

## USE OF EULERIAN MODEL OUTPUTS AS BACKGROUND CONCENTRATIONS FOR NITRATE PREDICTIONS IN CALPUFF SYSTEM

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### INTRODUCTION

Secondary particulate matter such as sulphate (SO<sub>4</sub>) and nitrate (NO<sub>3</sub>) are often important components of fine particulate matter in the environment. In addition to adverse health effects, hygroscopic nitrate and sulphate aerosols can have a strong impact on visibility degradation in pristine areas. The chemistry of nitrate aerosols formation depends strongly on the availability of ammonia, nitric acid and the temperature and relative humidity conditions in the atmosphere. In CALPUFF, an annual or monthly average concentration of ammonia is provided and is available on a puff by puff basis for nitrate aerosols formation. But in reality, ammonia is not constant, neither spatially nor temporally. A CALPUFF post-processing method called Ammonia Limiting Method (ALM) has been developed as a refined method for CALPUFF to take into account the non-linear effects of varying excess ammonia in the formation of nitrate. Instead of using a constant NH<sub>3</sub>, representing NH<sub>3</sub> gas in excess when all nitrates and sulphates have been formed in the background, the approach is to use a background environment temporally and spatially varying, composed of pollutants active in the nitrate formation. The outputs of a run of the EPA Community Multi-scale Air Quality (CMAQ) model are validated against two sets of observations gathered in the Southeastern United States. Its suitability for use as hourly background concentrations in the CALPUFF system for ALM application is discussed. Sensitivity to the monthly average background ammonia used in CALPUFF runs before ALM application is also discussed and some guidelines are provided accordingly.

### BACKGROUND ON NITRATE SIMULATION IN CALPUFF SYSTEM

The CALPUFF model (Scire *et al.*, 2000), a non-steady-state Lagrangian puff dispersion model, simulates the chemical conversion of nitric oxides (NO<sub>x</sub>) to nitric acid (HNO<sub>3</sub>) and nitrate aerosols (NO<sub>3</sub>) with a set of parameterized conversion equations. For either one of the two CALPUFF chemistry schemes, RIVAD and MESOPUFF, a monthly average constant background concentration of ammonia gas is entered into the model, and is used, together with an equilibrium relationship (equation 1) between nitric acid and nitrate aerosols (Stelson and Seinfeld, 1982) to predict nitrate aerosols for a given source.



$$\text{With } K = \frac{[HNO_3] \cdot [NH_3]}{[NH_4^+] \cdot [NO_3^-]}$$

This equilibrium equation is resolved at each puff and each time step. For each puff along the trajectory between the source and any receptor, the background value provided as input to CALPUFF is available to form ammonium nitrate if the conditions of relative humidity and temperature are adequate. This availability of ammonia in CALPUFF on a puff by puff basis has a cumulative effect on the quantity of ammonia used and tends to overestimate the ammonium nitrate formed at any receptor along the trajectory.

Since the relationship between nitric acid and ammonium nitrate is in balance, we can say that in the assumption of no deposition, the total nitrate (TNO<sub>3</sub>), sum of ammonium nitrate and nitric acid, stays constant, when it is advected along a trajectory. Because of this equilibrium, the repartitioning between HNO<sub>3</sub> and NO<sub>3</sub> is possible at each time step and each receptor with a corrected background NH<sub>3</sub>, more appropriate for the natural conditions than the cumulative effect of annual averaged or monthly averaged ammonia used in CALPUFF. A post-processor called POSTUTIL, in which the equilibrium chemistry equation from CALPUFF is implemented, allows the user to perform this repartitioning using either a concentration of free ammonia gas background provided as input in POSTUTIL or a total ammonia background (TNH<sub>3</sub>, sum of ammonia gas and ammonium particulate). In the option of TNH<sub>3</sub> background, other concentrations such as sulphate and TNO<sub>3</sub> are also needed to define the background for the POSTUTIL run. The repartitioning of NO<sub>3</sub> and HNO<sub>3</sub> done in POSTUTIL using this extended background is called the Ammonia Limiting Method (ALM).

### Description of Ammonia Limiting method

The Ammonia Limiting Method (ALM) was developed to refine the CALPUFF simulation of NO<sub>3</sub> aerosols concentrations in situations where sulphate concentrations are high or ammonia emissions are low and the atmosphere may be in an ammonia-limited regime relative to nitrate formation (*Escoffier-Czaja and Scire, 2002*). This method was also developed to palliate a lack of ammonia gas observations and to offer new possibilities other than using over conservative annual or monthly ammonia gas concentrations. This method does take into account the non-linear effects of varying excess ammonia in the formation of nitrate. A variation of the method described in *Escoffier-Czaja and Scire, 2002* is proposed here. Instead of observations, outputs concentrations of a photochemical eulerian model are tested. The approach is to assume that the nitrate aerosols emitted from a new source represent only a small perturbation to the background nitrate aerosols. Since nitrate aerosols and nitric acid are in equilibrium relationship (equation 1) at a given instant and given location, the equation (2) below can be resolved to estimate the nitrate aerosol from the source at this location. Indeed, the ratio NO<sub>3</sub>/(NO<sub>3</sub>+HNO<sub>3</sub>) is the same for the background alone, the background with a small perturbation or for the perturbation itself.

$$\frac{[NO_3]_{source}}{[HNO_3 + NO_3]_{source}} = \frac{[NO_3]_{source+background}}{[HNO_3 + NO_3]_{source+background}} \quad (2)$$

This requires a valid estimate of the background (SO<sub>4</sub>, TNO<sub>3</sub>, TNH<sub>3</sub>) provided by the photochemical model. By using model outputs, this background is available at every hour and with a high spatial resolution. The repartitioning of nitrate aerosol and nitric acid for the background + source at each instant is re-evaluated using the total ammonia background (ammonia gas + ammonium aerosols) and the nitrate aerosols for the source itself can be deducted from equation (2).

### USE OF DATA FROM PHOTOCHEMICAL MODEL CMAQ

The outputs of a CMAQ (*U.S. EPA, 1999*) model run performed by ENVIRON et al (2004) are evaluated. This run covers the United States of America for the year 2002. First, the ammonia gas (NH<sub>3</sub>) outputs are compared to several datasets of ammonia gas observations with different time resolutions: monthly averages at CENRAP and SEARCH sites, daily averages at St Louis Supersite. The results (not shown) demonstrate that the free ammonia from the model is very often too low compare to the ammonia observed. This underestimation is partly due to large uncertainties on ammonia emissions input into CMAQ

model. The ammonia gas model outputs are consequently not suitable to be used directly into POSTUTIL for repartitioning nitrate and nitric acid. This would generate too low concentrations of nitrate aerosols.

Separately, CMAQ concentrations such as SO<sub>4</sub>, NO<sub>3</sub>, HNO<sub>3</sub> and TNO<sub>3</sub> are compared against two datasets: the Interagency Monitoring of Protected Visual Environments (IMPROVE) daily averaged observations and the EPA Clean Air Status and Trend Networks (CASTNET) weekly averaged observations. From both datasets, a selection of stations was gathered in the Southeastern United States. The result of this comparison is a very good agreement between the model outputs and the observations for SO<sub>4</sub> and TNO<sub>3</sub> (not shown). However, CMAQ particulate NO<sub>3</sub> itself is larger (but still within a factor of 2) than IMPROVE and CASTNET nitrate observations (Figure 1), except for a few underestimation of the large concentrations when compared on a weekly basis to CASTNET.

HNO<sub>3</sub> and NO<sub>3</sub> concentrations from CMAQ model were tested as input into the CALPUFF equilibrium chemistry system implemented in POSTUTIL, using CMAQ TNH<sub>3</sub> concentrations for the repartitioning. The particulate NO<sub>3</sub> formed by this system were nearly identical to the NO<sub>3</sub> outputs of CMAQ itself as it is displayed in Figure 1. This result demonstrates the ability of CALPUFF equilibrium chemistry in repartitioning NO<sub>3</sub>/HNO<sub>3</sub>.

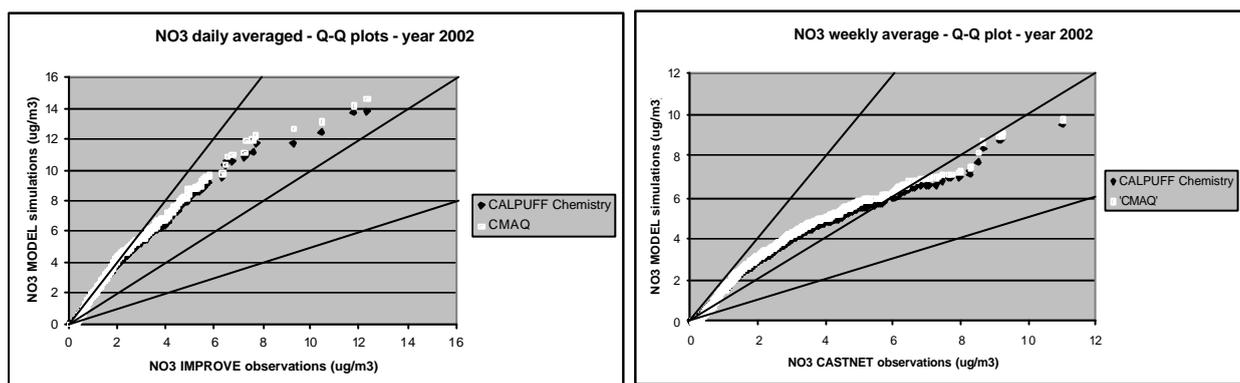


Figure 1; Quantile-Quantile plots of NO<sub>3</sub> aerosols modelled with CMAQ (white dots) and modelled with CALPUFF chemistry (black dots) as function of daily averaged NO<sub>3</sub> IMPROVE observations (left) and as function of weekly averaged NO<sub>3</sub> CASTNET observations (right)

## Application

A nitrate concentration impact from a hypothetical source is assumed to be 0.5µg/m<sup>3</sup> for each hour of a year at two receptors in the Southeastern United States. This application is provided for information to show the sensitivity of the repartitioning of NO<sub>3</sub> in POSTUTIL to the background ammonia chosen. At each location, two POSTUTIL runs are performed using first a constant background ammonia of 0.5ppb, then using ALM with CMAQ output concentrations to define the background at each location. The results are monthly averaged and plotted as time series on Figure 2. The POSTUTIL run using NH<sub>3</sub>=0.5ppb (dark line) shows a variability of NO<sub>3</sub> concentrations mostly created by the conditions of temperature and relative humidity different at each hour of every month and for each area. When ALM is applied (white line), the NO<sub>3</sub> concentrations is either smaller than the NO<sub>3</sub> concentrations simulated using NH<sub>3</sub>=0.5ppb for all months (as shown on the right plot of Figure 2) or as in the left plot sometime larger. It does show that the use of CMAQ model outputs in ALM

application with POSTUTIL to refine the simulation of particulate NO<sub>3</sub> from an individual source give more variability to the NO<sub>3</sub> formed than when a constant NH<sub>3</sub> is used.

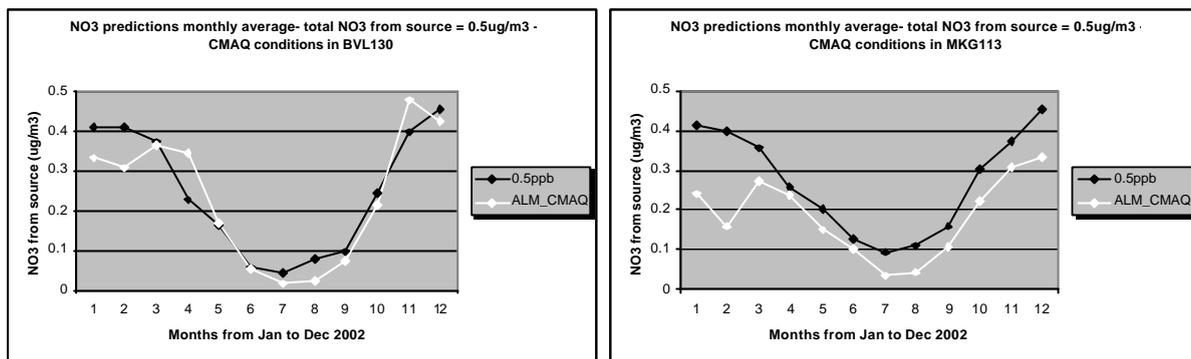


Figure 2; Monthly average time series of NO<sub>3</sub> concentrations simulated by two POSTUTIL runs with different NH<sub>3</sub> assumptions: 0.5ppb and ALM using hourly CMAQ background

### VALIDATION OF NO<sub>3</sub>/HNO<sub>3</sub> REPARTITIONING IN POSTUTIL

Finally, a set of experiments is performed to look at the impact of nitrate removal along the trajectory. It is tested with different values of background ammonia in the CALPUFF runs and the consequences on the nitrate aerosols simulated after repartitioning in POSTUTIL, are also tested with different value of ammonia. The experiment is performed for a full year run (year 2002) on the East coast of the United States. Visibility Improvement State and Tribal Association of the Southeast (VISTAS) CALMET Domain 5 dataset is used for the meteorology and a hypothetical source with SO<sub>2</sub> and NO<sub>x</sub>, emissions is placed on the West side of Shenandoah National Park (NP) in West Virginia State. Three CALPUFF runs (with deposition active) are performed, each with different annual average background ammonia gas: 0.5ppb, 1ppb and 10ppb. These runs outputs are saved and then post-process in POSTUTIL to repartition NO<sub>3</sub> and HNO<sub>3</sub> first with an ammonia gas of 0.5ppb, then with an ammonia gas of 10ppb.

At one of the receptor in Shenandoah NP, the nitrate concentrations of the three CALPUFF runs are plotted in a scatter plot on Figure 3 (left plot) as function of the nitrate concentration simulated using a CALPUFF/POSTUTIL combination, both using an ammonia gas of 0.5ppb. This figure clearly shows the cumulative effect of ammonia in CALPUFF where ammonia is applied on a puff by puff basis. The direct outputs of CALPUFF give larger nitrate aerosols concentrations (using any of the three ammonia gas) than the outputs of the combination of CALPUFF/POSTUTIL both using an ammonia of 0.5ppb.

On the right plot of Figure 3, when an ammonia gas of 0.5ppb is used in POSTUTIL to repartition the nitrates after any of the CALPUFF runs, all nitrate aerosols simulated agree to the nitrate concentrations produced by the CALPUFF(0.5ppb)/POSTUTIL(0.5ppb) combination. The concentrations are all aligned on the 1x1 line or slightly above. When an ammonia gas of 10ppb is used in POSTUTIL (not shown), the nitrate aerosols simulated by the CALPUFF(0.5ppb)/POSTUTIL(10ppb) and CALPUFF(1ppb)/POSTUTIL(10ppb) combinations are both lower than the nitrate aerosols simulated from CALPUFF(10ppb)/POSTUTIL(10ppb).

The results indicate that when CALPUFF is run with ample ammonia, repartitioning in POSTUTIL provide a very good estimate of the nitrate formed. The effects of variable deposition of HNO<sub>3</sub> and NO<sub>3</sub> are second order relative to the repartitioning effect. The

conclusion from this comparison is that repartitioning in POSTUTIL to account for total sulphate and total nitrate provides reasonable results, but that the CALPUFF simulation should include an abundant amount of ammonia.

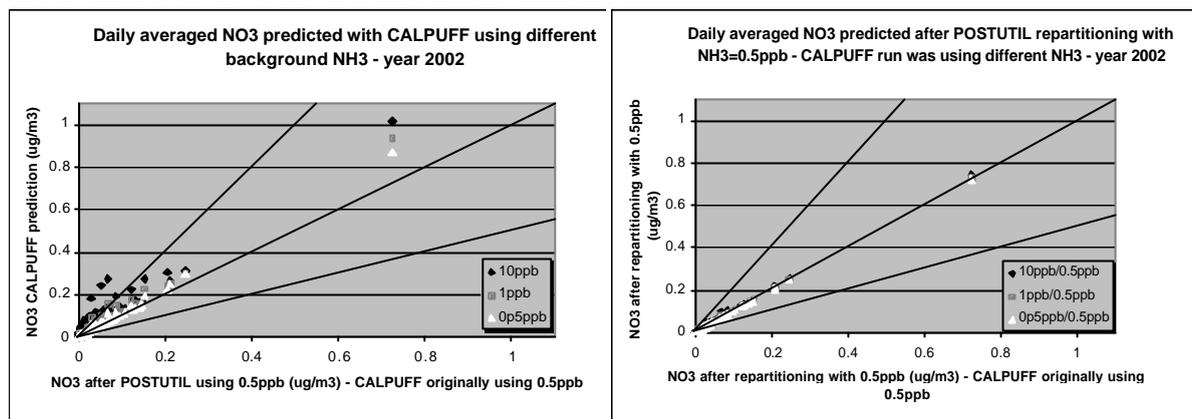


Figure 3; 24h-average scatter plot of  $\text{NO}_3$  simulated by three CALPUFF runs ( $\text{NH}_3=10\text{ppb}$  (black dot),  $1\text{ppb}$  (grey dot) and  $0.5\text{ppb}$  (white dot)) on the left and  $\text{NO}_3$  simulated by three CALPUFF/POSTUTIL runs (different  $\text{NH}_3$  in CALPUFF (same colours are used) and  $0.5\text{ppb}$  in POSTUTIL) on the right, both as function of  $\text{NO}_3$  simulated by a combination CALPUFF/POSTUTIL using both  $\text{NH}_3=0.5\text{ppb}$

## CONCLUSION

In this analysis, we first demonstrate that the  $\text{HNO}_3/\text{NO}_3$  equilibrium chemistry used in the CALPUFF system (implemented both in CALPUFF and in POSTUTIL) performed very closely to the equilibrium relationship used in CMAQ to simulate  $\text{NO}_3$  aerosols concentrations. Secondly, CMAQ outputs were validated to provide background data to better repartition  $\text{NO}_3$  and  $\text{HNO}_3$  in POSTUTIL rather than using simple constant background values of ammonia. The CMAQ outputs were tested in an ALM application and gave quite encouraging results for providing variable nitrate aerosols concentrations.

We also demonstrate that the repartitioning of nitrates in POSTUTIL is valid as long as the ammonia background used in CALPUFF is large enough to keep a conservative amount of total nitrate along the trajectory. The recommendation is to use an ample amount of ammonia background in the CALPUFF run before any repartitioning in POSTUTIL.

## REFERENCES

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