

Atmospheric Chemical Mechanisms

2020 Conference Abstracts

Date	Session
Monday, Nov. 9th	Fundamental Oxidation Chemistry
Tuesday, Nov. 10 th	Fundamental Oxidation Chemistry
Thursday, Nov. 12 th	Fundamental Oxidation Chemistry
Thursday, Nov. 12 th	COVID and Other Extreme Events
Friday Nov. 13 th	Wildfire Chemistry
Monday, Nov. 16 th	Indoor Chemistry and Emerging Anthropogenic Pollutants
Tuesday, Nov. 15 th	New Tools to 21st Century Air Quality Problems
Wednesday, Nov. 18 th	Current and New Atmospheric Chemical Mechanisms
Thursday, Nov. 19 th	Atmospheric Chemistry in Public Health and Regulatory Applications
Friday, Nov. 20 th	Keynote: How Reactive Organic Carbon Fuels Atmospheric Chemistry

CRI-HOM: A novel chemical mechanism for simulating Highly Oxygenated Organic Molecules (HOMs) in global chemistry-aerosol-climate models

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Abstract: We present a new mechanism, CRI-HOM, which we have developed to simulate the formation of highly oxygenated organic molecules (HOMs) from the gas phase oxidation of α -pinene, one of the most widely emitted BVOCs. This concise scheme adds 12 species and 66 reactions to the Common Representative Intermediates (CRI) mechanism v2.2 Reduction 5 and enables the representation of semi-explicit HOM treatment suitable for long term global chemistry- aerosol-climate modelling, within a comprehensive tropospheric chemical mechanism. The key features of the new mechanism are (i) representation of the autoxidation of peroxy radicals from the hydroxyl radical and ozone initiated reactions of α - pinene, (ii) formation of multiple generations of peroxy radicals, (iii) formation of accretion products (dimers) and (iv) isoprene-driven suppression of accretion product formation, as observed in experiments. The mechanism has been constructed through optimisation against a series of flow tube laboratory experiments. The mechanism predicts a HOM yield of 2-4.5% under conditions of low to moderate NO_x, in line with experimental observations, and reproduces qualitatively the decline in HOM yield and concentration at higher NO_x. The mechanism gives a HOM yield that also increases with temperature, in line with observations, and our mechanism compares favourably to some of the limited observations of [HOM] observed in the boreal forest in Finland and in the south east USA.

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A new database for the kinetics of the gas-phase atmospheric reactions of organic compounds

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Abstract: We present a digital, freely available, searchable, and evaluated compilation of rate coefficients for the gas-phase reactions of organic compounds with OH, Cl, NO₃ and O₃. Excellent compilations of much of these data exist, however, many are out of date, most have limited scope, and all are difficult to search and load completely into a digitized form.

This database builds on these efforts and we use the results of these previous reviews where possible, although many of our recommendations are updated to include new or omitted data or address errors. Furthermore, we provide recommendations for those myriad compounds that have yet to receive a previous evaluation. This database incorporates over 50 years of kinetic measurements and is approaching 3000 recommended bimolecular rate coefficients. It is a living document and will continue to grow as new data become available.

The primary motivation behind this work is to provide a large, reliable training dataset for the development and testing of structure-activity relationships (SARs), whose reliability depends fundamentally upon the availability of high-quality kinetic data. Furthermore, a comprehensive collation of data such as this provides us with a unique perspective on the state-of-the-knowledge in atmospheric chemistry, and allows us to identify some of the important challenges that our community is presented with.

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Photoproduction of singlet oxygen from aqueous organic aerosols

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Abstract: During their lifetime, organic aerosols will be subjected to atmospheric processing including exposure to sunlight. Photochemistry of chromophoric organic matter within aerosols can produce in-situ reactive oxygen species (ROS) capable of transforming chemical and physical properties of aerosols, with implications for air quality and climate. Singlet oxygen (1O_2) is a well-known ROS in biology and in surface waters, yet there is little knowledge of its atmospheric sources and sinks, and consequently of its ability to alter aerosol chemistry.

To address this knowledge gap, we generated secondary organic aerosols from aromatic anthropogenic precursors in a laboratory smog chamber. We then extracted the collected SOA filters and submitted the soluble extracts to atmospherically-relevant photochemical conditions. Using furfuryl alcohol as a probe for 1O_2 , we determined steady-state concentrations of this oxidant and calculated 1O_2 quantum yields for each SOA sample. Subsequent quantification of OH radicals and peroxides allowed for the comparison of degradation rates between ROS. We find that molecules such as amino acids, organo-nitrogen compounds and phenolic compounds have a shortened lifetime by more than half when 1O_2 reactivity is taken into consideration. Our ongoing work is looking at the photoproduction of 1O_2 in ambient PM₁₀ filter samples and its potential source apportionment.

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Primary radical effectiveness: Does the nature of the primary radical matter for ozone production?

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Abstract: The atmospheric oxidation of volatile organic compounds (VOCs) occurs primarily via reaction cycles involving gas phase radical species, catalysed by nitric oxide (NO), which result in the production of secondary pollutants such as ozone. For these oxidation cycles to occur they must be initialised by a primary radical, i.e. a radical formed from non-radical precursors. Once formed, these primary radicals can react with a VOC to produce peroxy radicals that, providing sufficient NO is present, can re-generate “secondary” radicals that react with further VOCs. Thus, one primary radical can result in the catalytic oxidation of multiple VOCs. Although the photolysis of ozone in the presence of water vapour to form two hydroxyl (OH) radicals is accepted as the dominant tropospheric primary radical source, multiple other primary radical sources exist and can dominate in certain environments. In this work we use a series of model simulations to investigate if the nature of the primary radical matters. The OH radical is the dominant tropospheric radical, with both primary and secondary sources. In contrast, atomic chlorine (Cl) has primary sources that show significant spatial heterogeneity throughout the troposphere but is not typically regenerated in catalytic cycles. Both primary OH and Cl can initiate VOC oxidation, but this work shows that the relative effectiveness with which they result in ozone production depends on the chemical environment in which they are produced.

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Singlet ($1\Delta_g$) O_2 as an efficient tropospheric oxidizing agent: the gas phase reaction with the simplest Criegee intermediate

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Abstract: The importance of atmospheric oxidants can hardly be overestimated. We have investigated, in this work, the possibility of singlet ($1\Delta_g$) O_2 as a potentially efficient oxidant of simplest Criegee intermediate (CH_2OO). High-level quantum chemical calculations including post-CCSD(T) corrections in terms of full triplets and partial quadratic excitations, along with core corrections have been employed to estimate the reaction energetics. The title reaction was found to be effectively barrierless with the transition state lying -22.85 kcal mol $^{-1}$ below the isolated reactants. Rate coefficients under tropospheric conditions have been calculated using the master equation. The calculated rate coefficients indicate the reaction to be very fast; the value of rate coefficient would be close to gas kinetic limit under the various tropospheric conditions. In order to check the atmospheric implications of the title reaction, comparison with other studied oxidation reactions of CH_2OO with $\bullet OH$ and O_3 has been made by means of lifetime calculations. The findings clearly suggest that $1\Delta_g$ O_2 could efficiently compete with the two well-known tropospheric oxidants in oxidizing simplest Criegee intermediate.

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Formic Acid Catalyzed Isomerization and Adduct Formation of an Isoprene-Derived Criegee Intermediate: Experiment and Theory

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Abstract: Methyl vinyl ketone oxide (MVK-oxide) is a four-carbon unsaturated Criegee intermediate generated with ~21-23% yield from isoprene ozonolysis. We present experimental and theoretical work that identifies two product channels in the rapid reaction of MVK-oxide with formic acid (FA). Multiplexed photoionization mass spectrometry experiments (298 K, 10 Torr) demonstrate the formation of a functionalized and highly oxygenated adduct, resulting from the barrierless insertion of MVK-oxide into FA. Isotopically labeled experiments reveal that FA also catalyzes the isomerization of MVK-oxide to a vinyl hydroperoxide product. Theoretical calculations provide mechanistic insight, rate coefficients, and branching of these pathways.

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Direct measurements of vinoxy radicals and formaldehyde from ozonolysis of trans- and cis-2-butenes: Quantification of syn- and anti-conformers of Criegee intermediate and new insights into OH radical formation mechanism

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Abstract: Ozonolysis reactions of alkenes are important oxidation pathways of alkenes in the atmosphere and significant sources of tropospheric hydroxyl radicals. The ozonolysis reactions proceed via Criegee intermediates (CIs), which have both syn- and anti-conformers. In the case of ozonolysis of trans- and cis-2-butene, it is believed that syn-CH₃CHOO (CI) isomerizes into vinylhydroperoxide and subsequently decomposes to OH and vinoxy radical. However, the syn- and anti-conformers of CI have not been quantified, and the fate of the vinoxy radical has not yet been completely elucidated. In this work, ozone reactions with trans- and cis-2-butene are studied using cavity ring-down spectroscopy (CRDS). Formation of vinoxy (CH₂CHO) radical is directly observed in these systems and is used to determine the syn-CH₃CHOO and OH yields. Formaldehyde (HCHO), a side-product in the ozonolysis reactions, is also monitored. Chemical kinetic modeling is performed to illustrate the reaction mechanisms and to quantify the reactive intermediate and product yields. For the first time, the yields of syn- and anti-CH₃CHOO conformers are determined to be 0.5 and 0.5 for trans-2-butene and 0.3 and 0.7 for cis-2-butene, respectively. It is also shown that secondary reaction of the vinoxy radical generates additional amount of OH radical, and HCHO is produced from both syn- and anti-CH₃CHOO. These studies have provided new insights into the ozonolysis reactions of alkenes and the OH formation mechanism.

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Mechanisms and yields of OCS from the low NO_x oxidation of dimethyl sulfide

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Abstract: Dimethyl sulfide (DMS), emitted from the surface ocean, contributes to aerosol particle formation and growth in the pristine marine atmosphere. DMS is primarily oxidized by the hydroxyl radical ultimately forming methane sulfonic acid and sulfuric acid. Current models of atmospheric sulfur chemistry often assume that 0.7% of DMS emitted from the ocean is oxidized to carbonyl sulfide (OCS), an abundant trace gas that contributes to the stratospheric sulfate aerosol load. Recently, a ubiquitous autoxidation product of the OH-initiated H-abstraction of DMS, hydroperoxymethyl thioformate (HPMTF), has been detected in the marine environment. Here, we report a potential mechanism for OCS formation and yields of HPMTF, SO₂ and OCS from OH-initiated oxidation of DMS conducted under conditions representative of the marine boundary layer. The HPMTF experiments were performed in a dark environmental chamber using alkene ozonolysis as the primary source of OH generation under low NO_x conditions. An OCS yield of >1% from OH-initiated DMS oxidation was found across a variety of different representative marine conditions. We proposed the formation of OCS from the decomposition of an alkyl radical, generated by a hydrogen abstraction of an aldehydic H atom, located on carbonyl carbons of various sulfur species, including HPMTF.

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Mechanistic Investigation of the Aqueous-Phase OH Oxidation of Pinic Acid

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Lightning Presentation Abstract: Atmospheric aqueous phases are important reaction media for water-soluble organic compounds in the atmosphere. Aqueous-phase OH oxidation can lead to both the formation and the decay of secondary organic aerosol (SOA) components. Currently, the kinetics and mechanism of many SOA components in the aqueous phase remain unknown. One of such examples is pinic acid. Pinic acid has been known as a major component of monoterpene SOA. Being a diacid, pinic acid is highly water soluble and can be readily introduced to the atmospheric aqueous phases. In this study, we have performed a mechanistic investigation of the aqueous-phase OH oxidation of pinic acid, with the main objective of identifying the major reaction pathway and products. Experiments were conducted in the lab using a photo-reactor equipped with UVB lamps. The reaction products were monitored using offline LC-MS. In addition to a C18 column, which is typically employed in SOA analyses, we also used a hydrophilic interaction chromatography (HILIC) column that can better retain polar organic compounds. A number of organic acids emerged as major oxidation products of pinic acid, including norpinic acid and terebic acid. A triple quadrupole MS with direct injection was employed to support the identification of these products. We have also observed a product with the identical elemental composition and similar fragmentation pattern of 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), a tracer for α -pinine oxidation.

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Ammonolysis of ketene as a potential secondary source of tropospheric acetamide: a theoretical investigation

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Lightning Presentation Abstract: In spite of being present in significant trace amount, not much is known about secondary sources of amides except via oxidation of amines. We examined the possibility of reaction between ammonia with simplest ketene as a potentially new secondary source of acetamide in troposphere. Electronic structure and chemical kinetics calculations were carried out and it was found that the reaction could occur via the addition of ammonia at either the C=C or C=O bonds of ketene. The reaction energetics as well as calculated rate coefficients indicate that under tropospheric conditions, ammonolysis would occur almost exclusively via ammonia addition at the C=O bond. The reaction of ketene with water has also been investigated in order to compare between hydrolysis and ammonolysis, as the former is known to be responsible for acetic acid formation under tropospheric conditions. The rate coefficient for the formation of acetamide was found to be $\sim 10^6$ to 10^9 times higher than that for the formation of acetic acid under tropospheric conditions. Based on relative rates of ammonolysis with respect to hydrolysis, it was found that acetamide formation would compete with acetic acid formation at lower altitudes while the former would dominate over the latter at higher altitudes in the troposphere.

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Particulate Matter (PM) chemical composition in different size fractions on Metropolitan Area of São Paulo (MASP)

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Lightning Presentation Abstract: Fine PM is mainly composed by SO_4^{2-} , NO_3^- , NH_4^+ , and Black Carbon (BC), whereas coarse PM has in its composition Si, Al, Ti, Fe, CaCO_3 and NaCl. However, how is the size distribution of PM chemical composition in MASP nowadays? In order to study this, twelve PM size fraction stages were sampled in Micro-Orifice Uniform-Deposit Impactor (model 110-R, MSP Corporation, EUA) in University of São Paulo (lat -23.56° and lon -46.73°) during 2017 and 2018 winters. To measure PM mass concentration, it was used gravimetric technique, an optical reflectometer to BC concentration, the x-rays fluorescence to elements and ionic chromatography to ions. The size distribution of PM average mass concentrations had two modes, with peaks on stages of 0.32 ($4.64 \pm 2.88 \mu\text{g.m}^{-3}$) and $3.2 \mu\text{m}$ ($3.21 \pm 2.41 \mu\text{g.m}^{-3}$). The highest BC average concentrations were observed on particles smaller than $0.32 \mu\text{m}$. The elements Al, Fe, Si, and Ti had average concentration peaks on the stage of $3.2 \mu\text{m}$ (49.4 ± 58.1 , 103 ± 90.3 , 130 ± 135 and $6.91 \pm 6.44 \text{ ng.m}^{-3}$, respectively). SO_4^{2-} , NH_4^+ and K^+ had peaks on $0.32 \mu\text{m}$ (763 ± 461 , 237 ± 173 and $64.6 \pm 77.7 \text{ ng.m}^{-3}$, respectively), whereas Na^+ , Cl^- , Ca^{2+} , Mg^{2+} and NO_3^- had the highest average concentrations on $3.2 \mu\text{m}$ (108 ± 132 , 65.6 ± 98.6 , 205 ± 118 , 46.1 ± 28.0 and $157 \pm 118 \text{ ng.m}^{-3}$, respectively). Al, Fe, Si and Ti; SO_4^{2-} and NH_4^+ ; Na^+ and Cl^- ; and Ca^{2+} and Mg^{2+} had similar size distributions with each other, what could indicate that they had the same sources.

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Oxidized Amines Enhance Particle Formation More Than Amines

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Lightning Presentation Abstract: Sulfuric acid plays a key role in atmospheric aerosol particle formation. Bases such as amines are known to stabilize sulfuric acid to form particles through salt formation. However, the role of oxidized amines in particle formation and growth is unknown. Trimethylamine oxide (TMAO), an oxidization product of trimethylamine, is studied. As a weak base in the aqueous phase and a strong base in the gas phase, TMAO offers an interesting perspective for an argument “base strength is a key factor in particle formation.” Another intriguing property of TMAO is related to its molecular structure: while steric hinderance of three methyl groups limits the hydrogen bonding sites to one, the zwitterionic bond causes a high dipole moment which enables the formation of stabilizing ion-dipole interactions. It seems clear that more than one base property is related to its capability to enhance aerosol particle formation. Molecular-level cluster formation mechanisms are resolved, and theoretical results on particle formation are confirmed with laboratory measurements. The enhancing effect of TMAO is compared to the other atmospheric bases and the factors, which make oxidized amines stronger stabilizer in clustering than amines, are discussed.

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Theory-based structure-activity relationships

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Abstract: The development of (semi-)explicit chemical kinetic models for atmospheric chemistry relies on an accurate assessment of the reaction rates and product yields for the elementary reactions in the model. For a large fraction of the reactions in an extensive oxidation mechanism, no direct experimental or theoretical data exists, or the information available does not span the required range of reaction conditions. Structure-activity relationships (SARs) are then used to predict the required data, where each SAR captures the known reactivity trends for a given reaction class. Preferably, the SAR links the molecular structure directly to the reactivity, without the need of additional input data beyond the molecular graph.

Experimental and theoretical studies are highly complementary to derive SARs. In recent years, the improved predictive capabilities of theoretical methods, and the ability to affordably examine systematic series of reactions in a given class theoretically, have allowed theory-based data to become an important source of information in the development of SARs.

A number of recent SARs will be discussed, in which theory-based methods have played an important role in their formulation. This includes recent SARs on the H-migration in alkylperoxy radicals, as well as systematic data on alkoxy radical decomposition, and the reactions of oxygenated Criegee intermediates. Where possible, the performance of these SARs will be compared to experimental data.

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Effect of Water Vapor on Oxidation of Aromatic Compounds

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Abstract: Aromatic compounds are ubiquitous pollutants in urban atmosphere. The oxidation of benzene and its alkyl substituents is initiated by their reactions with OH radicals, forming ring-retaining phenolic products and ring-opening carbonyl compounds. Preliminary smog chamber measurements found the production yield of phenolic compounds changes with the relative humidity, e.g., from 0.276 ± 0.011 at RH 60% down to 0.185 ± 0.012 at RH 5%. The change in yield might be somewhat explained by the strong interaction between the peroxy radicals and water, e.g., a stabilization of ~ 32 kJ/mol for C₆H₆-1OH-2OO-s and H₂O at M06-2X level, letting an equilibrium between C₆H₆-1OH-2OO-s + H₂O and C₆H₆-1OH-2OO-s--H₂O complex. The formation of peroxy-water complex reduces the effective route to ring-opening channel, resulting in increased yield of phenolic compounds.

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Structure-Activity Relations for Organic Photo-processes, Part 1: Absorption Cross Sections

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Abstract: Sunlight is absorbed by many organic molecules present in the atmosphere, leading to a wide range of photolysis and photoisomerization products with distinctly different behavior, e.g. highly reactive radical fragments, that can have a significant effect on atmospheric composition. Detailed chemical models such as GECKO-A predict thousands of multifunctional photo-labile organic molecules, for which absorption cross sections as functions of wavelength are needed. A review of laboratory measurements is made to attempt the development of estimation methods, or Structure Activity Relations (SARs), based on molecular structure, chromophores, and substituent functional groups. Fundamental gaps in knowledge are discussed.

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Unlumping monoterpenes: Identification of unique first-generation oxidation pathways for the most prevalent cyclic monoterpenes

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Abstract: Monoterpene oxidation is an important atmospheric mechanism in many regions of the world, contributing to secondary organic aerosol (SOA) formation, ozone formation, and NO_x cycling. Results from laboratory studies suggest that in spite of structural similarities, different monoterpenes behave differently, for example forming drastically different yields of SOA from one to another. However, in models monoterpenes are often lumped into one or two parameterizations, assuming that the structurally similar species will behave similarly. Using quantum chemical calculations of unimolecular reaction kinetics, we have demonstrated that the fate of the first-generation alkyl and/or alkoxy radical following NO₃ radical oxidation is quite different for 7 of the most prevalent cyclic monoterpenes: α -pinene, β -pinene, Δ -carene, sabinene, limonene, camphene, and α -thujene. Radical intermediates such as these can either continue propagating through additional oxidation steps or may terminate through uni- or bi-molecular chemistry. Our results show in general that the monoterpenes with higher observed SOA yields generate radical intermediates with readily available radical propagation pathways, whereas those with lower yields have dominant termination pathways early in the oxidation mechanism, thus suggesting that the key inter-terpene differences affecting other atmospheric chemistry may occur quite early in the oxidation mechanism.

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Experimental and theoretical study on the impact of a nitrate group on the chemistry of alkoxy radicals

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Abstract: Despite the important role of NO₃ as an oxidant, NO₃-initiated oxidation processes have not received as much attention as e.g. those by OH or O₃. As such, the corresponding degradation mechanisms of VOCs are significantly less understood. Though there are parallels between OH- and NO₃-initiated oxidation mechanisms, the available literature indicates that hydroxy- or nitrate substituents have a rather distinct impact on the reaction kinetics of the important peroxy, RO₂, and alkoxy, RO, radicals.

Within this study, the reactivity of nitrate-RO from C₂ to C₆ compounds, using a combination of experimental, theoretical, and modeling techniques was investigated. The theoretical work encompasses a series of quantum chemical and theoretical kinetic calculations on nitrate-substituted alkoxy radicals. These results are compared to earlier SAR predictions, improving the SAR predictive capabilities. The accompanying experiments performed in the atmospheric chamber SAPHIR together with modeling studies probe the fate of the nitrate-RO, firstly providing a measure for their relative rate coefficient of unimolecular decomposition or isomerization. Secondly allowing to investigate the implications of these reactions for LIF measurement of nitrated RO₂ in the atmosphere, and their impact on the night-time atmospheric degradation of VOCs.

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New Insights into the Radical Chemistry and Product Distribution in the OH-initiated Benzene Oxidation

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Abstract: Aromatic compounds are critical anthropogenic emissions, causing air pollution and detrimental health effects. There are growing interests in understanding the influences of aromatic chemistry in urban air quality, chemical evolution of biomass burning, and new-particle formation events. However, the fundamental oxidation mechanism of aromatic compounds in the atmosphere remains obscure. In this study, we investigate the reaction kinetics and the products of key radicals in benzene oxidation by means of experimental studies and theoretical calculations. We quantify the nitrate branching ratio of bicyclic peroxy radical reaction with NO, which has only been studied sparsely in the literature. The measured nitrate branching ratio is much lower than the value used in current models. The reaction of bicyclic peroxy radical with HO₂ is shown to largely regenerate OH radicals, instead of producing organic peroxide as typically assumed by conventional mechanism. The chemistry of alkoxy radical in benzene oxidation system is found to be diverse, because of the presence of C-C double bond and multiple functional groups in the radicals. New reaction pathways have been identified which carry a substantial fraction of carbon flow, but are not accounted for in current models. Overall, we will describe a nearly explicit chemical mechanism for benzene photooxidation.

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A new mechanistic overview for the removal of phenolic substituent from atmosphere in dark phase and its atmospheric importance.

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Abstract: A new mechanistic overview for the removal of Phenolic substituent from atmosphere in dark phase and its atmospheric importance

Phenol is mostly found from OH initiated oxidation of gasoline. Automotive gasoline contains aromatic hydrocarbons like toluene, ethyl benzene and xylene in 20-30% in volume. Apart from this phenolic species especially halo phenols are extensively used in pesticides. After releasing to atmosphere through different sources like vehicular emission, pesticide industries it reacts with different species abundant in troposphere like hydroxyl radical (OH), Chlorine radical (Cl), Nitrate radical (NO₃) and Nitrogen dioxide (NO₂). Among all the species NO₂ is highly abundant in atmosphere and it is also released through vehicular emission. So it is important to determine the fate of this type of phenolic substituent for the reaction with NO₂ and to understand the reaction mechanism and also to determine rate of the reaction.

Here we report the reaction of Phenol (PhOH) with NO₂ and also reaction of Orthochloro phenol(o-ClPhOH)-NO₂ in the gas phase.

In case of PhOH we have found ortho nitro PhOH, phenyl nitrite, nitric oxide and nitric acid as products and for o-ClPhOH nitric acid, nitric oxide and ortho chloro substituted phenyl nitrite as products. A new mechanism has been proposed to explain product formation. Termolecular rate constant calculated to be $(4.39 \pm 0.2) \times 10^{-35}$ and $(1.31 \pm 0.4) \times 10^{-35}$ cm⁶molecule⁻²s⁻¹ for reaction with PhOH and o-ClPhOH respectively.

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Chlorine radical oxidation of alkanes: effects of structural branching, NO_x, and relative humidity

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Abstract: Atmospheric chlorine radicals (Cl) have recently been observed in a variety of regions at concentrations significant enough to affect VOC oxidation. Experiments have shown that Cl oxidizes most VOC precursors, especially alkanes, more rapidly than hydroxyl radicals and that Cl-oxidation often results in higher SOA yields. As comparatively little is known about the mechanism and products of Cl reaction with alkanes, we investigated the Cl-oxidation of a series of C₁₀ hydrocarbon precursors with linear (n-decane), branched (2-methylnonane and 3,3-dimethyloctane), and branched cyclic (butylcyclohexane) structures through laboratory smog chamber experiments utilizing an iodide-adduct chemical ionization mass spectrometer (I- CIMS) with a filter inlet for gases and aerosols (FIGAERO) and an aerosol chemical speciation monitor (ACSM). Experiments were performed with or without added NO_x and at low (<5%) or medium (40-55%) relative humidity. Fragmentation to smaller molecules, as observed through early-generation oxidation products, was more common from branched alkanes and patterns in fragmentation products suggest that Cl are able to abstract primary hydrogen atoms, confirming prior theory. Oxidation of butylcyclohexane produced lower-volatility particle-phase products that were less likely to form oligomers compared to those of n-decane. Differences in particle-phase composition were also observed based on varying NO_x and RH conditions.

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Laboratory simulations of multiday chemical oxidation of organic carbon in the atmosphere

Lesly Franco

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Lightning Presentation Abstract: Organic carbon, emitted into the atmosphere from sources such as wildfires, vegetation, and vehicles, undergoes dramatic chemical changes over its atmospheric lifetime. Such chemical changes have a major influence on atmospheric composition, but many uncertainties remain about its chemical evolution (or “aging”), particularly over long timescales. Chamber studies that simulate the oxidation of organic carbon frequently cover atmospheric lifetimes from hours to days, but few are able to extend into the longer-term oxidation timescales. Here we carry out laboratory studies looking at the long-term oxidation and chemical evolution of gas-phase organic carbon, covering atmospheric lifetimes of ~two weeks to a month. Using a 150L “mini-chamber,” gas-phase organic carbon was exposed to OH concentrations that are hundreds of times higher than those in the atmosphere to simulate longer atmospheric lifetimes. The chemical evolution of gas-phase organic carbon is described and compared to results from the Master Chemical Mechanism. A particular focus of these experiments is to analyze the changes to gas-particle partitioning, carbon number distributions, and carbon oxidation state over long timescales. Understanding the multi-day chemical evolution of gas-phase organic carbon may provide insight into the atmospheric lifecycle of longer-lived gas-phase organic species and their impacts on atmospheric composition, especially in remote regions far from major sources of organic species.

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Novel reactions and treatments of atmospheric peroxides

Keith Kuwata

Professor and Chair of Chemistry, Macalester College

Lightning Presentation Abstract: Peroxides remain a challenge in atmospheric chemistry. My laboratory characterizes novel reactions of peroxides and estimates the importance of these reactions under atmospheric conditions. We apply two quantum chemical methods: (1) W1BD theory provides highly accurate relative energies for species well-described by a single electronic configuration; (2) equation-of-motion spin-flip coupled-cluster theory provides a tractable way of including more than one electronic configuration, which is necessary for treating singlet diradical species. One category of peroxides we have studied is the vinyl hydroperoxide (VHP) formed by isomerization of Criegee intermediates with syn-alkyl substituents. We have quantified two competing VHP pathways: the dissociation of the OH moiety vs. the roaming and re-attachment of OH to form hydroxycarbonyls. We have identified substitution patterns for VHPs that favor the OH roaming pathway, reducing its barrier far below the barrier to OH dissociation. For these VHPs, the reduction of free OH production will become important at lower temperatures. The other category is the hydrotetraoxides formed in peroxy + HO₂ reactions. Preliminary results suggest that our quantum chemical approach leads to total rate constants and branching ratios consistent with experimental measurements. The inclusion of multiple, non-degenerate conformers of pre-reactive complexes and covalently bonded intermediates is necessary to achieve agreement with experiment.

Additional Authors: None

Characterization of reactive gases during BIO-MAIDO campaign along the Maïdo slope on Indian Ocean tropical island (Reunion Island).

Manon Rocco
PhD Student, LaMP

Lightning Presentation Abstract: The characterization of Volatile Organic Compounds (VOCs) is fundamental to understand chemical processes and health and climate impacts. These compounds are emitted either by biogenic and anthropogenic sources. They play a large role in atmospheric chemistry, including the formation of ozone and Secondary Organic Aerosol (SOA). SOA are potential precursors of clouds and are not-well estimated in models. A better understanding of the chemical processes of VOCs will improve the quality of chemical modeling and prediction. The goal of the BIO-MAIDO campaign is to characterize the atmospheric dynamic and chemical processes and the cloud formation in a tropical climate (Reunion Island) along the Maïdo slope. To this end, a large instrumental campaign was set up during one month. For gas phase chemistry studies, three sites have been targeted (in Petite France (PF) at 900m, at the Maïdo hostel (MH) at 1500m and at the Maïdo observatory (MO) at 2200m). At all sites, meteorological conditions and reactive gases concentrations (including ozone, NO_x except MH site) have been recorded. VOC measurements were performed by PTR-MS from March 1st to April 4th, 2019. Results obtained from upslope and downslope sites (mixing ratios, diurnal variation, and influence of clouds) of this campaign are presented. The differences in concentrations show the influence of chemical reactions during transport from PF to the MO (1.5 ppb to 2.5 ppb for formaldehyde from PF to MO).

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Molecular understanding of biogenic volatile organic compound emissions and their atmospheric oxidation products as function of climate change-induced stress on plants

Ugo Molteni

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Lightning Presentation Abstract: Biogenic volatile organic compounds (BVOCs) comprise the largest fraction of the volatile organic compounds emitted to the atmosphere.¹ Atmospheric oxidation of BVOCs leads to the formation of highly oxygenated molecules (HOMs) and Secondary Organic Aerosol (SOA)^{2,3}

Climate models project for the next decades an increase of the average global temperature. Climate-change induced extreme events are expected to have stressful effects on plants, which the organisms react to by changing BVOC emissions composition and rates. These modifications may lead to subsequent changes in atmospheric oxidation chemistry processes. HOMs and SOA mass yield can decrease or increase depending on the cause of stress and the plant's reaction mechanism^{4,5}. Yet, most of the scientific work conducted in BVOCs oxidation so far focuses on single molecules which are, at the best, only representative for a particular type of biome. Real plant emission studies addressing a variety of plant conditions are needed to fill this gap of knowledge.

We present latest results from BVOCs oxidation experiments from real plant emissions under basal and stress conditions. We show how abiotic and biotic stressors modify plant BVOCs emission rate and composition, and how these impact on oxidation product composition and SOA yields.

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Photosensitization is in the air and opens new route for sulfate production

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Abstract: Northern China is regularly subjected to intense wintertime “haze events”, with high levels of fine particles that threaten millions of inhabitants. While sulfate is a known major component of these fine haze particles, its formation remains unclear especially under highly polluted conditions, with state-of-the-art air quality models unable to reproduce or predict field observations. These haze conditions are generally characterized by simultaneous high emissions of SO₂ and photosensitizing materials. In this study, we find that the excited triplet states of photosensitizers could induce a direct photosensitized oxidation of hydrated SO₂ and bisulfite into sulfate S(VI) through energy transfer, electron transfer or hydrogen atom abstraction. This photosensitized pathway appears to be a new and ubiquitous chemical route for atmospheric sulfate production. Comparing to other aqueous-phase sulfate formation pathways with ozone, hydrogen peroxide, nitrogen dioxide, or transition metal ions, the results also show that this photosensitized oxidation of S(IV) could make an important contribution to aerosol sulfate formation in Asian countries, particularly in China.

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Incorporation of Detailed Gas-Phase Furan Mechanism into a Young Biomass Burning Plume Box Model

Benjamin Brown-Steiner

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Abstract: We present the incorporation of a recently developed SAPRC-18-derived detailed gas-phase furan oxidation mechanism into a young biomass burning plume box model (ASP) and the impact this mechanism has on ozone and secondary organic aerosol (SOA) production under biomass burning conditions. The mechanism, which was derived from published data and the SAPRC mechanism generation system (MechGen), consists of furan, furan alkyl derivatives (2-MF, 3-MF, and 2,5-DMF), and their major oxidation products which consists of 15 chemical species and 291 oxidation reactions. The mechanism has been previously incorporated into simulations of chamber studies, while this work presents an extension into box model simulations of biomass burning plume conditions. The Aerosol Simulation Program (ASP) was developed to simulate ozone and SOA formation within young biomass burning plumes and has been used in chamber studies and Lagrangian model formulations, among others. In this work, we compare the standard ASP mechanism to the ASP + SAPRC-18-derived detailed furan mechanism for conditions consistent with the Williams Fire that burned in California in 2009. We describe the impact of the new furan mechanism on the time series and total production of ozone and SOA as well as the impact on plume oxidants and impacted chemical species. We also discuss challenges and future potential for the incorporation of the furan mechanism into other box, semi-Lagrangian, and 3D model simulations.

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Evaluating the sensitivity of radical chemistry and ozone formation to ambient VOCs and NO_x in Beijing

Lisa Whalley

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Abstract: Despite reductions in primary emissions of pollutants in China over the past decade, concentrations of the secondary pollutant, ozone, still exceed air quality threshold limits during the summertime. OH controls the oxidative chemistry in the atmosphere, being responsible for the transformation of primary emissions into secondary pollutants such as NO₂, O₃ and SOA. We present measurements of OH, HO₂, and RO₂ radicals taken in Beijing in the summer. Model comparisons have displayed varying levels of agreement as a function of NO_x. Under low NO conditions, a missing OH source is evident. Radical budget analysis demonstrates that this missing OH source can be resolved if unimolecular reactions of RO₂ radicals generate OH directly. In the presence of NO, the model overestimates the rate at which RO₂ propagates to HO₂ and we hypothesise that larger RO₂ species likely undergo multiple bimolecular reactions with NO, followed by isomerisation of the RO radical to another RO₂ species, before a HO₂ radical forms. By this process, the lifetime and the concentration of total-RO₂ radicals is extended. The ozone production efficiency of large, complex VOCs from which these RO₂ species are formed may be greater than currently appreciated, and so further efforts to understand the rate at which the larger RO₂ species propagate to HO₂ (or to OH directly) is necessary to accurately model ozone levels in urban centres and to fully understand how emission controls will impact ozone.

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Direct measurements of the kinetics of the reactions between the Criegee intermediates CH₂OO and CH₃CHOO and SO₂

Lavinia Onel

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Abstract: A significant fraction of unsaturated volatile organic compounds are oxidised by ozone, producing highly reactive Criegee intermediates, such as CH₂OO and CH₃CHOO, in the atmosphere. Previous studies have shown rapid gas phase reactions of CH₂OO and the two CH₃CHOO conformers, syn and anti, with SO₂ at 298 K.[1-3] The reactions are expected to generate SO₃,[4] which then leads to the production of H₂SO₄(g) and sulphate aerosols in the troposphere, impacting air quality and climate.

We have carried out direct kinetic measurements using flash photolysis of RI2 (R: CH₂ or CH₃CH)/SO₂/O₂/N₂ mixtures at 248 nm coupled with time-resolved multipass broadband UV absorption spectroscopy. We will report results from measurements of the kinetics of CH₂OO + SO₂ as a function of temperature and CH₃CHOO + SO₂ as a function of temperature and pressure. The measured temperature dependence and reported lack of a pressure dependence from 2–760 Torr of the rate coefficient of CH₂OO + SO₂ [5] have been modelled using MESMER (Master Equation Solver for Multi-Energy well Reactions) package.[6] A positive pressure dependence was found for the reactions of both CH₃CHOO conformers with SO₂, with the anti conformer reacting with SO₂ 4–5 times more rapidly than the syn conformer.

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The effect of COVID lockdown on the atmospheric air quality in China and northern Italy.

Frederico Bianchi

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Abstract: The 2020 pandemic are causing substantial reduction of anthropogenic emissions. China and Italy are among the countries that took the strongest measures to limit the spread of the virus by forcing their population to stay at home. This specific time provide a very unique opportunity to study the effect of the anthropogenic activities on air quality and atmospheric new particle formation. In my presentation, I will show long-term comprehensive observations before, during and after the COVID lockdown and how this has changed the atmospheric composition. Similarities and differences of the two sites will be also highlighted.

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Modeling the effects of COVID-19 measures on air quality using a chemical transport model: impacts on the Po Valley and the Swiss Plateau regions

Giancarlo Ciarelli

Postdoctoral Researcher., University of Helsinki. Institute for Atmospheric and Earth System Research (INAR).

Abstract: The spread of COVID-19 virus has posed serious challenges for the global communities. To try to reduce the circulation of the infection, governmental bodies have imposed different lockdown measures at various levels of complexity and duration. As a result, a substantial reduction in people's mobilities might have impacted air quality levels to a different extent.

In this study, we applied the Comprehensive Air-quality Model with eXtensions (CAMxv6.50) over northern Italy and Switzerland in order to investigate potential changes in air quality levels, and its chemical composition, during periods when lockdown measures were enforced. Impacts on air concentrations of nitrogen dioxide (NO₂), ozone (O₃) and fine particulate matter (PM_{2.5}) levels are presented for two regions, i.e. the Po Valley and the Swiss Plateau regions, and compared with air quality networks measurements. The impact on secondarily formed particulate species, i.e. inorganic and organic constituents, are also presented for daytime and nighttime periods.

Additionally, results from the Process Analysis (PA) probing tool, run in combination with CAMx and capable of disentangling the changes in various chemical reactions, are also presented.

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UK surface NO₂ levels dropped by 42% during the COVID-19 lockdown: impact on surface O₃

James Lee

Research Professor, University of York

Abstract: Human activity changed substantially during 2020 around the world due to government responses to COVID19. In the UK people were asked to work from home where possible on the 16th March and entered a period of “lockdown” on the 23rd March. During this lockdown period all non-essential travel was prohibited, and outdoor activity was limited to once per person per day. Many of these restrictions impacted activities that are considered antagonists for air quality, such as road transport. We examined NO₂ and O₃ measured by the UK’s Automatic Urban and Rural Network, focusing on those located in urban environments, between March 23rd and May 31st in 2020 compared to the previous 5 years. We observed reductions in NO₂ concentrations at sites across the UK, with a median reduction of 45 %. However, O₃ concentrations saw a median increase of 11 %. Total oxidant levels ($Ox = NO_2 + O_3$) increased slightly (3%), suggesting the majority of this change can be attributed to photochemical repartitioning due to the reduction in NO_x. Generally, we find larger, positive Ox changes in southern UK cities which we attribute to increased UV radiation and temperature in 2020 compared to previous years. The net effect of the NO₂ and O₃ changes is a sharp decrease in exceedances of the NO₂ air quality objective limit for the UK. Concurrent increases in O₃ exceedances in London emphasize the potential for O₃ to become an air pollutant of concern as NO_x emissions are reduced in the next 10-20 years.

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Minimal climate impacts from short-lived climate forcers following emission reductions related to the COVID-19 pandemic

James Weber

PhD student, University of Cambridge

Abstract: We present an assessment of the impacts on atmospheric composition and radiative forcing of short-lived pollutants following worldwide decrease in anthropogenic activity and emissions comparable to what has occurred in response to the COVID-19 pandemic, using the global composition-climate model UKCA. Changes in anthropogenic emissions reduce tropospheric hydroxyl radical and ozone burdens, increasing methane lifetime. Reduced SO₂ emissions and oxidising capacity lead to a decrease in sulphate aerosol and increase in aerosol particle size, with accompanying reductions to cloud droplet number concentration. However, large reductions in black carbon emissions increase aerosol albedo. Overall, the changes in ozone and aerosol direct effects (neglecting aerosol-cloud interactions which were not statistically significant) result in an instantaneous radiative forcing of -33 to -78 mWm⁻². Upon cessation of emission reductions the short-lived climate forcers rapidly return to pre-COVID levels, meaning these changes are unlikely to have lasting impacts on climate assuming emissions return to pre-intervention levels.

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Ozone pollution in the North China Plain spreading into the late-winter haze season

Ke Li

Postdoc, Harvard University

Abstract: Surface ozone is a severe air pollution problem in the North China Plain. Ozone concentrations are highest in summer, driven by fast photochemical production of hydrogen oxide radicals (HOx) that can overcome the radical titration caused by high emissions of nitrogen oxides (NOx) from fuel combustion. Ozone has been very low during winter haze (particulate) pollution episodes due to direct titration by emitted NO. However, the abrupt 60% decrease of NOx emissions following the COVID-19 lockdown in January 2020 reveals a switch to fast ozone production during winter haze episodes with MDA8 ozone of 60–70 ppb and PAN levels of 4 ppb. We reproduce this switch with the GEOS-Chem model, where the fast production of ozone and PAN is driven by HOx radicals from photolysis of formaldehyde, overcoming radical titration from the decreased NOx emissions. Formaldehyde levels are very high in the North China Plain because of high emissions of VOCs. This switch to an ozone-producing regime in January–February following the lockdown illustrates a more general tendency over 2013–2019 of higher winter-spring ozone in North China Plain, and increasing association of high ozone with winter haze events in late winter, as emission controls have targeted NOx (30% decrease) while VOC emissions have remained constant. This calls for stringent year-round VOC emission controls as NOx emissions continue to decrease to avoid further spreading of severe ozone pollution into the winter-spring season.

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How vegetation feedbacks during drought worsen ozone air pollution extremes in Europe, North America and Asia

Meiyun Lin

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Abstract: The most extreme ozone (O₃) pollution episodes are linked to heatwaves and droughts, which are increasing in frequency and intensity around the world, with severe impacts on natural and human systems. Biosphere-atmosphere interactions play a critical role in these air pollution extremes. The published literature has largely focused on the impact from increased BVOC emissions. Here we highlight a previously under-appreciated "climate penalty" feedback mechanism – namely, substantial reductions of O₃ removal by drought-stressed vegetation – as a key factor driving O₃ pollution extremes during heatwaves in Europe (e.g. 2003), North America (e.g. 2012) and Eastern China (e.g. 2019). Using six decades of observations and Earth system model simulations (1960-2018), we show that declining O₃ removal by drought-stressed vegetation in response to climate warming helps to explain why European O₃ pollution has not decreased satisfactorily in recent decades, despite marked reductions in regional emissions due to regulatory changes. Accounting for reduced O₃ removal by water-stressed plants leads to a three-fold increase in high-O₃ events above 80 ppb during European droughts. These vegetation feedbacks increased the sensitivity of O₃ extremes to increasing temperature by 20-30%. As hot and dry summers are expected to increase over the coming decades, effective emissions policies must consider the drought-vegetation feedbacks. Read Lin et al. (Nat. Climate Change) at <https://rdcu.be/b6xmD>

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Cl(2PJ) + Furan-2,5-dione (C₄H₂O₃, maleic anhydride) reaction in the gas phase: Temperature and Pressure dependent rate coefficients, end-products, reaction mechanism and atmospheric implications

APARAJEO CHATTOPADHYAY

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Abstract: Furan-2,5-dione (C₄H₂O₃, maleic anhydride) has been shown to be a significant emission of biomass burning that can be transported in wildfire plumes. The environmental and health impact of maleic anhydride necessitates a thorough understanding of its atmospheric chemical processing. In recent work from this lab, (Chattopadhyay et al. Int. J. Chem. Kinet. 2020, 52, 623-631) the OH + maleic anhydride reaction rate coefficient was measured and the results from that work will be discussed. In this study, rate coefficients for the gas-phase Cl(2PJ) + maleic anhydride reaction were measured over the 15–500 Torr (He and N₂ bath gas) pressure range at temperatures between 283 and 323 K. A pulsed laser photolysis - atomic resonance fluorescence (PLP-RF) method was used to quantify the reaction Fall-off behavior. An analysis of Cl-atom temporal profiles enabled an thermodynamic evaluation of the Cl•C₄H₂O₃ adduct reaction intermediate. A complementary relative rate (RR) measurement was also performed at room temperature (296 K) and 620 Torr pressure (syn. air). CO, CO₂, and HC(O)Cl were identified as the stable end-products with molar yields (80 ± 7), (188 ± 10), and (67 ± 10)%, respectively. On the basis of the observed reaction product yields, an atmospheric degradation mechanism will be presented that is also supported by electronic structure theoretical calculations.

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The chemical composition of Australian bushfire smoke and implications for population exposure during the 2019/2020 black summer bushfire crisis.

Clare Murphy (Paton-Walsh)
Professor, University of Wollongong

Abstract: The 2019/2020 Australian bushfire crisis saw unprecedented air pollution events with large populations exposed to hazardous air quality over extended periods of time. In addition to the fine particles that are damaging to human health, smoke from bushfires contains significant amounts of different gases that are also toxic (such as carbon monoxide, formaldehyde, acrolein and hydrogen cyanide). These additional airborne toxins are not measured at air quality monitoring stations (as they would usually be below the detection limits of available instruments) but nevertheless will impact on the health of those breathing the smoke. This presentation will describe some of what we know about the chemical composition of Australia bushfire smoke and likely implications for population exposure given the toxicological classes of the primary constituents of the smoke.

Additional Authors: To be confirmed

Detailed examination of the chemistry in fresh wildfire plumes using GECKO-A

Frank Flocke
Scientist, NCAR/ACOM

Abstract: We examine the gas phase chemistry during the first hours after emission in wildfire plumes sampled during the 2018 Western wildfire Experiment for Cloud chemistry, Aerosol absorption and Nitrogen (WE-CAN) field campaign. Fires exhibiting different NO_x to VOC ratios were selected from the roughly 20 different fires which were observed during the campaign using the NCAR/NSF C-130 aircraft, equipped with a state-of-the-art instrument suite for atmospheric chemical composition. The hyper explicit Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) box model is used to simulate plume chemistry. We attempt to use fire laboratory and other field data to reconstruct the un-sampled chemistry which has already occurred between the time of emission and the first sampling pass of the aircraft, which during WE-CAN often exceeded 30 minutes. The predicted product distribution is compared to the in-plume measurements, providing constraints on the fraction of reactive carbon actually measured by the suite of instrumentation deployed on the aircraft. The chemistry in the plumes can be very rapid, with simulated hydroxyl radical (OH) mixing ratios that can reach into the 10⁷ cm⁻³ range. The results can be used to improve the treatment of fire plume chemistry in large scale models, making use of typically available satellite and other remote sensing measurement data.

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Updating chemical mechanisms to include the OH oxidation of key reactive biomass burning non-methane organic gases

Matthew Coggon

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Abstract: Non-methane organic gases (NMOG) emitted by biomass burning constitute a large source of reactive carbon in the atmosphere. Once emitted, these compounds may undergo atmospheric chemistry to form ozone, secondary organic aerosol (SOA), and other secondary products. Highly reactive NMOG, such as furans and phenolic compounds, are significant contributors to the ozone and SOA formed downwind of wildfires, yet the detailed OH oxidation of these species is not widely represented in chemical mechanisms. In this talk, we will summarize work aimed at implementing the chemistry of furans and oxygenated aromatics into the Master Chemical Mechanism. We evaluate these mechanisms against measurements of laboratory and ambient biomass burning smoke collected during the 2016 FIREX Firelab campaign and 2019 FIREX-AQ airborne campaign. We will identify chemical tracers measured by mass spectrometry that link to the chemistry of furans and phenolic compounds. Finally, we will show the implications of this chemistry on reactive nitrogen (NO_y-) partitioning and ozone formation.

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Summer PM_{2.5} pollution extremes caused by wildfires over the western United States during 2017–2018

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Abstract: Complex chemical and physical processes in wildfire plumes pose challenges in assessing fire impacts on air quality and radiation. Using observations and Earth system model simulations, we show large year-to-year variability in western U.S. PM_{2.5} pollution caused by regional and distant fires. In 2017–2018, record-breaking wildfires, combined with stagnation, resulted in daily PM_{2.5} concentrations of 35–175 $\mu\text{g}/\text{m}^3$ across western U.S. sites. Wildfire emissions contributed 90% of PM_{2.5} levels on these days, with smoke transported from southwestern Canada explaining ~50% of PM_{2.5} pollution in northern states. Our study reveals substantial uncertainties in modeling surface PM_{2.5} and aerosol optical depth (AOD) due to uncertainties in fire emission. Our ESM4.1 simulation with a fire emission inventory constrained by satellite AOD captures the observed PM_{2.5} extremes. However, aerosol emissions from the widely used Global Fire Emissions Database must be increased by four to five times for ESM4.1 to match observations. While some studies suggest the importance of secondary organic aerosol (SOA) formation in aged fire plumes, a majority of field measurements have reported little net OA formation as SOA accumulation is compensated by primary OA evaporation. Published in *Geophysical Research Letter* (doi:10.1029/2020GL089429), our study indicates that fire emission uncertainties pose challenges to accurately assessing the impacts of fire smoke on air quality, radiation, and climate.

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Organic Chemical Composition of Gases and Particles Measured During the October 2017 Northern California Wildfire Plumes

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Abstract: Biomass burning is the largest source of organic aerosol to Earth's atmosphere. Fire suppression and climate change has led to larger and more frequent western US wildfires. Wildfire emissions, their atmospheric transformation, and what the downwind population is exposed to are not well-understood.

During the 2017 Northern California wildfires, we measured particle and gas phase organic compounds at the UCB campus, ~60 km downwind of the fire sites, using offline GC×GC-VUV/EI-HRTOFMS with ~4 hour time resolution filter samples, and online high time resolution PTR-ToF-MS, respectively. More than 200 gas phase VOCs and 500 particle phase species were tracked. Sugar-like compounds were the most abundant particulate organic compounds, followed by monocarboxylic acids and aromatic compounds. Knowledge of the health impacts of inhaling many of these compounds are still lacking. Primary BBOA tracers were clearly indicative of the vegetation burned, including diterpenoids for softwood and syringyls for hardwood. We identify a group of multifunctional aliphatic acids and oxygenated aromatic compounds produced during daytime transport that can serve as secondary chemical tracers. Gas phase VOC accounted for ~75% of observed organic carbon in the plumes, organic particles accounted for ~25%. Primary versus secondary VOC contributions to the composition of air at the receptor site were differentiated by their correlation with furan (primary) and maleic anhydride (secondary).

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Wildfire smoke at the transition from day to night to day - when all oxidants are at play.

Zachary Decker

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Abstract: Biomass burning emissions from both wildfires and agricultural fires include a suite of reactive volatile organic compounds (VOCs). At night or in opaque plumes smoke is oxidized mainly by O₃ and NO₃. In contrast, during the daytime when light penetrates the plume smoke is oxidized mainly by O₃ and OH. This work focuses on the transition between daytime and nighttime oxidation. We present wildfire smoke observations in this transition region made during FIREX-AQ (Fire Influence on Regional to Global Environments and Air Quality) aboard the NASA DC-8 and NOAA Twin Otter aircrafts. FIREX-AQ was a multi-platform campaign that took place in the United States in the summer of 2019 to study both wildfire and agricultural burning emissions and subsequent chemistry. We use an explicit chemical model analysis constrained by aircraft observations to understand the chemical evolution of smoke from emission through the night. We describe the distribution of VOC loss by each oxidant. We find that phenolics are mainly oxidized by O₃ with roughly equal oxidation by OH and NO₃, whereas furans and furfurals are mainly oxidized by O₃ or OH depending on the NO_x and O₃ abundance in the plume. Lastly, we use our model to support preliminary results from a Positive Matrix Factorization (PMF) analysis of I-chemical ionization mass spectrometer datasets from both aircraft. Our PMF analysis differentiates fresh emissions from secondary and aged smoke as well as center to edge VOC composition.

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Emissions of Volatile Chemical Products (VCPs) in China: insights from estimation of emission inventory, measurements of emission sources and ambient air

Bin Yuan

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Abstract: Volatile chemical products (VCPs) have been shown to contribute significantly to formation of ozone and secondary organic aerosol (SOA) in urban atmosphere of U.S. As the most populous country and the country with the largest industrial production, emissions of VCPs in China are potentially enormous. Here, combined analysis of VCPs emissions in China based on emission estimates, source measurements and ambient measurements will be presented. Firstly, we estimate the total emissions of VCPs in China in 2000-2017, considering recent control measures in industrial facilities and local emission profiles from various sources. We find different emission structure in China compared to US. Secondly, we perform measurements in various industrial facilities to characterize VCPs emissions. With the dataset, we identify the most important species from these sources. In the end, we use ambient measurements to evaluate the influence of VCPs sources to VOC concentrations in ambient air.

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Developing Models to Understand Atmospheric Reactions of Per- and Polyfluoroalkyl Substances (PFAS)

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Abstract: Per- and polyfluoroalkyl substances (PFAS) are a class of man-made compounds whose research has traditionally focused on exposure via water. More recently, air emissions have been identified as a likely pathway contributing to water concentrations via transport and deposition, although few studies examine the air concentration and deposition of PFAS. Thus, our understanding of basic information like the phase state of atmospheric PFAS is evolving rapidly. Most modeling studies have focused on individual compounds and very few have investigated atmospheric chemical transformations. We present results from the Community Multiscale Air Quality model (CMAQ) applied to a case study focused on a fluoropolymer manufacturer in North Carolina. This framework includes a suite of 53 compounds and their emission rates from this point source. One significant class of compounds emitted from this facility, acyl fluorides, are well-known to hydrolyze to carboxylic acids rapidly in the condensed phase, but the feasibility in the atmosphere is unknown. We find that the assumptions made about condensed-phase reaction time significantly impacts the partitioning and deposition of these compounds. Determining the time scale of simple reactions such as hydrolysis will be vital for understanding the environmental behavior of PFAS. Finally, we implement known PFAS chemistry into a box model framework and investigate the utility of a box model approach to understanding PFAS chemistry and partitioning.

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The Human Forest: Understanding the Impacts of Volatile Chemical Product Emissions to Urban Air Quality

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Abstract: With traffic emissions of volatile organic compounds (VOCs) decreasing steadily over the last decades, the contribution of other emission source categories, such as volatile chemical products (VCPs), has become more apparent in urban air. In this work, in-situ measurements of various VOCs are reported for urban environments in Europe, USA, and China. We show that VCP emissions are ubiquitous in cities around the world and scale with urban population density. We report significant VCP emissions for New York City (NYC), including an anthropogenic monoterpene flux (847–1400 kg/day) from fragranced VCPs comparable to that of a summertime forest. Positive matrix factorization is used to attribute hundreds of compounds to different anthropogenic emission sources for Boulder and NYC in the US, as well as Beijing, China. For Boulder and NYC, VCP emissions account for 42% and 78% of the anthropogenic VOC emissions, respectively. In Beijing, industrial VCP emissions account for 20% of the anthropogenic VOCs and account for 20–50% of the aromatic-species mass. The potential of VCP emissions to form secondary organic aerosol (SOA) is also investigated. The driving chemical and physical processes that increase SOA formation in polluted environments, particularly in Beijing, and the importance of regulating VOC emissions in order to reduce urban pollution are emphasized.

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Fast Unimolecular Reaction of Ozonolysis Initiated First Generation Peroxy Radicals of Limonene and its Impact on Indoor Chemistry

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Abstract: The volatile organic compounds (VOC) emitted to the atmosphere undergo a series of autoxidation processes and form highly oxygenated molecules (HOMs). HOMs have been recognized as key contributors to the formation of secondary organic aerosols (SOA), which have a great impact on climate and human health. Recently, SOA formation in the indoor environment has attracted widespread attention because an average person spends much more time indoors than outdoors. Indoor VOC concentrations can be orders of magnitude higher than outdoors due to the emission from humans and human activities such as cooking, cleaning, and the use of fragrance. Limonene, a widely used additive in indoor cleaning products, has shown a large potential for SOA formation. Since lack of direct sunlight limits the formation of OH, O₃ is considered the major oxidant in most indoor conditions. We have calculated the unimolecular reaction rate coefficients of the first-generation peroxy radical (RO₂) formed by limonene ozonolysis. The results showed these RO₂ have many fast unimolecular reactions. This suggest an important role of autoxidation for limonene, which would form HOMs and greatly contributing to the SOA formation in the indoor environment. Possible products formed from limonene ozonolysis are suggested along with formation pathways. The O₃, OH, NO₃, and Cl initiated oxidation of limonene are compared to have a more comprehensive understanding of limonene gas-phase oxidation.

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Indoor aerosol dynamics during cooking and cleaning activities: Insights from the HOMEChem study

Marina Vance

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Abstract: In the United States, as well as in most of the developed world, people spend about 90% of their time in indoor environments. Although many research efforts have focused on assessing the presence and quantity of chemical air pollutants that affect the indoor air quality, few comprehensive studies have attempted a deeper exploration into how indoor air chemical compounds may interact and transform throughout a normal day of activities. The HOMEChem (House Observations of Microbial and Environmental Chemistry) study was a month-long collaborative investigation into the chemistry of indoor environments that took place in the summer of 2018 at the University of Texas at Austin's test house, a three-bedroom, 2-bathroom manufactured home. This study investigated the effects of building occupants and their activities, such as cooking and cleaning, on the chemistry of the gas phase, particle phase, and surfaces in a simulated home environment. This study incorporates state-of-the-art atmospheric chemistry instrumentation from multiple research groups to build a shared dataset from those measurements. This presentation will focus on results from size-resolved particulate matter and black and brown carbon optical absorption measurements.

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Atmospheric fate of a new polyfluoroalkyl building block, C3F7OCHF2SCH2CH2OH

Shira Joudan

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Abstract: Many per- and polyfluoroalkyl substances (PFAS) have been regulated or phased-out of usage due to concerns about persistence, bioaccumulation potential, and toxicity. We investigated the atmospheric fate of a new polyfluorinated alcohol 2-(1,1,2-trifluoro-2-heptafluoropropoxy-ethylsulfanyl)-ethanol (C3F7OCHF2SCH2CH2OH; FESOH) by assessing the kinetics and products of the gas phase reaction of FESOH with Cl and OH. Experiments performed in a stainless-steel environmental chamber interfaced to an FTIR were used to determine reaction kinetics and gas phase products. We report reaction rate constants of $k(\text{Cl} + \text{FESOH}) = (1.5 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{OH} + \text{FESOH}) = (4.2 \pm 2.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Gas phase products of FESOH oxidation included at least two different aldehydes as primary products, likely C3F7OCHF2SCH2C(O)H and C3F7OCHF2SC(O)H, and terminal products including COF2, SO2 and a prominent ester-type acyl fluoride C3F7OC(O)F. Direct oxidation of the sulfur atom could not be confirmed. Experiments performed in a Teflon chamber were used to assess aqueous products by collecting gaseous samples offline into an aqueous bubbler prior to analysis with ultra-high performance liquid chromatography-tandem mass spectrometry. Two larger acids were identified as primary degradation products, C3F7OCHF2SCH2C(O)OH and C3F7OCHF2S(O)(O)OH, along with two smaller acids that appear to be terminal degradation products, C3F7OCHFC(O)OH and F5C2C(O)OH.

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Chemistry of perfluoroalkyl substances (PFAS): Formation and fate of strong atmospheric acids

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Abstract: Perfluoroalkyl substances (PFAS) are anthropogenic chemicals produced for several industrial and commercial products. PFAS includes many chemical classes, including perfluorocarboxylic acids and perfluorosulfonic acids. Despite being strong acids ($\text{pK}_a < 1$), these chemicals are found ubiquitously in the environment, including in locations far from PFAS production and use. Several volatile commercial PFAS can oxidize in the atmosphere to form acidic PFAS. Using spatially- and temporally-resolved atmospheric deposition samples, we can better understand how atmospheric formation contributes to the global distribution of these strong acids. Results from ice cores from the Canadian Arctic will be presented, along with a latitudinal transect from eastern Canada. By analogy to other strong atmospheric acids, wet and dry deposition has been assumed to dominate the fate of acidic PFAS. By this same analogy, processes such as reactive uptake to secondary inorganic aerosol, mineral dust, or sea spray aerosol may contribute to the fate and transport of acidic PFAS. Analytical limitations have previously precluded laboratory studies. Using a new chemical ionization mass spectrometry approach, flow tube experiments were used to explore the importance of these processes. The implications of aerosol uptake for the atmospheric fate of PFAS will be discussed.

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The Wonderful World of Indoor Air Chemistry: Insights from a Detailed Chemical Model.

Nicola Carslaw

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Abstract: In developed countries, we have been estimated to spend about 90% of our time indoors, for instance at home, at work, or commuting between the two. It therefore follows that our exposure to air pollution, whether to pollutants generated indoors or outdoors, happens mainly in the indoor environment. Despite this fact, air pollution research still focuses largely on outdoors. Given the important role that photolysis plays in initiating photochemical reactions outdoors, there is an often-held view that indoor air chemistry can't be important as there is not enough light indoors. However, there is now firm evidence that indoor air chemistry does exist, and that it can be initiated by indoor lighting, but also by a range of other mechanisms including mediation by surfaces. The importance of indoor air chemistry has been suggested by models for many years now, but more recently, a wealth of experimental evidence has become available (e.g. through the HOMEChem project). The experimental data have confirmed some of our model predictions, but also shown that there is much we still need to understand, not least the role of the human occupant in modifying indoor air quality. This presentation will therefore focus on the insight that has been gained from using a model with a detailed chemical mechanism to understand the indoor air chemistry that arises from cleaning indoors, the presence of surfaces including humans and other common activities.

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A boron dipyrromethene (BODIPY) based probe for selective passive sampling of atmospheric HONO indoors

Seyed Danial Nodeh Farahani
Graduate Student, York Univeristy

Lightning Presentation Abstract: Nitrous acid (HONO), is suspected to be the major source of hydroxyl (OH) radicals in an indoor environment, the dominant oxidant in the ambient atmosphere. It can easily photodegrade even under low light conditions; thus, it is thought to potentially control oxidation chemistry in this environment. Indoor sources of HONO from combustion via a gas stove or smoking cigarettes can result in emission of up to 100 ppbv, similar to NO_x. In indoor environments it is important to measure the quantities at which HONO is present by using methods that are non-intrusive to the activities of people, so the NO_x quantities have been mainly measured by passive sampling techniques. Nitrous acid is a quantitative interference for these passive sampling techniques, such that a strong positive bias occurs in indoors. These two issues necessitate the development of more selective sampling methods not only to sample HONO but also provide a correction for these NO_x measurements. In this work, a highly absorbing, and 'turn-off' fluorescent ($\Phi=32.99\%$), amino-functionalized BODIPY-based probe ($\epsilon=26900$ 1/M.cm, $\lambda_{\text{max}}=496$ nm) was synthesized to sample HONO. The product is also highly absorbing ($\epsilon= 21500$ 1/M.cm, $\lambda_{\text{max}}=506$ nm) enabling very sensitive quantitation by UV-Vis spectroscopy. The probe reacts efficiently with nitrite in an acidic medium ($k=0.87$ M/s) and the product absorption maximum undergoes a red-shift of 10 nm. The results from sampling gaseous phase HONO will be discussed.

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Analysis of Indoor/Outdoor ultrafine particles inside a retirement community in São Paulo, Brazil, and the potential health risk

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Lightning Presentation Abstract: Air pollution has a range of adverse health's effects. Concerning urban population, elderly's are distinctly more susceptible to air pollution adversities compared to younger adults because of pre-existing health conditions. Thus, this work aims to evaluate indoor/outdoor ultrafine particles (UFP) and quasi-ultrafine (q-UFP) ($PM_{<0.25}$) concentrations in a retirement home in São Paulo, Brazil. The particle concentrations were collected daily (24 hours) using (Sioutas PCIS, SKC) for q-UFP and UFP were monitored by portable condensation particle counters (P-Trak model 8525, TSI Inc., MN, USA) for 6 hours during the day and the human health risk assessment including non-carcinogenic and carcinogenic risks was carried out according methodology proposed by EPA-USA on q-UFP. The UFP concentrations were on mean 2.3×10^4 and 1.2×10^4 particles/cm³ for winter and 1.7×10^4 and 0.8×10^4 particles/cm for autumn, on outdoor and indoor, respectively. On average, outdoor UFP levels exceeded indoor measurements by 9017 particles/cm³ (95% confidence interval (CI): 10337, 7697). For cancer risk assessment, Cr, Pb and Ni indexes were higher than acceptable for chronic scenario, which might pose cancer risk to elderly's health. Our results point out indoor PM concentrations effected by infiltrating of outdoor. This study propose the importance of controlling emissions of atmospheric pollutants, from both external and internal sources and the care with elderly, especially in nursing homes

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Auto-Oxidation Mechanisms of Volatile Silicon Compounds in the Atmosphere

Zhonghua Ren

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Lightning Presentation Abstract: Volatile silicon compounds (VOSiCs) are air pollutants present in both indoor and outdoor environments. We have been using ab initio and RRKM theory / master equation kinetic modelling to study the atmospheric chemical mechanisms of VOSiC oxidation. Silanes and siloxanes are shown to undergo auto-oxidation mechanisms, in which the intermediate alkoxy radicals rearrange from Si-CH₂O to Si-OCH₂ with a very low reaction barrier, then react with a second O₂. Addition of the second O₂ is predicted to lead to the formation of esters, which are known oxidation products of VOSiCs. The production of highly oxygenated compounds following a single radical initiation reaction has implications for the ability of VOSiCs to contribute to ozone and particle formation in both outdoor and indoor environments.

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Indoor photochemistry: development of reference sensitizers for singlet oxygen quantum yield measurements

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Lightning Presentation Abstract: Singlet oxygen (1O_2) is an oxidant which is present in hydrometeors and in aerosols in the atmosphere. 1O_2 is an energetically excited form of ground state molecular oxygen and is formed in solution through indirect photochemistry. The formation process involves excitation of brown carbon with light and an energy transfer from the excited brown carbon to ground state oxygen to form the singlet state. Our group has ongoing research projects to study the sources and sinks of singlet oxygen in the atmosphere, and we are exploring its potential presence in indoor air. The first step to address this question is to insure that the irradiance from indoor light sources is able to sensitize organic molecules.

To address this goal, we tested a list of reference compounds for different light sources including UVA and UVB light as well as indoor lightning, such as LED and fluorescent tubes. Our preliminary results show that there are sensitizers, e.g. 2-imidazolecarboxaldehyde and perinaphthenone, which could be used as reference sensitizers. Our results suggest that there could be 1O_2 sensitization occurring under indoor lightning conditions. This discovery hints that singlet oxygen can be formed also from indoor organic aerosols, such as from cooking or smoking, and we will present preliminary results on these experiments.

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GEOS-Chem as a community model for air quality on urban to global scales in the satellite era

Daniel Jacob

Professor, Harvard University

Abstract: The GEOS-Chem atmospheric chemistry model is presently used by hundreds of research groups around the world for a very wide range of applications from air quality to climate forcing and biogeochemistry. It is managed as an open grass-roots community model with emphasis on nimble innovation, strong version control, traceability, documentation, and ease of use. The GEOS-Chem chemical module containing the mechanism (~250 species plus optional aerosol microphysics) can be used off-line (with archived meteorology) or on-line (coupled to weather/climate models) and for simulations ranging from global down to the 1-km scale. The urban scale is accessed through coupling of GEOS-Chem to WRF (WRF-GC model). A new stretched-grid capability enables seamless simulations over scales ranging from urban to global. New numerical methods are being developed for fast chemical integration. The global scale of GEOS-Chem enables the model to target problems such as intercontinental pollution transport and mercury cycling, and allows for the interpretation of column measurements from satellites. GEOS-Chem is an active participant in the design of MUSICA, the new multiscale version of the NCAR CESM that will include options for switching between different mechanisms. This talk will summarize new developments and recent applications of GEOS-Chem to air quality problems in the US and in Asia.

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Multi-scale modeling of air quality and mechanism comparison with MUSICA

Louisa Emmons

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Abstract: To explore the various couplings across space, time and between ecosystems in a consistent manner, atmospheric modeling is moving towards a unification of the range of scales inherent in the Earth System. The Multi-Scale Infrastructure for Chemistry and Aerosols (MUSICA) is intended to become the next generation community infrastructure for simulating atmospheric chemistry and aerosols. MUSICA is being developed collaboratively by the National Center for Atmospheric Research (NCAR) and university and government researchers, with the goal of serving the international research and applications communities. Results from MUSICA Version 0, a configuration of the CAM-chem global chemistry climate model with variable resolution, from 1° for most of the globe to ~14km over the conterminous U.S., will be presented. MUSICA is being built upon the standalone Model Independent Chemistry Model (MICM) that has a flexible design to handle a variety of gas phase and aerosol schemes and associated chemical modules such as deposition or photolysis. A box model encompassing MICM (MusicBox) has also been developed. The comparison of MusicBox results from several chemical mechanisms of varying complexity will be presented.

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Using TROPOMI to assess nitrogen dioxide air pollution inequality in major U.S. cities

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Abstract: Low-income and people of color experience higher levels of air pollution in U.S. cities. In a recently published paper, we demonstrated that TROPOMI, onboard the sun-synchronous Sentinel-5P satellite, captures similar relative nitrogen dioxide (NO₂) inequalities at the census-tract-level in Houston, Texas compared to those of higher resolution sub-orbital remote sensing. Here we expand on that analysis, evaluating weekday-weekend NO₂ patterns in the winter and summer seasons to assess the roles of diesel trucking emissions and changes in the NO₂ lifetime in air pollution inequality. To do this, we apply a physics-based oversampling algorithm to the first two years of observations from TROPOMI (June 2018–February 2020), producing NO₂ maps at 0.01 degree x 0.01 degree resolution. We then combine these maps with demographic data at the census-tract level to calculate population-weighted NO₂ inequality as a function of race, ethnicity, and income. Cities in this work exhibit a variety of racial, ethnic, and income segregation patterns that are relevant for further air pollution inequality research and evaluation of policy initiatives and strategies.

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Low-cost sensor platform: an emerging tool for air quality studies

Lekan Popoola

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Abstract: Direct observations of air quality are vital to our understanding of the physical and chemical processes relevant to air quality. These measurements are important for epidemiological/exposure studies, pollution trends analysis, formulation of policies, and monitoring impact of interventions and compliance. Traditionally, direct observations rely mainly on reference instruments which although highly precise and accurate, are limited by several factors including the cost associated with installation and maintenance, low spatial information on air quality due to sparse network and limited temporal data. These techniques cannot readily be applied in personal exposure and epidemiological studies.

Recent advancement in low cost sensors has made it possible to design portable air quality devices that are readily deployed both as static and mobile (personal) network. In this presentation, we will present results from some low-cost air quality studies including Sensor Network for Air Quality (SNAQ) project at London Heathrow airport, the Air Pollution and Human Health (APHH) project in Beijing, China and the Breathe-London project (<https://www.breathelondon.org>).

We will also show results from a sophisticated air quality model (ADMS), demonstrating how low-cost air quality data are utilised in the model to provide enhanced backcasting and forecasting capabilities.

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Multiphase and in-particle processes affecting SOA formation from organic compounds oxidation

Jean-Francois Doussin

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Abstract: Our current knowledge of oxidation pathways and chemical composition of SOA is still limited and poorly understood considering the difficulty of the chemical transport model to predict the OA mass in the atmosphere. Above all, the formation of SOA is often considered as being totally driven by volatility of organic precursors and often represented as a one condensation step process.

In this context, the aim of this work is to study SOA formation from oxidation of “simple” precursors (eg. long chain alkanes) and to use these model compounds to investigate the sensitivity to different reaction pathways of organic matter, i.e. fragmentation, functionalization or oligomerization, during atmospheric oxidation. As a results, we show that, depending on environmental conditions, complex in-particle transformations can take place and lead to products of unexpected volatility. These chemical processes are then inducing oscillating exchanges between gas- and particulate- phase that impact aerosol production as well as composition.

Experiments were carried out in the CESAM chamber which allows experiments to be conducted at different temperatures and humidities at constant pressure and under a very realistic actinic flux.

Together with aerosol formation efficiencies, molecular composition of both gas- and particulate-phase are presented and further complemented by high resolution mass spectra analysis of aerosol samples. Finally, mechanisms explaining observation are discussed.

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Oxidation of anthropogenic hydrocarbons – “unimolecular” autoxidation vs sequential ageing

Matti Rissanen

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Abstract: Urban air pollution is among the most severe threats to population health and well-being, and poses one of the humanity's greatest challenges in keeping our living environments habitable. Gas- and particle-phase pollutants deteriorate air quality and, more often than not, result from anthropogenic activities. The pollutant soup is heavily influenced by rapid in-situ oxidation of emitted anthropogenic volatile organic compounds (AVOC), which form a multitude of gradually oxidised reaction products, and their subsequent nucleated particulates.

The whole concept of anthropogenic volatile organic compounds (AVOC) is arbitrary as the same molecules are generated by biogenic and man-made processes, and the term ultimately only highlights the fact that this is the burden we leave to the environment. Although the definition is arbitrary, AVOC are usually grouped as resonance stabilised aromatics and saturated, simple alkanes, which manifest very different oxidation chemistry.

Recently we performed laboratory investigations of atmospheric pressure AVOC (auto-)oxidation initiated by OH radicals in flow tubes, and to some extent also in chamber environments. Ambient sampling chemical ionization time-of-flight mass spectrometry was used for detection of various oxygenated reaction products. In addition, theoretical computations were employed to supply insight into key reaction steps which are almost impossible to scrutinise by empirical means.

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Automating the Search for New Pathways in Atmospheric Oxidation Chemistry

Victoria Barber

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Abstract: Reactive organic carbon in the atmosphere undergoes radical initiated oxidation in a highly complex, multigenerational process. These reactions are critical in the secondary production of key atmospheric species including secondary organic aerosol (SOA). In recent years, a number of "exotic" transformations not found in standard atmospheric oxidation mechanisms (e.g. Peroxy radical isomerization, epoxide formation) have been shown to be of great atmospheric importance. These discoveries suggest that there may be other non-traditional mechanisms that play a role in oxidative aging, and point to the need for a systematic way to look for them. The Reaction Mechanism Generator (RMG) is an open-source program, typically applied to combustion systems, which automatically develops reaction networks. Here, we use RMG to systematize and automate the search for new mechanisms in atmospheric organic oxidation. Reaction networks are generated for the OH-initiated gas-phase oxidation of a set of approximately 200 substituted pentanes under atmospherically relevant conditions. In addition to the canonical reactions expected for organic radicals in the atmosphere, a number of "exotic" reactions are identified. These include the recently explored reaction mechanisms described above, as well as examples of novel radical chemistry. The results demonstrate the utility of RMG as a tool for atmospheric reaction discovery, and provide several interesting targets for further study.

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Graph Theory and Atmospheric Chemistry

Sam Silva

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Abstract: Graph theoretical methods have revolutionized the exploration of complex systems across scientific disciplines. Here, we demonstrate their applicability to the investigation and comparison of three widely-used atmospheric chemical mechanisms of varying complexity: the Master Chemical Mechanism v3.3, GEOS-Chem v12.6, and the Super-Fast chemical mechanism. We investigate these mechanisms using a class of graphical models known as species-reaction graphs and find similarities between these system of chemical reactions and other systems arising in nature. There are several properties of these graphs that are consistent across all mechanisms, including the strong disequilibrium of the dynamical system and clustering of chemically-related species. This formalism also reveals key differences between the mechanisms; for example, isoprene and peroxy radical chemistry exhibit substantially different graph properties in each mechanism. Graph theoretical methods provide a promising set of tools for investigating atmospheric chemical mechanisms, complementing existing computational approaches, and potentially opening new avenues for scientific discovery.

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A diagnostic package to facilitate and enhance chemical mechanism implementations within regional and global atmospheric chemistry models

Julie Nicely

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Lightning Presentation Abstract: We present plans to develop a machine learning-based diagnostic and emulator software package, aimed at understanding, inter-comparing, and condensing or replacing air quality model chemical mechanisms. We will discuss fundamental work leading up to this project, including use of neural networks to diagnose global model differences in short-lived radical concentrations and application of regression trees to predict evolution of an entire gas-phase chemical system. We will share approaches to designing this novel package, intended uses for the diagnostics, and possible applications of the emulator modules. Although this project is still in its infancy, we are eager to gather feedback on how this tool could best serve the interests of the atmospheric chemical mechanism and air quality modeling communities.

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Trace gases and organic aerosol at a rural site in Vietnam during large scale biomass burning

Simone Pieber

Postdoctoral Scientist, Empa

Lightning Presentation Abstract: Open biomass burning (BB) is a globally widespread phenomenon. The fires release pollutants harmful for human and ecosystem health and alter the Earth's radiative balance. Yet, the impact of various types of BB on the global radiative forcing remains poorly constrained concerning greenhouse gas emissions on the one hand, and BB organic aerosol (OA) chemical composition and related light absorbing properties on the other hand. Fire emissions composition is influenced by e.g., fuel and thereby vegetation-type, fuel moisture, fire temperature, available oxygen, and, due to regional variation, studies in different world regions are needed. Therefore, we investigate the influence of seasonally recurring BB on trace gas concentration and air quality at Pha Din (PDI) in rural Northwestern Vietnam (see Bukowiecki N., et al., AAQR, 2019). PDI is located in a sparsely populated area on the top of a hill (1466 m a.s.l.) and well-suited to study the large scale fires on the Indochinese Peninsula. We present continuous trace gas observations of CO₂, CH₄, CO, and O₃ conducted at PDI since 2014 during recurrent BB, and interpret the data with atmospheric transport simulations. We complement this analysis with carbonaceous PM_{2.5} chemical composition analyzed during an intensive campaign in March-April 2015, which includes measurements of EC/OC and more than 50 organic markers, such as sugars, PAHs, fatty acids and nitro-aromatics (Nguyen D.L., et al., in prep. for submission to ACPD).

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PRECIPITATION CHEMISTRY IN A BRAZILIAN RURAL AREA: ALKALINE SPECIES BEHAVIOUR AND AGRICULTURAL INPUTS

Jaqueline Pereira

Master student, Universidade Federal de Lavras

Lightning Presentation Abstract: Since 2000s, several studies have been reporting an increase of alkaline species in atmospheric deposition worldwide. This study aims to evaluate and give a better understanding about precipitation chemistry collected in Lavras, a Brazilian city with rural background. Bulk atmospheric deposition samples were collected from March 2018 to February 2019 and major ionic species were quantified. The pH values ranged from 5.52 to 8.29, with an average of 5.92 and most deposition samples (~94%) were alkaline ($\text{pH} > 5.60$). For the whole sampling campaign, the ions profile in volume weighted mean (VWM) was described as follows: Ca^{2+} (35.02) > NH_4^+ (11.26) > Cl^- (11.19) > Mg^{2+} (9.04) > NO_3^- (8.57) > Na^+ (5.65) > K^+ (2.61) > SO_4^{2-} (2.43) > H^+ (0.94) μmolL^{-1} . We identified Ca^{2+} and NH_4^+ as the most predominant species accounting for 53% of the total ionic species distribution. In addition, all samples showed neutralization factor (NF) higher than 1, with mean of 6.4. Regarding regression analysis, acidity neutralization precursors such as calcium and ammonia accounted for 50% and 4%, respectively. In order to identify the sources and atmospheric processes for the ionic compounds, we applied Principal Component Analysis (PCA). PCA produced 3 significant principal components, which explained 84% of the data variation. In general, the analysis suggested different scenarios for the sources, such as soil, agricultural activity, cement manufacturing and atmospheric processes neutralization.

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The development and application of HOM formation mechanisms for use in atmospheric models – updates, improvements and challenges

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Abstract: Highly oxygenated organic molecules (HOM) have been shown to be important for secondary organic aerosol (SOA) formation as well as new particle formation (NPF). HOM refers to a group of compounds produced through gas-phase autoxidation, which involves isomerization reactions of peroxy radicals (RO₂), allowing for the rapid addition of oxygen. HOM formation has been observed from all major atmospheric volatile organic compound (VOC) groups, including monoterpenes, aromatics and alkanes.

However, the detailed formation pathways remain elusive, largely because the reactions are complex, and occur in timescales and concentrations that are not easily accessible by existing instrumentation. Still, empirical parametrizations are finding their way into atmospheric chemistry transport models, and have been shown to improve measurement-model agreement.

It is an open question, to what extent the autoxidation potential of different VOC can be generalized into simple parametrizations. I will discuss recent findings on this topic, with examples from the most well-studied system of alpha-pinene ozonolysis, using both computational methods as well as various isotopic labeling experiments. These results confirm that the autoxidation pathways are extremely structure-dependent, and the rates and HOM yields will likely be very hard to extrapolate between VOC, even within compound groups with relatively similar structures, such as monoterpenes.

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GACM: Global Atmospheric Chemical Mechanism

Emily Saunders

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Abstract: The Global Atmospheric Chemical Mechanism (GACM) is the global version of the Regional Atmospheric Chemistry mechanism, version 2 (RACM2) and it was created to be chemically consistent with RACM2. To consider the marine environments that would be simulated with GACM marine chemistry reactions (i.e. Cl, Br, and I) were included into the mechanism. To maintain a compact size for GACM some volatile organic compound (VOC) chemistry was simplified to make room the additional marine chemistry and to maintain computational efficiency. GACM will be applicable to current global models and to be used in conjunction with RACM2 based modeling systems to more accurately predict the concentrations of pollutant species formed in highly polluted urban local and global communities across the nation and globe. The compatible VOC results from all model runs for RACM2 and GACM showed how both mechanisms would work in a global-regional modeling system, when using GACM provided boundary conditions. Improved global atmospheric chemistry models with GACM can be used to supply better initial and boundary conditions to regional air quality models that use RACM2 because GACM and RACM2 are designed to be highly compatible representations of atmospheric chemistry.

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The Importance of More Complex Isoprene and Terpene Chemistry for Simulating Surface Ozone in the Southeastern U.S. at Varying Horizontal Resolutions

Rebecca Schwantes

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Abstract: Ozone is a greenhouse gas and air pollutant that is harmful to human health and plants. During the summer in the southeastern U.S., many models are biased high for surface ozone compared to observations. Here, due to the high biogenic emissions in the southeastern US, more comprehensive and updated isoprene and terpene chemistry is added into CESM/CAM-chem (Community Earth System Model/Community Atmosphere Model with full chemistry) to evaluate the impact of chemistry on simulated ozone. A new configuration of CESM/CAM-chem has also been developed with the capability of regional refinement down to 14 km over the continental U. S. This new configuration along with the updated isoprene and terpene chemistry allows us to evaluate how horizontal resolution and chemical complexity impact ozone, ozone precursors, and NO_x reservoir compounds as compared to observations from the SEAC4RS (Studies of Emissions, Atmospheric Composition, Clouds, and Climate Coupling by Regional Surveys) aircraft campaign. We highlight the importance of chemical complexity in accurately simulating surface ozone at varying horizontal resolutions and in particular at finer horizontal resolutions where processes and emissions are better resolved. The chemical mechanism, MOZART-TS2, developed in this work is fully incorporated into the newest release of CESM2.2 and can be easily adapted for other atmospheric chemistry models as well.

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Intercomparison and optimization of aromatic oxidation mechanisms

Kelvin Bates

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Abstract: Aromatic hydrocarbons can account for a dominant fraction of ozone formation in urban and semi-urban areas, but the mechanisms used to represent their oxidation chemistry in global models are often highly simplified. Here, we use box model simulations to compare key outcomes of the oxidation cascades of benzene, toluene, and xylene (BTX) across a variety of published mechanisms (GEOS-Chem, MCM, MECCA, MOZART, RACM2, and SAPRC). We examine the effects of aromatic oxidation on ozone formation, oxidant cycling, and the yields of key VOC products (e.g. formaldehyde and glyoxal). We simulate oxidation in both ambient conditions and environmental chambers, and compare product yields from the latter to those from previous chamber studies. Using results from these simulations, we construct a new reduced mechanism for BTX oxidation, which adequately captures the key outcomes of interest with minimal computational burden, and show results from its implementation in GEOS-Chem, a global chemical transport model.

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Kinetic neural networks for atmospheric chemistry surrogate modeling

Christopher Tessum

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Abstract:

Atmospheric chemistry models—used as components in models that simulate air pollution and climate change—are computationally expensive. Previous studies have shown that machine-learned atmospheric chemical solvers can be orders of magnitude faster than traditional integration methods but tend to suffer from numerical instability. Here, we present a neural-network framework with an inductive bias specifically tailored for predicting atmospheric chemical kinetics. When this model is trained and tested on 10-day atmospheric chemical time series (randomly-initialized with typical atmospheric concentrations), it is accurate to within 16ppb in 90% of test cases and never experiences runaway error propagation. The same model (trained on 10-day time series) can also simulate 365 day time series, still without experiencing the runaway error propagation that has plagued previous efforts. Further research is required to test the performance of this framework within a full atmospheric model.

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Atmospheric Autoxidation of Amines

Kristian H. Møller

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Abstract: Autoxidation has been acknowledged as a major oxidation pathway in a broad range of atmospherically important compounds including isoprene, monoterpenes and very recently dimethyl sulfide (DMS). Using high-level theoretical multi-conformer transition state theory, we study the potential for atmospheric autoxidation in amines exemplified by the atmospherically-important trimethylamine (TMA) and dimethylamine (DMA) and generalized by the study of the larger diethylamine (DEA). For all, we find that the initial hydrogen shift reactions have rate coefficients greater than 0.1 s^{-1} and are thus able to compete with the bimolecular reactions. For TMA, this new oxidation pathway is found to dominate its reactivity under most atmospheric conditions. The amine autoxidation efficiently leads to the formation of hydroperoxy amides, a new type of atmospheric nitrogen containing compounds, and for TMA, we experimentally confirm this. The conversion of amines to hydroperoxy amides may have important implications for nucleation and growth of atmospheric secondary organic aerosols (SOA) and atmospheric OH-recycling.

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Evolution of OH reactivity in low-NO volatile organic compound photooxidation investigated by the fully explicit GECKO-A model

Zhe Peng

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Abstract: The evolution of OH reactivity (OHR) during volatile organic compound (VOC) oxidation is not well understood. We use the fully explicit GECKO-A model to study the OHR evolution in the low-NO oxidation of several VOCs. Total OHR (including precursor and products, OHRVOC) first increases for decane and m-xylene, as more reactive species are formed. For isoprene, C=C bond consumption leads to a rapid drop in OHRVOC before significant epoxydiol production. The saturated multifunctional species in the oxidation of different precursors have similar average OHRVOC per C atom. The latter oxidation follows a similar course for different precursors, involving multifunctional species fragmenting to C1 and C2 and oxidation to CO₂, leading to a similar evolution of OHRVOC per C atom. The total OH consumption during complete oxidation is ~3 per C atom. We show that differences in the OHRVOC evolution between the atmosphere, a chamber and an oxidation flow reactor (OFR) can be substantial, but are generally smaller than between precursors. Wall losses of oxygenated VOCs in chambers result in substantial deviations of OHRVOC from atmosphere, especially for the oxidation of larger precursors, where multifunctional species may suffer near-complete wall loss. For OFR, the deviations of OHRVOC evolution from the atmosphere are mainly caused by low HO₂-to-OH ratio that delays the conversion of rapidly produced RO₂ to stable products, and by lack of efficient organic photolysis.

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Towards a full representation of alkene ozonolysis for atmospheric chemistry modeling

Mike Newland

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Abstract: The reaction of alkenes with ozone produces Criegee intermediates (CI). In the atmosphere, these short-lived reactive species are an important non-photolytic source of radicals, participate in aerosol formation, and can themselves act as atmospheric oxidants.

In recent years there has been extensive progress on understanding the bimolecular reactions of stabilised CI with typical atmospheric trace gases. This has been facilitated by the use of photo-labile diiodo precursors. However, many kinetic and mechanistic uncertainties remain with respect to the formation of SCI species, as well as the generally accepted mechanism of alkene ozonolysis itself.

The ozonolysis system proceeds through a number of steps: from decomposition of the energy rich primary ozonide to give CI, that can be formed as syn or anti conformers with very different atmospheric fates; to the fraction of CI that are stabilised or undergo prompt decomposition / isomerisation. Each of these steps currently carries a large uncertainty, complicating the modelling of the full impact of alkene ozonolysis chemistry on atmospheric composition.

In this work we review the existing understanding of the dependencies of each of these steps, and look forward to what can be done to develop a full structure activity relationship of alkene ozonolysis chemistry for inclusion in automatic chemical mechanism generators such as MCM/GECKO-A.

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A recursive neural network chemical solver for fast long-term global simulations of atmospheric composition

Makoto Kelp

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Lightning Presentation Abstract: Numerical integration of chemical mechanisms in global models of atmospheric composition has relied on the application of implicit solvers to the stiff high-dimensional system of ordinary differential equations describing the mechanism, but this is computationally expensive. Machine-learned (ML) atmospheric chemical solvers can offer orders-of-magnitude speedup but past implementations have suffered from numerical instability and fast error growth. Here we explore the capability of ML methods for stable long-term global simulations of atmospheric composition by emulating the 15-species ‘Super-Fast’ chemical mechanism previously implemented in climate models. Our ML method uses an innovative multi-step recursive neural network algorithm to capture slower chemical modes and limit error growth, and an encoder/decoder to improve the ML fit over lower-dimensional manifolds. We implement the Super-Fast mechanism in the GEOS-Chem global 3-D atmospheric chemistry model for full-year simulations. We evaluate the ability of the ML method to reproduce the results from the standard 4th-order Rosenbrock solver in GEOS-Chem over varying time horizons from 1 week to 1 year. Preliminary results show that we are able to achieve +/- 10% accuracy for tropospheric ozone and are able to capture the transient spatiotemporal variability of the radicals driving chemical evolution.

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Mechanical study of toluene oxidation: development of a simplified chemical scheme for SOA formation

Victor Lannuque

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Lightning Presentation Abstract: Toluene is one of the main organic compounds emitted by road traffic. Innovative measurements of secondary organic aerosol (SOA) formation were carried out in an aerosol flow tube reactor (AFT) to determine the speciation of SOA from toluene oxidation in both the gas and condensed phases, under different environmental conditions of humidity and temperature.

In order to identify the reaction pathways driving SOA formation, we attempt to reproduce as closely as possible these toluene oxidation experiments with the SSH-aerosol box model (<https://github.com/sshaerosol/ssh-aerosol/releases>). SSH-aerosol represents the physicochemical transformations undergone by aerosols in the troposphere by (i) simulating the dynamics and the mixing state of atmospheric particles and (ii) calculating the partition of organic and inorganic compounds taking into account different processes (hygroscopicity, absorption in the aqueous phase of particles, etc.).

The RACM2 chemical scheme is modified and used in order to reproduce the experimental conditions in the AFT reactor. A simplified chemical scheme for toluene oxidation is developed to (i) identify the major species; (ii) better reproduce the speciation and concentrations observed in the different phases and (iii) identify the main pathways for SOA formation. This scheme is mainly based on those of MCM-v3.3.1 and GECKO-A, which are simplified and modified to take into account observations made by previous studies on toluene oxidation.

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Mechanistic Insights into the Night-time Chemistry of Isoprene

Alfred Mayhew

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Lightning Presentation Abstract: Although isoprene is the most highly emitted biogenic volatile organic compound (BVOC), its reaction with the nitrate radical (NO_3) is poorly understood, particularly when considering reactions beyond the initial oxidation steps. The work presented outlines efforts to combine existing isoprene oxidation mechanisms, as well as incorporating new chemistry of the secondary NO_3 oxidation of initial products. The mechanism produced was employed in box model simulations of a series of experiments performed in the SAPHIR Chamber designed to investigate the night-time chemistry of isoprene, including particle formation and growth. Comparisons of model outputs using the Master Chemical Mechanism (MCM) and Caltech Isoprene Mechanism show substantial differences in the temporal evolution of primary isoprene oxidation products, as well as in concentrations of HO_2 and OH . A hybrid mechanism combining the strengths of the two mechanisms has been developed to evaluate the chamber experiments. This work highlights areas where improvements are needed in current mechanisms with regards to the treatment of NO_3 chemistry, and indicates potential routes to an improved understanding of the night-time chemistry of isoprene in the atmosphere.

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Impacts of mechanistic changes in the oxidation of dimethyl sulfide on tropospheric chemistry and climate

Alexander ARCHIBALD

Reader, University of Cambridge & NCAS-Climate

Lightning Presentation Abstract: Dimethyl sulfide (DMS) is the most abundant naturally occurring sulfur compound emitted in the atmosphere. For the past five decades researchers have questioned the role that DMS plays in natural biogeochemical cycles, with no clear consensus. During this time our understanding of the chemistry of DMS has evolved with the recent discovery of unimolecular oxidation steps providing a paradigm shift. These autoxidation steps result in the formation of hydroperoxy methyl thio formate (HPMTF) which has been observed throughout the troposphere thanks to measurements made as part of the NASA ATom project. These measurements highlight that HPMTF may be formed as a major oxidation product of DMS and provide a challenge for the chemistry climate modelling community, as the fate of HPMTF is currently unknown.

In this talk we will review the current status of DMS chemistry in the wake of the discovery of autoxidation. We use a series of simulations with the UKCA model to investigate the impacts of improved representation of DMS chemistry in chemistry-climate models and to highlight key uncertainties in the DMS mechanism that require further work.

Additional Authors: Beatrice Cala (University of Cambridge), N. Luke Abraham (University of Cambridge & NCAS-Climate).

Ozone trend and its response to emission reductions in the South Coast of California

Chenxia Cai

Abstract: The South Coast Air Basin (SoCAB) of California is a region with a historically severe ozone (O₃) air quality issue. For many years, much of the SoCAB has been in a VOC limited chemical regime due to high NO_x emission and O₃ peaks are often higher on weekends despite lower NO_x emissions on those days. From year 2000 to 2020, the anthropogenic emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in SoCAB have been reduced by 70% and 55%, respectively, leading to a significant decrease in O₃ concentrations. The long term weekend to weekday ratio for O₃ has been steadily decreasing and is nearing 1 over the past few years. VOC emissions from natural sources such as biogenic emissions show strong seasonal variations. While in winter and spring, the biogenic VOC emissions are generally low, during the summer season VOC emissions from biogenic sources are comparable to those from anthropogenic sources in SoCAB. As a result, the O₃ response to emission reductions also show seasonal variabilities. Utilizing air quality model simulations along with satellite and ground based observations, we investigate the impact of COVID19 pandemic on the O₃ concentrations in SoCAB especially the potential causes for enhanced O₃ observed during the end of April and beginning of May in 2020. Further model analysis are conducted for spring and summer 2017 to illustrate how O₃ may respond to the same emission reduction in different seasons. Overall, both model simulations and observations show the SoCAB is gradually transitioning to a NO_x limited regime for O₃ formation.

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Persistent heavy winter nitrate pollution driven by increased photochemical oxidants in northern China

Tao Wang

Chair Professor, Hong Kong Polytechnic University

Abstract: Severe winter haze occurs frequently in northern China. Nitrate (NO_3^-) is a key and increasingly important component of fine particulate matter in haze events. Emission control measures in the past decade have been ineffective in reducing the winter nitrate concentrations. In this study, we use extensive regional observations and a model with state-of-the-art reactive nitrogen chemistry to identify the key factors that control the nitrate formation in the heavily polluted North China Plain (NCP). In contrast to the previous view of weak photochemistry in winter, we show that the productions of O_3 and OH are sufficiently high in winter to facilitate fast gas-phase and heterogeneous conversion of NO_x to NO_3^- over the NCP. Increasing O_3 and OH productions, from high levels of precursors (e.g. HONO) and fast ROX cycling, accelerate the nitrate generation during severe winter pollution episodes. We find that $\sim 32\%$ reduction of NO_x emissions from 2010 to 2017 in the NCP lowers the average surface NO_3^- concentrations by only 0.2% , and even leads to an increase of NO_3^- in some polluted areas. This is mainly due to the increase of O_3 and OH (by $\sim 30\%$), which has subsequently increased the conversion efficiency of NO_x to HNO_3 (by $\sim 39\%$). Future control strategies for the winter haze in the NCP should also aim to lower photochemical oxidants, via larger and synchronized NO_x and VOCs emissions reduction, to overcome the effects of non-linear photochemistry and aerosol chemical feedback.

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An odd oxygen framework for assessing NO_x and VOC emission controls to reduce wintertime ammonium nitrate pollution

Caroline Womack

Research Scientist, CIRES/NOAA CSL

Abstract: The Salt Lake Valley and the surrounding regions in northern Utah experience poor wintertime air quality during persistent cold air pool events (PCAPs). During a PCAP, emissions are trapped near the surface by warmer air aloft, stagnant winds, and mountainous topography. The emissions build up over many days and react to form PM_{2.5}, primarily in the form of ammonium nitrate. Reduction of this pollution requires a detailed understanding of the chemical processes that lead to ammonium nitrate aerosol formation via nitric acid (HNO₃). Using observations from the 2017 Utah Winter Fine Particulate Study (UWFPS), a photochemical box model, and a new definition of total odd oxygen that includes nighttime species and particulate nitrate, we demonstrate that formation of HNO₃ is NO_x-saturated and VOC-sensitive. This implies that efforts to reduce only NO_x emissions may initially worsen the PM_{2.5} pollution in Salt Lake City, and that VOC emission reductions would be more immediately effective. We also discuss how using this framework can elucidate chemical mechanisms in other regions that experience poor wintertime air quality.

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The Influence of Chemical Feedbacks on Wintertime Air Quality's Response to Emissions Reductions

Lyatt Jaeglé

Professor, University of Washington

Abstract: The past decade has seen dramatic reductions in anthropogenic SO₂ and NO_x emissions in the United States: 68% decrease in SO₂ emissions and 36% decrease in NO_x emissions between 2007 and 2015. Surface observations show that emission regulations have resulted in a ~30% decrease in PM_{2.5} concentrations in the NE US over that period. However, most of this decrease has occurred in summer, with winter trends being much weaker than summer trends. Thus, despite great effort invested in anthropogenic emission reductions, the air quality benefits in terms of PM_{2.5} reduction have been elusive in winter. During that season, formation of SO₄²⁻--NO₃⁻--NH₄⁺ PM_{2.5} from emitted precursors is governed by strong feedbacks depending on limited oxidant availability, cloud-water chemistry, and gas-particle partitioning. I will discuss some of our work using extensive airborne observations over the eastern United States from the 2015 Wintertime Investigation of Transport, Emissions, and Reactivity (WINTER) campaign; ground-based observations; and the GEOS-Chem chemical transport model to determine the controls on winter PM_{2.5} and its response to chemical feedbacks.

Additional Authors: Viral Shah (Harvard University), Joel Thornton (University of Washington), and WINTER Science Team

Comparing the Air Quality Impacts of Electrification and Gaseous Renewable Fuels

Michael MacKinnon

Senior Research Scientist, Advanced Power and Energy Program, UC Irvine

Abstract: Given the climate goals established in California, major transitions to strategies including electrification and renewable fuels will be required to meet targets. Technology assumptions within long-term low-carbon scenarios will also impact criteria pollutant emissions quantitatively, spatially, temporally, and in composition; all of which influence primary and secondary pollutant species including ozone and PM_{2.5}. Various viable technological and fuel pathways exist, and it is unclear which might be optimal in terms of associated metrics including air quality co-benefits. We characterize and quantify air quality and health impacts for a set of low-carbon scenarios in 2050 to provide insight into air quality co-benefits. A focus of this work is comparing the use of electrification and renewable gaseous fuels in different end-use sectors, including residential and commercial buildings and transportation. Output from the California PATHWAYS model is used to project emissions to 2050 which are then used as input into the CMAQ model to resolve impacts on ozone and PM_{2.5}. Pollutant changes are then translated into health impacts via BenMAP. Building electrification is found to improve air quality and public health outcomes, particularly in winter when reduced NO_x yields improvements in secondary PM_{2.5}. In contrast, the use of renewable gaseous fuels may be most effective in reducing GHG emissions from sectors that are harder to electrify including industry and transportation.

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How Much Further Do NO_x Emissions Need to Decrease Before We Achieve Ozone Benefits in California?

Michael Kleeman
Professor, UC Davis

Abstract: Model calculations and satellite measurements both suggest that major California cities are often in a regime where decreasing NO_x concentrations lead to higher O₃ concentrations. Continued NO_x reductions should eventually lead to a maximum O₃ concentration followed thereafter by O₃ reductions (benefits). The amount of NO_x control needed to achieve O₃ benefits is highly uncertain. Here we describe a unique measurement campaign involving three identical smog chambers operated in parallel to directly measure how O₃ responds to NO_x and VOC perturbations. Chambers are loaded with ambient air in late morning on each measurement day. Approximately 8 ppb of NO_x (as NO₂) is added to one of the chambers, and approximately 8 ppb of representative VOC is added to a second chamber. The third chamber acts as a control for comparison. All chambers are exposed to UV light typical of midday conditions in California during the summer for three hours. Final O₃ concentrations at the end of the experiment are compared to show the effects of NO_x and VOC perturbations. O₃ sensitivity measurements made in Sacramento from April – September 2020 will be discussed in this presentation. Day of week patterns for O₃ sensitivity will be identified, along with longer-term trends throughout the summer. The effects of wildfires on O₃ sensitivity will also be quantified. Finally, the implications for O₃ control programs will be discussed.

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Molecular mechanisms behind the health impacts of several organic aerosol components

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Abstract: adverse health effects leading to death. In this work, we studied the direct impacts of an OA model (i.e. fulvic acid (FA)) and three OA components; benzo[a]pyrene diol epoxide (BPDE), hopane (HOP), and 9,10-phenanthrenequinone (PQ). These are known for cytotoxic effects, but their detailed mechanism of action is not known. Metabolic analysis showed that BPDE, HOP and PQ can interrupt some metabolic pathways, but the low bioavailability of FA restricts its negative health effects. Molecular docking simulation revealed that just BPDE and PQ have the potential of wide distribution in human body and binding to DNA. Quantum chemical analysis of the ligand-DNA binding modes suggested that adenine nucleobases are more susceptible to mutation by the OA components. Further, detailed mechanistic evaluations at the ω B97X-D/def2-TZVP level under cell-like conditions (SMD water model, 310 K and 1 atm) indicated that PQ can undergo DNA adduct formation with adenines through the Michael addition mechanism, while BPDE cannot form any adduct following Michael addition or nucleophilic substitution. Similar quantum chemical calculations determined the oxidative cytotoxicity potential of both BPDE and PQ. However, the reaction energy profiles suggested that additional enzymatic contributions should be involved in the oxidative stress and DNA adduct formation processes.

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How Reactive Organic Carbon Fuels Atmospheric Chemistry

Colette Heald

Professor, MIT

Abstract: Organic molecules in the atmosphere play a major role in the production of secondary pollutants such as ozone and particles. These in turn, are central to some of the major environmental issues of our times (climate change, air pollution). Despite the vital role that these species play in our global environment, our understanding has been hampered by the complexity of this class of species and a fractured approach to studying their chemical evolution. In this talk I'll discuss the overall role of ROC in tropospheric chemistry, as well as recent progress and remaining challenges in understanding this role. I will also use field measurements from the CalNex, SOAS, and ATom field campaigns to contrast the abundance and role of ROC in terms of OH reactivity, ozone and SOA production.