



Evaluating evidence
for CI sources

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Evaluating evidence for CI sources and oxidation chemistry in a coastal, urban environment

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Abstract

The role of chlorine atoms (Cl) in atmospheric oxidation was traditionally thought to be limited to the marine boundary layer, where they are produced through heterogeneous reactions involving sea salt. However, recent observation of photolytic Cl precursors (ClNO₂ and Cl₂) formed from anthropogenic pollution has expanded the potential importance of Cl to include coastal and continental urban areas. Measurements of ClNO₂ in Los Angeles during CalNex showed it to be an important primary (first generation) radical source. Ratios of volatile organic compounds (VOCs) have been proposed as a sensitive method to quantify Cl oxidation, but have shown little evidence for a significant role of Cl outside of the Arctic. We used a box model with the Master Chemical Mechanism (MCM v3.2) chemistry scheme, constrained by observations in Los Angeles, to examine the Cl-sensitivity of the most commonly used VOC ratios (*i*-butane, *n*-butane, and propane) as a function of NO_x and secondary radical production. Model results indicated these and faster reacting VOC tracer ratios could not detect the influence of Cl unless the sustained ratio of OH to Cl was below 200. However, the model results also show that secondary (second generation) OH production resulting from Cl oxidation of VOCs is strongly influenced by NO_x, and that this effect can obscure the importance of Cl as a primary oxidant. Calculated concentrations of Cl showed a maximum in mid-morning due to a photolytic source from ClNO₂ and loss primarily to reactions with VOCs. The OH to Cl ratio was below 200 for approximately three hours in the morning, but Cl oxidation was not evident from the measured ratios of VOCs. Instead, model simulations show that secondary OH production causes VOC ratios to follow the values expected for OH oxidation despite the significant input of primary Cl from ClNO₂ photolysis in the morning. Despite the prevalence of secondary OH as an oxidant in Los Angeles, Cl may play an important role in tropospheric chemistry. The reactivity of Cl in Los Angeles during CalNex was more than an order of magnitude larger than that of OH. In addition, because of its reactivity toward different classes of VOCs and its greater propensity to participate in chain propagation rather than sink

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reactions, Cl atoms have a different impact on regional atmospheric oxidation than do OH radicals.

1 Introduction

Chlorine atoms (Cl) are extremely reactive towards volatile organic compounds (VOCs), with rate coefficients that are, with few exceptions, at least an order of magnitude larger than those of hydroxyl radicals (OH). In addition, Cl reacts rapidly with some compounds, such as alkanes, with which OH is relatively unreactive. As a result, if Cl is present in the troposphere in significant quantities, it can have an effect on tropospheric oxidation and impact the production of ozone in urban environments (Knipping and Dabdub, 2003; Chang and Allen, 2006). Historically, Cl was thought to be produced primarily from heterogeneous reaction cycles involving sea salt (Erickson et al., 1999; Keene et al., 1999; Knipping et al., 2000) and, consequently, the importance of Cl to atmospheric oxidation was limited to the marine boundary layer and coastal areas. Recent measurements of anthropogenically-derived photolabile Cl precursors (ClNO₂ and Cl₂) provide a mechanism for anthropogenic pollution to contribute to production of Cl (Osthoff et al., 2008; Lawler et al., 2009, 2011; Riedel et al., 2012). The detection of these species in mid-continental areas has expanded the potential impact of Cl to tropospheric oxidation chemistry (Thornton et al., 2010; Mielke et al., 2011).

Even in the presence of strong photochemical sources, predicted ambient Cl concentrations are exceedingly small ($< 10^5$ atoms cm⁻³), and reliable instrumental methods to measure Cl concentrations directly do not exist. Instead, the community has relied upon indirect methods to estimate the importance of Cl. Average concentrations of Cl on a near-global scale have been inferred using isotope ratios of methane (Allan et al., 2001, 2007; Platt et al., 2004) and removal rate of tetrachloroethylene (Singh et al., 1996). The spatially and temporally averaged (i.e. hemispheric to global scale over months to years) concentrations in the marine boundary layer were on the order of 10^3 atoms cm⁻³ (Singh et al., 1996; Allan et al., 2001). On local and regional scales,

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several indirect methods have been used to estimate the importance of Cl or its concentration. First, products of the addition reaction of Cl to unsaturated VOCs, such as the chlorinated product 1-chloro-3-methyl-3-butene-2-one (CMBO) from the addition of Cl to isoprene can be used as markers of chlorine oxidation (Nordmeyer et al., 1997).

5 Second, measurements of Cl precursors, including HOCl, ClO, Cl₂, and ClNO₂, enable estimations of the importance of Cl (Stutz et al., 2002; Osthoff et al., 2008; Lawler et al., 2011; Riedel et al., 2012). Finally, the most easily applied and commonly used method to infer Cl importance is VOC tracer ratios. These can determine the relative consumption of VOCs by Cl and OH (Jobson et al., 1994). A key characteristic of this
10 method is that it is sensitive to the total radical input, both primary (i.e. from photolysis of a precursor), and secondary (i.e. from radical propagation) sources. This method requires measurement of a set of three VOCs, where two have approximately equal reaction rate coefficients with OH and two have approximately equal rate coefficients with Cl; two examples are shown in Fig. 1. By tracking the ratios of these compounds
15 in air masses with different ages, it is possible to quantify the relative contribution of OH and Cl to oxidation. Although there remains considerable uncertainty in the analyses, these three indirect methods have shown that Cl may be an important oxidant in a number of locations, including Houston, Texas (Tanaka et al., 2003; Osthoff et al., 2008; Riemer et al., 2008), the east coast of the United States (Pzenny et al., 2007),
20 mid-continental North America (Thornton et al., 2010; Mielke et al., 2011), the Arctic (Jobson et al., 1994; Ramacher et al., 1999; Gilman et al., 2010), and Los Angeles, California (Gorham et al., 2010). Average concentrations estimated with these methods range from 10² to 10⁵ atoms cm⁻³ (Wingenter et al., 1996, 1999, 2005; Rudolph et al., 1997; Stutz et al., 2002; Pzenny et al., 2007; Riemer et al., 2008).

25 Although the VOC tracer ratio approach has been among the most commonly used methods to assess the importance of Cl to tropospheric oxidation, it has not been tested against the influence of factors such as nitrogen oxide concentrations, nor has it been used in conjunction with another method to assess the importance of Cl to tropospheric oxidation. Thus, further examination of the method and its applicability across

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a range of environments is of interest. In areas where primary radical production is the dominant radical source (e.g. very low or very high NO_x environments), VOC tracer ratios should be sensitive to the primary inputs. In areas where secondary radicals dominate (e.g. intermediate NO_x environments such as Los Angeles), VOC ratios may not be a good measure of the initiators of oxidation.

Recently, Cl was shown to be a significant contributor to the primary radical budget in Los Angeles during the CalNex campaign (Young et al., 2012; Mielke et al., 2013). Using measurements of ClNO_2 and other radical precursors, we demonstrated that ClNO_2 , as a source of Cl, accounts for 9% of all primary radicals on average, and for greater than half of ground-level primary radicals during some times in the morning. As such, it might be expected that VOC ratios would also show the impact of Cl oxidation in this location, especially immediately following sunrise. In this paper, we will examine: (i) VOC tracer ratios as descriptors of radical chemistry in the Los Angeles Basin during CalNex; (ii) the sensitivity of VOC tracer ratios to Cl chemistry; (iii) the effect of NO_x and secondary radical production on VOC tracer ratios; (iv) the impacts of secondary radicals on interpretations of VOC tracer ratios during CalNex; and (v) the impact of chlorine on tropospheric chemistry in Los Angeles.

2 Methods

2.1 Measurements

The CalNex Pasadena ground site was located on the campus of the California Institute of Technology in Pasadena, CA (34.1406°N , 118.1225°W , 236 m a.s.l.). The site operated from 15 May to 15 June 2010. Ground site measurements used in this analysis include speciated VOCs by gas chromatography coupled to mass spectrometry (Gilman et al., 2010); ozone by UV differential absorption; nitric oxide by chemiluminescence; carbon monoxide by vacuum UV fluorescence; formaldehyde by differential optical absorption spectroscopy (Wong et al., 2011); nitrogen dioxide, nitrous acid, and

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glyoxal by cavity-enhanced techniques (Washenfelder et al., 2011; Young et al., 2012); gas-phase acids by negative-ion proton transfer chemical ionization mass spectrometry (CIMS) (Roberts et al., 2010; Veres et al., 2011); OH and hydroperoxyl radicals by laser-induced fluorescence (Dusanter et al., 2008); and nitryl chloride by iodide CIMS (Mielke et al., 2011, 2013). Other relevant measurements include photolysis rate constants (Shetter and Muller, 1999) and meteorological parameters. Most measurements were made at 10 m a.g.l., with the exception of formaldehyde (average path height 55.5 m a.g.l.) and gas-phase acids (3 m). The measurements are summarized in Table 1.

Methane was not measured at the Pasadena ground site. In the absence of measurements, we assume a methane mixing ratio of 1.8 ppmv. Measurements of methane from the NOAA P-3 aircraft during CalNex observed mixing ratios up to 2.1 ppmv over the Los Angeles Basin (Peischl et al., 2013). Inclusion of a higher methane mixing ratio would modestly decrease the sensitivity of VOC tracer ratios to the presence of CI through consumption of a slightly larger fraction of these radicals to reaction with methane rather than VOCs. Thus, the modeled sensitivities of these ratios to CI presented in this paper can be considered modest upper limits.

The NOAA WP-3D research aircraft flew all or parts of 20 flights in and around the L.A. basin from 30 April through 22 June; VOCs were measured in whole air samples (Colman et al., 2001), periodically filled during all flights. In addition, the Research Vessel *Atlantis* cruised along the coast and within the harbors of California from 14 May through 8 June; a subset of VOCs were measured by an on board instrument. Ryerson et al. (2013) give details of these flights and cruise and the related measurements.

2.2 Reactivity calculation

Reactivity of OH and CI were calculated using averaged diurnal cycle concentrations of CINO₂, HONO, OH, HO₂, O₃, NO, NO₂, CO, acids, and speciated VOCs. The acid measurements included HONO (Young et al., 2012), HNO₃, HCl, and HCOOH (Veres et al., 2011). The VOC measurements included C₂–C₆ and C₉–C₁₁ alkanes, C₂–C₅

alkenes, ethyne, C₁–C₃ alcohols, C₆–C₉ aromatics, C₁–C₄ aldehydes, glyoxal, C₃–C₄ ketones, 2,3-butadione, acetonitrile, bromoform, isoprene, methyl vinyl ketone (MVK), methacrolein, α - and β -pinene and limonene (Gilman et al., 2010; Washenfelder et al., 2011; Wong et al., 2011). Kinetic parameters were taken from preferred or recommended values where possible (Atkinson et al., 2006, 2007; Sander et al., 2011). Rate constants were not available for Cl reaction with decane and a number of alkyl benzenes, as well as the reaction of OH with 1-ethyl-2-methylbenzene. For these reactions, rate constants for similar species were used. A complete list of included species, reaction rate constants, and references are included as Table S1 in the Supplement.

2.3 Modeling

We used a subset of the Master Chemical Mechanism (MCM) version 3.2 (Jenkin et al., 1997, 2003; Saunders et al., 2003) in the AtChem box model version 1.5 (Boronska et al., 2013) to study: (1) the impact of Cl/OH ratio on VOC tracer ratios; (2) the impact of NO_x on VOC tracer ratios; and (3) VOC tracer ratios that would be expected under conditions observed at CalNex, assuming no emission of VOCs. This model contains near-explicit degradation mechanisms and kinetics for gas-phase tropospheric chemistry. The subset used here includes all inorganic reactions and reactions for eighteen selected VOCs and their products, as described below. We modified the MCM scheme to include photolysis of ClNO₂ to yield Cl. Within MCM v3.2, Cl kinetics and mechanisms are included only for alkanes. We added Cl kinetics and degradation mechanisms for methanol, ethanol, isopropanol, formaldehyde, acetone, ethyne, ethene, and toluene (Yarwood et al., 1991; Taatjes et al., 1999; Wang et al., 2005; Atkinson et al., 2006; Yamanaka et al., 2007; Kaiser and Wallington, 2010), with the reaction rates given in Table S1. Concentrations for all alkanes and alcohols that were measured at the CalNex ground site were explicitly included (ethane, propane, *n*-butane, *i*-butane, *n*-pentane, *i*-pentane, hexane, nonane, decane, undecane, methanol, ethanol, and isopropanol). The chemistry of Cl with alcohols can be included with little modification of the model, because their reactions with Cl are well characterized and proceed by

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hydrogen abstraction leading to a radical species that is already explicitly included in the model. Radical yields for reaction of Cl with alcohols were taken from Taatjes et al. (1999) and Yamanaka et al. (2007).

Other classes of compounds have complex reactions with Cl that are poorly understood. For these other VOCs, a representative mixture was developed to model Cl chemistry. The compound that was found in highest concentration was used to represent that compound class. Formaldehyde represented aldehydes, acetone represented ketones, ethene represented alkenes (including biogenics), and toluene represented alkyl benzenes. For biogenic VOCs, current knowledge of reactions with Cl is insufficient for inclusion in the model. Biogenic VOCs accounted for approximately 7 % of total alkenes. Concentrations of all compounds in each class were summed and used to represent the concentration of the representative compound within the model. The chemistry and kinetics of each representative compound were assumed to represent the entire class. Average measured VOC concentrations from just before sunrise (04:30 Pacific Daylight Time (PDT = UTC – 7h)) were used to initialize the model, with no further emissions included. Conditions for the model can be found in the Supplement.

All model simulations were conducted using data from the Pasadena ground site. The date was constrained to 1 June 2010 (the midpoint of the campaign), temperature to 290 K, pressure to 2.46×10^{19} molecules cm^{-3} , and concentration of water to 4.2×10^{17} molecules cm^{-3} (equivalent to 90 % RH). Photolysis rate constants were calculated by the Tropospheric Ultraviolet and Visible (TUV) Radiation Model included within MCM v3.2. The photolysis rate constant for ClNO_2 is not included in the TUV model and was parameterized as a linear combination of measured J_{O_3} and J_{NO_2} , with J_{ClNO_2} derived from measured actinic fluxes and cross sections (Ghosh et al., 2011):

$$J_{\text{ClNO}_2} = J_{\text{NO}_2}(0.0267) + J_{\text{O}_3}(3.11) \quad (\text{R1})$$

The error in J_{ClNO_2} for this parameterization compared to the direct calculation is less than 30 % for all solar zenith angles. Concentrations of nitrate radicals were fixed to zero, although NO_3 oxidation would have little if any influence on the chosen VOCs due to the slow reaction rate coefficients of this radical with alkanes. Model simulations

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began just before sunrise (05:15 PDT) and continued past the end of the photochemical day (22:00 PDT).

We modeled three different scenarios to explore the role of Cl on VOC ratios. In the first (condition set 1), a fixed (i.e., time invariant) radical concentration of 5×10^6 molecules cm^{-3} was used, with concentrations of OH and Cl varying between different model runs to make up this total, to explore the impact of OH to Cl ratios on VOC tracer ratios under conditions of solely primary radicals. The concentration of NO_2 was fixed to zero. In the second (condition set 2), primary sources of OH (i.e. HONO and reaction of $\text{O}(^1\text{D})$ and water) were eliminated (i.e. by having a starting concentration of zero (HONO) or setting primary reactions that normally form OH to produce no products in the model ($\text{O}(^1\text{D}) + \text{H}_2\text{O}$)) and Cl was allowed to be formed as a product of ClNO_2 photolysis to better understand the impact of NO_x on VOC tracer ratios under the influence of chlorine oxidation only (condition set 2). Concentrations of NO_2 were fixed within a given simulation, but were changed between simulations. In the third scenario (condition set 3), two different radical conditions were simulated in order to explore the effect of the NO_x concentrations observed at CalNex. In the first (3a), OH was formed from reaction of $\text{O}(^1\text{D})$ with water and photolysis of nighttime accumulated HONO, while Cl was formed from photolysis of ClNO_2 . Under the second set of conditions (3b), reaction of $\text{O}(^1\text{D})$ plus water and HONO photolysis were unchanged, but photolysis of ClNO_2 was prescribed to produce OH instead of Cl in the model. For each condition in set 3, NO_2 was fixed at 18 ppbv, comparable to the mixing ratio observed during CalNex (Fig. S1).

3 Results and discussion

3.1 VOC tracer ratios from California

Ratios of VOC tracers are commonly used to assess the relative importance of VOC oxidation by Cl and OH. As described above, this involves a set of three VOCs, of which

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two have similar reaction rates with OH and two have similar reaction rates with Cl (Jobson et al., 1994). Use of VOC tracer ratios assumes that the primary influence on the relative changes in VOC concentrations is oxidation, which occurs at different rates with different radicals. Tracer ratios of VOCs are affected by mixing of air parcels that have different emission histories. Nevertheless, even in the presence of such mixing each ratio generally does provide a reasonably accurate determination of the average age of the more reactive VOC included in the ratio (Parrish et al., 2007) providing the difference is relatively large in the rate constants of the two VOCs composing the ratio.

Young et al. (2012) demonstrated that ClNO_2 was an important primary radical source in Los Angeles during CalNex. As such, we might expect the VOC tracer ratios to reflect the importance of Cl oxidation during the campaign. One of the most common sets of compounds used in VOC tracer ratios includes *i*-butane, *n*-butane, and propane (e.g. Jobson et al., 1994). The red points in Fig. 1 illustrate the Cl and OH rate coefficients for this set of alkanes, which is long-lived with respect to reaction with OH and has been often used to assess the importance of Cl atoms, including in Los Angeles (Gorham et al., 2010). A faster-reacting set of VOCs, toluene, acetylene, and *n*-hexane (blue points in Fig. 1), yield a more sensitive measurement. Rudolph et al. (1997) used a set of VOCs with benzene replacing acetylene. Here we will examine both of these two sets of tracer ratios.

All four ratios in the two sets of VOC tracer ratios were calculated from measurements made both at the Pasadena ground site and from the WP-3D aircraft on all flights within or offshore of California. This latter data set is concentrated in the Los Angeles Basin, but does include much of the state of California. These ratios are included in Fig. 2 along with lines indicating the slopes expected if solely OH or Cl oxidation were occurring. These lines were calculated so that they intersect at the average emission ratios of the respective VOCs based on those reported by Borbon et al. (2013).

In Fig. 2 there is little systematic change in either the average ratio of [*i*-butane]/[*n*-butane] relative to the change in [*i*-butane]/[propane] or the [toluene]/[*n*-hexane] ratio relative to the change in [toluene]/[propane], suggesting the VOCs are predominantly

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oxidized by OH. The relatively small systematic change in the average ratios is not in the direction that might indicate a significant contribution from CI atom oxidation; rather it is in the opposite direction for both sets of VOC tracer ratios. There is significant scatter in the data, suggesting that there is substantial variability in the measured VOC ratios that is unrelated to oxidation, arising from variability in VOC ratios in emissions from different sources and from experimental imprecision, which dominates at lower VOC ratios (see further discussion below). The WP-3D data shown in Fig. 2 include all measurements regardless of altitude or location within or offshore of California. Limiting data to a particular region (e.g. the Los Angeles Basin or the Central Valley) or to a specific altitude range (such as within the planetary boundary layer) did not reveal any significant differences in the systematic changes of the VOC ratios. In addition, *i*-butane, *n*-butane, and propane were measured on the Research Vessel *Atlantis* (Ryerson et al., 2013) during its cruise along the coast and within the harbors of California. Compared to the data in Fig. 2a, the ratios calculated from these data (not shown) exhibited greater scatter (presumably due to measurements made in close proximity to many different large emission sources), but the average systematic trends were not significantly different.

At small VOC ratios, the data in Fig. 2 fall significantly below the OH oxidation line in all three panels. This occurs at the lowest VOC concentrations where relative measurement precision decreases as the detection limit of the instrument is approached. Since the same VOC is used in the numerator of the VOC ratios on the ordinate and the abscissa in both sets of VOC tracer ratios, a positive correlation becomes apparent between the two ratios in these plots when instrument imprecision begins to dominate the scatter in the measured ratios. Parrish et al. (2007) and Fortin et al. (2005) further discuss such anomalous effects.

We also specifically examined VOC tracer ratios on the day of 3 June 2010 (Fig. 2c), for which the preceding night had the highest concentration of ClNO₂ (nocturnal maximum of 3.5 ppbv) observed at Pasadena during the campaign; hence that day may provide the best opportunity to observe the influence of CI oxidation at local scales.

During the morning (07:00 to 11:00 PDT), when Cl concentrations resulting from photolysis of ClNO_2 would be highest, the data from both Pasadena and the aircraft are scattered along, but generally below, the OH oxidation line, with no evidence for Cl oxidation. These data also indicate OH as the dominant oxidant.

The time evolution of the relative mixing ratios of the six VOCs in Fig. 2 provides no evidence for the influence of Cl oxidation in the total data or the data for the individual day selected for maximum nocturnal ClNO_2 concentration despite the demonstrably large input of Cl radicals from ClNO_2 photolysis. Similar conclusions are reached in examination of various subsets of these data, and the *i*-butane, *n*-butane, and propane ship borne data. Young et al. (2012) found Cl formation from photolysis of ClNO_2 accounted for approximately 9% of primary radicals formed during each day at the ground, where primary radical sources were assumed to include photolysis of nighttime accumulated HONO, O_3 photolysis and the subsequent reaction of $\text{O}(^1\text{D})$ with water vapor, and photolysis of ClNO_2 . In the same study, it was observed that photolysis of ClNO_2 accounted for approximately half of primary radicals formed between 06:00 and 12:00 PDT. By contrast, all data shown in Fig. 2 (and considered in other analyses not shown) suggest that Cl oxidation was not important at either the Pasadena location or throughout California during the CalNex time period.

3.2 Sensitivity of VOC tracer ratios

Further examination of the apparent discrepancy between primary radical sources and VOC tracer ratios is needed to assess the importance of Cl to oxidation in Los Angeles. We used the MCM v3.2 chemistry scheme with simplified Los Angeles conditions (described above as condition set 1) to assess the sensitivity of VOC tracer ratios to the presence of Cl. Figure 3 depicts the VOC tracer ratios expected under different OH to Cl ratios. A ratio of 1000 is observationally indistinguishable from OH reactions only, while a ratio of 1 is observationally indistinguishable from Cl reaction only. The sensitivity of VOC tracer ratios to the presence of Cl will depend on VOC tracer ratio measurement precision and variability. Based on the scatter in the available data (see

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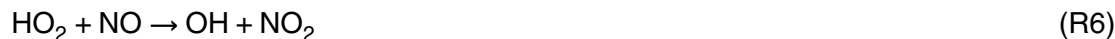
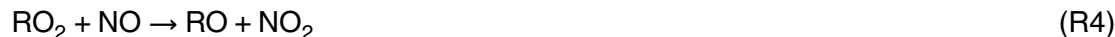
Fig. 2a), the minimum OH to Cl ratio required for detection of Cl oxidation using these VOC tracer ratios is estimated as approximately 200. Assuming scatter as observed in Fig. 2a, a daytime average concentration of OH of 2×10^6 molecules cm^{-3} , and an ideal case of an isolated air parcel with no injection of fresh VOC emissions, this OH to Cl ratio would have to be sustained for more than one day to be detectable. If Cl concentrations are elevated over only a short time period, the ratio of OH to Cl required for detection of the Cl influence would be higher.

3.3 Impact of NO_x and secondary radicals on VOC tracer ratios

Observations that Cl oxidation is important to VOC fate through the use of VOC tracer ratios have been made in low- NO_x environments (Jobson et al., 1994; Gilman et al., 2010). In a low- NO_x environment, peroxy radicals (RO_2 , HO_2) produced from reactions of radicals with VOCs react predominantly via self-reactions that lead to termination rather than with NO_x :



Conversely, in high- NO_x environments, such as Los Angeles, the input of a single radical can lead to radical propagation and the formation of many secondary radicals.



The cycle described by Reactions (R4) to (R6) can continue with the radical produced in Reaction (R6) leading to production of another RO_2 and further secondary radicals. In addition, $\text{R}'\text{CO}$ formed from Reaction (R5) is typically an aldehyde or ketone, which can photolyze or react with OH or Cl, substantially increasing the efficiency of propagation depending on the time scale for photolysis.

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In a moderate to high NO_x environment (i.e. where peroxy radical reactions with NO dominate over those with other peroxy radicals), the role of NO_x in secondary radical formation impacts the ability of VOC tracer ratios to show the importance of primary CI. In Pasadena during CalNex, observed daytime NO_x ranged from 1.3 to 82 ppbv, with a campaign daytime mean of 15.2 ppbv. The MCM model was used to explore the role of NO_x on secondary radical formation and VOC tracer ratios using simplified chemistry representative of conditions observed in Pasadena during CalNex (condition set 2). Within the chemistry scheme, concentrations of NO_2 were fixed, with initial concentrations of NO set to zero, to determine the impact of NO_x . Figure 4a depicts total integrated secondary OH produced from ClNO_2 photolysis-initiated chemistry. As the fixed NO_2 mixing ratio increases from 0 to 25 ppbv, production of secondary OH increases. As fixed NO_2 mixing ratios increase, total production of secondary radicals also increases, but the effect of additional NO_2 decreases at higher NO_2 mixing ratios. This occurs as a result of the importance of the radical sink reaction of NO_2 with OH to form HNO_3 .

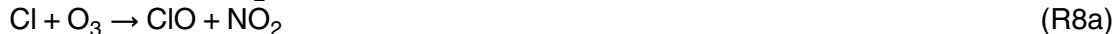
Using this same model simulation, we can determine the impact on VOC tracer ratios, shown in Fig. 4b. As fixed NO_2 mixing ratios increase from 0 to 2 ppbv, the VOC tracer ratios move from the CI oxidation line toward the OH oxidation line, even though there is no primary input of OH to the system. As NO_2 mixing ratios are further increased, ratios move slightly away from the OH oxidation line, following the same trend observed for secondary radical production. Despite the fact that CI is the sole primary oxidant in this simulation, production of secondary radicals in the presence of NO_x effectively masks the contribution of CI as the initiator of the oxidation process.

This simple simulation represents a proof-of-concept and should be interpreted as a qualitative depiction of the influence of CI on the time evolution of VOCs in Los Angeles during CalNex. The representative VOC mixture used in our model simulations is simplified, with the simplest available compound from many compound classes, which reduces the probability of radical recycling. In particular, reactive biogenics, many of which contain multiple double bonds, were represented in this simulation by ethene. It

has been suggested that isoprene may recycle OH efficiently (Lelieveld et al., 2008; Archibald et al., 2011) and representation of this species by ethene could impact calculated secondary radical production. Additionally, no emissions were included in this simulation, CINO₂ was used as the sole radical source, and there was no mechanism included to form secondary Cl (see discussion below). Despite these caveats, the model clearly shows that formation of secondary OH from Cl oxidation will reduce the apparent contribution of Cl to initiation of VOC oxidation cycles in NO_x-rich regions as inferred from VOC ratios.

3.4 Impacts of secondary radical chemistry on VOC tracer ratios in Los Angeles

Using measurements from CalNex, we can estimate the concentration of Cl present during the campaign. Up to this point, we have assumed that photolysis of CINO₂ is the only source of Cl. As this may not be the case, we assume that Cl produced from photolysis of CINO₂ provides a lower limit of primary Cl. Measurements aboard RV *Atlantis* taken off the coast of Los Angeles during CalNex indicate that other primary sources of Cl were present, but photolysis of CINO₂ dominated (Riedel et al., 2012). Secondary Cl can be formed as follows:



Based on measurements from CalNex and the steady-state approximation to determine concentrations of ClO (see Supplement), the secondary Cl source from (R7) and (R8) was determined to be approximately 23% of the calculated total and 30% of the source from CINO₂. Secondary Cl was more significant in late morning and early afternoon (Fig. 5a). Although the production of secondary Cl was not included in our model simulations, this source of Cl is judged to be small relative to primary Cl and secondary OH.

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Concentrations of Cl were calculated using measurements averaged over a diurnal cycle and the steady-state approximation (i.e., using ClNO_2 photolysis as a source balanced by Cl loss to oxidation of VOCs). The maximum concentration calculated during CalNex was $8.7 \times 10^3 \text{ atoms cm}^{-3}$ and the average daytime concentration was $2.3 \times 10^3 \text{ atoms cm}^{-3}$. This calculation may slightly underestimate the Cl concentration, since primary sources of Cl other than photolysis of ClNO_2 (e.g. Cl_2 , Oum et al., 1998) have not been included in this estimate. The lower-limit estimate for CalNex is slightly higher than calculated concentrations in the Mediterranean ($10^3 \text{ atoms cm}^{-3}$, Rudolph et al., 1997) and substantially lower than calculated concentrations on the east coast of the United States ($2.2\text{--}5.6 \times 10^4 \text{ atoms cm}^{-3}$, Pzenny et al., 2007) and in Houston, Texas (mean of $7.6 \times 10^4 \text{ atoms cm}^{-3}$, Riemer et al., 2008). However, instantaneous Cl atom concentrations are a balance between source and sink reactions, either of which may vary regionally and seasonally. The diurnal concentration calculated for Los Angeles is shown as a ratio to measured OH in Fig. 5b. A minimum OH to Cl ratio of 109 was calculated at approximately 08:00 PDT coincident in time with the maximum Cl concentration. The sensitivity of VOC tracer ratios determined above suggests a sustained OH to Cl ratio of less than 200 is needed to detect Cl oxidation. At the Los Angeles ground site during CalNex, OH to Cl ratios are calculated to have been below 200 for approximately two hours beginning at 07:00 PDT. Thus, we might expect to see evidence of Cl oxidation in the VOC tracer ratios in early morning in Los Angeles.

Using the AtChem model described in Sect. 2.3, we calculated the VOC tracer ratios expected in Los Angeles during CalNex (condition set 3) assuming the air masses measured at the site had a common history. The model was able to reasonably estimate observed conditions, considering the numerous simplifications made to the chemistry for this proof-of-concept analysis (Fig. S1). The influence of Cl was tested with the inclusion of ClNO_2 photolyzing to form either Cl or OH. Results of the simulations are shown in Fig. 6. In the simulation including Cl, there is an early-morning deviation from the OH oxidation consistent with the OH to Cl ratios presented in Fig. 5b. Following the removal of ClNO_2 by photolysis, oxidation follows a line parallel to the OH oxidation line,

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indicating that OH is the dominant oxidizer for the remainder of the day. As expected, VOC tracer ratios in the simulation producing OH from the photolysis of ClNO_2 are consistent with oxidation entirely by OH. The predicted difference in $\ln([i\text{-butane}]/[n\text{-butane}])$ between ClNO_2 reacting to form OH and Cl is less than 0.02 ($< 5\%$). It would be impossible to detect this difference given the data scatter of greater than 0.05 (10%) in VOC tracer ratio measurements (Fig. 2). In fact, the difference observed during CalNex between two subsequent VOC measurements exceeds the difference between the two simulated conditions (Fig. 6). Furthermore, the lifetimes of the alkanes used to generate the VOC tracer ratios are in excess of 100 h, with respect to both the observed OH and calculated Cl concentrations during CalNex. During the three hours in which the OH to Cl ratio is less than 200, Cl oxidation can only be expected to reduce the alkane concentrations by less than 3%, which is within the stated error of the VOC measurement (Table 1). As discussed above, sustained OH to Cl ratios of less than 200 are needed to detect the role of Cl using this method. Over the shorter time scale of high Cl concentrations observed during CalNex, the OH to Cl ratio was not low enough to overcome both the uncertainty in the measurements and the variability observed in Los Angeles for the most commonly used set of tracers (*n*-butane, *i*-butane, and propane).

Incorporation of faster-reacting compounds into VOC tracer ratios provides a more sensitive measure of the influence of Cl. Since reaction rate coefficients of Cl with alkanes approach the gas-kinetic limit, the toluene, *n*-hexane, and acetylene tracer ratios provide a more sensitive indicator of Cl oxidation. The ratio of toluene to *n*-hexane (Fig. 2b and c), having different Cl but similar OH rate coefficients, is more than 4 times as sensitive to Cl as the ratio of *n*-butane to *i*-butane ratio (Fig. 2a) primarily considered in the above consideration. However, the evolution of the toluene, *n*-hexane, and acetylene ratios considering both all data (Fig. 2b) and the morning of 3 June (Fig. 2c) reveals no indication of Cl oxidation.

3.5 Impact of Cl on tropospheric chemistry in Los Angeles

The models described above clearly indicate that VOC oxidation in Los Angeles during CalNex was dominated by reaction with secondary radicals. These results suggest that oxidation of VOCs by Cl leads to significant production of secondary OH that is much more important for atmospheric oxidation than are the primary Cl radicals themselves. However, Cl and OH react selectively with different species, as illustrated by the average reactivity of Cl and OH, shown in Fig. 7. Three key differences between the reactivity of Cl and OH affect tropospheric oxidation in Los Angeles. First, the reactivity of Cl with Los Angeles atmospheric composition is over an order of magnitude larger than that of OH, leading to faster reaction of Cl with VOCs, and a shorter radical lifetime and smaller abundances. Second, the single largest contributor to OH loss (30 % of daytime integrated reactivity) is the radical sink reaction with NO₂ to form nitric acid. This reaction is chain terminating, leading to permanent loss of OH, such that only ~ 70 % of primary OH would participate in oxidation cycles that lead to radical propagation. Reactivity of Cl, on the other hand, is due almost entirely to reactions that lead to radical recycling through oxidized VOCs. Although Cl also reacts with NO₂ (accounting for 5 % of total Cl reactivity), the reaction regenerates ClNO₂ or its isomers, which simply returns the Cl to the radical pool through subsequent photolysis. Chain termination for Cl is possible through reaction with O₃ (R9), which has the potential to form HOCl (R10a) if the resulting ClO does not react primarily with NO to regenerate Cl (R10b):



Reactions of Cl with OH also form HOCl, but this is a negligible loss process for either radical:



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The chemistry of HOCl is complex, and likely leads to further radical recycling through its heterogeneous uptake. Even if HOCl production were to be regarded as a Cl loss, we calculate that formation of HOCl through reactions (R10a) and (R11) accounts for less than a 1×10^{-6} fraction of the total Cl loss in Los Angeles. We note that in lower VOC, lower NO_x environments, such as remote ocean areas, HOCl production can be a significant fraction of total Cl loss (Lawler et al., 2009). Lastly, Cl reacts rapidly with species, such as alkanes, that are relatively unreactive with OH. These differences suggest that primary Cl may have impacts on tropospheric oxidation that cannot be assessed by a simple radical budget. Modeling studies have suggested the inclusion of Cl oxidation leads to increased production of O_3 in coastal urban areas, including Los Angeles (Knipping and Dabdub, 2003; Osthoff et al., 2008). Further study is required to fully assess the impacts of Cl on VOC oxidation, radical generation and propagation, and O_3 formation in light of recent field work showing a large Cl atom source through formation and photolysis of ClNO_2 .

4 Conclusions

The photolysis of ClNO_2 was an important primary radical source in Los Angeles during CalNex, but the influence of Cl oxidation was not detectable from the ratios of *i*-butane with *n*-butane and propane, the most common set of VOC tracers used to infer a Cl signature, or from the ratios of toluene with *n*-hexane and acetylene, faster reacting tracers that should be more sensitive to Cl oxidation. Modeling results indicate that secondary OH produced from Cl oxidation in the presence of NO_x obscures the impact of Cl as a primary radical on the VOC ratios. Thus, although Cl may initiate oxidation cycles in Los Angeles, its influence is not apparent in the time evolution of VOC ratios investigated here. These ratios should show Cl oxidation below a sustained OH to Cl ratio of approximately 200. However, since ClNO_2 photolysis is a strong radical source only for a few hours in the early morning, Cl concentrations of this magnitude are not sustained long enough to impact the VOCs used in these VOC tracer ratios. This

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result indicates that VOC tracer ratio interpretation is complex in moderate- and high- NO_x , urban environments. Ratios must be interpreted in the context of the role of NO_x and secondary emissions, as well as the timing of radical sources. The Los Angeles atmospheric composition during CalNex was more than an order of magnitude more reactive with Cl than with OH. The greater propensity of Cl for radical propagation, as well as rapid reaction rates with species that are long-lived with respect to OH oxidation, likely influences the oxidative impact of Cl. These differences between the behaviour of Cl and OH indicate that their contributions to tropospheric oxidation are not accurately captured through simple radical budgets.

Supplementary material related to this article is available online at:
<http://www.atmos-chem-phys-discuss.net/13/13685/2013/acpd-13-13685-2013-supplement.pdf>.

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Table 1. Relevant measurements acquired during CalNex 2010.

Species	Technique	Uncertainty (1σ)*	Frequency	Reference
O ₃	UV differential absorption	$\pm(0.4 \text{ ppbv} + 4\%)$	1 min	Thermo Scientific model 49c
OH	Laser induced fluorescence (LIF-FAGE)	$\pm(4 \times 10^5 \text{ cm}^{-3} + 18\%)$	15 min	Dusanter et al. (2009)
HO ₂	LIF-FAGE		15 min	Dusanter et al. (2009)
NO	Chemiluminescence	$\pm 4\%$	1 min	Thermo Scientific model 42i-TL
NO ₂	Cavity ringdown spectroscopy	$\pm 3\%$	1 min	Washenfelder et al. (2011)
HONO	Incoherent cavity enhanced absorption spectroscopy (IBBCEAS)	$\pm(52 \text{ pptv} + 30\%)$	10 min	Young et al. (2012)
ClNO ₂	Chemical ionization mass spectrometry (CIMS) with iodide ionization	$\pm 30\%$	30 s	Mielke et al. (2011)
CO	Vacuum UV fluorescence	$\pm 5\%$	1 s	Gerbig et al. (1999)
Gas-phase acids	Negative-ion proton transfer reaction CIMS	$\pm(30 \text{ pptv} + 35\%)$	1 min	Veres et al. (2011)
Speciated VOCs	Gas chromatography – mass spectrometry (GC-MS)	5–25 % (hydrocarbons) 20–35 % (oxygenates)	30 min	Gilman et al. (2010)
Formaldehyde	Differential optical absorption spectroscopy (DOAS)	$\pm 5\%$	Variable	Wong et al. (2011)
Glyoxal	IBBCEAS	$\pm(40 \text{ pptv} + 15\%)$	1 min	Washenfelder et al. (2011)
Photolysis	Scanning actinic flux spectroradiometer (SAFS)	$\pm 30\%$	1 min	Shetter and Muller (1999)

* For uncertainties given as $\pm(x \text{ pptv} + y\%)$, x represents the precision and y represents the accuracy.

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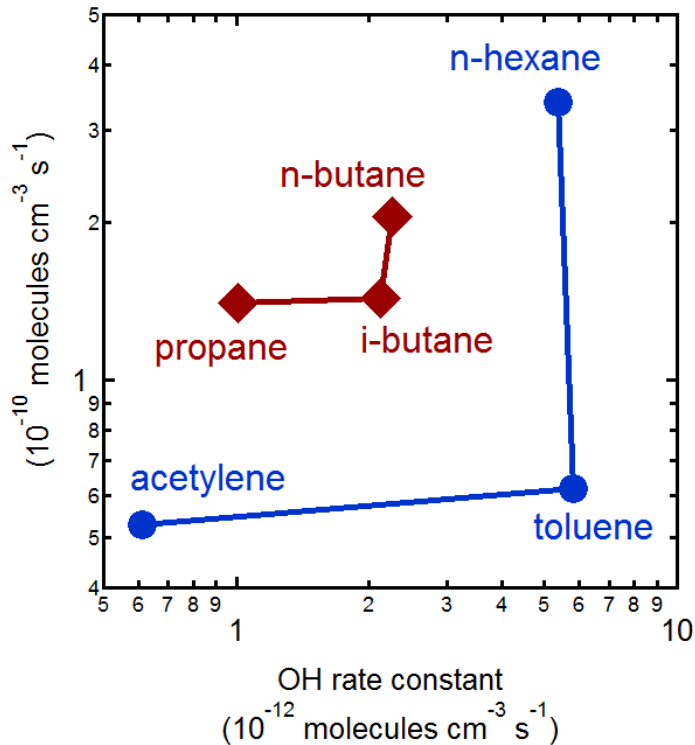


Fig. 1. Rate constants for reaction of Cl and OH with VOCs that are used to infer the influence of Cl oxidation. Rate constants are those used in the model, under conditions described in Table S4.

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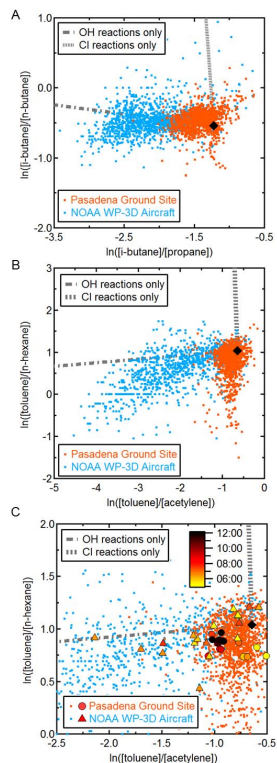


Fig. 2. VOC tracer ratios from the Pasadena CalNex ground site and the WP-3D aircraft. **(a, b)** All data for all days for the entire campaign. The lines indicate expected tracer ratio evolution for OH and Cl oxidation starting from Los Angeles Basin emission ratios (black diamonds) determined by Borbon et al. (2013). **(c)** Data from **(b)** on expanded axes with data from 05:00 to 13:00 PDT on 3 June 2010 collected at altitudes below 1000 m identified by large symbols, color-coded by time of day.

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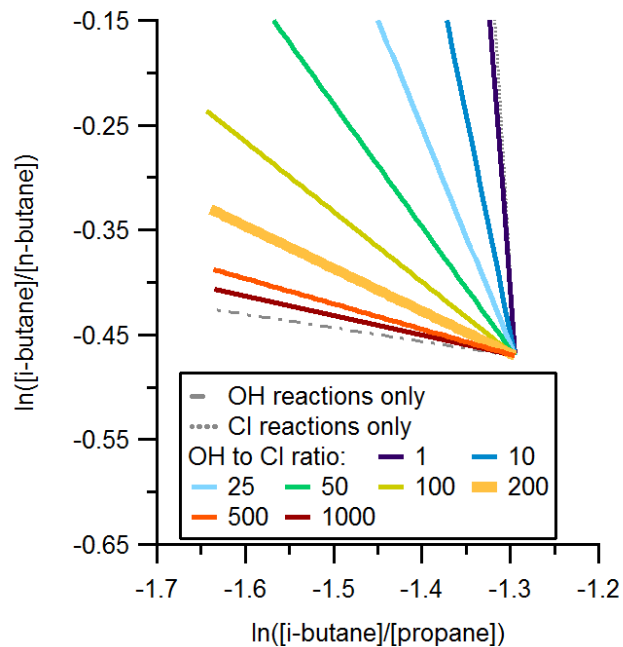


Fig. 3. VOC tracer ratios (*i*-butane, *n*-butane, and propane) under different ratios of OH to Cl (condition set 1) in the absence of NO_x .

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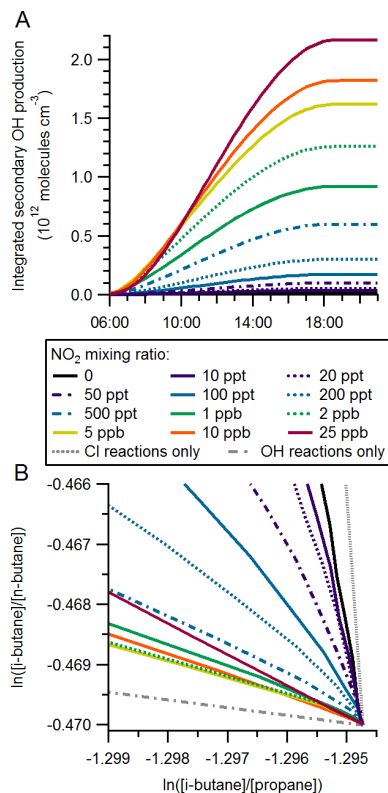


Fig. 4. MCM calculation results of ClNO_2 -initiated chemistry with different NO_x conditions (condition set 2): **(a)** integrated secondary OH under varying conditions of NO_2 ; and **(b)** VOC tracer ratios (*i*-butane, *n*-butane, and propane). Note that the x and y axis scales in **(b)** are expanded relative to Fig. 2 to show the influence of NO_2 on VOC ratios.

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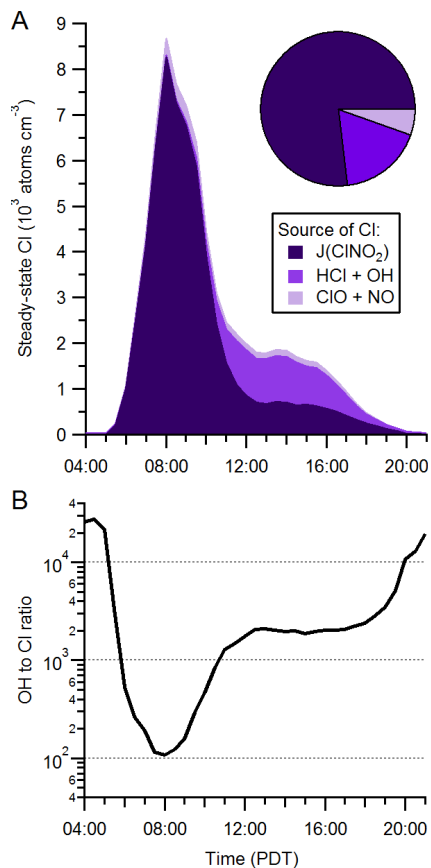


Fig. 5. (a) Calculated diurnal Cl concentration using measurements from the Pasadena ground site during CalNex; and **(b)** OH to Cl ratio using measured OH concentrations from the Pasadena ground site during CalNex and calculated Cl concentrations.



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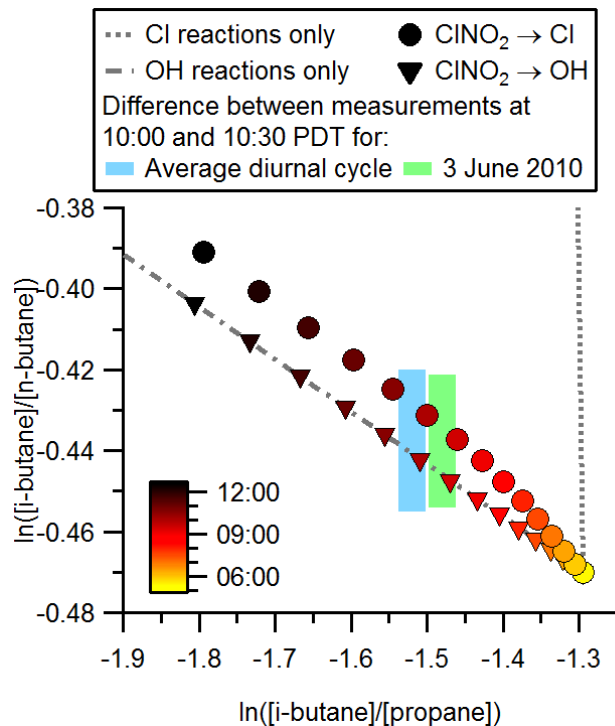


Fig. 6. MCM-calculated VOC tracer ratios (*i*-butane, *n*-butane, and propane) using Pasadena pre-sunrise measured concentrations of radical precursors and VOCs (condition set 3a), then changing the photolysis of ClNO₂ to produce OH instead of Cl (condition set 3b). Coloured bars show the difference between sequential VOC measurements at 10:00 and 10:30 PDT as a range for CalNex data from 3 June 2010 and the campaign diurnal average (shown in Fig. 2). Vertical scale is expanded to show the small influence of Cl.

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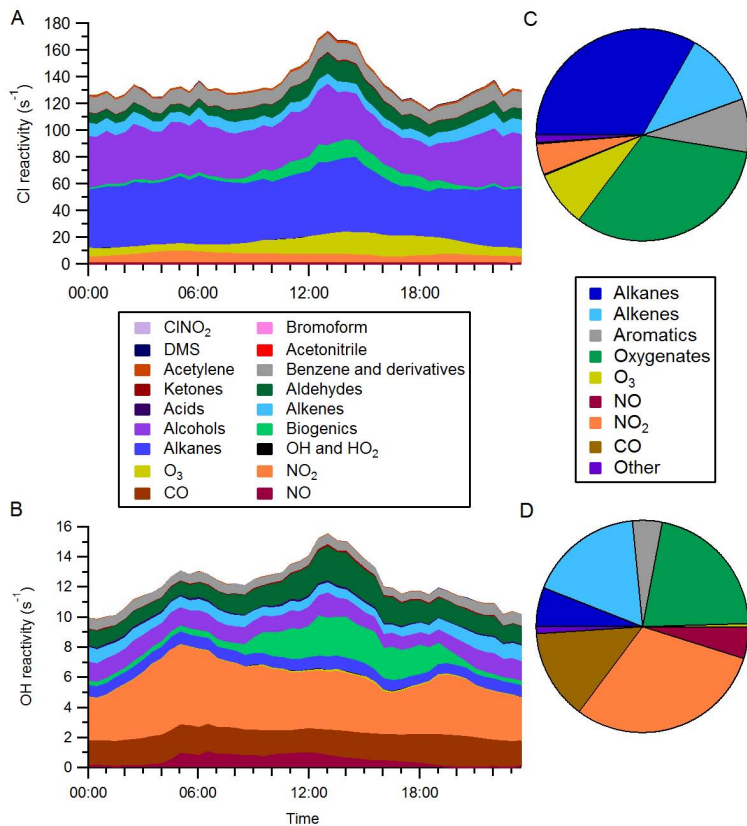


Fig. 7. Reactivity averaged over a diurnal cycle for (a) CI and (b) OH; Pie charts showing relative contributions to reactivity during daylight hours for (c) CI and (d) OH calculated from measurements made in Pasadena during CalNex campaign.