ABSTRACT

Title of thesis: CONTROLLING AMMONIA EMISSIONS FROM
CONCENTRATED FEEDING OPERATIONS

Chinmay Charuhas Satam, Master of Science in Chemical Engineering, 2002

Thesis directed by: Professor Sheryl H. Ehrman
Dept. of Chemical and Biomolecular Engineering

Ammonia is an essential component in the formation of particulate matter which has been a growing concern for areas along the Mid-Atlantic region. Also, animal husbandry operations have been isolated as the single largest sources of ammonia. Hale III (2005) suggests a strategy to reduce ammonia emissions from chicken manure using a dietary gypsum-zeolite infusion and slight crude protein reductions. A follow up study conducted by Wu-Haan et al. (2007) places the ammonia reduction values at 39 %. Simulations of this strategy for the MANEVU region find $PM_{2.5}$ reductions of up to 37.5% for the Delmarva Peninsula. Additionally, 6 hours of improved compliance (15 $\mu g/m^3$ standard) is seen in this region, during moderate $PM_{2.5}$ episodes. It was also observed that regions near the source, and down wind, with high available nitric to sulfuric acid ratios are benefited by this strategy which primarily targets ammonium nitrates.

CONTROLLING AMMONIA EMISSIONS FROM CONCENTRATED FEEDING OPERATIONS

by

Chinmay Charuhas Satam

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Advisory Committee:

Professor Sheryl H. Ehrman, Chair
Professor Raymond A. Adomaitis
Professor Russell R. Dickerson
Associate Professor Srinivasa R. Raghavan

DEDICATION

To my parents,

Charuhas Satam and Shailaja Satam

for their continual support and encouragement

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LIST OF ABBREVIATIONS

Variables	Description	Units
b_{ext}	Light extinction coefficient	$(Mm)^{-1}$
C	Concentration term	$\mu g/m^3$ or mol/m^3

Greek

μ	Micro

Full Forms

ACGIH	American Conference of Industrial Hygienists
AIRS	Atmospheric Infrared Sounder
BCON	Boundary Conditions Processor
CADDIS	Casual Analysis/Diagnosis Decision Information System
CAFO	Concentrated Animal Feeding Operations
CB05	Carbon Bond V
CCTM	CMAQ Chemistry Transport Model
CEC	Cation Exchange Capacity
CEN	European Committee for Standardization
CENRAP	Central Regional Air Planning Association
CIMS	Chemical Ionization Mass Spectrometer
CMAS	Community Modeling and Analysis
CMAQ	Community Multiscale Air Quality
COPD	Chronic Obstructive Pulmonary Disease
CP	Crude Protein
DC	District of Columbia
DE	Delaware
DRH	Deliquescent Relative Humidity
EPA	Environmental Protection Agency
EDT	Eastern Daylight Time
FEM	Front End Module
FTIR	Fourier Transform I
I.C	Ion Chromatography

ICON	Initial Conditions Processor
IMS	Ion Mobility Spectroscopy
IMPROVE	Interagency Monitoring of Protected Visual Environments
ISO	International Organization for Standardization
JPROC	Photolysis Rate Processor
MANEVU	Mid-Atlantic/North-East Visibility Union
MARAMA	Mid-Atlantic Regional Air Management Association
MCIP	Meteorology Chemistry Interface Processor
MD	Maryland
MDE	Maryland Department of Environment
MRPO	Midwest Regional Planning Organization
NAAQS	National Ambient Air Quality Standards
NARSTO	North American Research Strategy for Tropospheric Ozone
NESCAUM	Northeast States for Coordinated Air Use Management
NOAA	National Oceanic and Atmospheric Administration
NRC	National Research Council
PA	Philadelphia
PM	Particulate Matter
RH	Relative Humidity
RAMMPP	Regional Atmospheric Measurement Modeling & Prediction Program
RPO	Regional Planning Organization
SCC	Standard Classification Codes
SMOKE	Sparse Matrix Operator Kernel Emissions
TEOM	Tapered Element Oscillating Microbalance
TSP	Total Suspended Particles
UMD	University of Maryland
UV	Ultraviolet
US	United States
VISTAS	Visibility Improvement State and Tribal Association
WHO	World Health Organization
WRAP	Western Regional Air Partnership

INTRODUCTION

Air pollution generally occurs when substances like particulate matter or gases are present in amounts that pose a danger to humans, animals, plants or the general environment. Of these, there are certain common air pollutants which are commonly found everywhere within the United States (US). They are - ground level ozone, particulate matter, carbon monoxide, sulfur oxides, nitrogen oxides and lead. They are harmful to human health and can also cause property damage. They have been classified by the US Environmental Protection Agency (US EPA) as “criteria air pollutants” because their permissible levels are regulated using human health or environmental safety based criteria. Among these, the US EPA states, that ground level ozone and particulate matter or “PM” are the most widespread health threats (http://www.epa.gov/air/urbanair).

Particulate matter can be solid or liquid droplets. They vary in size from 0.01μm to 100 μm (Chow & Watson, 1998), and have been shown to either cause or aggravate problem related to the heart or lungs (United States Environmental Protection Agency [US EPA], 2006; Brook & Rajagopalan, 2009). Serious illness may result because of such particles and in some cases they may even cause death. Urban fine particulates has been a serious concern since the last decade (Chen, Doddridge, Dickerson, Chow & Henry, 2002; World Health Organization [WHO], 2003), primarily because they penetrate deeper into the lungs and heart than their coarser counterparts (United States Environmental Protection Agency [US EPA], 2003). Fine aerosols are essential to the formation of smog or haze that causes light extinction and reduces visibility. The heavily populated US eastern seaboard is among the regions where haze and smog are frequently observed (Malm, 1992 in Chen et al., 2002) and as such designing control strategies to bring the fine PM level into compliance with air quality standards will require knowledge of the aerosol chemical composition and source contribution (Chen et al., 2002).

1.1 Particulate matter

1.1.1 Sources and morphology

Atmospheric particles originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. They can be produced naturally from volcanic emissions, salt particles from seas sprays and soil-like particles from resuspended dust, or they can be generated by anthropogenic activities as in the case of combustion-generated particles, such as diesel soot or fly ash. There are also photochemically produced particles, such as those found in urban haze. Some particles are liquid; while some are solid (United States Environmental Protection Agency [US EPA] Vol. I, 2004; WHO, 2003). Others may contain a solid core surrounded by liquid (US EPA Vol. I, 2004). Furthermore aerosols are mixtures which can be classified as internal or external. Internal mixtures are characterized by chemically homogenous particles while external mixtures have individual particles with different chemical compositions. Internally mixed particles may also be externally mixed on the outside. (http://vista.cira.colostate.edu/improve/tools/reconbext/reconbext.htm).

1.1.2 Size distribution

Particles can be broadly classified into two groups: coarse particles and fine particles. The limit for fine particles is fixed by convention to be 2.5 μm aerodynamic diameter ($PM_{2.5}$) for measurement purposes (WHO, 2003). Whitby (1978), as mentioned in US EPA Vol. I (2004) has published an analysis of 1,000 particle size distributions measured at various locations in the United States. According to this data it was observed that numerically most of the particles are very small (<0.1 µm) while most of the particle mass however is found in the particles with aerodynamic diameter greater than 0.1 µm (US EPA Vol. I, 2004; WHO, 2003).

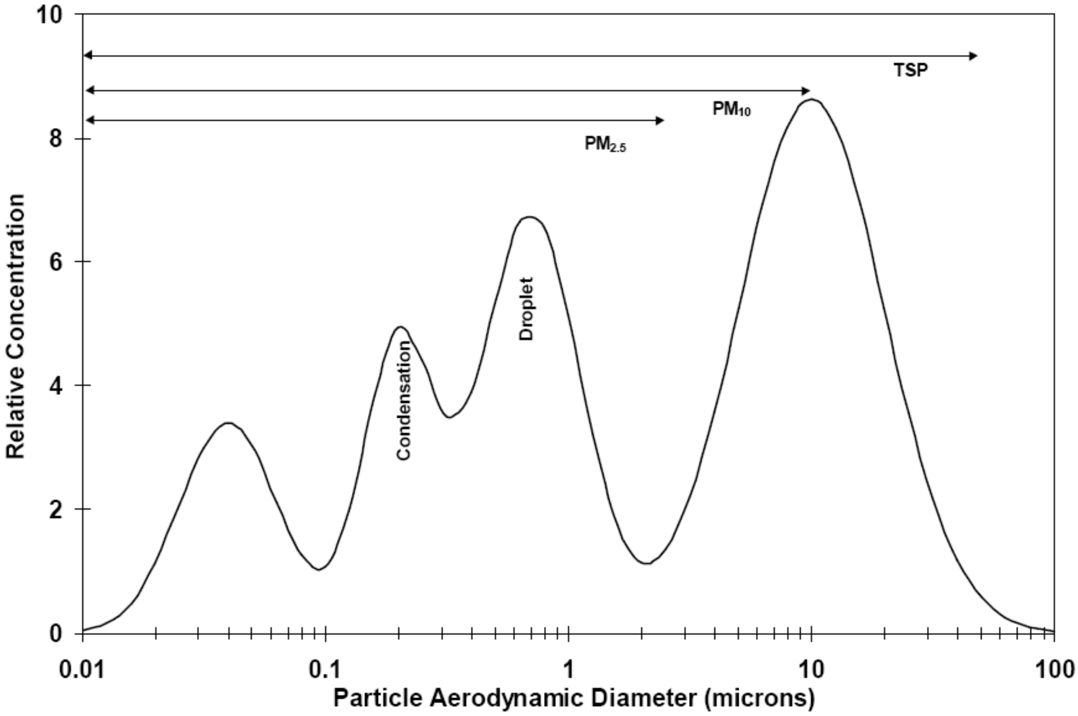


Fig 1.0 Ideal particle size distribution (Chow & Watson, 1998)

1.1.3 Measurement of particulate matter

Atmospheric aerosol particles are usually classified according to their aerodynamic diameter. The reasons for this are that most of the transport properties for emission, removal and deposition in respiratory organs are governed by the aerodynamic diameter. Also there seems to be some relation between the composition and the size of the particles. Smaller particles usually contain acidity (hydrogen ions) as well as mutagenic activity (WHO, 2003).

Particulate matter is usually measured in terms of $PM_{2.5}$ and PM_{10}. In 1987, the National Ambient Air Quality Standards (NAAQS) for particulate matter were revised to use PM_{10}, (Chen et al. , 2002) rather than total suspended particles (TSP), as the indicator for particulate matter. The use of PM_{10} was based on size-selective regulatory cuts. The cuts themselves are dependent on the separation and sampling methodology. The ACGIH-ISO-CEN penetration curve for thoracic particles (particles able to pass the larynx and penetrate into the bronchial and alveolar regions of the lung) has a 50% cut point at 10 μm aerodynamic diameter. The thus the selection PM_{10} as an indicator was based on health considerations and is a good indicator of particles that are small enough to enter the thoracic region of the human respiratory tract (US EPA Vol. I, 2004).

The North American Research Strategy for Tropospheric Ozone (NARSTO) Measurement Methods Compendium describes several methods for measurement of particulate matter as listed below.

1.1.3.1 PM_{10}: All of these methods are used for measurement in the concentration range of 30 to 300 $\mu g/m^3$ (US EPA [Procedures for determining comparability], 1998) for test conditions and are operated usually within a temperature range of -30 ^{0}C to + 45 ^{0}C. (US EPA, [Reference Method PM_{10}], 1998) Usually the lower detection limit is 5 $\mu g/m^3$ but may vary according to filter technology limitations (US EPA, [Reference method PM_{10}], 1998). The methods are as follows:

A. **Gravimetric:** An air pump is used to draw the surrounding air into a specially shaped inlet. Here, with the use of filters, the particulates are separated according to size where they are collected. Each filter is measured before and after use to determine the total amount of sample collected. The total volume of air filtered is known from the constant air flow, and the difference in filter weights is used to calculate the particulate matter concentration in micrograms per cubic meter (µg/m^3) of air. The main disadvantage of this method is that particulate matter may be lost during filter handling, transport and weighing procedures, especially if filter is exposed to heat. Also gaseous species may contaminate filters. Humidity may also be absorbed and may be difficult to control both during operations and when handling filters. As always meteorological conditions can affect flow rate and results. (US EPA, [Procedures for determining comparability], 1998; US EPA ,[Reference method PM$_{10}$], 1998;US EPA,[Procedures for Testing Performance],1998)

B. **Beta Attenuation Methods:** Beta particles are electrons with energies in the 0.01 to 0.1 MeV range. Some devices use ^{14}C as the beta source. These beta particles are allowed to pass through the particulate matter and are attenuated by them according to an approximate exponential function. The beta particles are then registered on a filter tape. Automated samplers use a continuous filter tape, using measurements from unexposed and exposed tape to obtain attenuation measurements due to particulate matter. Some devices convert these measurements directly to mass readings to avoid further analysis in laboratory. A disadvantage of the method is that particulate matter may be lost when the filter tape advances and due to subsequent vibrations especially if the filter is exposed to heat. Also gaseous species may contaminate filters. Humidity may also be absorbed and may be difficult to control both during operations. As always meteorological conditions can affect flow rate and results. Although this process offers continuous measurements and an improvement over gravimetric methods, the beta emission and detection process present additional on-site maintenance requirements.(US EPA [Procedures for determining comparability], 1998; US EPA [Reference method PM_{10}], 1998;US EPA,[Procedures for Testing Performance],1998 ; Watson et al.,1998)

C. **Tapered Element Oscillating Microbalance (TEOM) Methods (FEM):** Air is drawn in to a tapered glass element to which is attached a filter. The element oscillates according to a particular frequency which changes as PM- mass are deposited onto the filter. Measurement of the change in frequency converts is used to determine the accumulated mass. The main drawback of this method is that particulate matter may be lost due to vibration. Also gaseous species may contaminate filters. Humidity may also be absorbed and may be difficult to control both during operations. As always meteorological conditions can affect flow rate and results. The TEOM process offers improvement over gravimetric methods but the equipment presents additional maintenance requirements.(US EPA [Procedures for determining comparability] , 1998; US EPA [Reference method PM_{10}], 1998;US EPA,[Procedures for Testing Performance],1998 ;Watson et al. , 1998)

1.1.3.2. $PM_{2.5}$: The methods are used for measurement in the concentration range of 10 to 200 µg/m^3 (US EPA [Procedures for determining comparability], 1998) for test conditions and are operated usually within a temperature range of -30 ^{0}C to + 45 ^{0}C (US EPA, [Reference Method for Determination $PM_{2.5}$], 1998). Usually the lower detection limit is 2 µg/m^3 but may vary according to filter technology limitations (US EPA, [Reference Method for Determination $PM_{2.5}$], 1998). The methods are as follows:

Gravimetric: An air pump is used to draw the surrounding air into a spherical inlet. Here, with the use of filters, the particulates are separated according to size where they are collected. Each filter is measured before and after use to determine the total amount of sample collected. The total volume of air filtered is known from the constant air flow, and the difference in filter weights is used to calculate the particulate matter concentration in micrograms per cubic meter ($\mu g/m^3$) of air. The main disadvantage of this method is that particulate matter may be lost during filter handling, transport and weighing procedures, especially if the filter is exposed to heat. Also gaseous species may contaminate filters. Humidity may also be absorbed and may be difficult to control both during operations and when handling filters. As always meteorological conditions can affect flow rate and results. (US EPA [Procedures for determining comparability], 1998; US EPA, [Procedures for Testing Performance], 1998; US EPA, [Reference Method for Determination $PM_{2.5}$], 1998)

1.1.4 Chemical composition of particulate matter

Particles may be emitted directly from sources (primary) and their composition is closely related to the chemical composition of the source. However particles can also be formed from gases through chemical reactions in the atmosphere (secondary) involving atmospheric oxygen, water vapor and reactive species such as ozone, radicals such as the hydroxyl and nitrate radicals, and pollutants such as sulfur dioxide, nitrogen oxides, and organic gases from natural and anthropogenic sources in a diverse variety of ways. They can be produced by nucleation from low vapor pressure gases emitted from various sources or produced in the atmosphere by various chemical reactions, or aggregation with other particles in the atmosphere. Also gases may condense on already existing particles leading to heterogeneity in particles. Thus any particle in the atmosphere may contain elements from various sources and thus atmospheric particles may be considered a mixture of mixtures (US EPA Vol I, 2004).

There is some observed relation of the aerosol chemical composition with the size of the particles which can be explained in its mode of formation. The smaller particles contain the secondarily formed aerosols (gas-to-particle conversion), combustion particles and re-condensed organic and metal vapors. The larger particles usually contain earth crust materials and fugitive dust from roads and industries. The fine fraction contains most of the acidity i.e hydrogen ion (WHO, 2003).

Atmospheric particulate matter is generally a mixture of the following in various amounts:

- **Geological Material:** Also called as crustal composition**,** this consists mainly of oxides of aluminum, silicon, calcium along with other metal oxides. The actual composition varies according to region and the local industrial processes (like steel making, etc) which may contribute to the soil. Generally about 50 % of PM_{10} is geological material while its contribution to $PM_{2.5}$ is only 5-20% (Chow & Watson., 1998).
- **Sulfates:** Ammonium sulfate ($(NH4)_2SO_4$), ammonium bisulfate ($(NH_4HSO_4$), and sulfuric acid (H_2SO_4) are the predominant form so sulfate that occur almost exclusively in $PM_{2.5}$. These are water soluble and are mainly formed by gas to particle conversion processes which accounts for their exclusive abundance in $PM_{2.5}$. Sodium sulfate (Na_2SO_4) may be found in coastal areas due to sulfuric acid neutralization by sea salt. Gypsum ($CaSO_4$) and some other geological compounds contain sulfate but are water insoluble hence occur dominantly in coarse particulate matter (Chow & Watson, 1998).

- **Nitrate:** Ammonium nitrate (NH_4NO_3) is formed by an equilibrium reaction between HNO_3, NH_3 and is mostly found in fine particulate matter Sodium nitrate may be found near coastal areas due as a result of reaction of sea salt with nitric acid (Chow & Watson, 1998).
- **Ammonium:** Ammonium sulfate ($(NH_4)_2SO_4$), ammonium bisulfate (NH_4HSO_4), and ammonium nitrate (NH_4NO_3) are the most common compounds containing ammonium from irreversible reactions between sulfuric acid and ammonia gas and are found mainly in $PM_{2.5}$. (Chow & Watson, 1998).
- **Sodium Chloride:** Usually found in abundance in coastal regions and generally occurs as coarse fraction. However resuspension from water droplet or melting snow may cause formation of fine sea salt particles (Chow & Watson, 1998).
- **Organic Carbon:** Particulate organic carbon is a diverse series of carbon compounds usually more then 20 carbons in length. The exact compounds are difficult to fix and analyze because of the lack of molecular specificity and high volatility and it is usually analyzed and reported as “Organic Carbon” (Chow & Watson, 1998).
- **Elemental Carbon:** Elemental carbon is often called “soot” and consists of pure carbon as well as high molecular weight, dark colored non volatile organic materials such as tar, biogenic material and coke (Chow & Watson, 1998).
- **Liquid Water:** Soluble compounds like ammonium sulfate, ammonium nitrate take up liquid water and swell. Eventually during periods of high relative humidity they may absorb enough water to transition into a droplet (Chow & Watson, 1998).

The US EPA in association with state and local air quality agencies began implementing an ambient air quality network in 1999/2000 to provide a consistent data set for characterization and evaluation of trends in PM components. 13 initial sites were used for assessment. The data from them was used to determine the major chemical species on which subsequent measurements were analyzed, namely: sulfate, ammonium, nitrate, elemental carbon, organic carbon, and the five trace elements that go into the calculation of the crustal contribution to $PM_{2.5}$ (Al, Fe, Ca, Ti, and Si). Unfortunately, speciation data are not available for the $PM_{10-2.5}$ size fraction (US EPA Vol. I, 2004). One such dataset which lies in the MANEVU region is shown in Table 1.0 which shows that the dominant components (mean mass) of $PM_{2.5}$ are sulfate and ammonium ions followed by organic carbons and then nitrates.

Table 1.0 Summary data for Philadelphia, PA (AIRS Site code: 42010004) for October 2001 - September 2002 (US EPA Vol. I, 2004)

Parameter	**Mean ($\mu g/m^3$)**	**Max ($\mu g/m^3$)**	**Min ($\mu g/m^3$)**
$PM_{2.5}$ (FRM mass)	14.2	86.8	2.1
$PM_{2.5}$ (reconstructed mass)	16.0	239.0	0.0
Sulfate (calculated)	4.3	29.0	0.0004
Sulfate (by I.C)	4.4	30.5	0.020
Ammonium (by I.C)	2.0	11.4	-
Sodium ion (by I.C)	0.21	1.6	-
Potassium ion (by I.C)	0.042	0.83	-
Nitrate	2.1	8.7	0.050
Volatile Nitrate	0.84	4.0	0.030
Nonvolatile nitrate	0.61	5.6	0.020
Elemental carbon	0.66	2.3	-
Carbonate carbon	-	-	-
Organic carbon	3.1	50.5	-
Aluminium	0.019	0.54	-
Arsenic	-	0.006	-
Barium	-	0.12	-
Bromine	0.004	0.013	-
Cadmium	-	0.017	-
Calcium	0.037	0.18	-
Chlorine	0.011	0.68	-
Chromium	0.002	0.018	-
Copper	0.004	0.025	0.003
Iron	0.084	0.53	-
Lead	0.005	0.025	-
Magnesium	-	0.3	-
Manganese	0.002	0.009	-
Molybdenum	-	0.012	-
Nickel	0.006	0.13	0.001

Phosphorus	-	0.039	-
Potassium	0.053	1.1	-
Rubidium	-	0.003	-
Selenium	0.002	0.005	-
Silicon	0.086	1.1	-
Sodium	0.087	0.63	-
Strontium	-	0.016	-
Sulfur	1.45	9.6	-
Tin	-	0.035	-
Titanium	0.006	0.049	-
Vanadium	0.004	0.035	-
Zinc	0.015	0.095	0.007

1.1.5 Effects of particulate matter

The effects of PM on the environment can be analyzed in terms of the given factors as described in US EPA (2004) report Vol. I.

1.1.5.1 Effects on flora and fauna (direct and indirect)

Particulate matter contains a wide variety of compounds, and trace elements in varying amounts. Thus the effects of particulate matter on vegetation may be diverse because of the uncertainly in particulate matter. The effects also vary depending on the species of the plant in consideration. Also, many a times the effects are non-reproducible (Olszyk et al., 1989 in US EPA Vol. I, 2004). Particulate matter may affect vegetation directly through deposition on foliar surfaces or indirectly by deposition in soil/water and changing the chemistry or also by blocking incoming radiation from the sun. Observed effects include reduction in photo-synthesis and respiration rates. In certain cases it may also allow phytotoxic agents to penetrate leave surfaces more readily as observed in the case of ammonia. Permeability of leaves to ammonia was observed to increase on increasing the dust concentrations and decreasing on particle size (Farmer, 1993 in US EPA Vol. I, 2004). Deposition of dust particles on stomata can also physically block them.

Alkalinity in the dust is an essential phytotoxic property of the applied dusts. The range of effects includes lipid hydrolysis, coagulation of the protein compounds, and ultimately plasmolysis of the leaf tissue which reduce the growth and quality of plants (Guderian, 1986 in US EPA Vol. I, 2004). Sea salt which occurs in PM in coastal areas may cause salt injury because of sodium and foliar accumulation of airborne salt particles may lead to foliar injury (Smith, 1984 in US EPA Vol. I, 2004). Acidic deposition on plants has many well documented adverse effects like foliar injury. Heavy metal toxicity is an additional effect of particles which contain heavy metals either from human activities or from natural emissions (like volcanic activity). Additionally it has been shown that abundance of fungal growth has an intimate association with deposited particles (Smith, 1990 in US EPA Vol. I, 2004).

Particulate matter is also known to negatively affect animal health. The most extensive studies on health effects of particulate matter have been done on laboratory mice although several studies exist for human beings as well which document the negative effect of particulate matter on human health like Brook & Rajagopalan (2009) and the report by WHO (2003). It is difficult to estimate the direct effect of particulate matter on a particular species by extrapolation of data from another species because of the anatomical differences between species. In any case it has been shown that ambient particulate matter is responsible for increase in cardiac-related deaths and/or morbidity indicators and that the risk of related cardiac effects may possibly be greater than those attributed to respiratory causes. Both acute and chronic PM exposures have been implied to cause such affects mainly through direct particle uptake into the blood along with mediation by the nervous system. Figure 1.1 illustrates the hypothesized mechanisms involved in humans. Such effects may be especially problematic for individuals suffering from diseases like ischemic heart disease, cardiac arrhythmia, and COPD. Other indirect effects are related to UV radiation attenuation by particulate matter and its relation to Vitamin D production in skin (US EPA Vol. I, 2004). Particulate matter deposition also results in altering the nutrient content of the soil or water phase putting stress on the organisms that reside in that phase. Stress on a species of plant inherently places stress on the animals that depend on it for food or shelter (US EPA Vol. I, 2004).

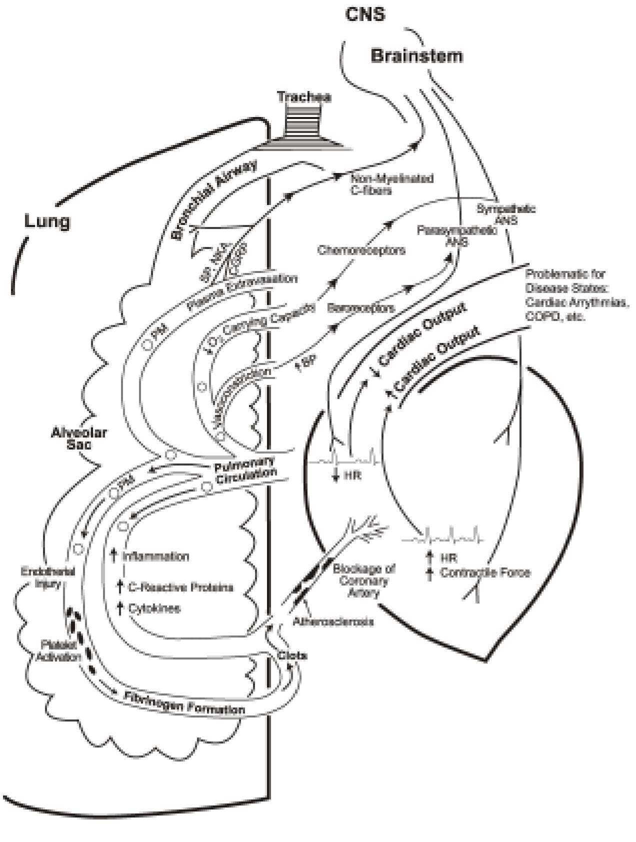


Fig 1.1 Hypothesized pathways to explain cardiovascular PM-related effects (United States Environmental Protection Agency [US EPA] Vol. II, 2004).

1.1.5.2 Effects on visibility

Haze has many effects on the appearance of objects. It washes out colors, reduces contrast and also renders distant objects indistinct or invisible. This is primarily due to the scattering and absorption of light by fine particles suspended in the atmosphere. One quantitative measure of visibility is the visual range which is defined as the farthest distance at which a large black object can be distinguished against the horizon sky (US EPA, 1979 in US EPA Vol. I, 2004). Another frequently used quantity is light extinction, which is the sum of the light scattered and absorbed by particles and gases, is and is used to estimate the effect of air pollution on visibility. Light extinction is usually quantified using the light extinction coefficient, which is the sum of the light scattering and absorption coefficients for gases and particles. The influence of particles in visibility is dependent on particle size, composition, and solubility (Pryor & Steyn, 1994 in US EPA Vol. I, 2004).Particles may absorb water and swell and thus humidity effects must also be considered. Fine particles which include sulfates, nitrates, organics, light absorbing carbon and soil (Malm et al., 1994 in US EPA Vol. I, 2004) tend to scatter light than their coarse counterparts. Several studies and reports (Chow et al. [Light Scattering], 2002; Samuels et al., 1973; Waggoner and Weiss, 1980; Waggoner et al., 1981 in US EPA Vol. I, 2004) indicate that the mass concentration of particles with diameter less than 3 μm correlates well with light scattering and visibility (under dry conditions).

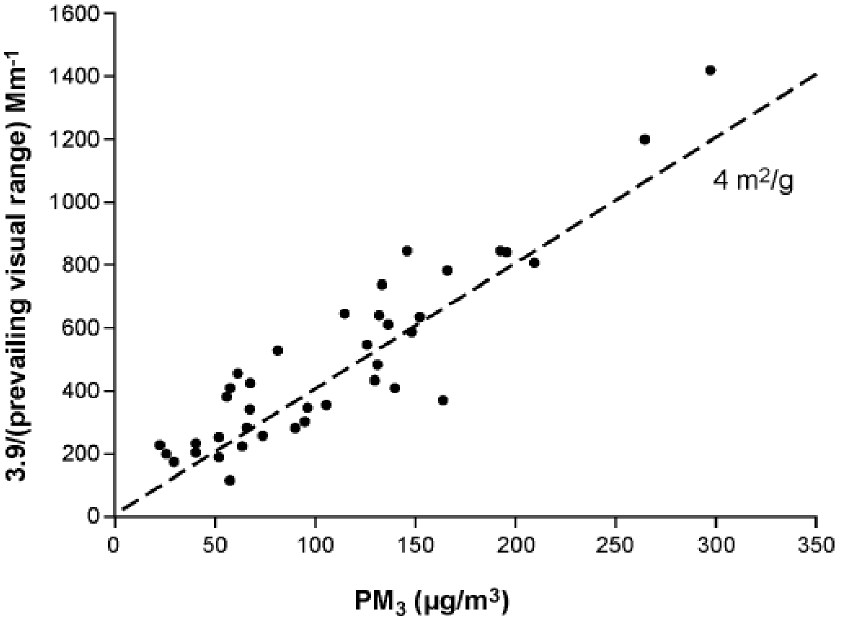


Fig 1.2 Observed daytime haziness is proportional to fine particle mass concentration obtained for 8h samples with Relative Humidity less than 30% (Chow et al, 2002 in US EPA Vol. I, 2004)

The Interagency Monitoring of Protected Visual Environments (IMPROVE) network which is a collaborative effort between federal, regional, and state organizations responsible for protection of visibility in the 156 mandatory Class I Federal areas (national parks and wilderness areas) and other areas of interest to land management agencies, states, tribes, and other organizations describe the algorithm listed as Eq. (1) for calculation of visibility. Here the concentration terms here are mass concentrations and f(RH) is a relative humidity function depending on the nature of the compound

$$b_{ext}=3f(RH)[Sulfate]+3f(RH)[Nitrate]+1.4[Organic\ Carbon]+1.0[Light\ Absorbing\ Carbon]+1.0[Soil]+0.6[Coarse\ PM]+10(Rayleigh\ scattering\ by\ gases) \quad \textbf{...(1)}$$

where, b_{ext} is the light extinction coefficient in $(Mm)^{-1}$.

(US EPA Vol. I, 2004)

1.1.5.3 Effects on man-made materials

Particulate matter, especially carbonaceous material has demonstrated a significant tendency for soiling buildings, monuments and even works of art. PM especially particles containing sulfates and nitrates can directly corrode building material or, through sorption of corrosive agents on deposited particles can accelerate natural weathering processes and can even affect stone structures. There is evidence that particles can act as carriers for corrosive pollutants (Cowling & Roberts, 1954 in US EPA Vol. I, 2004), promote discoloration, chalking, result in loss of gloss, cause erosion, blistering and peeling and thus reduce the durability of paint finishes. They can also stain and pit painted surfaces (Fochtman & Langer, 1957; Wolff et al., 1990 in US EPA Vol. I, 2004)

1.1.5.4 Relationship to climate change processes

Atmospheric gases as well as particulate matter always alter the amount of radiation that is transmitted by the atmosphere. Particulate matter can absorb or scatter incoming radiation and also can reflect and trap infrared radiation emitted by the earth's surface. This increased the heating of the earth's surface and lower atmosphere resulting in the commonly known effect –"The Greenhouse Effect". Thus there may be widespread impact of increasing concentrations of particulate matter on the global environment.

Aerosols may also nucleate cloud droplets depending on their composition. They increase the number of cloud droplets for constant water content. This means that smaller cloud droplets are formed that effectively scatter solar radiation. They also cause an increase in cloud lifetime and reduce the amount of precipitation. They increase the cloud albedo which is the "first" indirect effect. The consequent change in cloud lifetime due to reduced precipitation is the "second" indirect effect. Another "semi-indirect" effect is the reduction in cloud reflectivity. This may primarily be attributed to black carbon-containing aerosol within the cloud drops themselves or as interstitial aerosol (Hansen et al., 2000 in US EPA Vol. I., 2004). Sulfate aerosols which are greater then 50 um in diameter have the largest effect on clouds. They tend to nucleate cloud droplets and ice crystals efficiently (Twomey, 1974 in US EPA, Vol. I., 2004). Satellite observations have shown a reduction in cloud droplet ratio in polluted regions to below the precipitation threshold and consequent reduction in precipitation over the region (Rosenfeld, 1999 in US EPA Vol. I., 2004). If we include these indirect effects it is sufficient to reverse the effects of GHG-related forcing (Ramanathan et al., 2001 in US EPA Vol. I., 2004). Lesser consequences include alterations in the amount of ultraviolet solar radiation (especially UV-B, 290 to 315 nm) reaching its surface which can exert various effects on human health, plant and animal biota, and other environmental components.

1.1.6 Transport and fate of particulate matter

Particulate matter, their precursors and products are removed from the atmosphere mainly by deposition processes. This cleansing process reduces the concentration of particulate matter and prevents the long-term buildup of particulate matter and prevents lethal effects of their inhalation. Unfortunately, these same processes also introduce particulates into other phases and thus help in transfer of different atmospheric pollutants into the soil. There are two types of deposition processes. Wet deposition occurs when atmospheric particles get incorporated into cloud droplets and gases and eventually precipitate in rain. It can also occur because of scavenging nature of rain and snow and get incorporated into them as they fall to the earth (Lovett, 1994 in US EPA Vol. I, 2004). The other type of deposition is dry deposition in which particles are deposited by gravitational sedimentation and inertial impaction. This is generally for particles less than 5 μm diameter. Smaller particles, with diameters between .0.2 and 2 μm, are not readily dry-deposited and tend to travel long distances in the atmosphere until their eventual deposition, most often via precipitation. This long-distance transport of fine particles is largely responsible for the regional nature of acid deposition. Thus fine particles can affect larger areas than coarse particles. A major conclusion from atmospheric deposition research is the realization that dry deposition is usually a significant and, in some cases, a dominant portion of total atmospheric deposition to an ecosystem (Lovett, 1994 in US EPA Vol. I, 2004).

1.1.7 Regulations on particulate matter

The Clean Air act establishes two types of standards- primary and secondary. The primary standards set limits to protect public health including health of more sensitive populations like asthmatics, children and elderly. The secondary standards are more general to ensure public health and welfare and also to protect building, vegetation and animal life from the effects of air pollution.

The particulate matter standards deal with PM_{10} and $PM_{2.5}$. $PM_{2.5}$ was included later on because studies indicated significant links between $PM_{2.5}$ and health related problems. The current standard was established in 2006 during which the agency also revoked the annual PM_{10} standard, because available evidence does not suggest a link between long-term exposure to PM_{10} and health problems (http://www.epa.gov/air/criteria.html). The NAAQS standards are listed in Table 1.1.

Table 1.1 National Ambient Air Quality Standards for Particulate Matter effective December 17, 2006 (http://www.epa.gov/air/criteria.html)

Pollutant	Primary Standards	Averaging Times	Secondary Standards
Particulate Matter (PM_{10})	Revoked	Annual (Arithmetic Mean)	-
	150.0 $\mu g/m^3$	24-hour	Same as primary
Particulate Matter ($PM_{2.5}$)	15.0 $\mu g/m^3$	Annual (Arithmetic Mean)	Same as primary
	35.0 $\mu g/m^3$	24-hour	Same as primary

The following points may be noted:

1. The 24 hour PM_{10} standard may be exceeded only once per year on an average of 3 years.
2. The annual $PM_{2.5}$ standard is based on a 3-year average of the weighted annual mean concentrations from single or multiple community-oriented monitors which must not exceed 15.0 $\mu g/m^3$.

3. To attain the 24 hour $PM_{2.5}$ standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35 $\mu g/m^3$.

1.2 Ammonia

This section describes ammonia, its effect on the environment, its eventual fate and the relevant regulations on ammonia.

1.2.1 Introduction to ammonia

Ammonia is a colorless gas with a strong pungent odor. In nature it is a toxicant which is formed via natural processes and also through anthropogenic influences such as land application of fertilizer. It occurs in air as NH_3 gas but can also occur in water as NH_4^+ ion. It exerts a biochemical oxygen demand on water bodies in which it is present. Because of this, bacteria use dissolved oxygen to oxidize ammonia, thus reducing the available oxygen for fish and killing them. Additionally, it can also lead to heavy plant growth (eutrophication) because it is a nutrient (CADDIS: Vol. 2: Sources, Stressors & Responses). Ammonia as a gas is of particular concern because of its potential to create odors and negatively impact air and water quality and animal and human health (Becker & Graves, 2004).

1.2.2 Structure and physical properties

Ammonia is a compound formed from nitrogen and hydrogen with a chemical formula NH_3. The molecule has a trigonal pyramidal shape. The shape gives the molecule polarity and enables hydrogen bond formation. This is primarily responsible for its solubility in water (National Institute of Standards and Technology [NIST] Chemistry WebBook). With water it is basic in nature and is responsible for neutralizing several acidic gases in the atmosphere with unwanted effects like particulate matter formation (Harper, Flesch & Wilson, 2010). Relevant properties are listed in Table 1.2.

Table 1.2 Physical properties of anhydrous ammonia (MSDS:http://www.tannerind.com/anhydrous-msds.html)

Property	**Value**
Physical state	Gas
CAS registry No.	7664-41-7
Chemical family	Inorganic nitrogen compound
Molecular weight	17.03
Boiling point	-28 ^{0}F at 1 atm
pH	N/A
Specific gravity	0.596 at 32 ^{0}F
Critical temperature	271.4 ^{0}F
Gas specific volume	20.78 ft^3/lb at 32 ^{0}F, 1 atm
Approximate freezing point	-108 ^{0}F
Vapor pressure	114 psig at 70 ^{0}F
Solubility (water)	0.869 lb/lb-water at 32 ^{0}F, 51 lb/lb-water at 68 ^{0}F
Surface tension	23.4 dynes/cm at 52 ^{0}F
Critical pressure	111.5 atm

1.2.3 Sources of ammonia

As mentioned before ammonia is produced naturally as well as due to human influences. Ammonia typically results from bacterial decomposition of natural and anthropogenic organic matter that accumulates in sediment. The produced ammonia places a biological oxygen demand on the water body due to oxidation of ammonia by microbes (CADDIS: Vol. 2: Sources, Stressors & Responses). However a large fraction of ammonia also arises because of human influences and estimates suggest that ammonia derived from animal production operations makes up much as 81% of the total emissions from anthropogenic activity (Battye et al. 1994 in Becker & Graves, 2004). Smaller sources of ammonia include fertilizer application (9.5%), refrigeration (5.1%), municipal wastewater treatment systems (2.0%), and combustion processes (1.2%). Regional air and water quality affected by these ammonia emissions is primarily dependent on the size and density of these operations (Becker & Graves, 2004).

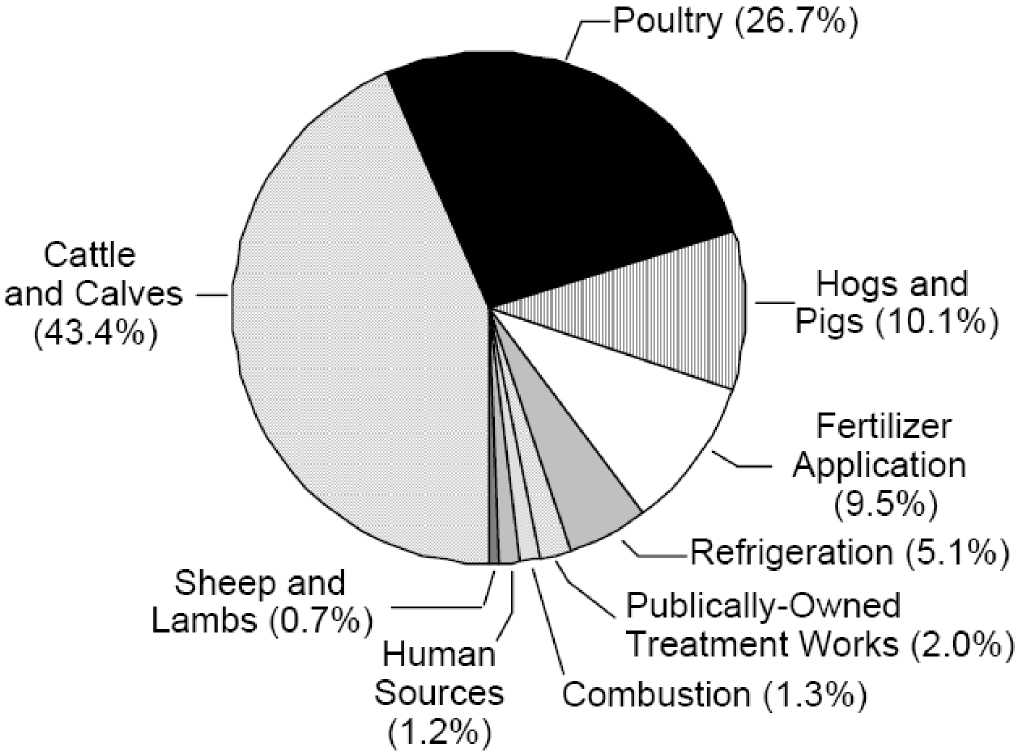


Fig 1.3 Ammonia emissions from human related activities (Battye et al. 1994 in Becker & Graves, 2004)

1.2.4 Measurement of atmospheric ammonia

Measuring atmospheric ammonia can be tricky because of the following reasons:

1. Atmospheric ammonia gets adsorbed onto surfaces very easily. Thus instrument surfaces may adsorb ammonia leading to erroneous readings. Also it may later get desorbed, leading to false positives.
2. The human body naturally produces ammonia which can lead to contamination of samples.

Some common techniques for measurement of atmospheric ammonia are:

1. Samplers which collect ammonia by using sulfuric acid bubblers and citric acid coated filters and denuders which can then be analyzed for ammonia content.

2. Chemiluminescence NO_x monitors which respond to ammonia when their molybdenum catalyst is operated at high temperatures. The exact sample measurement is done by measuring the difference between scrubbed sample and un-scrubbed sample.
3. NOAA developed chemical ionization mass spectrometer (CIMS) which uses citric acid denuders and can measure sub-ppb levels of ammonia with a 1 s response time.
4. NOAA developed ion mobility spectroscopy (IMS) which makes use of ammonia’s strong proton affinity and can sample at one-second intervals. It is a good candidate for on-road measurements.

Historically for large areas, point sampling measurement techniques were used that employed flux chambers or evacuated canisters. The samples later underwent gas analysis to determine the ammonia concentration in gas.

Remote sensing techniques are now available for measurement of ammonia over large heterogeneous sources like lagoons, wastewater treatment ponds, etc. These techniques measure ammonia in a column of air and the readings are reported in ppm-meter. Open-path FTIR spectroscopy is an important remote sensing technique and has received a lot of attention in the last decade (Atmospheric Ammonia: Sources and Fate, 2000).

1.2.5 Effects of atmospheric ammonia on the environment

Ammonia may be harmful to the environment in various ways. Ammonia may react with acidic gases in the atmosphere and form fine particulate matter which may deposit in water bodies. This causes over enrichment of nitrogen in the body leading to potential eutrophication. Approximately 35 to 60% of the total nitrogen loading to North Carolina coastal waters is estimated to be associated with ammonia deposition (Paerl, 1995 in Becker & Graves, 2004). Eutrophication tends to destroy the general biodiversity and leads to loss of species. In addition non-protonated ammonia is itself very toxic to aquatic animals like fish, because it can readily diffuse across gill membranes (Sampaio et al., 2002 in CADDIS Vol. 2: Sources, Stressors & Responses). On the other hand ionized ammonia does not pass as easily through gill membranes, hence it is less toxic (Camargo & Alonso 2006, in CADDIS Volume 2: Sources, Stressors & Responses).

Over fertilization of nitrogen on land may damage sensitive crops like tomatoes, cucumbers, and fruit cultures (van der Eerden et al. 1998 in Becker & Graves, 2004). Deposition of ammonium particulate matter may be of further concern than just over fertilization. The ammonia can get oxidized and lead to formation of nitrates which increases soil acidity in areas where the soil has a low buffering capacity. The formation of fine particles brings with it all the negative impacts of fine particulate matter as discussed (Becker & Graves, 2004).

Ammonia is corrosive and exposure to high concentrations of ammonia in air causes immediate burning of the nose, skin/eye irritation and irritation of throat and respiratory tract. Respiratory distress or failure may occur by inhaling dangerous doses of ammonia. At lower concentrations it causes respiratory irritation and coughing. It must be noted that its easy for the body to adapt to its pervasive odor at low concentrations and may it may become undetectable. Children have a risk of being exposed to higher concentrations of ammonia for the same dose because of their high lung surface area to body ratio. They are also shorter in height and can be subjected to a higher dose because ammonia is heavier than air and settles down (http://www.health.state.ny.us/environmental/emergency/chemical_terrorism/ammonia_tech.htm).

1.2.6 Fate of atmospheric ammonia

All ammonia emissions usually return to the ground. Ammonia readily undergoes dry deposition (Finlayson-Pitts & Pitts, 1999). Analysis shows that atmospheric ammonia is in dynamic equilibrium with ammonia in vegetation. There apparently is a "compensation point" related to the partial pressure of ammonia in leaf tissue of plants. The leaf surface acts as a sink when the ambient concentration is greater than the surface concentration but in other cases it can act as a source. This equilibrium process is not included in most air quality models, and contributes to the uncertainty in estimates of ammonia/ammonium transport and deposition.

In a more familiar fashion, ammonium also neutralizes nitrate, sulfate, or some other anion and leads to the formation of fine particulate matter as discussed before. The deposition process however is fairly complicated (Atmospheric Ammonia: Sources and Fate, 2000). Ammonium ion also reacts with OH^- but the reaction is fairly slow as compared to its reaction with sulfuric or nitric acid (Finlayson-Pitts & Pitts Jr., et al. 1999).

1.2.7 Regulations on atmospheric ammonia

Ammonia is mainly controlled in its aqueous phase due to its potential for eutrophication. The regulations are implemented mainly under the Safe Drinking Water Act. A notable regulation is the Concentrated Animal Feeding Operation (CAFO) Final Rule which requires concentrated animal feeding operations to safely manage manure due to their potential to pollute nearby streams, lakes, and other water bodies (http://water.epa.gov/lawsregs/rulesregs). As previously discussed animal operations constitute a large portion of total ammonia emissions, and a significant fraction of fine particulate matter appears to be ammonium based. Although there are no direct regulations for atmospheric ammonia emissions from concentrated feeding operations, regulations aimed at reducing $PM_{2.5}$ (fine particulate matter) specifically, the regulation of $PM_{2.5}$ as a criteria pollutant through the National Ambient Air Quality Standards may require reductions in ammonia emissions from animal agricultural operations (Becker & Graves, 2004).

1.3 Objectives

The following are the objectives of my study

1. Isolate ammonia as a significant cause of particulate matter formation through literature reviews on particulate matter formation.
2. Isolate the primary source of atmospheric ammonia from literature reviews and by studying published inventory of pollutants.
3. Review strategies to control atmospheric ammonia emissions from said source.
4. Apply best possible control strategy and simulate the effects of the same on regional particulate matter.

LITERATURE REVIEW

The following is a topic wise review of literature relevant to my study.

2.1 Ammonia as a source of particulate matter

Ammonia is a basic gas with a tendency to ionize into NH_4^+ ions in presence of water. Thus it can neutralize atmospheric acids like H_2SO_4 and HNO_3 and form secondary aerosols rapidly by the following reactions:

$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$ **… (2)**

$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$ **… (3)**

$NH_3 + HNO_3 \leftrightarrow NH_4NO_3$ **… (4)**

(Finlayson-Pitts & Pitts., 1999; Atmospheric Ammonia: Sources and fate, 2000).

Ammonia reacts rapidly with sulfuric acid to form ammonium sulfates. As such ammonium sulfate and bisulfate are one of the most common components of atmospheric aerosols. However the formation of sulfate is generally favored over the reaction to form bisulfate which in turn is favored over nitrates in majority of the cases and because of this most ammonium is present as ammonium sulfate although significant amount of ammonium nitrate can also formed in regions where the concentration of competing sulfate ion is low and nitrogen oxide is high. (Atmospheric Ammonia, Source and fate, 2000). Chow et al. (1996) in US EPA Vol. I, 2004) has shown an example in which sulfate mass is mainly present as neutralized ammonium sulfate, while ammonium bisulfate and sulfuric acid is not present in great abundance.

The ammonium nitrate formation reaction is an equilibrium reaction unlike the ammonium sulfate reaction and in addition to this ammonium nitrate is thermally unstable. (Finlayson-Pitts & Pitts., 1999, Atmospheric Ammonia: Sources and fate, 2000). Evidence suggests that in the gas phase ammonium nitrate formation involves a strong hydrogen bond rather than a proton transfer hence it suggests that water is also involved in the formation of atmospheric ammonium nitrate. (Finlayson-Pitts & Pitts., 1999).

The favorability of the reactions can be understood from their free energies of formation in aerosol generation schemes. The free energy of formation of ammonium sulfate from ammonia gas and sulfuric acid droplets is approximately -124 KJ/mol. The reaction equilibrium is towards the formation of ammonium sulfate and occurs in liquid phase with sulfate ions. The reaction to form ammonium nitrate is a gas phase reaction involving nitric acid gas and ammonia gas. As such its free energy of formation from nitrate ions is low of the order of -56 KJ/mol and that is based on the assumption that water is available for its formation. (Data from Kim et al., 1993 in Nenes et al. 1998)

These reactions allow for formation of new secondary aerosol particles or allow for the growth of existing particles. Laboratory measurements indicate that ammonium actually promotes the nucleation of sulfuric acid in the atmosphere which is not a well understood process. Also sulfates in general do not deposit readily and thus sulfates can travel long distances leading to spread of ammonium (Atmospheric ammonia: Sources and fate, 2000). Particles formed by gas reaction mechanisms are usually in the fine particle ($PM_{2.5}$) regime (US EPA Vol. I., 2004) and allow for efficient light scattering leading to observed haziness (Finlayson-Pitts & Pitts., 1999).

Studies conducted in the US indicate that much of the fine particulate matter is present as sulfate. Since ammonium is the only main basic constituent of the atmospheric almost all of it will be ammonium sulfate. Indeed studies conducted by Rogee et al. (1993) in Chow & Watson (1998) for two points in California, along with studies conducted in the Washington Baltimore by region Malm et al. (1994) in Chen et al., (2002), suggest that ammonium sulfate along with carbonaceous material dominate the $PM_{2.5}$ mass.

2.2 Primary sources of ammonia

As discussed earlier the ammonia can be emitted from both anthropogenic influences as well as naturally, although there is evidence (Bouwman et al., 1997 in Harper et al., 2010) to show that most ammonia emissions are largely anthropogenic in nature. Fig 2.0 gives an estimate of sector wise contributions to ammonia emissions. As seen in Fig 2.0, a large portion of this is from the agricultural sector mainly due to intensive animal husbandry operations (Atmospheric Ammonia: Sources and fate, 2000).

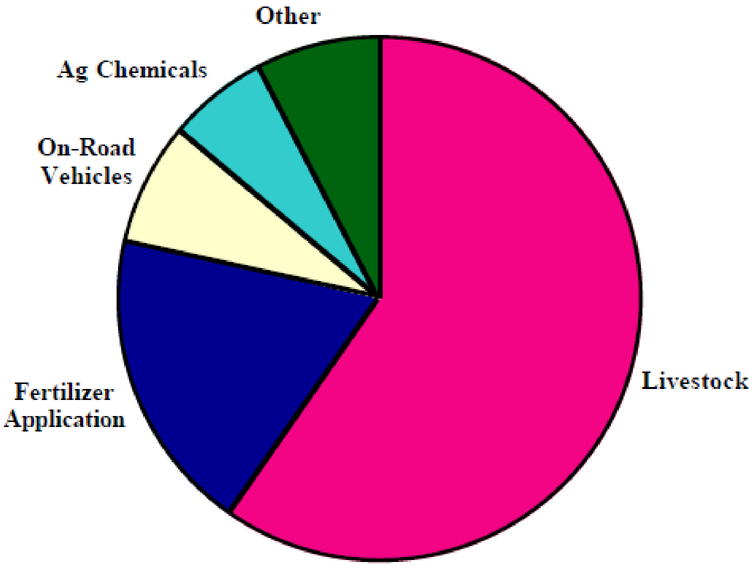


Fig 2.0 Total annual ammonia emissions by sector (EPA National Air Pollution Emissions Trends Update for the years 1970-1997, 1998 in Atmospheric Ammonia: Sources and fate, 2000)

The importance of agriculture as a major contributor to ammonia emissions is also evident from the ammonia emission density map of the US for 1997 shown in Fig 2.1. States with extensive animal-rearing operations involving cattle, hog or poultry were observed to have high ammonia emission densities.

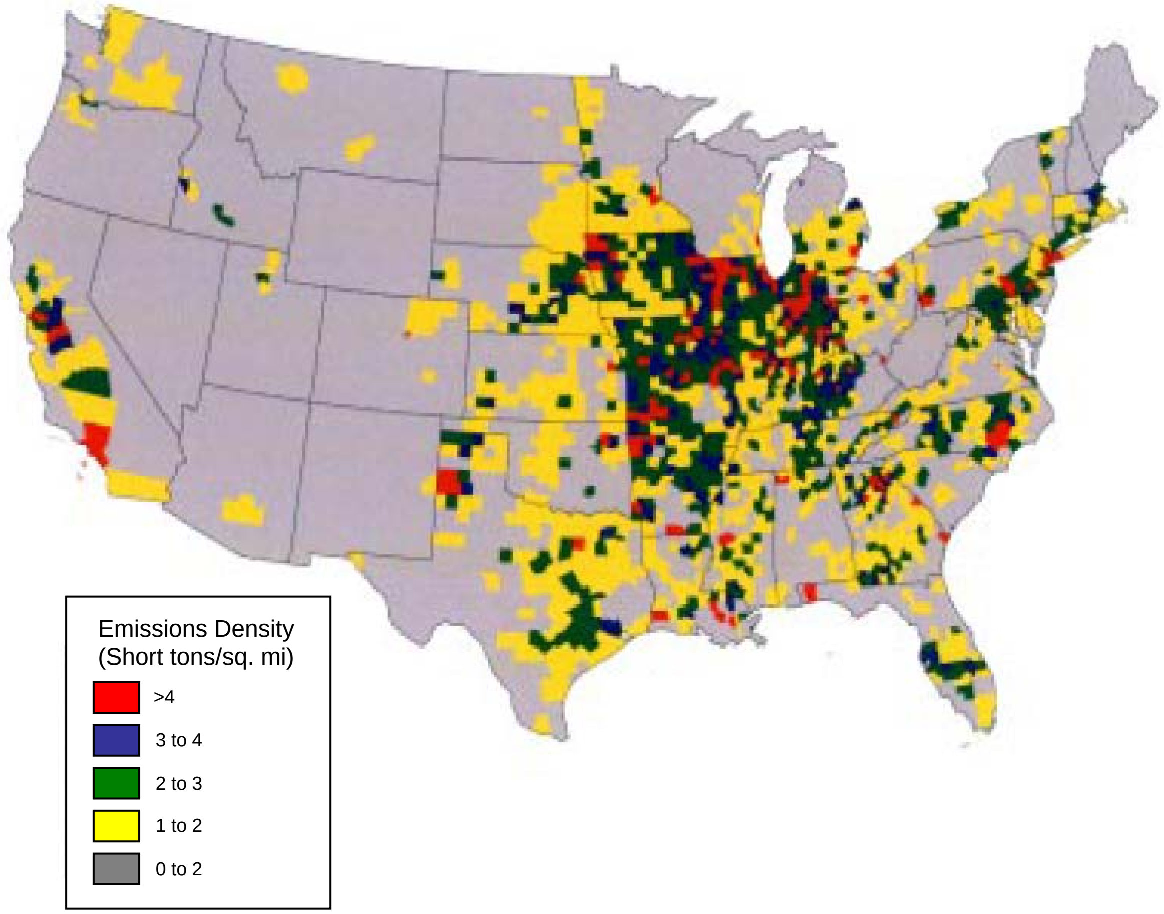


Fig 2.1 US Annual ammonia emissions by county for the year 1997 (US EPA, 1998 in Atmospheric Ammonia: Sources and fate)

Only a few studies of ammonia emissions from livestock have been done so far and there is an urgent need for such studies to be conducted (National Research Council [NRC], 2002 in Becker & Graves, 2004). This is because recent estimates are based on per animal emission factors and numbers of animal units. In any case, estimates indicate that ammonia derived from animal sources may contribute as much as 81% of the total ammonia emissions associated with human activities (Battye et al. 1994 in Becker & Graves, 2004).

The majority of the ammonia emitted as a result of livestock production is derived from cattle and calf operations, poultry and hog/pig rearing. The estimated contributions of various sectors are given in Fig 2.0 and are again reviewed during the study later on.

The trend toward increasingly intensive feeding operations will likely influence the environmental impact of ammonia emissions associated with livestock. For example, between 1982 and 1997, total livestock production increased approximately 10%, but the number of AFOs decreased 51% during this period. At the same time, production became more geographically concentrated. As the size and density of these ammonia sources increase, it is likely that their effects on regional air and water quality will also become more significant. (Becker & Graves, 2004)

2.2.1 Ammonia emissions from manure

The manure that is excreted is broken down by microbial or enzymatic activity and is an important process that releases the nutrients in the manure. In birds, the manure itself contains uric acid. In mammals, the manure mixed with urine contains urea. Breakdown of urea or uric acid requires the presence of an enzyme urease. This is usually present in feces. The conversion of urea or uric acid takes place rapidly (within a few days) while it is very slow in case of case of higher nitrogenous compounds, taking up to months or in some cases a few years. In both cases the released nitrogen is in the form of ammonium ion (NH_4^+). This is released as ammonia when the pH is high enough. The solubility of NH_4^+ ion is more than that of ammonia. Therefore, if NH_4^+ ion is formed it is not readily volatilized, whereas any dissolved ammonia that may be formed tends to volatilize out and is emitted from manure. Therefore pH plays a very important role in determining the rate of ammonia volatilization from manure. It is also influenced by a variety of other factors like the concentrations of manure NH_3 and urea, temperature, air velocity, surface area, and moisture. Understanding the effects of various conditions is the key to understanding how manure can be managed to minimize ammonia emissions (Becker & Graves, 2004).

2.2.2 Strategies to control ammonia emissions from husbandry animal operations

Ammonia emissions occur at different stages of the manure. The exact distribution is difficult to estimate as it is highly dependent on the management practices of the farm or establishment. Estimates suggest that the greatest ammonia losses are usually expected with land application of manure (35-45%) and housing (30-35%). Significant losses can also occur during grazing (10-25%) and manure storage (5-15%) if it is done (Meisinger & Jokela, 2000 in Becker & Graves, 2004). Thus there are multiple opportunities to reduce ammonia emissions at various stages.

The strategies to control ammonia emissions can be broadly grouped into two categories depending on how and when the control strategy acts. Pre-excretion strategies target excreta before excretion and thus control the amount of ammonia released into the atmosphere. Post excretion strategies control the amount of ammonia that is released into the atmosphere after it has passed out of the animal’s body. Again the applicability of these strategies may be suitable in certain cases only and varies on a case to case basis depending on economics and feasibility (Becker & Graves, 2004). Powers (2002) in Becker & Graves (2004) has described the various strategies to control ammonia emissions from animal operations which are described below.

2.2.2.1 Pre-excretionary strategies

Pre excretion strategies can again be classified as follows:

2.2.2.1.1 **Addition of acidogenic substances:** Addition of acidogenic substances like phosphorous sources and calcium salts in feed tends to decrease the pH of the resulting manure. This effect counteracts the increase in pH caused by urea hydrolysis that occurs later on in the manure. Thus a lowering in pH favors the formation of ammonium ion over ammonia and locks up the nitrogen in the feed as highly soluble and less volatile ammonium ion. Hence ammonia emissions are reduced.

2.2.2.1.2 **Feed additives:** Certain feed additives such as yucca plant extracts that purportedly inhibit urease activity may be useful as a control strategy. Such a strategy would target the urea hydrolysis reaction and would cause a slow release of ammonia. Also, certain feed additives tend to redistribute the feed nitrogen and cause more nitrogen to end up as complex nitrogenous compounds in manure rather than urine. These compounds degrade very slowly hence reduce the amount of ammonia released into the atmosphere. For example, inclusion of fermentable carbohydrates like sugar beet pulp into swine diets was shown to increase fecal nitrogen at the expense of urinary nitrogen and thus decreased ammonia emissions by changing excreted nitrogen distribution.

2.2.2.1.3 **Dietary feed manipulation:** While it is impossible to completely prevent feed nitrogen from ending up in animal feces, a careful manipulation of dietary sources can reduce the amount of nitrogen available for ammonia formation. Reduction of crude protein in the diets of swine (grower and finisher), poultry (broiler), and cattle (heifer) has also been shown to reduce ammonia emissions to the atmosphere.

2.2.2.2 Post-excretionary strategies

The post excretion strategies can be broadly classified as follows:

2.2.2.2.1 Prevention of hydrolysis: Application of urease inhibitors like N-(n-butyl) thiophosphoric triamide, cyclohexylphosphoric triamide, and phenyl phosphorodiamidate to cattle and/or swine manure has been shown to prevent urea hydrolysis in laboratory and field studies. Presumably, they would also be useful in case of poultry manure. However these are biodegradable and must be continuously applied to be effective. Also, another worthwhile strategy is the separation of urine and feces. This limits the amount of water available for hydrolysis and may be effective in case of mammals but not in the case of poultry. However such operations can be labor intensive and use of conveyor belts for the same are being investigated in case of pig manure handling.

2.2.2.2.2 Acidification of manure: Ammonia as stated before is released from manure under high pH conditions. The use of acidifying agents like, aluminum sulfate (alum), ferrous sulfate, phosphoric acid, and other proprietary products reduce pH and maintain ammonia in the non-volatile ionized form has been evaluated. Also, the addition of alum or ferrous sulfate introduces metal ions which tend to form insoluble compounds with phosphorus, and help to immobilize manure phosphorus. However if manure has sufficient buffering capacity, the pH may eventually increase, which results in a resumption of ammonia volatilization. In any case, significant reductions in ammonia emissions are observed associated with these strategies.

2.2.2.2.3 **Manure handling and storage strategies:** In addition to adding chemicals to feed several strategies can be used which are actually related to manure storage and handling. For example, sub-surface application of manure through the use of injectors or tillage equipment can reduce ammonia emissions due to land application of manure by preventing contact with air and preventing ammonia equilibration with the gas phase. Similarly, covering of manure storage facilities can also result in reduction. In addition to these housing ventilation systems can also be equipped with filters, scrubbers or other treatment systems that remove ammonia using physical/chemical or biological mechanisms.

2.2.3 Ammonia Emissions in MANEVU region

Ammonia emissions are a regional problem and hence in the discussion below we study ammonia emissions in the Maryland region which is the region used for study.

2.2.3.1 Regional Planning Organizations

Pollutants which can lead to haze formation can arise from a broad geographical area. Hence particulate matter and haze are a regional problem. The US EPA has thus encouraged States and Tribes to cooperatively handle the problem of particulate matter. As a consequence of this there exist five US EPA funded Regional Planning Organizations (RPOs), whose focus is twofold. First, they must evaluate technical information to better understand how their states and tribes impact national park and wilderness areas (Class I areas) across the country. Their second task is to develop regional strategies to reduce emissions of particulate matter and other pollutants leading to regional haze.

Fig 2.2 The five regional planning organizations (http://www.epa.gov/visibility/regional.html).

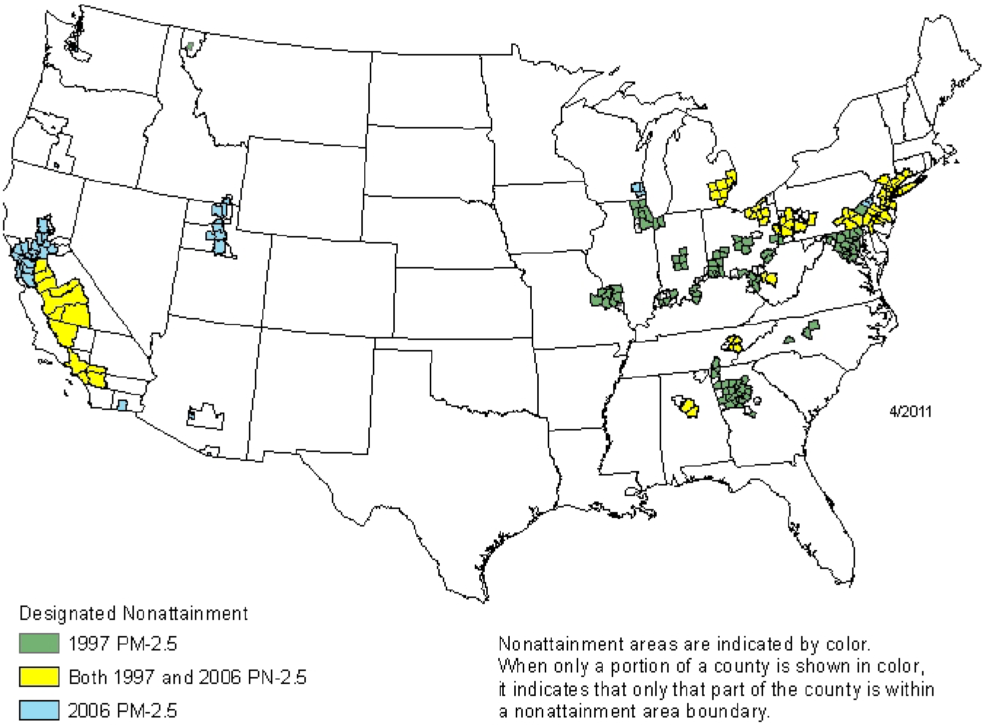
Maryland lies in the Mid-Atlantic/North-East Visibility Union (MANEVU) RPO and thus our main focus will hence be the MANEVU region (http://www.epa.gov/visibility/regional.html).

2.2.3.2 MANEVU Inventory

The Clean Air Act requires the states that do not attain the NAAQS standards (hence the associated term “Non-Attainment”) to submit “State Implementation Plans” to reveal their plans for implementation of strategies for attainment. For this, as mentioned before, the states must be able to analyze the cause of nonattainment. In order to help the states with this, the EPA’s regional haze rule requires states to maintain an inventory of pollutant emissions (Downs, Kheirbek, Klieman, Miller & Weiss, 2010). The inventory must include emissions for a baseline year, future (projected) year, and the most recent year for which data is available (District of Columbia [DC] Regional Haze State Implementation Plan, 2002). The data for compiling inventories is derived from the national emission inventories, Continuous Emission Monitors placed at strategic monitoring sites, and data that is obtained from other RPOs as a part of their data exchange program. Also some data is a result of best estimates from previous inventories or from the research conducted by universities, or dedicated bodies like NESCAUM. The emissions inventory is reported by the following source categories-point, area, highway mobile. These are usually reported by county for each state and tribe in the participating RPO and include all the primary PM ($PM_{2.5}$, PM_{10}) emissions and all precursor emissions like ammonia, oxides of sulfur, volatile organic compounds, NO_x and CO for the listed sources (MANEVU Technical Work Plan, 2003).

2.2.3.3 Ammonia emissions distribution in MANEVU region

From the EPA non-attainment national data in Fig 2.3, I observe that the MANEVU region has a significant $PM_{2.5}$. If the source of the problem is assumed to ammonia, which I have significant reasons to believe (Becker & Graves, 2004; US EPA Vol. I., 2004) the aim of the study is to locate and verify the most significant contributor of ammonia which is suspected to be animal husbandry operations (Bouwman et al, 1997 in Harper et al 2010, Atmospheric Ammonia: Sources and fate, 2000, Becker & Graves, 2004).



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Nonattainment areas are indicated by color. When only a portion of a county is shown in color, it indicates that only that part of the county is within a nonattainment area boundary.

Fig 2.3 $PM_{2.5}$ non-attainment areas by county according to various standards (http://www.epa.gov/oaqps001/greenbk/mappm25_2006.html)

A study was done to pin down the sector and source contributing the most ammonia. The MANEVU 2002 emission summaries are listed in Table 2.0.

Table 2.0 MANEVU 2002 emission summaries by source (http://www.marama.org/technical-center/emissions-inventory/2002-inventory-and-projections/mane-vu-2002-emissions-inventory/version-3-summaries)

Species	**Emissions in tons/year**				
	Area Sources	**Biogenic Sources**	**Nonroad Sources**	**Onroad Sources**	**Point Sources**
CO	1,325,853	274,451	4,553,123	11,749,819	357,645
NH3	249,795	NA	287	52,984	6,194
NOx	262,477	28,396	431,631	1,308,233	673,660
PM_{10} (Primary)	1,455,311	NA	40,114	31,561	89,150
$PM_{2.5}$ (Primary)	332,729	NA	36,084	22,107	55,447
VOC	1,528,141	2,575,232	572,751	789,560	97,300

The total ammonia emissions were obtained to be 309,260 tons/yr.

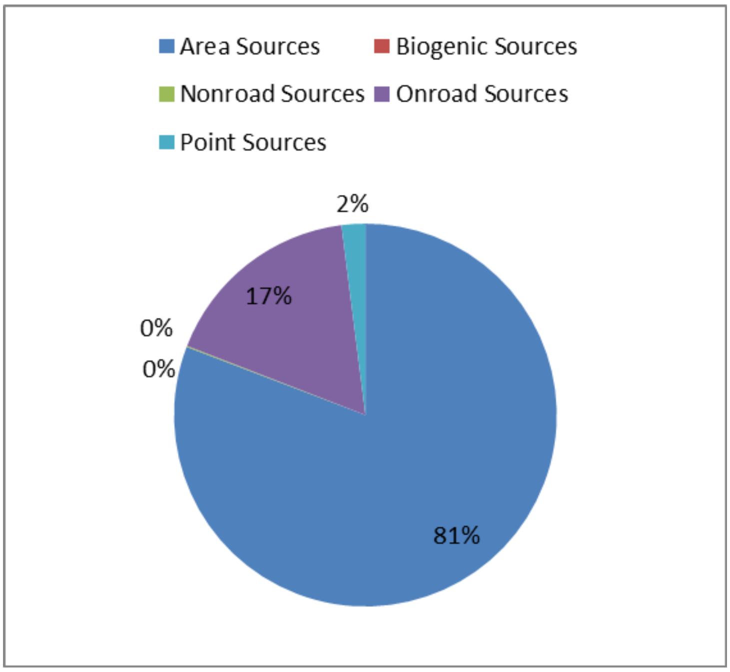

Fig 2.4 Ammonia emission contributions by source type

From Table 2.0 and Fig 2.4 we can clearly see that area sources contribute the greatest amount to the ammonia emissions over the MANEVU region.

I next took a look at the top 10 ammonia emitters in the region which are shown in Fig 2.5.

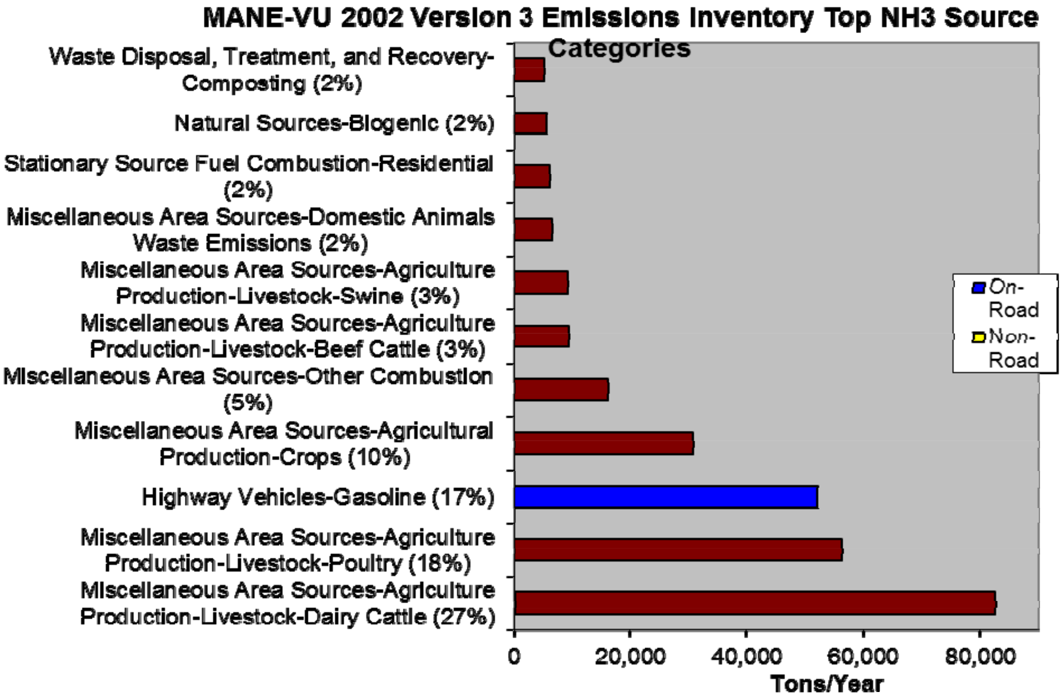

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Fig 2.5 Ammonia emission contributions by source type (http://www.marama.org/technical-center/emissions-inventory/2002-inventory-and-projections/mane-vu-2002-emissions-inventory/version-3-summaries)

From the above figure I can conclude that livestock operations, which is an area source, is the largest contributor to the total annual ammonia emissions in the region and of this 18 % of total ammonia emissions is contributed by poultry sources alone. Along with this I also obtained the SCC codes corresponding to sources of ammonia from animal husbandry operations. These were obtained from Technical Support Document: Preparation of Emissions Inventories for the 2002-based Platform, Version 3 Criteria Air Pollutants (2008) published by US EPA and are listed in Table 2.1 along with their percentage contribution to the area source ammonia emissions. Later on I used the SCC codes specific to broilers to conduct reduction studies, the details of which will be explained in Chapter 3.

Table 2.1 List of SCC codes for ammonia emissions as a result of animal husbandry operations, their descriptions and percentage contributions to total area sources.

SCC Code	Description	Percentage Contribution
2805000000	Agriculture – Livestock; Total	NA
2805001100	Beef cattle-finishing operations on feedlots (drylots); Confinement	1.19
2805001200	Beef cattle - finishing operations on feedlots (drylots); Manure handling and storage	0.00
2805001300	Beef cattle - finishing operations on feedlots (drylots); Land application of manure	0.95
2805002000	Beef cattle production composite; Not Elsewhere Classified	0.02
2805003100	Beef cattle - finishing operations on pasture/range; Confinement	2.02
2805007100	Poultry production - layers with dry manure management systems; Confinement	5.15
2805007300	Poultry production - layers with dry manure management systems; Land application of manure	0.12
2805008100	Poultry production - layers with wet manure management systems; Confinement	0.03
2805008200	Poultry production - layers with wet manure management systems; Manure handling and storage	0.08
2805008300	Poultry production - layers with wet manure management systems; Land application of manure	0.01
2805009100	Poultry production - broilers; Confinement	3.53
2805009200	Poultry production - broilers; Manure handling and storage	0.61
2805009300	Poultry production - broilers; Land application of manure	2.85
2805010100	Poultry production - turkeys; Confinement	0.73
2805010200	Poultry production - turkeys; Manure handling and storage	0.13
2805010300	Poultry production - turkeys; Land application of manure	0.65
2805018000	Dairy cattle composite; Not Elsewhere Classified	0.13
2805019100	Dairy cattle - flush dairy; Confinement	0.48
2805019200	Dairy cattle - flush dairy; Manure handling and storage	1.33
2805019300	Dairy cattle - flush dairy; Land application of manure	0.13

2805020001	Cattle and Calves Waste Emissions; Milk Cows	NA
2805020002	Cattle and Calves Waste Emissions; Beef Cows	NA
2805020003	Cattle and Calves Waste Emissions; Heifers and Heifer Calves	NA
2805020004	Cattle and Calves Waste Emissions; Steers, Steer Calves, Bulls, and Bull Calves	NA
2805021100	Dairy cattle - scrape dairy; Confinement	5.24
2805021200	Dairy cattle - scrape dairy; Manure handling and storage	5.80
2805021300	Dairy cattle - scrape dairy; Land application of manure	1.19
2805022100	Dairy cattle - deep pit dairy; Confinement	0.48
2805022200	Dairy cattle - deep pit dairy; Manure handling and storage	0.02
2805022300	Dairy cattle - deep pit dairy; Land application of manure	0.27
2805023100	Dairy cattle - drylot/pasture dairy; Confinement	4.27
2805023200	Dairy cattle - drylot/pasture dairy; Manure handling and storage	0.07
2805023300	Dairy cattle - drylot/pasture dairy; Land application of manure	5.67
2805025000	Swine production composite; Not Elsewhere Classified	0.42
2805030000	Poultry Waste Emissions; Not Elsewhere Classified	2.15
2805030001	Poultry Waste Emissions; Pullet Chicks and Pullets less than 13 weeks old	NA
2805030002	Poultry Waste Emissions; Pullets 13 weeks old and older but less than 20 weeks old	NA
2805030003	Poultry Waste Emissions; Layers	NA
2805030004	Poultry Waste Emissions; Broilers	NA
2805030007	Poultry Waste Emissions; Ducks	0.36
2805030008	Poultry Waste Emissions; Geese	0.00
2805030009	Poultry Waste Emissions; Turkeys	NA
2805035000	Horses and Ponies Waste Emissions; Not Elsewhere Classified	2.08
2805039100	Swine production - operations with lagoons (unspecified animal age);Confinement	0.48
2805039200	Swine production - operations with lagoons (unspecified animal age);Manure handling and storage	0.98
2805039300	Swine production - operations with lagoons (unspecified animal age);Land application of manure	0.08
2805040000	Sheep and Lambs Waste Emissions; Total	0.39
2805045000	Goats Waste Emissions; Not Elsewhere Classified	0.29

2805045002	Goats Waste Emissions; Angora Goats	NA
2805045003	Goats Waste Emissions; Milk Goats	NA
2805047100	Swine production - deep-pit house operations (unspecified animal age);Confinement	1.35
2805047300	Swine production - deep-pit house operations (unspecified animal age);Land application of manure	0.63
2805053100	Swine production - outdoor operations (unspecified animal age);Confinement	0.00
Total Contribution		52.41 %

MODELS AND SETUP

3.1 Selection of control strategy

As mentioned before, the control strategies for ammonia reductions are classified into two major types- pre excretion and post excretion. Post excretion strategies involving addition of acidifying agents like aluminium chloride may produce substantial reductions in ammonia emissions. However, they can also negatively affect feed intake of poultry at higher concentrations (Choi & Moore Jr., 2008). Also addition of acidifying agents like sulfates or chlorides especially aluminium salts can upset the pH and nutrient balance of the receiving soil. Other post excretionary strategies like manure handling and/or urine separation tend to be labor intensive, increasing cost of production. Addition of urease inhibitors may be potentially expensive and labor intensive.

Pre-excretionary strategies like addition of feed additives that inhibit urease activity have been tested in pigs but their effectiveness on poultry are unknown. Addition of pH increasing substances to diet and reduction in crude protein seem like the best approach for achieving ammonia emission reductions.

Hale III (2005) describes a method of feed reformulation of poultry feed using acidogenic substances, coupled with crude protein reduction. In this method, the author tested the effects of three different strategies for ammonia emissions from laying hen manure. The first strategy was to replace limestone with an acidifying substance like gypsum as a source of dietary calcium. 45 wt % of dietary calcium was replaced with gypsum in this particular case. It was found that that this produced a 15 % reduction in ammonia emissions. The author also states that based on a study done by Keshavarz (1991) as long as the gypsum is fine enough to ensure slow release of calcium and the net weight % is kept below 66 %, replacement of limestone with gypsum has no apparent effect on hen performance.

The second strategy the author tested was to add clinoptilolite zeolite to the acidogenic feed. Zeolites as a group generally exhibit a high cation exchange capacity (CEC) and resistance to acid attack and clinoptilolite zeolite especially exhibits a very strong preference for binding nitrogenous cations such as ammonium. The author also states that zeolites will pass through the gut with their CEC and nitrogenous reactivity intact. A diet consisting of 2 wt % (of diet) clinoptilolite along with 45 wt % (of dietary calcium) gypsum was tested. It was found that this diet provided significant reductions (47 %) in ammonia emissions. It was found that this was greater than the reductions from the first control strategy. A separate study conducted with only zeolite was found to actually increase ammonia emissions prompting the hypothesis that zeolite works synergistically with gypsum to produce higher reductions.

A third strategy involved reducing the fed crude protein (CP) such that the excess indigestible or unusable proteins are minimized (Powers et al., 1998 in Hale III, 2005). In order to maintain a comparable diet to the original baseline diet and to maintain the minimum nutritional value of the diet, the diet was supplemented with lysine. The modified diet comprised of powdered clinoptilolite at 2% by weight, gypsum providing 45% of the supplemental calcium in the diet, and CP levels reduced by 3.8%.It was found that the ammonia emissions were reduced by almost 77% compared to the standard diet. A further study optimized the various levels of zeolite-dietary calcium mixture.

To test the effects of an optimized diet, field tests were done in winter and in summer, in a high-rise layer house containing approximately 125,000 birds. These birds were fed a diet consisting of 1.25 wt. % zeolite, 35 wt. % of dietary calcium from gypsum, and 14.0% crude protein (as compared to the original 18.8%). A second house was used as a control case where the chickens were fed an unmodified diet. In winter, recirculation was used to conserve heat by reducing exhaust and during summer, exhaust fans were in operation to the maximum possible extent. Ten corresponding fans from each house were used as reference fans for readings and a hand held ammonia meter was used to take readings after equilibration. It was found that ammonia emission reduction of 54.3-85.6 % was obtained in winter and 32.8-63.3 % was obtained in summer. Although these values seem high it is a worthwhile study that needs to be taken into consideration.

A follow-up study was conducted by Wu-Haan, Powers, Angel, Hale III & Applegate (2007). The objectives of this particular study was to evaluate the effectiveness of feeding a diet containing 6.9% of gypsum-zeolite mixture that replaced 35% of the limestone along with slight crude protein reduction to laying hens of different ages. It was found that this reduced ammonia emissions by 39 % for hens of all ages. The diet reduced the emissions of certain gases like methane but increased H_2S concentration three fold. However the author states that the increased concentrations would not trigger federal reporting requirements. To do this 10 million hens would have to be present at the same site. Our control strategy is based on this particular paper. To simulate the strategy a 39 % ammonia emission reduction was applied with a 200 % increase in H_2S concentration.

3.2 Sparse Matrix Operator Kernel Emissions (SMOKE)

The SMOKE modeling system was developed for inventory processing using high performance computing algorithms under the UNIX/LINUX platform. It is primarily an emissions processing system that is used to create gridded, speciated emissions with hourly temporal variations. It is flexible and can produce outputs compatible with a wide variety of commonly used air quality modeling systems especially the Community Multiscale Air Quality (CMAQ) Model.

It supports different emission categories like area, biogenic, mobile and point sources and also supports different emission types like hazardous air pollutants and toxics. (http://www.smoke-model.org/overview.cfm)

3.3 Speciation mechanism

The Carbon Bond V (CB05) speciation mechanism was used for both speciation in SMOKE and CMAQ. It includes 156 reactions involving 52 species and is used by SMOKE to split inventory emissions (like NO_x) into speciated emissions (NO, HONO, NO_2).

(http://www.cmascenter.org/help/model_docs/cmaq/4.6/CB05_NOTES.txt)

3.4 CMAQ model

The US EPA Community Multiscale Air Quality (CMAQ) is a transport model that is used for a wide variety of studies ranging from regulatory to analysis of the complex interactions of the atmosphere. It is a 3 dimensional model that is capable of simulation of a wide variety of substances like particulate matter (PM), toxic airborne pollutants, acid rain, etc.

It is a eulerian model that uses coupled ordinary differential equations to predict changes in a fixed three dimensional grid. Thus it takes into account advection-diffusion, emission and losses of species and chemical transformation to predict the change in species concentration per unit cell per unit time.

Accordingly this can be mathematically represented as:

$$\partial C/\partial t = Adv + Diff + Rc + Ec - Sc \qquad \textbf{...(3)}$$

Where,

Adv = advection of species C

Diff = diffusion of species C

Rc = chemical transformation of species of species C

Ec = emissions of species C

Sc = loss processes for species C

Fig 3.0 gives a description of the general process involved in running CMAQ followed by the description of modules used during each simulation to perform various tasks.

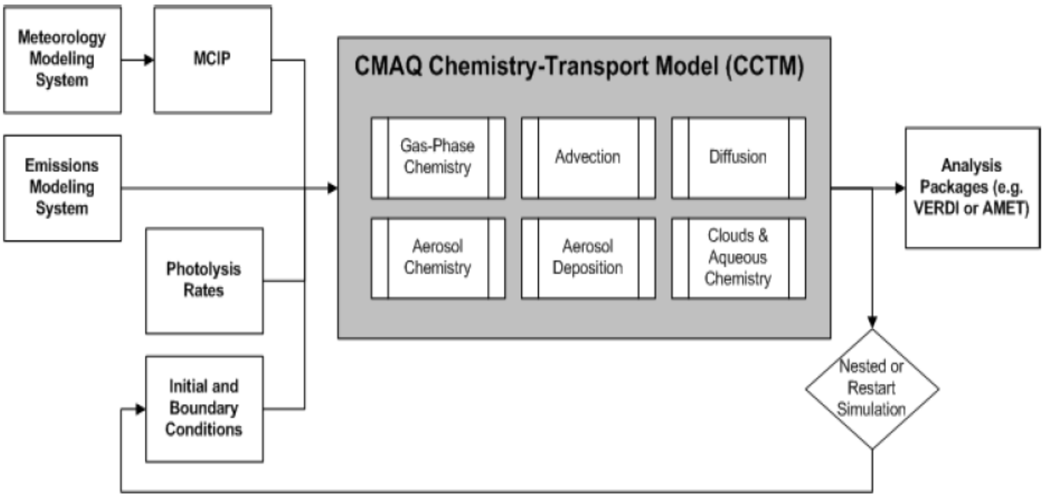

Fig 3.0 Description of various processes involved in a CMAQ process (CMAQv4.7.1 Operational Guidance Document, 2011)

1. **Photolysis Rate Processor (JPROC):** Calculates speciation mechanism specific gas phase chemical photolysis rates that are stored in lookup tables.
2. **Initial Conditions Processor (ICON):** Generates a initial conditions file containing the chemical conditions for the 1st hour of simulation.
3. **Boundary Conditions Processor (BCON):** Generates a boundary conditions file for the horizontal boundaries of the domain which can be static or time varying.
4. **Meterology Chemistry Interface Processor (MCIP):** Uses meteorological model files to create input meteorological data used by SMOKE and CMAQ
5. **CMAQ Chemistry Transport Model (CCTM):** It is the actual model which incorporates all the programs and solves for species concentrations, deposition velocities, aerosol mixing ratios, etc.

There are 3 main options available for solving chemistry in CCTM. They have been investigated for overall accuracy, generalization and computational efficiency to ensure a good balance between the three. They are as follows:

1. Rosenbrock (ROS3) solver (Sandu et al., 1997 in Operational guidance for CMAQ modelling system, 2011)
2. Euler Backward Iterative (EBI) solver (Hertel et al., 1993 in Operational guidance, 2010)
3. Sparse Matrix Vectorized GEAR (SMVGEAR) solver (Jacobson & Turco, 1994 in Operational guidance, 2011)

(CMAQ4.7.1 Operational Guidance, 2011)

3.5 Simulation Setup

A. Emissions Inventory: As mentioned before we used the MANEVU 2002 inventory along with the corresponding versions of other inventories for the surrounding regions like CENRAP, MRPO, CANADA, and VISTAS.

B. Inventory Processing: For this study we used SMOKE v2.2 for maximum compatibility with the 2002 inventories. The default binary that was available on the Community Modeling and Analysis System website (www.smoke-model.org) was downloaded and installed.

C. Meteorology: The MICP processed meteorology for the year 2002 was obtained from Maryland Department of Environment (MDE). This same meteorology has been used previously for several runs by the University of Maryland, and MDE.

D. Initial Conditions: Obtained from Maryland Department of Environment

E. Boundary Conditions: Obtained from Maryland Department of Environment

F. Grid: UMD, Eastern US grid with 12 kmx12km cells

G. Time step: The model progresses in 1 hour time steps. 25 hours (or time steps) constitute a daily emission files which is used for model analysis.

I. Chemical Speciation: Carbon Bond V (CB05)

J. Transport Model: CMAQ v 4.7.1b, which is the latest model version and is fully compatible with CB05 speciation, was used for processing the emissions.

K. Solver: EBI solver was used for CB05 chemistry

L. System: Debian GNU/Linux 2.6.26-2, on 8 Quad core AMD Opteron Processors (Ozone Cluster)

3.6 Cases:

3.6.1 Base case: The 2002 emissions for the month of May were processed in SMOKE with the 2002 meteorology using the UMD grid and CB05 mechanism. The model ready emissions files were then processed in CMAQ and the emissions data was obtained. This constitutes the base run. A convergence time of 15 days was allowed for convergence of the model based on previous simulation experiences. The actual base case run was done by Timothy Canty, RAMMPP group.

3.6.2. Reduced case: The 2002 area source emissions inventory for the MANEVU region and for the month of May was reduced for the SCC Codes listed in Table 3.0.

A 39% reduction in ammonia emissions was applied to each SCC entry found along with a 200 % increase in H_2S concentration. The latter was found to be unnecessary because the hydrogen sulfide emissions associated with each SCC entry were found to be zero. The reduced inventory was then processed in SMOKE to obtain a reduced emissions inventory. This was processed in CMAQ in a fashion similar to the base case to obtain the emissions that correspond with our selected control strategy.

Table 3.0 List of SCC codes for which ammonia reductions were done

SCC	Description
2805007100	Poultry production - layers with dry manure management systems; Confinement
2805007300	Poultry production - layers with dry manure management systems; Land application of manure
2805008100	Poultry production - layers with wet manure management systems; Confinement
2805008200	Poultry production - layers with wet manure management systems; Manure handling and storage
2805008300	Poultry production - layers with wet manure management systems; Land application of manure
2805009100	Poultry production - broilers; Confinement
2805009200	Poultry production - broilers; Manure handling and storage
2805009300	Poultry production - broilers; Land application of manure

The essential assumption in this case was that the SCC codes 2805007100-2805008300 correspond mostly to broilers, since there are separate categories listed for the other only poultry animal-turkeys.

The Fig 3.1 shows the original emissions and Fig 3.2 shows the emissions with the control strategy applied to them. Fig 3.3 gives a comparison between Fig 3.1 and Fig 3.2 in terms of percent reduction.

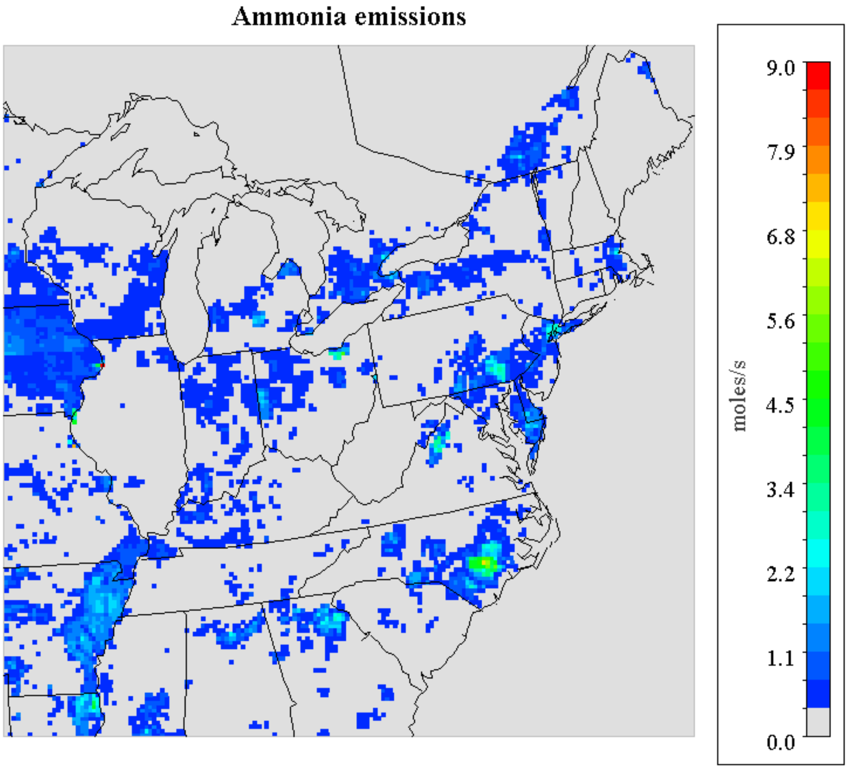

Fig 3.1 Ammonia emission data for MANEVU 2002 dataset with other RPO's incorporated for 15th May 2002, 12:00 EDT

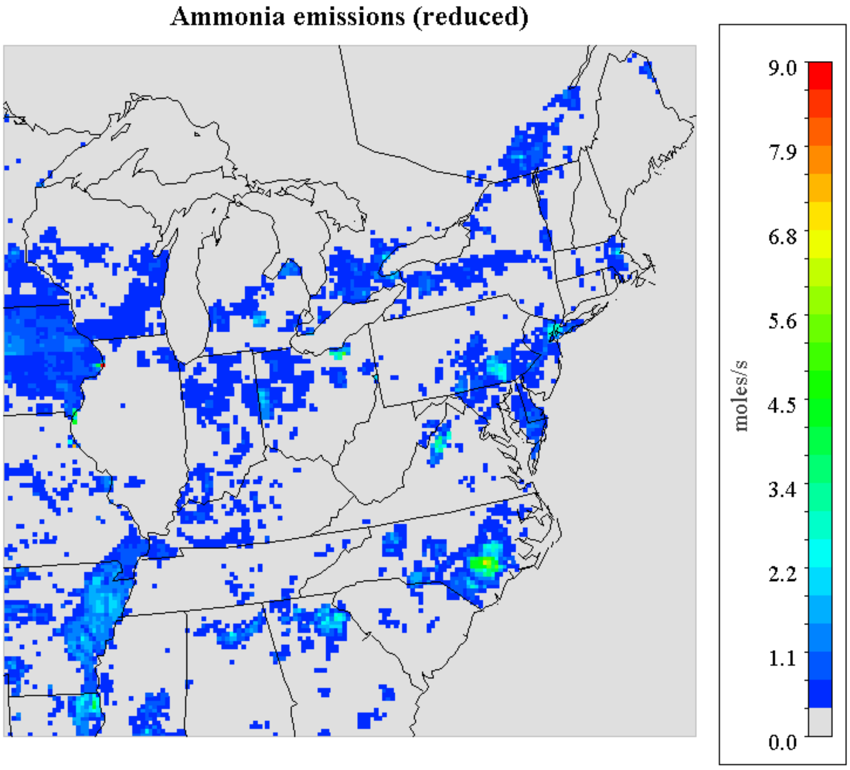

Fig 3.2 Ammonia emission data for MANEVU 2002 dataset from other RPO's incorporated after application of control strategy to the MANEVU 2002 dataset 15th May 2002, 12:00 EDT

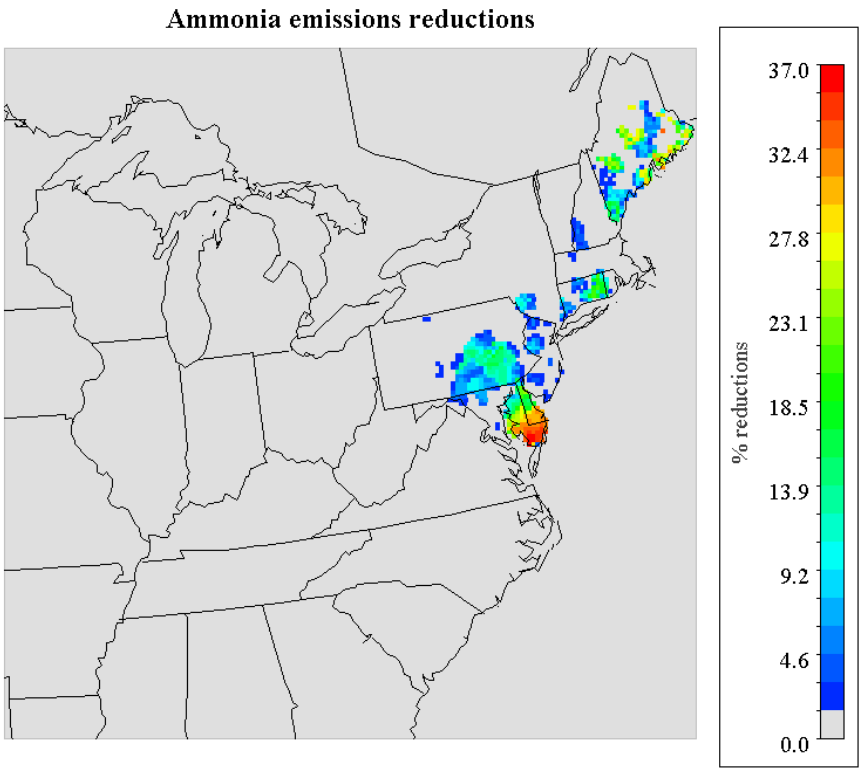

Fig 3.3 Percent reduction in ammonia emissions as a consequence of emission reduction scenario for the MANEVU region for 15th May 2002, 12:00 EDT

Fig 3.4 shows the ammonia emission curves over the day. It is observed that the emissions peak at 12:00 EDT. These curves are similar for the rest of the month.

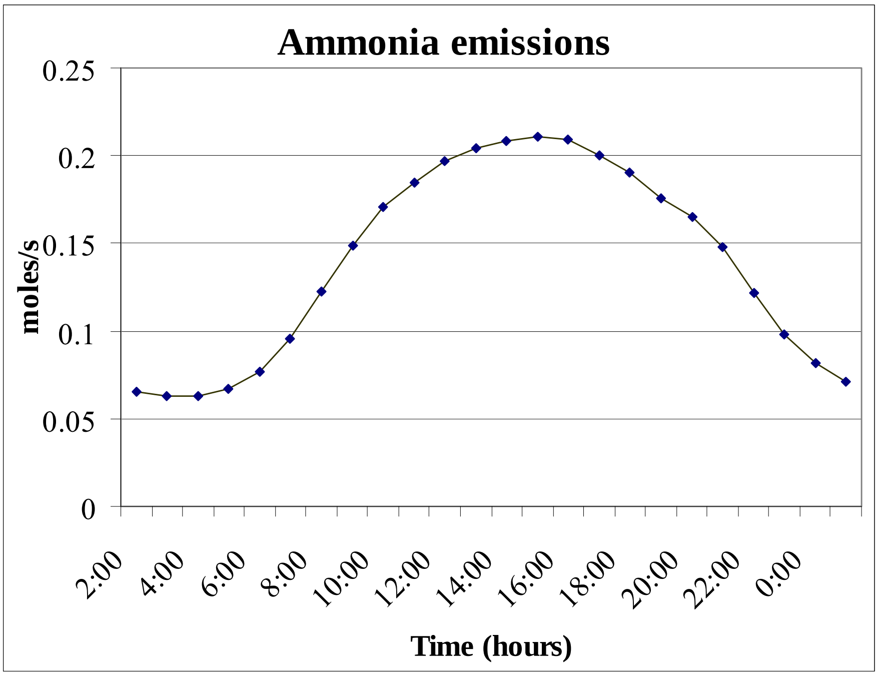

Fig 3.4 Average ammonia emission over the grid for 15th May 2002.

RESULTS AND DISCUSSION

I analyzed the simulation results obtained for the month of May, 2002. First, I looked at total $PM_{2.5}$ concentration over a period of 15 days from 15th of May to 30th of May. The average $PM_{2.5}$ values over the grid for each hour were taken into consideration and were plotted as shown in Fig. 4.0 for the days from 18th - 26th of May. The $PM_{2.5}$ values were found to have a daily maxima occurring at about 8:00 AM EDT.

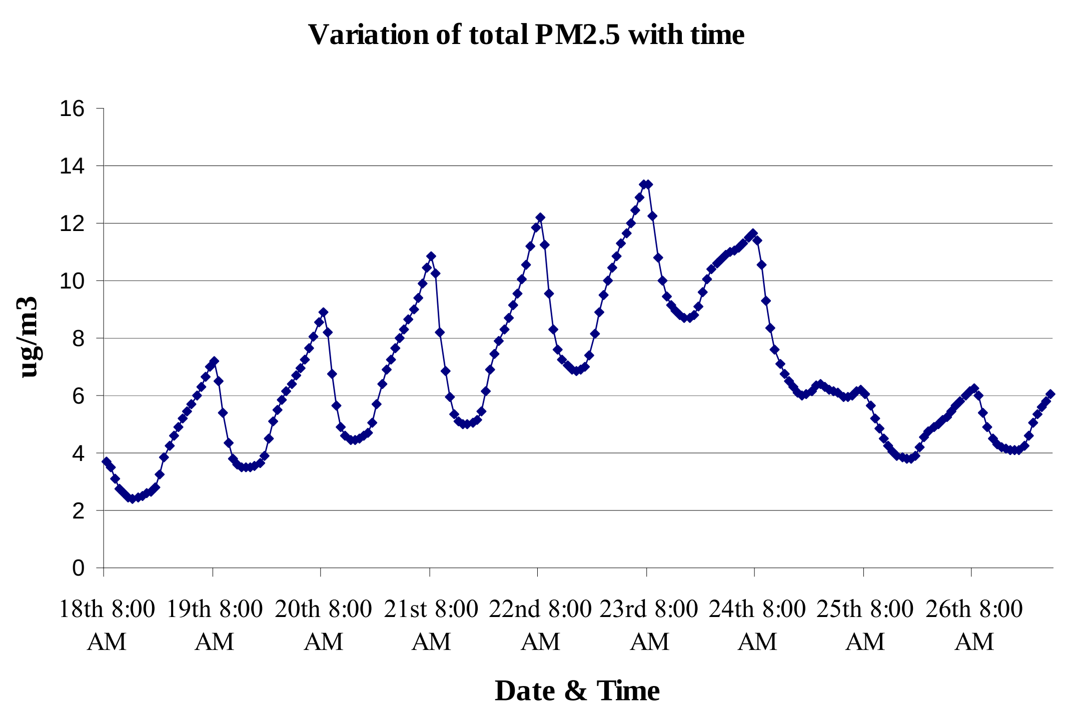

Fig 4.0 Average total $PM_{2.5}$ values for each hour (EDT) from 18th May to 26th May, 2002

According to Fig 4.0 the value of the maxima keep increasing till a peak is observed for 23rd of May after which the value of maxima begin to decline with each passing day suggesting a severe $PM_{2.5}$ episode at 8:00 AM EDT on 23rd of May for the whole grid. The hours of non compliance of each day leading till the 24th were also taken into consideration and, while the average $PM_{2.5}$ was higher for the 23rd throughout the grid, the 24th of May corresponds to a very high level of non-compliance over the Eastern United States and the MANEVU region. Thus, three days of 18thth, 22nd and 24th of May were selected to fully capture the episode for the evaluation of my proposed control strategy. Accordingly, each day corresponds to a comparatively low, moderate and high $PM_{2.5}$ episode respectively depending on their non-compliance of the 15 μg/m^3 standard. In my discussions "low $PM_{2.5}$" corresponds to 0-6 hours of non-compliance while "moderate $PM_{2.5}$" corresponds to 6 to 12 hours of non-compliance. Similarly, "High $PM_{2.5}$" corresponds to 12 to 24 hours of non-compliance.

4.1 Low $PM_{2.5}$ episode - May 18th, 2002, 8:00 EDT

4.1.1 Total $PM_{2.5}$

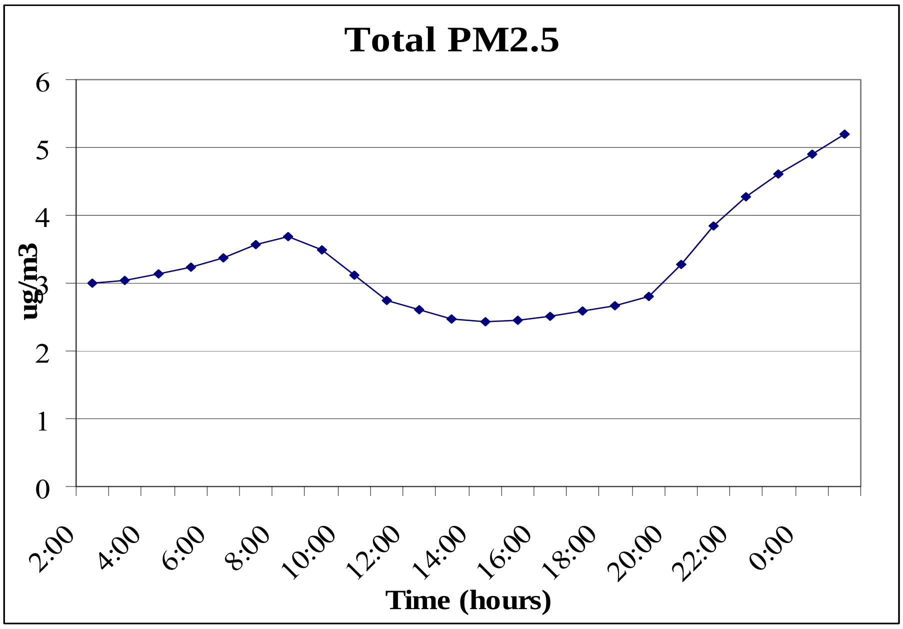

Fig 4.1 Total $PM_{2.5}$ for the base case showing maxima at 8:00 AM EDT, 18th May, 2002.

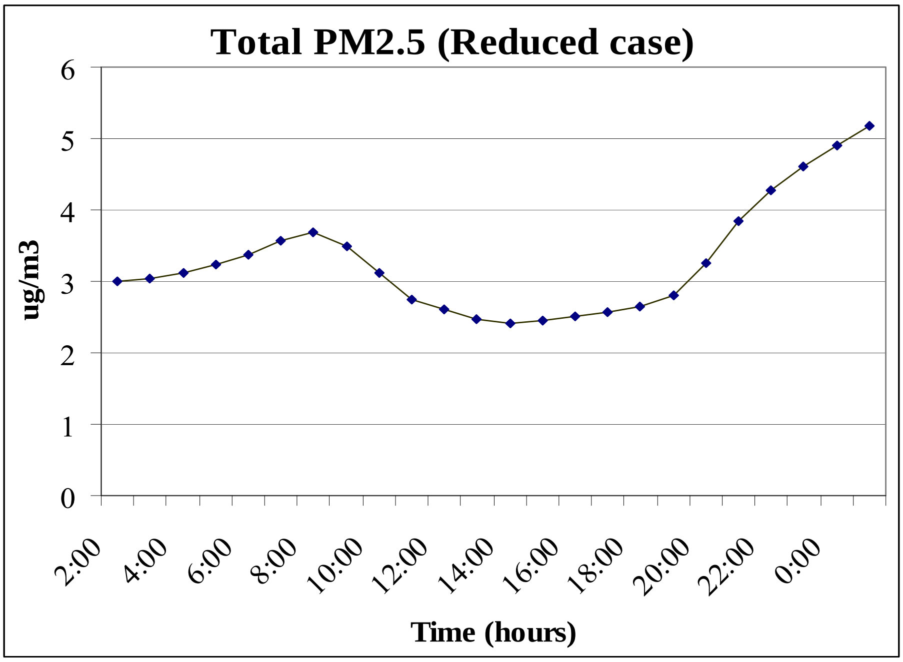

Fig 4.2 Total $PM_{2.5}$ for the reduced case showing maxima at 8:00 AM EDT, 18th May, 2002.

As can be seen from Fig 4.1 and Fig 4.2, both the base case, and the reduced cases show similar curves suggesting proportionality between their components. They both have maxima at 8:00 AM EDT and show $PM_{2.5}$ rising overnight to give maxima at 8:00 AM EDT the next day. However, not much can be said about the effectiveness of the control strategy from Fig 4.1 and Fig 4.2 because the differences in average $PM_{2.5}$ values are not apparent owing to low $PM_{2.5}$ concentrations.

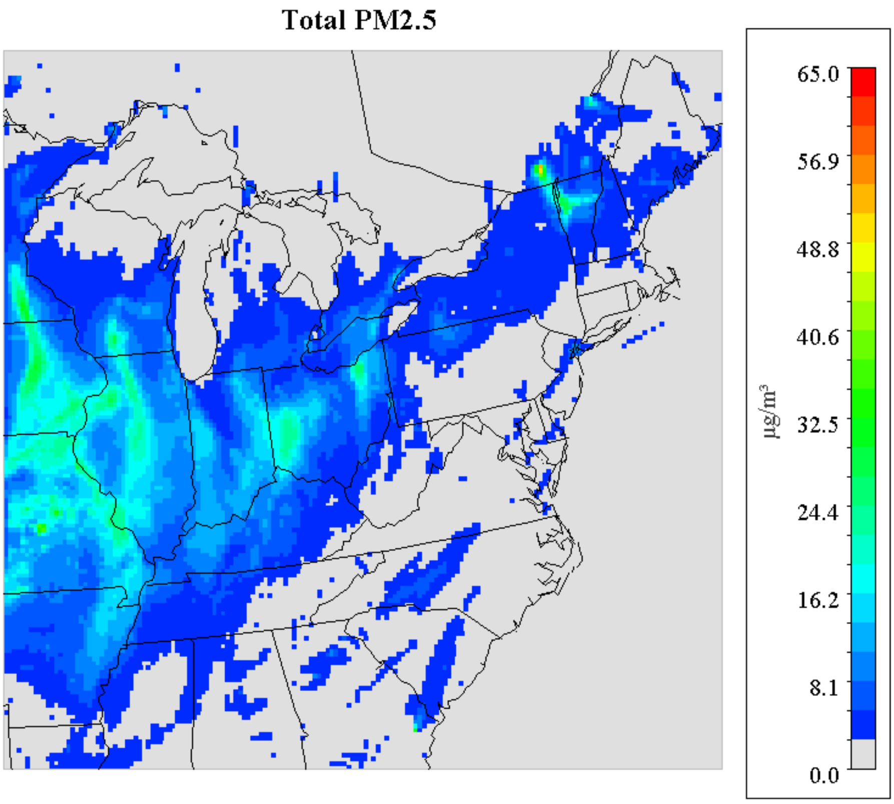

Fig 4.3 Total PM$_{2.5}$ over the eastern US showing maxima at 8:00 AM EDT, 18th May, 2002.

In general, the total PM$_{2.5}$ concentrations over the East Coast, as can be seen in Fig 4.3, were low with values ranging from 0 µg/m^3 to just above the 35 µg/m^3 (8 hour) limit. The central regions show higher PM$_{2.5}$ concentrations up to 40 µg/m^3. This is one of the reasons why this episode was chosen as the low PM$_{2.5}$ episode.

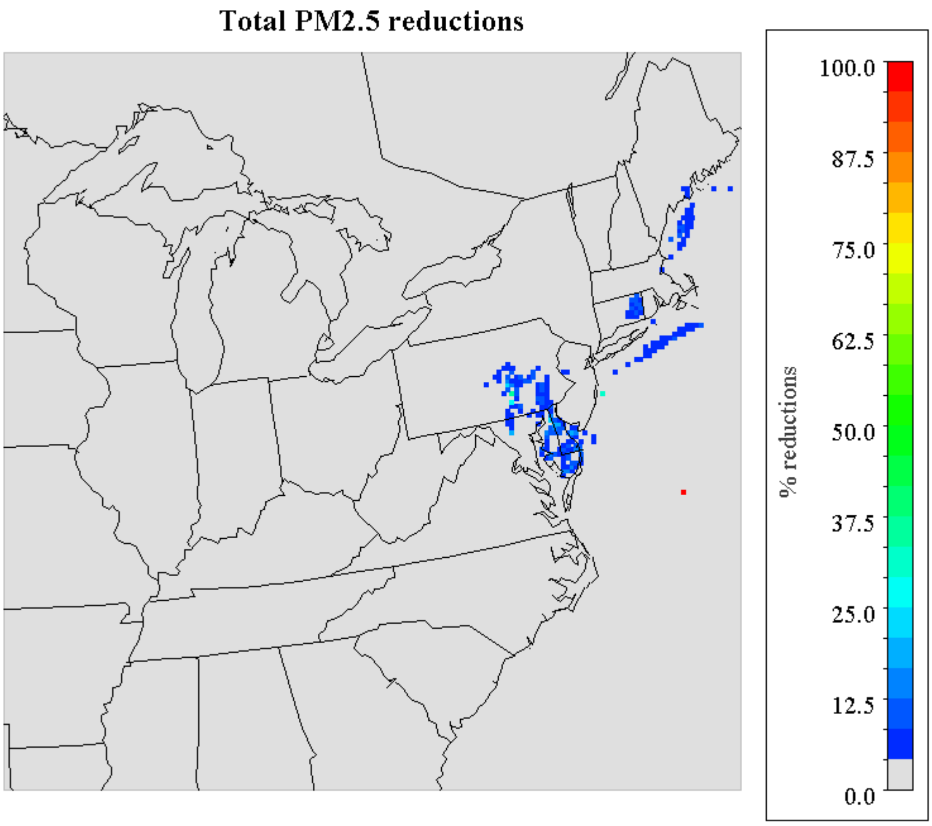

Fig 4.4 Total $PM_{2.5}$ percentage reductions achieved by control strategy at 8:00 AM EDT, 18th May 2002.

Also, seen here in Fig 4.4 the values of reductions obtained were low, ranging from 0% to 37.5 %. The reductions are local and are present near the source. If such trends are followed some benefits can be foreseen for the Chesapeake Bay region and central and southeastern Pennsylvania.

4.1.2 $PM_{2.5}$ Sulfate mass

Sulfate based fine particulate matter shows a rise in concentration throughout this episode, as can be seen in Fig 4.5 and Fig 4.6, suggesting an accumulation in sulfate based fine particulate matter. It is also important to note that both curves are qualitatively similar with no noticeable differences between the base and reduced cases.

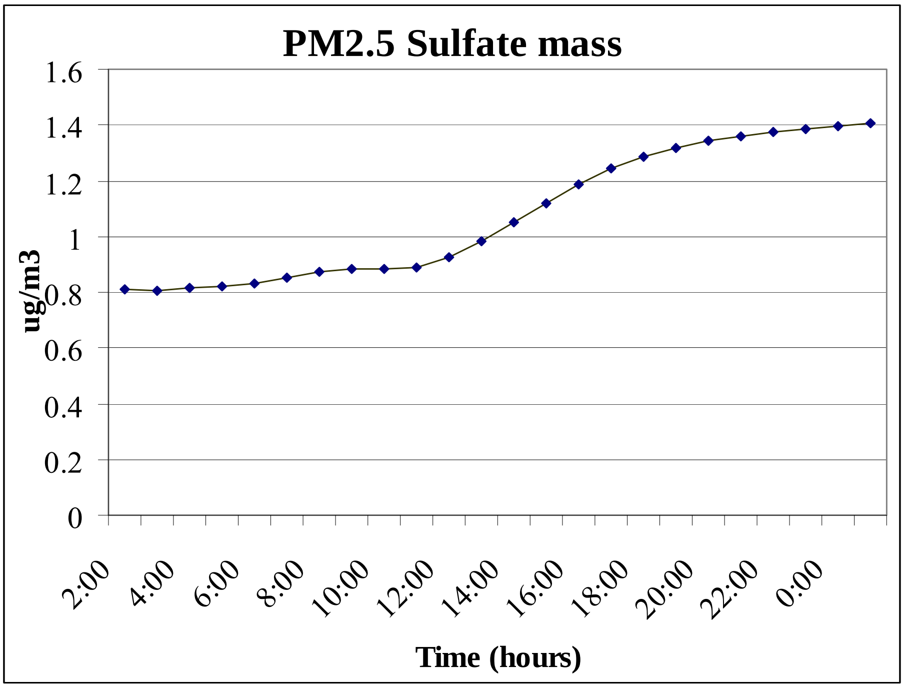

Fig 4.5 $PM_{2.5}$ sulfate mass showing a continual rise for 18th May, 2002.

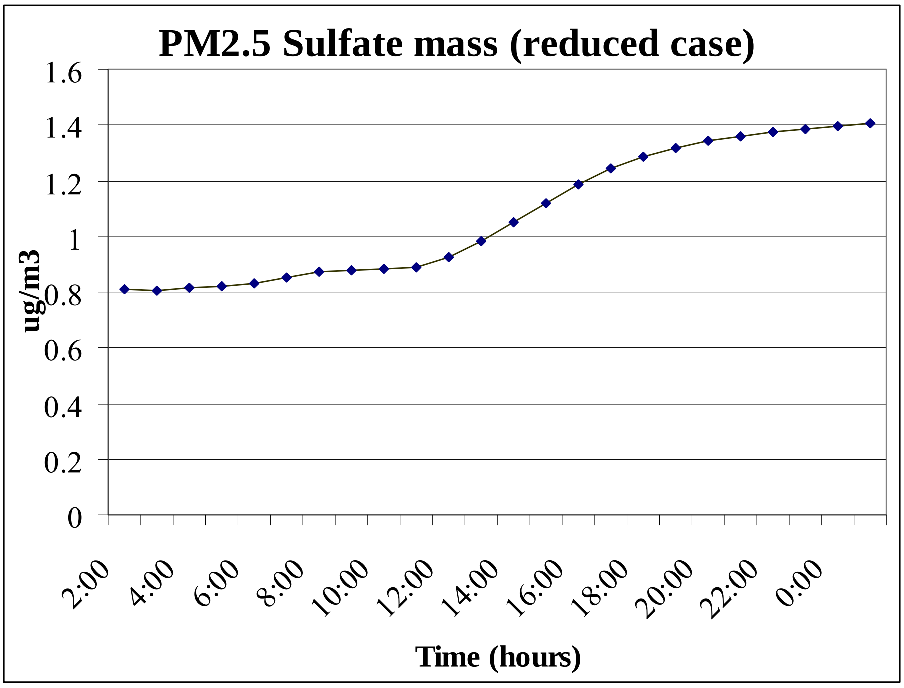

Fig 4.6 $PM_{2.5}$ sulfate mass showing continual rise for 18th May, 2002 even for reduced case

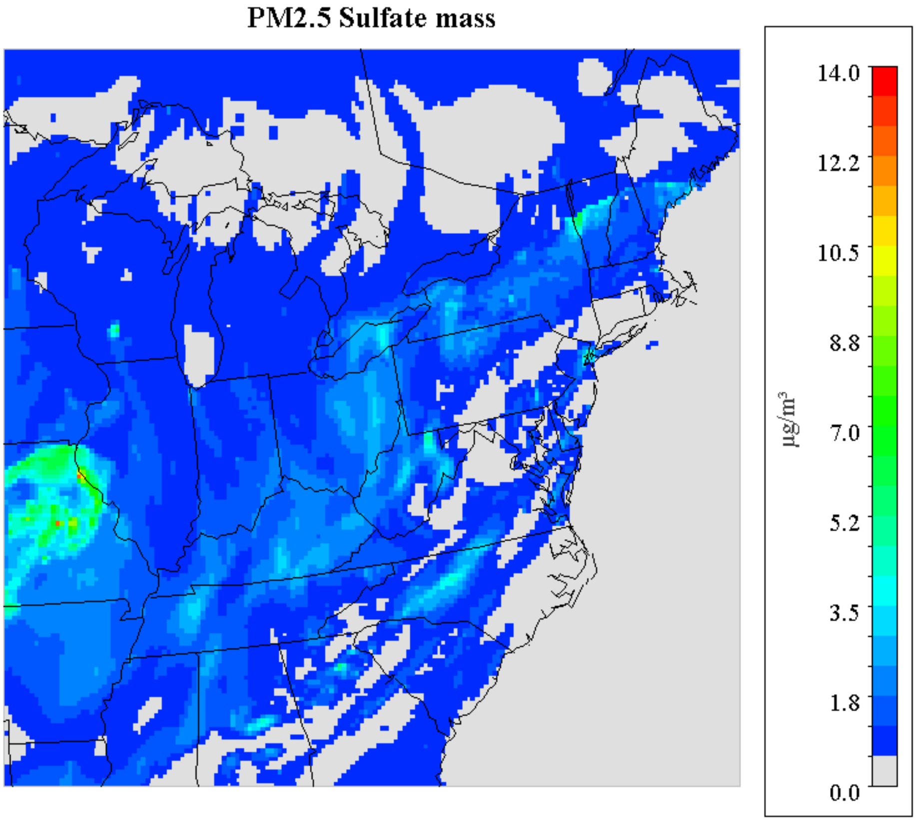

Fig 4.7 Sulfate based fine particulate matter over the eastern US at 8:00 AM EDT, 18th May, 2002

For this particular episode, it is seen from Fig 4.7 that the concentration of fine particulate sulfates over most of the eastern US ranges from 0 µg/m^3 to 5.2 µg/m^3. This is low as compared to the other cases. Again, as with the total $PM_{2.5}$, the central regions show higher concentrations than the east coast. However, it is not the concentration, but the accumulation trend, which could be seen in Figures 4.5 and 4.6, which is important and will play an important role in later episodes.

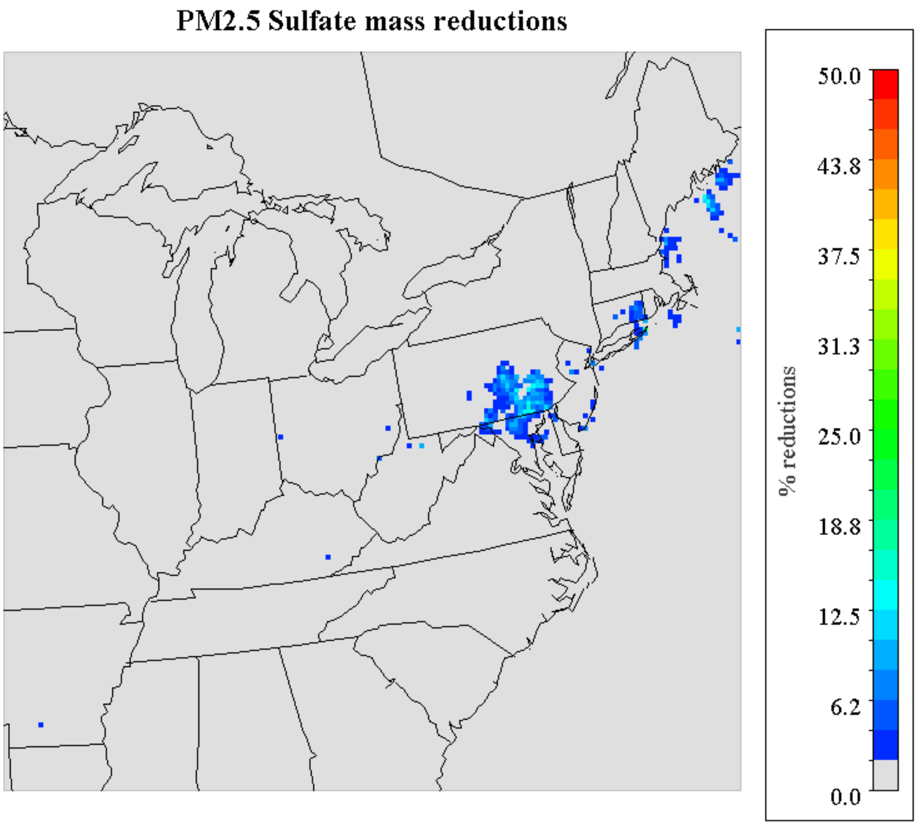

Fig 4.8 Reductions in sulfate based fine particulate matter achieved by control strategy at 8:00 AM EDT, 18th May, 2002

The control strategy shows some effect on sulfate based fine particulate matter, but it is mostly local and the reductions are low ranging from 0-15 %. It can be however be noted that the reductions over Pennsylvania are significant in the sense that Lancaster County, PA is the highest emitter of ammonia as per its tons/year emission rate (MANEVU, 2002) and has a non-attainment problem that might possibly be mitigated by enforcement of a stronger version of this control strategy (Susan Wierman, MARAMA, April 25th, 2011).

4.1.3 $PM_{2.5}$ Ammonium mass

From Figs 4.9 and 4.10 it is seen that like ammonium based fine particulate matter show a maxima at 8:00 AM EDT just like the total $PM_{2.5}$curves. Again as before, both curves are qualitatively similar.

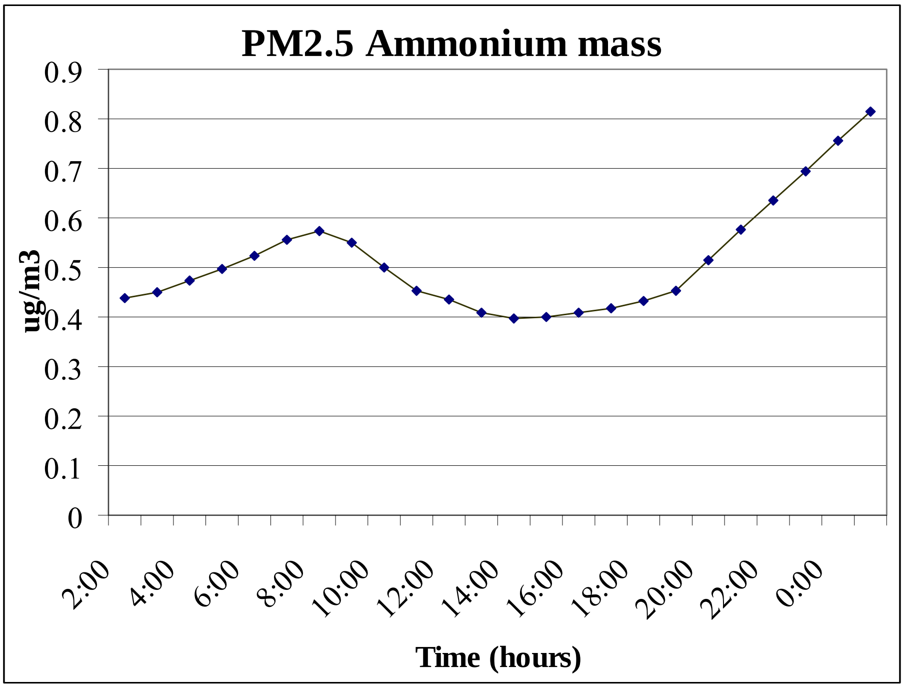

Fig 4.9 $PM_{2.5}$ ammonium mass showing maxima at 8:00 AM EDT, 18th May, 2002

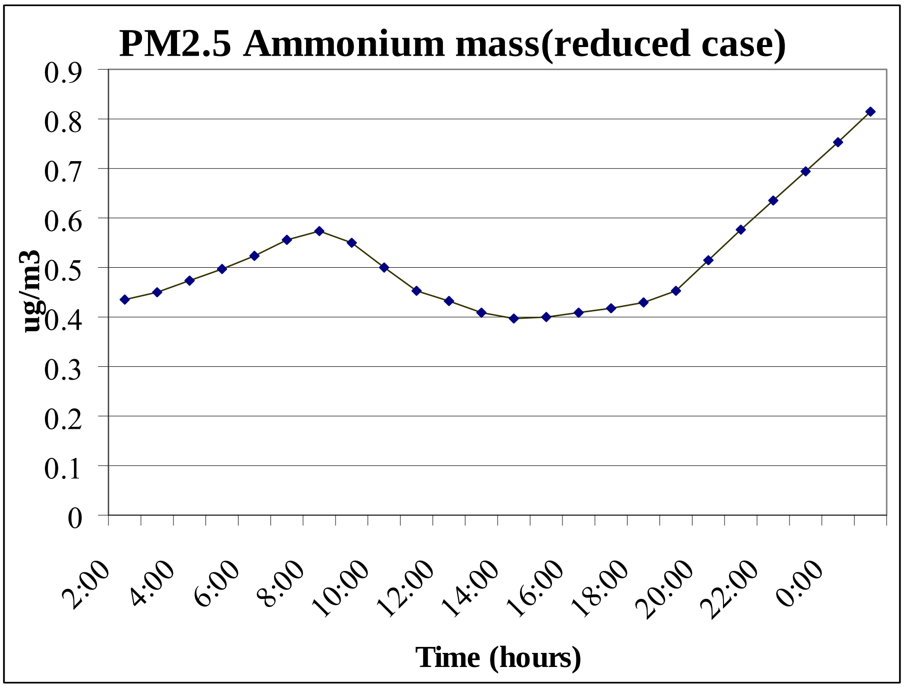

Fig 4.10 $PM_{2.5}$ ammonium mass showing maxima at 8:00 AM EDT, 18th May, 2002 for reduced case

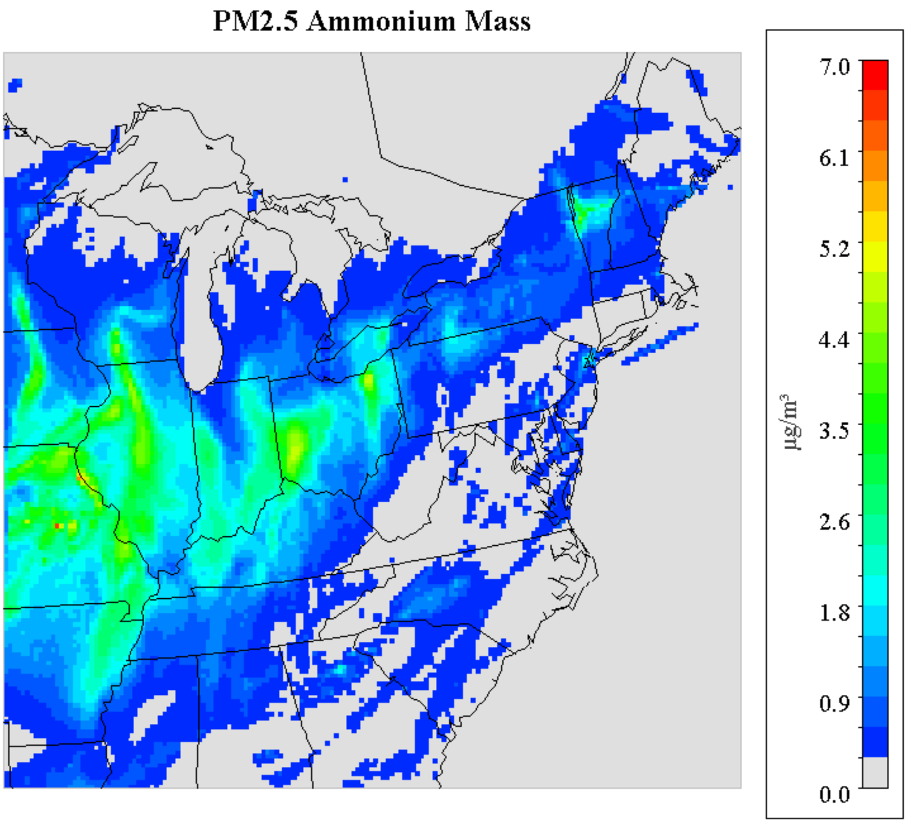

Fig 4.11 Ammonium based fine particulate matter, over the eastern US at 8:00 AM EDT, 18th May 2002.

Ammonium based fine particulate matter for this episode varies in concentration from 0 to 1.8 µg/m^3 over the MANEVU region. This low concentration is linked to the fact that $PM_{2.5}$ is low in this episode. As with the total $PM_{2.5}$, the concentrations in the central regions are higher with values up to 5.2 µg/m^3.

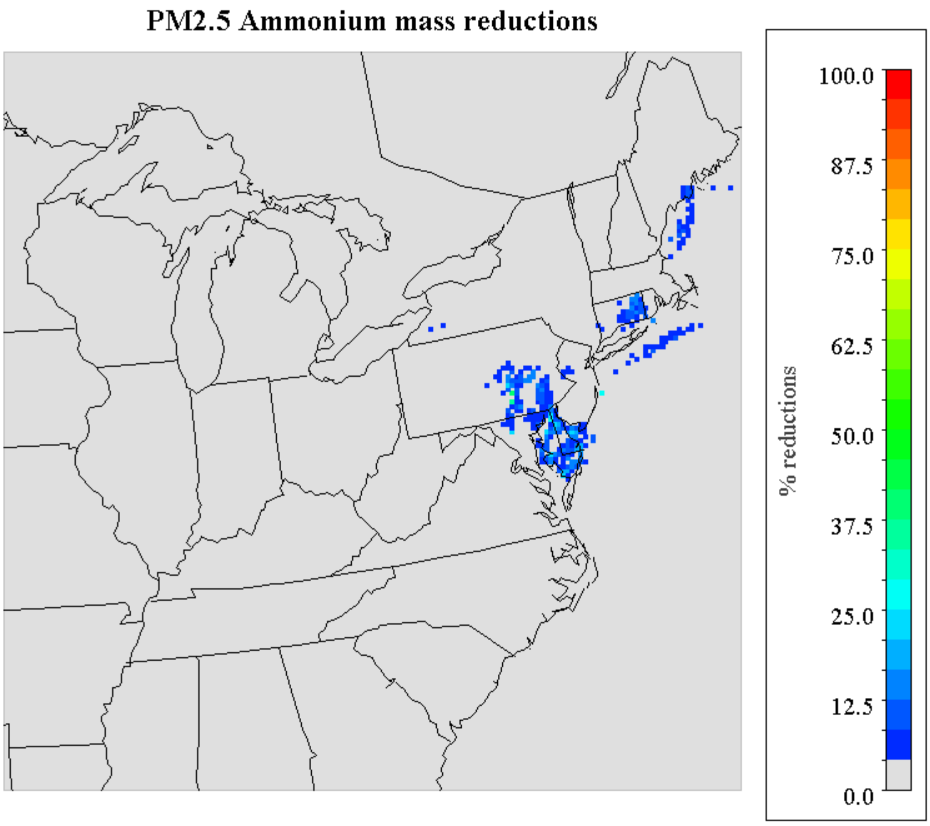

Fig 4.12 Reductions in ammonium based fine particulate matter achieved by control strategy at 8:00 AM EDT, 18th May, 2002.

The reduction strategy shows an analogous effect on ammonium based fine particulate matter as with total $PM_{2.5}$. This is actually expected as ammonium based fine particulate matter is mostly the sum of ammonium nitrate and ammonium sulfates and both together constitute a major part of $PM_{2.5}$. Hence their trends heavily influence the trends of total $PM_{2.5}$.

4.1.4 $PM_{2.5}$ Nitrate mass

Nitrate based fine particulate matter show a very distinct maxima at 8:00 AM EDT in Fig 4.13 which is similar to the total $PM_{2.5}$. However the maxima are more distinct. Also seen, is the rise in $PM_{2.5}$ leading to the maxima of the next day.

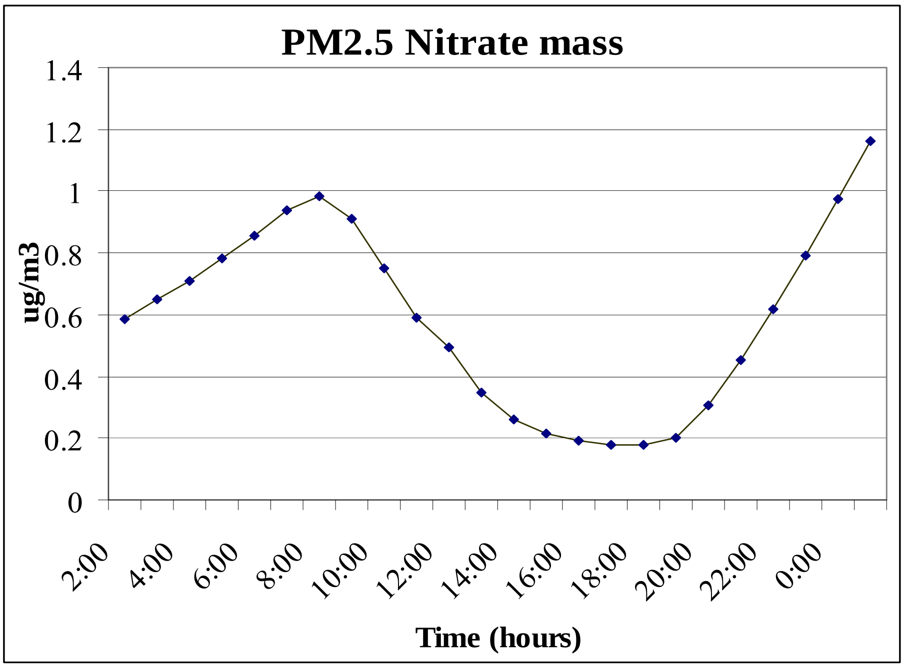

Fig 4.13 Nitrate based fine particulate matter showing maxima at 8:00 AM EDT, 18th May, 2002

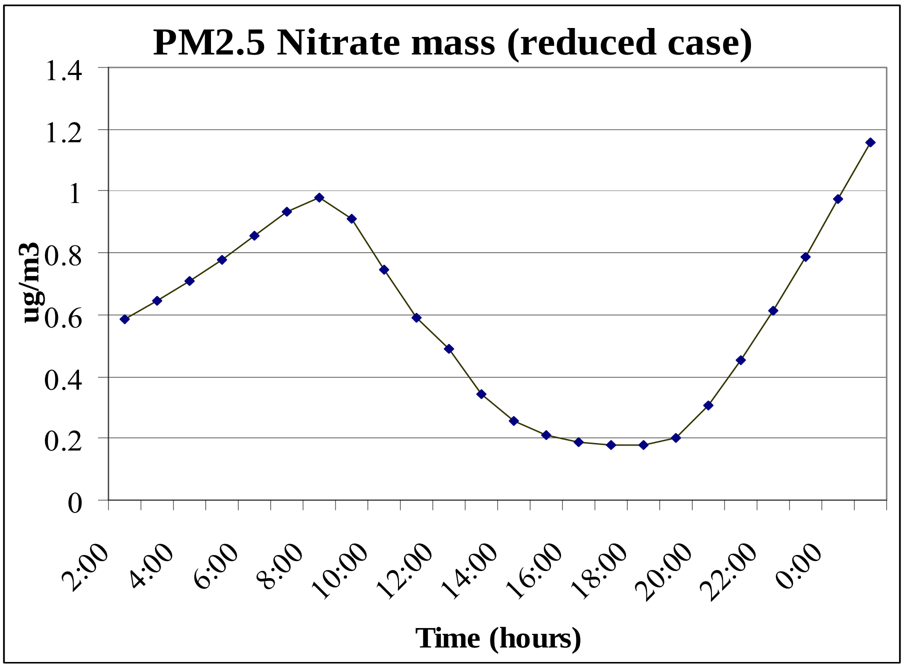

Fig 4.14 Nitrate based fine particulate matter showing maxima at 8:00 AM EDT, 18th May, 2002 for reduced case

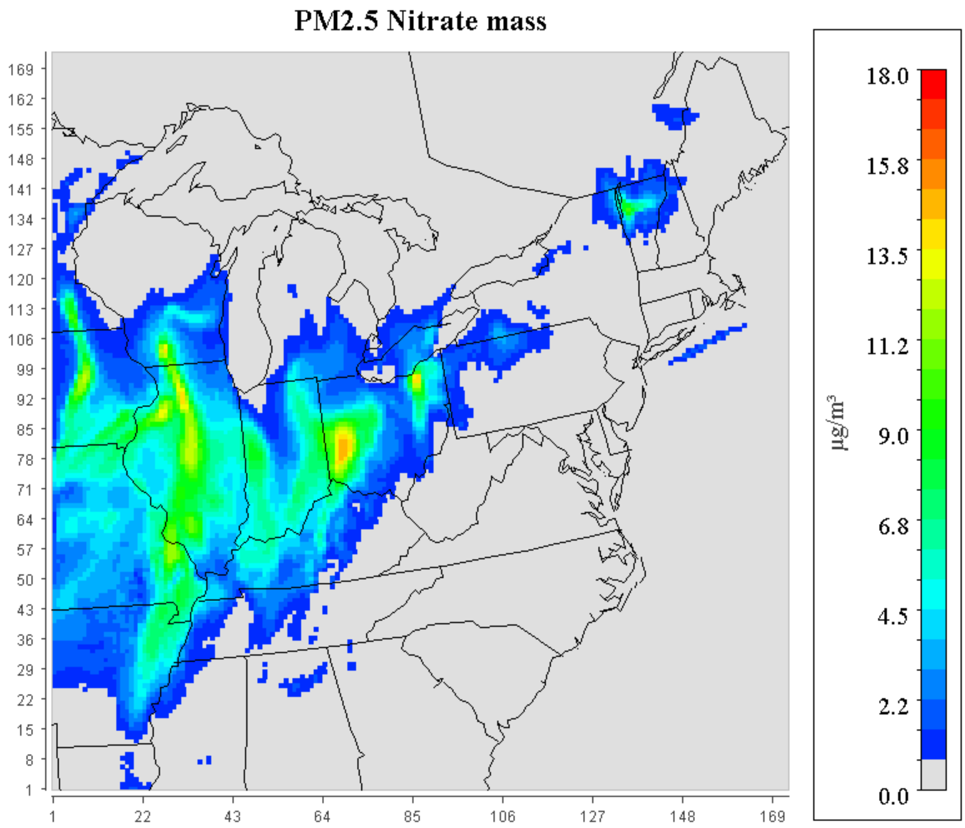

Fig 4.15 Nitrate based fine particulate matter over the eastern US at 8:00 AM EDT on 18th May, 2002

Nitrate based fine particulate matter in this case is low with most values close to zero along the Eastern Shore. The central regions however show much higher concentrations with values from 0 to 15.8 µg/m^3.

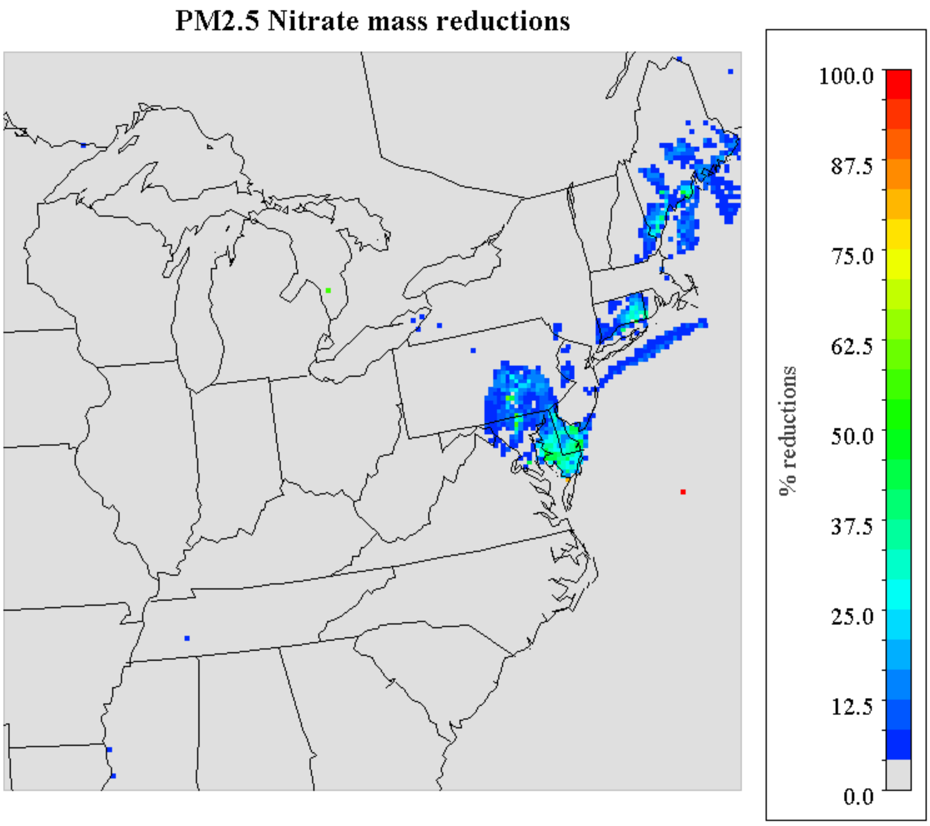

Fig 4.16 Reductions in nitrate based fine particulate matter at 8:00 AM EDT, 18th May, 2002 achieved by the control strategy.

In this case, more significant reductions of up to 63 % can be achieved over the Chesapeake Bay region, Southeastern Pennsylvania and the northern states like Maine, New Hampshire and Massachusetts. One can also argue that since the actual values of nitrate based fine particulate matter were already very low over these regions, these reductions may in fact be model fluctuations. However, this is clearly not the case because the reductions are situated close to the sources where the control strategy was applied and are certainly a result of my control strategy. Although the final values may not differ significantly over the initial values, it is important to note that nitrate based fine particulate matter shows more reductions than sulfate based fine particulate matter.

4.1.5 Ammonia

Free atmospheric ammonia curves show a double maxima once at 8:00 AM and once again at midnight as seen in Figs 4.17 and 4.18. The curves in these figures vary slightly as a result of our control strategy but still retain the same shape.

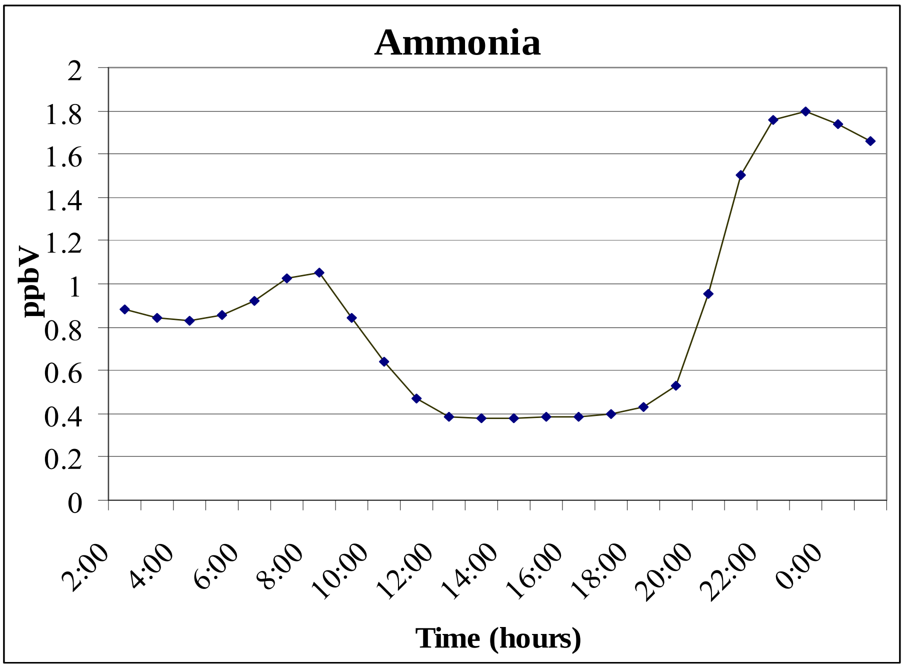

Fig 4.17 Atmospheric ammonia showing double maxima once at 8:00 AM and once at 12:00 midnight on 18th May, 2002

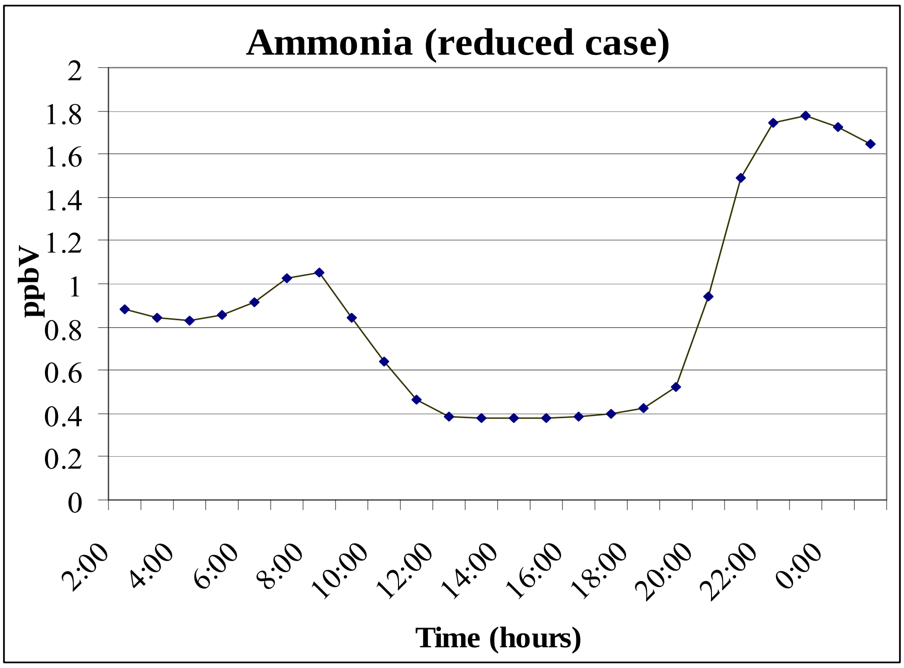

Fig 4.18 Atmospheric ammonia showing double maxima once at 8:00 AM and once at 12:00 midnight for reduced case on 18th May, 2002

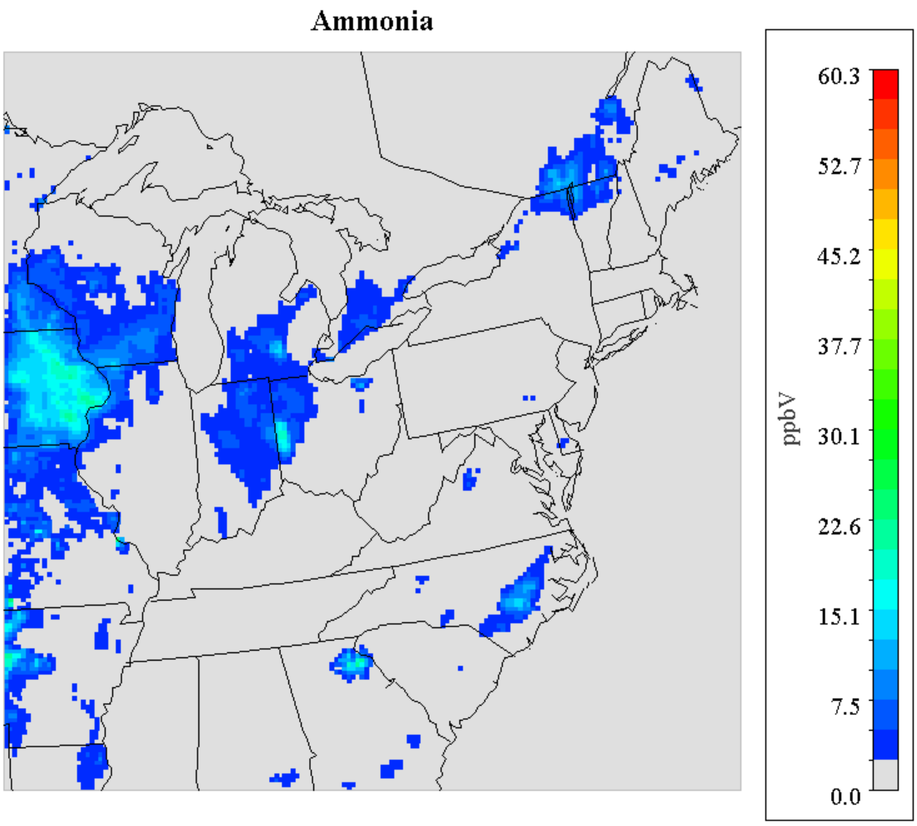

Fig 4.19 Atmospheric ammonia over the eastern US at 8:00 AM EDT, 18th May, 2002.

Atmospheric ammonia in this case behaves just like nitrates and is almost zero over the MANEVU region. The central regions however, show higher amounts of free atmospheric ammonia with values ranging from 0 to 22.6 µg/m^3.

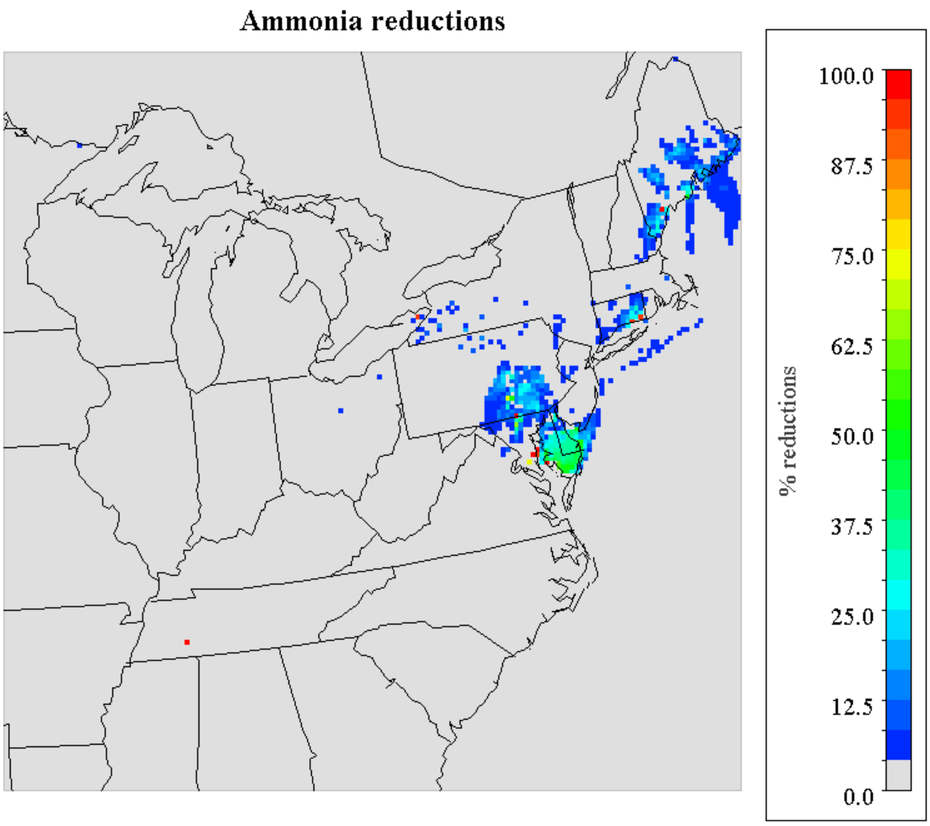

Fig 4.20 Atmospheric ammonia reductions at 8:00 AM EDT, 18th May, 2002 achieved by the control strategy

As is evident from Fig 4.20 significant reductions of up to 63 % can be achieved for ammonia. These reductions are the result of our control strategy, which knocks out 39 % of ammonia emissions, along with the fact that sulfates are formed before nitrates and thus reduce the amount of ammonia available for formation of ammonium nitrate which causes the reductions to increase further.

4.1.6 Hours of non-compliance

Fig 4.21 and Fig 4.22 shows the hours of non-compliance of the 15 $\mu g/m^3$ standard. Both show 1 to 8 hours of non-compliance for the Maryland area. No significant reductions in hours are seen and may not be expected because of the low $PM_{2.5}$ values.

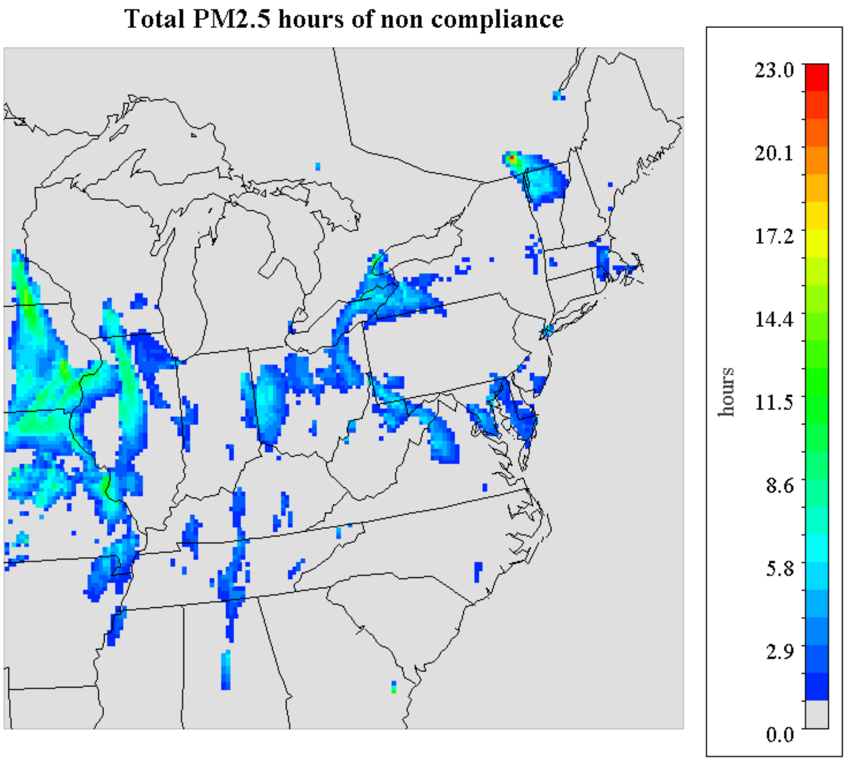

Fig 4.21 Hours of non-compliance for total $PM_{2.5}$ for base case on 18th May, 2002

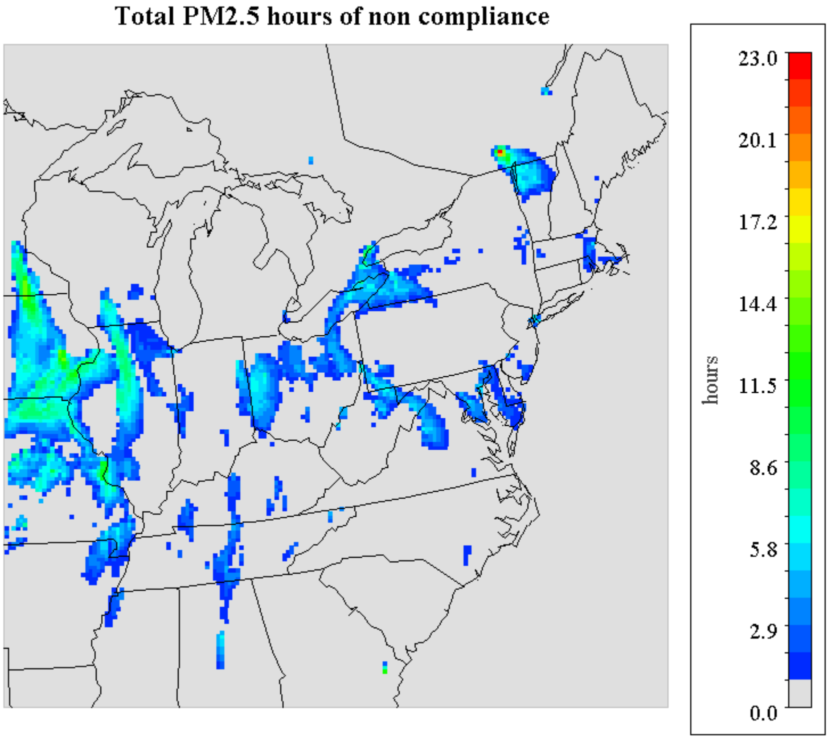

Fig 4.22 Hours of non-compliance for total $PM_{2.5}$ for reduced case on 18th May, 2002

4.2 Moderate PM Episode- May 22, 2002

4.2.1 Total $PM_{2.5}$

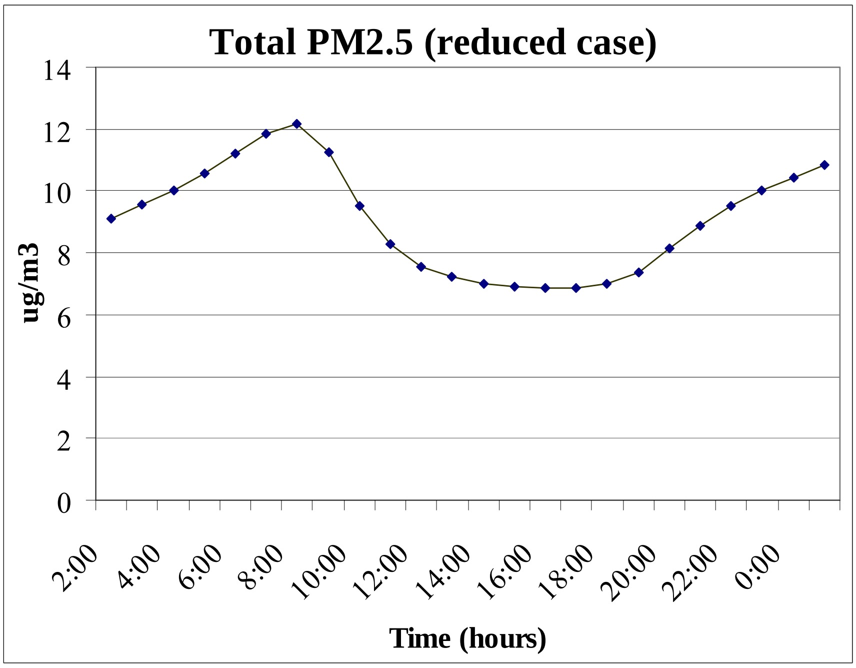

Fig 4.23 Total $PM_{2.5}$ for the base case showing maxima at 8:00 AM EDT on 22nd May, 2002.

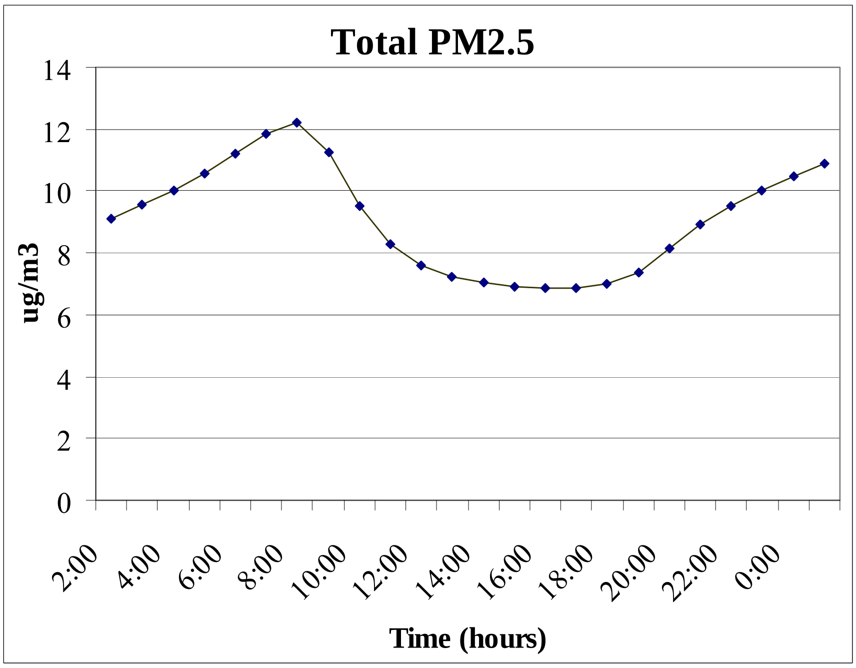

Fig 4.24 Total $PM_{2.5}$ for the reduced case showing maxima at 8:00 AM EDT on 22nd May, 2002.

Like in the previous cases, Figs 4.23 and 4.24 show that $PM_{2.5}$ has a maxima at 8:00 AM EDT. They also show $PM_{2.5}$ rising overnight and like before are qualitatively similar.

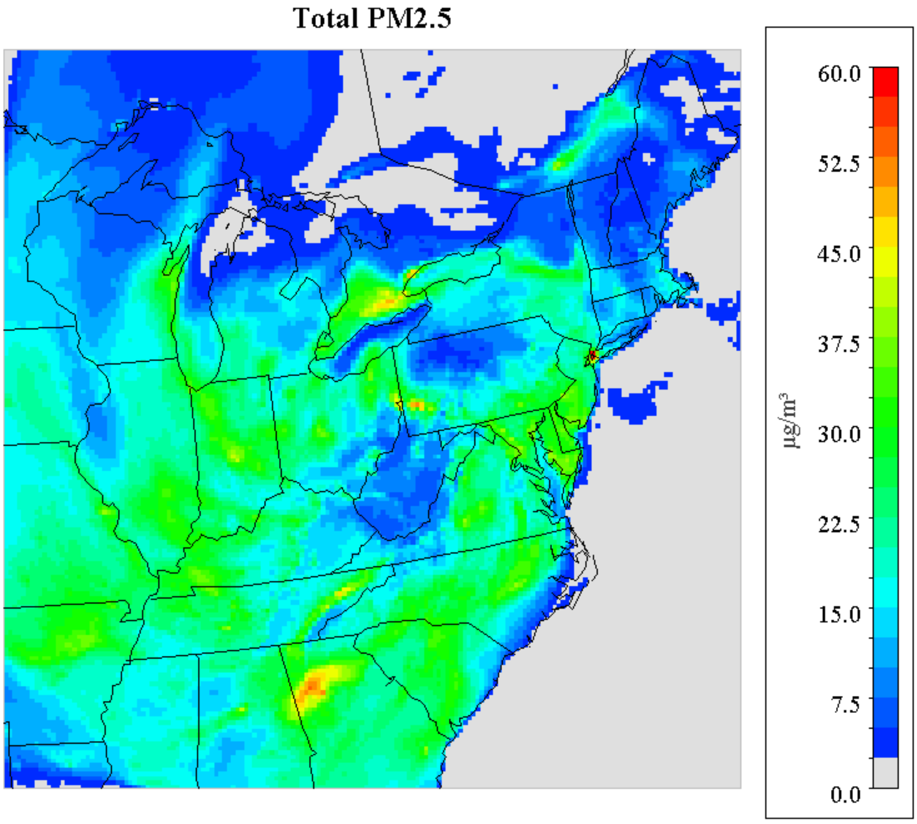

Fig 4.25 Total $PM_{2.5}$ over the eastern US showing maxima at 8:00 AM EDT 22nd May, 2002

In this particular case the total $PM_{2.5}$ concentrations over the entire region were observed to be moderate with values mostly above the 35 µg/m^3 limit as can be seen in Fig 4.25. This is why this episode was chosen as the moderate $PM_{2.5}$ episode the values are not very high, although they are above 35 µg/m^3.

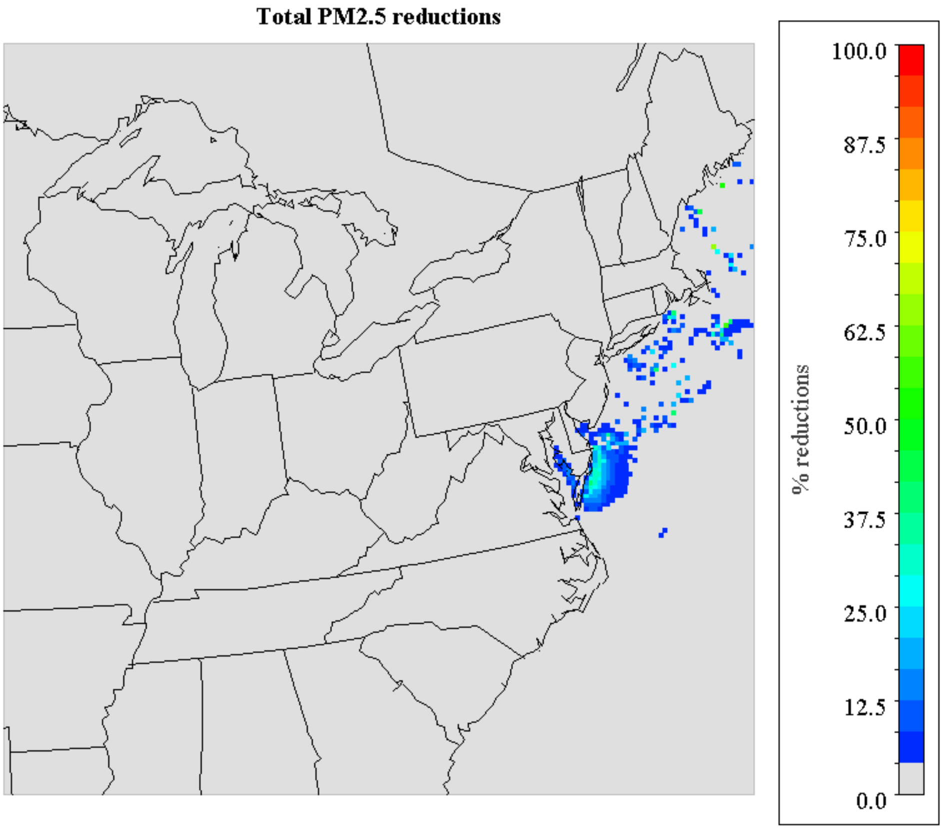

Fig 4.26 Total $PM_{2.5}$ percentage reductions achieved at 8:00 AM EDT, 22nd May, 2002 by the control strategy

In this case the reductions obtained are significant at about 25-37.5 %, however as can be seen in this picture they are mostly over the Chesapeake Bay and the Atlantic Ocean. It is suspected that prevailing winds blown away the low $PM_{2.5}$ parcels upwind of the source and over the ocean, replacing it with $PM_{2.5}$ laden parcels.

4.2.2 $PM_{2.5}$ Sulfate mass

Average sulfate based fine particulate matter over the grid shows a rise in concentration throughout this episode as can be seen in Fig 4.27 and Fig 4.28.

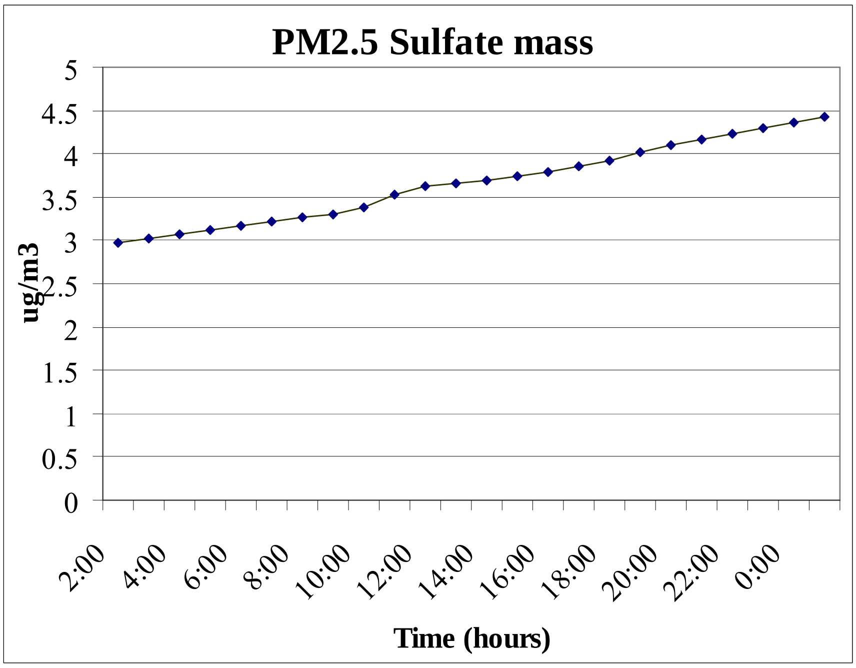

Fig 4.27 $PM_{2.5}$ sulfate mass showing a continual rise for 22nd May, 2002

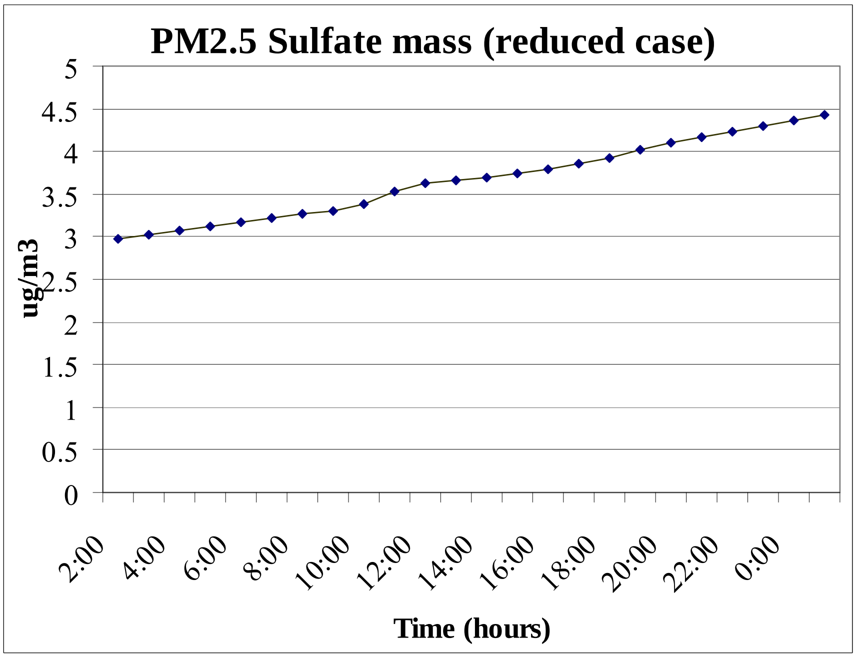

Fig 4.28 $PM_{2.5}$ sulfate mass showing a continual rise for 22nd May, 2002, even for the reduced case

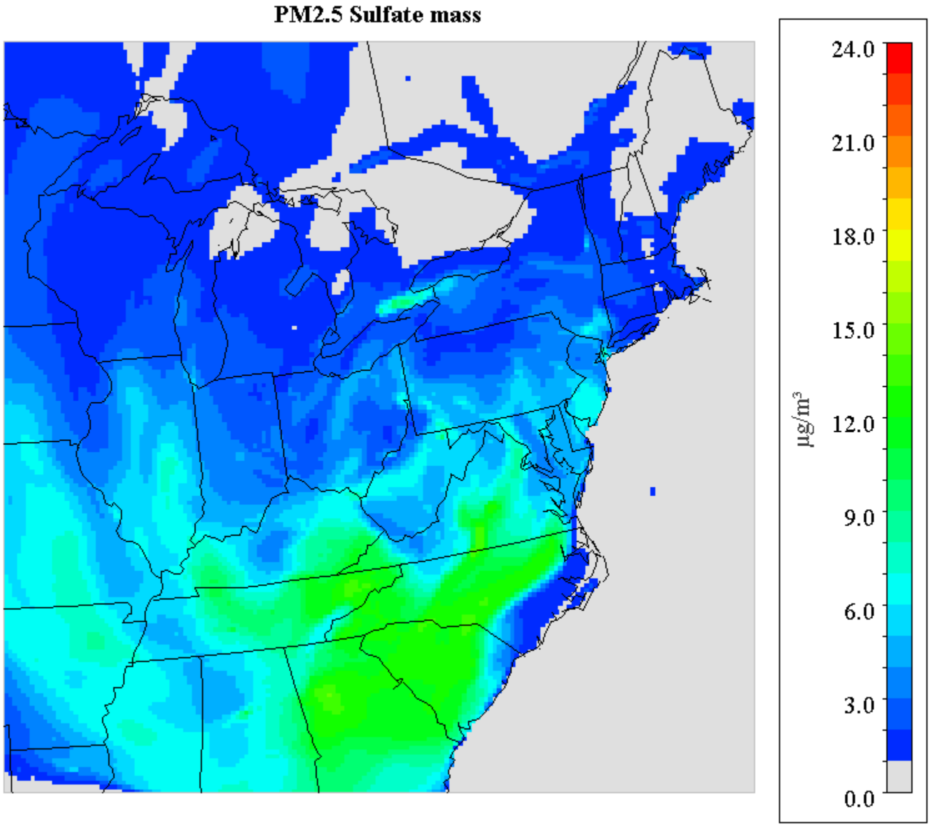

Fig 4.29 Total $PM_{2.5}$ sulfate mass over the eastern US at 8:00 AM EDT, 22^{nd} May, 2002

For this particular episode, it is seen from Fig 4.29 that the concentration of sulfates is higher than the previous episode. The MANEVU region has some areas in the 6-9 $\mu g/m^3$ range. A large mass of sulfates can be seen hanging over Tennessee, North Carolina, South Carolina, Georgia, Alabama and Missouri and moving upward.

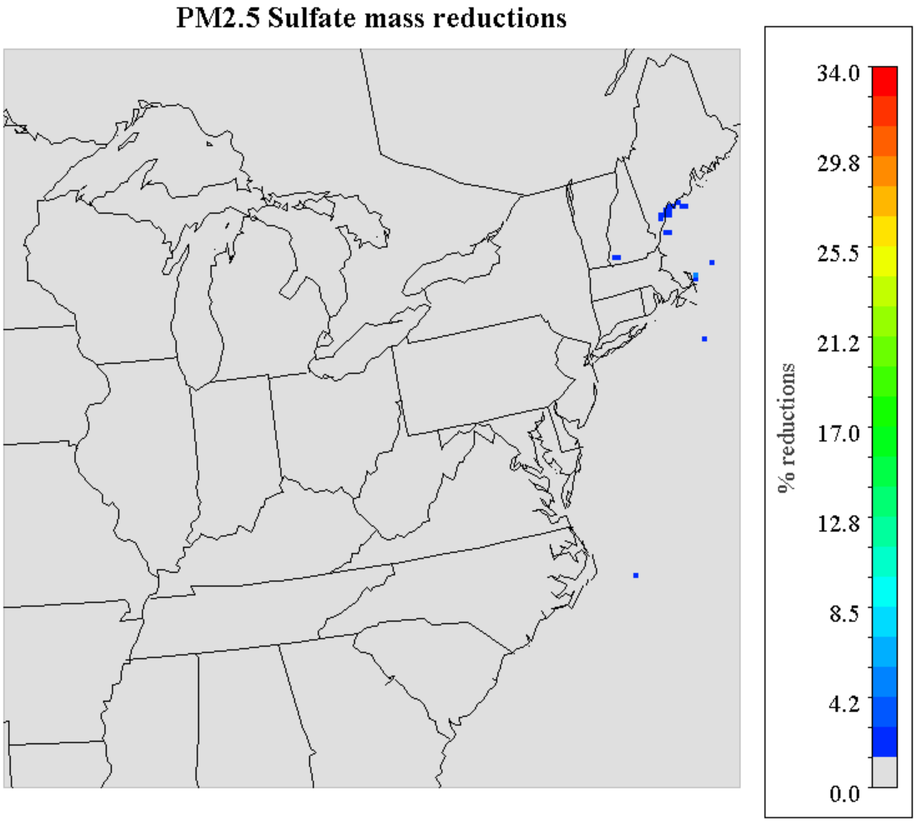

Fig 4.30 Reductions in sulfate based fine particulate matter achieved at 8:00 AM EDT, 22nd May, 2002 by the control strategy

The control strategy shows almost no effect on sulfates in this case. This marks an important event. This is primarily because of excess of ammonia in the atmosphere. Regions higher up with low ammonia to sulfuric acid ratios show minute amounts of reductions as seen in Fig 4.30.

4.2.3 $PM_{2.5}$ Ammonium mass

From Fig 4.31 and 4.32 it is seen that like before, ammonium based fine particulate matter show a maxima at 8:00 AM just like the total $PM_{2.5}$curves.

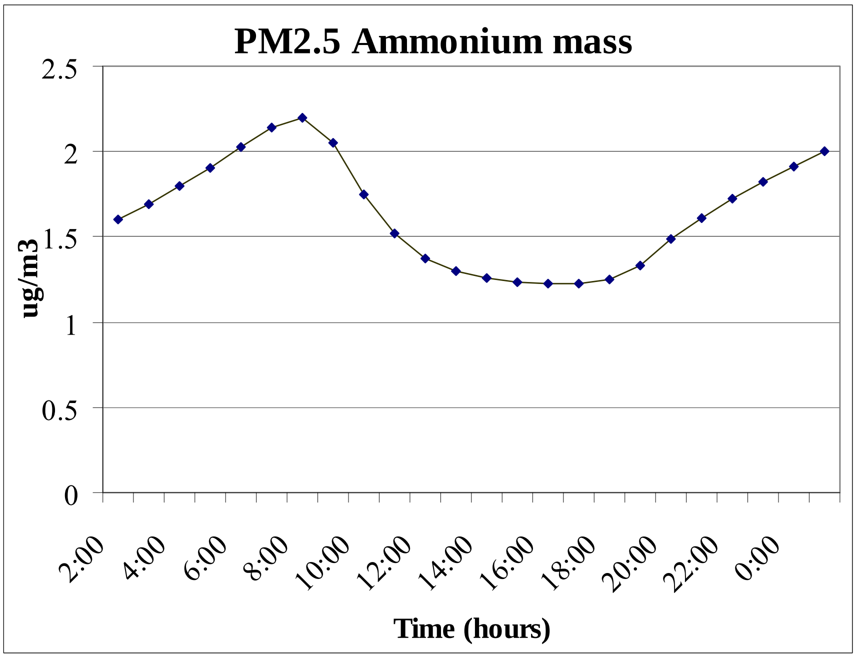

Fig 4.31 Ammonium based fine particulate matter showing maxima at 8:00 AM EDT, 22nd May, 2002

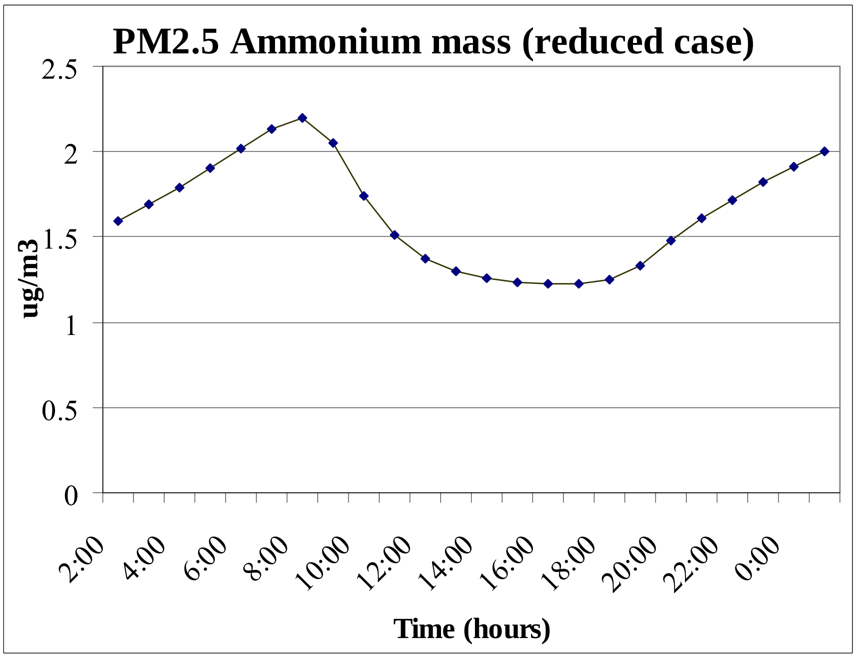

Fig 4.32 Ammonium based fine particulate matter showing maxima at 8:00 AM EDT, 22nd May, 2002 for reduced case

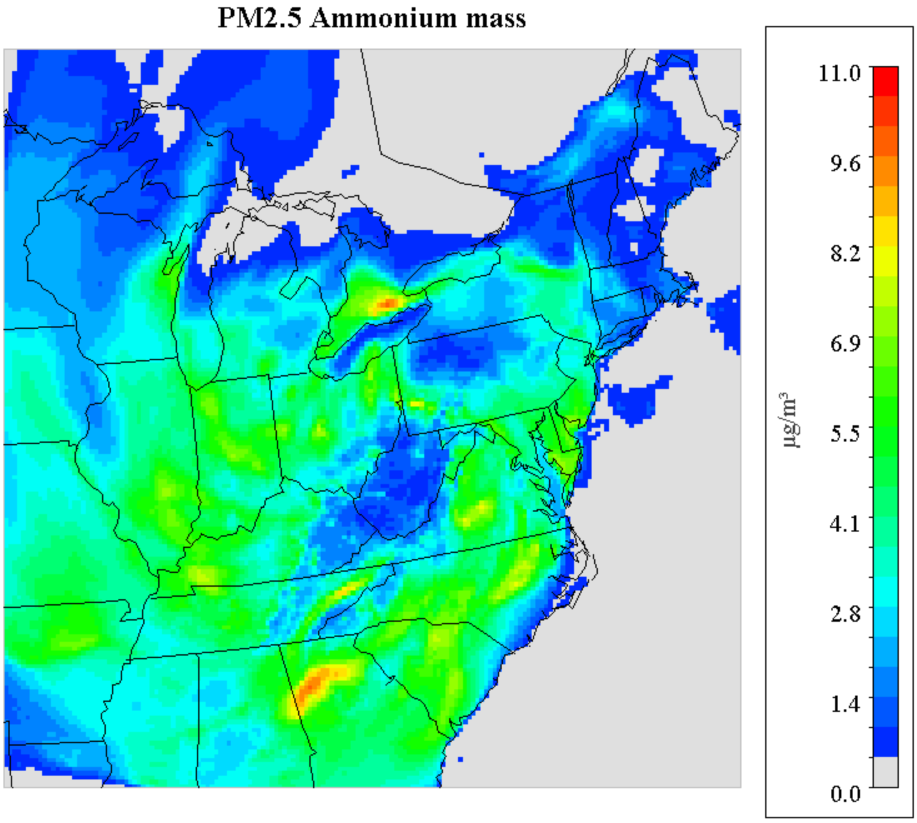

Fig 4.33 Ammonium based fine particulate matter over the eastern US at 8:00 AM EDT, 22nd May, 2002.

Ammonium based fine particulate matter for this episode varies in concentration from 2 to 7 µg/m^3 over the MANEVU region. Some regions in Georgia and Alabama show significantly higher levels of ammonium based PM$_{2.5}$ with values ranging between 8 and 10 µg/m^3.

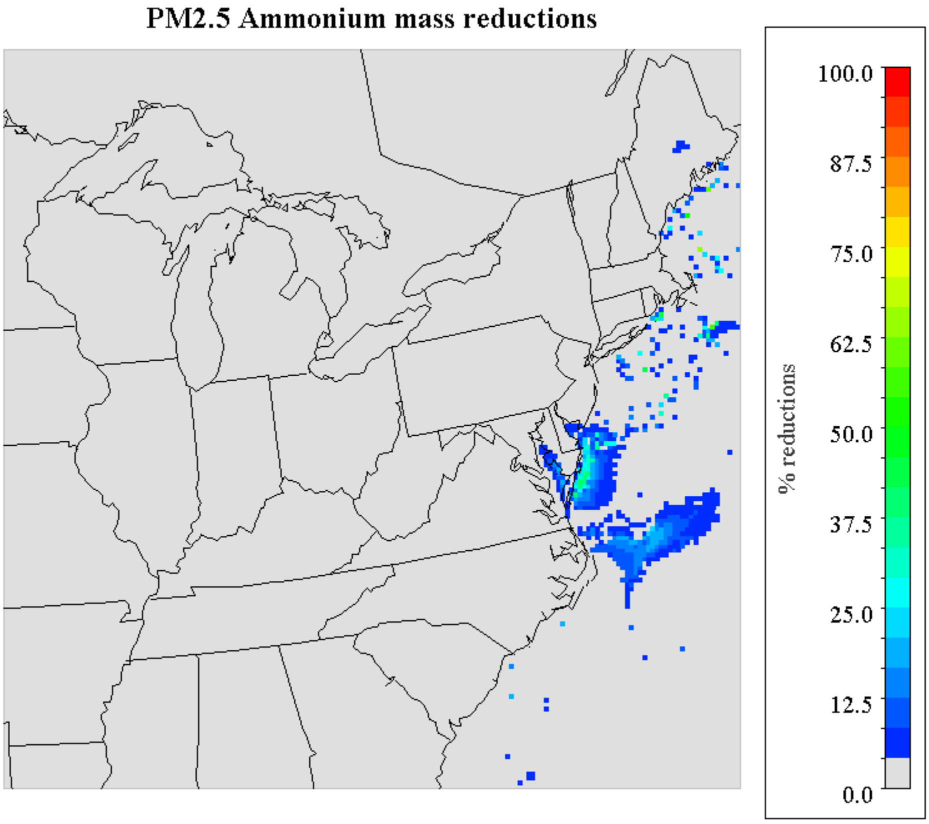

Fig 4.34 Reductions in ammonium based fine particulate matter achieved by control strategy at 8:00 AM EDT, 22nd May, 2002.

In this case the reductions of up to 50 % can be seen, but are blown over the ocean hence any benefit over land is lost. There may be some benefits for the Eastern Shore but a higher spatial resolution is needed to analyze these.

4.2.4 PM$_{2.5}$ Nitrate mass

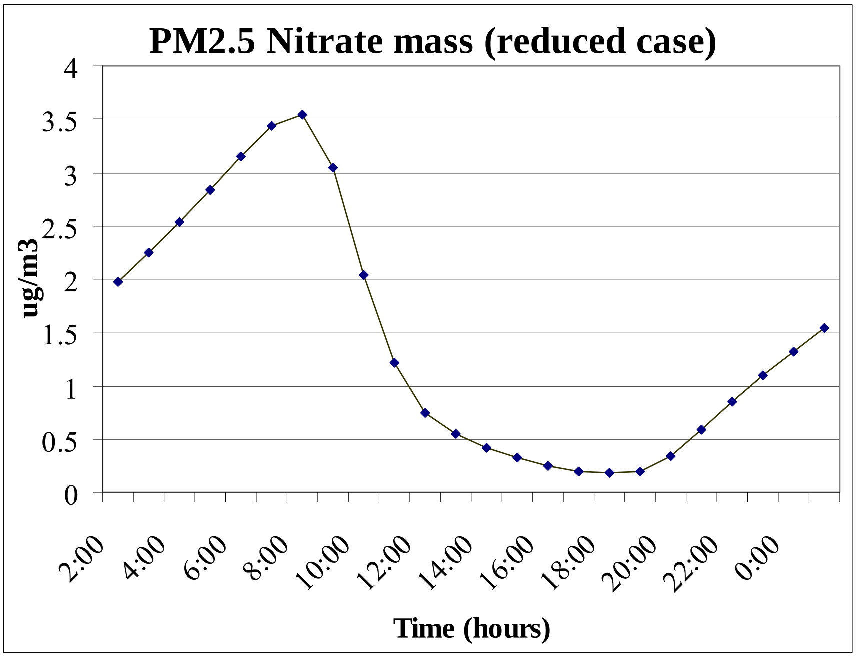

Fig 4.35 Nitrate based fine particulate matter showing maxima at 8:00 AM EDT, 22nd May 2002

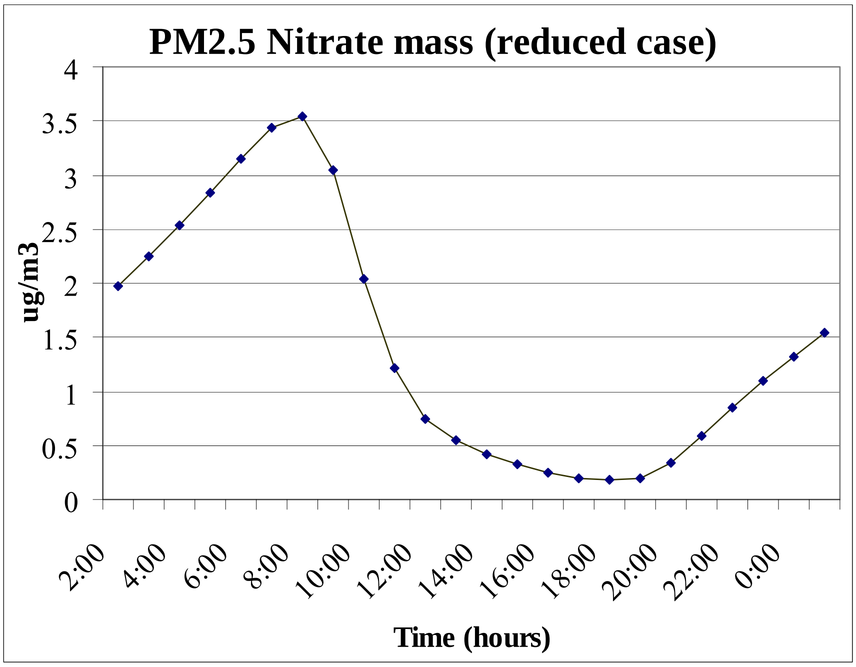

Fig 4.36 Nitrate based fine particulate matter showing maxima at 8:00 AM EDT, 22nd May 2002 for reduced case

Nitrate based fine particulate matter shows well defined maxima at around 8:00 AM.

All curves are qualitatively similar.

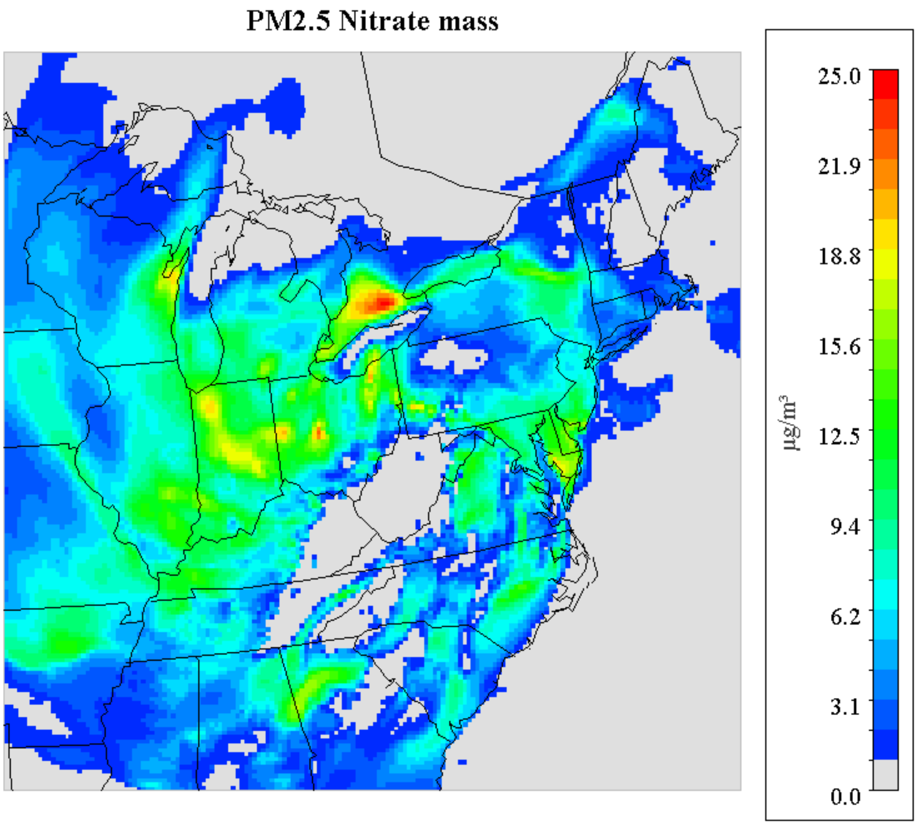

Fig 4.37 Nitrate based fine particulate matter over the eastern US at 8:00 AM EDT, 22nd May 2002

Fig 4.37 shows a high concentration of nitrate based particulates over areas of the MANEVU region with concentrations as high as 18 µg/m^3 can be seen over the regions of Delaware, Maryland and Washington D.C. This figure also shows nitrate hotspots over Ohio and Indiana. Ohio is the 2nd largest egg producer in the nation (www.ohpoultry.org) while Indiana is the 6th largest swine producer (www.stuffaboutstates.com/agriculture/livestock/hogs.htm). These operations may complement the already moderate PM$_{2.5}$levels to build up PM$_{2.5}$ hotspots.

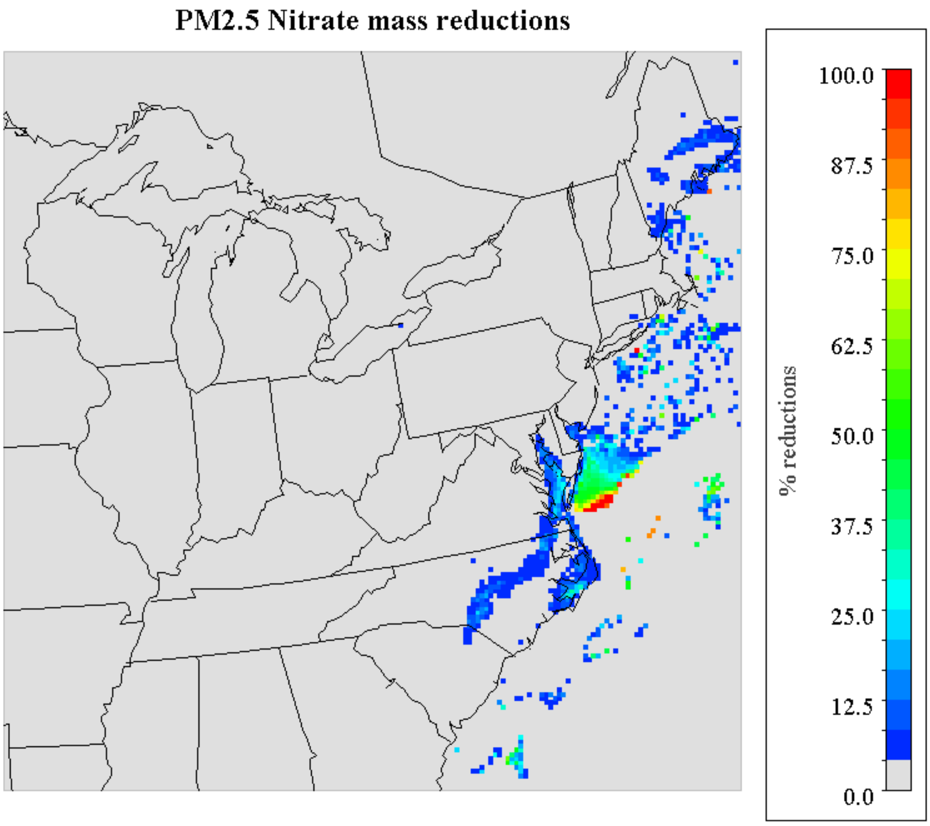

Fig 4.38 Reductions in nitrate based fine particulate matter at 8:00 AM EDT, 22nd May, 2002 achieved by the control strategy

Significant reductions in nitrates of up to 100 % can be achieved but are blown over the bay. Reductions of up to 12.5 % can be seen over North Carolina and the northeastern states of Maine and Massachusetts. There might be possible reductions in parts of Virginia, and Delaware.

4.2.5 Ammonia

Atmospheric ammonia for this case is significantly higher with the same kind of qualitative curve showing double maxima once at 8:00 AM EDT and once again at 12 midnight. Slight reductions in peaks can be seen as a result of our control strategy. This will be more evident in the reduction charts.

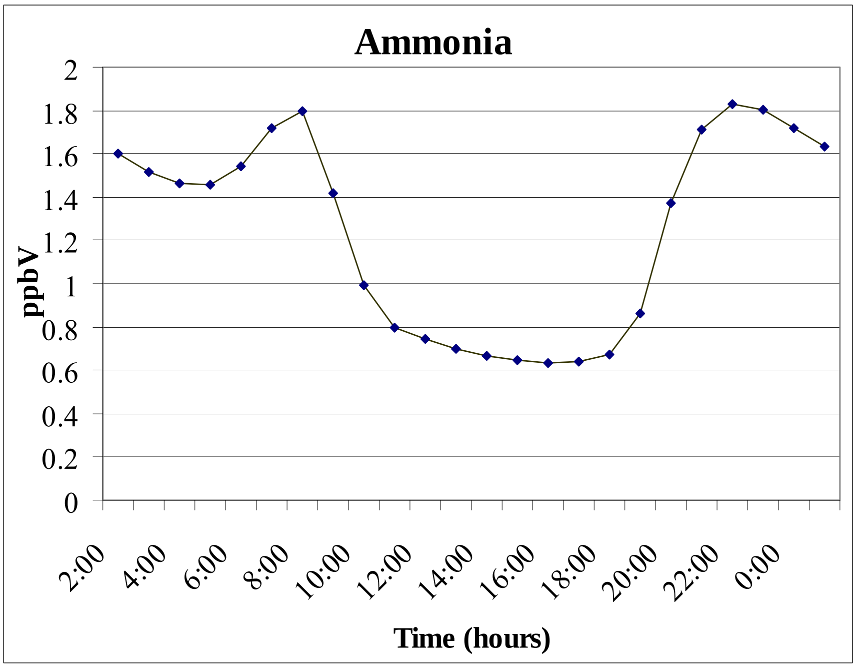

Fig 4.39 Atmospheric ammonia showing double maxima once at 8:00 AM and once at 12:00 midnight for 22nd May, 2002

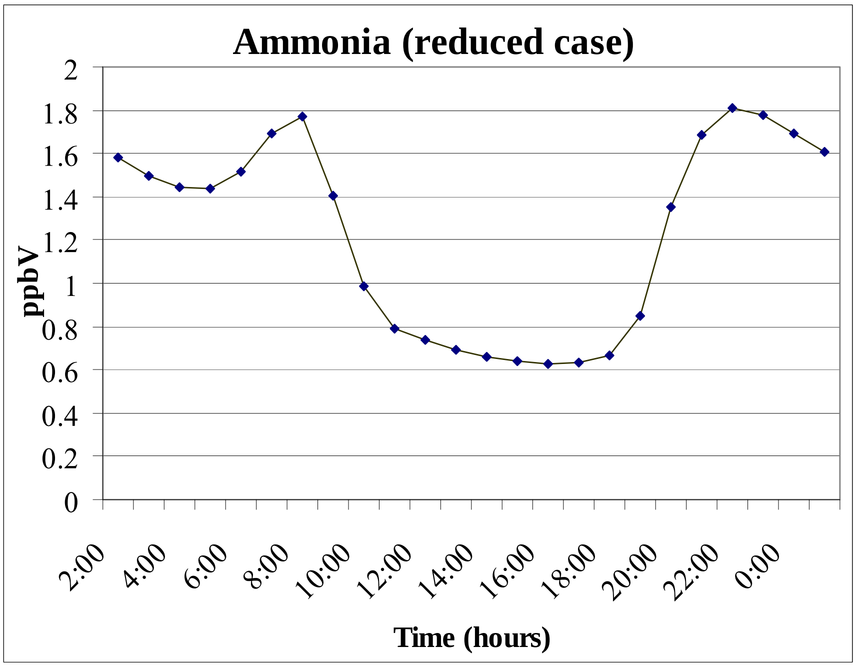

Fig 4.40 Atmospheric ammonia showing double maxima once at 8:00 AM and once at 12:00 midnight for reduced case for 22nd May, 2002

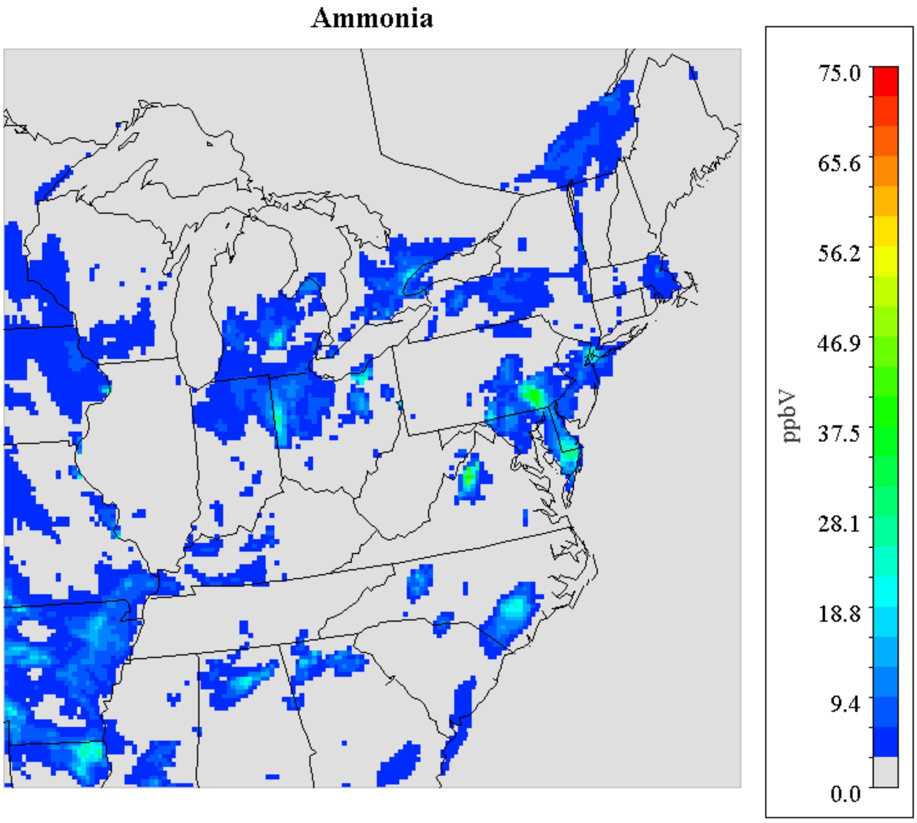

Fig 4.41 Atmospheric ammonia over the eastern US at 8:00 AM EDT, 22nd May, 2002

The overall ammonia concentrations varied from 0 to 50 ppbV in some cases. The figure shows patches of ammonia with some having high ammonia concentrations in the center. This is possibly from a large ammonia emitting source. Also, in Fig 4.41 we can clearly see ammonia hotspots over Pennsylvania, Delaware and North Carolina. These are the results of animal husbandry operations.

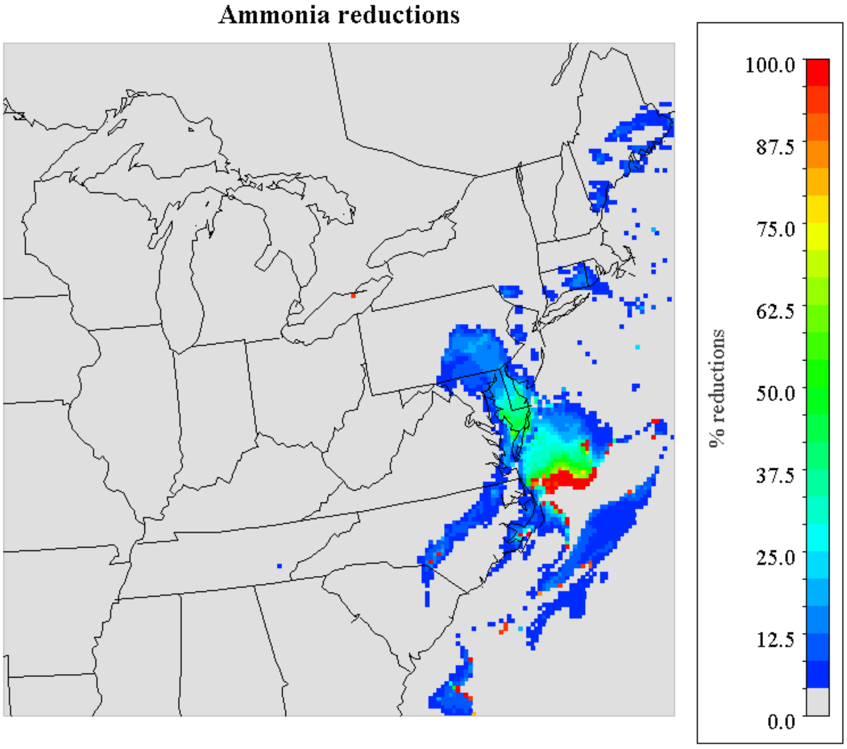

Fig 4.42 Atmospheric ammonia reductions achieved at 8:00 AM EDT, 22nd May, 2002 by the control strategy

In Fig 4.42 we see that ammonia concentrations have dramatically reduced over the ocean and over parts of Maryland and Delaware. Reductions of up to 63 % can be seen with reductions of up to 25 % seen over southeastern Pennsylvania. This can be attributed to the control strategy and the reactions of ammonia to form ammonium sulfates.

4.2.6 Hours of non-compliance

Figs 4.42 and 4.43 show the total hours of non-compliance for $PM_{2.5}$. At first glance the base case and the reduced case do not seem different. However upon closer inspection it can be seen that the red non-compliance over the MD-DE-DC region has now reduced from 24 hours of non-compliance to 18 hours of non-compliance. Also the 19-20 hour hotspot over southwestern Pennsylvania has now reduced to about 18-20 hours.

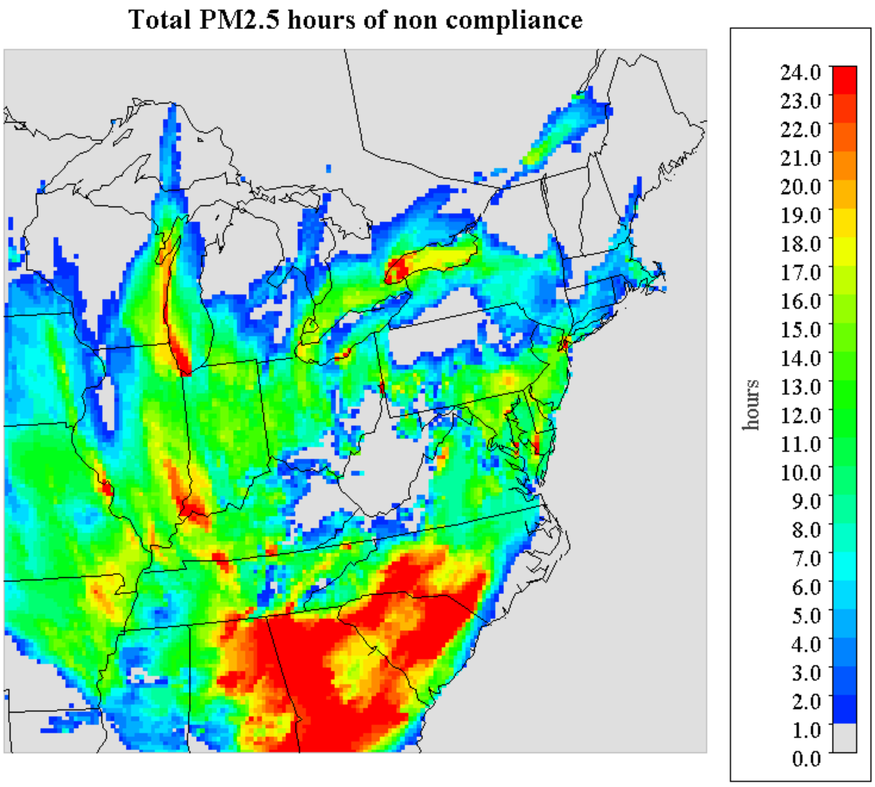

Fig 4.43 Hours of non-compliance for total $PM_{2.5}$ on 22nd May, 2002 for base case

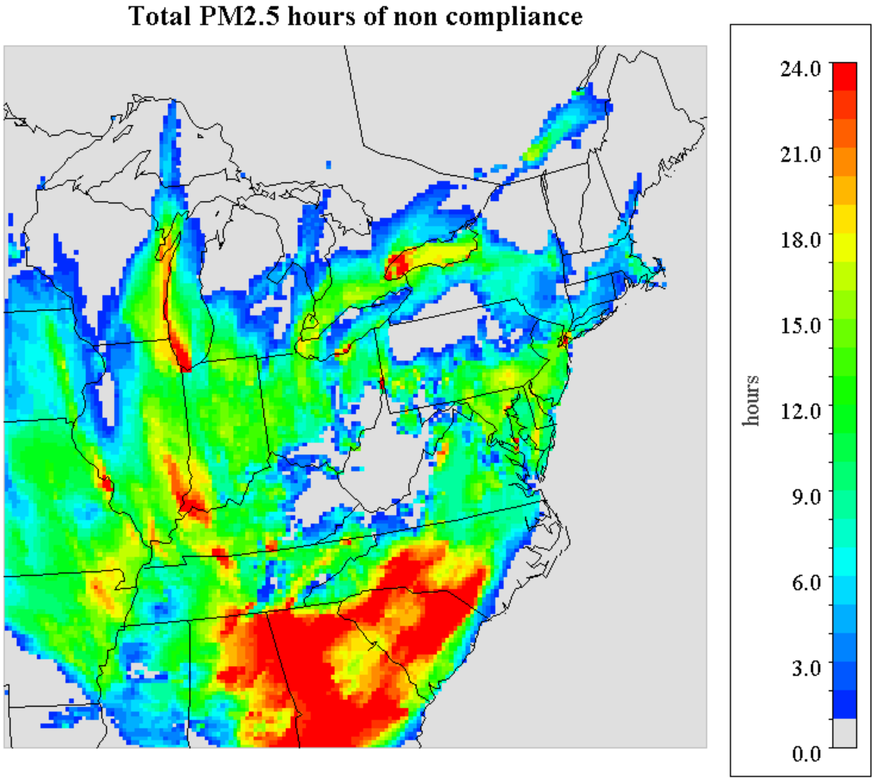

Fig 4.44 Hours of non-compliance for total $PM_{2.5}$ on 22nd May, 2002 for reduced case

4.3 High $PM_{2.5}$ Episode - May 24, 2002

4.3.1 Total $PM_{2.5}$

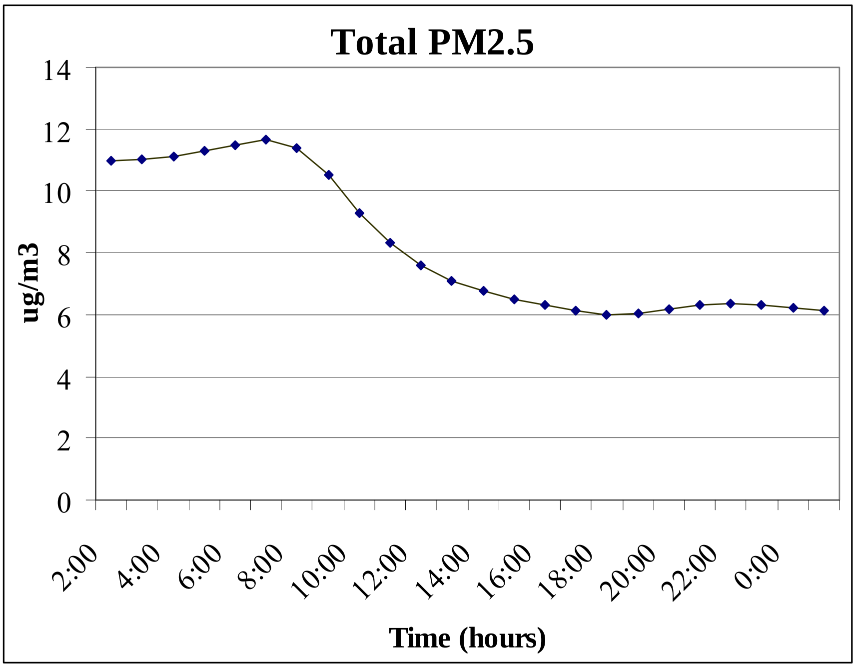

Fig 4.45 Total $PM_{2.5}$ for the base case showing maxima at 8:00 AM EDT, 24th May, 2002

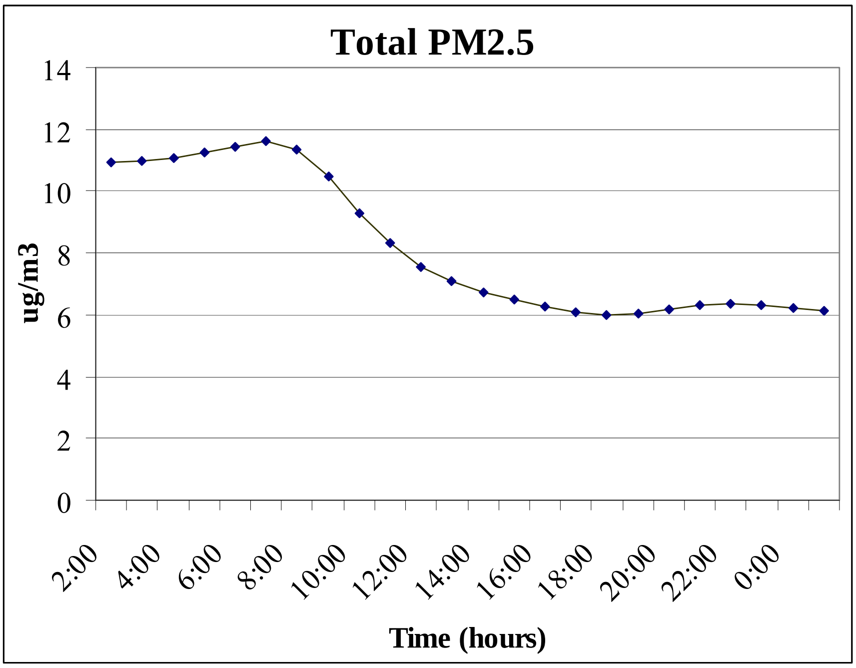

Fig 4.46 Total $PM_{2.5}$ for the reduced case showing maxima at 8:00 AM EDT, 24th May, 2002

In this episode the PM$_{2.5}$ reaches maxima at 8:00 AM EDT and decreases continually both in the base and the reduced case as seen in Figs 4.45 and 4.46 respectively. As before both curves are qualitatively similar.

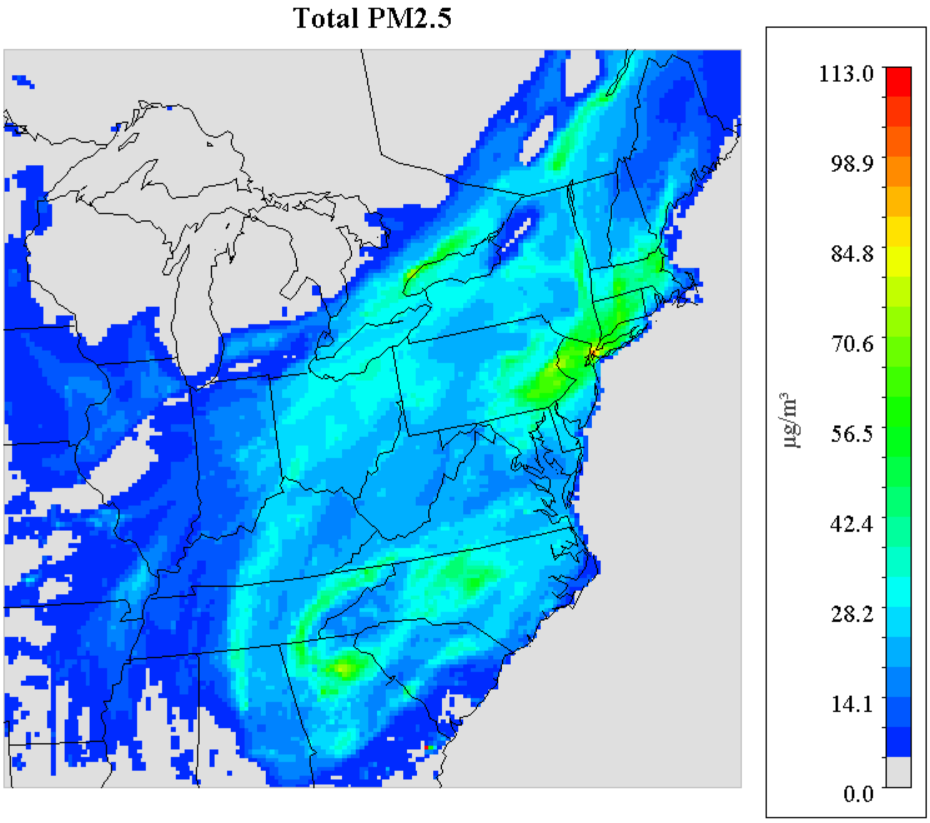

Fig 4.47 Total PM$_{2.5}$ over the eastern US showing maxima at 8:00 AM EDT, 24th May, 2002

As mentioned before and also as apparent in Fig 4.47, this episode corresponds to a decreasing PM$_{2.5}$ trend but at the maxima the PM$_{2.5}$ hangs over the east coast especially the MANEVU region. It remains there over the day reducing, to about 60 μg/m^3 and contributing to a high level of non compliance. PM$_{2.5}$ concentrations at the maxima vary from 28 μg/m^3 to 70.6 μg/m^3 with a hotspot of 113 μg/m^3 seen over southeastern New York Also seen in the figure are regions of high PM$_{2.5}$ over North Carolina and Georgia.

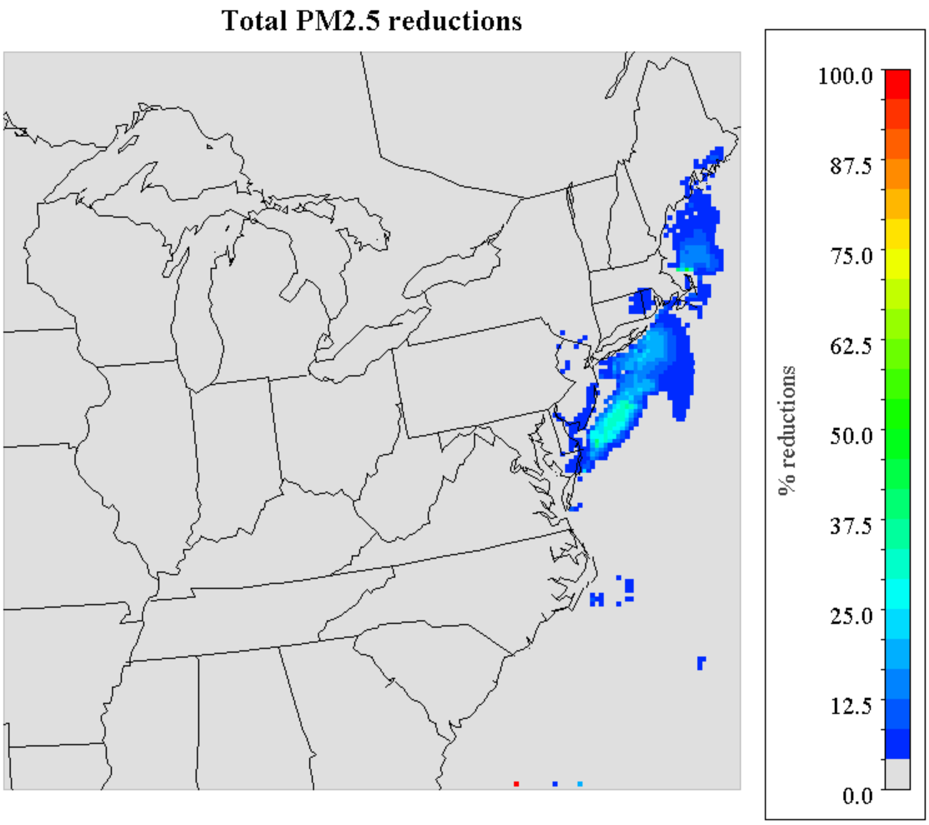

Fig 4.48 Total $PM_{2.5}$ percentage reductions achieved at 8:00 AM EDT, 24th May, 2002 by control strategy

Significant $PM_{2.5}$ reductions can be seen over the ocean with reduction values of 37.5 % in some regions. However most of these reductions are blown over the ocean as with the previous episode. Some benefits may can be foreseen for the northeastern states and the Chesapeake Bay regions where a 12.5-25 % reduction may occur over the shoreline regions.

4.3.2 $PM_{2.5}$ Sulfate mass

In this particular case the sulfate mass curves of Figs 4.49 and 4.50 show a continual decline and are similar for the base and the reduced case. They qualitatively indicate a reduction tendency in $PM_{2.5}$ as seen before.

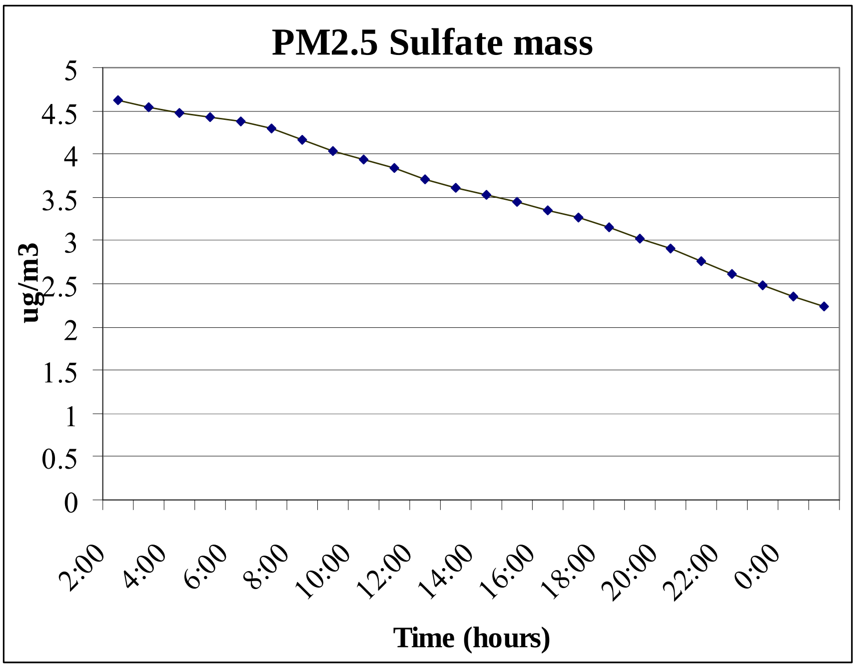

Fig 4.49 Total $PM_{2.5}$ sulfate mass showing a continual decline on 24th May, 2002

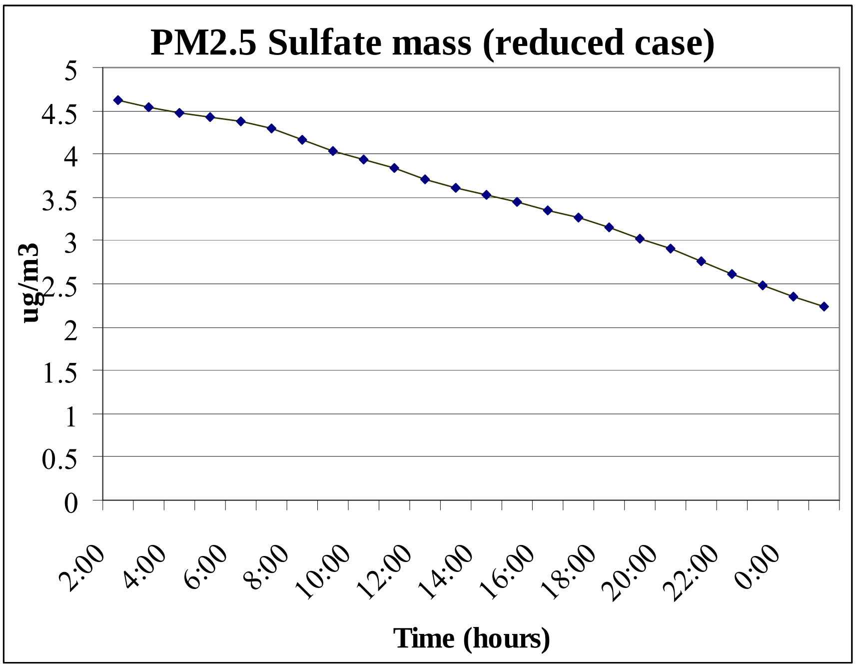

Fig 4.50 Total $PM_{2.5}$ sulfate mass showing a continual decline on 24th May, 2002 for the reduced case

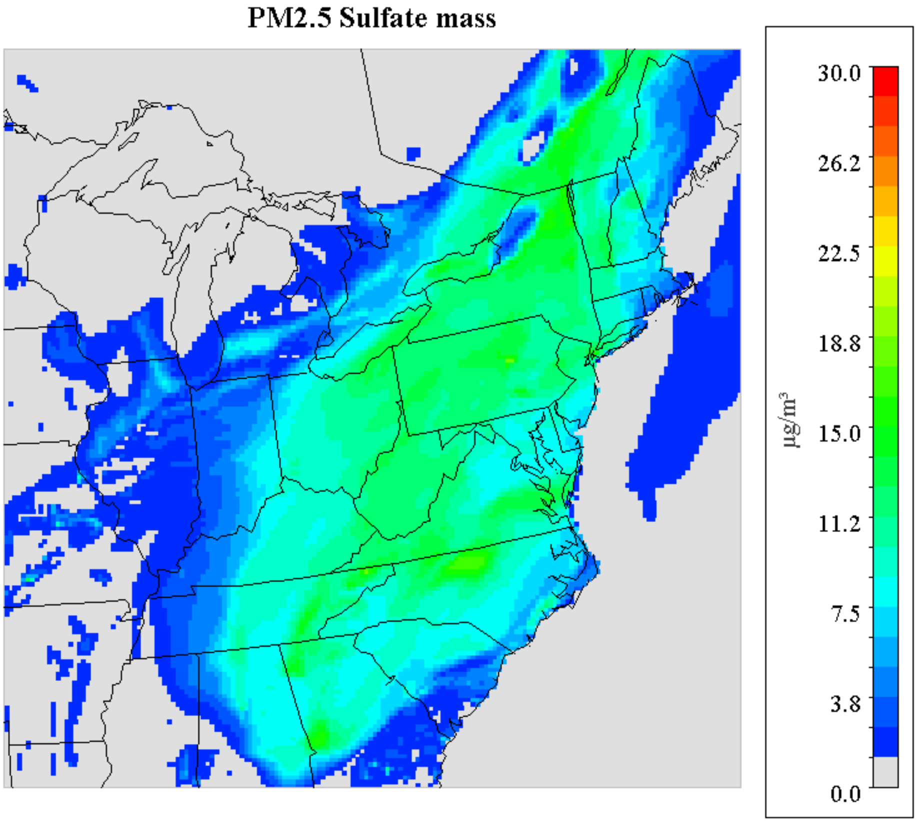

Fig 4.51 Total $PM_{2.5}$ sulfate mass over the eastern US at 8:00 AM EDT, 24th May, 2002

In the Fig. 4.51 we primarily see a large mass of sulfates hanging over the entire east coast. The sulfate concentrations vary from 7.5 to19 $\mu g/m^3$ with larger values seen at the center of the mass.

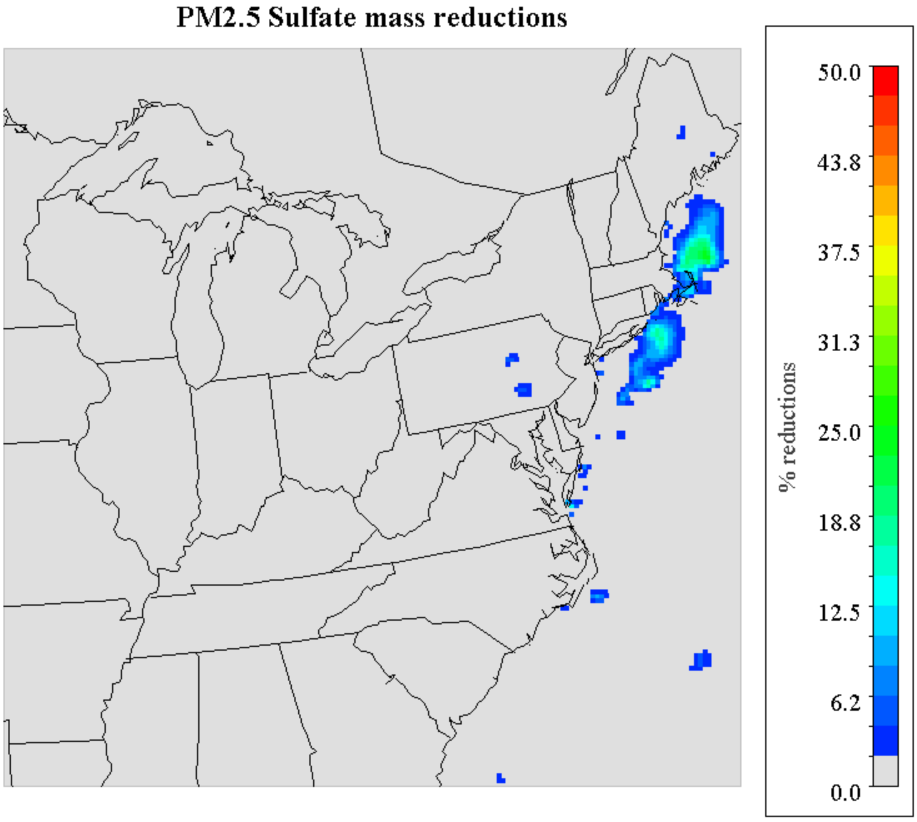

Fig 4.52 Reductions in sulfate based fine particulate matter achieved at 8:00 AM EDT for 24th May, 2002 by control strategy

Fig 4.52 shows reductions achieved as patches seen near the northeastern states. However as before the reductions are primarily over the ocean. The reductions are of the order of 5-32 %. Some small reductions of 5-7 % can be seen over Pennsylvania No sulfate reductions are seen elsewhere.

4.3.3 PM$_{2.5}$ Ammonium Mass

Fig 4.53 and 4.54 show a maxima at 8:00 AM EDT and then an asymptotic decrease in ammonium based fine particulate matter. Both curves are similar qualitatively.

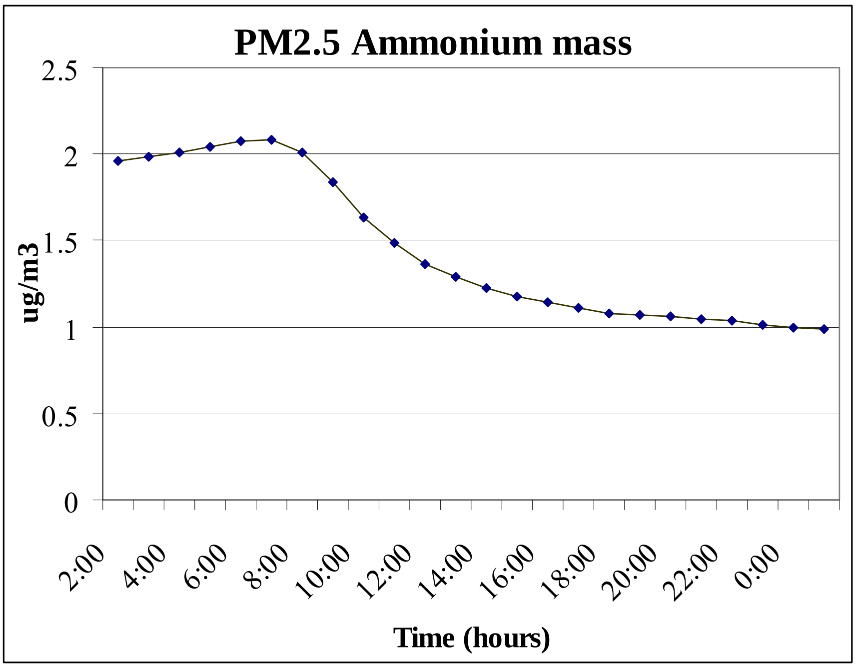

Fig 4.53 Ammonium based fine particulate matter showing maxima at 8:00 AM EDT, 24th May, 2002

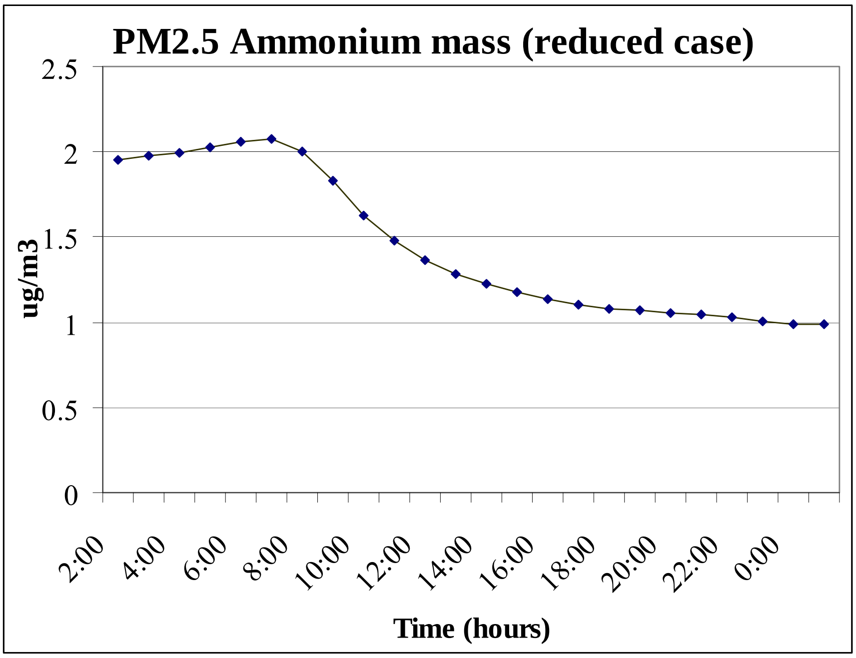

Fig 4.54 Ammonium based fine particulate matter showing maxima at 8:00 AM EDT, 24th May, 2002 for reduced case

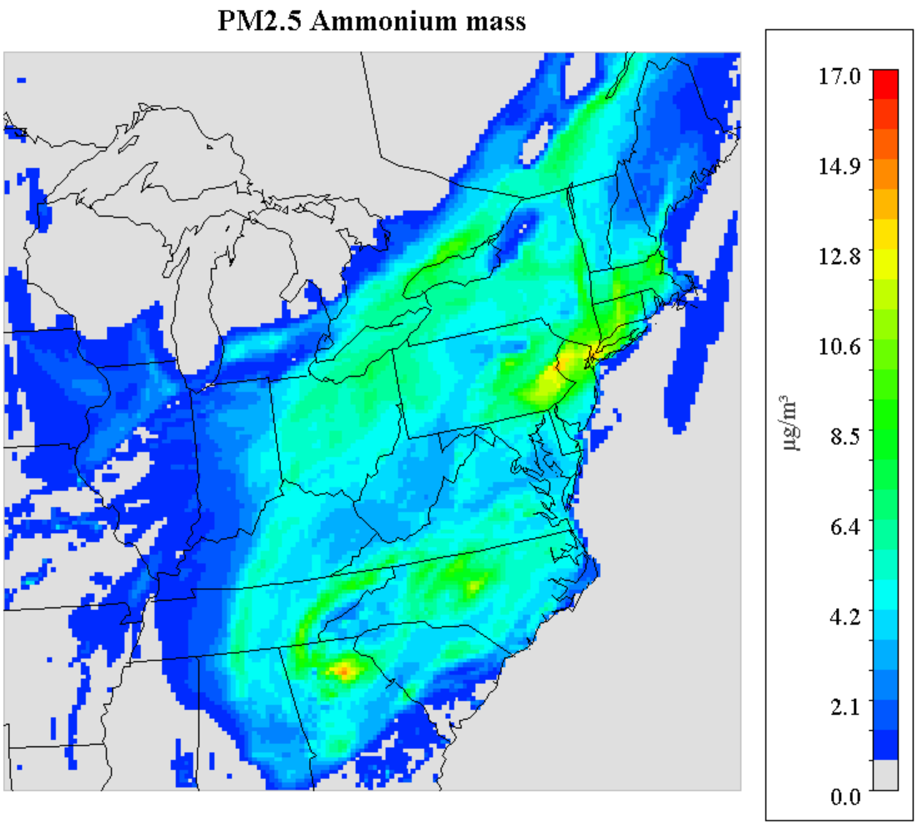

Fig 4.55 Ammonium based fine particulate matter over the eastern US at 8:00 AM EDT, 24th May, 2002

Fig 4.55 shows ammonium based fine particulate matter with hotspots over Pennsylvania, New Jersey and Southeastern New York. The values of ammonium based fine particulate matter vary from 6.5 µg/m^3, at the edges of the mass to 15.0 µg/m^3 at the hotspots. Also seen is a hotspot over Athens, Georgia which is not so apparent in the Fig 4.47. Athens has a few poultry and cattle farms near it which may have been aggravated by the moderate PM$_{2.5}$ levels.

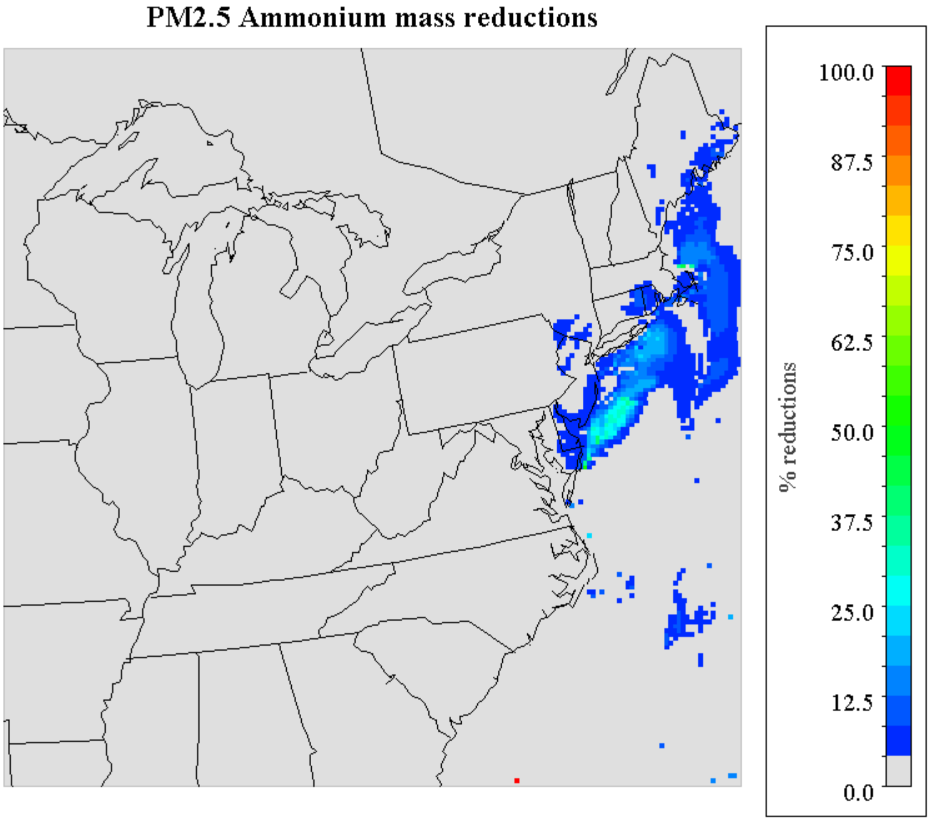

Fig 4.56 Reductions in ammonium based fine particulate matter achieved at 8:00 AM EDT, 24th May, 2002 by control strategy

As seen in Fig 4.56, ammonium based fine particulate matter is reduced by about 5-30 % primarily over the Chesapeake Bay and over the ocean. Some reductions also occur along the northeastern states with possible reductions occurring over land. Reductions of about 5% are seen over southeastern New York.

4.3.4 $PM_{2.5}$ Nitrate Mass

Nitrate based fine particulate matter shows maxima at 8:00 AM EDT. As before both curves are similar with the peaks slightly reduced for the reduced case.

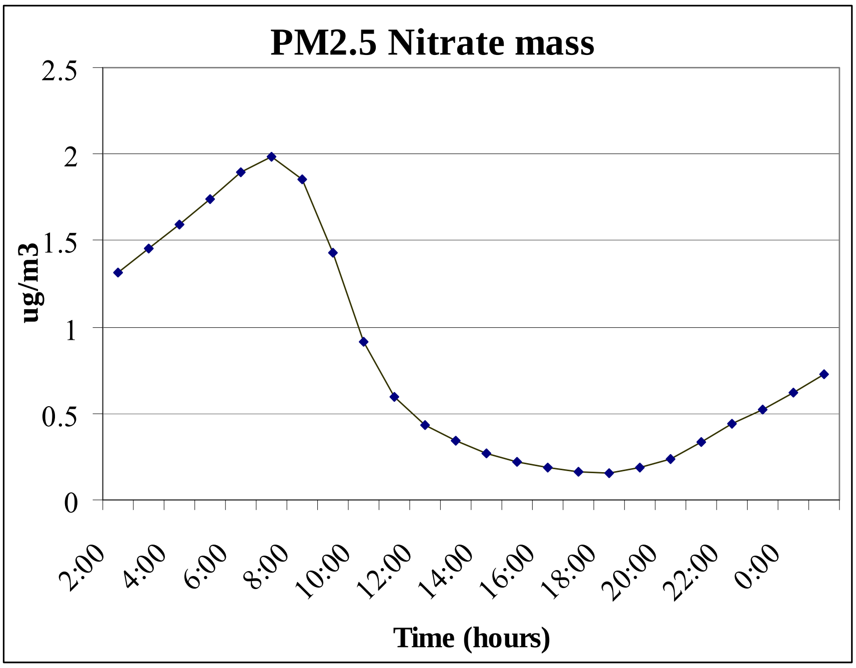

Fig. 4.57 Nitrate based fine particulate matter showing maxima at 8:00 AM EDT, 24th May, 2002

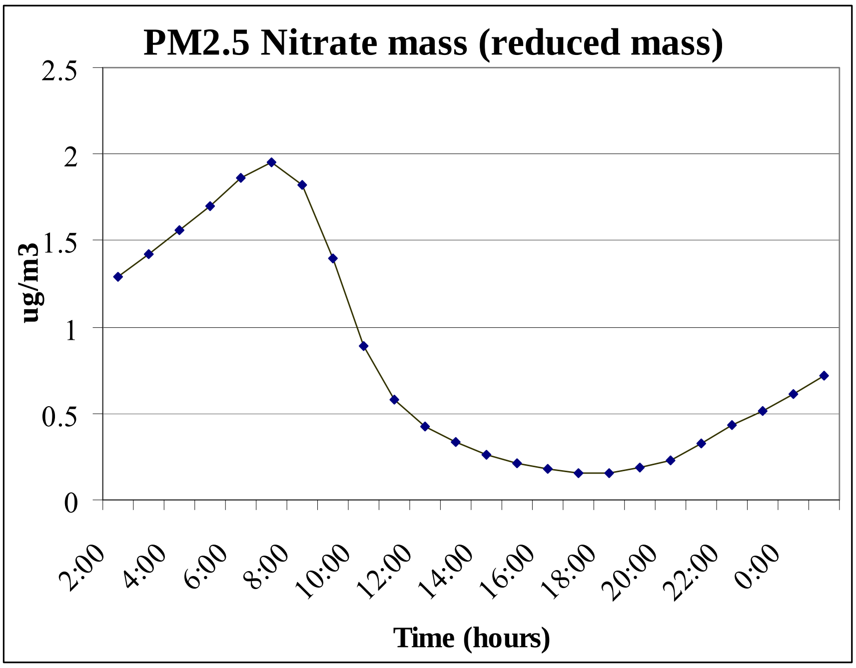

Fig. 4.58 Nitrate based fine particulate matter showing maxima at 8:00 AM EDT, 24th May, 2002 for reduced case

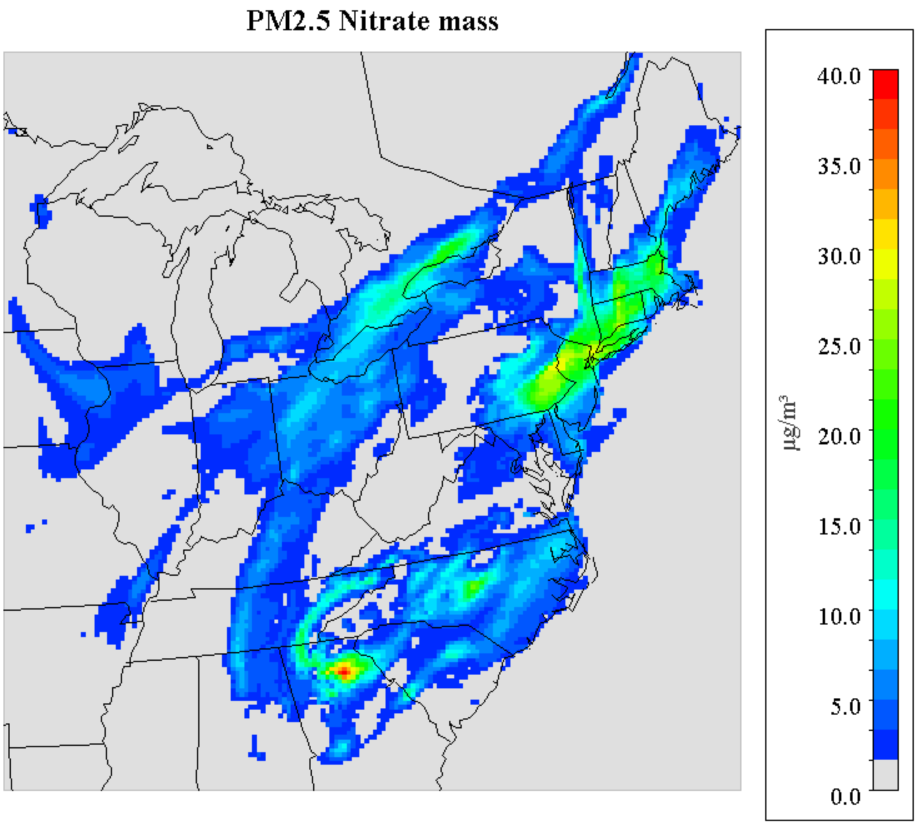

Fig 4.59 Nitrate based fine particulate matter over the eastern US at 8:00 AM EDT, 24th May, 2002

From Fig 4.59 significant nitrate base particulates can be seen hanging over the northeastern states with a hotspot over Pennsylvania-New Jersey border and over southeastern New York. Concentration values of 5 µg/m^3 can be seen at the edges of the mass with values as high as 30 µg/m^3 seen at the center of the mass. The hotspot over Georgia which was not so apparent in the total PM2.5 and ammonium based fine particulate matter curves is seen more distinctly in this figure suggesting it is primarily nitrate based.

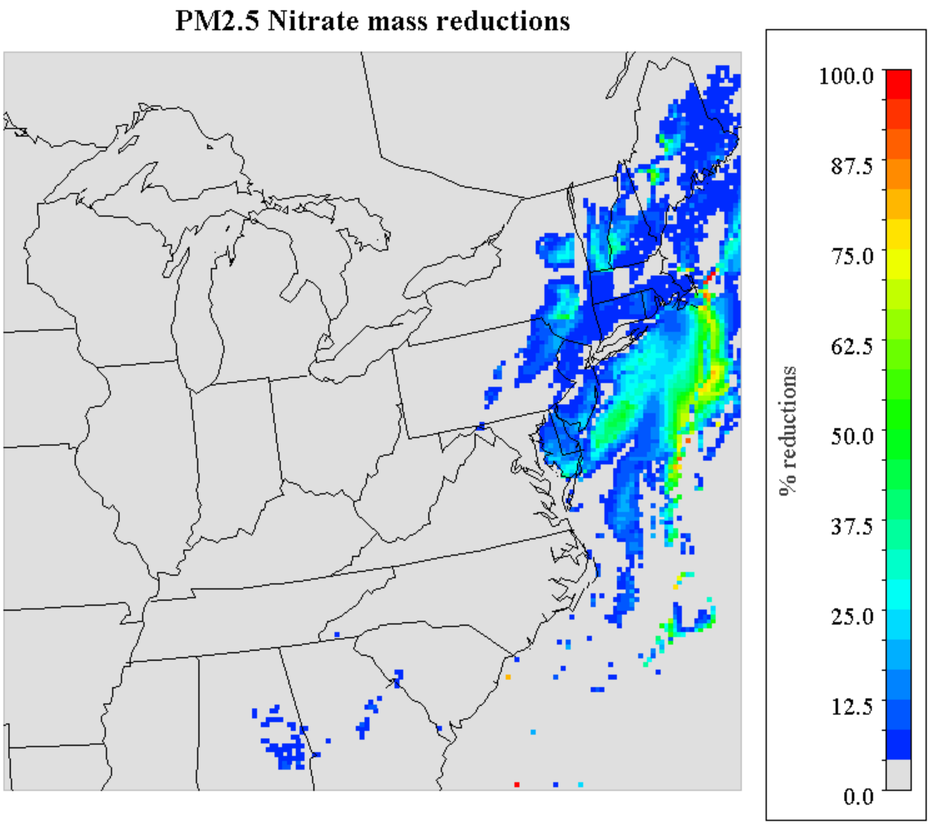

Fig 4.60 Reductions in nitrate based fine particulate matter achieved at 8:00 AM EDT, 24th May, 2002 by the control strategy

Significant reductions of about 75 % can be seen for nitrate based fine particulate matter in Fig 4.60, but most of these are seen over the ocean with some reductions over land in New York, and the northeastern states. Reductions of about 60 % can be seen close to the shoreline near the Chesapeake Bay and partly over it prompting the thought that there may be some benefit achieved over land of the proposed control strategy.

4.3.5 Ammonia

Atmospheric ammonia curves show double maxima at 8:00 AM EDT and 12 midnight like previous cases as can be seen in Figs 4.61 and 4.62. Also some reductions in ammonia are seen for the reduced case.

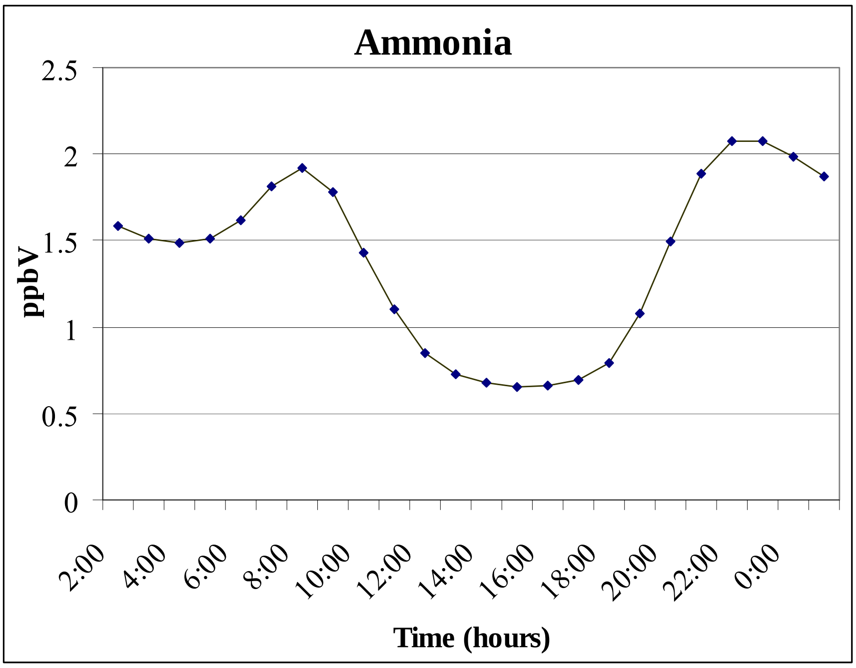

Fig 4.61 Atmospheric ammonia showing double maxima once at 8:00 AM and once at 12:00 midnight on 24th, May 2002

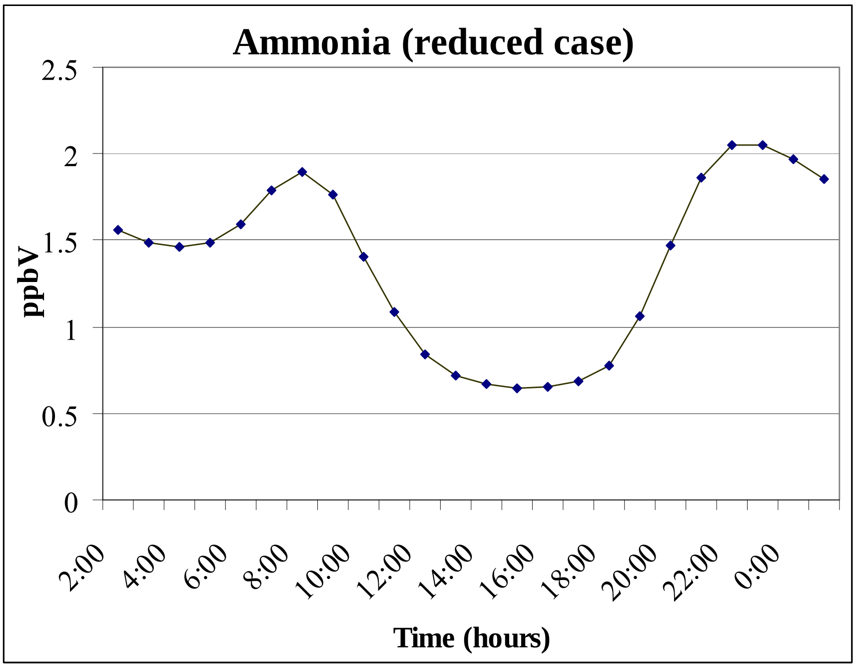

Fig 4.62 Atmospheric ammonia showing double maxima once at 8:00 AM and once at 12:00 midnight on 24th, May 2002 for reduced case

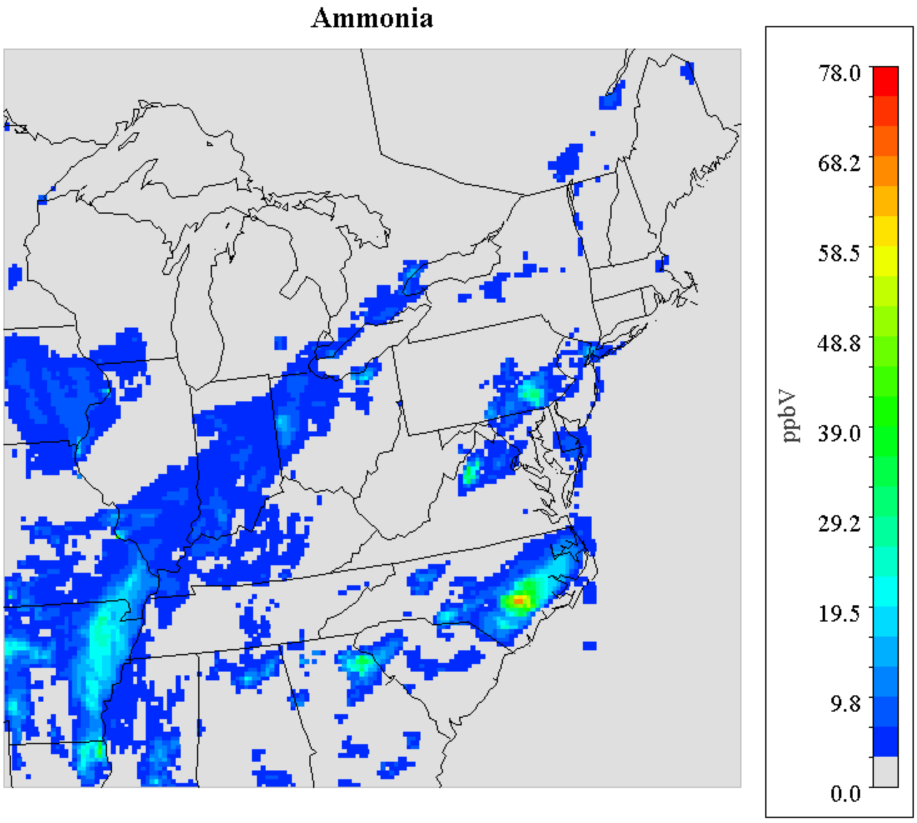

Fig 4.63 Atmospheric ammonia over the eastern US at 8:00 AM EDT, 24th May, 2002.

Atmospheric ammonia can be seen in Fig 4.63 looming over Pennsylvania and a hot spot can also be seen over North Carolina. The values of atmospheric ammonia are of the order of 5-9 ppbV over most of the regions where ammonia is present and 50-78 ppbV at the hotspots. Ammonia can also be seen looming over the central regions of the US.

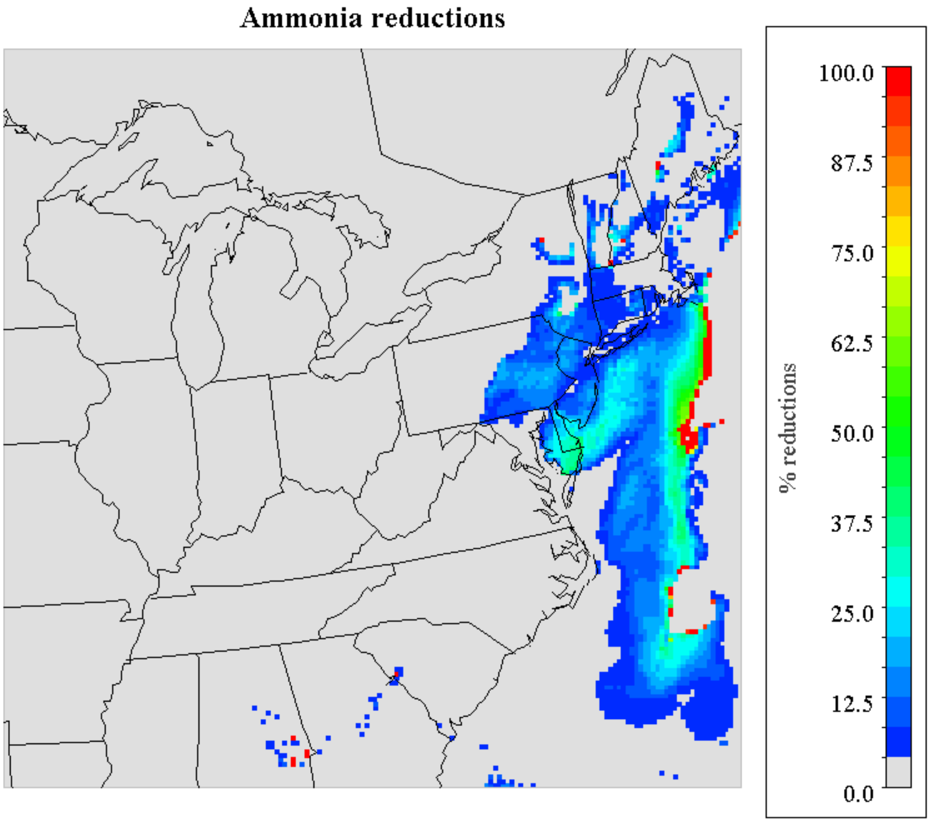

Fig 4.64 Atmospheric ammonia reductions achieved at 8:00 AM EDT, 24th May, 2002 by the control strategy

Fig 4.64 shows ammonia reductions primarily over Delaware-Maryland region with some reductions over Pennsylvania. The reductions are of the order of 30-60 % with significant reductions occurring of 50-70 % occurring over the ocean. This again can be attributed to the control strategy and the ammonia reaction mechanisms.

4.3.6 Hours of Noncompliance

Figs 4.65 and 4.66 show a high level of non-compliance over the most of the east coast with almost 24 hours of non-compliance for the MANEVU region. Because of this it is difficult to see the benefits of the control strategy. However, upon closer inspection a reduction in non-compliance from 24 hours to about 20 hours is seen in shoreline regions of New Jersey. Also there is a reduction in the 24 hour non compliance region over Connecticut and Rhode Island with the surrounding regions having 20 hours of non-compliance.

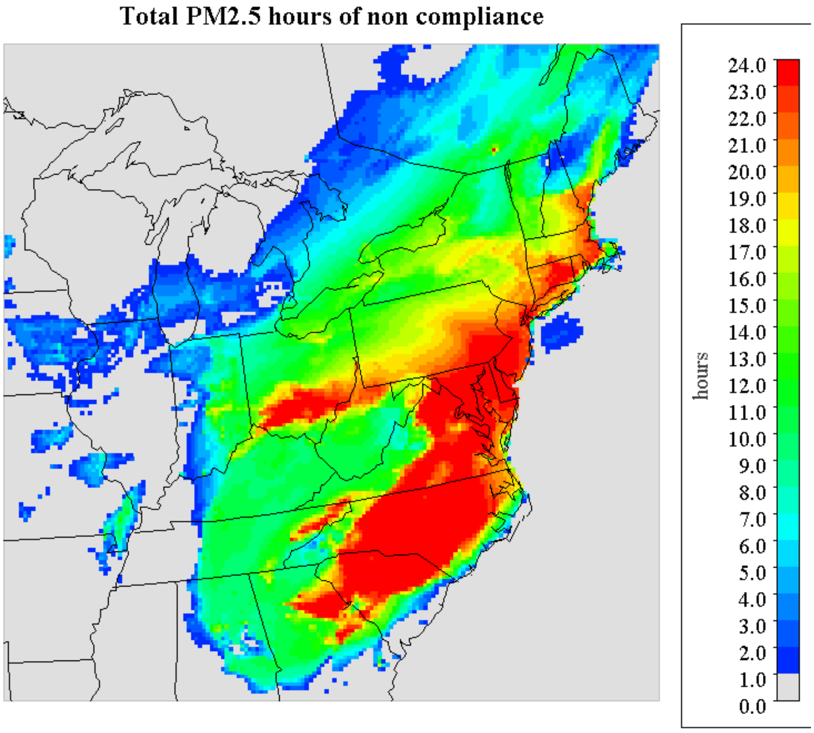

Fig 4.65 Hours of non-compliance for total $PM_{2.5}$ for base case for 24th May, 2002

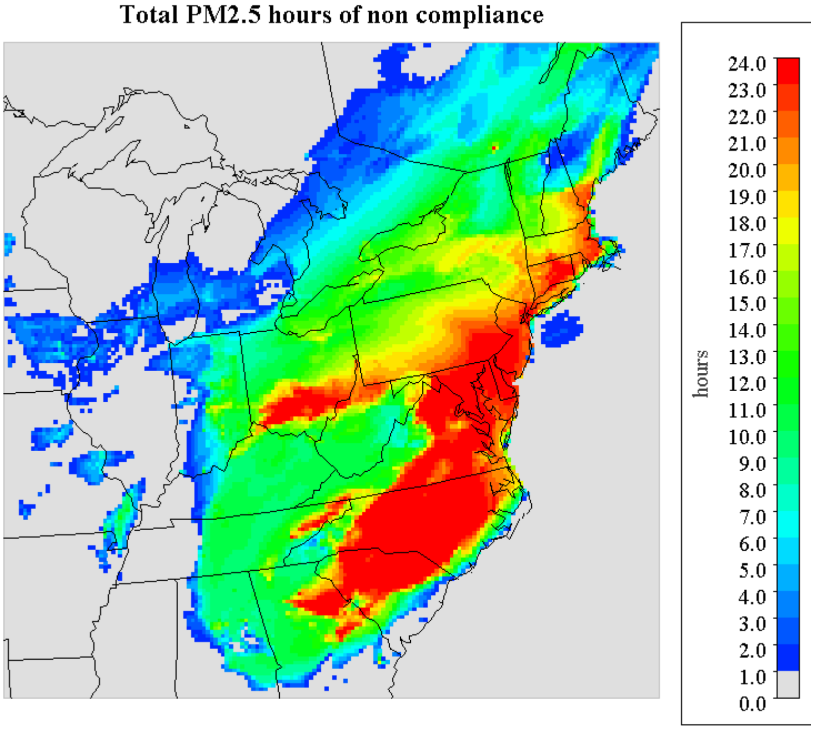

Fig 4.66 Hours of non-compliance for total $PM_{2.5}$ on 24th May, 2002 for reduced case

4.4 $PM_{2.5}$ sulfate to nitrate molar ratio

Fig 4.67, 4.68 and 4.69 show the sulfate to nitrate ratios in $PM_{2.5}$ for the selected days. These ratios are indicators of the amount of nitric acid and sulfuric acid available for reaction with ammonia. It is observed that regions with high nitrates to sulfates ratio upwind of the sources are reduced. Also regions near the source for which emissions have been reduced get a direct benefit of the reductions. This tells us that this strategy is primarily targeting nitrate based fine particulate matter. This also means that there is a lot of free ammonia in the atmosphere to react with sulfuric acid. Since sulfuric acid reacts first it consumes the required ammonia and the control strategy thus gets applied to nitric acid and hence nitrates.

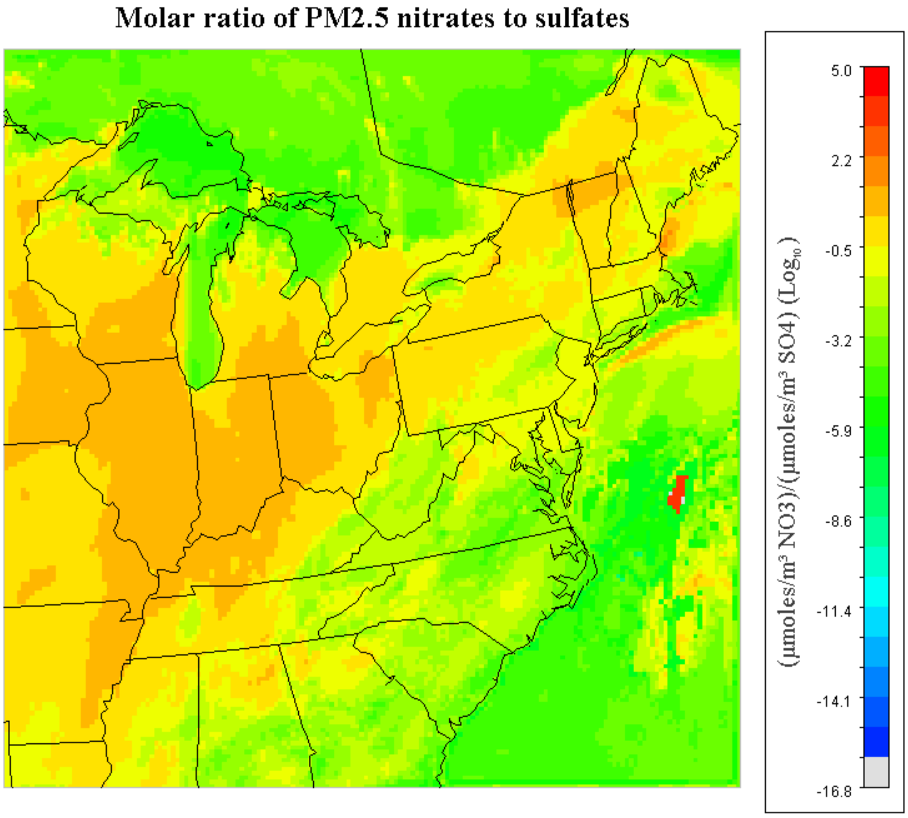

Fig 4.67 $PM_{2.5}$ nitrate to sulfate ratios at 8:00 AM EDT, 18th May, 2002

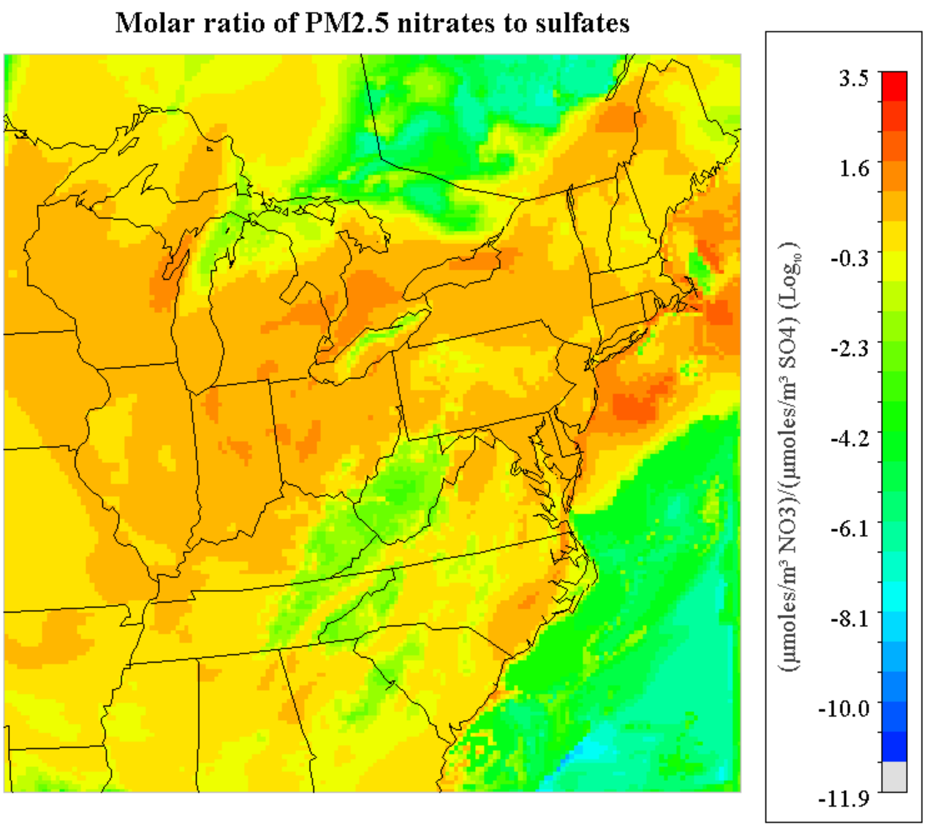

Fig 4.68 PM$_{2.5}$ nitrate to sulfate ratios at 8:00 AM EDT, 22nd May, 2002

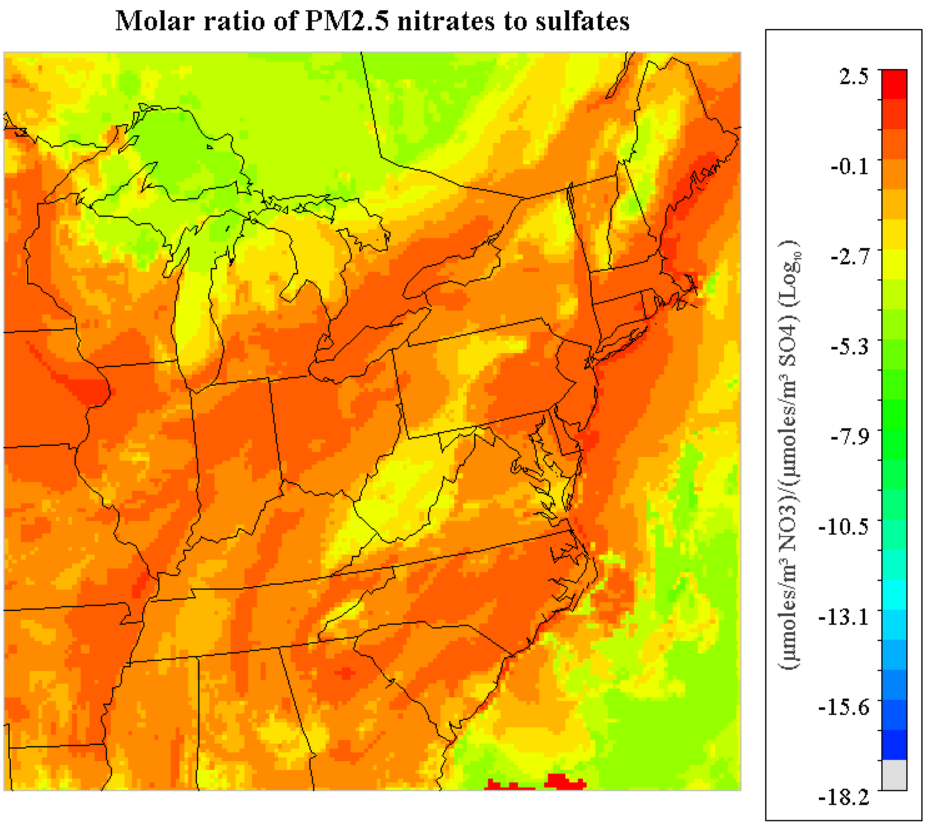

Fig 4.69 PM$_{2.5}$ nitrate to sulfate ratios at 8:00 AM EDT, 24th May, 2002

4.5 Aerosol thermodynamic equilibrium studies

The following is a description of the aerosol thermodynamic equilibrium studies performed to observe the percentage reductions in $PM_{2.5}$ obtained by reducing gas phase ammonia concentration. The main objectives of this study were as follows:

A. To observe the reduction in $PM_{2.5}$ obtained by reducing ammonia concentration using a simpler model than CMAQ.

B. To note any trends in $PM_{2.5}$ reductions corresponding to higher or lower ammonia phase reductions.

C. To compare the results with the existing equilibrium results from CMAQ studies.

An essential assumption in these studies is that percentage reductions in ammonia emissions are equal to percentage reductions in gas phase ammonia. In the following studies only aerosol and phase thermodynamic equilibrium is considered and transport has been neglected.

4.5.1 Thermodynamic equilibrium model (ISORROPIA-II)

For the following studies, ISORROPIA-II was used, which is a multi-component and multi-phase aerosol thermodynamic equilibrium model developed at the Schools of Earth & Atmospheric Sciences and Chemical & Biomolecular Engineering at the Georgia Institute of Technology (http://nenes.eas.gatech.edu/ISORROPIA/). ISORROPIA has been incorporated in the CMAQ aerosol module (http://www.epa.gov/AMD/ModelDevelopment/aerosolModule.html) and its primary aim is computational efficiency and speed. ISORROPIA-II is an extension of ISORROPIA and has a larger number of chemical species. It however uses the exact same calculation scheme as its predecessor (http://nenes.eas.gatech.edu/ISORROPIA/). In comparison with other models like SCAPE-II it has been seen that the ISORROPIA scheme has a stable and robust convergence (Nenes, Pandis, Pilinis; 1998). It also incorporates mutual deliquescence of multi-component salt particles, which lowers the deliquescence of aerosol particles, enabling realistic aerosol phase simulations.

4.5.2 Setup

ISORROPIA-II can run in two modes: forward and reverse. Forward mode can calculate gas, liquid phase aerosol and solid phase aerosol equilibrium concentrations from the known quantities: temperature, relative humidity and the total (i.e. gas+aerosol) concentrations of NH_3, H_2SO4, Na, (Ca, K, Mg), HCl and HNO_3.

Reverse mode can calculate gas, liquid phase aerosol and solid phase aerosol equilibrium concentrations from the known quantities: temperature, relative humidity and the aerosol phase concentrations of NH_3, H_2SO4, Na, (Ca, K, Mg), HCl and HNO_3.

In this study a point was chosen (130, 80) on the CMAQ grid. This corresponds to a location on the Delmarva Peninsula. The temperature, and water vapor mixing ratio, pressure, along with $PM_{2.5}$ sulfate, nitrate and ammonium mass concentrations were obtained for that particular point corresponding to 8:00 AM EDT, 22nd May 2002 from the meteorology fields previously used for CMAQ studies. The relative humidity corresponding to the given temperature, pressure and mixing ratio was calculated using the website http://www.johnsnhweather.com/mixingratio.html. The corresponding inputs were fed to ISORROPIA-II in reverse mode to obtain the desired total gas+aerosol phase compositions to use in the forward mode. Table 4.0 gives the ISORROPIA-II reverse mode inputs.

Table 4.0 Reverse mode inputs to ISORROPIA-II. Low values set to 0.

Variable	**Value**
Temperature	281.030 K
Pressure	102755.366 Pa
Water vapor mixing ratio	4.089 g-water vapor /g-air
Relative humidity (calculated)	62.830 %
Na, Cl, K, Mg conc.	0.000 μg/m^3
Sulfate conc.	4.570 μg/m^3
Ammonium conc.	5.739 μg/m^3
Nitrate conc.	13.860 μg/m^3

The reverse mode results were fed to the forward mode. The forward mode ISORROPIA simulations used total ammonia (gas+aerosol) linearly incremented values (step size of 0.00337 μmoles/m^3) from 0.000 μmoles/m^3 to 0.337 μmoles/m^3. The simulations were using batch mode input style that is supported by ISORROPIA-II.

4.5.3 Results

The results of the above batch mode simulations are shown in Fig, 4.70, 4.71 and 4.72. Specifics of sub-cases were obtained from the ISORROPIA source code listed on the NOAA website.

(http://www.nco.ncep.noaa.gov/pmb/codes/nwprod/sorc/aqm_fcst_5xpmwrf.fd/isofwd.f).

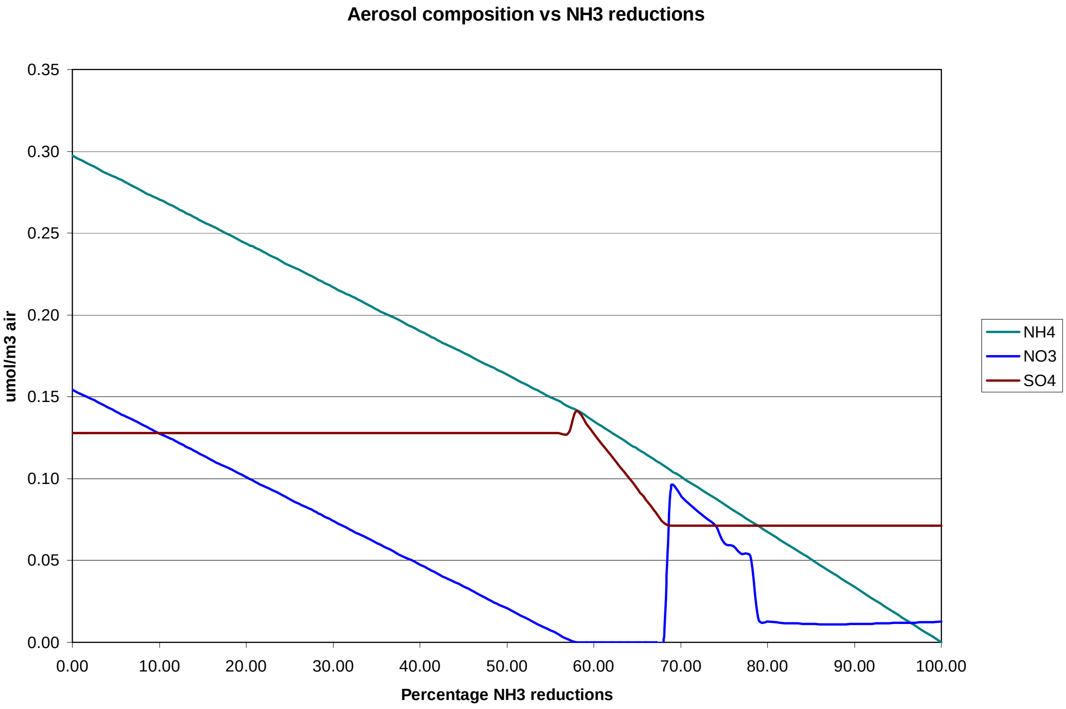

Fig.4.70 Effect of ammonia reductions on aerosol sulfate, nitrate and ammonium content (moles)

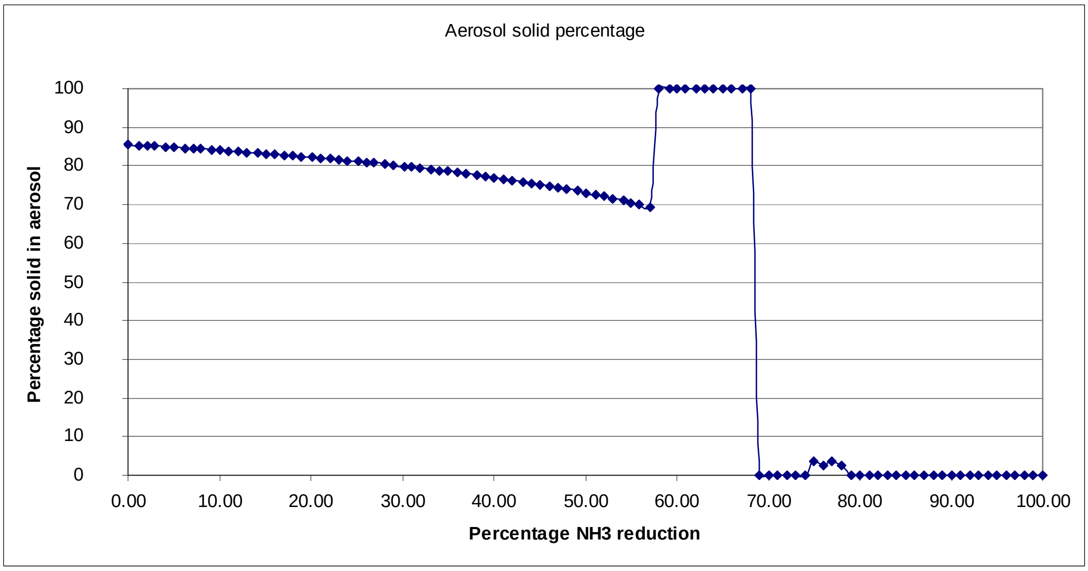

Fig.4.71 Effect of ammonia reductions on aerosol phase

The ammonia concentrations corresponding to a reduction range from 79 %-100 % corresponds to an aerosol which falls in ISORROPIA-II's F2 subcase regime. It is a sulfate rich regime with free sulfuric acid and very little nitric acid. Any nitric acid is assumed to be dissolved in the liquid phase as nitrate ions. ISORROPIA's phase calculations are based on deliquescence relative humidities (DRH) which represent the relative humidity (RH) required to liquefy the aerosol. The DRH of sulfuric acid is 0% and its high deliquescence causes the aerosol to liquefy with an almost 0 % solid throughout this range.

As the ammonia concentration increases more ammonium sulfate is precipitated due to the increasing ammonium ion concentration in the liquid phase. This makes way for more sulfate ion to dissolve in the aqueous phase causing an increase in its concentration. The nitrate ion concentration also increases due to increase in pH caused by the increase in ammonium ion, concentration however the bisulfate concentration decreases due to the same effect. This is because at higher pH the bisulfate-sulfate equilibrium tends to shift towards the sulfate side. At about 68 % ammonia reductions, the reduced ammonia concentration is sufficient to neutralize all of the free acid and the high heat of reaction (-179 KJ/mol) vaporizes the liquid phase. Thus only ammonium sulfate is left in the aerosol. This causes the DRH to rise abruptly above the present RH and causes the aerosol to solidify. Any bisulfate is now present as triammonium sulfate $(NH_4)_3H(SO_4)_2$. This corresponds to subcase 'E2' which is also a sulfate rich aerosol with no free acid. So far, the nitrate concentrations were low and were primarily because of free sulfuric acid which forms an aqueous phase for the nitric acid to dissolve. With the disappearing aqueous phase the nitrate ion concentration also abruptly decreases. The absence of any ammonium nitrate so far can be attributed to the preference of ammonia to react with sulfuric acid rather than nitric acid. This can be explained thermodynamically by the high standard free energy of formation of ammonium sulfate (-901.670 kJ/mol), ammonium bisulfate (-823.000 kJ/mol) as compared to ammonium nitrate (-183.870 KJ/mol) (Data from Kim et al.; 1993 in Nenes et al. 1998). This states that thermodynamically, the reaction to form ammonium sulfate is more favored over the ammonium. This continues till all of the sulfuric acid in the surrounding gas has transferred to the aerosol as ammonium sulfate.

After the end of the ammonium sulfate formation regime (58 % reductions) the aerosol becomes sulfate poor (given by ammonium to sulfate ratios).This shifts the aerosol into the 'D1' subcase 2 regime with a possible liquid phase. This regime is characterized by a primary solid aerosol with two main components-ammonium sulfate and ammonium nitrate. The regime is also characterized by increasing ammonium nitrate concentrations. The presence of ammonium nitrate reduces the DRH of the mixture such that the relative humidity is now greater than the maximum DRH of the mixture. There is also an accompanied removal of bisulfate ion from the mixture which is leftover from the liquefaction of triammonium sulfate due to rising pH. This causes the DRH of the mixture to increase because the bisulfate has a very low DRH and thus increases the solid fraction of the aerosol.

$PM_{2.5}$ was also calculated assuming ISORROPIA-II aerosol phase was almost all $PM_{2.5}$. This is valid because of the exclusion of coarse PM formation mechanisms in ISORROPIA-II (Pye, et al.; 2009). I have assume that 85 % of all $PM_{2.5}$ (concentration corresponding to 0% ammonia reductions) are sulfates and nitrates of ammonia. I have also assumed that this "other" PM is a constant quantity and is unaffected by the reductions. Hence the sum of nitrate, sulfate (sulfate+bisulfate) and ammonium is adjusted to give $PM_{2.5}$ mass by including a bias equal to the "other" PM concentration. Reductions were calculated based on $PM_{2.5}$ concentration at 0% ammonia reductions.

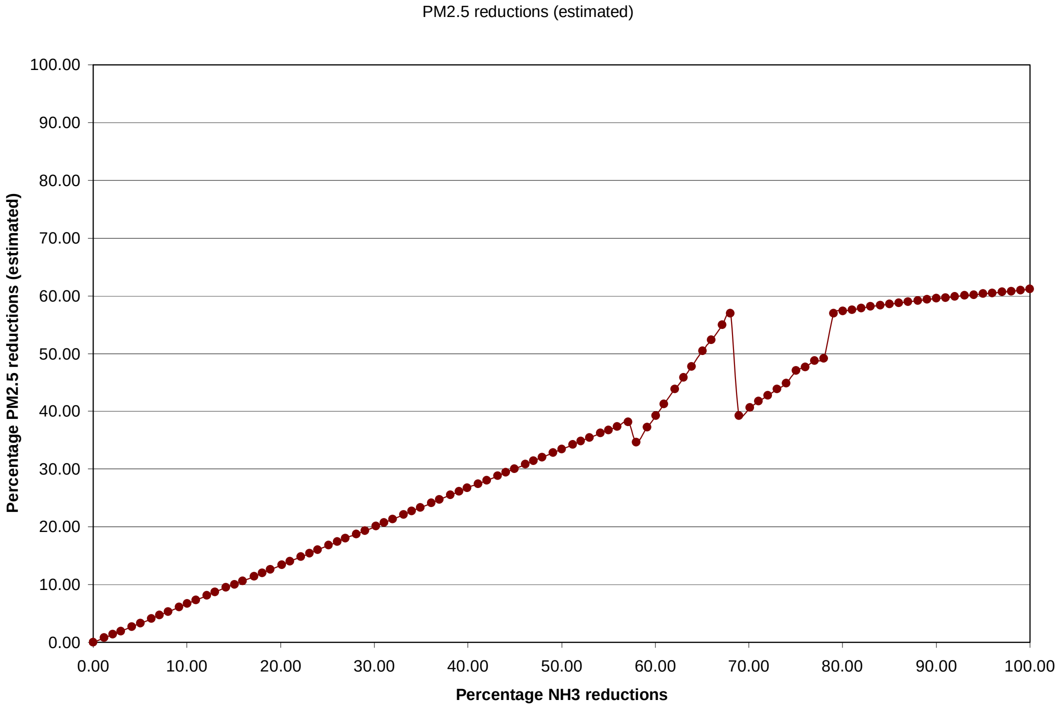

Fig4.72 Ammonia reductions vs $PM_{2.5}$ reductions

Based on fig 4.72 a good linear trend can be seen (R^2=1, slope=0.6689 and Y-intercept=-0.0332) between ammonia reductions and $PM_{2.5}$ reductions up to 50 % ammonia reductions. Also based on this graph, I can conclude that a maximum of 61 % $PM_{2.5}$ reductions can be obtained for 100 % ammonia reductions. This is because beyond 70 % ammonia reductions, the gas ammonia concentration is low enough to allow the existence of free sulfuric acid which tends to form droplets of sulfuric acid which are also classified as $PM_{2.5}$. Hence, although $PM_{2.5}$ mass may reduce, the number strength will reduce at a lesser rate than before. Still, despite all this, a region may have higher reductions in $PM_{2.5}$ because in this particular model transport has been ignored and removal mechanisms have not been considered.

Comparisons with the CMAQ simulations for 22nd of May for that region show reductions of 1.5 %. However, regions downwind show reductions of 20-30 % which is around the thermodynamic maximum achievable reductions of about 25 %. Also, as predicted from the CMAQ results, ammonium sulfate concentrations remain constant for 0-58 % ammonia reduction range, while ammonium nitrate concentrations decrease linearly for ammonia reductions. This is consistent with my theory that the strategy (which corresponds to 39 % ammonia reductions) targets ammonium nitrate as compared to ammonium sulfate. Thus we see that the reductions in the region are strongly transport dependent but still comply with this simple thermodynamic model which is used by CMAQ to calculate $PM_{2.5}$ fractions.

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

Through reviews of various EPA documents, published inventories and through this thesis, I have attempted to isolate ammonia as a significant source of particulate matter. The link between ammonia and particulate matter is well established and has been reaffirmed in this thesis. The atmospheric ammonia curves show a similar shape to the total particulate matter curves and both reach maxima at 8:00 AM EST. Ammonia is basic in nature and is found in abundance in the atmosphere. It reacts with atmospheric acids like sulphuric and nitric acid to form fine particulate matter which constitute most of the $PM_{2.5}$. This is reaffirmed through studies and also through the fact approximately 85% of all $PM_{2.5}$ was present as sulfates or nitrates of ammonia in my simulations. As such there is no scope of doubt that ammonia plays a major role in fine particulate matter formation.

I also reviewed various sources of ammonia and found that the major anthropogenic sources were a major contributor to atmospheric ammonia. More specifically, animal husbandry operations are the single largest source of atmospheric ammonia as per the US EPA and my studies. This fact is clearly illustrated by my previous discussions on the MANEVU inventories.

Next, I reviewed the different strategies to control atmospheric ammonia emissions from animal husbandry operations and I concluded based on cost, reduction efficiency along and no productivity loss critria that dietary feed manipulation (which is a pre-excretionary strategy) is the best possible strategy for controlling ammonia emissions from animal husbandry operations. I reviewed a paper by Hale III (2004), which dealt with reducing ammonia emissions from chicken manure using a combination of dietary crude protein reduction and acidification of diet with gypsum-zeolite mixtures. This particular paper described high values of reductions (upto 86 %) in field tests and was a source of inspiration for the this study which describes the effects of a possible control strategy for atmospheric fine particulate matter. Although the values seemed high, latter work done by Wu-Haan, et al. (2007) gave reasonable reductions of 39 % which I selected as the control strategy to be applied to the already existing inventories so as to establish whether such strategies would be effective towards controlling $PM_{2.5}$.

After conducting simulations, I found that such a strategy applied only to chickens in the MANEVU region helps mitigate episodes in which we have moderately high $PM_{2.5}$. The regions nearest to the ammonia reductions get direct benefits of the ammonia control strategy and regions downwind of the source are benefited by the reductions only if the sulfuric acid concentrations are low as compared to nitric acid. This is because, I found that there is abundance of atmospheric ammonia and thus sulfates react first to give ammonium sulfate based fine particulate matter. Thus, the control strategy is now applied only to the nitrate based particulate matter. For low $PM_{2.5}$ episodes, I did not observe any significant reductions in fine particulate matter because the ammonia concentrations were already low and the abundant sulfuric acid, which reacts first, dominated the $PM_{2.5}$ mass. Thus there was very little ammonia for the nitric acid to react with and any reductions here would not count too much towards $PM_{2.5}$ reductions. However for moderate $PM_{2.5}$ episodes significant reductions were seen. Some areas experienced the benefit of having 2-6 hours of compliance over the base case. However for high $PM_{2.5}$ episodes only 2 hours of benefits were seen in some areas. This was primarily because there was a lot of ammonia as compared to the sulfate and nitrates and any reductions here would not matter much.

In addition to this work, I also did a study using ISORROPIA which is a thermodynamic equilibrium model for aerosol formation. The effect of varying ammonia reductions was seen on $PM_{2.5}$ mass and its component sulfate, nitrate and ammonium masses. It was seen that low ammonia reductions till 50 % have a linear relation with $PM_{2.5}$ reductions. However, higher ammonia reductions may not be effective because $PM_{2.5}$ reductions are limited due to formation of sulfuric acid aerosol at high ammonia reductions. A theoretical maximum of 61 % reductions in $PM_{2.5}$ was obtained for 100 % reductions in ammonia emissions, however this particular model did not consider transport and removal mechanisms, hence a region may experience greater reductions than predicted thermodynamically.

5.2 Future work

It was found that the selected control strategy primarily affects ammonium nitrate and affects ammonium sulfate only if the ammonia concentration in the region is low. Even then we still see benefits of this strategy in some regions. Regions close to the sources where ammonia reductions were applied saw improved compliance with the 15 $\mu g/m^3$ standard. As such, it is a worthwhile strategy considering the fact that the reductions were only applied to chicken related operations while larger sources of ammonia like cattle were left unchanged. It might be worthwhile to apply this strategy to a particular site and conduct field tests to determine the exact reductions obtained. Also, simulations of application of these strategies can be done in a very limited region using Gaussian dispersion models. These can then be verified with $PM_{2.5}$ readings near the field test sites. It must be noted that this study was done for May which is primarily summer, but studies can also be done for different seasons. I would strongly advise repeating this study for winter to test the effectiveness of such strategies in different seasonal conditions.

Also, as mentioned before I have only applied this strategy to chickens because of the lack of field test data for other categories of animals and it has been mentioned in literature that that this particular strategy has the potential to be applied to cattle and swine. Thus, it may be worthwhile to conduct field tests and develop optimized diets for these animals.

Finally, if all of the above can be done it is definitely possible that this strategy can be used by policy makers to help mitigate the $PM_{2.5}$ problems. Already, this strategy shows potential to bring a few areas into better compliance and if there are any non-compliant monitoring sites in the vicinity then it may help push these sites towards compliance.

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