

LAGRANGIAN MODELLING OF PLUME CHEMISTRY FOR SECONDARY POLLUTANTS IN LARGE INDUSTRIAL PLUMES.

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INTRODUCTION

The UK Met Office NAME¹ model is used for national air quality forecasts². Previous applications include a sulphur dioxide episode, (Skinner, 2000), atmospheric chemistry campaigns (Redington et al., 2001) and formation of nitrate and sulphate aerosols (Redington and Derwent, 2002). We investigate a newly developed version NAME III (v2.1) for possible use as a regulatory modelling tool for large industrial plumes. We focus is on secondary pollutant formation: O₃ and NO₂. We explore the idea that a series of pre-defined scenarios might contribute to an objective Regulatory modelling process for such plumes. We consider the advantages of simple uniform meteorology and background fields whilst retaining Lagrangian dispersion processes and full NAME chemistry scheme.

Traditionally, NAME needed large arrays of numerical weather prediction (NWP) data from the Unified Model¹ (UM). Virtual 'particles' are released from the emission source to represent the advection and dispersion of plume species. Background chemistry fields (O₃, H₂O₂) have hitherto been initialised from the Met Office global chemistry model (STOCHEM¹) monthly mean values. These features of NAME II somewhat restricted its flexibility for Regulatory application to secondary pollutants in industrial plumes. New options in NAME III used here include:

- Single site, ADMS-format synoptic meteorological data generating uniform meteorology across the domain, instead of NWP meteorology.
- Suppression of turning of the wind with height when using simple uniform meteorology, facilitating plume chemistry visualisation.
- Lagrangian representation of a background domain with concentration fields of chemically reacting species (O₃, volatile organic compounds VOC) in addition to emitted plumes (SO₂, NO, NO₂). This enables the model to simulate plume chemistry with inhomogeneous mixing as the 'particles' from background and plume intermingle, representing reactive entrainment of background air.

Results for an elevated plume (domain 40×100 km, ~2.5 km deep) as the plume mixes and reacts with background air showed O₃ depletion from background air within the plume, nocturnal formation of NO₂ on the plume edges, and daytime photochemical elevation of O₃ at larger distances downwind. Possible regulatory control of secondary pollutants via a limited set of pre-defined scenarios will be discussed.

In the UK, regulatory responsibility for large industrial stacks and power stations rests with the Environment Agency³ (EA). Procedures for assessing NO₂ contributions to rural and urban air sheds have been both simple to apply (to facilitate the regulatory workload) and conservative (so that a worst case situation is regulated for). The procedure has simple assumptions for the amount of oxidation of emitted NO, ranging from 100% oxidation to NO₂ (worst possible outcome: most conservative) through 75% oxidation (less conservative) or 50% oxidation (less conservative still) down to 35% oxidation to NO₂ (even less

conservative) which is useful for evaluating annual mean concentrations. These fixed-ratio approaches have proved simple and clear to apply. The philosophy has been acceptable historically within the Agency, because in the UK the applicant must justify their protocol used to estimate their site's impact upon NO₂. For instance, if good monitoring data exist for location(s) downwind they can be used in the estimating process. Some operators have used the method of Janssen (see below) which was developed using aircraft data in *large* power station plumes, but the EA have rejected this for use on *smaller* plumes. Whilst unduly conservative, it is in practice the clarity of approach that supported such simple fixed-ratios. The EA has the ADMS⁴ model, which contains a simplified reaction scheme (the 2-reaction photo-stationary state reactions, or the 7-reaction General Reaction Scheme GRS). Currently the use of ADMS chemistry for NO₂ plume planning applications is difficult:

- uncertainty of knowing what background concentrations of O₃ or VOC species to use,
- uncertainty in representing photochemical episodes,
- unusual primary NO₂ emissions, e.g. land-fill gas burners or engines up to ~20%, or industrial processes like steel acid-pickling; nitrate drying up to ~100%, as NO₂.

EMPIRICAL FUNCTIONS FOR NO₂

Empirical functions summarise monitoring data in a form that regulators can use. Experience in Local Air Quality Management (LAQM) shows the practical value of such simple tools.

Motor vehicles, domestic and other sources, dominate urban NO₂. Tools to assess urban NO₂ in LAQM vary the yield of NO₂, rather than some fixed percentage as used above. They represent O₃ and NO_x limiting regimes. Empirical functions based on urban monitoring data by Derwent and Middleton (1996), Dixon et al. (2000; 2001) are used by local authorities in the UK. Carslaw et al. (2001) investigated further the concept of an empirical function for hourly mean NO₂ versus hourly mean NO_x. Clapp and Jenkin (2001) analyzed ambient *daylight* concentrations of O₃, NO and NO₂ as a function of NO_x from rural and urban stations. Their variable, *daylight* 'OX', is the total oxidant, [O₃]+[NO_x], in two parts:

- regional/background contribution - approximates to O₃; largely independent of NO_x
- local contribution - correlates with the contribution of local primary NO_x emissions to local NO₂, plus local oxidation of NO to NO₂ by O₂ (more significant at high [NO]), and local emissions of some species like HONO that can convert NO to NO₂.

Clapp and Jenkin (2001) investigate the variation of OX with NO_x, based on annual means, with functions for variation of annual mean NO₂ as a function of NO_x as the regional background of O₃ changes. Jenkin (2004) treats NO, NO₂ and O₃ as a coupled system when examining policy controls on NO_x emissions. A variety of monitoring sites were used, from kerb to rural. He establishes how OX varies with NO_x and how the partitioning or fractional contributions NO₂/OX and O₃/OX behave. He formulated empirical expressions for different parts of the UK and for future NO₂ concentrations. Chemical partitioning (NO₂ or O₃ as above) is decoupled from sources of oxidant to make predictions that distinguish regional O₃ from local primary NO₂ emissions. To conclude, UK empirical functions for urban NO₂ use polynomials from time-series monitoring results, not fixed NO₂:NO_x ratios.

Janssen (1986) analysed aircraft data from power station plumes; he modelled the effect of inhomogeneity in plume-atmosphere mixing on the conversion of NO to NO₂. He concluded that it is necessary to take account of *inhomogeneous* mixing. Janssen et al. (1988) gave an empirical equation (1) for the formation of NO₂ in a power station plume, with constants for different seasons, using data from aircraft measurements traversing plumes at different downwind distances. They measured the ratio NO₂:NO_x as a function of plume travel distance downwind. They expressed the rate of change of the ratio in terms of [O₃], wind speed *u* at

plume height, and downwind distance x . Their expression contained the rate constant for the $\text{NO}+\text{O}_3$ reaction, plus a constant derived by assuming the photo-stationary state at larger distances downwind. At these ranges, dispersion is slower than the chemical reactions.

$$\frac{[\text{NO}_2]}{[\text{NO}_x]} = \left(\frac{k_2}{k_1[\text{O}_3]} + 1 \right)^{-1} (1 - e^{-\alpha x}) \quad \text{where } \alpha = \frac{k_1[\text{O}_3]}{u} \quad (1)$$

and k_1 is the rate constant for $\text{NO}+\text{O}_3$. Also k_2 is the rate of photolysis (photo-dissociation) of NO_2 to NO by light (daytime). The units for k_1 and k_2 are $\text{ppm}^{-1} \text{min}^{-1}$ and min^{-1} respectively. Equation (1) assumes a *homogeneous* plume, ignoring variations in mixing and concentrations across the plume, but Janssen et al. (1988) said it was a first approximation to the $\text{NO}_2:\text{NO}_x$ ratio in a plume. They give a range of values for the constants according to season and background O_3 concentration. Equation (1) result in a higher yield of NO_2 in winter daytime than in summer, simply because actinic flux is lower (lower solar elevation at midday) and the photolysis reaction which removes NO_2 is slower.

Our study therefore uses complex modelling to explore the factors that influence the formation of NO_2 , and to identify possible simple methods of assessment of the NO_2 concentration in EA regulated plumes. We focus on ways of simplifying the use of the new NAME III model. This paper describes how we have used the new model, with point source, simple meteorological data, and concentrations for the background O_3 and VOC. The various scenarios can be pre-defined and run in sequence. Our Lagrangian plume is *inhomogeneous*.

MODEL SCENARIOS

This study investigates the sensitivities in plume chemistry as represented by the NAME 3 model. We model simple scenarios, looking to suggest a tool for Regulators. All these results are for concentrations in the lowest 100 m of atmosphere, below the plume. Our results showed a night/day contrast and change both across and down the plume. A continuous point source at the origin was 200 m above ground. The emission rates were: SO_2 , 8000 g s^{-1} ; NO , 950 g s^{-1} ; NO_2 , 50 g s^{-1} . Primary NO_2 from our point source is but 5% by mass of the total emitted NO_x . These data are typical of a power station in magnitude. As this is a Lagrangian model, 15 virtual 'particles' per second were released. The sensitivity of our results to this parameter was not investigated. Plume rise was not modelled.

Meteorological data were put in a small file in the same format as used by the ADMS model. These were artificial meteorological data, with the wind speed set at a steady 4 ms^{-1} blowing from due West to due East. The days simulated were 21 and 22 June to represent maximum solar elevation for driving the chemistry scheme. The model domain is the region 100 km downwind and 40 km wide. The plume passes symmetrically over the long axis of this domain area because the wind direction does not vary with height. Normally when running on single site met data (i.e. ADMS style surface synoptic data) the model calculates both the turning of the wind with height and the variation of its velocity with height. Initial runs showed how this turning causes the plume and its chemical products to curve with travel time, but here this option is turned off, so we have a uniform wind with altitude, in order to better delineate the response of the chemistry. In future runs we can include plume rise, the boundary layer profile, and switch to NWP data sets from the UM. More realistic situations may then be modelled.

In a long range model such as NAME, emissions across Europe can lead to atmospheric reactions and a burden of background pollutants in the air masses as they are modelled entering the UK. However to simplify the problem we have set up a uniform background

field. Background concentration fields were defined for O₃ and VOC. The VOC comprised 7 species types, according to reactivity, and as used in the PUMA study reported by Redington et al. (2001). The chemical reaction scheme is also summarised there. Total background VOC concentrations were varied for each run as 5, 10, 20, 50, 75 ppb. VOC species were in these constant mole ratios relative to each other: toluene 32.6%, ethane 23.4%, formaldehyde 15.6%, propene 13.48%, o-xylene 8.511%, acetaldehyde 3.546% and butadiene 2.837%. Background O₃ concentrations were 10, 20, 50, 100, 150 ppb, varied independently of VOC. To maintain a supply of background 'particles' to the Lagrangian domain, they were fed in through the top surface or lid, western up-wind face, and two down-wind walls to north and south. The Main Domain (105×40×2.3 km) is filled with 'particles at the start of the run. Each Side (105×4×2.3 km) & Top domain (105×40×2.3 km) steadily emits 'particles' carrying background O₃ and VOC during the run. 'Particles' were then allowed to exit the down-wind face. Masses of all species on each 'particle' once within the domain change independently of one another in accordance with the requirements of each chemistry step. Spurious edge effects during background 'emission' into the domain must be minimised.

Background supplies reactants able to combine with the plume pollution. Domain averaged concentration was checked at each 3-hour time-step. The background with no chemical reaction, emission of NO and NO₂ and background VOC all set to zero, was tested. It was a little below the target concentration at the start of the run and soon reached steady state. The fluctuation in the area averaged background over the domain grid squares from one 3-hour step to the next was typically within ±0.3% of the target O₃ background. This noise reflects the Lagrangian description of the background. It is dependent on 'particle' numbers.

Since NAME 3 is a Lagrangian model, it was necessary to calculate the mass of background species within the model domain, then allocate these in aliquots to 'background' imaginary model particles in this region, allowing them to be dispersed in the same manner as the 'particles' belonging to the point plume. As the two types of 'particles' dispersed and mixed, chemical reactions were modelled. To do this, 'particles' were sorted into virtual grid-boxes, their pollutant masses summed, and equivalent concentrations evaluated. Once the chemical kinetics had been solved, the new pollutant concentrations for plume and background were reallocated as pollutant masses on each 'particle'. 'Particles' were then ready for the next Lagrangian advection dispersion time-step. The model is thus able to represent the inhomogeneous concentrations and rates of reactions over the plume space. To reach steady state this set-up requires 7 hours to be modelled, the journey time for particles at 4 m/s to cross our 100 km domain. Day 1 shows the plume growing to cross the domain whilst Day 2 represents a pseudo-steady state (it still goes from night to day and back).

The model generates a spatial distribution of grid-box concentrations in which 'particles' are accumulated for a common model period, say a daily mean (24 hr) or 3-hourly mean. Since the grid boxes we have used represent 1 km × 1 km and 100 m depth, over 3 hours, significant spatial and temporal-averaging is implicit in our data. This may partly explain why our results for empirical functions give significantly different NO₂ values from those seen in earlier urban functions. In urban areas the monitoring point is usually surrounded by and relatively near to distributed sources, another difference from the plume situation. Work is needed to analyse the sensitivity of our results to spatial/temporal averaging; to investigate the effects of numbers of virtual 'particles' on concentration noise and the chemistry; to explore the influence of height, and the change from simple to NWP met-data.

CONCLUSIONS

The new NAME III model was run on simple single site ADMS-format data and used successfully for systematic sensitivity studies of plume chemistry. We have modelled the Lagrangian dispersion and Eulerian chemistry of a large point source plume, typical in scale of those regulated by the EA. Background O₃ and VOC were assigned to virtual 'particles' and their concentrations varied. The results showed:

1. Nocturnal NO₂ maxima on the plume-edges, by reaction of background O₃ with plume NO. They appear at night when there is no light to drive the photochemistry and dispersion is less. This leads to inhomogeneous concentrations across the plume, an important feature of plume chemistry identified by Janssen (1986).
2. A region of O₃ reduction nearer to the source.
3. If the hydrocarbon VOC concentrations are sufficient, in daylight with photochemistry, a region of raised O₃ concentrations further downwind.

A suite of scenarios with differing backgrounds can be pre-defined and run from a script and results plotted automatically for a point source. This facility represents a potentially useful Regulatory tool. It allows for systematic variation in key parameters: light/dark, background O₃, background VOC, and in meteorology, wind speed and cloud cover or NWP data.

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