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Accounting for Heterogeneous-Phase Chemistry in Air Quality Models – Research Needs and Applications

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BACKGROUND

Understanding the extent to which heterogeneous chemical reactions affect the burden and distribution of atmospheric pollutants is important because heterogeneous surfaces are ubiquitous throughout our environment. They include materials such as aerosol particles, clouds and fog, snow, dust particles, building surfaces, snow packs, and even vegetated surfaces such as grass and leaves.

While heterogeneous surfaces have long been known to be important reaction matrices for atmospheric chemistry^{1,2}, emerging laboratory, field and computational studies continue to demonstrate additional routes for atmospheric chemical reactions on heterogeneous surfaces. From a regulatory perspective, heterogeneous chemistry has the potential to affect several criteria pollutants, including ozone (O₃), nitrogen dioxide (NO₂), and fine particulate matter (PM_{2.5}), as well as the formation of acidic and toxic air pollutants.

While there is evidence that heterogeneous reactions occur, how much do they impact the chemical composition of the atmosphere, and where are the greatest impacts likely to be seen? This is difficult to answer because large uncertainties exist not only in characterizing the area and characteristics (size, age, composition, etc.) of reaction surfaces, but also the kinetics of surface reactions. The experimental set-up for measuring heterogeneous chemistry is challenging due to the need to introduce and characterize surface properties as well as gas-phase and wall chemistry. The wide variety of surface types also adds to the difficulty – building exteriors are very different than water droplets, for example. These surfaces may also be temporally variable; clouds are one example of an ephemeral medium.

For regulatory air quality model (AQM) applications, we need to know how uncertainties and inaccuracies in describing heterogeneous chemical reactions might affect predictions of harmful air pollutants. This paper lists recommendations to address some of the largest uncertainties, as identified at the Workshop on Future Air Quality Model Development Needs³. By identifying those aspects of heterogeneous chemistry with the greatest potential to affect AQM predictions, we can better focus resources to improve the treatment of heterogeneous chemistry and its role in atmospheric photochemistry.

RECOMMENDATIONS TO ADDRESS MULTIPHASE CHEMISTRY UNCERTAINTIES

- I. **Quantify the magnitude and uncertainties of aqueous phase chemistry impacts on secondary organic aerosol (SOA), oxidants, and hazardous air pollutants (HAPs).** The atmospheric aqueous phase - clouds, fog, snow, water layers on particles and other surfaces - provides many routes for chemical reaction. While more detail in describing chemistry is generally better from a scientific standpoint, complex schemes can dramatically slow down model simulations; AQMs require a careful balance between complexity and computational efficiency. How much detail is needed in aqueous chemistry for models to accurately predict air pollutant concentrations? We recommend using existing knowledge to develop upper bounds of the potential effect of aqueous reactions, including speculative pathways, on model predictions. These upper bound calculations would test the importance of aqueous chemical pathways on sulfate, ozone and SOA production, provide guidance on whether the inclusion of such detailed pathways in AQMs is warranted, and help identify additional, major aqueous phase organic SOA precursors and pathways.
- II. **Improve descriptions of heterogeneous dinitrogen pentoxide (N_2O_5) hydrolysis pathways.** Heterogeneous reactions of N_2O_5 with water provide a sink for NO_2 , producing nitric acid (HNO_3), and impacting O_3 and particulate matter formation. The physical parameters governing this reaction, including the reaction probability (γ), are uncertain⁴. The importance of this heterogeneous pathway relative to the homogeneous hydrolysis reaction also needs to be quantified. We recommend synthesizing and extending current studies to harmonize heterogeneous and homogeneous pathways and develop a "best estimate" for use in AQMs.
- III. **Determine the effect of nitryl chloride (ClNO_2) formation on criteria pollutants.** When N_2O_5 reacts heterogeneously with aqueous chloride instead of water, the resulting ClNO_2 provides an alternate pathway which can recycle NO_2 rather than terminate it as HNO_3 ⁵. Although this reaction was thought to be important near coastlines, recent measurements indicate that it could also be significant far inland^{6,7}. There is uncertainty in the ClNO_2 yield, the emissions of chlorine compounds, and in the potential affect on ozone and $\text{PM}_{2.5}$ over regional scales.
- IV. **Bound the effects of nitrous acid (HONO) formation from urban, soil, and possibly canopy surfaces on ozone, $\text{PM}_{2.5}$, and other species.** HONO is a powerful source of hydroxyl radicals which initiate photochemistry, but HONO concentrations are generally underestimated by AQMs. Heterogeneous, daytime sources of HONO from soils, building surfaces and vegetated canopies⁸⁻¹¹ have been proposed to account for this "missing" HONO. How much do model predictions of ozone, $\text{PM}_{2.5}$ and other regulated air pollutants depend on accurately reproducing heterogeneous sources of HONO? We recommend extending modeling studies¹² where surface sources of HONO chemistry are tuned to fit observations of HONO, and examining the effect on ozone predictions.

- V. **Evaluate the importance of snow and ice chemistry for O₃, PM_{2.5} and HAP formation.** The potential role of snow and ice surfaces in photochemically generating reactive trace gases has been recognized¹³. The impact of these reactive gases on modifying concentrations of radicals is another area of much uncertainty. There are ongoing field studies, particularly in the Western U.S.¹⁴, through which we hope to learn more about the role of frozen surfaces in ozone formation. We recommend that the community support and monitor these studies, and use the results to determine whether to invest more intensive resources.
- VI. **Assess the importance of chemistry on dust particles for regional pollutant concentrations.** Mineral dust is predicted to perturb the nitrogen, sulfur and photochemical oxidant cycles¹⁵, but these effects are highly dependent on properties of the surface, such as previous photochemical processing, number of activated sites, etc. It is unclear how much the uncertainty in our treatment of reaction on dust surfaces might contribute to model error compared to other components in the AQMs. A simple upper bounding study would help modelers determine how much effort should be invested in detailed descriptions of dust chemistry.

RECOMMENDATIONS FOR MODELING HETEROGENEOUS CHEMISTRY

- I. **Examine whether AQMs appropriately solve chemistry in all phases.** Current models employ operator splitting, whereby the gas and aqueous chemistry are solved separately. The inclusion of heterogeneous reactions necessitates consideration of feedbacks between chemistry occurring in various phases and surfaces. Consequently, the traditional approach of operator or time splitting employed in most atmospheric chemistry model formulations may need to be revisited. Alternate approaches, wherein homogeneous and heterogeneous chemistry is solved simultaneously, should be considered.
- II. **New Direction: Use detailed aqueous schemes to create condensed descriptions for regional models.** While highly detailed aqueous chemical schemes, such as CAPRAM¹⁶, are important for fully understanding aqueous chemistry, the use of such detail may be computationally prohibitive for most model applications. To account for aqueous chemistry in large-scale routine simulations, it will be necessary to derive and comprehensively evaluate condensed schemes that strike a balance between representation of reactant compounds and computational efficiency.
- III. **Improve gas-phase predictions and evaluations of species that participate in heterogeneous chemistry.** Even if we fully understood heterogeneous chemistry, it would be impossible to model correctly if the gas-phase precursors, on which they depend, are not accurately predicted. It is unclear how well current AQMs predict concentrations of non-criteria pollutants and individual VOCs^{17, 18} because these are rarely evaluated and not routinely measured¹⁹. We recommend greater emphasis on accurately describing the concentrations of pollutants in the gas phase which are key participants in heterogeneous phase chemistry. This would include measuring concentrations and evaluating model predictions of compounds such as carbonyls, organic acids, acid anhydrides, organic nitrates, hydroxyl and nitrate radical.

- IV. **Reduce uncertainties in meteorological parameters that affect heterogeneous chemistry.** The accurate representation of heterogeneous reactions also depends on several meteorological parameters and processes, especially relative humidity, aerosol liquid water, and cloud microphysics. Consequently, assessments of the relative importance of heterogeneous chemistry through modeling experiments must be conducted in the context of uncertainties in representation of these key meteorological processes and variables.

CONCLUSIONS

Numerous heterogeneous reactions occur in the atmosphere, with the potential to perturb gas phase photochemistry and contribute to secondary organic and inorganic aerosol formation. How important is it to represent heterogeneous chemistry in a detailed manner *for the purposes which AQMs are applied now and in the near future and with respect to uncertainties in other processes*? There are many gaps in our understanding of aqueous and surface chemistry. If detailed representation does matter, we need to identify which species/matrices are the most important and focus future research in those areas. We need to know whether addressing deficiencies in our current treatment of heterogeneous chemistry in AQMs will make a large difference in predictions of those species of greatest interest for regulatory and research purposes.

Several recommendations listed in this paper describe "bounding studies" using existing knowledge to determine upper limits of the effects of heterogeneous pathways on overall AQM concentration predictions. By identifying those processes which have the greatest potential to change predictions of regulated pollutants, we can focus research efforts where they might have the largest impact on improving human and ecosystem health.

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