to an initial n-butane concentration of 61.4±0.4 pptv (Figure 5 and Table 3). The self-consistently calculated C₂Cl₄ concentration from the second part of flight 12 was 24.2±0.4 and corresponds to an n-butane concentration of 52.9±2.4 pptv (Figure 6 and Table 3).

As a guide to how well the various combinations of the above parameters fit the observed losses, the Akaike information criterion (AIC) was calculated for each of these scenarios [Sakamoto et al., 1986]. The AIC takes into account the number of parameters used in fitting the data and how well the predicted values agreed with observations, as in (7),

$$AIC = n \ln(S) + 2m$$

where $n$ is the number of species being fitted and $m$ is the number of parameters used to fit the data. A smaller AIC implies a better fit. However, some caution should be used when relatively few species are being fit by so many parameters. Although the scenarios that best fit the data are quite clear, ranking these scenarios by AIC alone is less certain. Thus, some judgment when interpreting the results is necessary.

HO, CI, and mixing scenarios between flight 11 and the first part of flight 12. Table 4 shows the best fits to the seven different scenarios describing the NMHC and CII₃,CCl₃ concentration changes observed during the 11-hour period (5 hours of daylight) between flight 11 (2331±58 min) and the first part of flight 12 (1106±16 min). The HO-only scenario gives a poor fit to the observed losses as evidenced by its high AIC of 30. The AIC for the CI only case was also poor at 29. Thus HO or CI chemistry alone does not predict the observations well. When considering mixing only, the best fit (AIC of 24) was obtained when the SL air was completely replaced by ML air.

Varying both HO and CI in a combined scenario, the AIC value was 31, which is no better than for the HO- or CI-only chemistry scenarios. However, the HO chemistry plus mixing

| Table 3. Observed Initial, Observed Final and Calculated Final Mixing Ratios in the Surface Layer for the HO, CI and Mixing Scenario (see Table 4) Between the 1106±16 Min and 1325±3 Min Sampling Segments of Flight 12 |
|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Compound          | Measured Initial Mixing Ratio | Measured Final Mixing Ratio | Measured Loss | Calculated Final Mixing Ratio |
|                  | (1106 UT)         | (1325 UT)         |                  | (1325 UT)         |
|                  | $C_o$             | $C_f$             | $C_o-C_f$       | $C_{calc}$        | $C_o-C_{calc}$       | $C_f-C_{calc}$       | Measured Loss |
| Ethane            | 1021.0±1.8        | 987.5±14.2         | 33.5            | 986.5             | 34.5               | 1.0                |
| Propane           | 129.6±1.0         | 116.4±1.5          | 9.2             | 116.2             | 9.4               | 0.2                |
| n-Butane          | 61.5±0.4          | 52.9±2.4           | 8.6             | 53.6              | 7.9               | -0.8               |
| i-Butane          | 46.4±0.4          | 42.5±4.1           | 3.9             | 42.0              | 4.4               | 0.5                |
| i-Pentane         | 21.7±0.6          | 18.1±1.6           | 3.7             | 17.8              | 4.0               | 0.3                |
| CH₂CCL₃          | 177.3±0.3         | 177.4±1.8          | 0.1             | 177.3             | 0.0               | 0.1                |

Concentrations are in pptv.

<table>
<thead>
<tr>
<th>Note</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Initial concentrations taken from the appropriate linear regression plot of each species with C₂Cl₄ at a C₂Cl₄ concentration of 24.7 pptv.</td>
</tr>
<tr>
<td>b</td>
<td>Final concentrations taken from the appropriate linear regression plot of each species with C₂Cl₄ at a C₂Cl₄ concentration of 24.1 pptv.</td>
</tr>
</tbody>
</table>

The 1 sigma confidence intervals are calculated from the scatter about the linear regression.
Table 4. Estimates of Average HO, Cl, and Mixing for the 11-Hour Period (5 Hours of Daylight) Between Flight 11 (23:31 ± 58 min) and the First Part of Flight 12 (1106 ± 16 min), and for the 2.3-Hour Daytime Period Between the 1106 ± 16 min and 1325 ± 3 min Segments of Flight 12

<table>
<thead>
<tr>
<th>Scenario</th>
<th>HO</th>
<th>Cl</th>
<th>Mixing</th>
<th>AIC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x10^6 cm^-3</td>
<td>x10^4 cm^-3</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>HO only</td>
<td>1.5±0.2</td>
<td>—</td>
<td>—</td>
<td>30</td>
</tr>
<tr>
<td>Cl only</td>
<td>—</td>
<td>3.3±0.4</td>
<td>—</td>
<td>29</td>
</tr>
<tr>
<td>Mixing only</td>
<td>—</td>
<td>—</td>
<td>100</td>
<td>24</td>
</tr>
<tr>
<td>HO+Cl</td>
<td>0.3±0.2</td>
<td>2.9±0.9</td>
<td>—</td>
<td>31</td>
</tr>
<tr>
<td>HO+Cl+mixing</td>
<td>1.6±0.3</td>
<td>—</td>
<td>55±8</td>
<td>18</td>
</tr>
<tr>
<td>Cl+mixing</td>
<td>—</td>
<td>4.0±0.6</td>
<td>50±6</td>
<td>9</td>
</tr>
<tr>
<td>HO+Cl+mixing</td>
<td>0.3±0.5</td>
<td>3.3±1.1</td>
<td>50±9</td>
<td>10</td>
</tr>
</tbody>
</table>

Midday Period Between the First and Second Parts of Flight 12

<table>
<thead>
<tr>
<th>Scenario</th>
<th>HO</th>
<th>Cl</th>
<th>Mixing</th>
<th>AIC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x10^6 cm^-3</td>
<td>x10^4 cm^-3</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>HO only</td>
<td>4.7±0.8</td>
<td>—</td>
<td>—</td>
<td>1.8</td>
</tr>
<tr>
<td>Cl only</td>
<td>—</td>
<td>7.2±1.2</td>
<td>—</td>
<td>3.2</td>
</tr>
<tr>
<td>Mixing only</td>
<td>—</td>
<td>—</td>
<td>0±8</td>
<td>15.1</td>
</tr>
<tr>
<td>HO+Cl</td>
<td>2.6±1.1</td>
<td>3.7±1.7</td>
<td>—</td>
<td>-0.5</td>
</tr>
<tr>
<td>HO+Cl+mixing</td>
<td>4.7±1.0</td>
<td>—</td>
<td>0±1.47</td>
<td>3.8</td>
</tr>
<tr>
<td>Cl+mixing</td>
<td>—</td>
<td>10±2.6</td>
<td>39±22</td>
<td>3.0</td>
</tr>
<tr>
<td>HO+Cl+mixing</td>
<td>2.6±0.7</td>
<td>6.5±1.5</td>
<td>33±14</td>
<td>-6.1</td>
</tr>
</tbody>
</table>

The scenario gave a much lower AIC of 18. The combination of Cl chemistry and mixing gave the best fit to the observed data with an AIC of 9. This scenario estimated chlorine concentrations to be 4.0±0.6 x10^4 molecules cm^-3 and mixing to be 50±6%. A similar amount of mixing was predicted for both the HO and Cl cases. Therefore, although mixing cannot alone describe the observed concentration changes, it must be included with the chemical terms.

Combining all three HO, Cl, and mixing terms resulted in a slightly higher AIC of 10. However, this combination is the most reasonable scenario, and the calculated average daytime concentrations for HO and Cl of 0.3±0.5 x10^6 molecules cm^-3 and 3.3±1.1 x10^4 molecules cm^-3, respectively, with mixing estimated at 50±9%, yield a good fit to the observations. In this case the Cl reactions and mixing processes were seen to dominate the aging of this air mass, with the relative unimportance of the calculated HO levels leading to its wide range of possible HO concentrations.

Average HO, Cl, and mixing between the first and second parts of flight 12. The second set of fitted Lagrangian results were calculated from NMHC and CH_2CCL_3 concentration changes observed during the 2.3-hours period just before solar noon between the 1106 ± 10 min and 1325 ± 3 min sampling segments of flight 12. Seven samples were collected in the SL during the first part of flight 12, and these are compared for changes in concentrations with five SL samples from the second part.

Table 4 shows that the HO-only case, with an AIC of 1.8, fits most of the observations well. The Cl only loss mechanism (AIC of 3.2) gives a slightly worse AIC but still yields a good fit to the observed data. In the mixing-only scenario, the best fit was obtained when no mixing was involved. This is because the SL was slightly lower in concentration in four of the six gases, while CH_2CCL_3 and i-pentane had similar concentrations as the ML. Mixing did not improve the HO scenario, but the Cl and mixing scenario (AIC of 3.0) predicts significant mixing.

Considering both chemical removal processes together yields an AIC of -0.5. However, with an AIC of -6.1, the combination of HO, Cl, and mixing together by far gives the best fit to the observations. This fit was obtained with an HO concentration of 2.6±0.7 x10^6 molecules cm^-3, Cl at 6.5±1.4 x10^4 molecules cm^-3, and mixing of 33±14%. The differences between the expected and observed losses shown in Table 3 were no more than 1 pptv for any of the gases.

The average [HO] for this nighttime period is much higher (about a factor of 9) than the average for the 5 daylight hours following dawn. This increase is as expected for a photochemically produced radical such as HO. The chlorine concentrations were also higher for the later time period (about a factor of 2). This indicates that photochemistry plays an important part in the production of Cl and is consistent with the field results of Perner et al. [1993] and with recent laboratory experiments by Behnke and Zetzsch [1995] that produced Cl precursors from light, ozone, and sea-salt aerosol in the absence of NOx. However, our levels of Cl for the morning period are also consistent with a significant nighttime buildup of Cl atom precursors and a morning release of Cl. Additional experiments with better time resolution and under varying conditions would help to elucidate the diurnal Cl cycle.

Other possible loss processes. NMHC loss by reaction with nitrate and bromine radicals was also examined. Insignificant nitrate radical concentrations would have existed overnight as evidenced by the low levels (less than 40 pptv) of the photolysis product/precursor nitric oxide measured during both flights 11 and 12 (A. Turons, unpublished data, 1993). To examine the possible impact of bromine, the ozone concentrations [Kok and Schillawesi, unpublished data] are considered. Initially, ozone in the ML was 53.1 ppbv and the SL concentration was 50.1 ppbv. Hypothetically, if 100% of the SL air were exchanged with the ML and assuming no loss processes existed, the SL ozone levels would have increased to 53.1 ppbv. However, by the end of flight 12 the SL O_3 levels had increased only slightly to 50.7 ppbv. If it is assumed that this 2.4 ppbv (about 5%) difference between the hypothetical and measured O_3 levels was a loss caused by reaction with Br atom chemistry only, then it can be calculated that such levels
would have very little effect on the measured NMHC concentrations. This is because the rate of the reactions of Br with the alkanes are about 3 orders of magnitude slower than it is with O3. Even doubling the O3 loss to 10% would result in a less than 0.2% NMHC loss from Br. In addition, our calculations show that the measured O3 concentrations are consistent with the mixing, H2O, and Cl concentrations derived earlier. The excellent fit to the NMHC data also indicates that other removal processes and marine NMHC sources were not significant over the short time period of this experiment.

Conclusion

Position in the Lagrangian reference frame was indicated by using C2Cl4 as the principal tracer. Correlations of C2Cl4 and CH3CIC3 versus longitude were also used in identify regions of recent entrainment from the FT to the ML. Calculations fitting the observed temporal NMHC and halocarbon changes made possible the simultaneous, decoupled determination of mixing and time averaged hydroxyl and atomic chlorine concentrations. Daytime concentrations in the surface layer for the midnight to 1100 period were calculated to be 0.3+0.5 x10^6 molecules cm^-3 for HO, and 3.3+1.1 x10^4 molecules cm^-3 for Cl. Noontime concentration estimates were 2.6+0.7 x10^6 molecules cm^-3 for HO and 6.5+1.4 x10^4 molecules cm^-3 for Cl. The HO levels vary diurnally as expected, and the higher noon Cl levels also indicate a daytime photochemical source. However, the fact that the Cl variation was much smaller than for HO is also consistent with a nighttime precursor buildup of easily photolyzed Cl species.

This is the first field experiment for which HO, Cl, and mixing have been quantified simultaneously. The results suggest that, under the conditions encountered during the second Lagrangian experiment of ATEX/MAGE, all three processes were important in the photochemical and dynamical aging of this air mass.

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References


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