Tropospheric hydroxyl and atomic chlorine concentrations, and mixing timescales determined from hydrocarbon and halocarbon measurements made over the Southern Ocean

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Abstract. During the First Aerosol Characterization Experiment (ACE 1) field campaign, 1419 whole air samples were collected over the Southern Ocean, of which approximately 700 samples were collected in the marine boundary layer (MBL), 300 samples were taken in the free troposphere (FT), and the remainder were collected in the buffer layer (BuL), the layer between the MBL and FT. Concentrations of tetrachloroethene, ethane, ethyne, and propane decayed over the 24 day duration of the intensive portion of the field campaign, which began November 18, 1995. This decline was consistent with what is known about seasonal increase of HO and the seasonal decrease in biomass burning. Using a simple empirical model, the best fit to the observations was obtained when the average [HO] was $6.1 \pm 0.3 \times 10^5$ cm$^{-3}$, and an average [C1] of $720 \pm 100$ C1 cm$^{-3}$. The corresponding exchange times were 14 $\pm$ 2 days between the MBL and FT, and 49 $\pm$ 40/-13 days between the MBL in the intensive campaign region and the MBL region to the north (nMBL).

1. Introduction

Knowledge of the oxidative capacity of the atmosphere, and the contributions to it from various short-lived free radicals such as hydroxyl (HO), atomic chlorine (C1), and nitrate (NO$_3$), is crucial in assessing the lifetimes and impacts of many greenhouse gases and/or ozone-depleting gases, such as methane and methyl chloroform. In the troposphere, many important trace gases, such as hydrocarbons, hydrohalocarbons, carbon monoxide, and dimethyl sulfide (DMS), are primarily removed from the atmosphere by reaction with HO radicals. In some polluted air masses, oxidation by Cl and NO$_3$ can be significant [Blake et al., 1993; Wingenter et al., 1996]. The oxidation of DMS and its products can lead to the formation of sulfate aerosols, which affect the Earth's radiative budget [Charlson et al., 1987]. Several articles addressing the oceanic and atmospheric distribution of DMS in the First Aerosol Characterization Experiment (ACE 1) study region can be found in the first ACE 1 special section and in this issue [e.g., Curran et al., 1998; De Bruyn et al., 1998; Blake et al., this issue].

On a global and quarter hemispheric scale, HO concentrations and seasonality have been determined by methyl chloroform inference [Singh et al., 1979; Prinn et al., 1995]. Local quantification of HO mixing ratios has been achieved during only a limited number of field experiments, either by measurement [e.g., Wennberg et al., 1994; Eisele et al., 1994; Poppe et al., 1994], or indirectly from temporal changes in nonmethane hydrocarbon (NMHC) concentrations in well defined air masses [e.g., Wingenter et al., 1996; Blake et al., 1993; Roberts et al., 1984]. Unfortunately, many of these experiments employing NMHCs with different reactivities have yielded a wide range of [HO] estimates within the same data set [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], or to the influence of Cl chemistry [Finlayson-Pitts, 1993]. By simultaneously optimizing calculated mixing ratios of several different NMHCs to their observed mixing ratios, Wingenter et al. [1996] calculated HO and Cl concentrations and the amount of vertical mixing. Recently, Ehhalt et al. [1998] provided an outline on the use of NMHC data along with various model types for the determination of HO concentrations.

There has been considerable interest in recent years regarding the quantification of tropospheric Cl radicals and their impact on the oxidative capacity of the troposphere [Singh and Kasting, 1988; Keene et al., 1990; Finlayson-Pitts, 1993; Graedel and Keene, 1995; Singh et al., 1996a, b; Wingenter et al., 1996]. Three types of Cl atom precursor...
reactions have been identified, all of which require sea-salt aerosol and either NOₓ (NO, NO₂, N₂O₅, HNO₃, etc.), degassing of HCl, or the oxidation of Cl⁻ by O₃, HO, or HO₂. The NOₓ reactions generally proceed as

\[
\text{NO}_x\text{(gas)} + \text{NaCl}\text{(aq)} \rightarrow \text{XCl}\text{(gas)} + \text{products} \quad (1)
\]

\[
\text{XCl}\text{(gas)} + \text{hv} \rightarrow \text{Cl} + \text{products} \quad (2)
\]

where XCl is an easily photolyzed Cl species, such as Cl₂, NOCl, ClNO₂, or HOCl, which can accumulate overnight and dissociate within about 1 hour after sunrise [Green, 1972; Finlayson-Pitts, 1983; Zetzsch et al., 1988; Finlayson-Pitts et al., 1989].

Degassing of HCl is enhanced under polluted conditions, namely, when acidic compounds such as H₂SO₄ or HNO₃ are present. The subsequent reaction with HO, HO₂, or O₃ with Cl⁻ associated with sea-salt aerosols [see Keene et al., 1990 and references therein].

Recently, attempts have been made to estimate the average tropospheric Cl mixing ratio [Singh et al., 1996b; Rudolph et al., 1996]. The two dimensional (2-D) models used in these studies relied on assessing the budget of tetrachloroethene, which is emitted by anthropogenic sources and whose emissions are thought to be accurately inventoried. Once all the source and sink terms for tetrachloroethene are accounted for, the loss by reaction with Cl atoms is invoked to balance the budget. This method requires the accurate determination of the tetrachloroethene emissions, tetrachloroethene burden, and the HO field. Initial estimates have yielded average tropospheric Cl concentrations in the low 10^5 Cl atoms cm⁻³ range, with considerable uncertainty [Singh et al., 1996b; Rudolph et al., 1996].

Observations of the seasonal variation of halocarbons and hydrocarbons not only provide information on the average oxidative capacity of the atmosphere, but also on its seasonality. Seasonal variations of NMHCs and tetrachloroethene in the northern hemisphere (NH) [e.g., Blake and Rowland, 1986; Singh and Zimmerman, 1992; Penkett et al., 1993; Rudolph, 1995; Wang et al., 1995] have been reported but few observations exist for the southern hemisphere (SH) [Blake and Rowland, 1986; Rudolph et al., 1989; Wang et al., 1995]. Maximum background hydrocarbon levels are observed in winter months, with minimum levels occurring during summer. In the NH, longer lived gases tend to reach their minimum concentration later in the solar year compared to gases that react more quickly with HO [e.g., Penkett et al., 1993; Jobson et al., 1994b; Goldstein et al., 1995].

The International Global Atmospheric Chemistry (IGAC) sponsored First Aerosol Characterization Experiment (ACE 1) field campaign intensive period, mid-November to mid-December 1995, was conducted over the pristine Southern Ocean region south of Australia. The primary focus of ACE 1 was to observe the formation and growth of new particles from their precursors and observe their effect on cloud formation and radiative properties [Bates et al., 1998]. Measurements were made at two coastal sites, aboard two research ships, and aboard the National Center for Atmospheric Research (NCAR) C-130 aircraft, from which UC Irvine collected whole air samples [Bates et al., 1998]. One of the principal objectives for the UCI NMHC and halocarbon measurements was to indicate when any of the air masses sampled by the NCAR C-130 had been influenced by recent emissions [see also Blake et al., this issue].

Two Lagrangian experiments, similar to those that were performed during the Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange (ASTEX/MAGE) experiment in the North Atlantic [Wingenter et al., 1996] were conducted during ACE 1. However, with the exception of ethane [Sive, 1998], the much cleaner Southern Ocean boundary layer exhibited NMHC mixing ratios that were too low to observe temporal changes during the short timescale of these Lagrangian experiments. By contrast, temporal changes were observed during the period of the entire campaign, allowing an Eulerian reference frame to be employed. An Eulerian reference frame is one in which the observer moves relative to the air mass sampled. For example, a moving platform such as a ship steaming into the wind, or by remaining stationary on an island with air masses being advected past. This paper describes Eulerian observations of NMHCs and tetrachloroethene made during the intensive portion of ACE 1. From these observations, concentrations of HO and CI, as well as the vertical and horizontal mixing timescale between air masses, have been calculated using a simple, empirical three-box model. Lower tropospheric aircraft measurements of in situ HO concentrations were also made on board the NCAR C-130 [Mauldin et al., 1998]. The time average concentration of the in situ HO measurements is compared with the HO estimate derived from our Eulerian observations of NMHCs and tetrachloroethene.

2. Experiment

More than 2500 whole air samples were collected during 33 ACE 1 flights on board the NCAR C-130 aircraft. The samples were assayed for various halocarbons and NMHCs. Data used for part of this paper are the tetrachloroethene, ethane, ethyne, and propane mixing ratios made from more than 1500 samples collected on 18 local flights flown November 18 through December 12, 1995, out of Hobart, Tasmania, Australia (40°S-55°S latitude and 135°E-160°E longitude) and two transit flights made just north of this area on November 10 and December 15, 1995. The air sampling apparatus used for ACE 1 was very similar to the ASTEX system [Blake et al., 1996]. A maximum of 96 samples per flight could be collected. NMHCs and halocarbons from each whole air sample were quantified by complementary five-column gas chromatography using three electron capture detectors (ECD) and three flame ionization detectors (FID). Five different separation columns were contained in four independently programmed Hewlett-Packard 5890 Series II gas chromatographs (GCs). In the first GC a 50 m x 0.32 mm Al₂O₃/Na₂SO₄ porous layer open tubular (PLOT) column was coupled to an ECD to separate and quantify C₂-C₅ NMHCs. Installed in GC two was a 60 m x 0.25 mm DB-1 column with a 1 mm film thickness. The effluent separated by the DB-1 column was split. A portion of the flow was directed to an ECD, which measured C₁ and C₂ halocarbons, and the remainder of the flow went to an FID for quantification of C₃-C₅ NMHCs. In the third GC, a 60 m x 0.25 mm DB-5 MS column with the film thickness of 0.5 mm was coupled to an
ECD for separating and quantifying halocarbon compounds. The fourth GC contained two columns, a 60 m x 0.25 mm CD-B/Cyclodex column coupled to an FID, which separated and detected higher molecular weight NMHCs, and a composite column, which consisted of a 30 m of DB-1 column spiked to 30 m of a DB-5 MS column, which along with an ECD, separated and detected C1 and C2 halocarbons. The detector signals were sent to six Spectra Physics 4400 computing integrators and an IBM 486 personal computer using Labnet software for data capture and storage. This configuration allowed for six simultaneous yet separate chemical analyses from the same sample.

For ACE 1, a 1520 cm³ (at STP) aliquot of each sample was trapped on a preconcentration loop filled with 3 mm diameter glass beads, immersed in liquid nitrogen. Once the sample was trapped, the preconcentration loop was isolated and warmed to 80°C, then injected and directed by hydrogen carrier gas to the GCs. The split was reproduced with high precision, and 27.0% of the carrier flow was directed to the PLOT column, 18.9% was directed to the DB-1/ECD, 16.1% was directed to the DB-1/FID, 16.2% was directed to the DB-5MS/ECD, 11.0% was directed to the Cyclodex-B/FID, and 10.8% was directed to the DB-1/DB-5MS/ECD composite column. A 40 L x 2000 psig whole air sample collected at the Scripps Institute for Oceanography pier, La Jolla, California, was used as the working standard. The standard was assayed after every four samples in the same manner used to analyze the canister samples [Blake et al., 1996]. Two other pressurized whole air standards were periodically assayed to ascertain the integrity of the working standard over time.

An upper estimate of the measurement precision for the gases quantified during the ACE 1 local flights can be determined from eight samples collected in the MBL, at about 500 feet, during a 34 min period of flight 16. The mean mixing ratios, along with the corresponding 1σ precisions were (in parts per trillion by volume (pptv)): Tetrachloroethene, 1.39 ± 0.05; ethane, 314.4 ± 1.0; ethyne, 20.4 ± 1.4; and propane, 6.3 ± 1.5. The absolute calibration standards were periodically assayed to ascertain the integrity of the working standard over time.

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3. Eulerian Observations and Model Description

Meteorological parameters provided by NCAR describing relative humidity, temperature, potential temperature (THETA), and equivalent potential temperature (THETA E) enabled the samples from each flight to be grouped into three vertical layers, the marine boundary layer (MBL), free troposphere (FT), and buffer layer (BuL). Typically, the MBL extended from the surface to about 500-1000 m, while the FT was above an altitude of approximately 3000 m. One example from flight 18 is shown in Figure 1. Figure 2 displays the average concentrations and one standard deviation of the mean error bars for tetrachloroethene, ethane, ethyne, and propane for each of the local flights. Best fit curves to the average temporal mixing ratio data were calculated, employing a function with two exponential terms, in order to approximately describe atmospheric mixing and photochemistry. The average FT mixing ratios are plotted in Figure 3.

Comparison of Figures 2a and 3a reveals that there is no statistical difference between the tetrachloroethene mixing ratios measured in the MBL and the FT. Because 93% of tetrachloroethene emissions occur in the NH (P. Midgley, personal communication, 1997) and its lifetime is of the order of 4 months, tetrachloroethene is expected to be well mixed in the SH. However, the scatter about the curve is larger in the FT, indicating greater atmospheric variability compared to the MBL. In contrast to tetrachloroethene, the FT ethane mixing ratios shown in Figure 3b are considerably greater than in the MBL (Figure 2b). Ethane has a lifetime of approximately 2.5 months (these lifetimes are based on our HO and CI estimates and the rate constants evaluated by DeMore et al. [1997]). Thus a substantial southern hemispheric source of ethane originating outside the high southern latitude region is necessary to maintain this observed vertical gradient. The most likely source of ethane into this region is from biomass burning [Rudolph, 1995; Blake et al., this issue].

An empirical three-box model was constructed to represent the MBL and FT in the region of the ACE 1 intensive. The model is designed to estimate [HO] and [CI] in the MBL, and the exchange times between the MBL and the FT (τex1), as well as between the MBL and the nMBL, τex2. The concentrations in the buffer layer (BuL) were very similar to those measured in the MBL, and mixing between the MBL and the BuL mainly recycles air between these two layers. Thus this layer acts to "buffer" dilution by impeding direct mixing with the FT as described by Wingenter et al. [1996]. Therefore this layer was not included in the following calculations. A detailed
description of the BuL observed during ACE 1 is given by Russell et al. [1998]. Thus the average mixing time constant calculated for the exchange between the MBL and the FT (and similarly the exchange between the MBL and nMBL) represents the time needed to reduce the gradient between the MBL and the FT by a factor of 69% (the natural log of 2) in the absence of any other sources or sinks. The MBL and FT concentrations used in the model were taken from the measurements shown in Figures 2 and 3 and those from the marine boundary layer directly to the north (nMBL). The nMBL concentrations employed in the model are from the linear fit to the average concentrations of samples collected between 30°S and 40°S on the transit flights before and after the ACE 1 intensive flights (Table 1).

The model calculates [HO], [CI], and the two exchange times by varying these parameters such that the sum of the weighted residuals, simultaneously calculated from the predicted MBL values of tetrachloroethene, ethane, ethyne, and propane and the measured mixing ratios in the MBL, are minimized. This is described as follows:

\[
C_{MBLcalc}(t) = C_{MBL}(0) - \left\{ \frac{C_{MBL}(0)}{t} + \frac{C_{FT} - C_{MBL}}{t_{ex1}} + \frac{C_{nMBL} - C_{MBL}}{t_{ex2}} \right\} t
\]

(4)

where \( C_{MBLcalc}(t) \) is the calculated MBL concentration of species \( i \), either tetrachloroethene, ethane, ethyne, or propane in the MBL at time \( t \) and \( C_{MBL}(0) \) is the initial concentration. \( C_{MBL}(0)/t \) is the change in concentration due to chemical loss, where \( t \) is in the sum of the HO and CI lifetimes \( 1/t = \left[ k_{HO}[HO] + k_{CI}[CI] \right] \). The rate constants, \( k_{HO} \) and \( k_{CI} \), are taken from DeMore et al., [1997] (see Table 2), and [HO] and [CI] represent the time-averaged concentrations of HO and CI. The next term, \( \left[ C_{FT} - C_{MBL} \right]/t_{ex1} \), is the change in concentration resulting from mixing of FT air with the MBL. Similarly, the last term is the change in concentration in the MBL as a result of exchange with the nMBL. It is noted here that the model does not have direct sources and all input occurs because of mixing. Figure 4, for example, shows that no plumes were observed in the MBL, supporting this assumption [Blake et al., 1999, and this issue].
Figure 3. Measured FT (a) tetrachloroethene, (b) ethane, (c) ethyne, and (d) propane results for the ACE 1 local flights. The diamonds represent the average measured concentration with standard deviation of the mean error bar. The solid curve is the best fit (having two exponential terms) of the measurements. The outer dashed curves represent the 95% confidence interval for the measurements.

The program simultaneously recalculates equation (4), for all four gases to minimize $S$, the sum of individual $X^2$ in equation (5), until it obtains the best fit for the parameters used:

$$S = \sum w_i (C_{MBL}^{obs}(t) - C_{MBL}^{fit}(t))^2$$  \hspace{1cm} (5)

where $w_i$ is the statistical weight defined in equation (6),

$$w_i^{-1} = \sigma R_{MBL}^{obs}(t)^2$$  \hspace{1cm} (6)

where $\sigma$ is the estimated error (the sum of the relative analytical error and the scatter of the data about the best fit curve) and $R_{MBL}^{obs}(t)$ is the ratio of the observations at $t$ over the initial observations.

The model MBL values, average MBL concentrations, and the prediction intervals for the best fit curves to the average MBL measurements are plotted in Figure 2. In Figure 2a the modeled tetrachloroethene values compare well with the tetrachloroethene best fit to the data. The model values were on average 0.01 pptv greater than the best fit curve. The modeled ethane values in Figure 2b agree to within an average of 0.5 pptv with the best fit curve of the measurements.

Ethyne values predicted by the model agree well with the best fit curve to the data, with a maximum deviation from the curve of 0.3 for pptv (Figure 2c). Predicted propane values were on average 0.6 pptv below the measurement best fit, but still within the 2 $\sigma$ prediction interval of the best fit to the data. In general, the predicted values agree well with the measurements.

Optimal model fits were obtained when HO and Cl values were $6.1 \pm 0.3 \times 10^5$ HO cm$^{-3}$ and $720 \pm 100$ Cl cm$^{-3}$, with

| Flight | Tetrachloroethene | Ethane | Ethyne | Propane |
|--------|------------------|--------|--------|---------|
| Flight 8 | 1.47 ± 0.03 | 369.9 ± 1.2 | 31.6 ± 0.3 | 11.0 ± 0.4 |
| Flight 29 | 1.09 ± 0.02 | 253.8 ± 0.8 | 14.3 ± 0.04 | 5.4 ± 0.5 |

Table 1. Average Mixing Ratios for Samples Collected in the MBL North of the Intensive MBL Before and After the Hobart Local Flights

Mixing ratios are in pptv.
Table 2. HO and Cl Rate Constants, Ratios of Rate Constants, and Calculated Percent Contribution of HO and Cl to Chemical Loss

|                | $k_{HO}$  | $k_{Cl}$ | $k_{HO}/k_{Cl}$ | Calculated Percent Loss By$^a$ |
|----------------|-----------|----------|-----------------|-------------------------------|
| Tetrachloroethene$^{b,b}$ | 1.2E-13$^c$ | 4.0E-11  | 323             | HO  72 Cl  28                 |
| Ethane         | 1.8E-13   | 5.6E-11  | 304             | HO  74 Cl  26                 |
| Propane        | 9.2E-13   | 1.4E-10  | 150             | HO  85 Cl  15                 |
| Ethyne$^{b,d}$ | 6.7E-13   | 5.9E-11  | 88              | HO  91 Cl  9                  |
| Methane        | 4.0E-15   | 7.0E-14  | 17              | HO  98 Cl  2                  |
| Methyl chloroform | 6.7E-15 | 4.4E-15  | 0.7             | HO  100 Cl  0                 |
| DMS$^e$        | 4.7E-12   | 3.3E-10  | 70              | HO  92 Cl  8                  |
| Methyl bromide | 2.0E-14   | 3.3E-13  | 16              | HO  98 Cl  2                  |

All rate constants (DeMore et al. [1997] or Stickel et al. [1992]) are expressed as second-order reactions having units of cm$^3$ molecules$^{-1}$ s$^{-1}$. The average MBL temperature used was 277 K.

$^a$Percent loss is $kX \cdot [X]/(k_{HO} \cdot [HO] + k_{Cl} \cdot [Cl])$; where $X$ is either HO or Cl.

$^b$The $k_{Cl}$ is the three-body rate constant taken at a pressure equivalent to 350 m.

$^c$Read 1.2E-13 as 1.2x10$^{-13}$.

$^d$The $k_{HO}$ is the three body rate constant taken at a pressure equivalent to 350 m.

$^e$Here $k_{Cl}$ is from Stickel et al. [1992].

vertical mixing between the MBL and FT 14 ± 2 days and horizontal mixing 49 +40/-13 days. Error estimates are arbitrarily based on varying one parameter while holding the other three constant until $S$ (equation (5)) was 3 times greater than the best fit.

4. Discussion and Comparison of ACE 1 Eulerian Results

Four day back trajectory analysis [Whittlestone et al., 1998] (for an overview of the meteorology, see also Hainsworth et al. [1998]) shows that the air parcels reaching the intensive sampling region originated between 40°S and 60°S latitude, with a mostly westerly flow. This indicates that the air masses were representative of the mid-latitude/subpolar region. Potential interference with our results could occur if direct emissions of tetrachloroethene, ethane, ethyne, and propane were introduced upstream of the ACE 1 intensive region, and remained in the MBL. However, the homogeneous air masses encountered indicate a lack of recent emissions in the region (see Figure 4 and Table 3 and Blake et al. [this issue]), and NOAA advance very high resolution radiometer (AVHRR) satellite imagery shows virtually no biomass burning occurring in any part of this region for either November or December 1993, the most recent year in which the data are fully processed for these regions (http://shark1.esrin.esa.it/). In addition, 93% of tetrachloroethene is emitted in the NH (P. Midgley, personal communication, 1997) and is well mixed in this region (Figures 2a and 3a). The largest emissions of ethane, ethyne

Figure 4. Latitudinal profile of more than 700 (a) ethane, and (b) ethyne samples collected in the ACE 1 intensive MBL. The samples were normalized for the temporal trend shown in Figure 2 to the midpoint time of the experiment. The solid curve is the linear least squares best fit.
and propane in the SH are from seasonal biomass fires [Rudolph, 1995; Singh and Zimmerman, 1992; Andreae et al., 1994]. The majority of these emissions occur in the southern Tropics between July and October [Justice et al., 1996; Cahoon et al., 1992]. The lack of recent direct emissions contributed to the homogeneity of the region. This coupled with the large number of observations and the considerable time period of the experiment allowed for the observation of the decay of tetrachloroethene, ethane, ethyne, and propane in an Eulerian reference frame.

4.1. Comparison of Inferred HO With Measurements

Our diurnally averaged HO values compare well with the diurnal averaged HO measurements of Mauldin et al. [1998] made on board the NCAR C-130 during this project. From the in situ measurements it is apparent that HO noontime mixing ratios have a bimodal distribution with average diurnal concentrations of $1 \times 10^6$ and $4 \times 10^5$ HO cm$^{-3}$ depending on whether clear-sky or cloudy conditions, respectively, were encountered. Satellite imagery of the region suggests approximately 60-70% cloudy conditions, yielding average diurnal concentration of $6 \times 10^5$ HO cm$^{-3}$ based on the direct measurements. However, simply averaging the measurements diurnally for each flight also yields an average diurnal HO concentration of $6 \times 10^5$ HO cm$^{-3}$ during the study period. Thus our calculated [HO] is in excellent agreement with experimental values.

4.2. Comparison of [Cl] in Polluted and Pristine Environments

The springtime Southern Ocean CI concentration estimate of $720 \pm 100$ CI cm$^{-3}$ are 2 orders of magnitude lower than estimated for polluted NH air masses [Wingenter et al., 1996; Pszenny et al., 1993]. During the ASTEX/MAGE project, CI concentrations were estimated from a single polluted air mass [Wingenter et al., 1996] with high sea-salt aerosol concentrations [Clarke et al., 1996]. The ACE 1 CI concentration estimate is the diurnal average over 24 days, which included periods after storms when sea-salt aerosol had been washed out [Clarke et al., 1998a]. Ozone and HO concentrations during ACE 1 were not low enough in comparison to ASTEX/MAGE to account for the 2 order of magnitude differences in calculated CI. However, concentrations of NO$_y$ were most likely very much lower during ACE 1 (e.g., reactions (1) and (2)) because these air masses were clean marine. Unfortunately, NO$_y$ was not measured during ACE 1. Furthermore, the low concentrations of NO, observed in the boundary layer on board the NCAR C-130 (-3 pptv) during ACE 1, shifts the ClO$_x$ photostationary state in favor of reduced CI and increased ClO. In comparison with the pristine background conditions over the Southern Ocean, it appears that polluted NH air masses considerably favor the production of atomic CI compared to clean southern hemispheric marine air masses.

Singh et al. [1996b] estimate that because CI is generated by sea-salt aerosol, about 90% of tropospheric chlorine atoms resides in the MBL. Employing this assumption would lead to an integrated tropospheric CI value over the Southern Ocean in springtime of approximately 100 CI cm$^{-3}$. This estimate is an order of magnitude less than the global estimates of Singh et al. [1996b] and Rudolph et al. [1996].

4.3. Comparison of the Oxidative Capacity of HO and Cl

Chemical loss by CI in the MBL during the springtime Southern Ocean is significant for tetrachloroethene, ethane, propane, and to a lesser extent ethyne (Table 2). Chemical loss by CI and HO at the concentrations determined in this work are also compared in Table 2 for some stratospheric ozone-depleting substances such as methyl bromide and methyl chloroform, the greenhouse gas methane, and DMS, the main precursor to new sulfate particle growth in the clean MBL [Clarke et al., 1998b]. At the average CI levels encountered during ACE 1, CI oxidation has little impact on methyl bromide, methyl chloroform, or methane. However, 8% of the chemical removal of DMS in the MBL is a result of CI oxidation.

4.4. Vertical Transport of Methyl Nitrate

Transport times from the boundary layer to the FT can also be estimated by employing the vertical distribution of short-lived gases having surface sources [Davis et al., 1996]. Methyl nitrate concentrations of the 1419 samples collected during the ACE 1 intensive experiment were partitioned into 0.5 km bins. The averages are plotted versus altitude in Figure 5. The ocean is the only known significant direct source of methyl nitrate to the atmosphere (E. Atlas et al., manuscript in preparation, 1999). The primary removal process for methyl nitrate is photolysis, having a lifetime of about 29 days in the midlatitude MBL near the equinox [Talukdar et al., 1997] and a hydroxyl lifetime of about 100 days at $6 \times 10^5$ HO cm$^{-3}$ for an overall MBL lifetime of about 22 days. During ACE 1 the average MBL methyl nitrate mixing ratio was about 19 pptv,

### Table 3. Summary of Results for the Linear Regressions Plotted in Figure 4

| Compound          | Gradient (pptv/Latitude) | $R^2$ | Total (ppbv) | Average Mixing Ratio (ppbv) | Percent (%) |
|-------------------|---------------------------|-------|---------------|-----------------------------|-------------|
| Tetrachloroethene | 1.1E-03                   | 1.1E-03 | 1.5E-02      | 1.29                        | 1.1         |
| Ethane            | 6.1E-01                   | 8.0E-02 | 8.5E+00      | 326                         | 2.6         |
| Ethyne            | 7.5E-02                   | 1.1E-02 | 1.1E+00      | 19.7                        | 5.3         |
| Propane           | 1.1E-02                   | 1.2E-04 | 1.6E-01      | 8.7                         | 1.8         |

*a*Total change in concentration over the entire latitudinal range.

*b*The average mixing ratios were determined from the best fit curves in Figures 2-5 at midpoint time.

*c*Total divided by the average mixing ratio multiplied by 100.
timescale of this experiment to be useful. Therefore, other
being predicted from the time series of only four gases.
therefore, unsuitable for the analysis in this paper. Gases such
hydrocarbons were often times below detection limit and
Unfortunately, shorter lived gases such as butanes or larger
as CFCs or HCFCs are too long lived in comparison to the
in magnitude to the nMBL, our estimates of HO, C1, and
were not measured before and after the project, so that the
in the springtime ACE 1 intensive experiment.
700 ± 100 Cl cm⁻³ may help elucidate the mechanism(s) responsible for Cl production. Although Cl concentrations were 3 orders of magnitude less than HO, Cl is a significant oxidizer for some trace gases in the MBL because of its greater reactivity with these compounds. Transport times from the MBL to the FT and from the nMBL to the MBL in the intensive study region were 14 ± 2 days and 49 ± 40/-
13, respectively. The methyl nitrate vertical gradient was employed for validation of the MBL/FT exchange time calculated using the three-box model. Results from this study may help constrain 2-D and 3-D model values of HO and Cl concentrations as well as transport time scales in this region.

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5. Conclusion

The average hydroxyl estimate of 6.1 ± 0.3 x 10⁵ HO cm⁻³ for the MBL over the Southern Ocean during the springtime ACE 1 project agrees well with the measured diurnal average. The corresponding Cl concentration estimate in this pristine region of 720 ± 100 Cl cm⁻³ may help elucidate the mechanism(s) responsible for Cl production. Although Cl concentrations were 3 orders of magnitude less than HO, Cl is a significant oxidizer for some trace gases in the MBL because of its greater reactivity with these compounds. Transport times from the MBL to the FT and from the nMBL to the MBL in the intensive study region were 14 ± 2 days and 49 ± 40/-
13, respectively. The methyl nitrate vertical gradient was employed for validation of the MBL/FT exchange time calculated using the three-box model. Results from this study may help constrain 2-D and 3-D model values of HO and Cl concentrations as well as transport time scales in this region.

References

Andreae, M. O., B. E. Anderson, D. R. Blake, J. D. Bradshaw, J. E. Collins, G. L. Gregory, G. W. Sachse, and M. C. Shipham, Influence of plumes from biomass burning on atmospheric chemistry over the equatorial and tropical South Atlantic during CITE 3, J. Geophys. Res., 99, 12,793-12,808, 1994.

Bates, T. S., B. J. Huebert, J. L. Gras, F. B. Griffiths, and P. A. Durkee, The International Global Atmospheric chemistry (IGAC) project’s First Aerosol Characterization Experiment (ACE 1): Overview, J. Geophys. Res., 103, 16,297-16,318, 1998.

Blake, D. R., and F. S. Rowland, Global atmospheric concentration and source strength of ethane. Nature, 321, 231-233, 1986.

Blake, D. R., D. F. Hurst, T. W. Smith Jr., W. J. Whipple, T. Y. Chen, N. J. Blake, and F. S. Rowland, Summertime measurements of selected nonmethane hydrocarbons in the Arctic and subarctic during the 1988 Arctic Boundary Layer Experiment (ABLE-3A), J. Geophys. Res., 97, 16,559-16,588, 1992.

Blake, D. R., T. W. Smith Jr., T. Y. Chen, W. J. Whipple, and F. S. Rowland, Effects of biomass burning on summertime nonmethane hydrocarbon concentrations in the Canadian wetlands, J. Geophys. Res., 99, 1699-1719, 1994.

Blake, D. R., N. J. Blake, T. W. Smith Jr., O. W. Wingenter, and F. S. Rowland, Nonmethane hydrocarbon and halocarbon distributions
Singh, H. B., et al., Low ozone in the marine boundary layer of the tropical Pacific Ocean: Photochemical loss, chlorine atoms, and entrainment, *J. Geophys. Res.*, 101, 1793-1808, 1996a.

Singh, H. B., A. N. Thakur, Y. E. Chen, and M. Kanakidou, Tetrachloroethene as an indicator of low Cl atom concentrations in the troposphere, *Geophys. Res. Lett.*, 23, 1529-1532, 1996b.

Sive, B. C., Atmospheric nonmethane hydrocarbons: Analytical methods and estimated hydroxyl radical concentrations, Ph.D. dissertation, Univ. of Calif., Irvine, 1998.

Stickel, R. E., J. M. Nicovich, S. Wang, Z. Zhao, and P. H. Wine, Kinetic and mechanistic study of the reaction of atomic chlorine with dimethyl sulfide, *J. Phys. Chem.*, 96, 9875-9883, 1992.

Talukdar, R. K., J. B. Burkholder, M. Hunter, M. K. Gillis, J. M. Roberts, and A. R. Ravishankara, Atmospheric fate of several alkyl nitrates, 2.. U. V. absorption cross sections in photodissociation quantum yields, *J. Chem. Soc. Faraday Trans.*, 93, 2797-2805, 1997.

Wang, C. J.-L., D. R. Blake, and F. S. Rowland, Seasonal variations in the atmospheric distribution of a reactive chlorine compound, tetrachloroethene (CCl2=CCl2), *Geophys. Res. Lett.*, 22, 1097-1100, 1995.

Wennberg, P. O., et al., Removal of stratospheric O3 by radicals: In situ measurements of OH, HO2, NO, NO2, ClO, and BrO, *Science*, 266, 398-404, 1994.

Whittlestone, S., J. L. Gras, and S. T. Siems, Surface air mass origins during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, 103, 16,341-16,350, 1998.

Wingenter, O. W., M. K. Kubo, N. J. Blake, T. W. Smith, D. R. Blake, and F. S. Rowland, Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights, *J. Geophys. Res.*, 101, 4331-4340, 1996.

Zetzsch, C., G. Pfahler, and W. Behnke, Heterogeneous formation of chlorine atoms from NaCl aerosols in a smog chamber, *J. Aerosol Sci.*, 19, 1293-1296, 1988.