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Modeling heterogeneous $ClNO_2$ formation, chloride availability, and chlorine cycling in Southeast Texas

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ABSTRACT

Nitryl Chloride ($ClNO_2$) mixing ratios above 1 ppbv have been measured off the coast of Southeast Texas. $ClNO_2$ formation, the result of heterogeneous N_2O_5 uptake on chloride-containing aerosols, has a significant impact on oxidant formation for the Houston area. This work reports on the modeling of $ClNO_2$ formation and describes the sensitivity of $ClNO_2$ formation to key parameters. Model sensitivity analyses found that: (1) Chloride availability limits the formation of nitryl chloride at ground level but not aloft; (2) When excess particulate chloride was assumed to be present at ground level through sea salt, $ClNO_2$ concentrations increased in some locations by a factor of 13, as compared to cases where sea salt chloride was assumed to be limited; (3) Inland formation of $ClNO_2$ seems feasible based on chloride availability and could have a large impact on total $ClNO_2$ formed in the region; and (4) $ClNO_2$ formation is quite sensitive to the assumed yield of $ClNO_2$ from N_2O_5 uptake. These results demonstrate that there is a need for further field studies to better understand the geographic extent of $ClNO_2$ formation and the atmospheric conditions which control partitioning of chloride into the particle phase. In addition, this work examined the role of $ClNO_2$ in the cycling of chlorine between chloride and reactive chlorine radicals. The modeling indicated that the majority of reactive chlorine in Texas along the Gulf coast is cycled through $ClNO_2$, demonstrating the importance of including $ClNO_2$ into photochemical models for this region.

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1. Introduction

Ambient measurements of Nitryl Chloride ($ClNO_2$) were made for the first time during the TexAQS II/GoMACCS field campaign in 2006 (Osthoff et al., 2008). $ClNO_2$ mixing ratios measured on board the *Research Vessel Ronald H Brown* reached over 1 part per billion by volume (ppbv) off the coast of southeast Texas. This compound is potentially significant for several reasons. First, $ClNO_2$ serves as a NO_x reservoir at night which prevents nitrogen from being lost to inactive forms such as nitric acid. Second, $ClNO_2$ represents a largely unstudied form of chlorine in the atmosphere that may be a key step in a pathway that converts particulate chloride into reactive chlorine radicals. The effect of this chemistry on both NO_x and chlorine cycling has the potential to increase ozone production in regionally polluted areas (Simon et al., 2009; Osthoff et al., 2008).

Finlayson-Pitts et al. (1989) first suggested that $ClNO_2$ could form from heterogeneous reactions between N_2O_5 and aqueous sea salt aerosols. Osthoff et al. (2008) showed strong temporal correlations between $ClNO_2$ and N_2O_5 concentrations measured in the Gulf of Mexico. Their results make a compelling case that the dominant mechanism for nitryl chloride formation is this heterogeneous pathway. Studies that have investigated heterogeneous $ClNO_2$ formation in the laboratory suggest that the mechanism is the same as that of heterogeneous N_2O_5 hydrolysis [Reaction (1)] (Behnke et al., 1997; Schweitzer et al., 1998).

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$$N_2O_5 \xrightarrow{\text{aqueous sea salt}} NO_2^+ + NO_3^- \quad (1)$$

The Cl^- ions in aqueous aerosol compete with H_2O to react with NO_2^+. Therefore the reaction can either result in $2HNO_3$ or $ClNO_2 + HNO_3$ as shown in Reactions (2)–(4).

$$NO_3^-(aq) + H^+(aq) \rightarrow HNO_3(g) \quad (2)$$

$$NO_2^+(aq) + Cl^-(aq) \rightarrow ClNO_2(g) \quad (3)$$

$$NO_2^+(aq) + 2H_2O(aq) \rightarrow HNO_3(g) + H_3O^+(aq) \quad (4)$$

The yield of nitryl chloride from this reaction [i.e. the fraction of NO_2^+ ions that proceed to Reaction (3) instead of Reaction (4)] is strongly dependent on the chloride ion concentration in the aerosol (Behnke et al., 1997; Roberts et al., in press; Schweitzer et al., 1998; Thornton and Abbatt, 2005). Yields close to 1 at high molarities (1 M) suggest that Cl^- ions outcompete H_2O as discussed in Section 3.2.3. In fact, both Behnke et al. (1997) and Roberts et al. (in press) report nitryl chloride formation on aerosols as dilute as 0.01 M. Most laboratory studies are in relative agreement on their measurements of reactive uptake coefficients for N_2O_5 on chloride aerosols (0.01–0.03) (Behnke et al., 1997; Schweitzer et al., 1998; Thornton and Abbatt, 2005).

Previous articles have described the impact of $ClNO_2$, once formed, on ozone formation (Simon et al., 2009; Osthoff et al., 2008). The work presented here incorporated heterogeneous $ClNO_2$ formation on ambient aerosol, as well as other related heterogeneous N_2O_5 chemistry, and investigated the sensitivity of $ClNO_2$ formation to various model parameters. Specifically, this work studies the dependence of $ClNO_2$ formation on available chloride and its sensitivity to the assumed yield of $ClNO_2$. Finally, the implications of this chemistry for chlorine cycling and the total reactive chlorine budget in Southeast Texas are investigated.

2. Methods

2.1. Photochemical simulations

Photochemical modeling was performed using the Comprehensive Air quality Model with extensions (CAMx) version 4.2 (Environ, 2008). This program is a three-dimensional Eulerian model which calculates the effects of emissions, chemistry, deposition, advection, and dispersion on chemical concentrations in the atmosphere. A full description of the model treatment of these processes as well as the nesting schemes and numerical solvers can be found in the CAMx User's Guide (Environ, 2008). Evaluations of CAMx model performance have been carried out by Tesche et al. (2006) and Morris et al. (2005). CAMx was chosen for this work to facilitate comparison with previous studies of chlorine and nitryl chloride in the Houston area (Chang and Allen, 2006a,b; Wang et al., 2007; Simon et al., 2009).

The modeling domain consisted of three two-way nested grids, as shown in Fig. 1. The two largest of these grids had cells with horizontal dimensions of 36 km by 36 km and 12 km by 12 km. These two grids have 17 vertical layers covering the lowest 15 km of the atmosphere. The finest of the grids, which was centered over the Houston area, had cells with horizontal dimensions of 4 km by 4 km and 28 vertical layers covering the lowest 15 km of the atmosphere. The layers are more finely divided at lower altitudes, with 12 of the 28 layers in the lowest 1000 m. A full description of the thickness of each vertical layer is described by the Texas Commission on Environmental Quality for their SIP mid-course review modeling (http://www.tceq.state.tx.us/implementation/air/airmod/data/hgb1_camx_domain.html). The model simulation was run for the dates of August 30, 2006 through September 9, 2006, one of the time periods when the *R.V. Ronald H. Brown* was taking measurements in the Houston area. August 28 and 29 were used as model spin-up days. Meteorological inputs for the modeled days were developed at the University of Houston (Ngan, 2008), as described by Simon et al. (2009) and in the supplemental information.

Emissions inputs for ozone precursor compounds (NO_x and VOCs) are described by Simon et al. (2009). In addition, emissions of anthropogenic Cl_2, primary particulate matter (PM), SO_2, and ammonia were included in the modeling. A full description of these emissions and the associated boundary conditions can be found in the supplemental information.

2.2. Updated model chemistry

Current versions of the CAMx software include a standard CB IV chemical mechanism (Gery et al., 1989), and two enhanced mechanisms: one with added chlorine chemistry described in Tanaka et al.

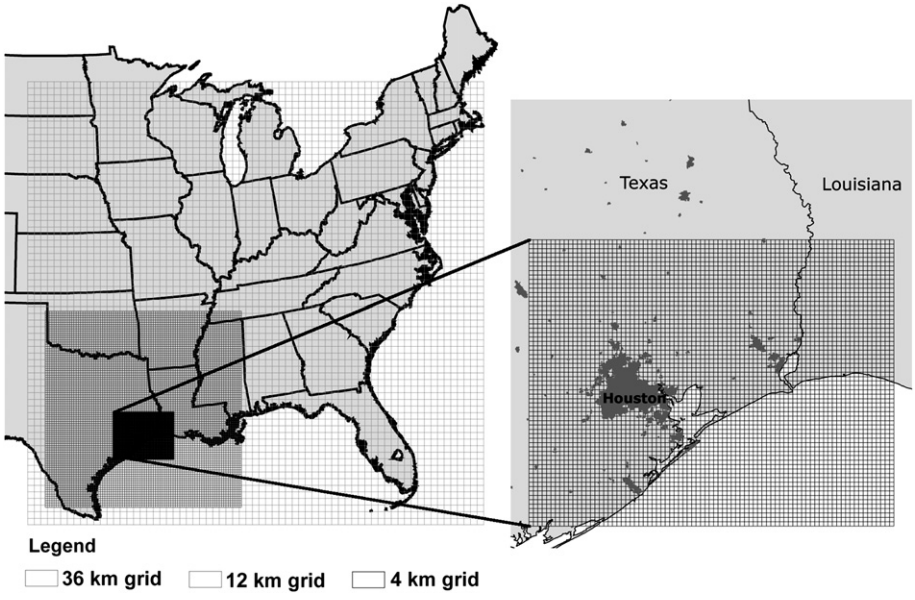

Fig. 1. Nested domains used in CAMx modeling.