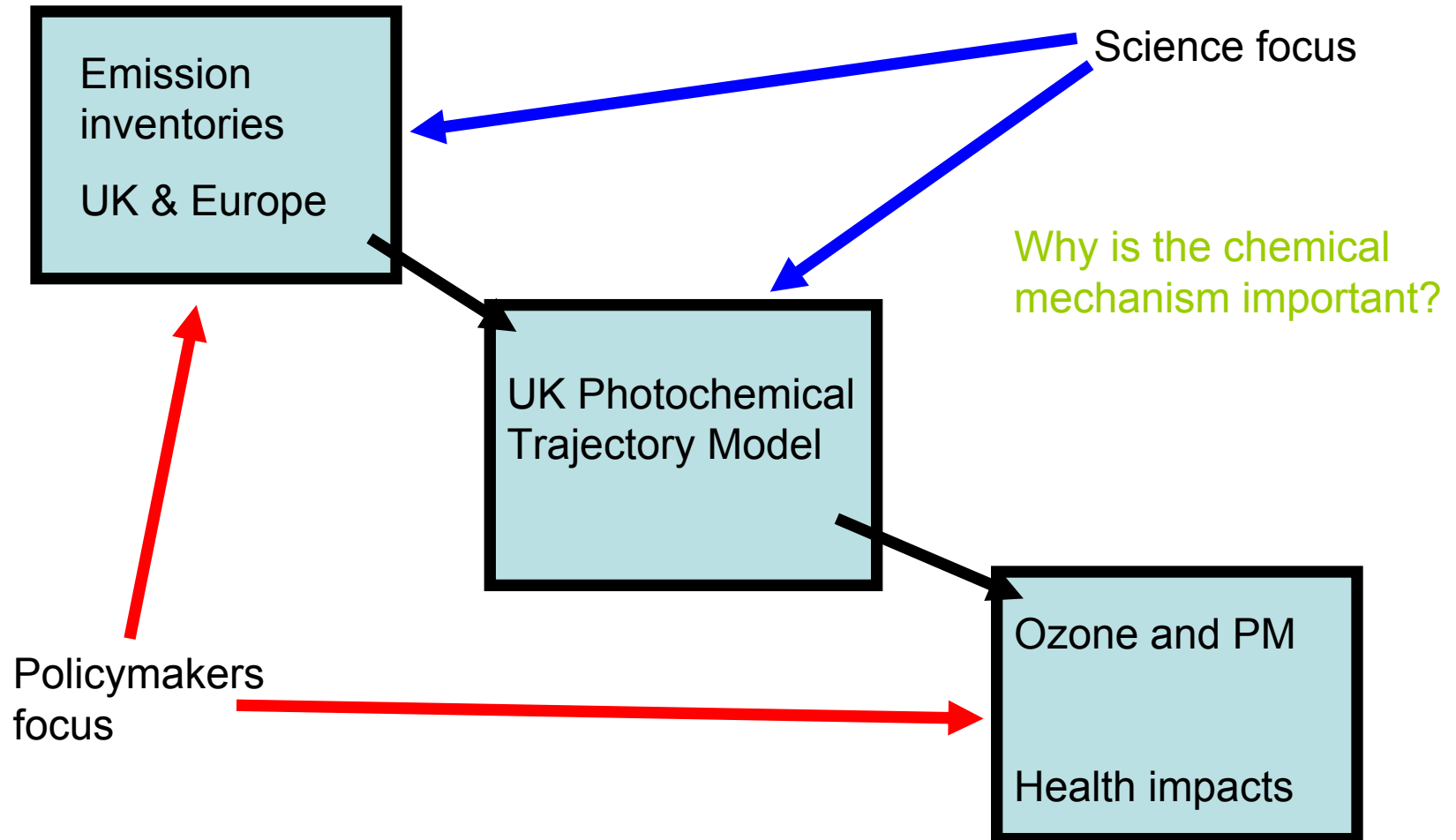


APPLICATION OF A MASTER CHEMICAL MECHANISM (MCM) TO OZONE POLICY ASSESSMENTS IN EUROPE

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rdscientific

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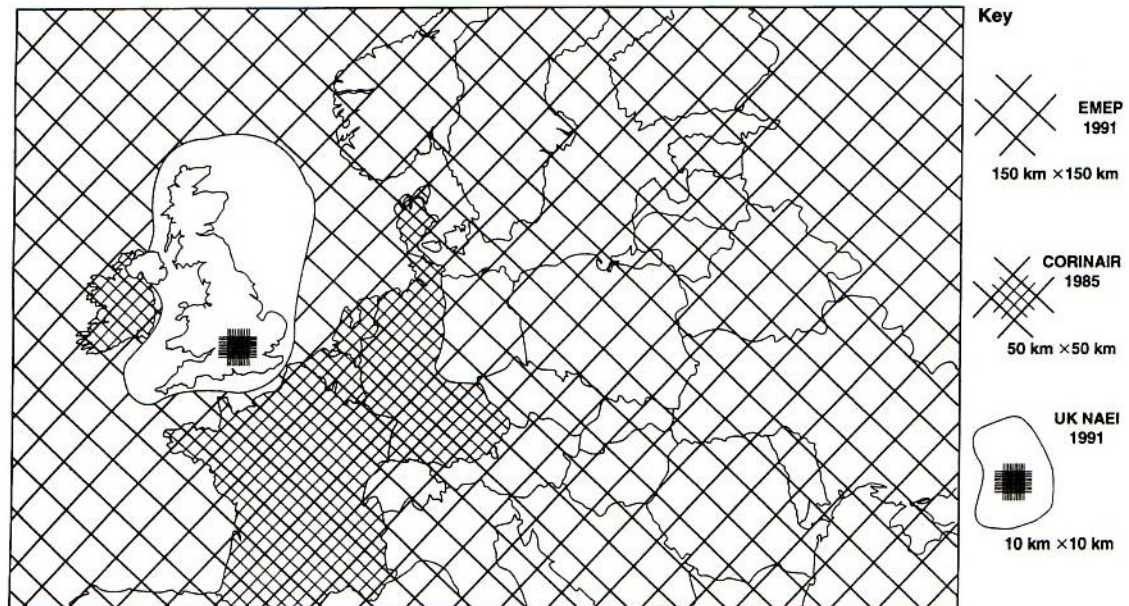
AIM OF THE STUDY



UK PHOTOCHEMICAL TRAJECTORY MODEL

- moving box model
- box height changes with time of day
- emissions of SO₂, NO_x, CO, CH₄, organic compounds
- spatial resolution is 10 km x 10 km , 50 km x 50 km and 150 km x 150 km depending on distance from arrival point
- single standard 5 – day trajectory case from Austria to the UK

GRIDDED EMISSION INVENTORIES



SPECIATION OF THE EMISSIONS OF ORGANIC COMPOUNDS

- UK National Atmospheric Emissions Inventory NAEI
- 248 separate emission source categories
- each emission source has a separate species profile
- species profiles contain 663 individual VOC species
- UK PTM utilises the 248 x 663 speciation matrix
- <http://www.naei.org.uk>

SPECIATION MATRIX

Policy makers

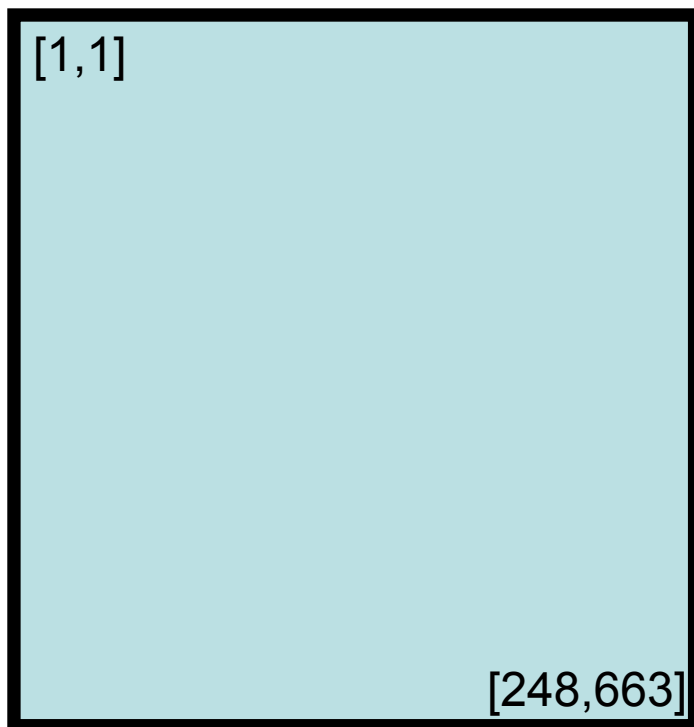
Emission source categories



Organic species



Science community



[248,663]

MASTER CHEMICAL MECHANISM

UK PTM uses MCMv3.1

- 176 emitted organic compounds
- 4,414 reaction products
- 12,871 chemical reactions

Detailed near-explicit chemical mechanism MCM v3.1 to represent the contribution made by methane and 136 individual organic species to ozone formation.

MCM-CRI common reactive intermediates mechanism (Jenkin et al.) used for addition 40 organic species

- 248 x 176 matrix of category x species
- 90% coverage of total VOC mass emissions
- fractional speciation held constant across Europe

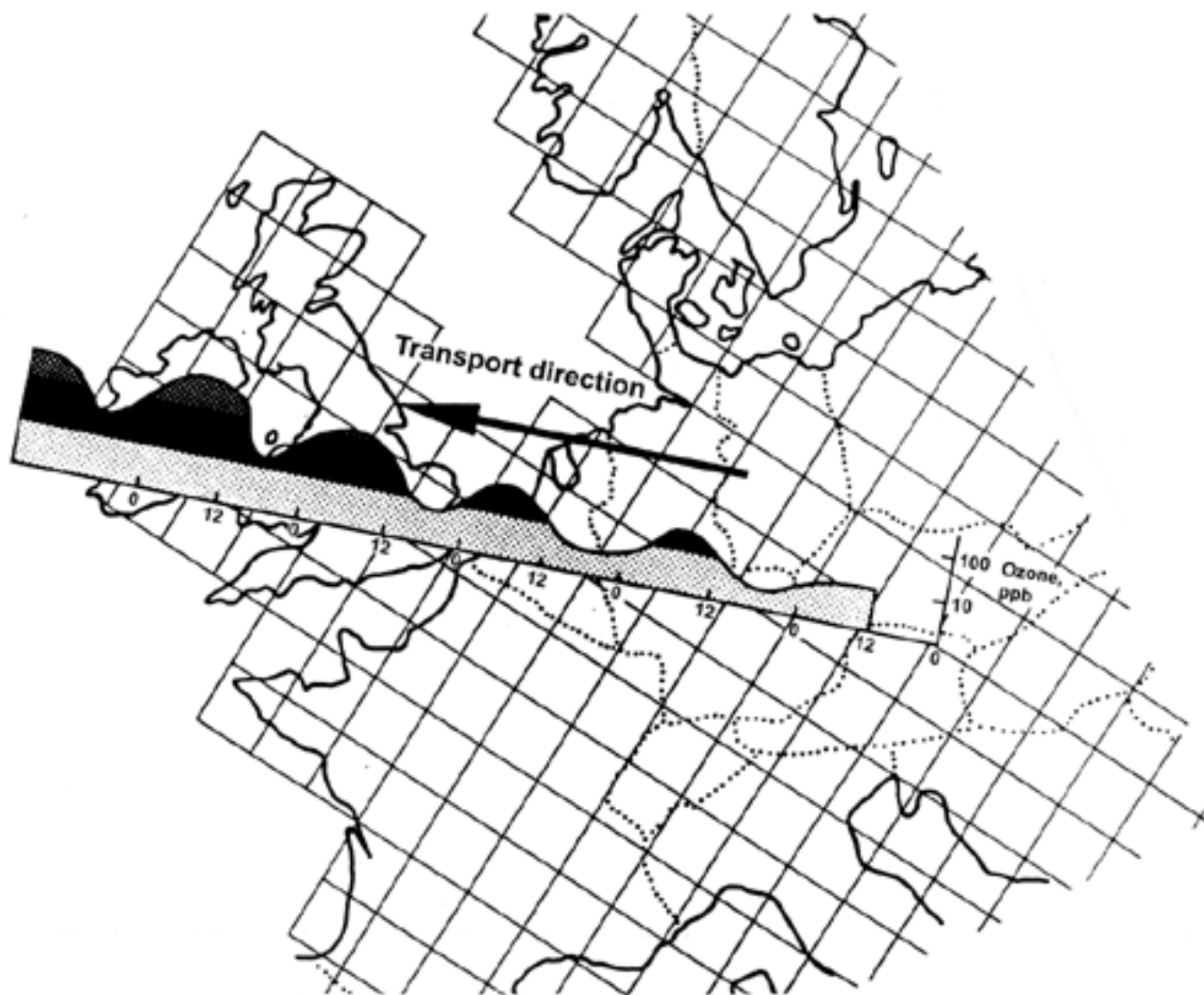
MASTER CHEMICAL MECHANISM

Generates the same picture of regional ozone formation across Europe as other mechanisms such as CBM-4

Used here because it is the only mechanism that treats enough emitted organic species in explicit detail

VOC emission source categories can only be treated explicitly with a chemical mechanism that treats each species in detail

UK PHOTOCHEMICAL TRAJECTORY MODEL



REACTIVITY SCALES

Incremental reactivity

- this is the increase in ozone ΔO_3 in ppb divided by the fractional increase in the emissions from that source category:

$$IR_i = \frac{\Delta O_3}{\frac{\Delta VOC_i}{VOC}}$$

Incremental reactivities depend on the environmental conditions and are not geophysical quantities

SENSITIVITY EXPERIMENTS

An additional emission was added in turn for each of the 176 VOC emission source categories across Europe and the model was rerun.

The extra emission amounted to a 2.9% increase in the emissions for that VOC species.

The increase in emission was applied everywhere across Europe.

The increase in ozone above the base case ΔO_3 was different for every VOC species.

PHOTOCHEMICAL OZONE CREATION POTENTIAL POCP

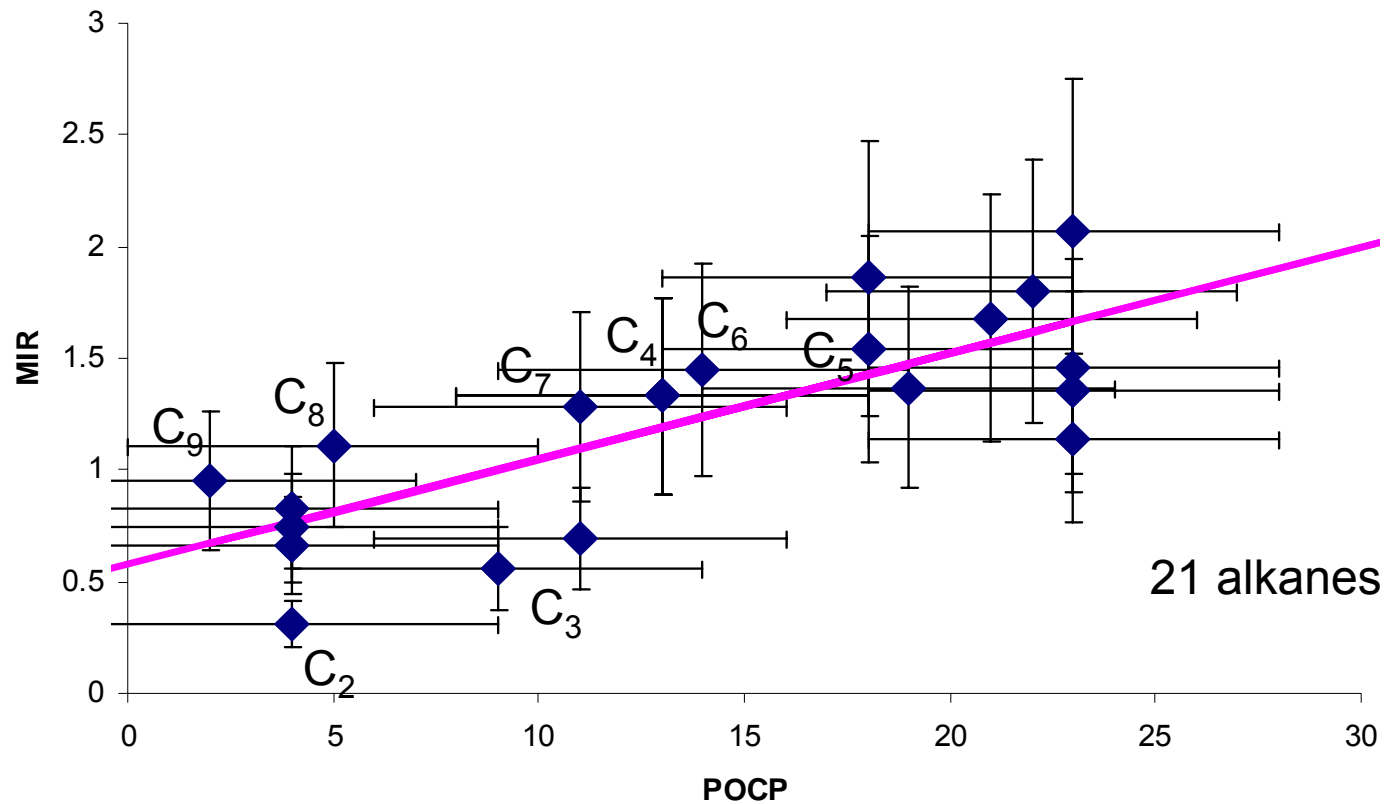
Incremental reactivity for VOC_i expressed relative to ethylene = 100

They depend on environmental conditions such as NO_x and VOC emissions and some policy assumptions.

Determined for:

- single-day Los Angeles situation
- multi-day European situation

COMPARISON OF MIR REACTIVITIES FOR THE ALKANES WITH POCP INDICES FOR LOS ANGELES SINGLE-DAY SITUATION



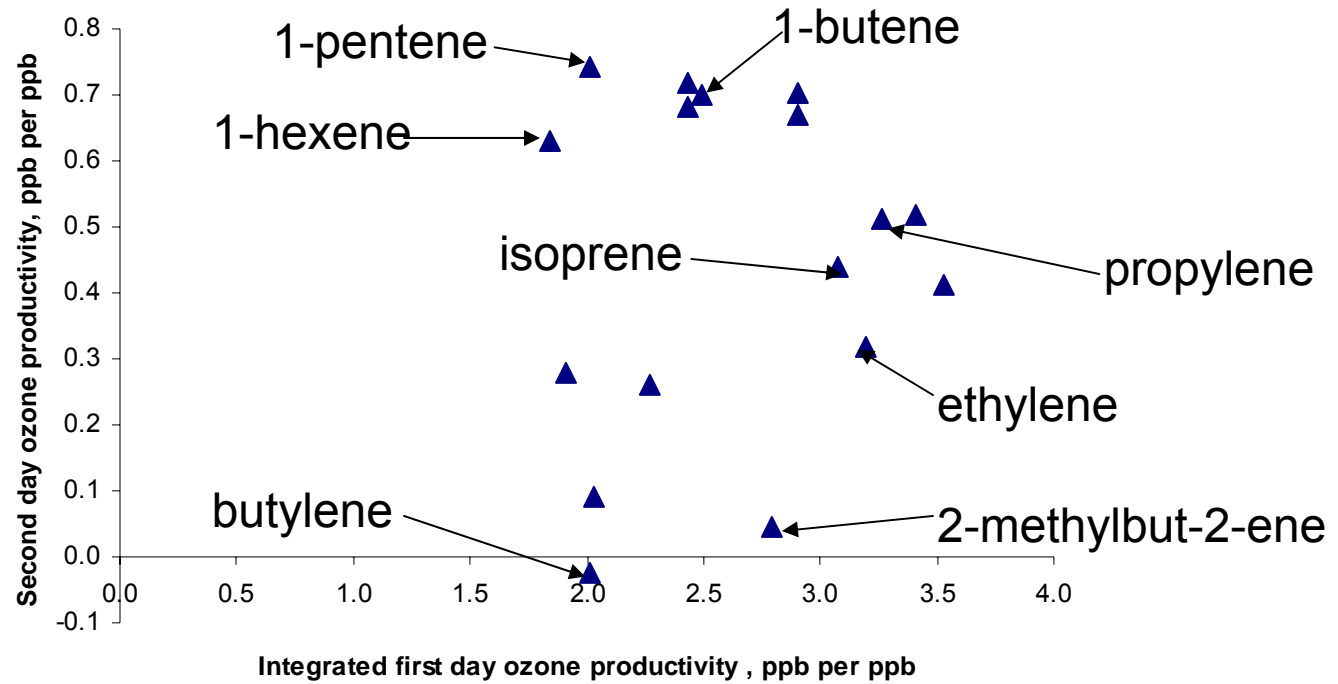
Acknowledgement: W P L Carter for MIR values

CONCLUSIONS ABOUT REACTIVITY SCALES

- can represent a huge amount of atmospheric chemistry in a single number
- can see that OH-reactivity is not the major term determining reactivity
- other determining factors included organic NO_y formation, formation of photochemically-labile molecules, formation of unreactive molecules, competition between pathways
- new chemistry, eg. for aromatics, can drastically change reactivities

MULTI-DAY OZONE FORMATION AND THE REACTIVITIES OF THE OLEFINS

All completely
reacted on 1st day



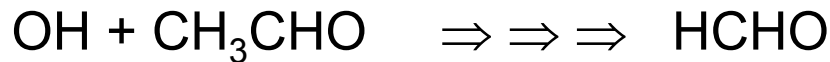
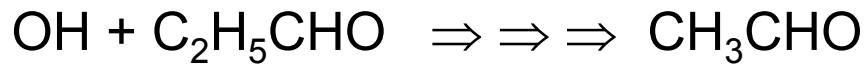
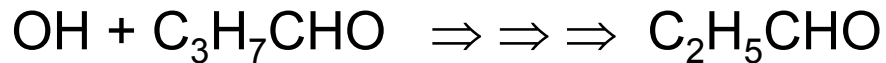
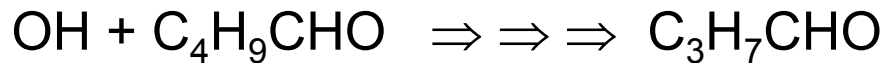
17 olefins

European conditions

FIRST DAY AND SECOND DAY OZONE PRODUCTION WITH THE OLEFINS

- Conclude that all olefins have some ozone production on the second day and that it is highly species dependent
- Second day ozone production occurs even with the almost complete decay (>99%) of the parent olefin on the first day
- There are routes in the Master Chemical Mechanism that allow a VOC to continue making ozone on the second day despite its almost complete decay on the first day

DEGRADATION OF TERMINAL OLEFINS

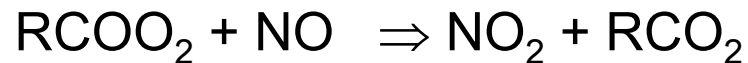
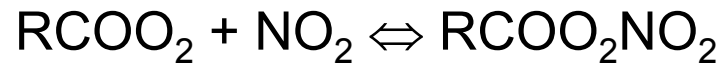


Aldehydes and ketones are longer-lived than olefins and some may survive past the end of the first day.

Formaldehyde is often the end of the decay chain and its production is delayed towards the end of the first day.

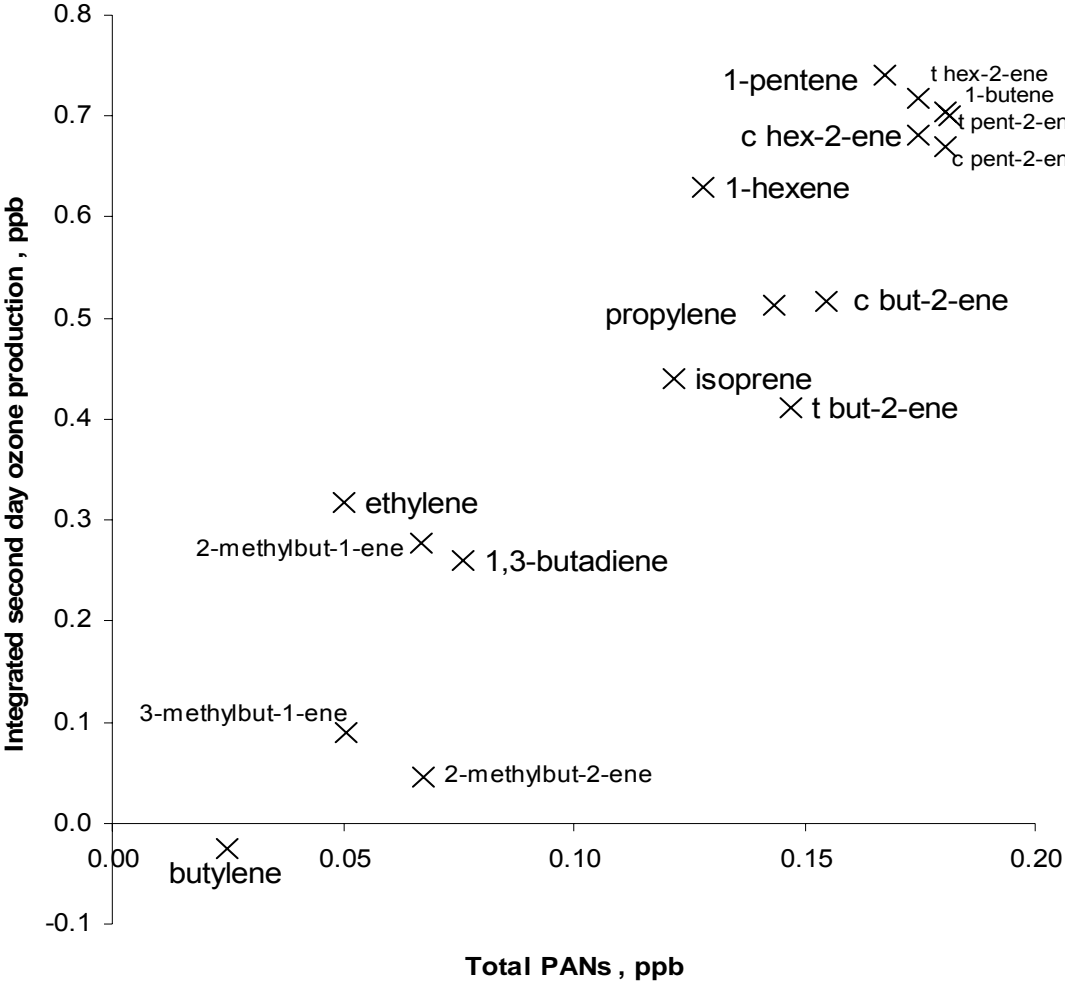
PEROXYACYLNITRATES - PANs

- important set of temporary reservoir species for NO_y
- thermally unstable with a lifetime of many hours



- MCM v3.1 contains 207 individual PAN-type species
- peroxyacetylnitrate PAN is usually present in the highest concentration

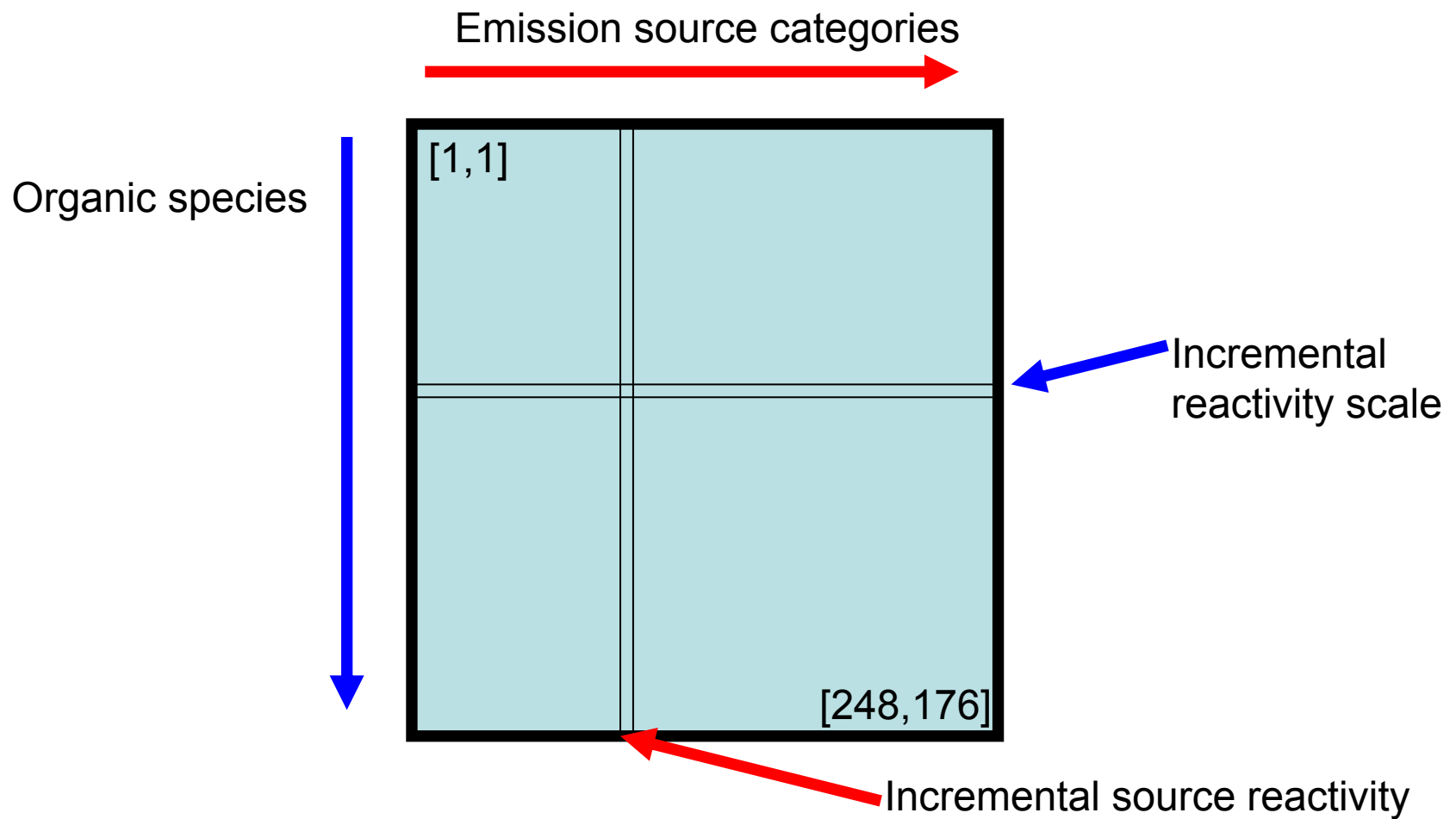
SECOND DAY OZONE PRODUCTION vs OVERNIGHT PANs FOR OLEFINS



CONCLUSIONS ON MULTI-DAY REACTIVITY

- All highly reactive organic compounds have some multi-day ozone formation potential
- Some of the routes are impossible to represent in simplified chemical mechanisms
- PAN formation is an important route and this can be represented in simplified mechanisms

PERTURBING THE SPECIATION MATRIX



INCREMENTAL REACTIVITY IR OF A VOC EMISSION SOURCE

This is the increase in ozone ΔO_3 in ppb divided by the fractional increase in the emissions from that source category:

$$IR = \frac{\Delta O_3}{\frac{\Delta VOC}{VOC}}$$

Incremental reactivities depend on the environmental conditions and are not geophysical quantities

SENSITIVITY EXPERIMENTS

An additional emission was added in turn from each of the 248 VOC emission source categories across Europe.

The extra emission amounted to a 7.3% increase in VOC emissions.

The speciation of the extra emission was given the same species profile as the emission source category.

The increase in emission was applied everywhere across Europe.

INCREMENTAL REACTIVITIES – TOP 12 SOURCE CATEGORIES

Chemical waste incineration	53.8
Blast furnaces_Coke-oven gas	49.5
Iron & steel (Flaring)_Coke-oven gas	49.0
Iron & steel industry_Coke-oven gas	48.9
Other industrial combustion_Coke-oven gas	48.9
Industrial coatings (drum)	47.5
Printing (metal decorating)	47.1
Printing (heatset web offset)	47.0
Industrial coatings (marine)	46.5
Railways (Freight)_Gas oil	46.2
Road transport (rigid HGVs)_DERV	46.2
Other industrial (off-road)_Gas oil	46.0

Expressed
relative to
ethylene = 100

CONTRIBUTION TO OZONE FORMATION

Ozone formation from a particular source category

= Incremental Reactivity x Fractional contribution
to total VOC emissions

Sum of all 248 source category contributions to ozone formation

= 31 ppb

out of the peak ozone concentration of 87.8 ppb

CONTRIBUTION TO OZONE FORMATION IN 2000 - TOP 15 SOURCE CATEGORIES

	% emissions	incremental reactivity	ozone ppb
Road transport (cars without catalysts)_Petrol	11.524	41.387	4.769
Road transport (cars with catalysts)_Petrol	5.264	41.578	2.189
Onshore loading of crude oil	5.098	31.532	1.608
Chemical industry	5.364	28.337	1.520
Offshore loading of crude oil	3.739	31.026	1.160
Spirit manufacture (maturation)	3.401	30.890	1.051
Refineries (process fugitives)	2.091	41.291	0.863
Petrol stations (vehicle refuelling with unleaded petrol)	2.709	31.327	0.849
Other solvent use	3.370	20.229	0.682
Gas leakage	4.648	13.527	0.629
Decorative paint (trade decorative)	1.811	31.395	0.569
Industrial coatings (metal & plastic)	1.627	34.835	0.567
Aerosols (cosmetics and toiletries)	1.883	28.638	0.539
Decorative paint (retail decorative)	1.669	31.313	0.523
Industrial adhesives	1.822	28.569	0.520

CONCLUSIONS

- The detailed representation of the atmospheric degradation pathways for organic compounds can be handled in near-explicit chemical mechanisms such as the MCM
- Reactivity scales represent a means of reducing all the detailed mechanistic information into a single number for each organic compound.
- There are policy implications particularly for the formation and long-range transport of ozone in the detailed representation of the degradation pathways for organic compounds.