

Interactive comment on “Examining the impact of heterogeneous nitryl chloride production on air quality across the United States” by G. Sarwar et al.

G. Sarwar et al.

sarwar.golam@epamail.epa.gov

Received and published: 5 June 2012

Anonymous Referee 3

General comments

Comment: This paper presents a continental scale model of the influence of CINO₂ formation and photolysis on ozone and particulate nitrate. The paper presents model results from two months, February and September 2006. The choice of these two months facilitates comparison with the limited field data for CINO₂ currently available (Houston, TX in September 2006, Boulder CO in February 2009, Calgary, Canada in early spring 2010).

C3300

Predicted and observed CINO₂ levels agree well enough to justify the use of this model for further predictions of impacts of its formation. The model finds a modest influence of CINO₂ production on ozone averaged across the domain, with larger effects for specific days and within specific grid cells (e.g., Los Angeles). It also finds a modest influence on particulate nitrate, especially in winter. Since the only previous air-quality model analysis of the influence of CINO₂ was for specific conditions in Houston, TX, this paper is a new and useful contribution that will help to define the impact of this chemistry on air quality models.

Response: We appreciate the reviewer's thoughtful comments and suggestions to improve the article.

Comment: The methodology and improvements to the chemical mechanism to include chlorine chemistry is well described. The only potential inconsistency is the treatment of the partitioning between gas phase HCl and particulate chloride, which is not described in detail (see comments below). The only potential omission is some discussion of the vertical distribution and mixing of pollutants (NO_x and chloride) that produce CINO₂ in a poorly mixed nighttime boundary layer structure. This aspect was identified as a potential uncertainty in the prior work of Simon et al. and should be mentioned here as well to the extent that it was considered in this study.

Response: We agree that examining the vertical distribution of pollutants can further illuminate the factors affecting CINO₂ formation. We have added an analysis of vertical profiles on two days at several locations of interest. We plan to include the following text and Figure in section 3.3 of the paper:

Vertical profiles of CINO₂ and its main precursors (N₂O₅ and particulate chloride) are examined for one day before sunrise in February and one day in September at a few locations with high CINO₂ concentrations: Los Angeles and Indiana in February; Los Angeles and Idaho in September. The profiles shown in Figure 1 are average concentrations over the identified regions and present mean values over hundreds of square

C3301

km. These vertical profiles reveal some interesting relationships between ClNO₂ and its precursors at these times and locations. All four instances shown in Figure 1 display ClNO₂ concentrations highest at the surface. Variation in the nighttime boundary layer height by location and season is demonstrated by ClNO₂ being concentrated in the lowest 40 m of atmosphere in Los Angeles on February 9, 2006, but being mixed up to a height of 200-400 m in both locations on September 12, 2006. In contrast to ClNO₂, N₂O₅ appears to peak in the residual layer aloft at between 200 and 400 m depending on the location and season. The exception to this is the Idaho location on September 12, 2006, where N₂O₅ is mostly depleted at all heights. Since the Idaho ClNO₂ concentrations are associated with a large fire plume, it is possible that the loss of N₂O₅ by the end of the night was a result of large amounts of particulate surface area available for hydrolysis reactions. In all four examples shown here, the vertical profiles of ClNO₂ appear to mirror the profiles of particulate chloride suggesting that chlorine probably limits ClNO₂ formation aloft, especially given the elevated N₂O₅ concentrations above the boundary layer. These plots also demonstrate that the chlorine may come from either fine or coarse particulate chloride since the Los Angeles profiles show very little fine chloride while the Indiana profile demonstrates a predominance of fine chloride over coarse chloride.

Specific comments

Comment: Page 6152, line 5: ClNO₂ influences ozone by producing radicals (source) and by reacting with O₃ (sink). In the later model analysis, is there a way to separate the magnitude of the two effects? In other words, is the modest effect determined here due to approximately equal ozone sources and sinks, or to a small source countered by a much smaller sink?

Response: The photolysis of ClNO₂ produces Cl and NO₂. VOCs can react with Cl to produce HO₂ and RO₂ which convert NO into NO₂. The photolysis of NO₂ then enhances O₃. However, Cl also consumes O₃ by directly reacting with it. O₃ production rate can be defined as the conversion of NO into NO₂ and calculated using

C3302

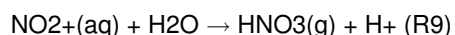
the following equation (Sadanaga et al., 2005; Chen et al., 2010; Mao et al., 2010):

$$P(\text{O}_3) = k_1[\text{NO} + \text{HO}_2][\text{NO}][\text{HO}_2] + \sum k_i[\text{NO}][\text{RO}_2]$$

We calculated O₃ production rates without and with the heterogeneous production of ClNO₂. Monthly mean O₃ production rate was zero at night which started to increase during the morning hours and peaked in the afternoon hours. The monthly mean peak O₃ production rates without the heterogeneous production of ClNO₂ ranged up to 25 ppbv/hr. The heterogeneous production of ClNO₂ enhanced the monthly mean peak O₃ production rate by less than 0.3 ppbv/hr. The monthly mean morning O₃ production rates without the heterogeneous production of ClNO₂ ranged between 5-20 ppbv/hr. The heterogeneous production of ClNO₂ enhanced the mean morning O₃ production rate by up to 1.0 ppbv/hr. The heterogeneous production of ClNO₂ enhanced O₃, thus the consumption rate of O₃ by its reaction with Cl was lower than the O₃ production rates indicated above.

Comment: Page 6153, reaction (R9). This reaction is typically written as between NO₂+ and liquid water rather than NO₂+ and OH-.

Response: We changed the reaction (R9) as follows:



Comment: Page 6155, top. Chlorine mass is conserved between ClNO₂ and particulate chloride. Does the model include a gas phase reservoir of HCl, as implied by the field observations? Is there explicit repartitioning between HCl and particulate chloride? Does this affect mass balance?

Response: CMAQv5.0 uses ISORROPIA 2.1 (Fountoukis and Nenes, 2007) to calculate the equilibrium distribution of chlorine and other compounds between gas and particle phases. The model accounts for the production of HCl via gas-phase chemistry as described in Table 1 and also accounts for fine and coarse-mode particulate chloride. Particulate chloride mass is reduced by the amount of chlorine in ClNO₂ formed

C3303

via the heterogeneous reaction on fine as well as coarse particles. However, equilibrium is achieved quickly through the use of ISORROPIA; thus mass balance affects both HCl and particulate chloride.

We plan to change the text of sections 2.1 and 2.4 as follows: Section 2.1: This study uses the Community Multiscale Air Quality (CMAQ) modeling system (version 5.0; beta version) (Binkowski and Roselle, 2003; Byun and Schere, 2006; Foley et al., 2010) to simulate air quality. This version of CMAQ includes several updates to the aerosol treatment including tracking of trace metals in fine particles and an updated inorganic partitioning module, ISORROPIA 2.1 (Fountoukis and Nenes, 2007). ISORROPIA 2.1 calculates equilibrium partitioning of inorganic compounds (chlorine, ammonia, nitrate, and water) between the gas and particle phases. This partitioning is dependent on ionic concentrations in the particles of Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺, Cl⁻, SO₄²⁻, and NO₃⁻ and gas-phase concentrations of NH₃, HNO₃, and HCl.

Section 2.4: In this study, we replace R6 with R11 in CMAQ. The yield and reactions rates are calculated separately for coarse and fine particles and use the chloride and water contents in the appropriately-size particles. The yield for R11 is calculated with Eq 3 on both fine and coarse particles. Reactive uptake (γ N₂O₅) is calculated based on Davis et al.(2010) for fine particles (as is done in the base version of CMAQ) and is calculated based on Eq 4 (using k₃₄/k₃₃ from Bertram and Thornton (2009)) for coarse particles. To conserve mass of chlorine, particulate chloride mass is reduced by the amount of chlorine in ClNO₂ formed via the heterogeneous reaction on fine as well as coarse particles. Equilibrium between particulate chloride and gas-phase HCl is achieved quickly through the use of ISORROPIA 2.1 (Fountoukis and Nenes, 2007) in CMAQ, so the formation of ClNO₂ can affect ambient concentrations of both particulate chloride and HCl. If no particulate chloride is present, then Y=0 according to Eq 3 and no ClNO₂ is formed.

Comment: Section 3.1: Same comment. Is there any prediction of the gas-phase HCl reservoir associated with the modeled particulate chloride? Gas phase HCl is likely a

C3304

better predictor of ClNO₂ formation potential from a mass balance standpoint than is fine mode particulate chloride.

Response: Please see our response above.

Comment: Page 6158, end of section 3.2: Is it possible to be more quantitative about the last statement? For example, is the integrated N₂O₅ production available from the NO_x inventory and the amount of this NO_x oxidized through N₂O₅, and can this number be compared with the chlorine / chloride inventory? Such a comparison may identify regions that are more or less Cl limited relative to NO_x. It may also require substantial effort that is beyond the scope of this manuscript, so this comment is at the author's discretion.

Response: While we appreciate the comment for more detailed information, we also agree that it will require a substantial effort that is beyond the scope of this manuscript. We, however, remove line 19-20 and replace it with the following sentence:

These results suggest that the heterogeneous production of ClNO₂ can further increase O₃ and reduce TNO₃ if elevated particulate-chloride levels are present in the atmosphere.

Comment: Section 3.3, Figures 2, 3: Legends on the color scales are difficult to read and should be printed with larger font size. Modeled yields of ClNO₂ are large in many regions – does the ClNO₂ formation deplete particulate chloride over the course of individual nights?

Response: We have printed Figures 2 and 3 with larger font. The revised Figure 2 is presented here and the revised Figure 3 was presented earlier (please see responses to comments from anonymous Referee 2).

While modeled yields of ClNO₂ are large in many regions, it does not deplete particulate chloride over the course of individual nights. Higher ClNO₂ are predicted when particulate chlorides are also high; thus particulate chloride levels are not depleted.

C3305

Comment: Figure 3 also shows no ClNO₂ in Colorado, though the text cites levels roughly in agreement with field observations there. Why the difference?

Response: The minimum scale in Figure 3 (maximum ClNO₂ plot) is 0.5 ppbv (500 pptv) and it uses white color. The largest predicted value in Boulder, Colorado is 200-300 pptv; thus it does not explicitly show up in the Figure.

Comment: Section 3.4: Is it possible to determine the individual contributions of the Cl atom input and the recycling of the NO₂ to increased ozone production? Another way to ask this question: Is the next day ozone model more sensitive to inclusion of ClNO₂ (Cl atom source plus NO_x recycling) or to changes in the uptake coefficient for N₂O₅ (NO_x recycling only)? Again, although this would be a useful metric from a chemical mechanism standpoint, it is at the author's discretion to determine if it fits within the scope of the paper.

Response: While we appreciate the comment for more detailed information, we also agree that it will require a substantial effort that is beyond the scope of this manuscript. We opted not to include such analysis.

Comment: Page 6163, section 3.4.4: There are larger effects on ozone within certain grid cells. Is ClNO₂ likely to influence the number of days above the air quality standards in Los Angeles?

Response: We analyzed the number of days any grid-cells exceed the National Ambient Air Quality Standards (NAAQS) of 75 ppbv. The addition of ClNO₂ heterogeneous chemistry indeed increases the number of days any grid-cells exceed the NAAQS in Los Angeles and other areas. We add the following sentence in section 3.4.4:

The addition of ClNO₂ heterogeneous chemistry also increases the number of days any grid-cells exceed the National Ambient Air Quality Standards of 75 ppbv in Los Angeles and other areas (the maximum increase 7 days in September).

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6145, 2012.

C3306

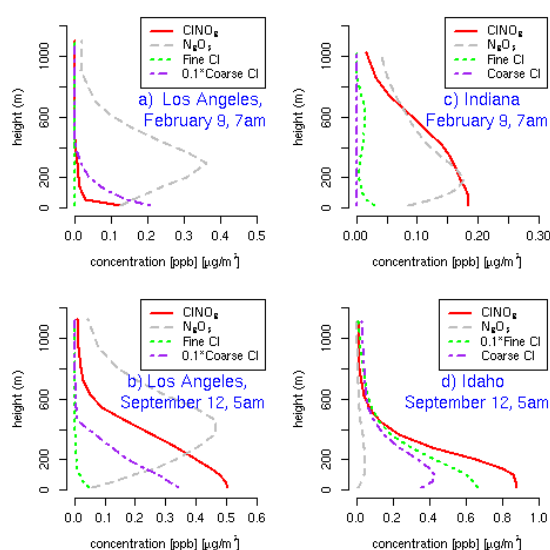


Fig. 1. Vertical profiles of ClNO₂, N₂O₅, coarse Cl, and fine Cl for (a) Los Angeles on Feb. 9 (b) Los Angeles on Sep. 12 (c) Indiana on Feb. 9 (d) Idaho on Sep 12

C3307

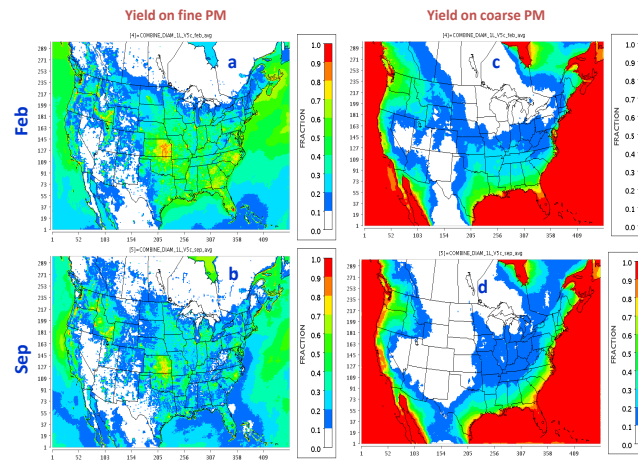


Fig. 2. (a) Predicted mean yield for ClNO₂ on fine particles in (a) February and (b) September. Predicted mean yield for ClNO₂ on coarse particles in (c) February and (d) September.