MODELLING THE SPECIATION OF PARTICULATE MATTER

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Airborne Particles
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Society of Chemical Industry
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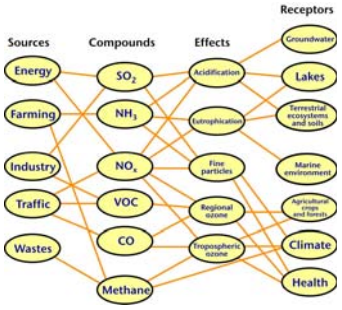
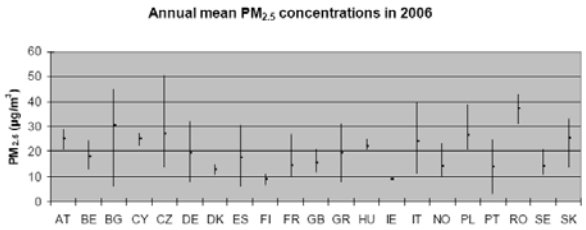
REGIONAL AIR QUALITY PROBLEMS



THE PM SITUATION ACROSS EUROPE



European Environment Agency

CURRENT AIR QUALITY POLICY SITUATION IN EUROPE

EU - Brussels

- CAFÉ Thematic Strategy
- Revision of the National Emissions Ceilings Directive

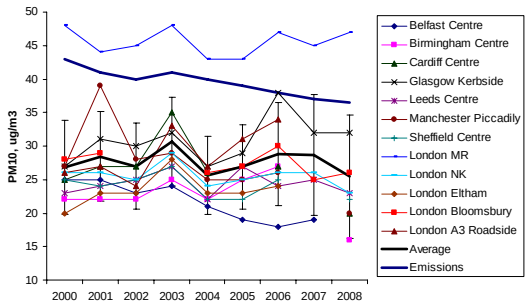
UN ECE - Geneva

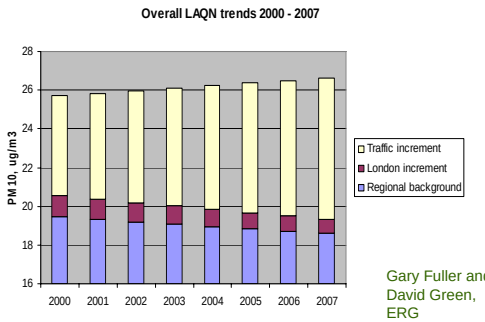
- Review of the Gothenburg Protocol on acidification, eutrophication and ground-level ozone formation

The policy focus is most definitely on PM, driven by their urban health effects.

DESPITE A DECADE OF DECREASING VEHICLE EMISSIONS OF PM URBAN LEVELS REMAIN STUBBORNLY CONSTANT

WHY IS THIS ?



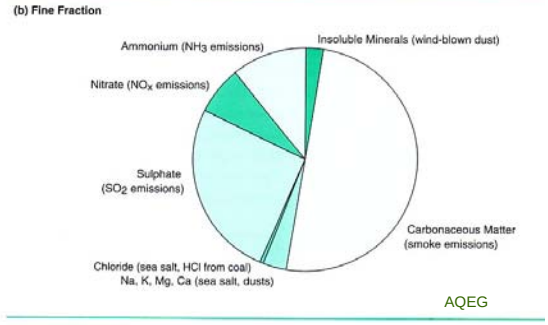


Gary Fuller and David Green, ERG

Modelling The Speciation of Particulate Matter

COMPOSITION OF AIRBORNE PARTICULATE MATTER $PM_{2.5}$

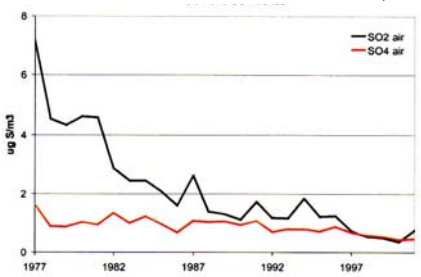
CAN WE MODEL THESE PM SOURCES ?



AQEG

OBSERVATIONS OF PM FINE SULPHATE SHOW MARKED NON-LINEARITIES WITH SO_2 EMISSIONS

Eskdalemuir, Scotland



HOW ARE THESE OBSERVED NON-LINEARITIES TO BE INCLUDED IN POLICY ASSESSMENTS?

- International regional scale assessments use the Unified EMEP Eulerian model (Tarrason et al. 2007)
- UK assessments use a Lagrangian trajectory model approach Photochemical Trajectory Model

PHOTOCHEMICAL TRAJECTORY MODEL

- UK NAEI & EMEP emissions of PM, SO_2, NO_x, NH_3, VOCs, CO, CH_4
- natural biogenic emissions of isoprene and terpenes from GEIA
- Carbon Bond IV or Master Chemical Mechanism
- model for mid-afternoon boundary layer 15:00z
- initial and boundary conditions from literature data
- Met Office NAME 3-D trajectories 96-hour long
- 30 per mid-afternoon for 365 days of 2006
- arrival point Harwell, Oxfordshire

LOCATION OF THE RURAL MONITORING SITE AT HARWELL, OXFORDSHIRE, UK

PRIMARY CARBONACEOUS PM

Elemental carbon emitted mainly from combustion sources

Diesel-engined vehicles are a major source

Biomass burning sources are difficult to assess

Modelling The Speciation of Particulate Matter

FORMATION OF PM SULPHATE

Homogeneous oxidation of SO_2

$$OH + SO_2 + M = HOSO_2 + M$$

$$HOSO_2 + O_2 = HO_2 + SO_3$$

Cloud-phase oxidation by H_2O_2 and O_3

$$SO_2 + H_2O_2 = H_2SO_4$$

FORMATION OF PM NITRATE

Daytime oxidation of NO_2

$$OH + NO_2 + M = HNO_3 + M$$
$$NH_3 + HNO_3 = NH_4NO_3$$
$$NaCl + HNO_3 = NaNO_3 + HCl$$

Nightime oxidation

$$NO_2 + O_3 = NO_3 + O_2$$
$$NO_3 + NO_2 + M = N_2O_5 + M$$
$$N_2O_5 + H_2O = HNO_3 + HNO_3$$
$$N_2O_5 + 2NaCl = 2NaNO_3 + HCl$$

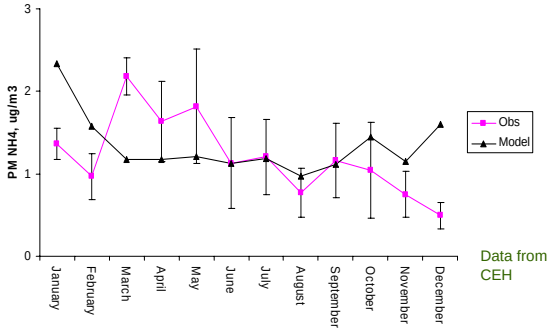
PHOTOCHEMICAL FORMATION OF OZONE AND PARTICULATE MATTER

$$OH + C_{10}H_{16} = \text{reaction products}$$
$$NO_3 + C_{10}H_{16} = \text{reaction products}$$
$$O_3 + C_{10}H_{16} = \text{reaction products}$$

OH + toluene = reaction products

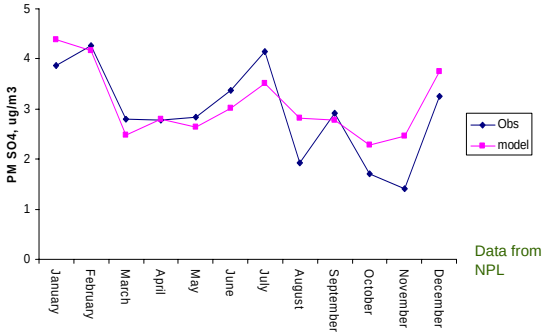
Low vapour pressure reaction products may be scavenged by the pre-existing aerosol.

CHECKING MODEL PERFORMANCE FOR PM NH_4^+



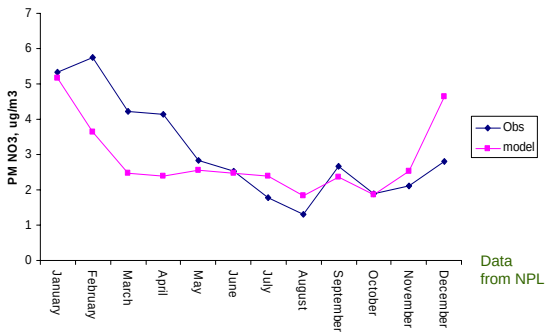
Data from CEH

CHECKING MODEL PERFORMANCE FOR PM SO_4^{2-}



Data from NPL

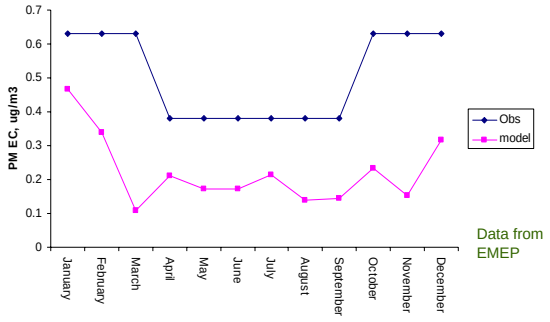
CHECKING MODEL PERFORMANCE FOR NO_3^-



Data from NPL

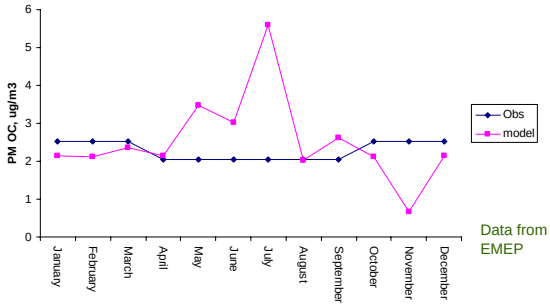
Modelling The Speciation of Particulate Matter

CHECKING MODEL PERFORMANCE FOR ELEMENTAL CARBON PM



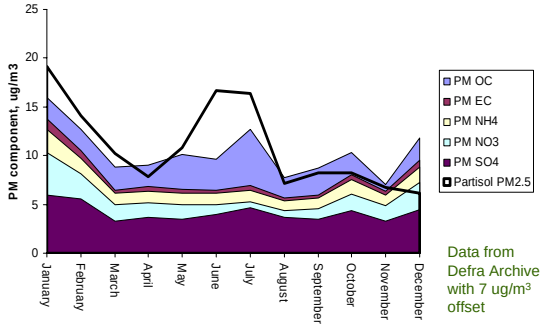
Data from EMEP

CHECKING MODEL PERFORMANCE FOR ORGANIC PM



Data from EMEP

CHECKING MODEL PERFORMANCE FOR $PM_{2.5}$



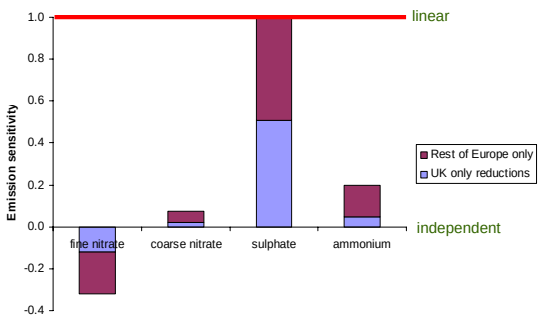
Data from Defra Archive with 7 ug/m³ offset

EMISSION SENSITIVITIES

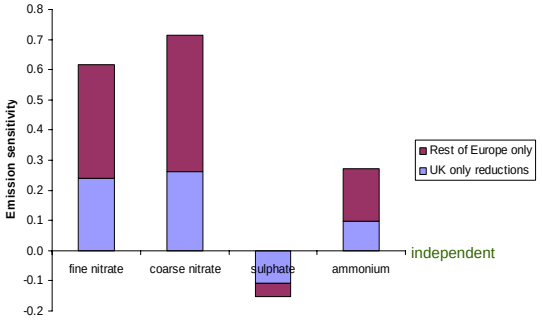
$$\frac{\frac{PM_{reduction\ case} - PM_{base\ case}}{PM_{base\ case}}}{\frac{EMISSION_{reduction\ case} - EMISSION_{base\ case}}{EMISSION_{base\ case}}}$$

In the ideal case of linearity, these sensitivities would either be exactly 1.0 or 0.0
These have been defined by 30% cuts in emissions across-the-board.

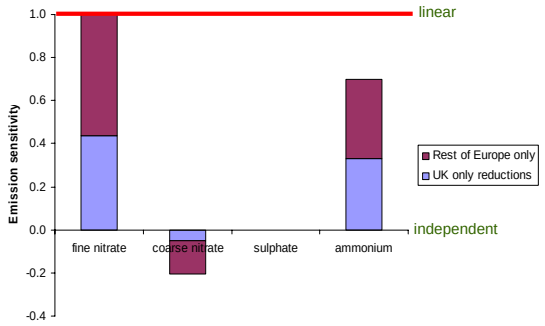
SENSITIVITY OF PM TO ACROSS-THE-BOARD REDUCTIONS IN SO_2 EMISSIONS



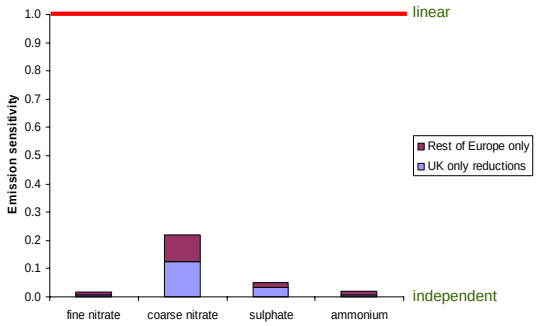
SENSITIVITY OF PM TO ACROSS-THE-BOARD REDUCTIONS IN NO_x EMISSIONS



SENSITIVITY OF PM TO
ACROSS-THE-BOARD REDUCTIONS IN NH_3 EMISSIONS



SENSITIVITY OF PM TO
ACROSS-THE-BOARD REDUCTIONS IN VOC EMISSIONS



CONCLUSIONS – PM FINE SULPHATE

- PM fine sulphate is linear in SO_2 emissions and has an important –ve non-linearity with NO_x emissions
- the PM fine sulphate is of both domestic and foreign origins
- the non-linearity is largely with domestic NO_x emissions

CONCLUSIONS – PM FINE NITRATE

- PM fine nitrate is linear in NH_3 emissions and has important +ve non-linearity with NO_x emissions and –ve non-linearity with SO_2 emissions
- PM fine nitrate is of both domestic and foreign origins
- the non-linearities are generally with the foreign emissions
- non-linearities are crucial

CONCLUSIONS – PM COARSE NITRATE

- PM coarse nitrate has +ve non-linearities with NO_x, SO_2 and VOC emissions and –ve non-linearity with NH_3 emissions
- the majority of the PM coarse nitrate is of foreign origins
- the NOx, NH_3 and SO_2 non-linearities involve foreign emissions but the VOC non-linearities involve domestic emissions
- non-linearities are crucial

CONCLUSIONS – PM FINE AMMONIUM

- PM fine ammonium has non-linearities with NO_x, SO_2 and NH_3 emissions
- PM fine ammonium has more or less equal foreign and domestic contributions
- the non-linearities with NO_x and SO_2 involve foreign emissions
- non-linearities are crucial

ACKNOWLEDGEMENTS

• AQIP Defra for support through contract numbers AQ0704 and AQ3508
• NPL for providing access to the daily PM observations for Harwell
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• Gary Fuller and David Green, ERG, for access to the LAQN data