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Journal

Geophysical Research Letters, 33(11)

ISSN

0094-8276

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Publication Date

2006-06-01

DOI

10.1029/2006GL025799

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Measurement of Cl₂ in coastal urban air

B. D. Finley¹ and E. S. Saltzman¹

Received 18 January 2006; revised 3 April 2006; accepted 19 April 2006; published 6 June 2006.

[1] Measurements of Cl₂ in coastal urban air were made in Irvine, California from Aug.-Nov., 2005, using negative ion atmospheric pressure chemical ionization with tandem mass spectrometry. Cl₂ ranged from <2.5 to 20 ppt with a two month mean of 3.5 ± 3.5 ppt (1 σ) and an average noon photolysis rate of 44 ppt hr⁻¹ Cl₂. Model calculations suggest that Cl₂ photochemistry results in an increase of 5–8 ppb in daily maximum O₃ levels, relative to a base case scenario without Cl₂. **Citation:** Finley, B. D., and E. S. Saltzman (2006), Measurement of Cl₂ in coastal urban air, *Geophys. Res. Lett.*, 33, L11809, doi:10.1029/2006GL025799.

1. Introduction

[2] The OH-initiated oxidation of volatile organic compounds (VOCs) is the primary pathway leading to O₃ formation in urban air. Another pathway to O₃ formation is oxidation of organic compounds by Cl atoms, generated from photolysis of Cl₂ or other precursors, or from the reaction of OH with HCl [Singh and Kasting, 1988]. The reaction rate constants of Cl atoms with many VOCs are 1–2 orders of magnitude faster than the corresponding OH reactions [DeMore et al., 1997]. As a result, Cl competes effectively with OH at much lower concentrations. To date, there have been few direct measurements of reactive halogens in air, and halogen chemistry is not included in standard air quality models.

[3] A variety of indirect methods have been used to infer the levels of reactive chlorine in air. These include observations of chlorine isotope ratios [Volpe et al., 1998], aerosol chloride deficits [Johansen et al., 2000], tandem mist chamber measurements of volatile inorganic halogen species [Keene et al., 1993; Pszenny et al., 2004], and the ratios of various nonmethane hydrocarbons [Jobson et al., 1994; Singh et al., 1996; Wingenter et al., 1999]. These studies suggest that reactive chlorine precursors may be present in marine air at ppt levels, and that oxidation of organics by Cl atoms has a significant role in tropospheric photochemistry. Spicer et al. [1998] reported the direct detection of Cl₂ over Long Island by API/MS/MS, at levels of up to 150 pptv at night in air with marine air mass back trajectories.

[4] The origin of reactive chlorine in air is not fully understood. Sander and Crutzen [1996] proposed an autocatalytic, acid-catalyzed mechanism for Cl₂ production from marine aerosols, involving heterogeneous uptake of HOCl and subsequent oxidation of Cl⁻ ions. Laboratory studies

demonstrated Cl₂ production from the interaction of gas phase free radicals with aerosols, and led to the proposal of a non acid-catalyzed surface reaction between OH and Cl [Oum et al., 1998; Finlayson-Pitts and Hemminger, 2000; Knipping et al., 2000; Knipping and Dabdub, 2002]. Laboratory measurements have shown that seasalt aerosol reactions with N₂O₅ produce ClNO₂ [Behnke et al., 1997; Schweitzer et al., 1998]. The reaction of O₃ with seasalt and ferric ions has also been suggested as a source of Cl precursors [Sadanaga et al., 2001]. Model simulations investigating the potential role of chlorine in urban ozone formation indicate that Cl₂ levels on the order of 10 ppt result in ozone increases of several ppb in urban air [Tanaka and Allen, 2001; Knipping and Dabdub, 2002; Chang et al., 2002].

2. Detection of Molecular Chlorine (Cl₂)

[5] Molecular chlorine (Cl₂) levels were measured in this study using negative ion atmospheric pressure chemical ionization with tandem mass spectrometry [Spicer et al., 1998]. The instrument was run nearly continuously from Aug. to Nov., 2005. The sampling site was at Croul Hall on the UCI campus, approximately 4 km inland from Newport Bay. The air sample inlet was situated 3 m above ground level near a parking lot. Concurrent measurements of O₃ (10–70 ppb) and NO_x (1–100 ppb) were also made using Thermoelectron models 49C and 42C, respectively. Regional meteorological data for this period was obtained from NCEP Reanalysis and local conditions were obtained from measurements recorded at John Wayne International Airport in Santa Ana, about 3 km from the measurement site (National Climate Data Center, Unedited Local Climatological Data, <http://cdo.ncdc.noaa.gov/ulcd/ULCD>). Air mass back trajectories were computed using the Hysplit v4.7 model [Draxler and Hess, 1997, 1998].

[6] Cl₂ is highly surface active, and a laminar flow, multi-stage inlet was used to minimize wall interactions during transit of the air to the instrument. The sample inlet consisted of a 6 m long 2" ID plastic pipe (ABS and PVC) operated with an air flow rate of 0.5 m/s (64 SLPM). A 1/2" ID Teflon tube sampled isokinetically from the center of the larger pipe (2.25 SLPM) to deliver air to the atmospheric pressure ionization source. The ion source was a 1/4" ID SS tube lined with a ⁶³Ni beta-emitting foil. The source tube sampled air isokinetically from the center of the 1/2" tube at 1 L/min. This inlet arrangement resulted in a nearly wall-less sampling line with a residence time of 3 seconds and a passing efficiency for Cl₂ of 85 ± 10%.

[7] Cl₂ was measured by tandem quadrupole mass spectrometry of Cl₂⁻ in single reaction mode (ThermoFinnigan Quantum). The Cl₂⁻ parent ions were mass filtered in the first

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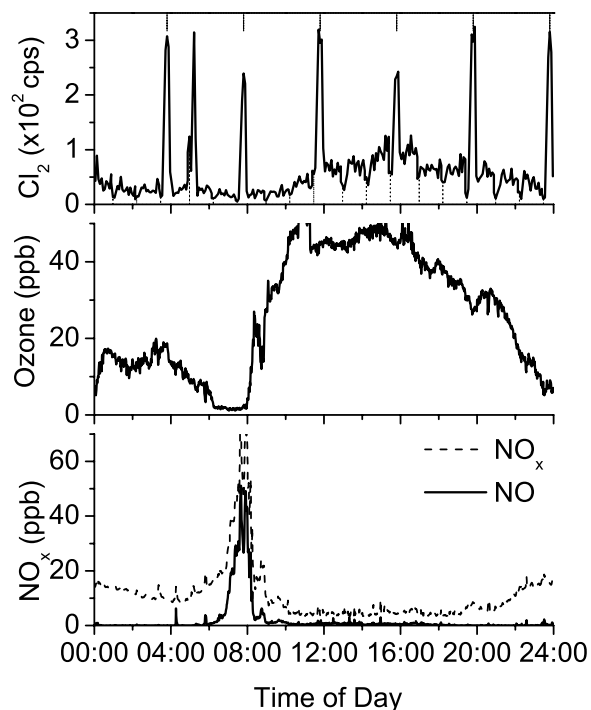


Figure 1. Cl_2 , O_3 and NO_x in Irvine air (9/14/2005). Top: APCI-MS/MS analysis of Cl_2 at the 70/35 transition ($^{35}\text{Cl}^{35}\text{Cl}^- \rightarrow ^{35}\text{Cl}^-$), 5 minute average signals. Blanks marked by lower dotted lines, standards (25 ppt) by upper dotted lines.

quadrupole, then dissociated by collision with Ar at a pressure of 1 mtorr and 20 eV to form daughter Cl^- ions which were mass filtered in the final quadrupole. The two natural isotopes of chlorine (^{35}Cl and ^{37}Cl) result in four possible mass transitions (70/35, 72/35, 72/37, 74/37) for Cl_2 . The ratios of the various transitions are determined by the unique isotopic distribution of chlorine ($^{35}\text{Cl}:^{37}\text{Cl} = 3:1$).

[8] Instrument blanks were taken every hour by diverting the inlet air stream through a section of ABS pipe filled with fiberglass wool treated with a 1% (w/w) NaCO_3 solution. Every four hours, a Cl_2 standard was added to blank air to measure instrument sensitivity changes. A VICI Metronics permeation device was used as a source of Cl_2 in N_2 . A dilution system [Gallagher *et al.*, 1997] was used to generate low-level (ppt) standards that were then introduced to the sample flow. Full instrument calibrations were carried out weekly. These consisted of sequentially adding Cl_2 gas standards to scrubbed ambient air at four mixing ratios from 10 to 60 ppt. Several months after this study, the permeation source was calibrated by bubbling through neutral potassium iodide solution and monitoring the formation of triiodide ion (I_3^-) by UV absorption at 352 nm. The emission of oxidant (expressed as Cl_2) was about half of that inferred from the gravimetric calibration. This is consistent with previous observations by Keene *et al.* [1993]. As a result of this calibration, a correction factor was retroactively applied to the absolute calibration of the field measurements. The gravimetric

calibration was constant throughout the measurement and post-calibration period. This correction introduces an uncertainty of $\pm 25\%$ into the absolute calibration of these measurements.

[9] Figure 1 illustrates the typical instrument response for a 24 hour period, including blanks and 25 ppt standards added to scrubbed air. The instrument blank signal follows a reproducible diurnal pattern, with lower blank signals in the early morning, increasing around mid-day and reaching a maximum during the late afternoon. The blank remains high until well after sunset, and returns slowly to morning levels. When determining ambient Cl_2 levels, these blanks are subtracted from the observed Cl_2 signal. The identity of the compound(s) causing these blanks is unknown. The blank appears to be caused by a photochemically produced substance with a lifetime of several hours. We speculate that the blank may be due to a polyhalogenated hydrocarbon which decomposes to form Cl_2 following ionization in the mass spectrometer source. The nocturnal decrease in the blank suggests a heterogeneous loss mechanism for the compound(s).

[10] Instrument sensitivity at the $^{70}\text{Cl}/^{35}\text{Cl}$ transition is approximately 5 cps ppt $^{-1}$ and the instrument blank ranges from 0.5–60 cps. The detection limit for Cl_2 is estimated at 2.5 ppt (S/N = 2), imposed by the variability in the blank. All four Cl_2 mass transitions are detected in air. The ratio of the signal intensities of the four Cl_2 transitions observed in ambient air is consistent with that observed in Cl_2 gas standards and with the natural abundance of chlorine isotopes.

[11] It is important to note that the possibility of positive interference in these measurements cannot be completely ruled out. An interferent would need to both: 1) generate Cl_2^- in the ion source either by decomposition or ion-molecule reactions, and 2) be effectively removed by the carbonate scrubber. Laboratory tests investigated and eliminated dichloroacetic and trichloroacetic acids (breakdown products of tetrachloroethene and 1,1,1-trichloroethane) and NCl_3 (a by-product of wastewater treatment). Aerosols were

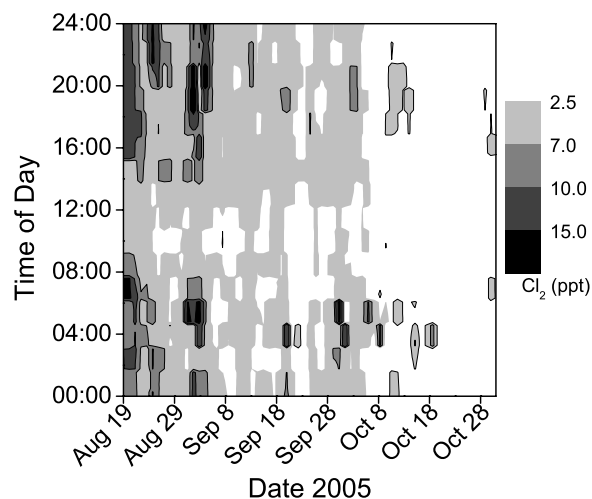


Figure 2. Cl_2 mixing ratios in surface air at Irvine, CA plotted against time of day during August, September, and October, 2005.

not removed from the air stream, and remain a potential interferent.

3. Results and Discussion

[12] Cl_2 mixing ratios during this study ranged from <2.5 ppt (below detection limit) to 20 ppt (Figure 2). Daily average Cl_2 mixing ratios ranged from <2.5 to 15 ppt. Over the entire measurement period, the average mixing ratio was 3.5 ± 3.5 ppt (1σ). Early in the study (August 24–30), a consistent diurnal pattern was observed, with low Cl_2 mixing ratios during the morning (<2.5–5 ppt) and an increase beginning around noon up to 5–10 ppt by the evening. The higher evening Cl_2 levels decreased overnight or during the next morning. For the remainder of the study, this diurnal pattern disappeared, and there was little difference between daytime and nighttime Cl_2 mixing ratios. There were two periods (August 19–22 and September 1–4) which had elevated Cl_2 levels (up to 15 and 7.5 ppt, respectively) that persisted over 24 hours. During the final two weeks of the study, Cl_2 was consistently below the detection limit.

[13] There is no obvious correlation between Cl_2 levels and meteorological conditions (wind speed/direction, temperature, relative humidity) or local pollutant levels (NO_x , O_3). Five day air mass back trajectories show a predominantly marine origin for air masses during the study. Most of the air mass trajectories were northwesterly, originating over the Pacific ocean at northern mid-latitudes. Aug 24–27 was a period of southwesterly trajectories originating over the subtropics. The last two weeks of the study (October 13–27) were characterized by cloudy or overcast skies with regular drizzle and rainfall.

[14] These are the first extensive measurements of Cl_2 over full diurnal periods. Daytime values typically ranged from below detection to 5 ppt, but on occasion reached levels as high as 15 ppt. The observation of such high daytime levels is surprising, given the short photolysis lifetime of Cl_2 .

4. Comparison With Previous Measurements

[15] The only previously published mass spectrometric measurements of Cl_2 are those of Spicer *et al.* [1998], who reported Cl_2 levels ranging from <10–150 ppt in marine air over Long Island from sundown to shortly after sunrise. Keene *et al.* [1993] reported 13–127 ppt of Cl^* ($\text{Cl}_2 + \text{HOCl}$, as Cl_2) in Miami using a tandem mist chamber. Pszenny *et al.* [2004] reported <6 to 38 ppt Cl^* in Oahu with the same technique. There is considerable overlap between the ranges of these published studies and the Cl_2 levels reported in this study.

5. Implications for Ozone Production in Coastal Urban Air

[16] The photolysis rate of Cl_2 was estimated based on the mixing ratios observed in this study, absorption coefficients from Maric *et al.* [1993], and a two-stream radiative transfer model [Madronich and Flocke, 1999]. These calculations yield a noontime photolysis lifetime of 3.7 minutes for 33.6° latitude, -117.8° longitude, Julian day 244, 287 DU total ozone column, and an albedo of 0.5. The short lifetime of Cl_2

implies that it must have a daytime source, presumably photochemical in nature. At night, one expects surface deposition to deplete Cl_2 , and there must be some nighttime production to balance this relatively slow loss.

[17] Based on the observed ambient mixing ratios, Cl_2 photolysis represents a source of Cl atoms on the order of 88 ppt/hr. In urban air, Cl atoms react primarily with VOC's to form peroxy radicals. These peroxy radicals ultimately result in the oxidation of NO to NO_2 , which photolyzes to produce O_3 . A photochemical box model incorporating the gas phase chemistry of Cl_2 , Cl, ClO, HCl, HOCl, and ClONO₂ was used to simulate the study conditions. Simulations suggest that chlorine-mediated oxidation of VOC's can account for several ppb per hour of additional ozone production during daylight hours. Assuming a constant Cl_2 mixing ratio of 3.5 ppt, the model yielded a noon Cl atom concentration of $1.2 \times 10^5 \text{ cm}^{-3}$ and a noon OH concentration of $8.5 \times 10^6 \text{ cm}^{-3}$. The Cl_2 increases peak O_3 levels by 5–8 ppb over a base case scenario with no chlorine chemistry.

[18] These model results are consistent with previously published simulations using a 3-dimensional regional air quality model of the California South Coast Air Basin with detailed chlorine chemistry [Knipping and Dabdub, 2003]. In those simulations, 12 pptv of Cl_2 at sunrise led to an O_3 increase of 12 ppb, compared with no-chlorine conditions. If the observations in this study of detectable Cl_2 levels throughout the day are correct, then Cl-mediated ozone production constitutes a substantial fraction of the total ozone production.

6. Implications for Cl_2 Production Mechanisms

[19] The observed Cl_2 levels may reflect either gas phase/aerosol interactions or direct emissions from anthropogenic sources such as industrial and water treatment plants, cooling towers, chlorinated domestic water supplies, fuel combustion, or incineration. The field observations place some constraints on the mechanism of Cl_2 formation. For Cl_2 to be present during daylight hours, when the photolysis lifetime is only minutes, requires a large production rate. The fact that Cl_2 does not exhibit a large and consistent diurnal cycle suggests that the rates of production and photolysis covary. This implies a production mechanism involving photochemical precursors. The OH-mediated surface reaction mechanism [Knipping *et al.*, 2000] is a potential source of daytime Cl_2 , but it does not appear sufficient to explain the observed levels. Box model calculations [Yvon *et al.*, 1996] were carried out using the parameterization of Knipping and Dabdub [2002], with a seasalt aerosol surface area of $145 \text{ um}^2 \text{ cm}^{-3}$, estimated from Lewis and Schwartz [2004], for 10 m height, 5 m s^{-1} wind speed, 80% RH, and an aerosol Cl concentration of 5 M [Herrmann *et al.*, 2003]. Under these conditions, the noontime concentration of Cl_2 reached only 0.5 ppt, a factor of 7 less than observed. By itself, the OH surface mechanism also leads to a diurnal pattern with a midday maximum. The rate of production of Cl_2 involving the seasalt aerosol surface reaction of ClONO₂ was also estimated using a similar approach [Caloz *et al.*, 1996; Knipping and Dabdub, 2003]. Inclusion of this mechanism leads to a Cl_2 level of about 1 ppt. These two mechanisms together

account for 44% of the observed average Cl₂. Inclusion of a ClONO₂ mechanism better models the observed temporal behavior by smoothing out the diurnal variations compared to the OH-only surface reaction. Clearly, future studies incorporating both gas phase and aerosol measurements are needed in order to rigorously test various production mechanisms.

7. Conclusions

[20] The ambient levels of Cl₂ observed in this study suggest that current air quality models in coastal regions may either underestimate the overall daily ozone formation rate or misattribute a significant amount of ozone production to OH-mediated, rather than Cl-mediated, oxidation of VOC's. Further research is needed to: 1) verify these observations and explore the ambient distribution of Cl₂ and other reactive halogen species, and 2) fully understand the mechanisms by which reactive halogen compounds are formed in the troposphere.

[21] **Acknowledgments.** The authors wish to thank John Greaves of the UCI mass spectrometer facility and Brad Hart of ThermoFinnigan Corp. for analytical advice. We also wish to thank an anonymous reviewer for raising the important issue of Cl₂ permeation tube artifacts. This research was supported by the NSF Atmospheric Chemistry Program (ATM-0403421).

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