

A61A-0069 0830h POSTER

Measurement of Total Non-volatile and Semi-volatile Organic Carbon Associated with PM2.5 in Vancouver during Pacific 2001

Xinghua Fan¹ (1-416-946-7736; xfan@chem.utoronto.ca)Jeffrey R. Brook² (1-416-739-4916; Jeff.Brook@ec.gc.ca)Scott A. Mabury¹ (1-416-978-1780; smabury@chem.utoronto.ca)¹ University of Toronto, 80 St. George St., Toronto, ON M5S 3H6, Canada² Environment Canada, 4905 Dufferin St., Toronto, ON M3H 5T4, Canada

The behavior and chemical speciation of organic carbon (OC) is one of the poorest understood aspects of fine particulate matter (i.e., PM_{2.5}). In the Lower Fraser Valley, which was the region studied during Pacific 2001, understanding OC is especially important because it is the dominant fine particle component. Accurate determination of the concentration of OC is difficult due to the lack of appropriate sampling methods. Traditional samplers such as a filter pack (FP) have inherent artifacts during sampling, which leads to underestimates of the actual particle phase OC during some conditions and overestimates in other cases. In our study, a denuder-based integrated organic gas and particle sampler (IOGAPS) was employed. The IOGAPS is able to reduce the sampling artifacts, since the gas phase organics are removed first by the denuder placed upstream of a quartz filter while the semi-volatile organic carbon (SVOC) evaporated from the particles is collected by backup sorbent impregnated filters (SIFs). Both denuder and SIF are coated with XAD resin to retain organics. The quartz filter and the SIF can be analyzed directly for non-volatile OC and SVOC, respectively, using thermal-optical transmission analysis. This sampling and analysis method was tested in Toronto in July 2001 and then applied at the urban site (Slocan Park) on seven days during Pacific 2001. In both locations, samples were collected twice a day to investigate the diurnal pattern of OC, SVOC and EC. Compared with the OC determined by the filter pack sampler, lower OC on the quartz filter of the IOGAPS confirmed that the denuder could efficiently remove positive artifacts. Higher nighttime SVOC levels were observed in both cities, suggesting that more of the SVOC from primary sources and secondary formation condenses onto particles at night due to the decreased ambient temperature. At Slocan Park, the amount of the total particle phase OC found to be SVOC ranged from 0% to 32% during the day and 2% to 27% during the night.

A61B MCC: Hall D Saturday 0830h

Oxygenated VOCs II: New Developments Posters

Presiding: R J Yokelson, University of Montana; S Paulson, University of California, Los Angeles

A61B-0070 0830h POSTER

Direct Emission of Methylvinylketone from Birch (*Betula pendula*)Achim Folkers¹ (x49-(0)2461-618679; a.folkers@fz-juelich.de)Ralf Koppmann² (x49-(0)2461-615118; r.koppmann@fz-juelich.de)Jürgen Wildt¹ (x49-(0)2461-618684; j.wildt@fz-juelich.de)¹ ICG-III: Phytospäre, Forschungszentrum Jülich, Jülich 52425, Germany² ICG-II: Troposphäre, Forschungszentrum Jülich, Jülich 52425, Germany

Volatile organic compounds (VOCs) are of central importance for the chemistry of the troposphere. They have a significant impact on photochemical processes that lead to the formation of ozone and other photooxidants in the planetary boundary layer. With estimated global emission rates of 520 Tg yr⁻¹ [Guenther *et al.* 1995], biogenic emissions of short chained oxygenated VOCs (SOVOCs) like methanol, ethanol, acetaldehyde, and acetone cannot be neglected for atmospheric chemistry. In addition to the direct emissions by plants SOVOCs are produced by chemical reactions of VOCs in the atmosphere. For some SOVOCs such as methanol, acetone, or leaf alcohols it is known

that they have a large biogenic source strength. Other SOVOCs are believed to be only produced by atmospheric processes. For example methacrolein, and methylvinylketone (MVK) are believed to be exclusively produced during atmospheric isoprene oxidation. Thus, up to now the only known source of MVK in the atmosphere is the oxidation of VOCs like isoprene.

We analysed SOVOC emissions from different plant species under well defined conditions in our plant chambers and determined the temperature- and light intensity dependence of their emission rates. During these measurements we also observed a direct MVK emission from birch. The emission rates exhibit a temperature and light intensity dependence. Artificial MVK formation was excluded by a series of experiments. Due to the direct emission of MVK probably also from other plant species than birch, measurements of ambient concentrations of this compound have to be carefully investigated. The fact that there may be a primary source for MVK has to be considered in model calculations concerning the photochemistry and the concentrations of OH radicals in the lower troposphere.

References

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klünger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P. (1995), A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, **100**, 8873-8892.

A61B-0071 0830h POSTER

Bimolecular Reaction of SO₂ with Thermalized Syn Carbonyl Oxide from Isoprene OzonolysisDan Zhang¹ (979-458-1822; dzhang@ariel.met.tamu.edu)Renyi Zhang¹ (979-845-7656; zhang@ariel.met.tamu.edu)¹ Department of Atmospheric Sciences, Texas A&M University, College Station, TX 77843

Cycloaddition of O₃ to isoprene yields carbonyl oxides consisting of chemically activated syn and anti configurations. The excited carbonyl oxides then undergo prompt unimolecular isomerization or collisional stabilization. Prompt reaction of syn or anti carbonyl oxides has been shown to be a source of hydroxyl radical OH. The thermalized syn carbonyl oxides also decompose to form OH or engage in bimolecular reactions with SO₂, H₂O, CO₂, aldehydes, etc. The reaction with SO₂ can contribute to oxidation of SO₂ to H₂SO₄, a crucial step in the formation of sulfate aerosols. In order to assess the role of isoprene ozonolysis in OH formation and SO₂ oxidation, we have performed a theoretical study of the bimolecular reaction between syn carbonyl oxide and SO₂. A mechanism involving the addition of SO₂ to carbonyl oxide, followed by decomposition pathways leading to SO₃ formation is proposed. Rate constant of each reaction step is evaluated based on Transition State Theory and compared with other competing reactions in atmospheric SO₂ oxidation. The results reveal a profound impact of the title reaction on SO₂ oxidation and OH formation yield from isoprene ozonolysis under atmospheric conditions.

A61B-0072 0830h POSTER

Quantification of Carboxylic Acid Formation from the Reaction of Ozone with Alkenes

Suzanne Paulson¹ (3102064442; paulson@atmos.ucla.edu)Grazyna Orzechowska¹ (paulson@atmos.ucla.edu)Ha Nguyen¹¹ Dept. of Atmospheric Sciences, UCLA, 7127 Math Sciences, Los Angeles, CA 90095-1565, United States

This study focuses on identification and quantification of carboxylic acids from the ozonolysis of C₃ to C₁₀ alkenes under dry and humid conditions. Analysis was performed using solid phase microextraction for smaller simple acids, and in-inlet derivatization for larger and multifunctional acids. Both techniques were used in conjunction with GC/FID/MS. Acid yields from 2 to 10 percent were observed. Yields decreased somewhat at higher humidities, indicating that the water reaction with the so-called stabilized Criegee intermediate is not the source of acids from these reactions. A possible mechanism for their formation will be discussed.

A61B-0073 0830h POSTER

Ozonolysis of a series of alkenes in a large simulation chamber

Sonia Rodriguez-Bares¹ (s.rodriguez-bares@fz-juelich.de)Franz Rohrer¹ (f.rohrer@fz-juelich.de)Theo Brauers¹ (th.brauers@fz-juelich.de)Andreas Wahner¹ (a.wahner@fz-juelich.de)¹ Forschungszentrum Jülich, ICG-II, Jülich 52425, Germany

The simulation chamber SAPHIR on the campus of the Forschungszentrum Jülich provides a volume of 300 m³ in which chemical processes of atmospheric relevance can be studied under conditions of ambient trace gases mixing ratios. In this study we examined the ozonolysis of ethene, propene, and 4 different isomers of butene (iso-, n-, trans-, and cis-butene) at different conditions: dry (p(H₂O)=0.1 hPa) and humid (10 hPa), with and without CO. Experiments with CO (500 ppm) were used to avoid the reaction of OH with the alkene in order to follow the loss of alkene due to the ozone reaction. These experiments provide data for the ozone alkene rate constants which were within the error margin given in the literature. By a specific data analysis of the experiments without CO we have been able to determine the OH and HO₂ yields for these reaction systems. The results show a distinct water dependence of the OH yields for most alkenes, not observed before.

A61B-0074 0830h POSTER

Validation Of VOC Measurements By PTR-MS Using A Gas Chromatographic Pre-Separation Technique

William C Kuster¹ ((303)497-3819; bkuster@al.noaa.gov)Joost A de Gouw² (jdegouw@al.noaa.gov)Carsten Warneke² (cwarneke@al.noaa.gov)Paul D Goldan¹ (pgoldan@al.noaa.gov)¹ NOAA Aeronomy Laboratory, R/AL-7 325 Broadway, Boulder, CO 80305, United States² NOAA Aeronomy Laboratory CIRES University of Colorado, R/AL-7 325 Broadway, Boulder, CO 80305, United States

Proton-transfer-reaction mass spectrometry (PTR-MS) has emerged as a useful tool to measure volatile organic compounds (VOCs), including many oxygenated VOCs, in the atmosphere. In PTR-MS, organic trace gases are ionized by proton-transfer reactions with H₃O⁺ and are detected with a quadrupole mass spectrometer. The technique combines a fast time response (a few seconds or less) with a high sensitivity (10-100 pptv), which enables applications in rapidly changing air masses, such as encountered in airborne measurements or when measuring VOCs close to a source. In PTR-MS, only the mass of the ions produced in the instrument is determined, which is a useful but not a unique indicator of the identity of a VOC. Therefore, the selectivity of PTR-MS for different VOCs needs to be investigated. In this work, we have coupled a gas chromatographic column to a PTR-MS instrument to study the selectivity of PTR-MS in different air masses. Using this so-called GC-PTR-MS combination we have analyzed a large number of urban air samples as well as standard gas mixtures. The database that has emerged from this work is a useful tool in interpreting the mass spectra observed by PTR-MS, and a number of VOCs have been identified that can be uniquely detected by PTR-MS. Secondly, we have quantitatively inter-compared on-line PTR-MS measurements with GC-PTR-MS analyses of samples collected in parallel. The good quantitative agreement between the independent measurements infers generally insignificant interferences from such compounds as organic acids and peroxides in the PTR-MS system while the slightly decreased response for certain OVOC's in the GC-PTR-MS system can be attributed to the more involved sample treatment.

A61B-0075 0830h POSTER

Comprehensive Laboratory Measurements of the Emissions From Fires in Indonesian and African Fuels Measured by FTIR, PTR-MS, and GC

Ted J. Christian¹ (1-406-329-4878;theo@selway.unt.edu); Robert J. Yokelson¹; Rupert Holzinger²; Betina Kleiss²; Paul J. Crutzen²; Wei Min Hao³

¹Chem Dept, U Montana, Missoula, MT 59812, United States

²Air Chem Dept, Max Planck Institute for Chemistry, Mainz 55020, Germany

³Fire Chem, USFS Fire Sciences Laboratory, Missoula, MT 59802, United States

In large-scale laboratory experiments at the USFS Fire Sciences Laboratory we captured and measured the emissions produced by 46 separate burns of 16 fuel types from Indonesia, southern Africa, Canada, the U.S., and Germany. Five of the most significant Indonesian fuel types (rice straw, peat, grass, litter, brush) and two of the most significant African savanna fuel types (miombo, dambo) are represented here by 32 experimental fires. We deployed both a closed cell and open-path FTIR to quantify CO₂, CO, VOC, NO_x, HCN, and NH₃, and a proton transfer reaction mass spectrometer (PTR-MS) to measure VOC. We included dedicated instruments to measure CO₂ and CO and filled numerous canisters for analysis by GC-FID for CO₂, CO, and hydrocarbons.

PTR-MS can quantify VOC emissions at pptv levels and can detect compounds with a wide range of molecular weights. Drawbacks to using PTR-MS include molecular mass signals complicated by more than one compound, insensitivity to compounds with proton affinities near or below that of water, and reduced signal for compounds that may stick to sample lines. FTIR is capable of positive identification based on many spectral features for each compound. Open-path FTIR is not subject to sampling artifacts. Drawbacks include lower sensitivity which limits the range of expected analytes, dependence on absorption cross-section, which is low for certain trace gases, and complicated spectra that require de-convolution. The combination of these two techniques, however, provides a very powerful analytical tool.

The trace gases emitted from Indonesian biomass burning have never been fully characterized. This study provides initial emission ratios and emission factors for five important Indonesian fuel types for 20 compounds, half of which are OVOC. Results from the African fuels are being carefully interwoven into our recent field results to supplement a list of the top trace gas emissions from African savanna fires. These results constitute the most comprehensive measurements of fire emissions to date and also the first direct inter-comparison between FTIR and PTR-MS.

A61B-0076 0830h POSTER

Modeling the Climate Variability of Biogenic Isoprene and Monoterpenes

Vaishali Naik¹ (217-333-6296; vnaik@atmos.uiuc.edu)

Christine Delire² (608-262-5961; cldelire@facstaff.wisc.edu)

Donald J. Wuebbles¹ (217-244-1568; wuebbles@atmos.uiuc.edu)

¹Department of Atmospheric Sciences, University of Illinois at Urbana-Champaign, 105 S. Gregory St., Urbana, IL 61801, United States

²Center for Sustainability and the Global Environment, Gaylord Nelson Institute for Environmental Studies, University of Wisconsin-Madison, 1710 University Avenue, Madison, WI 53726, United States

Emissions of volatile organic compounds (VOCs, including isoprene, monoterpenes, and others) from terrestrial vegetation are known to influence the global tropospheric chemistry, atmospheric composition and the global carbon cycle. Since biogenic VOC emissions respond to changes in temperature, precipitation, and radiation, they have the potential to feedback on the radiative balance of the atmosphere through their chemical interactions. Therefore, a comprehensive assessment of the response of biogenic VOC emissions to climate variability is required to ascertain the relative importance of the environmental factors. Thus, the goal of this study is to explore the independent and combined effects of observed fluctuations in temperature, precipitation, and atmospheric CO₂ distribution in the past three decades on emissions of isoprene and monoterpenes. Here, we only consider isoprene and monoterpenes, as they are the dominant VOCs emitted by vegetation. We use the Integrated Biospheric Simulator (IBIS), a dynamic global ecosystem model, to simulate emission rates of VOCs being considered. IBIS derived vegetation canopy properties are coupled to control algorithms that relate the emission rates of isoprene to light and temperature, and the monoterpenes to temperature to simulate terrestrial ecosystem-specific emission rates. We present the seasonal, interannual, and spatial changes in the simulated biogenic emission rates of isoprene and monoterpenes in response to variations in temperature, precipitation, and atmospheric CO₂.

A61B-0077 0830h POSTER

Product Analysis of the OH Oxidation of Acrolein and Methacrolein in the Presence of NO

Timothy J Dransfield¹ (617-495-5922; dransf@fas.harvard.edu); Michele M Sprengnether² (spreng@huarp.harvard.edu); Yi-wen Huang¹ (ywhuang@fas.harvard.edu); Neil M Donahue³ (nmd+@cmu.edu); Kenneth L Demerjian² (kld@atmos.albany.edu); James G Anderson¹ (anderson@chemistry.harvard.edu)

¹Harvard University, Department of Chemistry and Chemical Biology, 12 Oxford Street, Cambridge, MA 02138, United States

²State University of New York at Albany, Atmospheric Sciences Research Center, Albany, NY 12203, United States

³Carnegie Mellon University, Departments of Chemistry and Chemical Engineering, 1106 Doherty Hall, Pittsburgh, PA 15213, United States

The oxidation of acrolein and methacrolein by OH in the presence of high NO was studied under "wall-less" conditions in Harvard's High Pressure Flow System. The experiment was conducted at 450 torr with a reaction time of several seconds. In the present work, first stage products are formed at 10¹³ molecules/cm³ levels and analyzed in-situ by FTIR spectroscopy. The use of Reaction Modulation Spectroscopy allows for accurate measurement of the very small (~1%) change in unsaturated aldehyde and NO reactants, in addition to product concentrations. Observed products from the acrolein oxidation include: formaldehyde(CH₂O), glyoxal(CHOCHO), glycolaldehyde(CH₂OHCHO), ketene(CH₂CO), nitrogen dioxide, carbon dioxide and carbon monoxide. The methacrolein oxidation produces: formaldehyde, methylglyoxal(CH₃COCHO), hydroxyacetone(CH₂OHC(O)CH₃), ketene, nitrogen dioxide, carbon dioxide and carbon monoxide. Both reactions also produce peroxy nitrates and alkylnitrates that have proven difficult to spectrally resolve. We observe elevated yields of ketene relative to previously published experiments conducted on longer timescales. We interpret this as evidence of rapid ketene removal in these systems. The mechanisms for ketene formation are discussed.

A61B-0078 0830h POSTER

Laboratory Studies of the Tropospheric Loss Processes for Acetic and Peracetic Acid

John J Orlando¹ (303-497-1486; orlando@acd.ucar.edu)

Geoffrey S Tyndall¹ (303-497-1472; tyndall@acd.ucar.edu)

¹Atmospheric Chemistry Division National Center for Atmospheric Research, 1850 Table Mesa Drive, Boulder, CO 80305, United States

Organic acids are ubiquitous components of tropospheric air and contribute to acid precipitation, particularly in remote regions. These species are present in the troposphere as the result of direct emissions from anthropogenic and biogenic sources, and as the result of photochemical processing of hydrocarbons. Production of organic acids can occur following ozonolysis of unsaturated hydrocarbons, while both organic acids and peroxyacids are formed from the reactions of HO₂ with acylperoxy radicals. For example, both acetic and peracetic acid are known products of the reaction of HO₂ with acetylperoxy radicals. In this paper, data relevant to the gas-phase tropospheric destruction of both acetic and peracetic acid are reported, including studies of their UV absorption spectra and of their rate coefficients for reaction with OH radicals. The data, the first of their kind for peracetic acid, show that the gas-phase lifetime of this species will be on the order of 10 days, with OH reaction occurring more rapidly than photolysis. Data on the rate coefficient for reaction of OH with acetic acid appear to resolve some conflicting data in the previous literature, and show 1) that reaction of OH with the acetic acid dimer is slow compared to the monomer and 2) that the rate coefficient possesses a negative temperature dependence near room temperature.

A61B-0079 0830h POSTER

On the seasonal change of fluxes and the climatology of acetone and methanol at a rural mountain site in California

Gunnar W Schade¹ (gws@nature.berkeley.edu)

Allen H Goldstein¹ (ahg@nature.berkeley.edu)

¹University of California Berkeley ESPM Ecosystem Sciences Division, 151 Hilgard Hall, Berkeley, CA 94720-3110, United States

Methanol and acetone are oxygenated volatile organic compounds (VOCs) with long atmospheric lifetimes. They are transported higher into the troposphere, where they can influence the odd hydrogen budget and thereby ozone chemistry. At our research site near Blodgett Forest Research Station, elevation 1300 m, on the western slope of the Sierra Nevada mountains, we have measured the seasonal cycle of acetone and methanol mixing ratios and fluxes since spring 2000. Owing to their long atmospheric lifetimes and local emissions, methanol and acetone are the most abundant VOCs throughout the seasons, with highest levels in summer (methanol = 60 ppb, acetone = 9 ppb) and lowest levels in winter (methanol = 0.4 ppb, acetone = 0.1 ppb). Both methanol and acetone fluxes were close to zero in the spring, increasing towards the summer and dropping during the fall. Both showed a typical, exponential temperature-dependence as demonstrated for this site before ($F_{30^\circ C} = 0.35$ and

$0.8 \text{ mg C m}^{-2} \text{ h}^{-1}$ for acetone and methanol, respectively). Temperature-normalized fluxes did not show a strong seasonality for either acetone or methanol, however, both were slightly elevated during active leaf growth, acetone fluxes appeared to increase again in the fall, and methanol fluxes increased during a routine thinning procedure in the plantation. Rain events did not seem to increase OVOC deposition, and low-temperature data indicate that the dry deposition velocity was likely less than 0.1 cm s^{-1} for acetone and 0.3 cm s^{-1} for methanol. Emissions of both OVOCs were correlated with their mixing ratios and the local biogenic VOC MBO. As the mixing ratio correlations continued throughout the winter, it is likely that both OVOCs show net emissions all year round.

A61B-0080 0830h POSTER

Relationships Between Total Alkyl Nitrates, Total Peroxy Nitrates, Biogenic VOCs and O₃ at Granite Bay, CA

Patricia A Cleary¹ (510-642-8001;

pcleary@uclink.berkeley.edu); Douglas A Day¹ (pollywo@uclink4.berkeley.edu); Paul J

Wooldridge¹ (pjwool@socrates.berkeley.edu);

Dylan Millet² (dylanbm@nature.berkeley.edu);

Megan McKay² (megan@nature.berkeley.edu);

Allen H Goldstein² (ahg@nature.berkeley.edu);

Ronald C Cohen^{1,3,4} (cohen@cchem.berkeley.edu)

¹Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720, United States

²Department of Environmental Science, Policy and Management, University of California, Berkeley, Berkeley, CA 94720, United States

³Department of Earth and Planetary Science, University of California, Berkeley, Berkeley, CA 94720, United States

⁴Energy and Environment Technologies Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd, Berkeley, CA 94720, United States

Observations of total alkyl nitrates (ΣANs) using thermal dissociation-laser induced fluorescence show they make up 15% of total NO₂ ($\text{NO}_2 \equiv \text{HNO}_3 + \Sigma\text{ANs} + \text{total peroxy nitrates}$, (ΣPNs)). The total alkyl nitrates peak midday at about 0.95 ppb and are at a minimum at night (0.35 ppb). The ΣANs also show a strong correlation to O₃ and isoprene oxidation products methacrolein and methyl vinyl ketone. Total peroxy nitrates show diurnal cycles and concentrations similar to total alkyl nitrates. Photochemical implications of these correlations will be explored.

A61B-0081 0830h POSTER

Preliminary Results from Regional Modeling of the KIE, in the Oxidation of Hydrocarbons

Farida - Dehghan¹ (416 7362100-Ex.20264; farida@yorku.ca)

Diane V Michelangeli¹ (416 7362100-Ex.77713; dvm@yorku.ca)

¹Farida Dehghan, Earth and Space Department York University 4700 keel ST., Toronto, ON. M3J1P3, Canada

The modeling of the reactions with the OH-radical of stable isotopes of Non Methane Hydrocarbons (NMHC) can help to understand important pollution sources. Modeling the stable isotope ratio ($\delta^{13}\text{C}$) also can be used to study the contribution of air pollution transport. The effect of isotopes on a rate constant is referred to as a kinetic isotope effect (KIE). The OH radical will tend to abstract the most weakly bound hydrogen atom in the molecule. So in NMHC reactions

with OH the overall rate constant reflects the number of available hydrogen atoms and the strengths of C-H bonds, therefore the effect of one ^{13}C atom in a molecule of NMHC will change the rate constant. The rate constants of NMH13C reactions with the OH-radical were determined from recent and on going laboratory measurements of KIE (Professor Rudolph's Group York University). The model used for this study was the MC2AQ model. The model includes on-line gas phase chemistry, and covers part of Eastern US and Canada on a 21km grid scale. The model was modified to include isotope information for Propene, Toluene, Propane, Benzene, Xylenes, and Isoprene. These compounds (both ^{12}C and ^{13}C were included as tracers reacting only with OH, with no feedback on the main chemistry in the model. This will help to test and verify the OH-radical concentration predicted by the chemistry model. The changes in ($\delta^{13}\text{C}$) of less reactive (or more reactive) NMHC due to the mixing of air masses is studied from the output of the model.

A61B-0082 0830h POSTER

Carbon Kinetic Isotope Effects in the Reactions of Atmospheric Non-methane Hydrocarbons with Hydroxyl Radicals, Chlorine Atoms and Ozone

Rebecca S Anderson¹ (416-736-2100 x44608; rebeccah@yorku.ca); Richard Iannone¹ (416-736-2100 x44608; riannone@yorku.ca); Jochen Rudolph¹ (416-736-5410; rudolphj@yorku.ca); Alexandra E Thompson¹ (416-736-2100 x77033; alext@yorku.ca); Lin Huang² (lin.huang@ec.gc.ca); Darrell Ernst² (darrell.ernst@ec.gc.ca)

¹Centre for Atmospheric Chemistry, York University, 006 Steacie Science Library 4700 Keele Street, Toronto, ON M3J 1P3, Canada

²Meteorological Service of Canada, 4905 Dufferin Street, Toronto, ON M3H 5T4, Canada

Recently it has been shown that stable carbon isotope measurements are extremely useful for better understanding of atmospheric processes involving NMHC. Interpretation of these measurements requires both the knowledge of the isotopic composition of hydrocarbon emissions as well as of the isotopic fractionation associated with the removal of NMHC from the atmosphere. Oxidation by OH-radicals is by far the most important atmospheric removal process of NMHC. To some extent oxidation by chlorine atoms and ozone also contribute to the removal of NMHC from the atmosphere. KIEs for the reactions of C2-C9 NMHC with atmospheric oxidants hydroxyl radicals, chlorine atoms and ozone will be presented and discussed with respect to studying atmospheric processes.

A61B-0083 0830h POSTER

The Carbon and Hydrogen Kinetic Isotope Effects of Non-methane Hydrocarbons in Their Reactions with OH Radicals, Cl Atoms and Ozone

Richard Iannone¹ (416-736-5410; riannone@yorku.ca); Rebecca S Anderson¹ (416-736-5410; rebeccah@yorku.ca); Eva Czuba¹ (eva@yorku.ca); Aileen Vogel¹ (416-736-5410; aileen@yorku.ca); Jochen Rudolph¹ (416-736-5410; rudolphj@yorku.ca); Paul S Eby² (250-721-6183; peby@uvic.ca); Michael J Whitticar² (250-721-6154; whitticar@uvic.ca); Lin Huang³ (lin.huang@ec.gc.ca); Darrell Ernst³ (darrell.ernst@ec.gc.ca)

¹Centre for Atmospheric Chemistry, York University, 006 Steacie Science Library 4700 Keele Street, Toronto, ON M3J 1P3, Canada

²Biogeochemistry Facility, School of Earth and Ocean Sciences, University of Victoria, 3800 Finnerty Road, Victoria, BC V8W 2Y2, Canada

³Meteorological Service of Canada, 4905 Dufferin Street, Toronto, ON M3H 5T4, Canada

A quantitative understanding of atmospheric oxidation processes can be attained through studies of the isotopic composition of non-methane hydrocarbons (NMHCs). Rudolph and Czuba (2000) have demonstrated that such isotopic studies can be used to determine the average photochemical age of an air mass. One of the prerequisites is the knowledge of the kinetic isotope effects associated with the removal processes for NMHCs in the atmosphere. We have measured the carbon and hydrogen kinetic isotope effects (KIEs) of NMHCs in reaction with species of atmospheric relevance (OH and Cl radicals, ozone) using continuous flow-isotope ratio mass spectrometry (CF-IRMS). The NMHCs studied include alkanes, alkenes, and aromatics

such as toluene and p-xylene. This presentation will focus on the results of these experiments and will explain their significance and utility in atmospheric chemistry.

A61B-0084 0830h POSTER

Trends of Formate, Acetate, and Oxalate in Alpine Ice Cores over the Twentieth Century: Implications for their Natural and Anthropogenic Budgets in the Atmosphere over Europe

Susanne Preunkert¹ (33-476-824207; ps@lgge.obs.ujf-grenoble.fr)

Michel Legrand¹ (33-476-824243; legrand@lgge.obs.ujf-grenoble.fr)

Ingrid Etchevers¹ (33-476-824233; etchevers@lgge.obs.ujf-grenoble.fr)

Martin Schock² (49-6221-546315; Martin.Schock@IUP.uni-heidelberg.de)

¹CNRS Laboratoire de Glaciologie et Geophysique de l'Environnement, BP 96, St Martin d'Heres 38402, France

²Institut fuer Umweltpophysik, Universitaet Heidelberg, INF 229, Heidelberg 69120, Germany

A continuous high-resolution record from a Col du Dome (Mt Blanc, 4250 m a.s.l., French Alps) ice core in addition to discontinuous samples from a Colle Gnifetti (Monte Rosa, 4450 m a.s.l., Swiss Alps) ice core were used to investigate the partitioning between natural and anthropogenic sources of mono- and dicarboxylates in the European atmosphere. It is found that with a mean summer level close to 100 ppb formate dominates other monocarboxylates such as acetate (~15 ppb) and lactate (~8 ppb). With levels close to 15 ppb, oxalate and succinate are the two most important di-carboxylates of the present-day Alpine precipitation. Together, these 4 species represent on average 30% of the DOC level, which ranges between 100 and 300 ppb C.

The long term trends of formate and acetate show an increase by a factor of two after 1950 and a decrease after 1980. At present more than 80% of formate and acetate present in Alpine precipitation is of natural origin (likely continental biogenic emissions). The changes of formate and acetate after 1950 follow rather well the course of expected change of COV emissions related to vehicular traffic. The absence of a temporal trend for oxalate suggests an insignificant impact of anthropogenic emissions for this species. Likewise it is shown that the oxalate produced in biogenic soils and emitted during biomass burning events does not dominate the atmospheric budget of this species. A comparison of the Alpine oxalate levels with those obtained at sites located at lower elevation, suggests that a secondary production of this species takes place in the troposphere. Finally, in contrast to oxalate, succinate whose atmospheric budget is poorly understood exhibits a well marked anthropogenic trend (a factor of 10 between the pre-industrial era and present).

A61B-0085 0830h POSTER

Development of Laser Induced Fluorescence Sensor for Measurements of Atmospheric HCHO

Scott T Sandholm¹ (404-894-3824; scott.sandholm@eas.gatech.edu)

Anne T Case¹ (404-385-0927; atc@minitower.gtri.gatech.edu)

David K Tan¹ (404-385-1821; tan@minitower.gtri.gatech.edu)

Joe N Mastromarino (404-385-0927; joe@minitower.gtri.gatech.edu)

Hann-Wen Guan (404-894-3895; hwg@minitower.gtri.gatech.edu)

¹GA TECH School of EAS, Baker bldg room 107, ATL, GA 30332

Formaldehyde has been identified as a source of free radicals that ultimately leads to the formation of pollutants, particularly ozone. Formaldehyde is formed from the oxidation of both anthropogenic and biogenic organics; it is also directly emitted by anthropogenic sources such as motor vehicles. Currently, there are pronounced discrepancies between measured formaldehyde and model predictions, especially within the upper troposphere. In order to understand the atmospheric oxidation capacity and the ozone formation/destruction cycle more fully, it is essential for formaldehyde measurements to be accurate and precise. We present results from the ongoing development of field-deployable LIF (laser induced fluorescence) based on a real-time sensor for formaldehyde with one-minute signal integration time. Its projected limits of detection in the free troposphere and boundary layer are 5 pptv and 30 pptv respective

URL: <http://lif.gtri.gatech.edu/web/experiments/hcho>

A61B-0086 0830h POSTER

The Role of Organic Compounds in Precipitation Development Using an Explicit Microphysical Model

Lester Alfonso¹ (52-555-622-4053; lester@ccaunam.atmosfcu.unam.mx)

Graciela Raga¹ (52-555-622-4053; raga@servidor.unam.mx)

¹Centro de Ciencias de la Atmosfera. Ciudad Universitaria, Circuito Exterior S/N. Ciudad Universitaria, Mexico, DF 04510, Mexico

In order to estimate the anthropogenic influence of gas and aerosol emissions from the Petroleum Industry in maritime zones with clouds of small vertical extent, a numerical 1D Eulerian cloud-chemical model with detailed microphysics (Alfonso and Raga 2002) is used to simulate the influence of water soluble organic compounds (WSOC) and organic+inorganic gas emissions on cloud development. Following Mircea et al. (2002), we tested the sensitivity of the cloud and precipitation development in the classical inorganic case (CIC) and the inorganic+organic case (IOC) with respect to CCN compositions. The results indicate an increase in the droplet concentration for the IOC, and a delay in the development of precipitation. The pH spectral evolution was studied during both the development and precipitation stages. The influence of the diffusion of formic acid and its generation by oxidation of hydrated formaldehyde in the aqueous phase result in a reduction in the acidity of precipitation in the range between 0.05 and 0.15 pH units (from 1 to 3%) for the high ambient SO₂ concentration (20 ppb) and between 0.8-1.6 pH units for the low ambient SO₂ concentration (1ppb) case.

A61C MCC: Hall D Saturday 0830h

Recent Advances in Global Climate Modeling I Posters (joint with NG, B, H, OS, GC)

Presiding: D Stephenson-Hawk, The Stephenson Group

A61C-0087 0830h POSTER

Simulations of Global Climate With a High Resolution Model of the Atmosphere

Philip B. Duffy¹ (925-422-3722; pduffy@llnl.gov)

Bala Govindasamy¹ (925-423-0771; bala@llnl.gov)

¹Lawrence Livermore National Laboratory, 7000 East Ave. L-103, Livermore, CA 94550, United States

One factor limiting the realism of global climate simulations is lack of spatial resolution. We have performed simulations of global climate at spectral truncations of T170 and T239 (resolutions of 75 km and 50 km, respectively) using the NCAR CCM3 atmospheric climate model. We performed simulations of the present climate and of the effects of increased greenhouse gases. We performed a first-order "retuning" of the model physics at T170. We will discuss how the model's ability to simulate the present climate, and its response to increased greenhouse gases, depend on horizontal resolution.

A61C-0088 0830h POSTER

Development of a High-Resolution Climate Model for Future Climate Change Projection on the Earth Simulator

Hiroshi Kanzawa³ (+81-298-50-2431; kanzawa@nies.go.jp); Seita Emori¹ (+81-45-778-5614; emori@jamstec.go.jp); Teruyuki Nishimura¹ (+81-45-778-5574; nt@jamstec.go.jp); Tatsuo Suzuki¹ (+81-45-778-5628; tsuzuki@jamstec.go.jp); Takahiro Inoue⁴ (+81-3-3712-5321; don@tokyo.rist.or.jp); Hiroyasu Hasumi² (+81-3-5453-3961; hasumi@ccsr.u-tokyo.ac.jp); Fuyuki Saito² (+81-3-5453-3950; fuyuki@ccsr.u-tokyo.ac.jp); Ayako Abe-Ouchi^{1,2} (+81-3-5453-3955; abeouchi@ccsr.u-tokyo.ac.jp); Masahide Kimoto² (+81-3-5453-3957; kimoto@ccsr.u-tokyo.ac.jp); Akimasa Sumi² (+81-3-5453-3951; sumi@ccsr.u-tokyo.ac.jp)