

Chlorine chemistry in urban atmospheres: a review

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Environmental context. Atmospheric chlorine radicals can affect the chemical composition of the atmosphere through numerous reactions with trace species. In urban atmospheres, the reactions of chlorine radicals can lead to effects such as increases in ozone production, thus degrading local and regional air quality. This review summarises the current understanding of atmospheric chlorine chemistry in urban environments and identifies key unresolved issues.

Abstract. Gas phase chlorine radicals (Cl^\bullet), when present in the atmosphere, react by mechanisms analogous to those of the hydroxyl radical (OH^\bullet). However, the rates of the Cl^\bullet -initiated reactions are often much faster than the corresponding OH^\bullet reactions. The effects of the atmospheric reactions of Cl^\bullet within urban environments include the oxidation of volatile organic compounds and increases in ozone production rates. Although concentrations of chlorine radicals are typically low compared to other atmospheric radicals, the relatively rapid rates of the reactions associated with this species lead to observable changes in air quality. This is particularly evident in the case of chlorine radical-induced localised increases in ozone concentrations. This review covers five aspects of atmospheric chlorine chemistry: (1) gas phase reactions; (2) heterogeneous and multi-phase reactions; (3) observational evidence of chlorine species in urban atmospheres; (4) regional modelling studies and (5) areas of uncertainty in the current state of knowledge.

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Introduction

Most management plans for the reduction of photochemical smog focus on reducing emissions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x), leading to reduced formation of photochemical air pollutants, such as ozone, through various chemical pathways involving HO_x radicals. A growing body of observations and modelling studies, however, indicates that halogen radicals, particularly the chlorine radical and related species, can play a significant role in urban atmospheric chemistry. This may occur through both emissions of chlorine radical precursors and through the involvement of chlorinated species in $\text{VOC-NO}_x\text{-HO}_x$ pathways. This review will summarise the current understanding of the role of chlorine

radicals in urban photochemistry and will highlight key issues that are unresolved. The review is organised into five sections: gas phase chlorine chemistry in urban atmospheres, heterogeneous (gas-particle) and multi-phase chlorine chemistry in urban atmospheres, observations, regional modelling studies and critical gaps in current understanding.

Gas phase chlorine chemistry in urban atmospheres

Various forms of chlorine (e.g. particulate chloride, inorganic gas species, organohalogenes) are present in the atmosphere. Analyses of natural emissions indicate an atmospheric loading of 23 Tg of Cl, of which 8.4 Tg comprises reactive species. The



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Table 1. Photolysis rates ($\times 10^3 \text{ min}^{-1}$) of gas phase atomic chlorine sources compared to other common photolysis rates

Photolysis rates from parameterisations developed for the SAPRC-07 condensed chemical mechanism.^[89] O_3 produces $\text{O}(^1\text{D})$ by photolysis reaction

Chemical species	Zenith angle		
	30	50	70
Cl_2	158.9	125.2	50.2
ClONO_2	24.0	17.3	5.5
HOCl	18.6	14.1	5.2
HONO	0.106	0.085	0.0356
NO_2	676.3	559.8	253.4
O_3	2.2	1.1	0.1

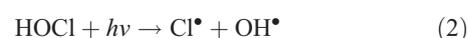
two dominant reactive species are CH_3CCl_3 (29% of reactive species) and CH_3Cl (43%), with inorganic species accounting for 7% of reactive atmospheric chlorine.^[1] Other common species include HCl , CHClF_2 , Cl_2 , HOCl , $\text{CCl}_2=\text{CCl}_2$, CH_2Cl_2 , COCl_2 and CHCl_3 . Photodissociation of chlorinated species, the sources of which may be natural or anthropogenic, is one of the most common routes to global tropospheric chlorine radical production. Other gas phase chemical pathways to the global formation of chlorine radicals include reactions of HCl or chlorocarbons.^[2,3] Gas phase species also participate in reactions involving particulate matter, which will be described in subsequent sections of this review.^[3]

Although important globally, photodissociation and oxidation of many of the most common chlorinated organic species occur at rates that are generally not fast enough to contribute significant concentrations of chlorine radicals in urban atmospheres. For example, the rate constant for chlorine radical generation by the oxidation of HCl by the hydroxyl radical at 298 K is reported to be $7.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^[4,5] This rate constant is approximately two orders of magnitude lower than the rate constant for hydroxyl radical formation from the reactions of $\text{O}(^1\text{D})$ and H_2O (1.63×10^{-10}).^[5] Given that H_2O is also typically present in the urban atmosphere at concentrations far greater than those of HCl , the result is a smaller rate of generation for chlorine radicals compared to hydroxyl radicals. For chlorocarbon photolysis, rates of reaction are very low, approaching zero, in the urban atmosphere. For example, the photolysis of CH_3Cl has only been reported to occur during exposure to radiation at wavelengths below 216 nm.^[6] In the urban atmosphere, radiation of this wavelength is negligible.

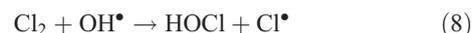
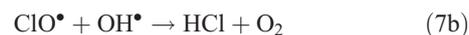
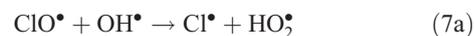
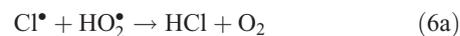
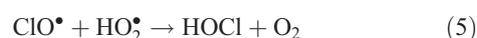
Production of chlorine radicals through routes other than photolysis of chlorocarbon species and oxidation of common chlorinated species such as HCl can proceed at rates that are significant in urban atmospheres, however. The photolysis of Cl_2 is expected to proceed rapidly with a quantum yield of unity.^[4,7,8] One comparison of radical generation from 3 ppb HONO , a photolytic source of the hydroxyl radical, and 0.1 ppb Cl_2 in a polluted region estimates corresponding radical generation rates of 5×10^6 and $4 \times 10^5 \text{ radicals cm}^{-3} \text{ s}^{-1}$ respectively for hydroxyl radicals and chlorine radicals.^[8] Thus, if concentrations of species such as HOCl , ClONO_2 or Cl_2 are sufficiently high, photolysis reactions can provide an important source of chlorine radicals in urban atmospheres. In some regions, direct anthropogenic emissions of these chlorine radical precursors can be significant. One estimate^[7] suggests that anthropogenic HOCl and Cl_2 emissions in the Houston area are $\sim 10^4 \text{ kg day}^{-1}$, coming from cooling towers, swimming pools and industrial

point sources.^[9] In the vicinity of large anthropogenic sources of Cl_2 or HOCl , the reactions of Cl and related radicals can significantly affect photochemistry. Thus, although photolysis of many chlorocarbon species and oxidation of the most common gas-phase chlorine species is not a significant contributor to radical production in urban atmospheres, there are situations where anthropogenic emissions of chlorine radical precursors can produce significant radical concentrations through photolysis pathways. Table 1 below shows a comparison of photolysis rates for some chlorine species and some other common atmospheric species involved in the photochemical cycle.

Chlorine radicals produced photolytically or through other mechanisms may react with and oxidise VOCs. The examples in Reactions 1–3 represent typical photolysis reactions and the initiating reaction for the oxidation of a generic VOC, denoted as RH .^[4,5,7,8,10,11]



The presence of reactive chlorine species can also modify HO_x levels and the $\text{HO}_2^\bullet/\text{OH}^\bullet$ ratio. This occurs from reactions resulting in the inter-conversion of OH^\bullet and HO_2^\bullet . Examples of known reactions are shown in Reactions 4–8.^[4,5,10,11]



Unlike OH^\bullet , chlorine radicals are not regenerated within the oxidation cycle. However, chlorine radicals can be regenerated by heterogeneous cycling from chloride containing aerosols (discussed in the next section) or by the volatilisation and oxidation of HCl (Reaction 9).^[2–5,10,11]



Another important difference between the hydroxyl and chlorine radicals is the rates at which they oxidise hydrocarbons. The reactivity of chlorine with most VOCs is greater than that of the hydroxyl radical, such that even concentrations of chlorine radicals an order of magnitude or more lower than hydroxyl radicals can compete with normal atmospheric concentrations of hydroxyl radicals.^[12] The reaction rates of chlorine radicals with many alkanes, aromatics, alcohols and ethers typically range between one to two orders of magnitude greater than the identical reaction with the hydroxyl radical.^[11,13–15] This high reactivity causes the rates of such reactions to approach the collisional limit. For alkenes and alkynes, the difference is slightly smaller ($k_{\text{Cl}}/k_{\text{OH}} \approx 4–13$). One exception to the increased reactivity of chlorine is the reaction with benzene, for which the ratio $k_{\text{Cl}}/k_{\text{OH}}$ is on the order of 10^{-4} .^[11,16]

Table 2. Comparison of rate constants for OH• (K_{OH}) and Cl• (K_{Cl}) for reactions with common volatile organic carbons (VOCs) at 298 K

Rate constants were compiled from Sander et al.,^[5] Aschmann and Atkinson,^[15] Finlayson-Pitts et al.,^[109] Stutz et al.,^[110] Gill and Hites,^[111] Atkinson et al.^[112] and Aschmann et al.^[113] and are given in units of cubic centimetres per molecule per second

VOC	K_{OH}	K_{Cl}
Methane	6.3×10^{-15}	1.0×10^{-13}
Ethane	2.4×10^{-13}	5.7×10^{-11}
Propane	1.1×10^{-12}	1.4×10^{-10}
<i>n</i> -Decane	1.25×10^{-11}	4.87×10^{-10}
Propene	3.01×10^{-11}	1.58×10^{-10}
Isoprene	1.01×10^{-10}	3.05×10^{-10}
α -Pinene	5.05×10^{-11}	4.70×10^{-10}

Table 3. Relative radical loss rates (R_{OH} and R_{Cl}) for a surrogate volatile organic carbon (VOC) mixture typical of urban atmospheres

Urban VOC mixture taken from Carter et al.^[114] More details are available in the Supplementary material. Rates are given in parts per billion per second at 298 K and rate constants for calculations are from Manion et al.^[115] Cl• and OH• concentrations of 1 ppt were used for rate calculations. R_{Cl}/R_{OH} ratios were calculated with full precision rates. Rates in this table are rounded to one decimal place

VOC	ppb ppm C ⁻¹	$R_{OH} \times 10^{23}$	$R_{Cl} \times 10^{23}$	R_{Cl}/R_{OH}
<i>n</i> -Butane	70.7	-67.8	-61.4	0.9
<i>n</i> -Octane	22.3	-0.7	-34.6	49.4
Ethylene	13.4	-0.5	-5.4	11.6
Propene	10.4	-1.3	-6.7	5.2
<i>t</i> -2-Butene	10.4	-2.7	-16.9	6.3
Toluene	13.3	-0.3	-3.1	9.4
<i>m</i> -Xylene	16.3	-1.6	-9.3	5.7
Formaldehyde	7.9	-0.3	-2.3	7.8
Acetaldehyde	7.6	-0.5	-2.2	4.4
Inert or lost carbon	193.1	-	-	-
Total	365.4	-75.7	-141.9	11.2 ^A

^AAverage ratio from mixture.

Reactions of biogenic VOCs (BVOCs) with chlorine also proceed more rapidly than corresponding reactions with OH•, with rate constants typically $>10^{-11}$ cm³ molecules⁻¹ s⁻¹.^[17] The oxidation of the common biogenic, isoprene, by chlorine radicals takes place primarily through chlorine addition, with ~10% of the reaction proceeding through the hydrogen abstraction pathway.^[18] Unique reaction products such as 1-chloro-3-methyl-3-butene-2-one (CMBO), and isomers of chloromethylbutenal (CMBA) result.^[18–20] Although not a BVOC, the reaction of chlorine radicals and 1,3-butadiene also produces unique tracer species, 4-chlorocrotonaldehyde (CCA) and chloromethyl vinyl ketone, with yields varying depending on the presence or absence of NO.^[21] Table 2 shows a comparison of the rate parameters of OH• and Cl• for some common alkanes, alkenes and BVOCs.

These differences in reactivities contribute to the overall loss rates for each radical as well as the relative loss rates of different VOCs. Table 3 shows a comparison of reaction rates for a VOC mixture^[22] that was formulated to represent a typical urban mixture of reactive organic gases. More details on this mixture are available in the Supplementary material (see http://www.publish.csiro.au/?act=view_file&file_id=EN13026_AC.pdf). The comparisons shown in Table 3 indicate that relative

rates of reaction with chlorine and hydroxyl radicals vary among hydrocarbon species. This difference in relative rates can be used, as will be described later in this review, to infer chlorine and hydroxyl radical concentrations, based on the relative rates of reaction of selected hydrocarbons.

Heterogeneous and multiphase chlorine chemistry mechanisms

Chlorine in particulate matter is generally in the form of unreactive chloride; however, a variety of heterogeneous and multi-phase reaction processes can lead to the conversion of particulate chloride into gas phase, reactive chlorine species. Multiphase reactions include the reactions of dissolved gas phase species within aqueous droplets, whereas reactions taking place at the interface between two phases are considered heterogeneous.^[23,24] These processes include acid displacement and reactions of N₂O₅, ozone and other species with chloride-containing aerosol.

Acid displacement and reactive chlorine cycling

Acid displacement involves the replacement of particulate chloride anions by anions associated with H₂SO₄, HNO₃, methane sulfonic acid (MSA) or other acids, and has been observed in particles of marine origin.^[25–28] In the case of HNO₃ or H₂SO₄, the process may be represented as the heterogeneous reaction of a gas phase acid with NaCl aerosols.^[3,27,29,30] In the examples in Reactions 10 and 11, the subscripts (g) and (cd) respectively denote gas phase and condensed phase species.

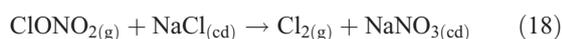
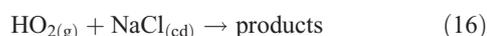
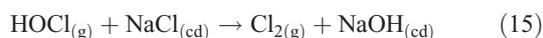
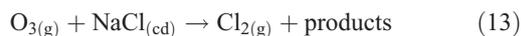


The uptake of HNO₃ is more effective when the particle is aqueous or in the presence of surface adsorbed water (SAW).^[29] Reduction in aerosol pH can also enhance HCl production, which may increase by up to a factor of 20 between pH 5.5 and 3.^[31] The presence of MgCl₂ in a particle increases SAW and thus increases the reactive uptake at lower relative humidity. It is therefore expected that this reaction will proceed at normal conditions in the marine boundary layer (MBL) and that sea salt chloride can be depleted within several hours of aerosol generation.^[29,30] HCl production by acid displacement is more efficient within the smaller size fractions of typical aerosol populations.^[32,33]

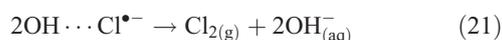
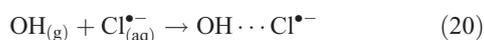
The efficiency of chloride loss from aerosols is often quantified in terms of a particulate chloride deficit. This is defined as the amount of particulate chloride that is necessary to balance the observed concentrations of sea salt tracer cations, such as Na⁺, that have no associated chloride.

Reactive uptake of gases and volatilisation of reactive chlorine

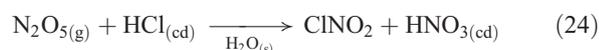
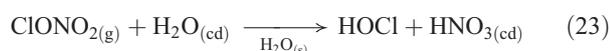
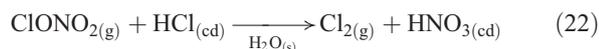
Additional multi-phase and heterogeneous chlorine reactions include the reactive uptake of other, non-acid gases, leading to the accumulation of photoreactive chlorine species. Most known mechanisms require the presence of reactive nitrogen gases.^[34] Many of these reactions can take place on dry, solid salt particles as well as aqueous droplets, although the reactions are typically slower in the absence of water.^[35] Some examples of these reactions, which can compete with the acid displacement reactions described above, are shown in Reactions 12–19.^[11,24,30,36–40]



A mechanism involving the formation of a surface complex between particulate chloride and OH^\bullet ($\text{OH}\cdots\text{Cl}^{\bullet-}$) (Reactions 20, 21) has been proposed to explain the processes involved in Reaction 14.^[41,42]



Gas phase chlorine species have also been found to react in the presence of ice surfaces or particles to produce other chlorine species (Reactions 22–24).^[36,37,39,43]

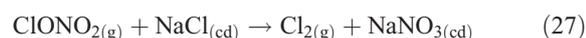


The direct uptake and scavenging of HCl by dust particles has also recently been observed, resulting in dust particles composed of up to 9% HCl by mass.^[44] In general, the cycling of chlorine can be summarised in the steps listed below.^[3,45]

1. Volatilisation of Cl_2 , HOCl or other photolytic chlorine species from NaCl aerosols or other source.
2. Photolysis of the volatilised species to produce Cl^\bullet .
3. Hydrogen atom abstraction from non-methane hydrocarbons to produce HCl.
4. Removal of HCl by reaction with OH^\bullet , wet or dry deposition or scavenging by aerosols.

N₂O₅ and ClNO₂ production

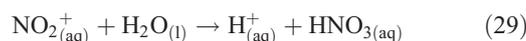
One heterogeneous mechanism that has been suggested and confirmed as a source of reactive chlorine (gas phase ClNO_2) is the reaction of N_2O_5 with chloride aerosols. It is known that heterogeneous uptake of N_2O_5 plays a critical role in overall NO_x chemistry, with up to 50% of NO_x removal being attributed to its heterogeneous mechanisms.^[46] Reactions that involved chloride activation include those shown in Reactions 25–27.^[38,47,48]



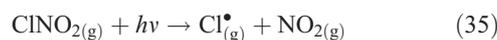
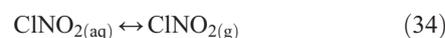
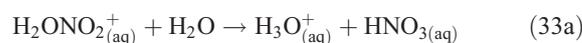
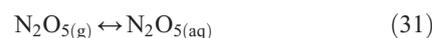
Of these three, Reaction 25 is not thought to be important.^[47] However, Reaction 26 plays an important role in the activation of chloride and ClNO_2 production,^[49,50] although the process may involve multiple steps, as outlined below. Acid displacement by HNO_3 is up to two orders of magnitude slower than the interaction with N_2O_5 .^[51] Atmospheric implications of this reaction are important, because tropospheric concentrations of N_2O_5 can range from 1 to 15 ppb.^[36,51] The reaction results in a build up of ClNO_2 in the morning, limited by N_2O_5 uptake. N_2O_5 formation, which occurs from a reversible reaction between NO_3 and NO_2 , is favoured at night due to the photochemical instability of NO_3 .^[51] Although ClNO_2 can form by homogeneous gas phase chemistry, the reactions are extremely slow,^[5] preventing significant production of ClNO_2 .

Hints that Reaction 26 existed arose during studies of the rates of chlorine radical production from irradiated NaCl aerosols in the presence of NO_x . A smog chamber experiment using initial NO_2 , O_3 and NaCl concentrations of 200 ppbv, 108 ppbv and 1.5 mg m^{-3} , found a large chlorine radical source upon irradiation of the mixture after 100 min in the dark. The observed source, if occurring from the reaction between gas phase HCl and OH radical species, would have required a 1.5-ppmv HCl mixing ratio at OH concentrations of $1.7 \times 10^7 \text{ cm}^{-3}$.^[52] Similar smog chamber studies following up these unexplained observations indicated that ClNO_2 was produced at a high yield when the relative humidity was in the range of 71–92%.^[53]

A mechanism was proposed to explain the characteristics of the reaction, including the dependence of ClNO_2 yields on particle chloride concentrations. Due to the fact that N_2O_5 does not react directly with chloride ions, there is no observable dependence of the uptake coefficient on chloride concentrations present in the aqueous solution. This is because aqueous chloride ions react not with aqueous N_2O_5 but with its dissociation products as shown below in Reactions 28–30.^[47] Direct hydrolysis was found to account for approximately only 20% of the overall reaction, and dissociation of N_2O_5 has since been cited as the rate limiting step.^[40,47,54]



Taking this proposed mechanism a step further, Bertram and Thornton^[55] proposed a reaction scheme involving the initial uptake of N_2O_5 into the aqueous phase and formation of a hypothetical protonated nitric acid intermediate as the initiating step in the production of ClNO_2 .^[55] ClNO_2 then partitions into the gas phase where it can undergo photolysis to produce chlorine radicals (Reactions 32–35).^[46,56]



An experimental study to examine the kinetics of this mechanism concluded that either **Reaction 31** or **32** is the rate limiting step at 50 % relative humidity, thus corroborating previous suggestions that mass accommodation and hydrolysis of N_2O_5 are the processes limiting the overall reaction rate. This same study showed that the decay of gas phase N_2O_5 concentrations in the presence of simulated sea salt aerosols is log-linear, implying a first order loss mechanism.^[56] A coexisting reaction pathway producing Cl_2 , in which ClNO_2 is an intermediate, is observed below pH 2.^[49,54]

ClNO_2 can also undergo reactions within particles instead of being released into the gas phase. The uptake and solubility of ClNO_2 into aqueous particles is inhibited by the presence of chloride due to its dissociation reaction in the aqueous phase (**Reaction 36**).^[57]

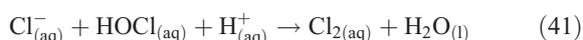
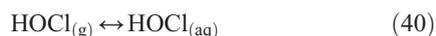
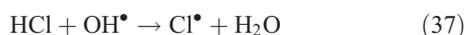


Observations of atmospheric chlorine radicals and related species

The preceding sections have summarised gas phase, heterogeneous and multi-phase reactions of chlorine radicals and related species, believed to be important in urban atmospheres. The relative importance of these pathways has been examined in a variety of observational studies. In this section, observational evidence of the presence of various atmospheric chlorine species will be explored.

Observations of chloride deficits and volatilisation

Overall, depending on region and aerosol size, particle chloride volatilisation of 70–80 % is possible.^[32] A study of volatile chlorine over the North Atlantic Ocean determined that the concentrations of volatilised chlorine from aerosols, as determined from particulate chloride deficits, tended to be approximately equal to measured HCl concentrations, ranging from below detection limits up to 125 nmol m^{-3} (3 ppbv).^[45] A separate study of chlorine chemistry in polluted air that had been advected offshore noted that the cycling of chlorine between phases can lead to a $\text{Cl}_{2(\text{g})}$ increase of 90 parts per trillion by volume (pptv) in no wind scenarios and 125 pptv in high wind scenarios.^[58] Shown below (**Reactions 37–42**) are the dominant reactions cited as being responsible for this increase. The sequence is initiated by acid displacement (**Reactions 10–11**).^[58]



The correlation between particulate chloride deficits and HCl concentrations was observed to be much higher in air polluted with combustion products, nearing a $[\text{HCl}]/[\text{Cl}^- \text{ deficit}]$ ratio of 1 in polluted air masses compared to 4.5 in cleaner air masses.^[45]

Deficits vary regionally, and air in the southern hemisphere exhibits lower particulate chloride deficits whereas chloride deficits in the northern hemisphere have approached 100 %. However, once particulate chloride is removed, HCl serves as a chloride reservoir and can be scavenged by aerosols to replenish particulate chloride concentrations.^[46] It is predicted that HCl has a lifetime in the MBL of 10 min before it is scavenged by sea salt aerosols.^[44]

Observations of hydrogen chloride (HCl) and molecular chlorine (Cl_2)

Surface concentrations of HCl in remote ocean regions range from 100 to 300 pptv, whereas peak concentrations in urban areas can be ~ 1500 pptv. Multiple studies note that peak HCl concentrations typically occur in the afternoon, coinciding with peak photochemical smog production and HNO_3 concentrations.^[59–63] This is generally attributed to the volatilisation of chloride from aerosol particles.^[3,62,63] HCl generally exhibits a trend of vertical distribution, decreasing with altitude. Previous reviews of continental tropospheric HCl observations have reported peak concentrations of up to 1–3 ppbv in urban areas.^[3] A marked drop off in concentration to 50–100 pptv typically occurs at altitudes above the boundary layer.^[3,45]

In Virginia Key, Florida, mist chamber techniques^[64] were used to measure total HCl^* (HCl and possibly ClNO_x species), which ranged between 40 and 268 pptv Cl. The same technique was used to measure total Cl_2^* (Cl_2 + some HOCl) and found concentrations ranging from below the detection limit of 26 pptv up to 254 pptv Cl. Cl_2^* built up during the night and sharply decreased after sunrise corresponding with a HCl^* increase. This suggests the photolysis of Cl_2 or HOCl at sunrise, followed by VOC oxidation by hydrogen atom abstraction by Cl^\bullet , producing HCl. Photochemical modelling performed in this study indicated that if the observed levels of Cl_2^* were completely photolysed, it would lead to Cl^\bullet concentrations of 10^4 – 10^5 radicals cm^{-3} .^[65] It was observed that higher levels of Cl_2 and HOCl were present in winds coming from the Atlantic as opposed to those from the North, suggesting a marine origin.^[65]

Other authors have also noted high concentrations of molecular chlorine in incoming marine air along the coasts of North America.^[66] Using the mist chamber technique in the Hawaii boundary layer, respective HCl^* and Cl_2^* concentrations up to 250 and 38 pptv were detected.^[67] Cl_2 concentrations in La Jolla, California, have been observed to average 2.3 pptv.^[68] In Irvine, California, Cl_2 concentrations ranging from 2.5 to 20 pptv with a 2-month mean of 3.5 pptv have been reported. Modelling the photochemistry of this observed Cl_2 showed a 5–8-ppb increase in daily maximum O_3 concentrations.^[69] Earlier evidence of O_3 production increases from the presence of chlorine was observed in industrial plumes in Telemark, Norway.^[70] In Houston, Texas, the detection of the tracer species (CMBO) at peak concentrations of 12–126 pptv^[71] provided evidence of chlorine radical concentrations estimated to be approximately $< 5 \times 10^3$ to 3.3×10^5 radicals cm^{-3} (2×10^{-4} to 1.3×10^{-2} pptv).^[20] Associated enhanced ozone production rates of > 75 ppbv h^{-1} were observed when small amounts of Cl_2 were injected into captive ambient air during chamber experiments.^[71]

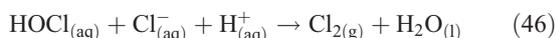
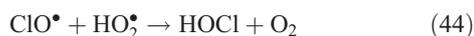
Off the coast of Long Island, New York, a concentration up to 150 pptv of Cl_2 was observed at night, with a rapid decline to less than 15 pptv after sunrise. Such amounts of Cl_2 would lead to chlorine radical concentrations of 1.3×10^5 radicals cm^{-3}

Table 4. Summary of ranges of HCl and Cl₂ observations

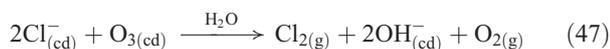
Concentrations are in parts per trillion by volume. Data from studies reporting HCl* or Cl₂* are included

Environment	HCl	Cl ₂
Marine	50–1200	–
Coastal or island	40–268	2.3–254
Urban	39–8000	2.5–20
Arctic coastal	–	9.0–100

(5.1×10^{-3} pptv) and require a daily source of ~ 330 pptv Cl₂. In this case, the air was again of marine origin.^[66] The authors suggest that a mechanism aside from photolytically driven aqueous phase mechanisms^[64,72] is needed to explain these observations. A study in the arctic coastal location of Alert, North-West Territories utilised the photoreactive halogen detector method^[73] to detect levels of photolysable Cl, which ranged between <9 and 100 pptv. Concentrations were reported as Cl₂, although they may have also included HOCl or other photolysable species. A nocturnal build up of photolytic chlorine species followed by a rapid decline after sunrise was once again observed. To explain the night time build up of these species, the nocturnal mechanism in Reactions 43–46 was proposed^[74]:



In Charlottesville, Virginia, ~ 250 miles (~ 400 km) inland, researchers using the tandem mist chamber technique^[64] found HCl* concentrations ranging from <39 to 2800 pptv, with most measurements falling under 300 pptv. Most measurements of Cl₂ and HOCl in the same study were under the 26 pptv Cl* detection limit, indicating that HCl (and possibly ClNO_x) was the dominant form of volatile chlorine.^[75] Because of results such as this, another proposed explanation of the marine origin of Cl₂ has been made by suggesting a heterogeneous reaction between particulate chloride and either ozone or the hydroxyl radical.^[3,34,45,74] An alternate reaction (Reaction 47) explaining the mechanism described in Reactions 20 and 21 was put forward as an explanation^[45,76]:



Assuming a steady-state between Cl₂ volatilisation by Reaction 47 and reuptake of HCl into aerosols, this mechanism results in a Cl₂ source of ~ 1 ppbv h⁻¹ with corresponding net O₃ production rates of 1.4 ppbv h⁻¹ during the day.^[45] Table 4 contains a summary of observations from the studies discussed in this section.

Reactions 43–47, or other pathways that also lead to nocturnal buildup of photolytic chlorine species, can potentially lead to increases in VOC oxidation, NO-to-NO₂ conversion and O₃ production early in the day. The effects of the sudden introduction of a large source of chlorine radicals would be analogous to the effect elicited by the nocturnal buildup and sunrise photolysis of a hydroxyl radical source such as HONO.

Observations of chlorine (Cl[•]) and chlorine monoxide (ClO[•]) radicals

Analysis of non-methane hydrocarbon (NMHC) decay rates has led to estimates of chlorine radical concentrations on the order of 10⁵ molecules cm⁻³ (4×10^{-3} pptv) in the Pacific MBL. These concentrations were deduced from observed decay rates of VOCs such as ethane, propane and acetylene by back calculating necessary chlorine radical concentrations to compensate for a lack of sink strength from the OH[•] reaction alone.^[77] At Appledore Island, Maine, observations of increased NMHC reactivity implied chlorine radical concentrations of 2.2×10^4 to 5.6×10^4 radicals cm⁻³ (8.6×10^{-4} to 2.2×10^{-3} pptv). These concentrations were deduced by measuring C₂–C₁₀ NMHC compounds, calculating the back trajectories of sampled air parcels and then calculating the chlorine radical concentration necessary to explain observed NMHC decay rates that were too fast to be fully explained by OH[•] concentrations.^[78] In the Southern Ocean, average Cl[•] concentrations of 720 radicals cm⁻³ (2.8×10^{-5} pptv) have been reported.^[12] At Great Lake, Utah, 3.8×10^8 molecules cm⁻³ of ClO[•] (15 pptv) was observed, suggesting mobilisation of chloride from salt beds in the area.^[79] This observation also implied a chlorine radical concentration on the order of 10⁵ radicals cm⁻³ (4×10^{-3} pptv), which would double the reactivity of the air in the area, increase OH[•] concentrations by up to 50% through radical propagation and convert NO_x into halogenated nitrates.^[79]

Observations of nitryl chloride

Direct correlations between ClNO₂, N₂O₅ and aerosol surface area concentrations have been noted in field observations.^[80] During the Texas Air Quality Study II (TEXAQS II), concentrations of ClNO₂ up to 1200 pptv were found in ship engine plumes, near NO_x sources in the Houston Ship Channel and in surrounding urban areas.^[80,81] Contemporaneously measured N₂O₅ concentrations and consumption rates suggest that anthropogenic pollutants contributed significantly to the observed ClNO₂.^[80]

In addition, ClNO₂ concentrations up to 450 pptv have also been found as far inland as Kohler Mesa outside of Boulder, Colorado. The Kohler Mesa is 1400 km from any coastal area, but it is thought that the air masses during the measurement period were potentially influenced by long distance chlorine transport from coastal areas or inland salt beds and pollution from combustion in the Boulder, Colorado area.^[46] More recent observations in Los Angeles, California, revealed concentrations of ClNO₂ up to 2100 pptv.^[82] In 2011, observed ClNO₂ mixing ratios up to 250 pptv were observed in Calgary, Alberta, Canada.^[83] Arctic observations of N₂O₅ and ClNO₂ were made during the International Chemistry in the Arctic Lower Troposphere (ICEALOT) campaign. Respective ClNO₂ and N₂O₅ ranges, on average, of 150–250 and 150–200 pptv were observed.^[84] Table 5 summarises observations of ClNO₂ in several locations.

Observations of chlorine tracer species

CMBO and CMBA are known tracer compounds of chlorine's oxidation of isoprene. Observations of these compounds were made during the Texas Air Quality Study (TEXAQS) in Houston, Texas.^[71] Chlorine radical concentrations were deduced from CMBO and CMBA concentrations and were determined to range between 5×10^3 and 3.3×10^5 radicals cm⁻³ (2×10^{-4} and 1.3×10^{-2} pptv).^[20] In comparison, Maben et al.^[75]

Table 5. Detection of ClNO₂ chemistry in continental North America
Texas Gulf Coast data are from Osthoff et al.^[80] Boulder, Colorado, data are from Thornton et al.^[46] Los Angeles, California, data are from Riedel et al.^[82] Calgary, Ontario, data are from Mielke et al.^[83] Only NO_y data for Los Angeles and Calgary were reported in this study

Locale	N ₂ O ₅ (ppbv)	ClNO ₂ (pptv)	N ₂ O ₅ loss rate, k_{het} (s ⁻¹)
Texas Gulf Coast	0–0.750	0–1200	$(0.1–3) \times 10^{-3}$
Boulder	0–1.5	0–450	–
Los Angeles	0–25	0–2100	–
Calgary	1.9–60	0–250	–

approximated chlorine radical concentrations to be less than 10^4 radicals cm⁻³ (4×10^{-4} pptv) in continental air over eastern North America, at the lower end of the range of the Houston observations. During the Atlantic Stratospheric Transition Experiment/Marine Aerosol and Gas Exchange (ASTEX/MAGE), observed hydrocarbon concentrations were used to determine average chlorine radical concentrations between 0600 and 1100 hours local time, which were approximated at $(3.3 \pm 1.1) \times 10^4$ molecules cm⁻³ ($(1.2 \pm 0.4) \times 10^{-3}$ pptv). Midday concentrations were calculated to be $(6.5 \pm 1.4) \times 10^4$ molecules cm⁻³ ($(2.6 \pm 0.6) \times 10^{-3}$ pptv), and the authors suggest a nocturnal build up of photolysable chlorine as the source.^[34]

Summary of observations

Observational evidence suggests that chlorine chemistry is occurring over both oceanic and continental areas, with observed chlorine radical concentrations on the order of 10^3 – 10^5 molecules cm⁻³ (4×10^{-5} to 4×10^{-3} pptv) not being uncommon.^[3,20,34,45,65,75,85] Although observations have generally supported known gas phase chemical pathways, observational evidence^[46,65,66,80] hinting at a more complex role for chlorine illuminated gaps in the understanding of reactive gas phase chlorine sources in the atmosphere. Such observations have led to the proposal and investigation of heterogeneous mechanisms to explain the volatilisation of chloride from aerosol particles.^[24,41,42,49,54,56,72] More recently, daytime concentrations of chlorine species such as HCl and ClNO₂ on the order of 1–2 ppbv have been reported inland in regions such as Dallas–Fort Worth^[59] and Boulder, Colorado.^[46] These observations may suggest sources other than sea salt for atmospheric chlorine.

Modelling studies

As the importance of chlorine as an atmospheric oxidant has become increasingly apparent, atmospheric chemistry models have been supplemented with basic gas phase chlorine chemistry mechanisms. This section describes condensed chlorine mechanisms, and their use in regional photochemical modelling studies.

Condensed chlorine mechanism development

A critical component of regional models is a condensed photochemical mechanism that is computationally efficient while retaining enough accuracy to be used in the study of atmospheric chemical processes. The Carbon Bond mechanism^[86,87] is one of the most commonly used condensed chemical mechanisms;

reactions representing chlorine chemistry in urban atmospheres were devised and added to a modified version of the Carbon Bond mechanism by Tanaka et al.^[88] for use in the Comprehensive Air quality Model with extensions (CAMx). The mechanism included the reaction of chlorine with ozone and VOCs through condensed reactions for olefins and paraffins. Reactions with ethene, methane, 1,3-butadiene and isoprene were explicitly represented in order to account for the unique products of these reactions while enabling comparisons between observations and predictions of the concentrations of these molecular tracers. Photolysis reactions for Cl₂ and HOCl were included, and the rates of photolysis for these species were scaled to the respective photolysis rates of NO₂ and isoprene oxidation products.^[88] Since the creation of this initial mechanism, chlorine reaction sets have been implemented as adjunct mechanisms in both the Carbon Bond 05 (CB05) and the SAPRC-07 mechanisms,^[86,89] and these mechanisms have been used in both box^[90] and regional^[7,71,91–94] modelling.

Recent chlorine mechanism development has involved the addition of heterogeneous pathways, including ClNO₂ production chemistry^[91,92,94] and the OH[•]-mediated formation of gas phase Cl₂.^[24,41,42] Simon et al.^[91] implemented a surrogate gas phase reaction for investigating ClNO₂ chemistry (Reactions 28–30); Simon et al.^[92] improved upon the scheme by using a heterogeneous parameterisation.^[23,56,95] Parameter values cited from the literature were used and varied by region based on proximity to the Gulf Coast.^[92] Further work on ClNO₂ chemistry included dependencies^[55] on particle liquid water, particle nitrate and particle chloride in the parameterisation of ClNO₂ chemistry for modelling within the continental United States.^[94] A parameterised^[23,95] version of Reactions 20 and 21 was implemented to study the effect of sea salt and related chlorine emissions on coastal urban ozone in the South Coast Air Basin, California.^[24]

Regional modelling of atmospheric chlorine chemistry

Photochemical models are used to probe the effects of atmospheric chlorine chemistry on a continental to global scale. The focus in this section will be on regional models because the reduced computational intensity of these models, relative to global models, has allowed more detailed treatments of chlorine chemistry.

In Houston, Texas, the inclusion of anthropogenic chlorine emissions in regional modelling revealed a maximum localised ozone increase of 16 ppb and moderate increases over a larger spatial area. The maximum modelled O₃ increase coincided with a maximum CMBO mixing ratio of 59 ppt.^[71] Another study found that chlorine increased 1- and 8-h ozone levels during peak ozone hours by 8 and 9 ppb. This same study also found a maximum increase during morning hours, at the times of maximum rates of Cl₂ and HOCl photolysis, of 45 ppbv.^[96,97] Because some of the peak enhancements of ozone concentrations predicted in these models are highly localised near chlorine radical precursor sources, the maximum predictions of the models are very sensitive to the grid cell dimensions used in the work. Wang et al.^[96,97] used a nested grid with horizontal spatial resolutions as small as 4 km. In similar work, but with horizontal grid cell dimensions of 12–36 km, Sarwar and Bhave^[98] modelled the effect of chlorine chemistry on ozone levels over the eastern half of the United States. The study found major effects only in the Houston, Texas, and New York–New Jersey areas, where 1-h O₃ level averages increased by 12 and

Table 6. Summary of grid cell sizes used in regional photochemical modelling

Regions of focus were those of the highest resolution grid. For simplicity, the largest urban metropolitan area within the finest mesh grid is cited where appropriate. – indicates that no value was explicitly reported in this study. SOCAB, South Coast Air Basin; CMBO, 1-chloro-3-methyl-3-butene-2-one

Region	Nested	Grid size (km)	Maximum 1-h O ₃ enhancement (ppbv)	Chlorine species reported	Maximum predicted Cl species concentration (pptv)	References
SOCAB, California	No	5	12.7	Cl ₂	12	[24]
Houston, Texas	Yes	36, 12, 4	16	CMBO	59	[71]
Houston, Texas	Yes	36, 12, 4	72	CMBO	100	[7]
Houston, Texas	Yes	36, 12, 4	48	–	–	[96,97]
Eastern USA	Yes	36, 12	12	–	–	[98]
SOCAB, California	No	5	80	Cl ₂	1000	[99]
Houston, Texas	Yes	36, 12, 4	–	CINO ₂	>3200	[91]
Houston, Texas	Yes	36, 12, 4	1.5	CINO ₂	719	[92]
Continental USA	No	12	13.3 ^A	CINO ₂	4500	[94]

^A8-h average O₃ increases were reported in this study.

6 ppbv respectively and 8-h increases were 8 and 4 ppbv. Similarly, a study of a photochemical pollution episode in September 2000 in south-east Texas, using a 4-km horizontal spatial resolution, found highly localised non-peak O₃ concentration increases up to 70 ppbv, with peak hour concentration increases typically below 10 ppbv.^[7] Yet another study in Texas found a 1-h average O₃ level increase of 1.5 ppb from inclusion of CINO₂ production and photolysis.^[91]

Modelled CINO₂ concentrations in south-east Texas have ranged from 256–1210 pptv, compared to previous field measurements in the region of 1300 pptv. A limiting factor in the modelling was the modelled availability of chloride. Scenarios assuming excess particulate chloride resulted in peak ground-level CINO₂ concentration increases of up to 3200 pptv compared to a base case scenario without excess particulate chloride.^[92] More recently, modelling of CINO₂ chemistry across the continental USA revealed monthly mean 8-h O₃ increases of 1–2 ppbv (3–4%), with maximum daily 8-h maximum increases of up to 13 ppbv in the north-eastern United States. Resulting reductions in total nitrate ranged from 11 to 21%. This study used a single domain of 12-km grid cells.^[94] Regional modelling of the South Coast Air Basin (SOCAB) suggests that sea salt-derived chlorine chemistry reduces weekend ozone levels while increasing average weekday peaks, thus reducing the difference between the two.^[99] A separate study in the SOCAB^[24] included several chlorine reaction mechanisms (Reactions 10, 11, 20–22, 28–30) and found a maximum 1-h ozone enhancement of 12.7 ppbv with a corresponding peak in Cl₂ concentrations of 12 pptv. In both of these cases, 5-km grid cells were used.^[24,99] A summary of the results from the studies discussed above is shown in Table 6.

The concentrations predicted from these modelling studies correspond well with documented observations of reactive chlorine. However, in order to model chlorine radical concentrations at magnitudes that are consistent with observed concentrations, modellers must assume rates for the most likely heterogeneous mechanisms. Along with uncertainties in anthropogenic and natural source strength approximations, the values of these rate parameters in heterogeneous reactions remain a gap in the current understanding of urban atmospheric chlorine chemistry.

Critical gaps in current understanding

This section addresses two primary areas of uncertainty in the understanding of atmospheric chlorine chemistry. The first area

of uncertainty is accurate estimation of the parameters used to model heterogeneous chlorine chemistry. The parameters involved in the heterogeneous CINO₂ mechanism that was described in previous sections is included as a case study of the range of predictions that can result from application of models, employing reaction rate parameters within accepted ranges. The second area of uncertainty is the issue of the chlorine emissions sources driving the chemistry.

Sensitivity analysis of heterogeneous CINO₂ production

The parameters that must be known to model heterogeneous reactions include^[23]:

1. Particle surface area.
2. The phase(s) in or on which the reaction is taking place.
3. Chemical composition of the phases.
4. Concentrations of species involved in the reaction.
5. A reactive uptake coefficient for the gas species involved.

These physical parameters can be lumped into a single rate constant.^[23,95]

$$k = \frac{\gamma_{\text{obs}} \omega A}{4} \quad (48)$$

Here, γ_{obs} is the observed reactive uptake coefficient, ω is the average molecular velocity of the reactant and A is the surface area density of particles ($\text{cm}^2 \text{cm}^{-3}$). The reactive uptake coefficient is the number of molecules lost through the surface relative to the number of molecules hitting the surface and is a unit-less parameter.^[57] In addition to these parameters, the fractional yield of the product can be included on the right hand side of Eqn 48 when competitive reaction pathways are present within the condensed phase.

A wide variety of yield and reactive uptake values for reactions producing CINO₂ have been reported in the literature.^[30,36,46–48,51,56,80,95,100–103] The range of heterogeneous reaction rate parameters reported in the literature was used to develop a range for the values of the reactive uptake coefficient (γ) and the CINO₂ yield (Y_{CINO_2}) for the reaction of N₂O₅ with particulate chloride. Previous regional modelling studies of this mechanism used limited, and typically fixed, parameter values.^[91,92] One recent study^[94] has implemented parameterisations^[46,54,55] which account for influences from particulate species such as H₂O and NO₃[–] for continental-scale modelling

within the USA. These parameterisations are shown in Eqns 49–51, where f and r subscripts indicate directionality of the reversible reactions that are referenced.^[54,55]

$$Y_{\text{ClNO}_2} = \frac{\Delta \text{ClNO}_2}{\Delta \text{N}_2\text{O}_5} = \left(\frac{k_{33a}[\text{H}_2\text{O}]}{k_{33b}[\text{Cl}^-]} + 1 \right)^{-1} \quad (49)$$

$$\gamma_{\text{N}_2\text{O}_5} = Ak'_{32f} \left(1 - \frac{1}{\left(\frac{k_{33a}[\text{H}_2\text{O}]}{k_{32r}[\text{NO}_3]} \right) + 1 + \left(\frac{k_{33b}[\text{Cl}^-]}{k_{32r}[\text{NO}_3]} \right)} \right) \quad (50)$$

$$k'_{32f} = \beta - \beta e^{(-\delta[\text{H}_2\text{O}])} \quad (51)$$

The ratio of k_{33b}/k_{33a} has been determined by several studies to range between 450 ± 100 and 836 ± 32 .^[40,50,54,55] For the other parameters involved, A is 3.2×10^{-8} s, β is $(1.15 \pm 0.3) \times 10^5$ s⁻¹ and δ is $(1.3 \pm 0.5) \times 10^{-1}$.^[55] Although the introduction of parameterisations such as in Eqns 48–50 is an important advance over fixed parameter values, the parameterisation still assumes that heterogeneous rate parameters can be quantified with precision.

The objective of the sensitivity analysis described here is to quantify upper and lower limits to the effect of this mechanism with respect to O₃ formation chemistry. Effects of varying VOC concentrations and composition as well as NO_x availability were tested. Changes in peak O₃ and ClNO₂ concentrations between simulations were quantified and compared to a base case scenario lacking heterogeneous chemistry. Methods used in the sensitivity analyses are summarised in the Supplementary material.

Using well established parameter ranges, the heterogeneous reaction of N₂O₅ with aerosol chloride is able to reproduce ClNO₂ concentrations at levels that have been observed. Depending on the combination of heterogeneous parameters, VOCs and NO_x, the mechanism contributed to both peak ozone reduction as well as peak ozone increases. The range of effect was a -10.5 to 27% change in peak O₃ concentrations relative to a base case scenario with no heterogeneous reactions. The decreases in ozone typically resulted from low values of ClNO₂ yield (0–15%, depending on the amount and types of VOCs present). Relative decreases in O₃ occurred in simulations including the heterogeneous chemistry due to the fact that the mechanism served as a NO_x sink, particularly in cases with low ClNO₂ yields. This NO_x sink was not present in the simulations without heterogeneous chemistry. Combinations of yields above 25% and reactive uptake coefficients greater than zero resulted in increases in peak ozone levels.

The effect of changing base VOC concentrations was also examined. Four scenarios with differing initial VOC concentrations were used: (1) 0 ppb C VOCs; (2) 300 ppb C VOCs; (3) 1000 ppb C VOCs and (4) 300 ppb C *t*-2-butene. The reason for isolating the effects of *t*-2-butene within a single scenario is that it rapidly reacts with NO₃[•], thus producing HNO₃ instead of N₂O₅ through the reaction of NO₃[•] with NO₂. For all values of γ examined, the effect of increasing the value of the yield parameter from 0 to 100% at a fixed γ was a linear increase in peak ozone concentrations. These results are summarised in the Supplementary material. Increasing the reactive uptake at a fixed yield value resulted in an intensification of the effect on peak ozone concentrations elicited by the value of the yield parameter. These, and additional, results are also shown in the Supplementary material.

The range of the effect that heterogeneous ClNO₂ production has on peak ozone levels in the scenarios described above reflects the potential significance of this chemistry to ozone formation. However, the broad range of reported parameter values and the potential for both increases and decreases in ozone production from this mechanism highlight the importance of accurate parameter estimation. Maximum changes in peak O₃ concentrations ranged from -10.5 to 27%. ClNO₂ formation by this mechanism resulted in concentrations up to 4.0 ppb at the highest combination of parameter values, with peak concentrations of 1.0–2.0 ppb being typical of more moderate parameter value combinations (e.g. 20–50% yield and a reactive uptake of 0.03). It should be noted that this analysis excluded the consideration of effects from meteorology, mass transport and dilution. However, it serves in identifying an upper boundary of effects for the chemistry alone.

Uncertainty in emissions estimates

Traditionally, sources of molecular chlorine, and other inorganic sources of chlorine radicals, have not been included in photochemical modelling. Studies covered in the section on regional modelling^[7,71,91,92,94,96–99] highlighted the effects of including chlorine emissions into the modelling of photochemical episodes. Inventories have been developed for both anthropogenic^[104,105] and natural^[1,32,106–108] sources. However, uncertainties exist within these inventories. Uncertainty in inventory development can stem from uncertainty in observations used to deduce source strengths and the methods or assumptions associated with extrapolating these measurements to larger scales.^[1] Assumptions in emissions factors as well as approximations in their implementation into models are two additional sources of uncertainty.^[106] In general, any uncertainty in the understanding of the biogeochemical processes involved in the natural chlorine cycle can lead to a corresponding uncertainty within inventories.^[107]

Chang et al.^[104] developed a comprehensive inventory for Houston, Texas, that evaluated industrial point sources, cooling tower use, water and wastewater treatment, swimming pool chlorination, tap water use, sea salt chloride and chlorinated organics as potential chlorine radical precursor sources in the region. The authors cite particularly high uncertainty in the emission rates of chlorinated organics and sea salt aerosols. Uncertainty in the form of volatile reactive chlorine species (HOCl and Cl₂) produced by anthropogenic sources such as cooling tower operation has also been noted.^[104] The contribution of inorganic chlorine from biomass burning, and particularly the anthropogenic contribution by this mechanism, is inherently uncertain due to the problem of accurately estimating the natural rate of fires in a scenario in which humans are not present. One study noted that although biomass burning could potentially contribute up to 25% of total HCl emissions, the source strength is highly uncertain and not likely to be a significant source of particulate chloride globally.^[106] Sinks and removal processes for chlorine species can also be a source of uncertainty.^[107] Emissions estimates from coal combustion also suffer from uncertainty in the amount of chloride present in the coal.^[105]

Summary

Most of the studies cited in this review have presumed that sea salt is the dominant source of atmospheric chlorine, however, markers

of chlorine chemistry such as HCl and ClNO₂, observed at inland locations such as Dallas–Fort Worth,^[59] may suggest sources other than sea salt for atmospheric chlorine. An important step in improving the understanding of chlorine's role in urban atmospheres would be to more accurately model the processes underlying emissions of the various chlorine radical precursors that have been observed. Improved emission inventories could be coupled with the increasing knowledge of heterogeneous processes in order to produce more meaningful computational predictions of the effect that chlorine species have in urban environments. As seen from the evidence related to enhanced ozone production from the presence of chlorine, this would prove extremely useful to researchers addressing issues in urban air quality.

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