# An improved estimate of inorganic iodine emissions from the ocean using a coupled surface microlayer box model

Ryan Pound, Postdoctoral Research Associate, University of York

**Poster Number:** 1

## Abstract:

Iodine at the ocean's surface impacts climate and health by removing ozone (O3) from the troposphere both directly, via ozone deposition to seawater, and indirectly via the formation of iodine gases which are emitted into the atmosphere. We present a new box model of the ocean surface microlayer that couples oceanic O3 dry deposition to inorganic halogen chemistry to predict inorganic iodine emissions. This model builds on the previous work of Carpenter et al. (2013), improving both chemical and physical processes. We incorporate the results of this box model into the global chemical transport model GEOS-Chem to predict global inorganic iodine emissions and their effect on tropospheric O3. Inorganic iodine emissions from tropical waters decrease by as much as half, while higher latitude emissions increase by a factor of ~10. Despite these large local changes, global total inorganic iodine emissions increased by only ~ 4% (2.83 Tg to 2.95 Tg) compared to the previous parameterization. This results in a negligible change in average tropospheric OH).

# Modelling the stochastic dependence structure of extreme tropospheric ozone and simulating events

Kyle Jex, PhD Student, Lancaster University

**Poster Number:** 2

## Abstract:

Given the well-established negative impacts of extreme episodes of tropospheric ozone on human and plant health, accurately modelling and forecasting such events are essential in mitigating any potential effects. We apply a univariate extreme value theory technique known as the peaks-over-threshold approach to model the marginal distribution of ozone observations from the UK's Automatic Urban and Rural Network. Multivariate extreme value methods are then employed to estimate the extremal dependence and stochastic behaviour within the observed extreme episodes. Model-based estimates for the probability an extreme event persists over T days are generated through simulations. These statistical models are then used to perform real-time forecasts and to simulate extreme scenarios.

# Wintertime formation of HONO from aerosol surfaces in Fairbanks, Alaska

Rae James, University of Leeds

**Poster Number:** 3

## Abstract:

As a high-latitude city, Fairbanks, Alaska, undergoes prolonged, cold winters with limited sunlight, and strong surface temperature inversions. These conditions coupled with its position at the bottom of the Tanana Valley lead to cold, dark, stagnant weather conditions, which when combined with demands for heating and transportation contribute to substantial degradations in air quality. These factors have led to Fairbanks exceeding the Environment Protection Agency PM2.5 standard and being classified as a serious nonattainment area for air quality.

The ability to mitigate harmful pollution concentrations in Fairbanks is hampered by a lack of knowledge of the physicochemical processes which drive localised extreme pollution episodes during wintertime. For example, low levels of sunlight and ozone concentrations inhibit the well-established formation mechanisms of HOx via photolysis or radical reactions. However, nitrous acid (HONO) can be a major source of OH radicals even in cold, dark, polluted environments. Despite being a major source of OH radicals, the formation of HONO is poorly represented in models. HONO is directly emitted from vehicles or formed via gas-phase reactions or via heterogeneous reactions such as those occurring on the surface of aerosols.

Using observations made during the Alaska Layered Pollution and Chemical Analysis Campaign (ALPACA), which took place in Fairbanks during January – February 2022, we conducted constrained chemical box model experiments to investigate HONO and oxidant sources during the ALPACA campaign. Our results show that gas-phase only reactions cannot account for observed HONO concentrations nor correctly reproduce diurnal trends. This suggests additional sources of HONO present in Fairbanks, potentially including formation on the surface of aerosols, which is not currently well constrained, especially at temperatures and relative humidities pertinent to wintertime Fairbanks.

Here, we present preliminary laboratory results aimed at addressing the lack of studies into HONO formation on the surface of aerosols in cold, dark environments and provide a wider atmospheric context via chemical box modelling constrained to observations from the ALPACA campaign. We purpose-built a chamber designed to reach temperatures similar to wintertime conditions in Fairbanks to study the formation

of HONO from aerosol samples collected on filters during the ALPACA campaign, as well as filters collected from idealised single-source emission experiments in the laboratory. The generated HONO was detected in the gas-phase following its photolysis at 355 nm to OH and NO, with the OH detected via OH laser-induced fluorescence spectroscopy.

# An Updated Structure Activity Relationship to Determine Site Specific Rate Coefficients for Multifunctional Compounds

Niamh Robertson, Postgraduate Researcher, School of Chemistry, University of Leeds

**Poster Number:** 4

**Abstract:**

Multifunctional compounds are released directly and formed in situ in the atmosphere. In situ formation follows the oxidation of simpler hydrocarbons and can result in highly oxidised molecules (HOMs). Increased functionality leads to increases in intermolecular interactions that can stabilise transition states and decrease volatilities, increasing the potential for secondary organic aerosol (SOA) formation, thus influencing human health and climate. Furthermore, functionality increases the number of initial reaction sites.

Site-specific rate coefficients are rate coefficients for a particular reaction site within a molecule. Determining site-specific rate coefficients is important to truly understand the atmospheric fate of a molecule, as reactions at different sites often lead to different products, and hence have different atmospheric impacts.

Esters, R-O-C(=O)R’, with an ether linkage and a carbonyl functionality are simple examples of multifunctional compounds. As one of the major components of biofuels, ester emissions are likely to increase as interests in biofuels soar. Esters are also formed following the oxidation of ethers, whose emissions are also on the rise as for example, due to their use as sustainable solvents. Laser flash photolysis coupled with laser induced fluorescence has been used to determine the OH initiated site-specific kinetics of methyl formate (CH3OCHO) via deuterated isotopomers to give a room temperature branching ratio of 44 % abstraction from the methyl group, decreasing with increasing temperature. The site-specific kinetics of tert-butyl formate ((CH3)3COCHO), have determined methyl abstraction dominates.

Due to the large variety of multifunctional compounds in the atmosphere, experimentally determining each rate coefficient is unfeasible. Structure activity relationships (SARs) are one way of predicting rate coefficients based on the structure of a molecule and are inherently site-specific. However, SARs for multifunctional compounds are unreliable due to a lack of experimental data, particularly on site-specific rate coefficients. Despite this, they are widely used in chemical modelling, for example in the Master Chemical Mechanism. Trained on the experimentally determined site-specific rate coefficients, this work presents a revised SAR for the esters.

# Testing the capabilities of Chemistry Transport Models to predict heat waves episode over the United Kingdom and their impact on ozone levels changes.

Andrea Mazzeo, Lancaster Environment Centre - Lancaster University

**Poster Number:** 5

**Abstract:**

Heat waves are weather episodes of a few days of unusually high temperatures occurring with higher frequency due to climate change. Their higher occurrence causes economic disruption across multiple sectors (Costa et al., 2016), impacting human health and ecosystems. In the context of a warming climate, higher temperature is expected to impact air contaminants, in particular exacerbating O3 pollution, possibly offsetting the benefits from the primary emission reduction making the O3 season longer. This phenomenon called the “climate change penalty” has already been shown to have an impact on heat-related deaths (Johnson et al., 2005, Green et al., 2016) and morbidity (Arbuthnott, Hajat, 2017). Therefore, the capability to predict these weather events and plan measures to mitigate their effects on O3 levels is becoming progressively more important for research and policymakers.

Chemistry Transport Models (CTMs) represent suitable tools for this task given their ability to reproduce regional weather patterns and chemical physical parameters acting in the low troposphere, allowing analysis, forecasts and what-if scenarios. Here we implement the CTM WRF-Chem (Grell et al., 2005) to simulate the heat wave episode of July 2019 in the UK. During this episode, the highest temperature recorded (38.7 °C) set a record for the UK. We validate the CTM performance to reproduce the main weather parameters (namely, surface temperature, relative humidity wind speed and direction) using Met Office network data and reproducing Ozone levels using AURN-Defra network data divided by rural and urban background. WRF-Chem’s best configuration is used to forecast future heat wave occurrence, predict the relative changes in ozone levels and evaluate the impact on health burden.

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# Investigating radical processes at the surface of secondary organic aerosols

Abigail McConnell, PhD Student, School of Chemistry, University of Leeds

**Poster Number:** 6

**Abstract:**

Secondary Organic Aerosols (SOAs) have been estimated to be the highest proportion by mass of atmospheric aerosols averaged globally and a significant fraction of particulate matter below 2.5 µm (PM2.5). Previous studies have established its formation pathways, but fewer studies have focused on the processing of SOAs and how SOAs interact with trace gas species in the atmosphere. Concentrations of HO2, a critical radical in many atmospheric processes, are often overestimated in atmospheric models. These discrepancies have sometimes been attributed to the heterogeneous uptake onto atmospheric aerosols. There is a significant lack of data with respect to the uptake of HO2 onto secondary organic aerosols. The principal objective of this project is to explore the heterogeneous reactions of HO2 occurring on the surface of atmospherically relevant secondary organic aerosols.

Atmospherically relevant SOA has been produced in a Potential Aerosol Mass Chamber (PAM) from the oxidation with OH and ozone of volatile organic compounds, α-pinene, d-limonene and 1,3,5 – trimethyl benzene. A scanning mobility particle sizer (SMPS) characterised the aerosol's physical properties. Results from these chamber studies show that the size distribution of the SOA can be altered by changing the initial mixing ratio of the VOC or oxidant. A flow tube coupled to a Fluorescence Assay Gas Expansion (FAGE) detection cell, which utilises laser-induced fluorescence (LIF) spectroscopy, is used to measure radical species in the gas phase.

HO2 uptake is observed by an increased loss of HO2 with increasing aerosol surface area. There is competition between the uptake of HO2

onto SOAs and the production of HO2 from SOAs. Thus, both processes must be well understood to obtain an HO2 uptake coefficient for SOAs and are investigated in this presentation.

# Marine biogenic benzene and toluene emissions impact secondary organic aerosol in the polar regions

Charel Wohl, Senior Post-doctoral Research Assistant, University of East Anglia, UK

**Poster Number:** 7

**Abstract:**

We present seawater measurements of benzene and toluene in surface underway seawater and depth profiles in the polar regions, namely the open Southern Ocean and the Arctic marginal sea ice zone. Previously thought to have predominant anthropogenic sources, the distribution of their concentrations in the water column and correlations with other biogenic gases suggest a biological source of benzene and toluene in seawater. Combined with concurrently measured atmospheric mole fractions, we calculate that the oceans were supersaturated in benzene and toluene. We assessed the atmospheric impact of this outgassing using the global chemical transport model CAM-Chem. Our modelling results show that by including our average benzene and toluene flux, total secondary organic aerosol increased less than 1 % in the Arctic, but by 7 % over the Southern Ocean. Overall, this work contributes to a better understanding of the impact of the variety of gases emitted by biological processes in the ocean.

# Alternative laboratory precursors for Criegee intermediates

Kate Livesey, PhD student, University of Leeds, NERC

**Poster Number:** 8

**Abstract:**

Air quality and climate are determined by atmospheric composition and chemistry. Gas phase oxidation processes dominate the chemistry in the lower atmosphere, with OH, NO3 and O3 being the main oxidants. Ozone-initiated oxidation of unsaturated volatile organic compounds produces zwitterionic Criegee intermediates (R2COO) with high internal energy. Collision with a bath gas (typically N2), produces stabilised Criegee intermediates (SCIs), which are potentially important oxidants. Knowledge of the kinetics and products of SCI reactions is therefore important for understanding air quality and climate. Until 2012, the kinetics of SCIs were investigated in indirect studies, leading to large uncertainties in the chemistry of SCIs. After establishing that photolysis of diiodo-alkyl compounds can be used to produce SCIs in the laboratory (1), direct studies have demonstrated that SCIs are up to 10,000 times more reactive than initially shown in indirect studies (1, 2).

Laser flash photolysis (LFP) of CH2I2 in the presence of O2 forms CH2OO, which can be observed in the laboratory using UV absorption spectroscopy. The UV absorption cross-sections of CH2I2 and CH2OO overlap, creating issues in single wavelength studies. However, a recent study has used CH2IBr as an alternative precursor for CH2OO (3), which could be advantageous over CH2I2 owing to less overlap in the UV spectra between CH2OO and CH2IBr. The secondary species produced from CH2IBr-O2 photolysis are yet to be determined.

Time-resolved broadband UV absorption spectroscopy coupled with LFP was used in this work to investigate the products of CH2IBr-O2 photolysis and to determine the yield of CH2OO from CH2IBr. The probe beam used in the experimental set-up multi-passes through the reaction cell to increase sensitivity, with transmitted light wavelength resolved by a spectrograph and detected by a 2D detector which also gives microsecond to millisecond time resolution. The light intensities are converted to absorbance via the Beer-Lambert law, giving absorbance as

a function of time and wavelength. Reference spectra are fitted to the experimental absorbance giving concentration-time profiles of the species present, which enable determination of CH2OO yields and kinetics.Time-resolved broadband analysis of the CH2IBr-O2 system indicated contributions from other species. BrO was identified, which has overlapping absorption with CH2OO and may interfere in single wavelength analysis at ~340 nm. Yields of CH2OO produced via CH2IBr-O2 photolysis were lower than those from CH2I2-O2, however there is evidence to suggest that CH2Br + O2 is forming CH2OO as well as CH2I + O2.

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# Significant missing OH reactivity measured at a remote Tropical marine site

Samuel Seldon, PhD student, School of Chemistry, University of Leeds

**Poster Number:** 9

## Abstract:

The OH radical is the dominant daytime tropospheric oxidising agent, reacting with almost all Volatile Organic Compounds (VOCs). The majority of global methane is removed in the tropical troposphere by OH. The oxidation of VOCs by OH forms peroxy radicals, $HO_2$ and $RO_2$, with formaldehyde (HCHO) often formed as a product. In remote marine environments, ozone ($O_3$) is destroyed during the day by reaction with OH or $HO_2$, or photolysis.

Ground-based measurements of OH, $HO_2$, $RO_2$, OH reactivity and HCHO, together with a comprehensive suite of supporting measurements, were made at the Cape Verde Atmospheric Observatory (CVAO), situated on the island of São Vicente located in the Tropical North Atlantic Ocean, during February 2023 as part of the NERC-funded PEROXY project. With no nearby emissions and prevailing winds from over the ocean, the clean marine air sampled was representative of the open ocean.

In this work, time series and diurnal variations of the measured species are presented, and production and destruction rates of OH, $HO_2$. Reactions of the halogen oxides, IO and BrO, are shown to be important for understanding the chemistry of OH, $HO_2$ and $RO_2$. The $CH_3O_2$ reactions with halogen oxides are an important sink for $RO_2$ and a possible source of $HO_2$ that likely enhances $O_3$ destruction in remote marine environments. Heterogeneous losses are also shown to be important for $HO_2$. The OH budget analysis shows a possible minor missing source of OH while net $HO_2$ production is observed, indicating either an overestimation of $HO_2$ sources or an underestimation of $HO_2$ sinks. Measured OH reactivity was ~2 $s^{-1}$ while modelled OH reactivity was ~1.5 $s^{-1}$ indicating missing OH reactivity of ~0.5 $s^{-1}$. This missing reactivity suggests the presence of an unknown or unmeasured VOC that may also regenerate OH.

# Glyoxal Yields from Selected Hydrocarbon Oxidations

Danny McConnell, Postgraduate Researcher, University of Leeds

**Poster Number:** 10

## Abstract:

Glyoxal is a second-generation product of atmospheric volatile organic compound (VOC) oxidation. Measurements of glyoxal provide information on the mechanism of precursor oxidations. This can include information on site specific OH abstraction reactions and branching ratios of peroxy and alkoxy reactions. Glyoxal's low vapour pressure means that glyoxal is relevant in the formation and growth of secondary organic aerosols, impacting human health and climate. Due to glyoxal's strong and distinct UV absorption spectrum, measurements of atmospheric glyoxal concentrations via satellite are possible allowing spatial distributions on global and regional scales. Ratios of formaldehyde and glyoxal formation vary widely across different compound oxidation pathways, hence satellite measurements of formaldehyde and glyoxal can give information of initial VOC distributions.

Glyoxal is present in the marine boundary layer where there are inconsistencies between measured and modelled glyoxal concentrations. Compounds such as acetaldehyde have been considered as an unaccounted-for source of glyoxal. This presentation reports glyoxal yields from VOC oxidation processes.

Experiments were carried out in the HIRAC chamber with direct detection of glyoxal via laser induced phosphorescence. Precursors and stable intermediates were tracked with PTR-MS or FTIR instruments, concentrations of relevant radicals were measured using FAGE or ROxLIF and O3 and NOx via commercial analysers.

The implications of these glyoxal measurements on VOC oxidation mechanisms and observed atmospheric glyoxal concentrations will be discussed.