Evaluation of a hierarchy of chemical mechanisms to model net ozone production from seasonal biomass burning in boreal North America over the western boundary of the North Atlantic

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1. BORTAS: Quantifying the impact of BOReal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites

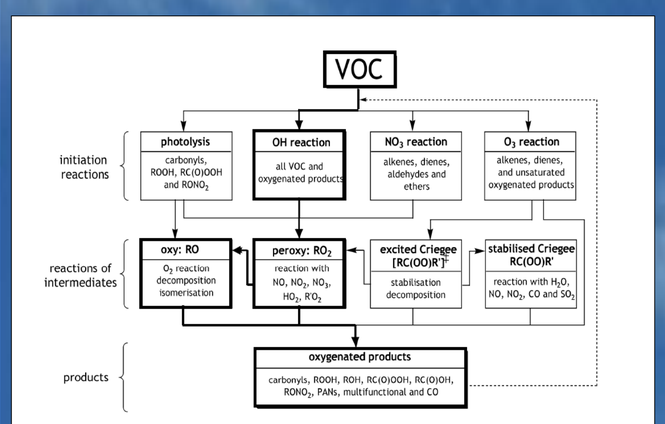
• Boreal forest fires are a significant source of atmospheric trace gases and aerosols and consequently play an increasingly important role in the chemical state of the atmosphere and global climate. Accurately estimating the impact relies on understanding the connection between measurements over the source region and downwind, involving uncertain atmospheric chemistry within these plumes as they evolve. .

• BORTAS is a 3-year multi-national project with the overall goal of quantifying the connections between the composition and the distribution of biomass burning outflow, O_3 production and loss within the outflow, and the resulting perturbation to atmospheric chemistry in the troposphere from seasonal biomass burning in boreal North America.

• Leeds will evaluate a hierarchy of chemical mechanisms (from explicit (MCM) to those suitable for integration by global CTMs (CRI-tuned)) in order to model multi-day secondary pollution formation within the plumes.

• The work described will feed into the development and evaluation of GEOS-CHEM variants for the interpretation of the aircraft and satellite data in order to estimate the impact of boreal burning on the composition of the northern hemisphere

2. The Master Chemical Mechanism http:/mcm.leeds.ac.uk/MCM



Flow chart indicating the major reactions, intermediate classes and product classes considered in the MCM protocol. The highlighted sections include free-radical propagated chemistry

• MCMv3.2 contains 144 primary emitted VOCs which leads to a mechanism containing ~6900 species and 16700 reactions.

• The MCM is a near-explicit chemical mechanism describing the detailed gas phase tropospheric degradation of a large series of volatile organic compounds (VOCs) emitted from a wide variety of anthropogenic and biogenic sources.

• It is often employed as a benchmark mechanism by the atmospheric science community in a wide variety of science and policy applications where chemical detail is required and also acts as a reference mechanism for the development and evaluation of reduced or lumped mechanisms.

• The latest version, MCMv3.2, includes a number of targeted extensions with specific emphasis on extending the range of reactivity of biogenic compounds, including the addition of detailed degradation schemes for DMS, limonene and β-caryophyllene.

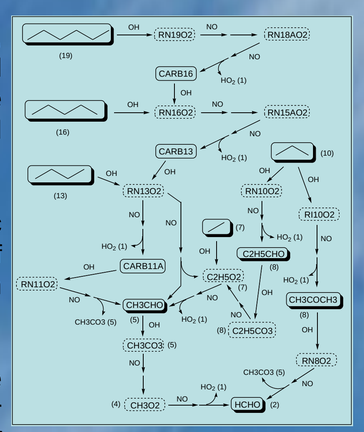
3. The Common Representative Intermediates Mechanism (CRImech) and its variants

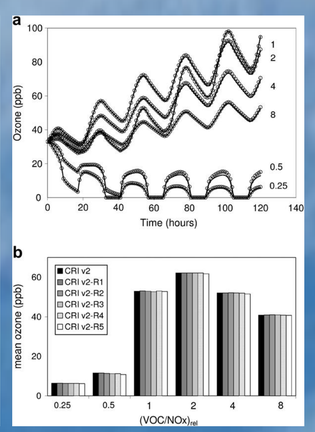
• Developed in parallel with the MCM, CRImech provides a more economical description of ozone formation from the degradation of a detailed speciation of emitted VOC.

• CRImech contains a series of generic intermediate radicals and products, each of which can represent a larger set of species in the MCM.

• These generic intermediates mediate the breakdown of larger VOC into smaller fragments (e.g. HCHO), the chemistry of which is treated explicitly.

• Previous studies using the MCM demonstrates that the potential for a given VOC to form O_3 can be related to the number of reactive bonds it contains (C-C and C-H bonds) – this quantity defines the basis of the generic intermediate groupings in the mechanism.





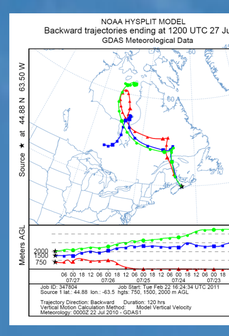
• Lumping of emissions into appropriate surrogates has resulted in a much reduced version of CRImech ("CRI-reduced") which contains 196 species, 555 reactions (factor of 2 reduction).

CRI version	v2	v2-R1	v2-R2	v2-R3	v2-R4	v2-R5
VOCs	115	67	55	42	33	22
Percentage redistribution (%)	0	5	10	20	33	44
Species	434	373	352	296	219	196
Reactions	1183	1012	988	882	643	555

4. Case Studies

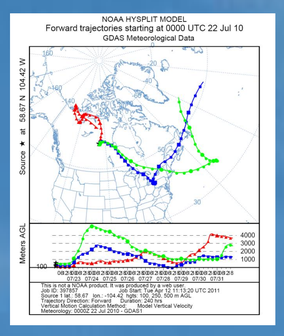
Trajectory A

• 5 day back trajectory ending 27th July 2010 starting at Halifax (blue line):



Trajectory B

• 10 day forward trajectory ending 22nd July 2010 from an area of intense fire activity (blue line):



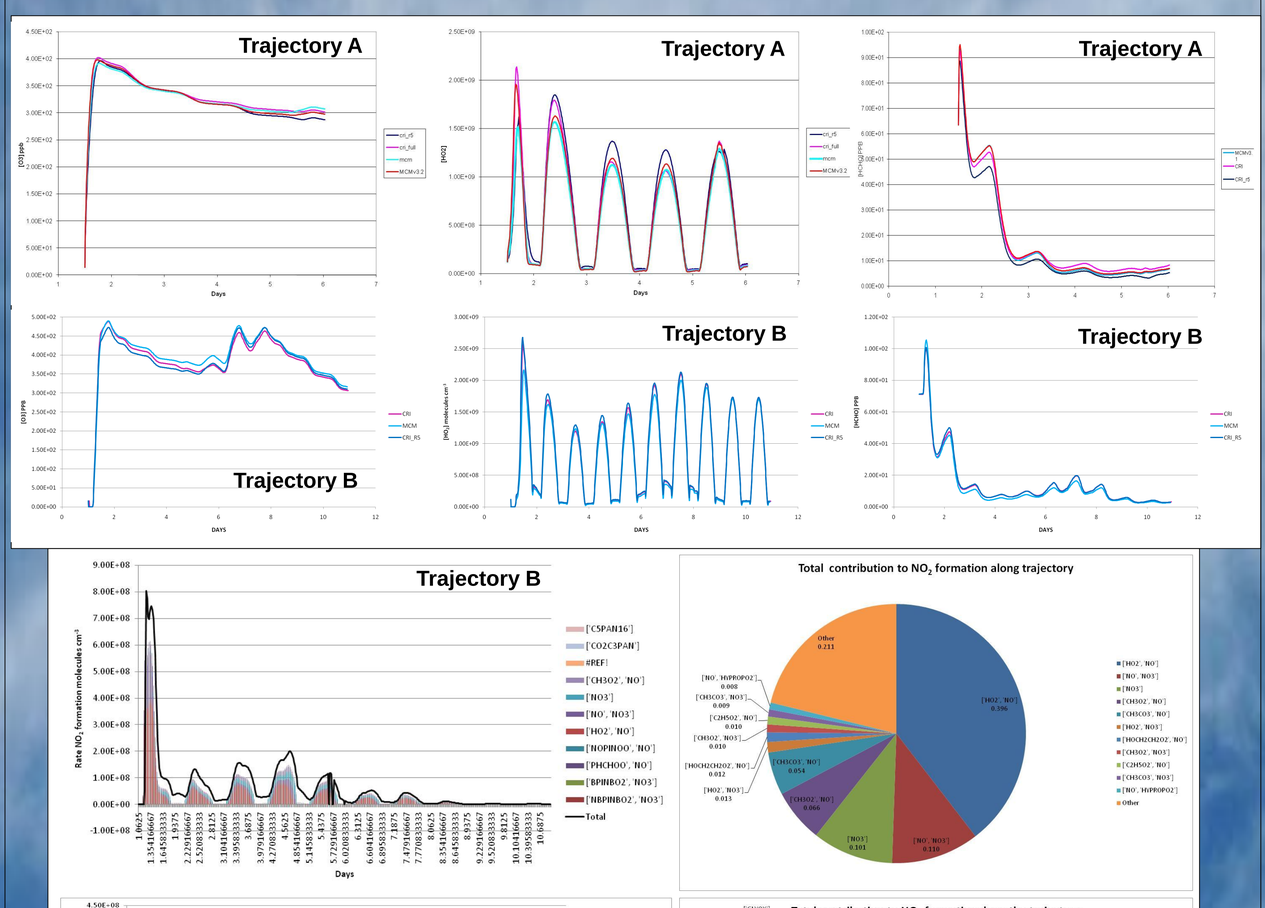
5. Initialisation I. – Hays et al., (2002)

• Speciated gas-phase VOC emissions from controlled open burning of six fine foliar fuels common to fire-prone U.S. ecosystems.

• Concentrations for CO_2, CO, CH_4, C_2H_4. C_2H_2, HCHO, CH_3OH, CH_3COOH, HCOOH, NO, NO_2, O_3 taken from observations reported in Mason et al., (2006) for a young Alaskan BB plume.

• Other species initialised by using emission ratios relative to C_2H_4 from Hays et al, (2002).

• Initialisation emissions were assigned to surrogate where species do not exist in CRImech.



6. Initialisation II. – Simpson et al., (2011)

• CO initial concentration taken from GEOS-Chem output, other species initialised relative to this using emissions ratios defined in Simpson et al – these were derived from observations of 5 Canadian boreal fires (ARCTAS).

• Further species were initialised using emissions ratios from Hays et al., (2002).

• Initialisation emissions were assigned to surrogate where species do not exist in CRImech.

References

Jenkin et al., Atmos Env., 31, 81 (1997)

Saunders et al., ACP., 3, 161 (2003)

Watson et al., Atmos Env., 42, 7196 (2008)

Hays et al., ES&T., 36, 2281 (2002)

Mason et al., J. Atmos. Chem., 55, 273 (2006)

Simpson et al., ACPD., 11, 9515 (2011)