J5.13   THE EFFECTS OF AMMONIA LIMITATION ON NITRATE AEROSOL
FORMATION AND VISIBILITY IMPACTS IN CLASS I AREAS

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1.   INTRODUCTION

Secondary pollutants such as sulfate (SO_4), organics and nitrate (NO_3) are significant components of the visibility degradation-producing aerosols in Class I areas in the United States. Because ammonia (NH_3) is preferentially scavenged by sulfate, the formation of nitrate may be limited by the availability of ammonia (Stelson et al., 1983). In areas where sulfate concentrations are high or ammonia emissions are low, the atmosphere may be in an ammonia-limited regime relative to nitrate formation.

CALPUFF (Scire et al., 2000) is recommended by the Federal Land Managers Air Quality Related Values Workgroup (FLAG) and the Interagency Workgroup on Air Quality Modeling (IWAQM) for evaluating visibility impacts in Class I areas. We have implemented refinements in CALPUFF to evaluate the effects of ammonia limitation on nitrate formation. Although the technique can be used with either modeled or measured values for the background contributions of sulfate and nitrate, we demonstrate the technique using an observational dataset from the EPA Clean Air Status and Trend Networks (CASTNET) at the Mammoth Cave National Park Class I area. We will focus on the impact of ammonia limitation on predicted visibility. The limitations of current observational datasets and the effects of their uncertainties on the maximum change in light extinction will be discussed.

2.   METHOD

In the CALPUFF model, total nitrate (TNO_3 = HNO_3 + NO_3) is partitioned into each species according to the equilibrium relationship between HNO_3 and NO_3. This equilibrium varies as a function of time and space, in response to both the ambient temperature and relative humidity. In addition, the formation of nitrate is subject to the availability of NH_3 to form ammonium nitrate (NH_4NO_3), the assumed form of nitrate in the model. In CALPUFF, a continuous plume is simulated as a series of puffs, or discrete plume elements. The total concentration at any point in the model is the sum of the contribution of all nearby puffs from each source. Because CALPUFF allows the full amount of the specified background concentration of ammonia to be available to each puff for forming nitrate, the same ammonia

may be used multiple times in forming nitrate, resulting in an overestimate of nitrate formation. In order to properly account for ammonia consumption, a program called POSTUTIL was introduced into the CALPUFF modeling system in 1999. POSTUTIL allows total nitrate to be repartitioned in a post-processing step to account for the total amount of sulfate scavenging ammonia from all sources (both project and background sources) and the total amount of TNO_3 competing for the remaining ammonia. In POSTUTIL, ammonia availability is computed based on receptor concentrations of *total* sulfate and TNO_3, not on a puff-by-puff basis. The total concentration includes background and the project sources. This avoids the double (or multiple) counting of ammonia in forming nitrate. In the refined method, the background ammonia concentration, instead of being a constant, is determined hourly using the equilibrium between NO_3 and HNO_3, hourly temperature and relative humidity from CALMET meteorological database. The amount of available ammonia in the gas phase (Stelson and Seinfeld, 1982) is:

$$[NH3(g)] = K [NH4NO3] / [HNO3(g)] \qquad (1)$$

where the concentrations are in ppb, K is an equilibrium constant which is a function of temperature and relative humidity. The total amount of background ammonia is the gas phase component plus the amount associated with ammonium sulfate and ammonium nitrate.

Nitrate and nitric acid of the project pollutants are then re-partitioned using the temperature and humidity dependent K while accounting for background + project source concentrations of SO_4, NO_3 and NH_3.

3.   DATA

The data we are using to demonstrate the method come from the CASTNET monitoring network. SO_4, NO_3 and HNO_3 are measured as weekly averages at each CASTNET site. This induces uncertainties in the estimation of hourly NH_3. However, by allowing the temperature and relative humidity to vary hourly, the diurnal variations are reflected in NH_3 estimation. Another uncertainty is the use of Teflon filters to collect nitrate in the CASTNET network. Due to volatilization effects, these measurements may underestimate the true amount of nitrate (Ames and Malm, 2001). Tests results on the sensitivity of this source of uncertainty are presented in the next section.

Developments are continuing to evaluate the use of IMPROVE data and other sources of background sulfate and nitrate to supplement or replace the CASTNET observational data. This work will be reported in future papers.

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4. RESULTS

We applied the refined method to the Mammoth Cave National Park Class I area for a one-year period, 1990. The emission source is located about 75 km West of the Park. The closest CASTNET site to the National Park is Mackville (MCK). Taking into account the background concentrations from this site, the maximum change in light extinction changes from 7.4% (base run of CALPUFF with a constant 0.5 ppb of NH_3) to 5.5% (refined method) on day 356 when the peak value was observed. It represents a 30% decrease of the impact on visibility (Table 1).

The change in light extinction comes from a decrease in NO_3 due to repartitioning when the ammonia-limited method is applied. Figure 1 shows the changes in NO_3 concentrations due to ammonia limiting effects for a constant input NO_3 concentration. Temperature, humidity, and background sulfate are allowed to vary hourly. The effect can be large in summer when NH_3 is preferentially scavenged by SO_4, so less NH_3 is available to form NH_4NO_3.

Scenario	Backgrd NO_3 (ppb)	Total NH_3 (ppb)	Total NH_3 yr (ppb)	Max change (%)
Base	N/A	N/A	N/A	7.40
Mackville; MCK	0.085	1.17	7.41	5.50
Vincennes; VIN	0.429	2.00	17.55	5.82
Lilley C.W.; LCW	0.080	0.84	8.70	5.52
EdgarEvins; ESP	0.031	1.29	5.50	5.50
VIN NO3*2	0.882	3.38	31.62	6.22

Table 1. *Averages of background NO_3 and total NH_3 on day 356 (in ppb) and annual averages of total NH_3 (in ppb). Last column is the maximum change in daily light extinction.*

There are uncertainties associated with the spatial representativeness of any single CASTNET measurement. To test the sensitivity of the method to this uncertainty we used three other CASTNET sites. They represent together a large range in NO_3 concentrations. Annual NO_3 average is 0.8ppb at VIN, 0.15ppb at LCW and 0.38ppb at MCK. On the day when the maximum of extinction change occurs, daily NO_3 is 0.429ppb at VIN, more than four times larger than at MCK while the maximum in extinction change is only 0.32% higher at VIN than at MCK.

Another uncertainty is associated with volatilization of NO_3 from the CASTNET samples. According to Hering and Cass (1999), measurements of NO_3 on a Teflon filter produced aerosol mass up to 61% (summer) and 28% (overall) less than those from a denuded nylon filter, which is less susceptible to volatilization. A sensitivity test with NO_3 concentrations increased by 200% above the highest measured value produces only little change in visibility. The difference in predicted light extinction change is 0.4%. The reason for the lack of sensitivity is that there is little response to increased ammonia until the ammonia concentrations exceed levels that are scavenged by background + source sulfate.

5. CONCLUSION

The use of a constant ammonia concentration that is independent of background sources and applied on a puff-by-puff basis overestimates the incremental nitrate formation in the situation evaluated in this study. The difference in extinction predicted by the refined ammonia limited method including time-varying cumulative consumption of ammonia was significant for regulatory applications. The ammonia-limited method is an important improvement in estimating source impacts on visibility in Class I areas. It has the advantage of allowing the effect of background sulfate and nitrate to be accounted for in the calculation of the source contribution in a manner that is consistent with the observational data.

For the Mammoth Cave case, the sensitivity of the method to NO_3 measurement uncertainties associated with spatial changes in NH_3 and potential volatilization effects is small, suggesting the situation evaluated is highly ammonia limited.

For additional explanations and results see the following web site: http://www.src.com.
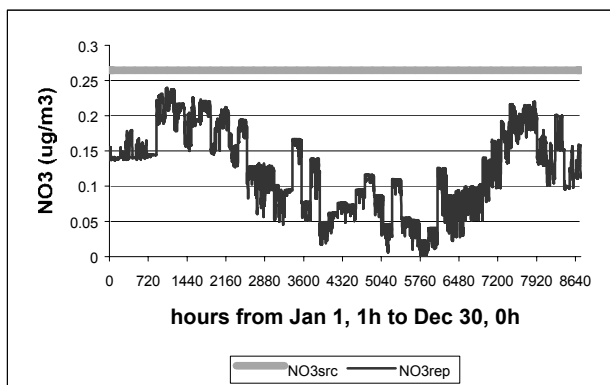
Figure 1. *NO_3 concentration (0.264 $\mu g/m^3$) from the source is repartitioned using the refined method. Atmospheric conditions varying hourly are tested.*

6. REFERENCES

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