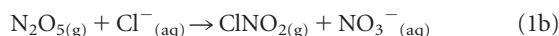


A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry

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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 mercury¹ and hydrocarbons such as the greenhouse gas methane². Chlorine atoms also influence cycles that catalytically destroy or produce tropospheric ozone³, 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 phenomenon⁴. 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 regions⁵. We also suggest that a significant fraction of tropospheric chlorine atoms⁶ may arise directly from anthropogenic pollutants.

Night-time reactions of nitrogen oxides are known to convert inorganic chloride into chlorine atom (Cl[•]) precursors⁷ (for example, Fig. 1). N₂O₅, a nocturnal NO_x reservoir (NO_x = NO + NO₂), can react on airborne particles to produce only HNO₃ (reaction (1a)), or both nitryl chloride (ClNO₂) and nitrate (NO₃⁻) (reaction (1b)).



The ClNO₂ yield depends on water and chloride concentrations within particles⁸. The latter is often sufficient for efficient ClNO₂ production⁵. 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 particles⁹. Depending on the environment, soluble chloride or NO_x availability and reactivity may limit ClNO₂ production. The few prior observations of ClNO₂ 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).

ClNO₂ production has an impact on NO_x and Cl budgets, both of which affect the troposphere's oxidizing capacity¹². Current atmospheric chemistry models predict reaction (1a) accounts for 30–50% of total NO_x removal in polluted regions¹³, but they typically neglect

reaction (1b). Owing to efficient deposition of HNO₃, reaction (1a) represents a terminal NO_x sink in the lower troposphere, whereas reaction (1b) recycles NO_x through ClNO₂ photolysis (reaction (2)) within a few hours after sunrise¹⁴.



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[•] 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

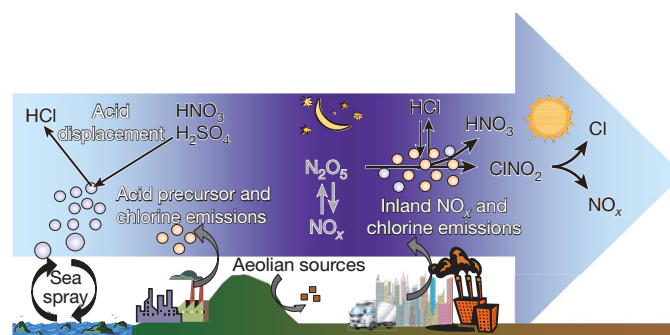


Figure 1 | Schematic of chlorine activation by night-time NO_x chemistry. The emphasis here is on inland ClNO₂ production, although production also occurs in coastal and marine regions. Globally, sea spray is the dominant source of tropospheric inorganic chloride⁹, which can be transported as fine-mode sea spray particles or gaseous HCl following acid displacement by HNO₃ or H₂SO₄. Locally, other sources of chloride from industrial activities⁹, biomass burning⁹, or transport of wind-blown soil dust¹⁵ may be important. Reactions of N₂O₅ on chloride-containing particles produce ClNO₂, which photochemically converts to chlorine atoms and NO₂ 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 areas⁹ or inland salt beds¹⁵, and by anthropogenic sources including combustion and transportation⁹. 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 phase¹⁶, 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^- alone⁵ (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 areas⁹, and with the $\text{pCl}^- \leftrightarrow \text{HCl}_g$ equilibrium predicted using thermodynamic models constrained by our measurements¹⁷ (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 water¹⁷ (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 area¹⁹, 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 challenging²⁰. 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

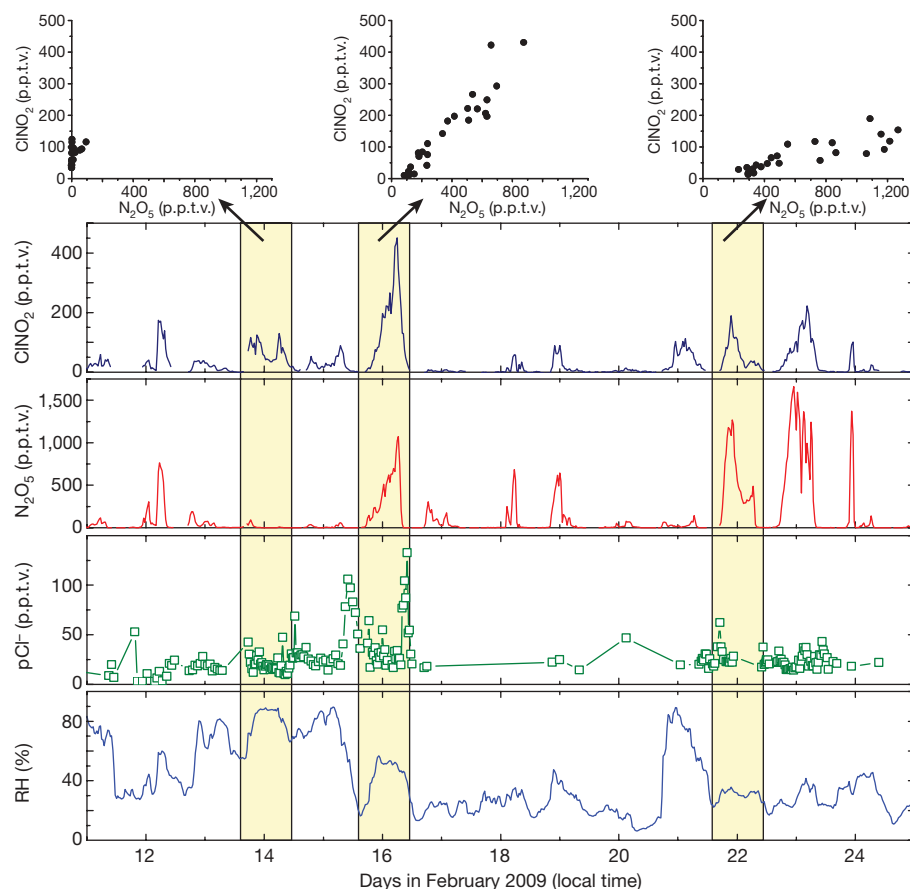


Figure 2 | Time series of key quantities observed in Boulder, Colorado, from 11 to 25 February 2009. Main panels: from top to bottom, ClNO_2 , N_2O_5 , pCl^- shown in mixing ratio units (p.p.t.v.) for comparison with gases, and relative humidity (RH). Insets (top) are point-to-point comparisons of ClNO_2 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.

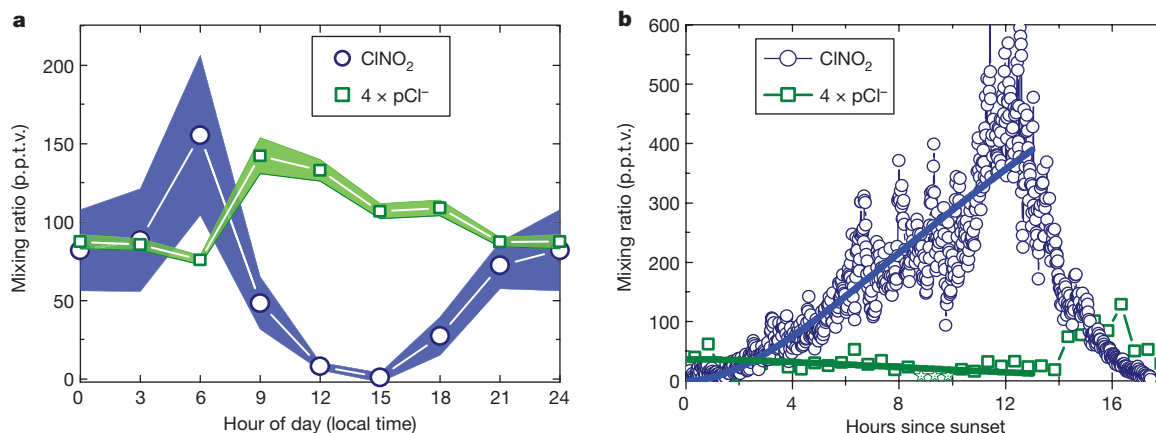


Figure 3 | Observed and modelled relationships of ClONO₂ and particulate chloride. **a**, 3-h averages of coincident ClONO₂ and 4 × pCl⁻ versus time of day. Shading indicates the standard error of means; each bin contains more than 15 points. **b**, Observed and modelled evolution of ClONO₂ and pCl⁻ over the 12-h period from sunset on 15 February. Symbols as in **a**, stars denote

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 ClONO₂.

Assuming lower tropospheric NO_x is in steady-state, we calculate a total annual ClONO₂ production rate as a sum over seasonal averages (*s*) via the following equation:

$$P_{\text{ClONO}_2} = \sum_s P_{\text{ClONO}_2}^s = \sum_s \sum_r E_{\text{NO}_x}^s(r) f_{\text{N}_2\text{O}_5}^s(r) \phi_{\text{ClONO}_2}^s(r) \quad (3)$$

where *r* denotes a 1 × 1° grid cell in the contiguous US or its coastal regions, $E_{\text{NO}_x}^s(r)$ is the anthropogenic NO_x emission rate from the EDGAR database²¹, $f_{\text{N}_2\text{O}_5}^s(r)$ is the fraction of NO_x removed by N₂O₅ heterogeneous chemistry predicted by the GEOS-Chem global model¹³ and $\phi_{\text{ClONO}_2}^s(r)$ is the ClONO₂ yield. We constrained

pCl⁻ below the detection threshold, and solid lines represent model predictions. The model reasonably reproduces the night-time evolution of ClONO₂ with a constant ClONO₂ yield of 0.14, and matches the ozone, NO₂ and N₂O₅ observations 12 h after sunset. See Supplementary Information for a more complete description of the model.

$\phi_{\text{ClONO}_2}^s(r)$ 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) network²³, respectively. This approach provides ϕ_{ClONO_2} consistent with all existing ClONO₂ 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), $f_{\text{N}_2\text{O}_5}$ (Fig. 4b), ϕ_{ClONO_2} (Fig. 4c), and the resulting P_{ClONO_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_{ClONO_2} for the contiguous US lies in the range 3.2–8.2 Tg yr⁻¹, providing a photolytic Cl* source of 1.4–3.6 Tg Cl yr⁻¹. This US ClONO₂ source is far larger than the first global estimate of

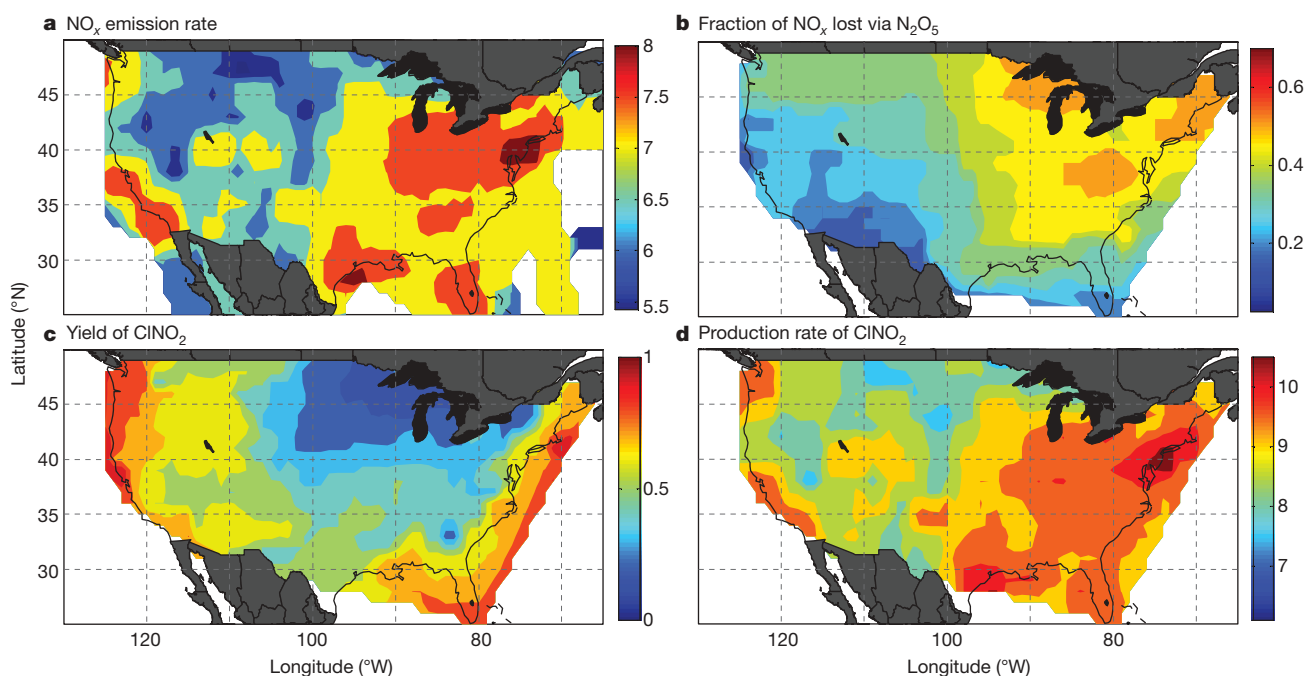


Figure 4 | Annual average components of P_{ClONO_2} over the US. **a**, US NO_x emissions (kg yr⁻¹) given by the EDGAR database with a logarithmic colour scale starting at 10^{5.5} kg NO_x yr⁻¹; **b**, annual average fraction of total nitrate (0–2 km) formed by N₂O₅ reactions on particles predicted by the GEOS-Chem global model; **c**, annual average yield of ClONO₂ calculated from

IMPROVE and NADP network observations; and **d**, the ClONO₂ production rate, P_{ClONO_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 Tg Cl yr⁻¹ (ref. 24), and is similar to the recent 3.2 Tg Cl yr⁻¹ estimated for global coastal and marine regions⁵. More than half of the predicted ClNO₂ 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 ClNO₂, 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 suggest²⁵, we estimate the global Cl^{*} source from ClNO₂ to be 8–22 Tg Cl^{*} yr⁻¹, which is of the same order as that inferred from methane isotopes in remote regions (25–35 Tg Cl^{*} yr⁻¹)^{2,6}. ClNO₂ production will mostly occur in polluted regions; as such, Cl^{*} from ClNO₂ will react with other hydrocarbons as well as methane. Thus, the Cl^{*} source from ClNO₂ may be in addition to that inferred from methane isotopes^{2,6}. Some fraction of the Cl^{*} from ClNO₂ may also convert to temporary reservoirs, such as HOCl and ClONO₂, possibly enhancing Cl^{*} production not captured by our estimates¹¹.

Although likely to be the most rigorous observationally constrained estimate of continental-scale ClNO₂ production to date, the accuracy of the above approach (and probably any other) is limited by significant uncertainty in $f_{\text{N}_2\text{O}_5}$ and ϕ_{ClNO_2} that arise from an incomplete understanding of N₂O₅ reactivity^{26,27} and of chloride partitioning across the particle distribution¹⁹. More studies of the NO_x–ClNO₂–pCl⁻–HCl system around the globe are critical to refine these predictions.

Our results imply that a significant fraction of the tropospheric Cl^{*} 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 nitrates²⁸, or NO_x emissions from irradiated snow packs²⁹, 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 formation³⁰. 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, HNO₃). Widespread ClNO₂ 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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- Donohoue, D. L., Bauer, D. & Hynes, A. J. Temperature and pressure dependent rate coefficients for the reaction of Hg with Cl and the reaction of Cl with Cl: a pulsed laser photolysis-pulsed laser induced fluorescence study. *J. Phys. Chem. A* **109**, 7732–7741 (2005).
- Platt, U., Allan, W. & Lowe, D. Hemispheric average Cl atom concentration from ¹³C/¹²C ratios in atmospheric methane. *Atmos. Chem. Phys.* **4**, 2393–2399 (2004).
- Knipping, E. M. & Dabdub, D. Impact of chlorine emissions from sea-salt aerosol on coastal urban ozone. *Environ. Sci. Technol.* **37**, 275–284 (2003).
- Von Glasow, R. & Crutzen, P. J. in *The Atmosphere* (ed. Keeling, R. F.) 21–64 (Oxford Univ. Press, 2007).
- Osthoff, H. D. et al. High levels of nitryl chloride in the polluted subtropical marine boundary layer. *Nature Geosci.* **1**, 324–328 (2008).
- Allan, W., Struthers, H. & Lowe, D. C. Methane carbon isotope effects caused by atomic chlorine in the marine boundary layer: global model results compared with Southern Hemisphere measurements. *J. Geophys. Res.* **D 112**, D04306, doi:10.1029/2006JD007369 (2007).
- Finlayson-Pitts, B. J., Ezell, M. J. & Pitts, J. N. Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N₂O₅ and ClONO₂. *Nature* **337**, 241–244 (1989).

- Behnke, W., George, C., Scheer, V. & Zetzsch, C. Production and decay of ClNO₂ from the reaction of gaseous N₂O₅ with NaCl solution: bulk and aerosol experiments. *J. Geophys. Res.* **D 102**, 3795–3804 (1997).
- Graedel, T. E. & Keene, W. C. Tropospheric budget of reactive chlorine. *Glob. Biogeochem. Cycles* **9**, 47–77 (1995).
- Kercher, J., Riedel, T. & Thornton, J. Chlorine activation by N₂O₅: simultaneous, *in situ* detection of ClNO₂ and N₂O₅ by chemical ionization mass spectrometry. *Atmos. Meas. Techn.* **2**, 193–204 (2009).
- Pechtl, S. & von Glasow, R. Reactive chlorine in the marine boundary layer in the outflow of polluted continental air: a model study. *Geophys. Res. Lett.* **34**, L11813, doi:10.1029/2007GL02976 (2007).
- Logan, J. A., Prather, M. J., Wofsy, S. C. & McElroy, M. B. Tropospheric chemistry: a global perspective. *J. Geophys. Res.* **86**, 7210–7254 (1981).
- Alexander, B. et al. Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition (Δ¹⁷O) of atmospheric nitrate. *Atmos. Chem. Phys.* **9**, 5043–5056 (2009).
- Nelson, H. H. & Johnston, H. S. Kinetics of the reaction of Cl with ClNO and ClNO₂ and the photochemistry of ClNO₂. *J. Phys. Chem.* **85**, 3891–3896 (1981).
- Abuduwailli, J., Gabchenko, M. V. & Xu, J. R. Eolian transport of salts — a case study in the area of Lake Ebinur (Xinjiang, Northwest China). *J. Arid Environ.* **72**, 1843–1852 (2008).
- Thornton, J. A., Braban, C. F. & Abbatt, J. P. D. N₂O₅ hydrolysis on sub-micron organic aerosols: the effect of relative humidity, particle phase, and particle size. *Phys. Chem. Chem. Phys.* **5**, 4593–4603 (2003).
- Wexler, A. S. & Clegg, S. L. Atmospheric aerosol models for systems including the ions H⁺, NH₄⁺, Na⁺, SO₄²⁻, NO₃⁻, Cl⁻, Br⁻, and H₂O. *J. Geophys. Res.* **D 107**, 4207, doi:10.1029/2001JD000451 (2002).
- Roberts, J. M., Osthoff, H. D., Brown, S. S. & Ravishankara, A. R. Laboratory measurements of ClNO₂ yields from N₂O₅ reactions as a function of chloride molarity in various inorganic salt solutions. *Geophys. Res. Lett.* **36**, L20808, doi:10.1029/2009GL040448 (2009).
- Moffet, R. C., de Foy, B., Molina, L. T., Molina, M. J. & Prather, K. A. Measurement of ambient aerosols in northern Mexico City by single particle mass spectrometry. *Atmos. Chem. Phys.* **8**, 4499–4516 (2008).
- Keene, W. C. & Savoie, D. L. The pH of deliquesced sea-salt aerosol in polluted marine air. *Geophys. Res. Lett.* **25**, 2181–2184 (1998).
- Olivier, J. G. J. & Berdowski, J. J. M. in *The Climate System* (eds Berdowski, J., Guicherit, R. & Heij, B. J.) 33–78 (Balkema, and Swets and Zeitlinger, Lisse, The Netherlands, 2001).
- National Atmospheric Deposition Program Office. *National Atmospheric Deposition Program (NRSP-3)* (Illinois State Water Survey, Champaign, Illinois, 2010).
- Malm, W. C., Sisler, J. F., Huffman, D., Eldred, R. A. & Cahill, T. A. Spatial and seasonal trends in particle concentration and optical extinction in the United States. *J. Geophys. Res.* **D 99**, 1347–1370 (1994).
- Erickson, D. J., Seuzaret, C., Keene, W. C. & Gong, S. L. A general circulation model based calculation of HCl and ClNO₂ production from sea salt dechlorination: reactive chlorine emissions inventory. *J. Geophys. Res.* **D 104**, 8347–8372 (1999).
- Zhang, Q. et al. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes. *Geophys. Res. Lett.* **34**, L13801, doi:10.1029/2007GL029979 (2007).
- Bertram, T. H. et al. Direct measurements of N₂O₅ reactivity on ambient aerosol particles. *Geophys. Res. Lett.* **36**, L19803, doi:10.1029/2009GL040248 (2009).
- Brown, S. S. et al. Variability in nocturnal nitrogen oxide processing and its role in regional air quality. *Science* **311**, 67–70 (2006).
- Singh, H. B. & Hanst, P. L. Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere — an important reservoir for nitrogen oxides. *Geophys. Res. Lett.* **8**, 941–944 (1981).
- Grannas, A. M. et al. An overview of snow photochemistry: evidence, mechanisms and impacts. *Atmos. Chem. Phys.* **7**, 4329–4373 (2007).
- Shindell, D. T. et al. Improved attribution of climate forcing to emissions. *Science* **326**, 716–718 (2009).

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

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