



Chlorine as a primary radical: evaluation of methods to understand its role in initiation of oxidative cycles

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Abstract. The role of chlorine atoms (Cl) in atmospheric oxidation has been 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 (California Nexus – Research at the Nexus of Air Quality and Climate Change) showed it to be an important primary (first generation) radical source. Evolution of ratios of volatile organic compounds (VOCs) has been proposed as a method to quantify Cl oxidation, but we find no evidence from this approach for a significant role of Cl oxidation in Los Angeles. We use 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 commonly used VOC ratios as a function of NO_x and secondary radical production. Model results indicate VOC tracer

ratios could not detect the influence of Cl unless the ratio of [OH] to [Cl] was less than 200 for at least a day. 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 obscures 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 3 h 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 ratio evolution to follow that expected for OH oxidation, despite the significant input of primary Cl from ClNO₂ photolysis in the morning. Even though OH is by far the dominant oxidant in Los Angeles, Cl atoms do play an important role in photochemistry there, constituting 9 % of the primary radical source. Furthermore, Cl–VOC reactivity differs from that of OH, being more than an order of magnitude larger and

dominated by VOCs, such as alkanes, that are less reactive toward OH. Primary Cl is also slightly more effective as a radical source than primary OH due to its greater propensity to initiate radical propagation chains via VOC reactions relative to chain termination via reaction with nitrogen oxides.

1 Introduction

Chlorine atoms (Cl), even if present in the troposphere in small concentrations, can have a significant effect on tropospheric oxidation and can impact the production of ozone in urban environments (Chang and Allen, 2006; Knipping and Dabdub, 2003). Atomic chlorine is 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. Historically, Cl was thought to be produced primarily from heterogeneous reaction cycles involving sea salt (Keene et al., 1999; Knipping et al., 2000; Erickson et al., 1999) and, consequently, the importance of Cl to atmospheric oxidation was believed to be limited to the marine boundary layer and coastal areas. Recent measurements of anthropogenically derived photolabile Cl precursors (ClNO_2 and Cl_2) identify a mechanism for anthropogenic pollution to contribute to production of Cl (Osthoff et al., 2008; Riedel et al., 2012; Lawler et al., 2009, 2011). 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).

Indirect methods must be used to estimate the importance of Cl in tropospheric photochemistry, since reliable instrumental methods to directly measure Cl concentrations do not exist. Even in the presence of strong photochemical sources, predicted ambient Cl concentrations are small ($< 10^6$ atoms cm^{-3} ; e.g., Riedel et al., 2012). 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 the 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 estimated to be on the order of 10^3 atoms cm^{-3} (Allan et al., 2001; Singh et al., 1996). On local and regional scales, several indirect methods have been used to estimate the concentration of Cl or its contribution to tropospheric oxidation. First, measurements of Cl precursors, including HOCl, ClO, Cl_2 , and ClNO_2 , enable estimates of the importance of Cl (Osthoff et al., 2008; Riedel et al., 2012; Lawler et al., 2011; Stutz et al., 2002). Second, products of addition reactions 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

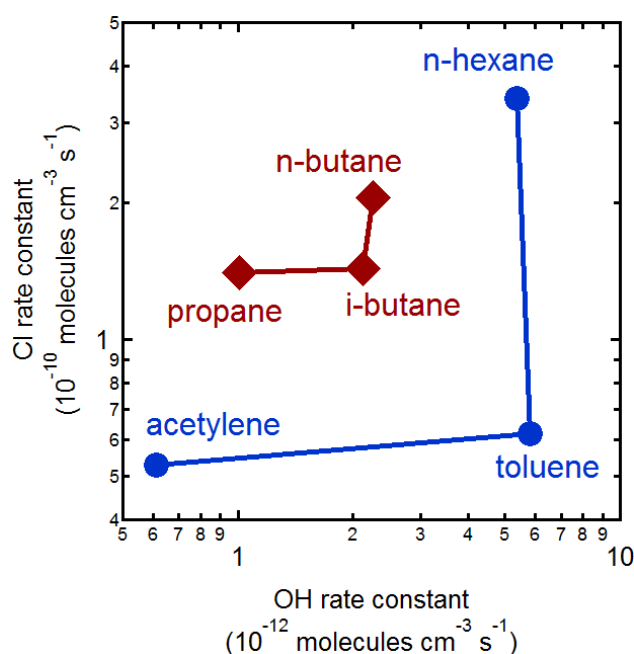


Fig. 1. Rate constants for reaction of Cl and OH with VOCs that are used to infer the influence of Cl oxidation. Rate constants are those used in the model, under conditions described in Table S4.

isoprene, can be used as markers of chlorine oxidation (Nordmeyer et al., 1997). Finally, the most easily applied and commonly used method to infer Cl importance is examination of VOC tracer ratios. These ratios can determine the relative contributions to oxidation of VOCs by Cl and OH (Jobson et al., 1994). 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 in air masses with different ages, it is possible to quantify the relative contribution of OH and Cl to oxidation. A key characteristic of the second and third methods is their sensitivity to the total radical concentrations, which result from both primary production (i.e., from photolysis of a precursor) and secondary formation (i.e., from radical propagation reactions). Although there remains considerable uncertainty in the analyses, results of these three indirect methods have been interpreted as indicating that Cl is an important oxidant in a number of locations, including Houston, Texas (Riemer et al., 2008; Tanaka et al., 2003; Osthoff et al., 2008), the east coast of the United States (Pzsenny et al., 2007), mid-continental North America (Thornton et al., 2010; Mielke et al., 2011), the Arctic (Jobson et al., 1994; Gilman et al., 2010; Ramacher et al., 1999), and Los Angeles, California (Gorham et al., 2010). Average concentrations estimated with these methods range from 10^2 to 10^5 atoms cm^{-3} (Riemer et al., 2008; Rudolph et al., 1997; Pzsenny et al., 2007; Stutz et al., 2002; Wingenter et al., 1999, 1996, 2005).

The VOC tracer ratio approach has been among the most commonly used methods to assess the importance of Cl to tropospheric oxidation. It is sensitive to the relative concentrations of Cl and OH radicals. In areas with high nitrogen oxide levels, the use of this method can be complicated by the influence of secondary OH radical generation through radical propagation cycles, and thus would not necessarily provide an accurate test of primary radical sources. A low [Cl] to [OH] ratio may not imply that Cl is not important as a primary radical source. Effects of this secondary radical generation on [OH] to [Cl] ratio interpretation have not been fully evaluated and quantified, though recent field studies suggest a large source of primary Cl radicals in areas with large NO_x concentrations through the nighttime formation and daytime photolysis of ClNO₂. Furthermore, use of the VOC tracer ratio approach has not been compared with another method to assess the importance of Cl to tropospheric oxidation. Thus, further examination of this method and its applicability across 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 are expected to reflect the overall contributions of Cl and OH oxidation, but cannot be expected to accurately reflect the relative contribution to the initiation of radical reactions.

Recently, Cl was shown to be a significant contributor to the primary radical budget in Los Angeles during the CalNex (California Nexus – Research at the Nexus of Air Quality and Climate Change) campaign (Young et al., 2012; Mielke et al., 2013). Using measurements of ClNO₂ and other radical precursors, it was demonstrated that ClNO₂, 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 in this location should show the impact of Cl oxidation, especially immediately following sunrise; however it has not been possible to identify such an impact. In this paper, we will examine (i) VOC tracer ratios as descriptors of radical chemistry in the Los Angeles (L.A.) 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 mechanisms through which chlorine impacts tropospheric chemistry in Los Angeles. Our ultimate goal is to reconcile the evidence for the significant contribution of Cl as a primary radical source with the lack of evidence for a direct role of Cl in VOC oxidation.

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 above sea level). The site operated from 15 May to 15 June 2010. Ground site measurements used in this analysis 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 WP-3D aircraft during CalNex showed mixing ratios up to 2.1 ppmv over the Los Angeles Basin (Peischl et al., 2013). In addition, many other VOC species are likely present at low levels, but were not included in this study.

The NOAA WP-3D research aircraft flew 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 R/V *Atlantis* cruised along the coast and within the harbors of California from May 14 through June 8; 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

The reactivities of OH and Cl with other species (i.e., $\text{reactivity}_{\text{Cl}/\text{OH}+\text{X}} = k_{\text{OH}/\text{Cl}+\text{X}} \times [\text{X}]$) in the ambient atmosphere were calculated using averaged diurnal cycle concentrations of ClNO₂, HONO, OH, HO₂, O₃, NO, NO₂, CO, acids, and speciated VOCs. The acid measurements included HONO, HNO₃, HCl, and HCOOH (Young et al., 2012; 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-butadiene, acetonitrile, bromoform, isoprene, methyl vinyl ketone (MVK), methacrolein, α - and β -pinene and limonene (Washenfelder et al., 2011; Wong et al., 2011; Gilman et al., 2010). 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] to [OH] ratio on

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)	30 min	(Gilman et al., 2010)
		20–35 % (oxygenates)		
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 ($x \text{ pptv} + y \%$), x represents the precision and y represents the accuracy.

VOC tracer ratios; (2) the impact of NO_x on VOC tracer ratios; and (3) the evolution of VOC tracer ratios that would be expected under conditions observed at CalNex, assuming no continuing emissions of VOCs into the box. 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 18 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 (Taatjes et al., 1999; Atkinson et al., 2006; Yamanaka et al., 2007; Kaiser and Wallington, 2010; Zhou et al., 2005; Yarwood et al., 1991), 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 was included with little modification of the model, because their reactions with Cl are well characterized and proceed by 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 measured in highest concentration was used to represent that compound class and the chemistry and kinetics of reaction with Cl atoms for that compound were added into the model. 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 – 7 h) 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 % relative humidity). 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, to avoid significant modification of TUV, 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 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 concentrations on the evolution of VOC ratios. The first (Condition Set 1) explored the impact of [OH] to [Cl] ratios on VOC tracer ratios under conditions of solely primary radical production. A fixed (i.e., time invariant) radical concentration of 5×10^6 molecules cm^{-3} was used, with relative amounts of OH and Cl varying between different model runs to make up this total. Keeping the total number of radicals constant allowed us to explore the effect of [OH] to [Cl] ratios, which have been used as a common metric for the influence of Cl in past studies (Pzsenny et al., 2007). The concentrations of NO and NO_2 were fixed to zero throughout the simulation. The second scenario (Condition Set 2) explored the impact of NO_x on VOC tracer ratios with Cl atoms as the sole primary radicals. Primary production of Cl as a product of ClNO_2 photolysis was included, while primary sources of OH (i.e., HONO photolysis and reaction of $\text{O}(^1\text{D})$ with water) were eliminated by fixing the initial HONO concentration at zero and setting the $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ reaction to produce no products in the model. Initial 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 more fully 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 . In the second (3b), reaction of $\text{O}(^1\text{D})$ plus water and HONO photolysis was unchanged, but photolysis of ClNO_2 was prescribed to produce OH instead of Cl in the model. Thus, simulation 3b maintained the same production rate and temporal distribution of primary radicals and changed only the identity of the radical between OH and Cl. In both cases,

NO_2 was fixed at 18 ppbv, comparable to the mixing ratio observed in the morning 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. Tracer ratios of VOCs are affected by mixing of air parcels that have different emission and photochemical histories. Nevertheless, even in the presence of such mixing, each ratio generally does provide a reasonably accurate determination of the degree of photochemical processing of the more reactive VOC included in the ratio (Parrish et al., 2007) provided the difference between the rate constants of the two VOCs composing the ratio is relatively large.

Here we examine VOC tracer ratios measured during the campaign for evidence of VOC oxidation by Cl atoms. The set of compounds that includes *i*-butane, *n*-butane, and propane has been used for this purpose (e.g., Jobson et al., 1994) including in Los Angeles (Gorham et al., 2010). 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. A faster-reacting set of VOCs, toluene, acetylene, and *n*-hexane (blue points in Fig. 1), yield more sensitive indicator ratios. Rudolph et al. (1997) used a similar 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], indicating the VOCs are predominantly oxidized by OH. The relatively small systematic change in the average ratios is not in the direction that indicates a significant contribution from Cl 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 aircraft data shown in Fig. 2 include all measurements regardless of altitude or

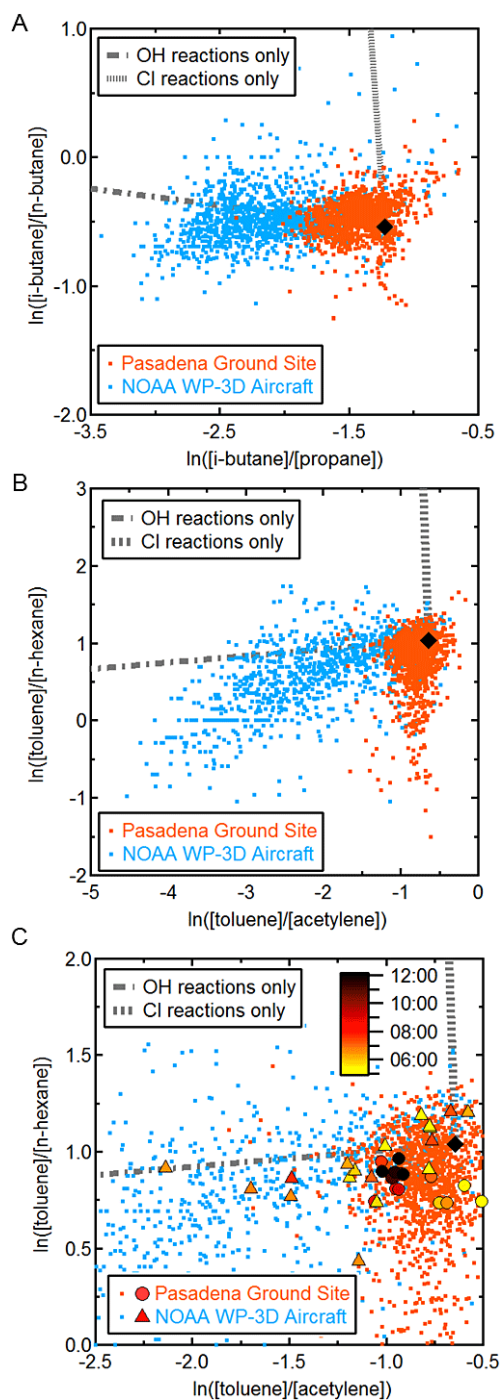


Fig. 2. VOC tracer ratios measured at the Pasadena CalNex ground site and on the WP-3D aircraft. (A, B) All data for all days for the entire campaign. The lines indicate expected tracer ratio evolution for OH and Cl oxidation starting from Los Angeles Basin emission ratios (black diamonds) determined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

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 R/V *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.

We also specifically examined VOC tracer ratios on the day of 3 June 2010 (large, color-coded symbols in Fig. 2c), for which the preceding night had the highest concentration of ClNO_2 (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 Cl oxidation at local scales. During the morning (07:00–11:00 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 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 shipborne measurements of *i*-butane, *n*-butane, and propane. 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 was not important for direct VOC oxidation at either the Pasadena location or throughout California during the CalNex time period. Examination of this apparent discrepancy between the quantification of the primary radical sources and evolution of VOC tracer ratios is needed to understand the importance of Cl to VOC oxidation and ozone formation in Los Angeles. The following sections investigate the evolution of the VOC tracer relationships within the box-model calculations described in Sect. 2.3

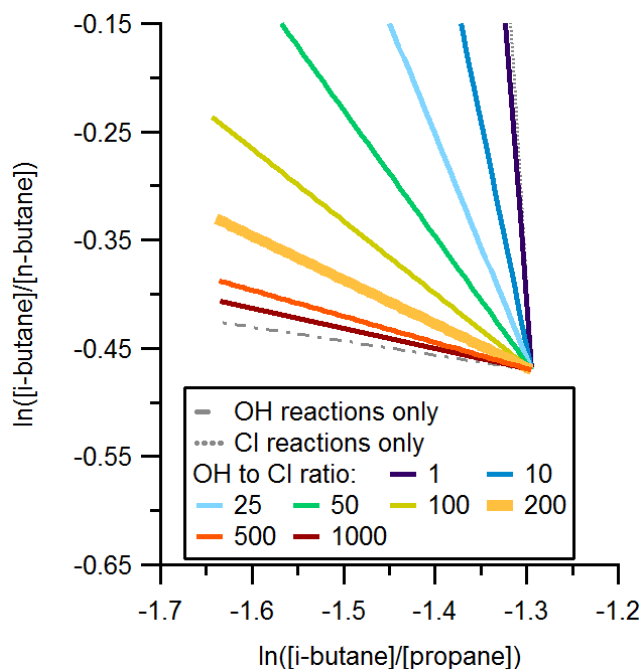


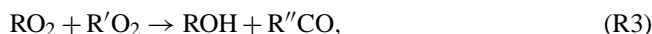
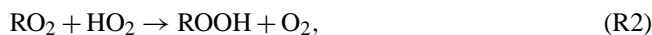
Fig. 3. Evolution of one set of VOC tracer ratios (*i*-butane, *n*-butane, and propane) under different ratios of [OH] to [Cl] (Condition Set 1) in the absence of NO_x . The total radical concentration was held at 5×10^6 molecules cm^{-3} and photochemical processing was allowed to proceed for 17 h.

3.2 Sensitivity of VOC tracer ratios to Cl radicals

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 ratio evolution expected for different OH to Cl ratios for a constant radical concentration of 5×10^6 molecules cm^{-3} . A ratio of 1000 is observationally indistinguishable from OH reactions only, while a ratio of 1 is observationally indistinguishable from Cl reactions 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 Fig. 2a), the maximum OH to Cl ratio allowing 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 1 day for the Cl reactions signature to be detectable. With a faster-reacting set of VOC tracers, this time period would decrease. 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

A very important characteristic of the photochemistry of the urban atmosphere is the formation of secondary radicals through chain reaction mechanisms. An OH or Cl radical initiates the VOC oxidation process by directly reacting with the VOC, and (through multiple steps) forming a peroxy radical of the form HO_2 or RO_2 , where R represents an organic group formed from part of the VOC reactant. In the absence of NO_x , peroxy radicals react predominantly via self-reactions that lead to radical termination:



Although RO_2 radicals can self-react leading to radical propagation, this is not their dominant fate. Conversely, in high- NO_x environments, such as Los Angeles, the input of a single radical can lead to radical propagation and formation of many secondary radicals:



The cycle described by Reactions (R4)–(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 timescale for photolysis. Two important features of this cycle should be noted. First, initiation of radical propagation through Reaction (R4) requires the presence of NO_x . Second, even if the initial radical is Cl, the secondary radical produced in Reaction (R6) is an OH.

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 . The reactions responsible for primary production of OH were turned off, so that OH could only be produced through secondary production following primary production of Cl. The impact of NO_2 increases on VOC tracer ratios is shown in Fig. 4a. As NO_2 mixing ratios increase from 0 to 2 ppbv, the VOC tracer ratios move from the Cl oxidation line toward the OH oxidation line, even though there is no primary production of OH within the system. Figure 4b depicts the change in integrated secondary OH produced from ClNO_2 photolysis-initiated chemistry as a function of NO_2 mixing ratio. As the fixed NO_2 mixing

ratio increases from 0 to 1.5 ppbv, the integrated production of secondary OH increases, as radical propagation initiated through Reaction (R4) is enhanced. The effect of additional NO₂ decreases at higher NO₂ mixing ratios. This occurs as a result of the growing importance of the radical sink reaction of NO₂ with OH to form HNO₃. As NO₂ mixing ratios are further increased, ratios move slightly away from the OH oxidation line as the importance of OH radical loss to HNO₃ increases. Despite the fact that Cl is the sole primary radical produced in this simulation, production of secondary OH radicals in the presence of NO_x effectively masks the contribution of Cl as the initiator of the oxidation process.

The chain length for radical propagation may be defined as the instantaneous ratio of the rate of conversion of HO₂ to OH to that of total radical termination. In a separate set of simulations where the OH reactivity with respect to VOCs was similar to CalNex, the chain length of radical propagation was determined as a function of NO_x. The chain length for radical propagation varied from 1 to 6, with an initial increase with increasing concentration of NO_x, followed by a decrease with further concentration increase (similar to the trend for secondary radicals in Fig. 4b). This implies that the reaction of a single Cl atom could lead to the production of 1–6 OH radicals. Radical propagation chain lengths were similar for Cl and OH.

This simple simulation in Fig. 4 is a qualitative depiction of the influence of Cl on the time evolution of VOCs. These model results describe a single total VOC concentration. Results are qualitatively similar when total concentrations of VOCs are changed (Fig. S2). 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 likely underestimates calculated secondary radical production. Additionally, no emissions were included in this simulation, ClNO₂ 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 greatly reduce the apparent contribution of Cl to VOC oxidation as inferred from VOC ratios in NO_x-rich regions, even if Cl is the sole driver initiating the oxidation cycle.

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

We can estimate the concentration of Cl present during CalNex using measurements averaged over a diurnal cycle and the steady-state approximation, i.e., using ClNO₂ photolysis as a source balanced by Cl loss to oxidation of VOCs

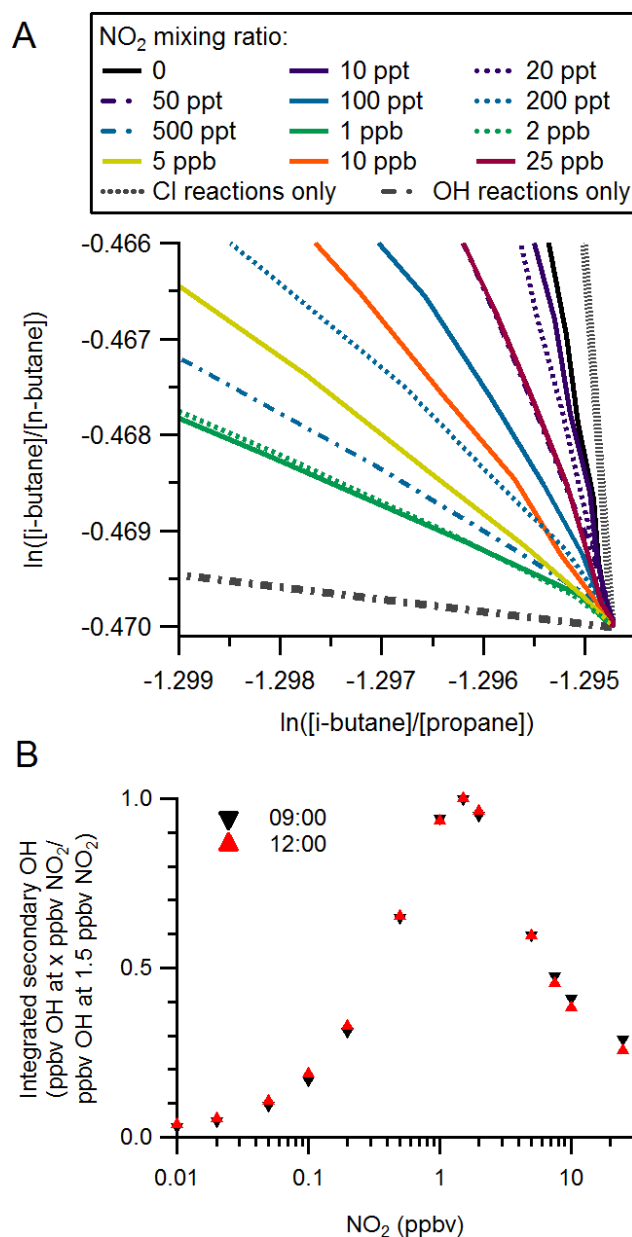


Fig. 4. MCM calculation results of ClNO₂-initiated chemistry with different NO_x conditions (Condition Set 2): (A) evolution of one set of VOC tracer ratios (*i*-butane, *n*-butane, and propane), and (B) integrated secondary OH under varying conditions of NO₂. Note that the *x* and *y* axis scales in (A) are expanded relative to Fig. 2 to show the influence of NO₂ on VOC ratios.

(Fig. 5). Up to this point, we have assumed that photolysis of ClNO₂ is the only source of Cl. Measurements aboard R/V *Atlantis* taken off the coast of Los Angeles during CalNex indicate that other primary sources of Cl were present (e.g., Cl₂; Oum et al., 1998), but photolysis of ClNO₂ dominated (Riedel et al., 2012). Formation of secondary Cl atoms is also possible. Based on measurements from CalNex, the secondary Cl source was determined to be approximately

23 % of the calculated total Cl production, and 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 is small relative to the primary Cl source. The maximum Cl concentration calculated during CalNex was 8.7×10^3 atoms cm^{-3} and the average daytime concentration was 2.3×10^3 atoms cm^{-3} . This calculation may slightly underestimate the Cl concentration, since minor primary sources have not been included. The lower-limit estimate for CalNex is of the same order as calculated by Knipping and Dabdub (2003) for Los Angeles, but substantially lower than calculated for Houston, Texas (mean of 7.6×10^4 atoms cm^{-3} ; Riemer et al., 2008). A minimum [OH] to [Cl] ratio of 109 was calculated at approximately 08:00 PDT coincident in time with the maximum Cl concentration (Fig. 5b). 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, calculated [OH] to [Cl] ratios are below 200 for approximately two hours beginning at 07:00 PDT. Thus, VOC tracer ratios, which are sensitive to radical concentration but not their primary sources, would show at best marginal evidence for Cl oxidation, and only over a short period during early morning, despite the relatively much larger contribution of ClNO₂ photolysis as a primary radical source operative during that time.

Using the MCM modeling described in Sect. 2.3, we calculated the VOC tracer ratio evolutions for a simplified Los Angeles case during CalNex (Condition Set 3). These can be compared with measured VOC ratios assuming the air masses measured at the Pasadena site had a common history. The model does not attempt to replicate the complex meteorology or emissions within the Los Angeles Basin, but is instead used to assess the sensitivity of a more realistic VOC and radical precursor mixture to Cl reactions. The influence of Cl was tested with the inclusion of ClNO₂ 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 loss of ClNO₂ by photolysis, oxidation follows a line parallel to the OH oxidation line, 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 ClNO₂ are consistent with oxidation entirely by OH. The predicted difference in $\ln([i\text{-butane}]/[n\text{-butane}])$ between ClNO₂ reacting to form OH and Cl is less than 0.02. This difference is impossible to detect given the data scatter of approximately 0.5 in VOC tracer ratio measurements (Fig. 2a). 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 timescale 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 An-

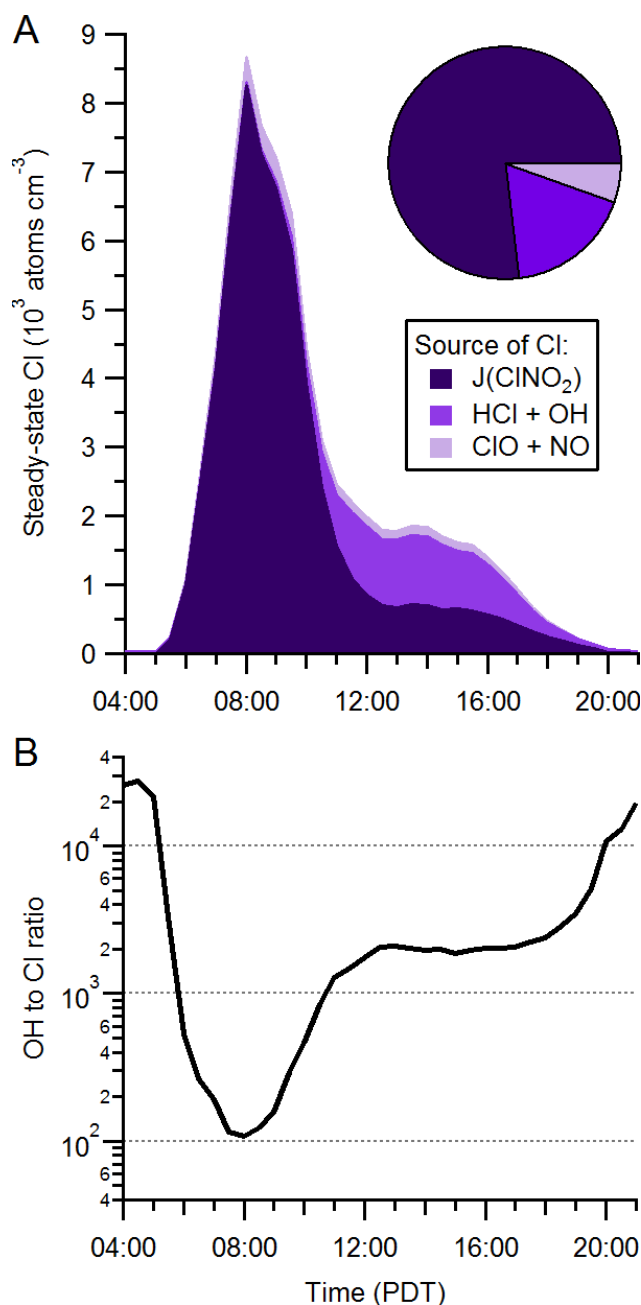


Fig. 5. (A) Calculated diurnal Cl concentration using measurements from the Pasadena ground site during CalNex; and (B) calculated [OH] to [Cl] ratio using measured OH concentrations from the Pasadena ground site during CalNex and calculated Cl concentrations.

geles for the most commonly used set of tracers (*n*-butane, *i*-butane, and propane).

Incorporation of faster-reacting compounds into VOC tracer ratios can provide a more sensitive measure of the influence of Cl. 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, c), having different

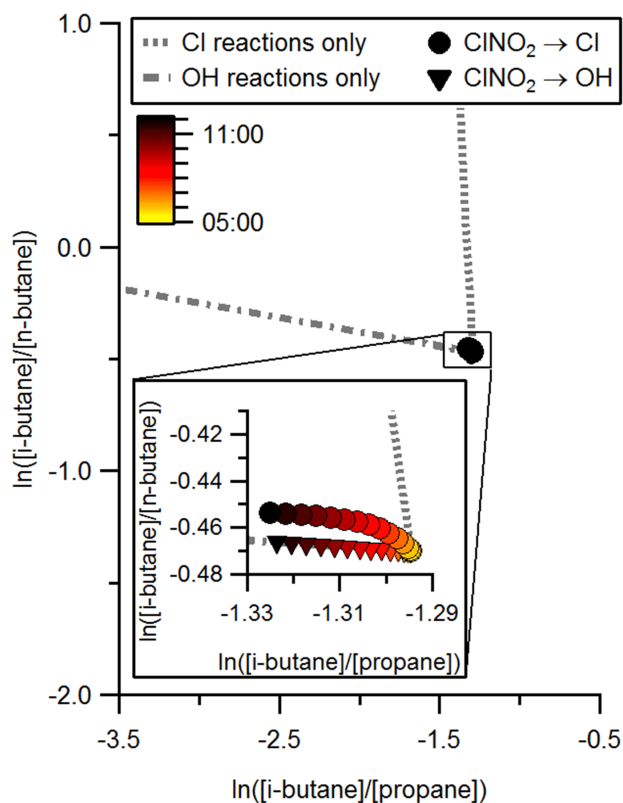


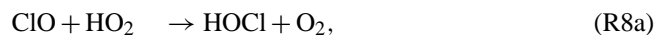
Fig. 6. MCM-calculated VOC tracer ratio evolution (*i*-butane, *n*-butane, and propane) using Pasadena pre-sunrise measured concentrations of radical precursors and VOCs (Condition Set 3a), then changing the photolysis of ClNO₂ to produce OH instead of Cl (Condition Set 3b). Scale is identical to that in Fig. 2a and expanded in the inset.

Cl but similar OH rate coefficients, is more than four times as sensitive to Cl as the ratio of [*n*-butane] to [*i*-butane] ratio (Fig. 2a) primarily considered above. However, the evolution of the toluene, *n*-hexane, and acetylene ratios considering all data (Fig. 2b) and the morning of 3 June (Fig. 2c) also reveals no indication of Cl oxidation. Results of Condition Set 3a indicate that uncertainty and variability in these ratios must be less than 0.06 to be detected, which is far less than the typical observed variability of 0.5 (Fig. 2b, c).

3.5 Differences Between Cl and OH radicals

Three key differences between the reactivity of Cl atoms and OH radicals 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 par-

ticipate 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 (Reaction R7), which has the potential to form HOCl (Reaction R8a) if the resulting ClO does not react primarily with NO to regenerate Cl (Reaction R8b):



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



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 (R8a) and (R7) 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 has 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 O₃ 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 O₃ formation in light of recent fieldwork showing a large Cl atom source through formation and photolysis of ClNO₂.

4 Conclusions

Previous studies have shown that Cl radicals play a significant role in Los Angeles photochemistry (Young et al., 2012; Mielke et al., 2013). Here we investigate why the evolution of VOC ratios in Los Angeles show no indication that these Cl radicals play a significant role in their oxidation (Figs. 1, 2). Box modeling based upon the MCM indicates that VOC ratios do evolve as expected (Fig. 3) when the relative amounts

of Cl and OH are artificially held at fixed ratios. However, even when the model is constrained so that the only primary radical source is photolysis of ClNO₂ producing Cl (i.e., primary production of OH radicals from all sources are turned off), the VOCs evolve similarly to that expected for OH oxidation (Fig. 4a) over a range of NO_x concentrations. The reason for this behavior is that VOC oxidation by the secondary OH produced from Cl oxidation of VOCs 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 measured ambient VOC ratios. These ratios are expected to show Cl oxidation signatures only below a sustained OH to Cl ratio of approximately 200. However, since ClNO₂ 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.

These results indicate that VOC tracer ratios do accurately reflect the relative oxidation of VOCs by the Cl and OH radicals present in the atmosphere, and when properly interpreted with appropriate consideration of the confounding effects of mixing (cf. Parrish et al., 2007), do provide useful indirect determinations of the average ratio of Cl to OH concentrations. However, in moderate- and high-NO_x urban environments, the ratio of the radical concentrations do not provide an accurate indication of the relative impacts of the primary sources of the Cl and OH radicals, and it is these primary sources that drive urban photochemistry.

Any method that relies upon the ratio of Cl to OH concentrations to gauge the relative impacts of Cl and OH radicals may be biased without careful consideration of the impact of secondary radical formation. Both Cl atoms and OH radicals form secondary radicals through radical chain reactions, but these radicals are almost exclusively OH rather than Cl. This secondary OH formation can then (depending upon NO_x concentration) greatly enhance the OH concentration over the Cl concentration compared to that produced from the primary radical sources. Derivation of the average ratio of [Cl] to [OH] from analysis of measurements of Cl atom-isoprene addition products (such as reported by Riemer et al., 2008) suffers from the same potential bias as analysis of VOC ratios for exactly the same reason – secondary production of OH by Cl. Interpretation of model results (e.g., Knipping and Dabdub, 2003) based upon calculated Cl to OH ratios will likewise be complicated by secondary radical production. To accurately gauge the relative impacts of Cl and OH in moderate- and high-NO_x environments requires a time-integrated analysis of the primary radical production of both Cl and OH radicals.

Differences in radical chemistry also affect the relative impacts of Cl and OH formed in the primary formation processes. The Los Angeles atmospheric composition during CalNex was more than an order of magnitude more reactive with Cl than with OH (Fig. 7) and Cl reacts more rapidly

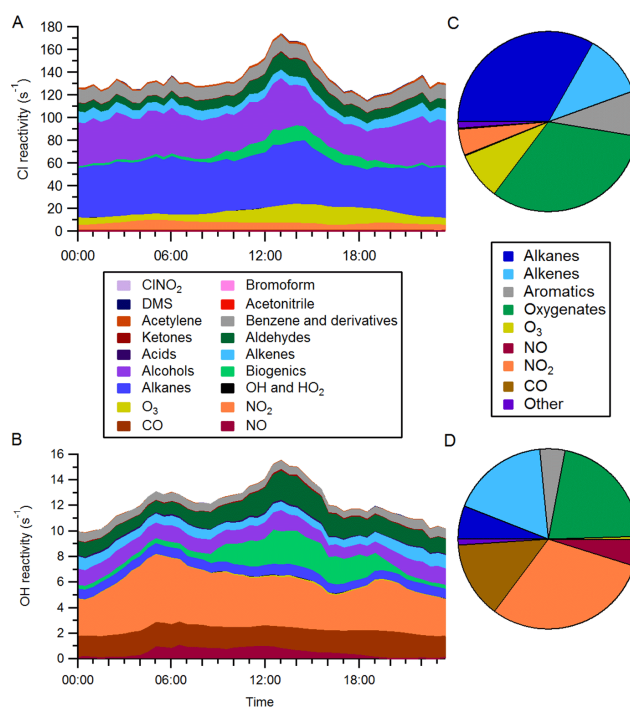


Fig. 7. Reactivity averaged over a diurnal cycle for (A) Cl and (B) OH; Pie charts showing relative contributions to reactivity during daylight hours for (C) Cl and (D) OH calculated from measurements made in Pasadena during the CalNex campaign.

with some VOC species that are long-lived with respect to OH oxidation. Cl also more efficiently forms secondary radicals than OH, since a significant fraction of OH, but not Cl, is lost to a chain termination reaction with NO₂. All of these differences between the behavior of Cl and OH indicate that their contributions to tropospheric oxidation are not accurately captured through simple radical counting. The different effects of Cl and OH on tropospheric oxidation and ozone production should be explored quantitatively.

Supplementary material related to this article is available online at <http://www.atmos-chem-phys.net/14/3427/2014/acp-14-3427-2014-supplement.pdf>.

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