Use of Eulerian Model outputs as background concentrations for Nitrate Predictions in CALPUFF system

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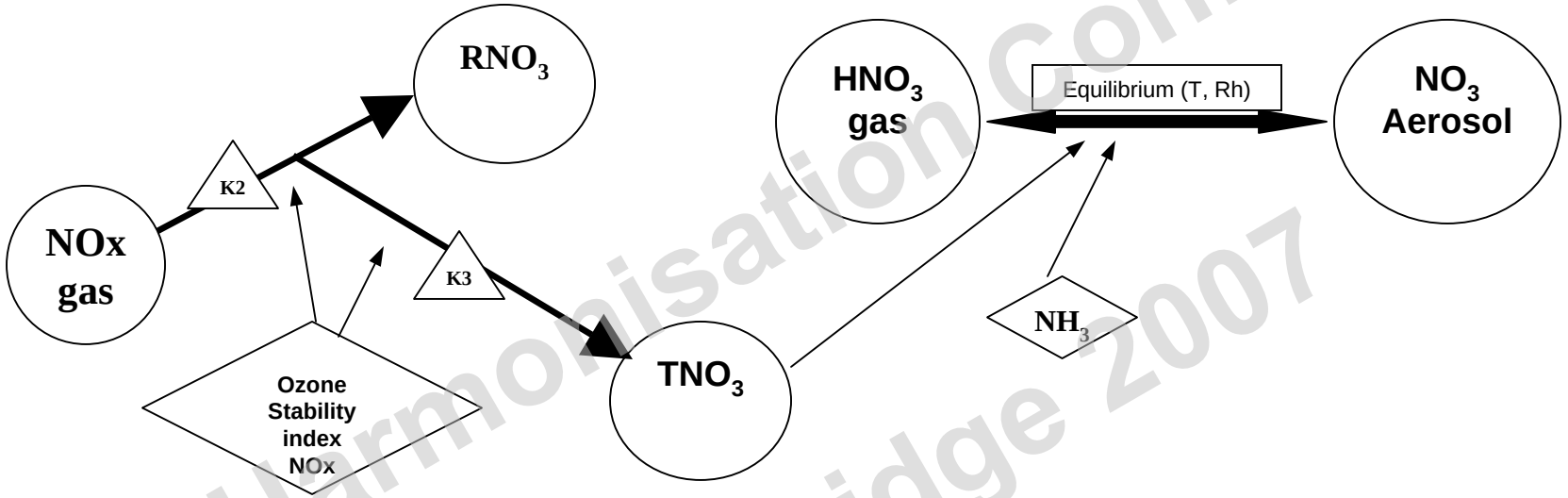
NITRATE – SECONDARY AEROSOLS - FINE PARTICULATE MATTERS COMPONENTS

- Adverse effect on Health
- Strong impact on visibility degradation in pristine areas (hygroscopic)

- Refinement in CALPUFF system NO_3 prediction

NO_x OXIDATION CALPUFF MESOPUFF II SCHEME



CALPUFF is a non-steady state dispersion model

- It has a choice of two chemistry schemes (MESOPUFF II and RIVAD) or a user entry for dissociation constant of each equation
- Each scheme resolves SO_2/SO_4 and NO_x/NO_3 chemistry parameterization

NO_3 FORMATION DEPENDS ON NH_3 CHEMISTRY

(1) $HNO_3\,(g) + NH_3\,(g) \leftrightarrow NH_4NO_3\,(a)$

Equation (1) is an equilibrium relationship, depending on T and RH and availability of NH_3

A second equations scavenging NH_3:

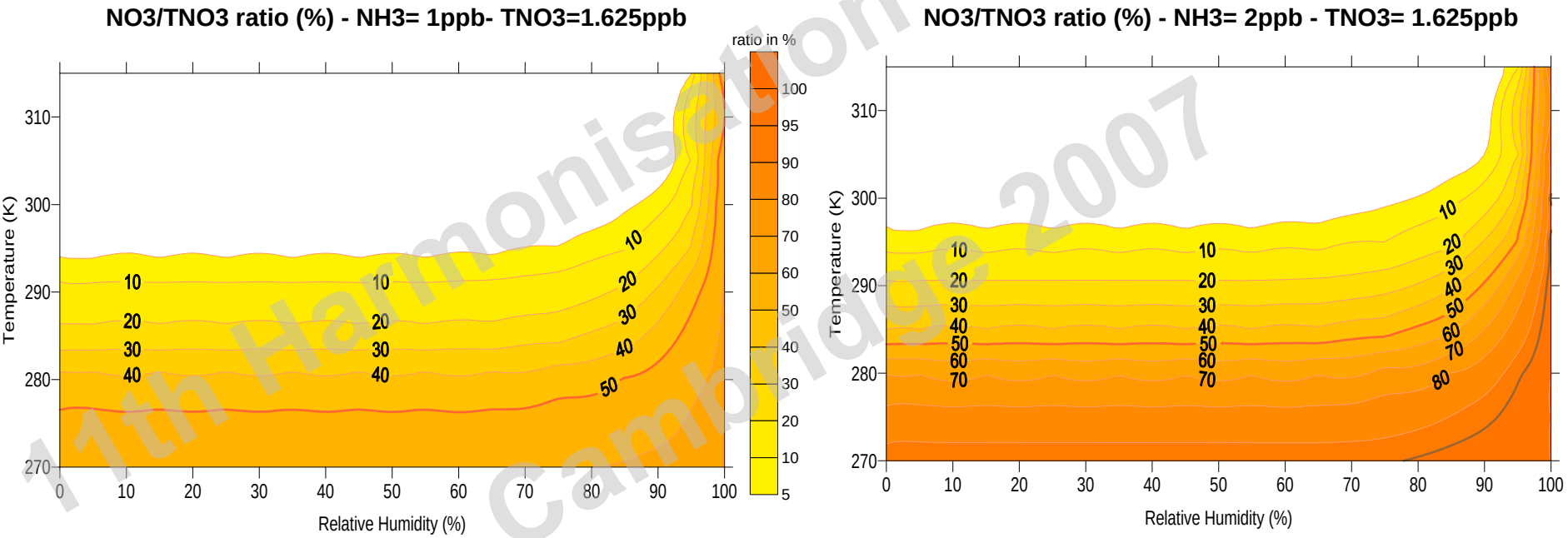
SO_4 preferentially over NO_3

(2) $SO_4^{2-} + NH_3\,(g) \rightarrow (NH_4)_2SO_4$

(g) stands for gas, (a) stands for aerosol

NO_3/HNO_3 Equilibrium Depends on Temperature, Relative Humidity

here, total $TNO_3 = NO_3 + HNO_3$

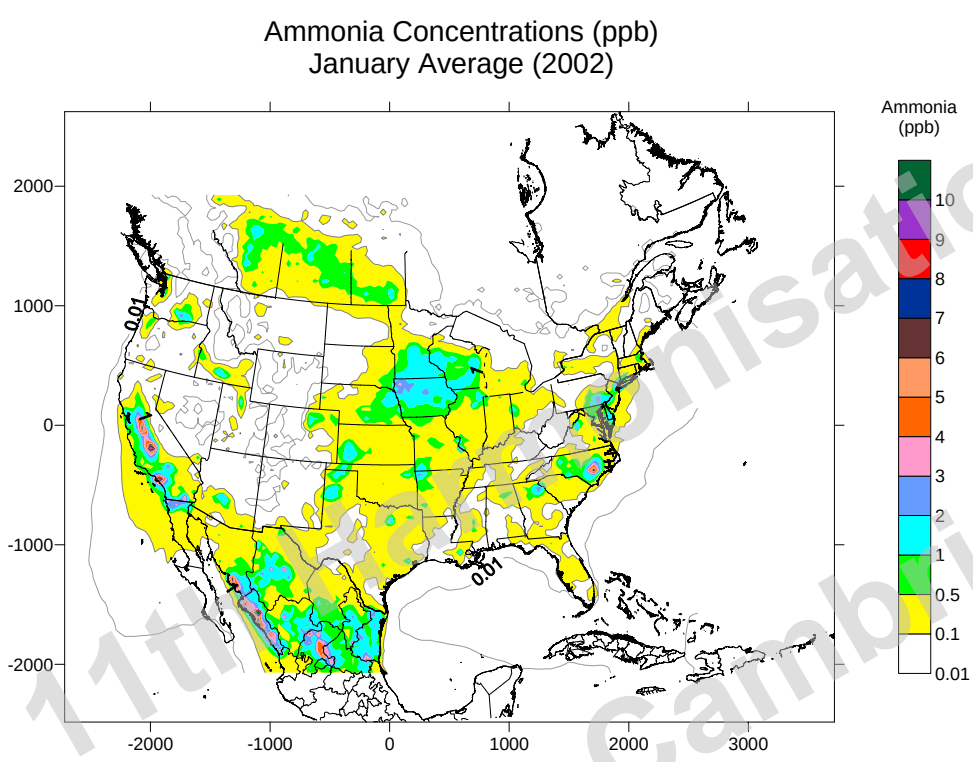


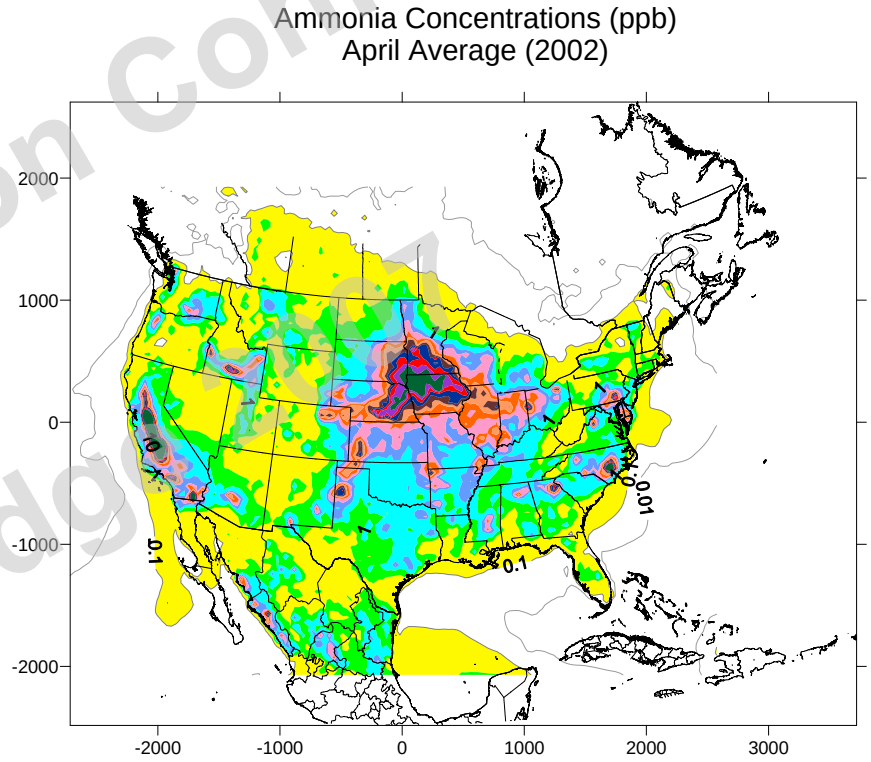
(Stelson and Seinfeld, 1982) dissociation constant, applied in CALPUFF and POSTUTIL

USE OF NH_3 IN CALPUFF SYSTEM

- **In CALPUFF code, NH_3 is constant (on a puff-by-puff basis)**
  - 0.5 ppb for forest; 1 ppb for arid land; Up to 10 ppb for grassland (IWAQM, 1998)
  - NH_3 =0.5ppb or 1ppb, usually large enough to form NH_4NO_3 in every season, but may lead to too much overprediction
  - In reality, Ammonia not constant

CMAQ NH3(gas) MONTHLY AVERAGE





JANUARY 2002

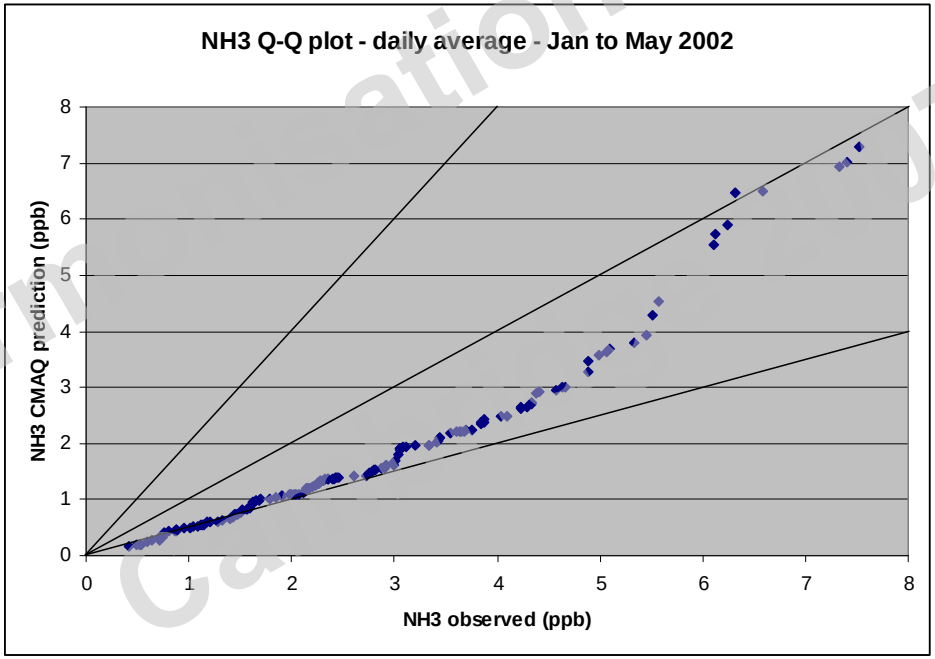
APRIL 2002

USE OF NH_3 IN CALPUFF SYSTEM (cont'd)

- **In POSTUTIL, a CALPUFF post-processor – has also the algorithm to repartition NO_3/HNO_3 with either**
  - **1 - Constant, monthly or hourly variable NH_3 gas**
    - From Observations (Difficult - very local and not always available)
    - From Model (source inventory of Ammonia still poor, large Domain)
  - **applied hour by hour and receptor by receptor**

CMAQ NH_3(gas) COMPARED TO OBSERVATIONS – daily averaged

January to May 2002 – Daily average at St Louis Supersite, Illinois



Quantile-Quantile PLOT

USE OF NH_3 IN CALPUFF SYSTEM (cont'd)

- **In POSTUTIL, a CALPUFF post-processor – has also the algorithm to repartition NO_3/HNO_3 with either**
  - **1 - Constant, monthly or hourly variable NH_3 gas**
    - From Observations (Difficult - very local and not always available)
    - From Model **(CMAQ NH_3 – too low compared to observations)**
  - **2 - Ammonia Limited Method (ALM) - take into account the background concentrations and total NH_3 (gas + aerosol) = Total NH_3 = 2 SO_4 + NO_3 + $NH_{3(gas)}$**
    - Model output of background pollutant (including time-varying Total NH_3.
  - **Both applied hour by hour and receptor by receptor**

DESCRIPTION OF ALM APPLICATION

- Refined the Nitrate prediction for an individual source
- Repartition the source + background $(NO_3/HNO_3)_{all}$ once NH_3 necessary to scavenge SO_4 is removed from TNH_3

$$NO_{3\,src\_after} = \frac{TNO_{3\,src\_after}}{TNO_{3\,src+bckg}} \times NO_{3\,src+bckg}$$

with

$$TNO_{3\,source} = TNO_{3\,src\_after} = TNO_{3\,src\_before}$$

and

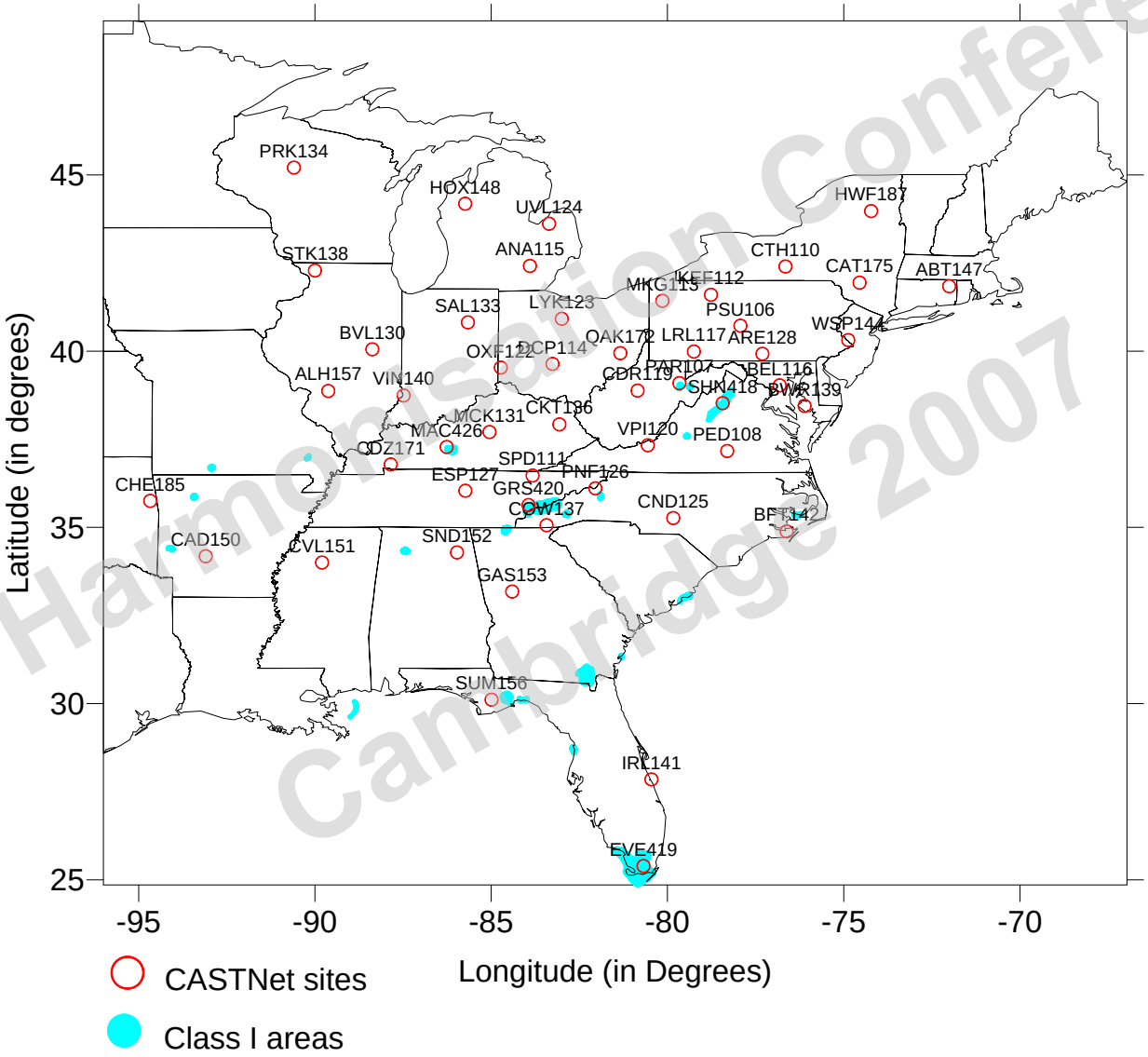
$$TNO_3 = NO_3 + HNO_3$$

src_after = from source after repartitioning
src_before = from source before repartitioning
src+bckg = from source + background

USING CMAQ OUTPUTS FOR ALM

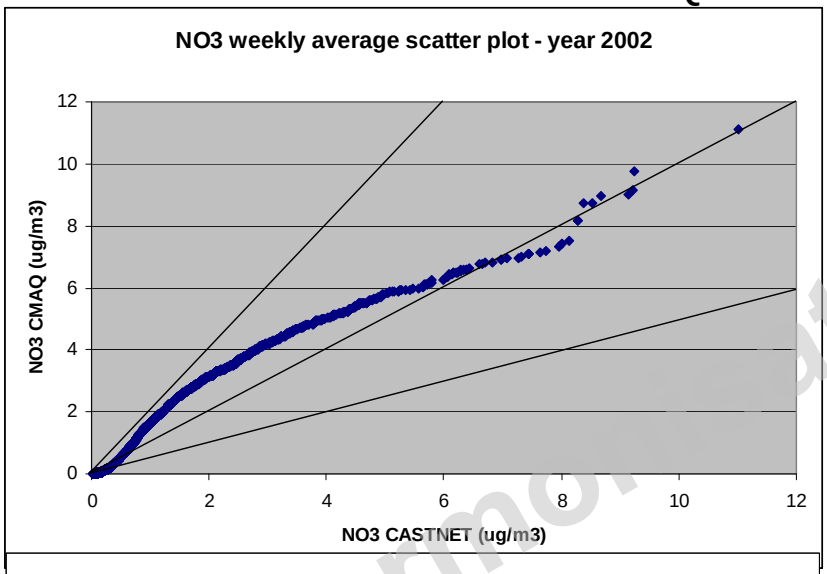
- VALIDATION of 2002 CMAQ run (ENVIRON)
- NO_3, SO_4 and total NO_3 (NO_3+HNO_3) comparison to observations from CASTNet and IMPROVE networks
- 52 CASTNet sites (23 in VISTAS states) – weekly average
- 46 IMPROVE sites (16 in VISTAS states) – daily average (not shown)

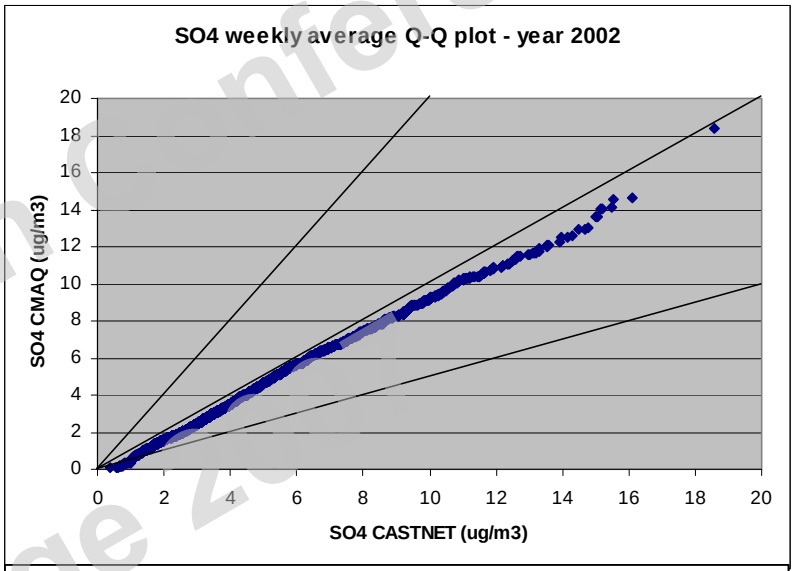
Location of CASTNet sites Used and Class I areas in the SouthEast

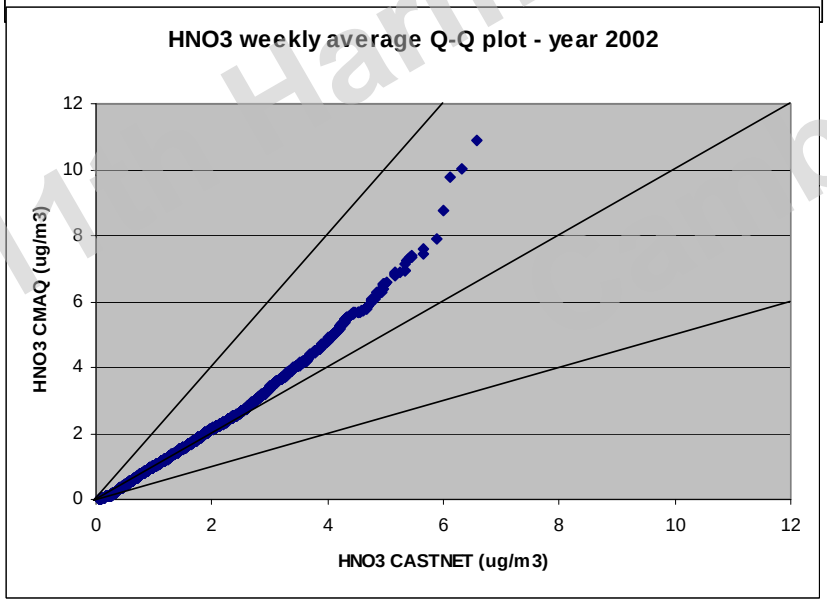


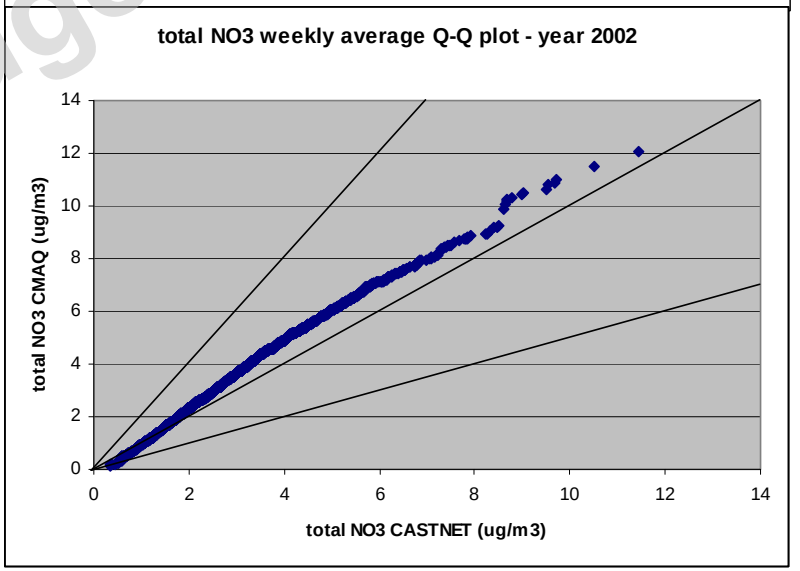
CMAQ versus CASTNet

Quantile-Quantile PLOTS

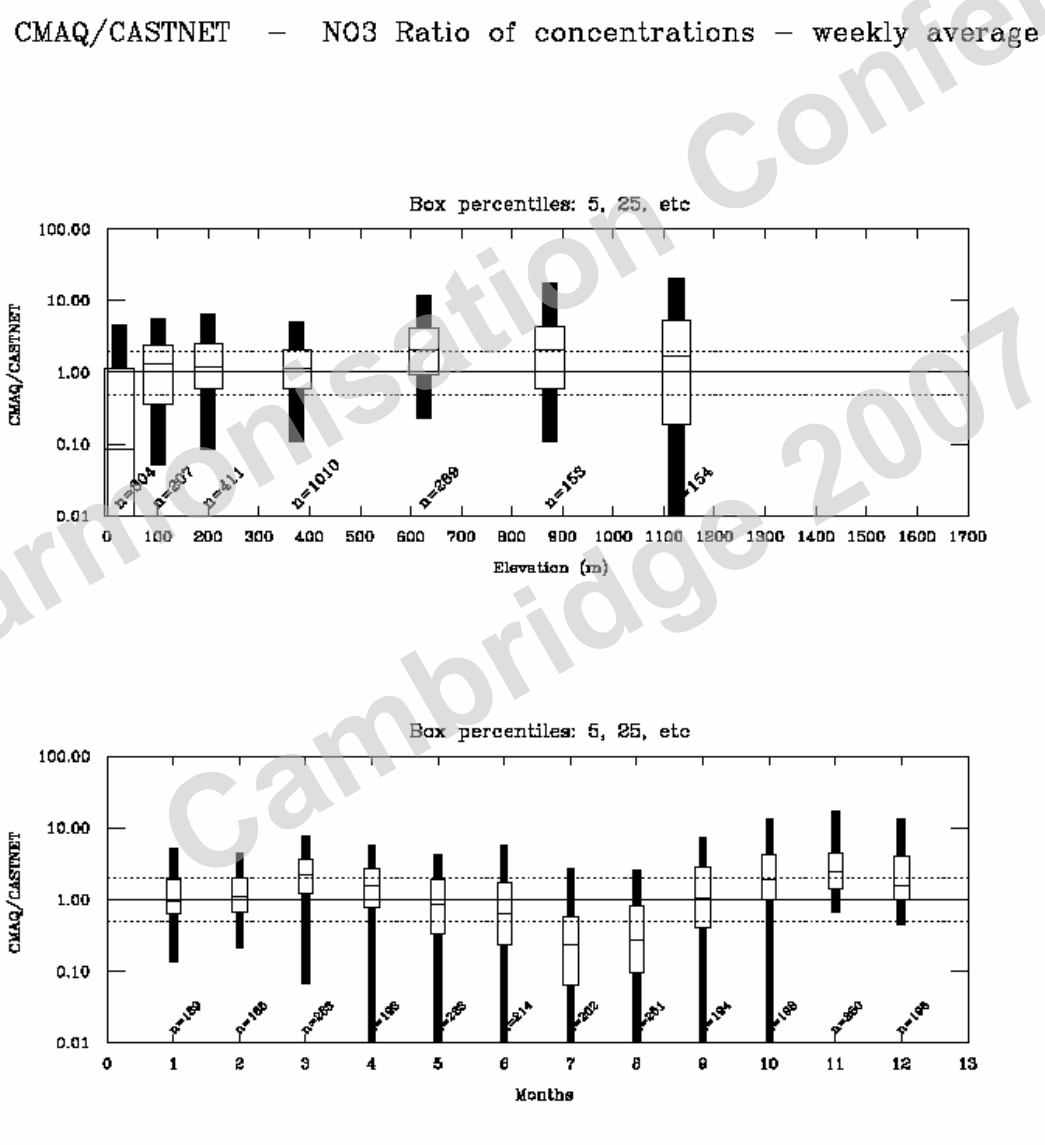




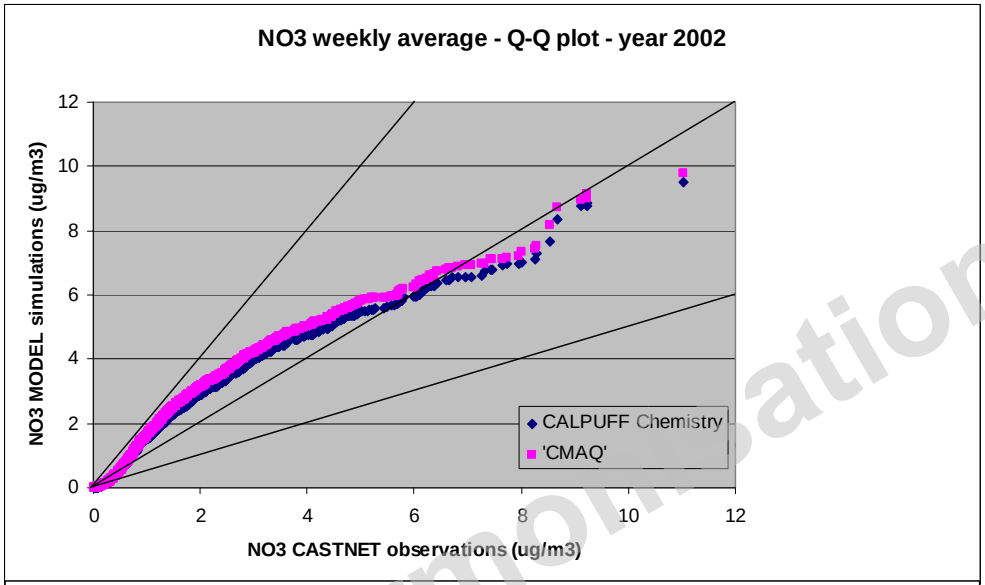


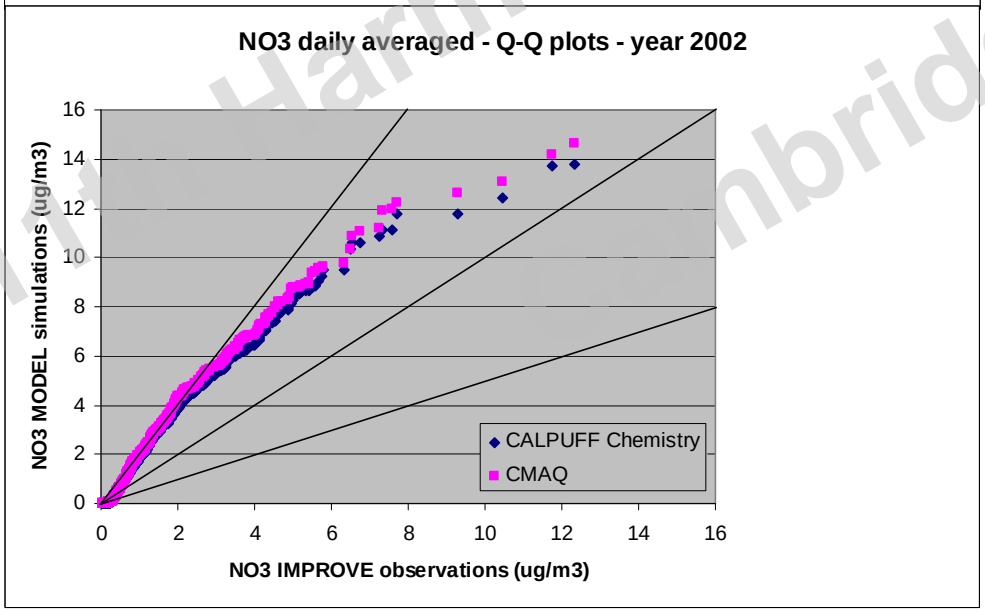


CMAQ/Observation as function of elevation and months



CMAQ data INPUT in POSTUTIL for NO_3 predictions





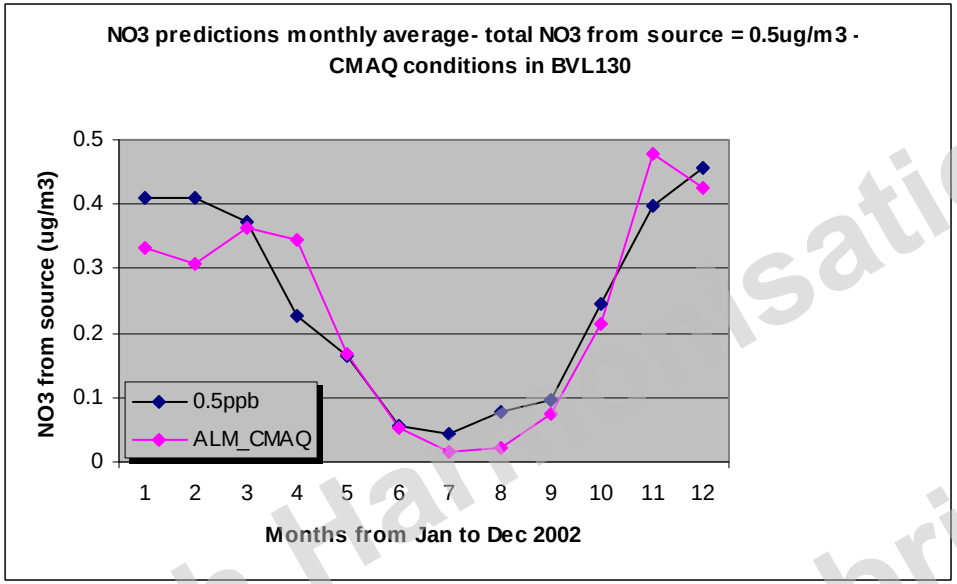
- Pink – NO_3 CMAQ output
  - Mozurkewich, 1993 is used in CMAQ for NO_3/HNO_3 equilibrium parameterization
- Blue – NO_3 POSTUTIL output: CMAQ concentrations input in POSTUTIL + CMAQ hourly $NH_3 = NH_3g+NO_3+2SO_4$
  - Stelson and Seinfeld, 1982 is used in CALPUFF and POSTUTIL for NO_3/HNO_3 equilibrium parameterization

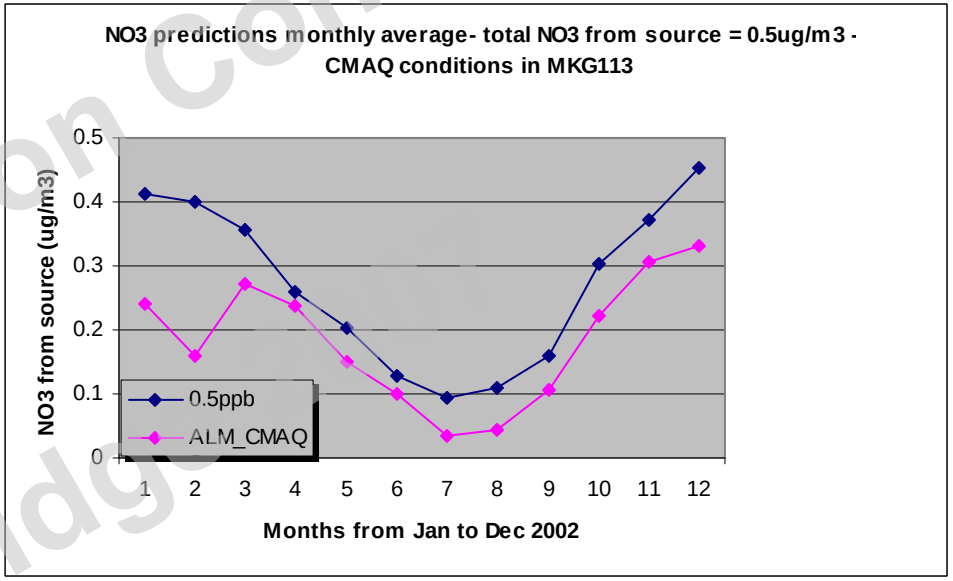
Quantile-Quantile PLOTS

CONCLUSION ON CMAQ EVALUATION

- SO_4 concentrations from CMAQ in very good agreement with observations (both CASTNet and IMPROVE)
- Total NO_3 ($=NO_3+HNO_3$) concentrations from CMAQ are in good agreement with observations (from CASTNet and IMPROVE)
- Conservative NO_3 concentrations predictions at most sites
- NO_3/HNO_3 equilibrium parameterization similar in CMAQ and CALPUFF system.

APPLICATION : NO_3 predictions monthly averaged time series





-Total NO_3 = 0.5µg/m^3 (constant every hour of the year)
-T_1, RH_1 hourly varying

Repartition using NH_3=0.5ppb or ALM (with CMAQ background) SIMILAR RESULTS – NOT AMMONIA LIMITED

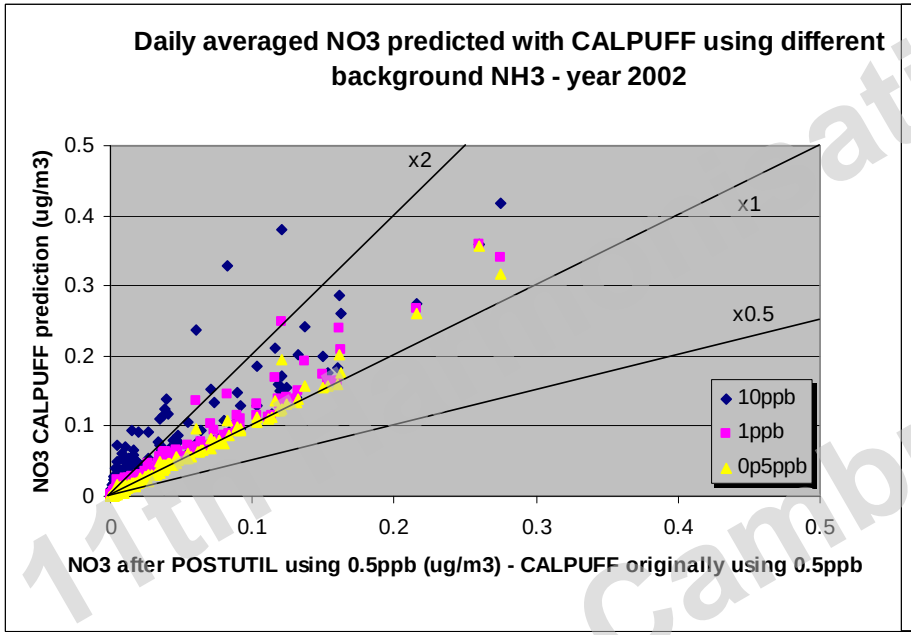
-Total NO_3 = 0.5µg/m^3 (constant every hour of the year)
-T_2, RH_2 hourly varying

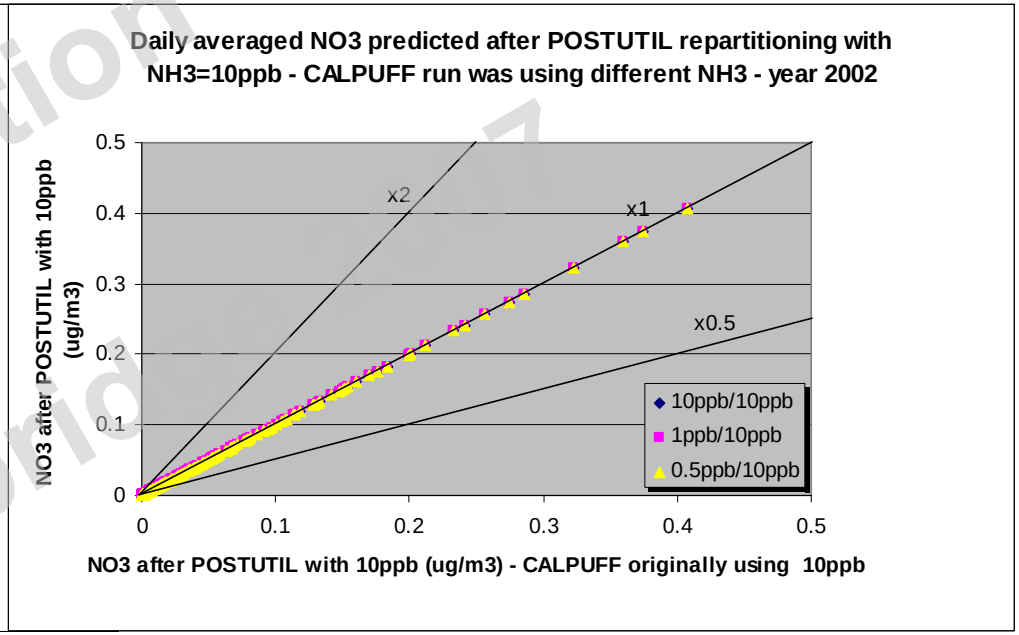
Repartition using NH_3=0.5ppb LARGER than when ALM (with CMAQ background) - MAY BE AMMONIA LIMITED

VALIDATION OF REPARTITIONING IN POSTUTIL – NO DEPOSITION

- Modelling of an individual source located west of Shenandoah NP (US)
- Look at the impact at 1 receptor in Shenandoah National Park
- Total Nitrate stay constant along the trajectory of a plume

SCATTER PLOTS





CALPUFF RUN WITH DIFFERENT NH_3:
0.5ppb, 1ppb, 10ppb

- Show the cumulative effect of NH_3 used in CALPUFF on a puff-by-puff basis

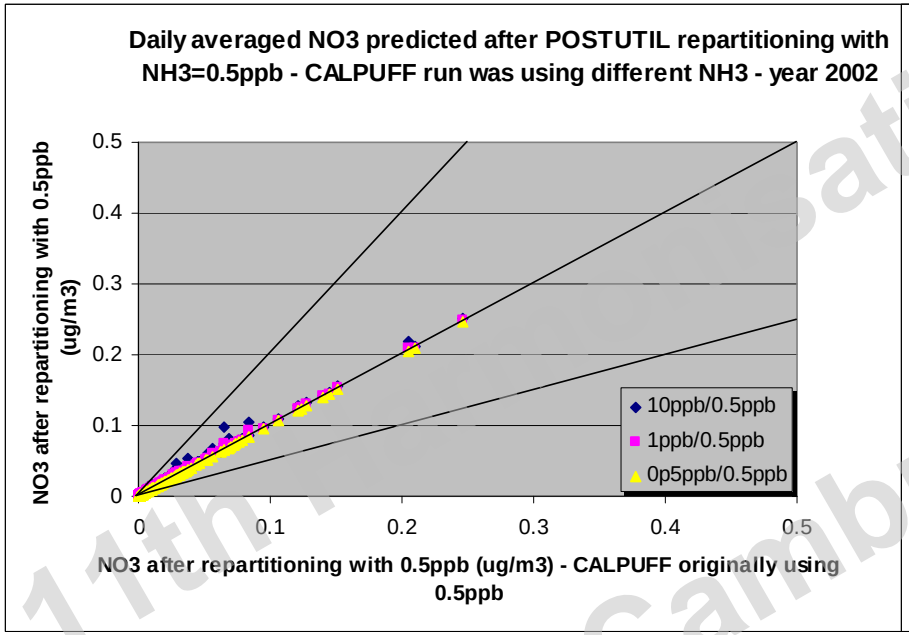
CALPUFF RUN WITH DIFFERENT NH_3:
0.5ppb, 1ppb, 10ppb then repartition in POSTUTIL with 10ppb (same results with 1ppb or 0.5ppb)

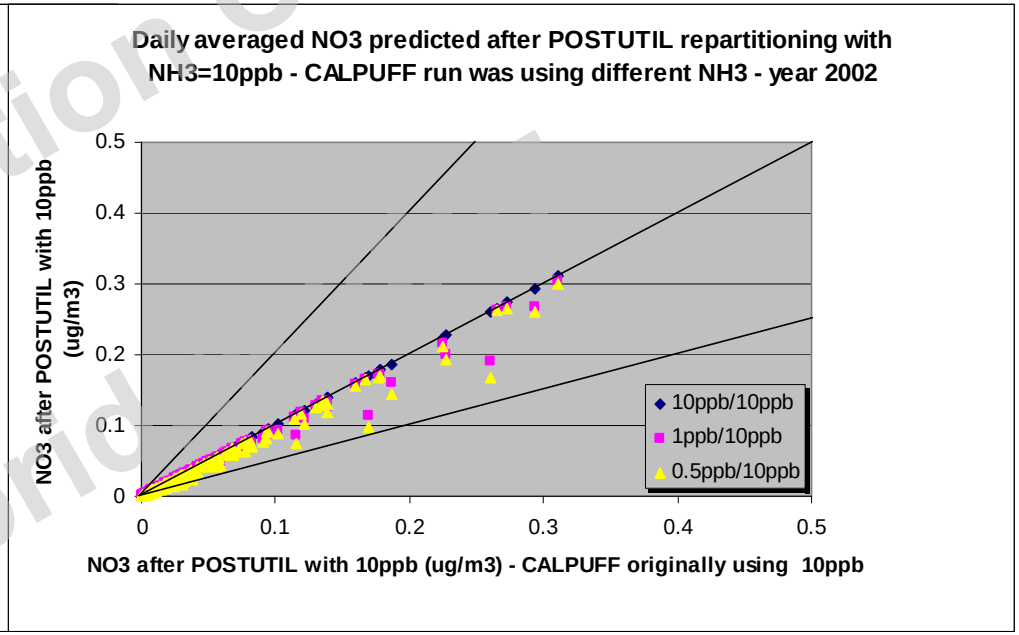
- Show conservation of Total NO_3, whatever NH_3 used in CALPUFF, results after repartitioning in POSTUTIL is the same

VALIDATION OF REPARTITIONING IN POSTUTIL - WITH DEPOSITION

- Same source model and impact in Shenadoah NP (US)
- Total Nitrate is not constant anymore along the trajectory

SCATTER PLOTS





CALPUFF RUN WITH DIFFERENT NH_3:
0.5ppb, 1ppb, 10ppb then repartition in POSTUTIL with 0.5ppb

- If repartitioning in POSTUTIL with lower or equal NH_3 than in CALPUFF – almost same NO_3 results with any NH_3 used in CALPUFF

CALPUFF RUN WITH DIFFERENT NH_3:
0.5ppb, 1ppb, 10ppb then repartition in POSTUTIL with 10ppb

- If repartitioning in POSTUTIL with larger NH_3 than in CALPUFF – NO_3 predicted too small

CONCLUSION

- CMAQ NH_3(gas) can not be used to replace constant NH_3 in CALPUFF - too much underprediction at most sites analyzed

- Varying Background from CMAQ to be used in ALM: hourly SO_4, total NO_3 and total NH_3 = NH_3(gas)+NO_3+2SO_4 gives conservative prediction of NO_3 background concentrations in POSTUTIL at most sites
  - Create a good varying background (including total NH_3) to refine estimation of NO_3 concentration for an individual source

- HNO_3/NO_3 equilibrium used in CALPUFF give similar results as the one used in CMAQ

- Validation of HNO_3/NO_3 repartitioning after CALPUFF in POSTUTIL as long as Ammonia used in CALPUFF is large enough to avoid Ammonia limitation