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LETTERS

A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry

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Halogen atoms and oxides are highly reactive and can profoundly affect atmospheric composition. Chlorine atoms can decrease the lifetimes of gaseous elemental mercury[1] and hydrocarbons such as the greenhouse gas methane[2]. Chlorine atoms also influence cycles that catalytically destroy or produce tropospheric ozone[3], a greenhouse gas potentially toxic to plant and animal life. Conversion of inorganic chloride into gaseous chlorine atom precursors within the troposphere is generally considered a coastal or marine air phenomenon[4]. Here we report mid-continental observations of the chlorine atom precursor nitryl chloride at a distance of 1,400 km from the nearest coastline. We observe persistent and significant nitryl chloride production relative to the consumption of its nitrogen oxide precursors. Comparison of these findings to model predictions based on aerosol and precipitation composition data from long-term monitoring networks suggests nitryl chloride production in the contiguous USA alone is at a level similar to previous global estimates for coastal and marine regions[5]. We also suggest that a significant fraction of tropospheric chlorine atoms[6] may arise directly from anthropogenic pollutants.

Night-time reactions of nitrogen oxides are known to convert inorganic chloride into chlorine atom ($Cl^{\bullet}$) precursors[7] (for example, Fig. 1). N_2O_5, a nocturnal NO_x reservoir ($NO_x = NO + NO_2$), can react on airborne particles to produce only HNO_3 (reaction (1a)), or both nitryl chloride ($ClNO_2$) and nitrate (NO_3^-) (reaction (1b)).

$$N_2O_{5(g)} + H_2O_{(aq)} \rightarrow 2HNO_{3(aq)} \qquad (1a)$$

$$N_2O_{5(g)} + Cl^-{}_{(aq)} \rightarrow ClNO_{2(g)} + NO_3^-{}_{(aq)} \qquad (1b)$$

The $ClNO_2$ yield depends on water and chloride concentrations within particles[8]. The latter is often sufficient for efficient $ClNO_2$ production[5]. However, the moles of particulate chloride per volume of air (pCl^-) is typically small, and would limit reaction (1b) except that gaseous HCl can almost always provide a larger reservoir through equilibrium repartitioning to particles[9]. Depending on the environment, soluble chloride or NO_x availability and reactivity may limit $ClNO_2$ production. The few prior observations of $ClNO_2$ within polluted marine air have shown it is produced in high yields during spring and summer, and exceeds previously predicted values by factors of 2–30 (refs 5, 10, 11).

$ClNO_2$ production has an impact on NO_x and Cl budgets, both of which affect the troposphere's oxidizing capacity[12]. Current atmospheric chemistry models predict reaction (1a) accounts for 30–50% of total NO_x removal in polluted regions[13], but they typically neglect reaction (1b). Owing to efficient deposition of HNO_3, reaction (1a) represents a terminal NO_x sink in the lower troposphere, whereas reaction (1b) recycles NO_x through $ClNO_2$ photolysis (reaction (2)) within a few hours after sunrise[14].

$$ClNO_2 + h\nu \rightarrow Cl^{\bullet} + NO_2 \qquad (2)$$

Models incorporating reactions (1b) and (2) differ in their predicted impacts, but generally show summer ozone concentrations in coastal urban areas to be enhanced by faster cycling of oxidants produced from $Cl^{\bullet}$ attacking hydrocarbons[3,5].

These previous studies have been restricted to coastal or marine regions. However, our observations made near Boulder, Colorado, an urban location in the middle of North America, demonstrate that this chemistry extends well inland, and are consistent with calculations based on network observations of aerosol and precipitation composition.

We made *in situ* measurements on 11–25 February 2009 at the National Oceanic and Atmospheric Administration's Kohler Mesa facility, just west and 150 m above Boulder, Colorado. The site, subject to large variability in pollutant levels, receives either the urban plume from nearby cities, or much cleaner air from the Rocky Mountain

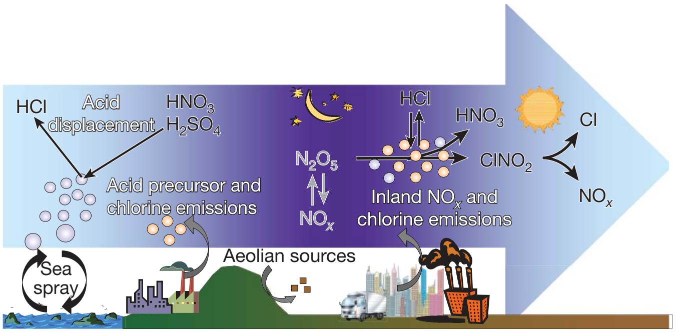

Figure 1 | Schematic of chlorine activation by night-time NO_x chemistry. The emphasis here is on inland $ClNO_2$ production, although production also occurs in coastal and marine regions. Globally, sea spray is the dominant source of tropospheric inorganic chloride[9], which can be transported as fine-mode sea spray particles or gaseous HCl following acid displacement by HNO_3 or H_2SO_4. Locally, other sources of chloride from industrial activities[9], biomass burning[9], or transport of wind-blown soil dust[15] may be important. Reactions of N_2O_5 on chloride-containing particles produce $ClNO_2$, which photochemically converts to chlorine atoms and NO_2 in the morning. The chlorine atoms react with hydrocarbons, returning to HCl or forming an organo-chlorine compound.

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region. Typically residing above the urban nocturnal boundary layer, the site is often minimally affected by direct, local night-time emissions. It therefore allows overnight observation of the chemical evolution of air masses characteristic of this region. More information on the site and measurement methods is provided in Supplementary Information.

There are three salient features of the February 2009 time series (Fig. 2). First, $ClNO_2$ production was routinely observed in a region of North America far removed from sea spray, but possibly affected by chloride transport from coastal areas[9] or inland salt beds[15], and by anthropogenic sources including combustion and transportation[9]. Second, $ClNO_2$ mixing ratios consistently reached 100–450 parts per trillion by volume (p.p.t.v.) whenever the urban plume was sampled. These levels are unexpectedly large, reaching a third to a half of the maximum values observed in polluted coastal areas[5,10]. Third, consistent with the above mechanism, $ClNO_2$ was observed only at night or in the early morning, and often correlated with N_2O_5 (Fig. 2, top). However, their relationship was variable, probably due to changes in: (1) the N_2O_5 heterogeneous loss rate, which depends on humidity, particle composition and phase[16], and surface area density (S_a); (2) air mass age and non-aerosol losses of N_2O_5 (Supplementary Information); and (3) chloride availability. We observed similar levels of N_2O_5 and $ClNO_2$ in February 2008 at a nearby location, suggesting year-to-year consistency (Supplementary Information).

As expected, the 2009 observations also indicate total available chloride for $ClNO_2$ production is greater than pCl^- alone[5] (Fig. 3a). The inferred minimum abundance of total available chloride (100–500 p.p.t.v.) is consistent with admittedly uncertain HCl observations in other urban areas[9], and with the $pCl^- \leftrightarrow HCl_g$ equilibrium predicted using thermodynamic models constrained by our measurements[17] (Supplementary Information).

We performed time-dependent chemical box modelling to develop a quantitative relationship between measured pCl^- and the $ClNO_2$ yield from reaction (1) (ϕ_{ClNO_2}) needed to explain the observations. The box model integrates explicit N_2O_5, $ClNO_2$ and pCl^- mass balance equations initialized with observations of NO_2, O_3, S_a, pCl^-. The N_2O_5 reaction probability and ϕ_{ClNO_2} are adjusted between 0.005–0.03 and 0.07–0.36, respectively, so the model matches the observed NO_2, O_3, N_2O_5 and $ClNO_2$ at a specific time. Model details and additional output are given in Supplementary Information.

The night of 15–16 February illustrates the time evolution of $ClNO_2$ under low wind, providing a model-to-measurement comparison least affected by air mass variations due to transport. A constant model ϕ_{ClNO_2} of 0.14 adequately reproduces the observed $ClNO_2$ and pCl^- evolution (Fig. 3b), as well as NO_2, O_3 and N_2O_5 at specific times after sunset. These species are more sensitive to fresh emissions or land-surface interactions caused by slight changes in transport, and therefore exhibit larger deviations from the model curve (Supplementary Information). This night did not show evidence of a chloride limitation, and had the highest 24-h average pCl^- and $ClNO_2$ of the campaign. Most other nights did not allow comparison to the box model with a single set of initial conditions mainly because of transport effects (Supplementary Information).

The box-model-derived ϕ_{ClNO_2} are generally lower than calculated from laboratory parameterizations[8,18] using measured pCl^- and estimated particle water[17] (Supplementary Information). Several possible reasons for the apparent discrepancy exist. First, although sufficient total chloride mass may exist, it probably partitions to a fraction of the particle surface area[19], reducing the population average efficiency of reaction (1b) which our model-derived ϕ_{ClNO_2} values represent. A more accurate calculation would require size-resolved particle composition and pH measurements, which are challenging[20]. Additionally, the ϕ_{ClNO_2} required in the model is different for different nights, and even decreases within some nights, suggesting significant variability in the factors controlling $ClNO_2$ production as well as a possible limitation by available chloride.

The existence of a mid-continental $ClNO_2$ source was unknown before the observations we report here. Yet, the ingredients for this source, NO_x and particulate chloride, are known from various

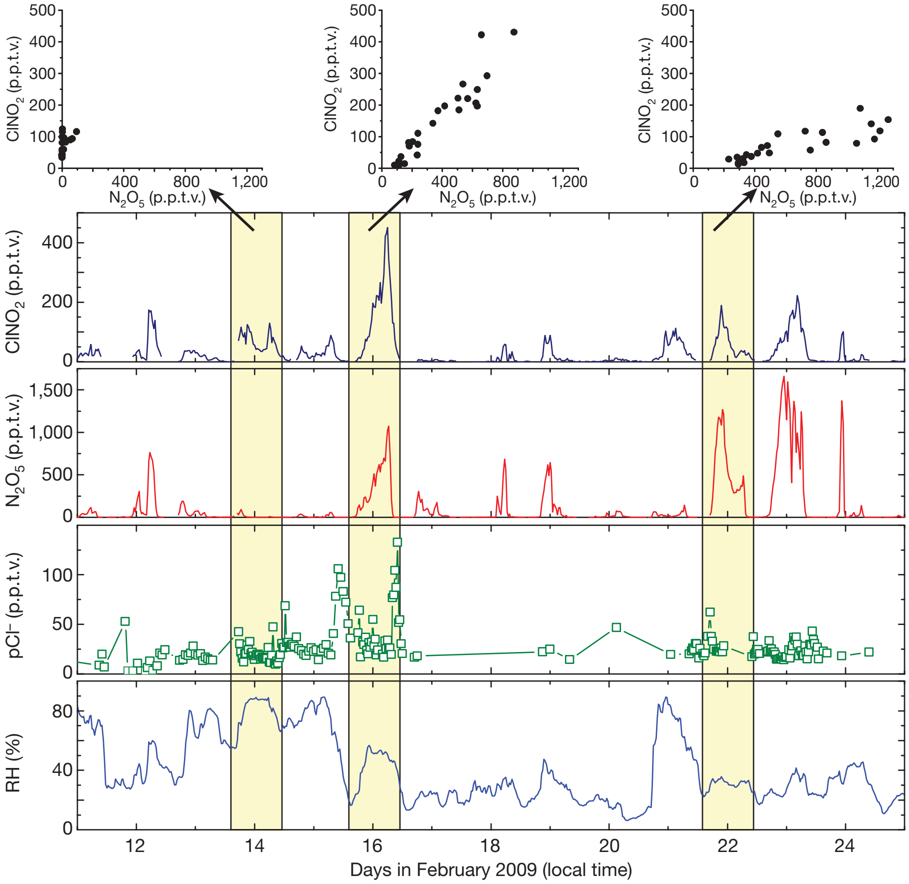

Figure 2 | Time series of key quantities observed in Boulder, Colorado, from 11 to 25 February 2009. Main panels: from top to bottom, $ClNO_2$, N_2O_5, pCl^- shown in mixing ratio units (p.p.t.v.) for comparison with gases, and relative humidity (RH). Insets (top) are point-to-point comparisons of $ClNO_2$ to N_2O_5 on 13–14 February (left), 15–16 February (centre) and 21–22 February (right). These nights are characterized by high (85%), moderate (50%) and low (35%) RH; and high, moderate and low ratios of $ClNO_2$:N_2O_5, respectively. The $ClNO_2$:N_2O_5 ratio is not solely a function of RH. For example, on 14 February we sampled air from the urban surface layer containing fresh NO_x emissions which can titrate N_2O_5. See Supplementary Information for additional details.

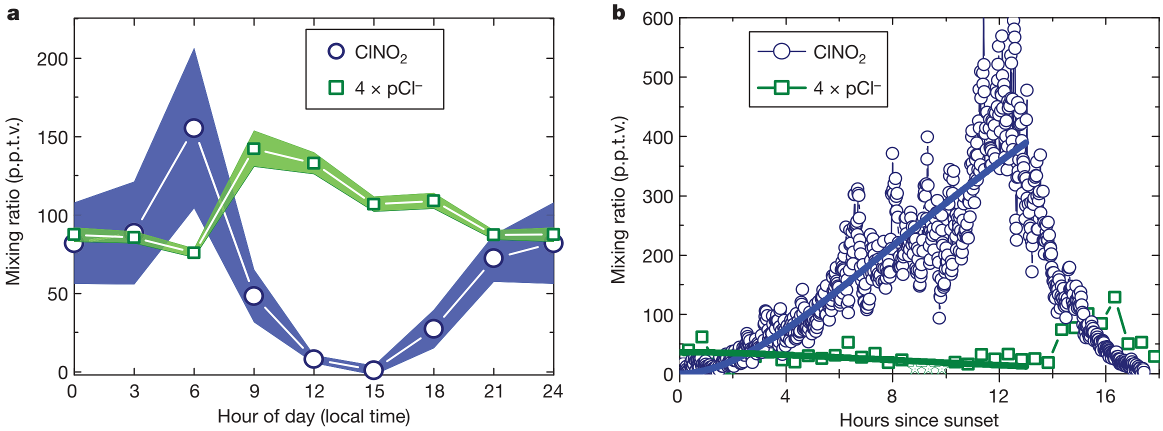

Figure 3 | Observed and modelled relationships of ClNO$_2$ and particulate chloride. **a**, 3-h averages of coincident ClNO$_2$ and 4 × pCl$^-$ versus time of day. Shading indicates the standard error of means; each bin contains more than 15 points. **b**, Observed and modelled evolution of ClNO$_2$ and pCl$^-$ over the 12-h period from sunset on 15 February. Symbols as in **a**, stars denote pCl$^-$ below the detection threshold, and solid lines represent model predictions. The model reasonably reproduces the night-time evolution of ClNO$_2$ with a constant ClNO$_2$ yield of 0.14, and matches the ozone, NO$_2$ and N$_2$O$_5$ observations 12 h after sunset. See Supplementary Information for a more complete description of the model.

long-term databases to be ubiquitous across the North American continent (and elsewhere). With these data sets, we now estimate the magnitude of this halogen source across wider scales and compare these estimates to multi-location observations of ClNO$_2$.

Assuming lower tropospheric NO$_x$ is in steady-state, we calculate a total annual ClNO$_2$ production rate as a sum over seasonal averages (s) via the following equation:

$$P_{\mathrm{ClNO_2}} = \sum_s P^s_{\mathrm{ClNO_2}} = \sum_s \sum_r E^s_{\mathrm{NO}_x}(r) f^s_{\mathrm{N_2O_5}}(r) \phi^s_{\mathrm{ClNO_2}}(r) \qquad (3)$$

where r denotes a 1 × 1° grid cell in the contiguous US or its coastal regions, $E^s_{\mathrm{NO}_x}(r)$ is the anthropogenic NO$_x$ emission rate from the EDGAR database[21], $f^s_{\mathrm{N_2O_5}}(r)$ is the fraction of NO$_x$ removed by N$_2$O$_5$ heterogeneous chemistry predicted by the GEOS-Chem global model[13] and $\phi^s_{\mathrm{ClNO_2}}(r)$ is the ClNO$_2$ yield. We constrained $\phi^s_{\mathrm{ClNO_2}}(r)$ with a combination of precipitation and aerosol composition measurements from the National Atmospheric Deposition Program (NADP)[22] and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network[23], respectively. This approach provides $\phi_{\mathrm{ClNO_2}}$ consistent with all existing ClNO$_2$ observations in Boulder and coastal regions[5,10], while reproducing the likely spatial distribution in total available chloride.

Figure 4 shows the annual average fields of E_{NO_x} (Fig. 4a), $f_{\mathrm{N_2O_5}}$ (Fig. 4b), $\phi_{\mathrm{ClNO_2}}$ (Fig. 4c), and the resulting $P_{\mathrm{ClNO_2}}$ (Fig. 4d). Based on the seasonal values of these components, the variability in the Boulder and network data, and alternative approaches to equation (3), all of which are presented in the Supplementary Information, we estimate that $P_{\mathrm{ClNO_2}}$ for the contiguous US lies in the range 3.2–8.2 Tg yr^{-1}, providing a photolytic Cl$^\bullet$ source of 1.4–3.6 Tg Cl yr^{-1}. This US ClNO$_2$ source is far larger than the first global estimate of

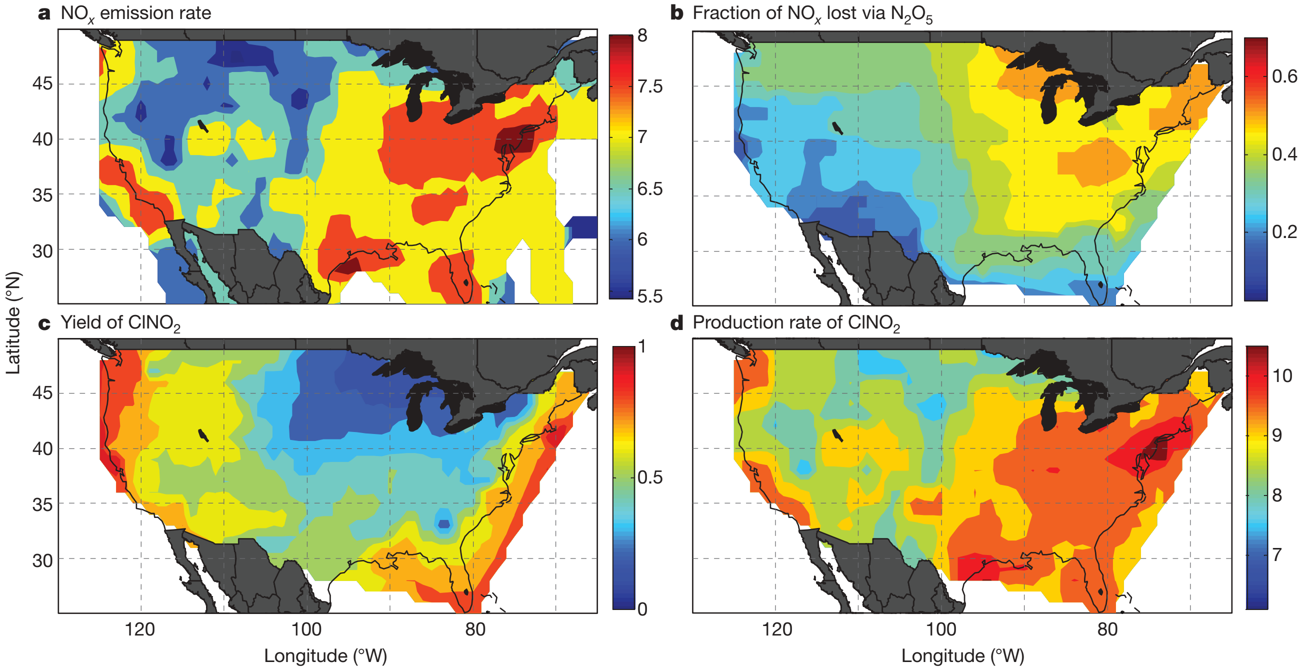

Figure 4 | Annual average components of $P_{\mathrm{ClNO_2}}$ over the US. **a**, US NO$_x$ emissions (kg yr^{-1}) given by the EDGAR database with a logarithmic colour scale starting at $10^{5.5}$ kg NO$_2$ yr^{-1}; **b**, annual average fraction of total nitrate (0–2 km) formed by N$_2$O$_5$ reactions on particles predicted by the GEOS-Chem global model; **c**, annual average yield of ClNO$_2$ calculated from IMPROVE and NADP network observations; and **d**, the ClNO$_2$ production rate, $P_{\mathrm{ClNO_2}}$, in g Cl yr^{-1}, obtained from the product of quantities shown in panels **a**, **b** and **c** with a logarithmic colour scale starting at $10^{6.5}$ g Cl yr^{-1}. Boulder, Colorado, is at approximately 40° N, 105° W.

$0.06\,\mathrm{Tg\,Cl\,yr^{-1}}$ (ref. 24), and is similar to the recent $3.2\,\mathrm{Tg\,Cl\,yr^{-1}}$ estimated for global coastal and marine regions[5]. More than half of the predicted $ClNO_2$ production occurs over land, and 40% occurs during winter (December–February). It also suggests that, in the US, an amount of NO_x equivalent to 8–22% of that emitted cycles through $ClNO_2$, potentially forming a non-negligible fraction of reactive nitrogen at night's end, primarily during winter above the nocturnal surface layer (see Supplementary Information).

If the global distribution of pCl^- and NO_x sources are similar to those in the US, as independent measurements suggest[25], we estimate the global $Cl^\bullet$ source from $ClNO_2$ to be $8\text{–}22\,\mathrm{Tg\,Cl^\bullet\,yr^{-1}}$, which is of the same order as that inferred from methane isotopes in remote regions ($25\text{–}35\,\mathrm{Tg\,Cl^\bullet\,yr^{-1}}$)[2,6]. $ClNO_2$ production will mostly occur in polluted regions; as such, $Cl^\bullet$ from $ClNO_2$ will react with other hydrocarbons as well as methane. Thus, the $Cl^\bullet$ source from $ClNO_2$ may be in addition to that inferred from methane isotopes[2,6]. Some fraction of the $Cl^\bullet$ from $ClNO_2$ may also convert to temporary reservoirs, such as HOCl and $ClONO_2$, possibly enhancing $Cl^\bullet$ production not captured by our estimates[11].

Although likely to be the most rigorous observationally constrained estimate of continental-scale $ClNO_2$ production to date, the accuracy of the above approach (and probably any other) is limited by significant uncertainty in $f_{N_2O_5}$ and ϕ_{ClNO_2} that arise from an incomplete understanding of N_2O_5 reactivity[26,27] and of chloride partitioning across the particle distribution[19]. More studies of the NO_x–$ClNO_2$–pCl^-–HCl system around the globe are critical to refine these predictions.

Our results imply that a significant fraction of the tropospheric $Cl^\bullet$ source is anthropogenic, distributed over a relatively small area of the Earth's surface—polluted continental and coastal regions—and concentrated in a fraction of each day (morning). Long-range transport of NO_x reservoirs, such as peroxy nitrates[28], or NO_x emissions from irradiated snow packs[29], may also affect halogen activation far from anthropogenic emissions, albeit on a smaller concentration scale. Therefore, past and future trends in continental NO_x emissions may represent an important global influence on tropospheric halogen sources that has largely gone unrecognized.

NO_x influences climate by directly and indirectly regulating oxidant budgets that determine the methane lifetime and affect aerosol formation[30]. Nocturnal processing of NO_x is typically considered a reduction in the troposphere's oxidizing capacity due to the conversion of NO_x and ozone into soluble, largely non-reactive species (for example, HNO_3). Widespread $ClNO_2$ production instead renders nocturnal NO_x chemistry a potential source of oxidants and ozone in polluted regions, and may have as yet unrecognized influences in remote regions. Thus, anthropogenic NO_x may have an even larger effect on the oxidizing power of the lower troposphere than current models estimate.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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