



Modeling nitric oxide emissions from biosolid amended soils

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Abstract

Utilizing a state-of-the-art mobile laboratory in conjunction with a dynamic flow-through chamber system, nitric oxide concentrations [NO] were measured and NO fluxes were calculated during the summer, winter and spring of 1999/2000. The field site where these measurements were conducted was an agricultural soil amended with biosolids from a municipal wastewater treatment facility. These NO flux values were then used to assess the impact of including biosolid amended soils as a land-use class in an air quality model. The average NO flux from this biosolid amended soil was found to be exponentially dependent on soil temperature [NO Flux ($\text{ng N m}^{-2} \text{s}^{-1}$) = $1.07 \exp(0.14 T_{\text{soil}})$; $R^2 = 0.81$ —NO Flux = $71.3 \text{ ng N m}^{-2} \text{s}^{-1}$ at 30°C]. Comparing this relationship to results of the widely applied biogenic emissions inventory system (BEIS2) model revealed that for this field site, if the BEIS2 model was used, the NO emissions would have been underestimated by a factor of 26. Using this newly developed NO flux algorithm, combined with North Carolina Division of Water Quality statistics on how many biosolid amended acres are permitted per county, county-based NO inventories from these biosolid amended soils were calculated. Results from this study indicate that county-level biogenic NO emissions can increase by as much as 18% when biosolid amended soils are included as a land-use class. The multiscale air quality simulation platform (MAQSIP) was then used to determine differences in ozone (O_3) and odd-reactive nitrogen compounds (NO_y) between models run with and without the biosolid amended acreages included in the inventory. Results showed that during the daytime, when atmospheric mixing heights are typically at their greatest, any increase in O_3 or NO_y concentrations predicted by the model were small (<3%). In some locations during late evening/early morning hours, ozone was found to be consumed by as much as 11%.

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1. Introduction

It is well established that the primary source of nitric oxide (NO) emissions into the troposphere is anthropogenic activity. Soil emissions, however can also make a significant contribution to the NO inventory (Warneck, 2000). Depending on which NO budget is considered, soil emissions and biomass burning rank

either second or third behind fossil fuel combustion as the largest source of NO emissions. In fact, in some regions the soil contribution has been reported to be approximately equal to the emissions from anthropogenic sources (Yienger and Levy II, 1995). Because of its role in tropospheric ozone (O_3) formation, accurate inventories of NO are required to confidently run air quality models and to design and implement O_3 control strategies.

Williams et al. (1992) presented a model based on the strong dependence of biogenic NO emissions on soil temperature and land-use type. The algorithm which

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Table 1
Characteristics of grab samples of the soil at the research site and of the biosolids which are applied to the field

| Soil, grab sample | | Biosolids, grab sample | |
|--|--------------------------|--|---------------------------|
| Parameter | Quantity | Parameter | Quantity |
| Ammonia nitrogen (NH ₃ -N) | <28.6 mg-N/kg dry weight | Ammonia nitrogen (NH ₃ -N) | 23,080 mg-N/kg dry weight |
| Nitrate nitrogen (NO ₃ ⁻ -N) | <5.7 mg-N/kg dry weight | Nitrate nitrogen (NO ₃ ⁻ -N) | <256 mg-N/kg dry weight |
| Nitrite nitrogen (NO ₂ ⁻ -N) | <5.7 mg-N/kg dry weight | Nitrite nitrogen (NO ₂ ⁻ -N) | <443 mg-N/kg dry weight |
| Total Kjeldahl nitrogen | 753 mg-N/kg dry weight | Total Kjeldahl nitrogen | 41,700 mg-N/kg dry weight |
| pH | 5.83 | Phosphorus | 37,350 mg-N/kg dry weight |
| Soil class | Mineral | Percent Solids | 3.4% |
| Bulk density | 1.27 g/cm ³ | | |
| Particle density | 2.44 g/cm ³ | | |

Total Kjeldahl nitrogen = organic N + NH₃-N + NH₄⁺-N.

Williams et al. (1992) developed is one of the principal methods which researchers currently use to derive global and regional inventories of soil NO emissions (Yienger and Levy II, 1995; Thornton et al., 1997). In fact, many current air quality models derive the biogenic NO input data from the biogenic emissions inventory system (BEIS2) model which is based on a temperature and land-use algorithm proposed by Williams et al. (1992). While many studies have been conducted on fallow soils, forested soils, grassland, golf course soils, agricultural soils, etc., there are comparatively fewer studies on emissions from biosolid amended soils and therefore no land-use type for this category currently exists in the BEIS2 model.

Biosolids are often applied to the soil for their beneficial nutrient content (Table 1) and as a cost effective way to dispose of this byproduct of the wastewater treatment process. This nitrogen-rich source, through nitrification and denitrification processes, has the potential to result in increased emissions of NO (Warneck, 2000). Currently in the United States, approximately 6,000,000 metric tons of biosolids are generated annually (Peirce and Aneja, 2000). In this paper, a flux algorithm which has been previously developed to estimate NO emissions from biosolid amended soils is applied to those acreages in North Carolina which receive biosolid applications (Roelle et al., 2001). The field site where the measurements were made is located in central North Carolina, approximately 30 mile west of Raleigh. The sampling site, crop characterization and sampling scheme are described in Roelle and Aneja (2002) and the chamber design, associated mass balance equation and calibration procedures are described in Roelle et al. (1999).

The updated NO inventory, derived from the previously developed NO flux algorithm, will then be used to model changes in ozone concentrations ($\Delta[\text{O}_3]$) using the multi scale air quality simulation platform (MAQSIP). These ($\Delta[\text{O}_3]$) will be assessed by comparing the O₃ produced using the updated NO inventory (modified

case) to the estimated O₃ produced using the existing NO inventory (base case). The oxidized nitrogen species (NO_y = NO + NO₂ + HNO₃ + HONO + NO₃ + N₂O₅ + HNO₄ + PAN + RONO₂ + ROONO₂) and ratios of these species will also be modeled to help determine the end products of the increased NO emissions. This comparison will help to determine whether a significant error may exist in an air quality model by neglecting biosolid-amended soils as a land-use class when developing the NO emission inventories.

2. Description of model and inputs

2.1. Model

MAQSIP is a publicly available, fully modularized, three-dimensional modeling framework which has been developed through a cooperative agreement between the North Carolina Supercomputing Center and the US Environmental Protection Agency's (EPA) National Exposure Research Laboratory (NERL). The current MAQSIP model was developed with various options for describing regional and urban-scale air quality through physical and chemical processes. The spatial resolution used in this study was a 4 × 4 km grid cell, 38 m high, where one concentration per species per hour was calculated for each grid cell. The episode being examined is a 13-day period from 19 June–1 July 1996, and the model domain (480 km × 276 km) covers the majority of North Carolina. It should be noted that only the portion of North Carolina which coincided with the MAQSIP modeling domain is being used in this comparison.

2.2. Emissions data

Emission inputs into MAQSIP are provided by the sparse matrix operator kernel emissions (SMOKE) modeling system. The submodels for SMOKE are

Table 2
Estimated NO flux at field site sampled throughout 1999–2000

| Season | Existing BEIS2 model (g N) | New algorithm (g N) |
|--------------|----------------------------|---------------------|
| Winter | 28.2 | 265.5 |
| Spring | 58.7 | 1161.5 |
| Summer | 116.7 | 4089.7 |
| Fall | 64 | 1410 |
| Yearly total | 267.6 | 6926.7 |

First column represents estimates using existing BEIS2 model while the second column represents estimated NO flux using algorithm developed as part of this study.

biogenic, mobile, area and point emissions, which eventually are merged to produce emissions that are ready for input into the models timeline and grid system. The biogenic emissions processing submodel is essentially the biogenics emissions inventory system 2 (BEIS2) model which has been slightly modified to be compatible with SMOKE (Birth and Geron, 1995; MCNC, 2001). Currently, biogenic nitric oxide emissions are estimated in BEIS2 through a temperature and land-use relationship described in Williams et al. (1992) is given by

$$\text{NO Flux (ng N m}^{-2} \text{ s}^{-1}) = A \text{Exp}(0.071 T_{\text{soil}}), \quad (1)$$

where T_{soil} is in °C and the coefficient (A) is an emission factor that is experimentally derived and based on land-use. For each of the 4×4 km grid cells (= 1600 ha) in the model domain, statistics are available which describe the land-use in that grid cell. While this land-use approach is a significant improvement over the earlier methods which assumed constant NO emissions across all crops or forest types, it still fails to capture the emissions from all land-use types.

Table 2 shows the seasonal and yearly averaged NO emissions for this field site (~1 ha) using both the emissions algorithm determined for this site [$\text{NO Flux (ng N m}^{-2} \text{ s}^{-1}) = 1.07 \text{exp}(0.14 T_{\text{soil}}); R^2 = 0.81$] and the Williams model (Eq. (1)) where the corresponding A factor is based on the crop planted at this site (Rye). Table 2 highlights how the BEIS2 model would have underestimated the NO emissions during all seasons and for the entire year would have underestimated emissions by a factor of 26. Currently no land-use type exists for soils amended with biosolids, and the A factor used for biosolid amended soils is based on the crop-type planted at that field. Considering the significant source strength observed at this field site, it is possible that ignoring biosolids as a land-use class may result in underestimations in the regional biogenic NO emission inventories. Therefore, this study will modify the current land-use class (base case) so that these

biosolid amended acreages are represented in a regional biogenic NO inventory (modified case).

2.3. Source apportionment

The process of applying biosolids to soils in North Carolina requires a permit from the North Carolina Division of Water Quality. The Division of Water Quality maintains a database of all existing permits on a county-basis and although restrictions do exist that dictate where and when the biosolids can be applied, there is no restriction upon which crop they are applied (Barnett, 2000). For the purposes of this study, the acreages of biosolid amended soils within each county are assumed to be equal to the existing permits issued. It is not possible to ascertain where within each county the biosolids are applied, therefore the procedure used to apportion the biosolids within a county was to distribute them so that each 4×4 km grid cell within the county had the same percentage of biosolid amended soil in its respective cell.

County boundaries do not follow the same boundaries as the grid cells, and therefore there were often cells that contained acreages in two counties. In these instances, the county surrogate data, which identifies the fraction of a grid cell within a county, were used to apportion the biosolids accordingly. The increase in biogenic emissions of NO, resulting from the biosolid applications, was determined for each of the counties in the model domain to produce a modified NO inventory. The average increase of biogenic NO emissions in each of the North Carolina counties in the model domain can be seen in Fig. 1 which, as expected, shows the largest increase in those counties receiving the highest application rate of biosolids. (Note: The five counties with the highest biosolid application rates were: Gaston County, Brunswick County, Forsyth County, Granville County and Wake County) For example, in Gaston County NC, approximately 18% of the biogenic NO is due to biosolid amended soils, and in Brunswick County, Forsyth County, Granville County and Wake County, the contribution from biosolid amended soils increases the biogenic NO emissions by 10%, 14%, 9% and 7% respectively.

3. Results and discussion

In Figs. 2a and b, $\Delta[\text{O}_3]$ (modified case–base case) in pptV is plotted for a weekend episode during the early morning (4:00 a.m.—Fig. 2a) and also after sunrise (10:00 a.m.—Fig. 2b). In Fig. 2a, the areas of greatest $\Delta[\text{O}_3]$ are observed to coincide with the areas where the largest increases in biogenic NO emissions were observed (Fig. 1). Furthermore, these areas are all negative in value, as shown by the scale to the side of the figure,

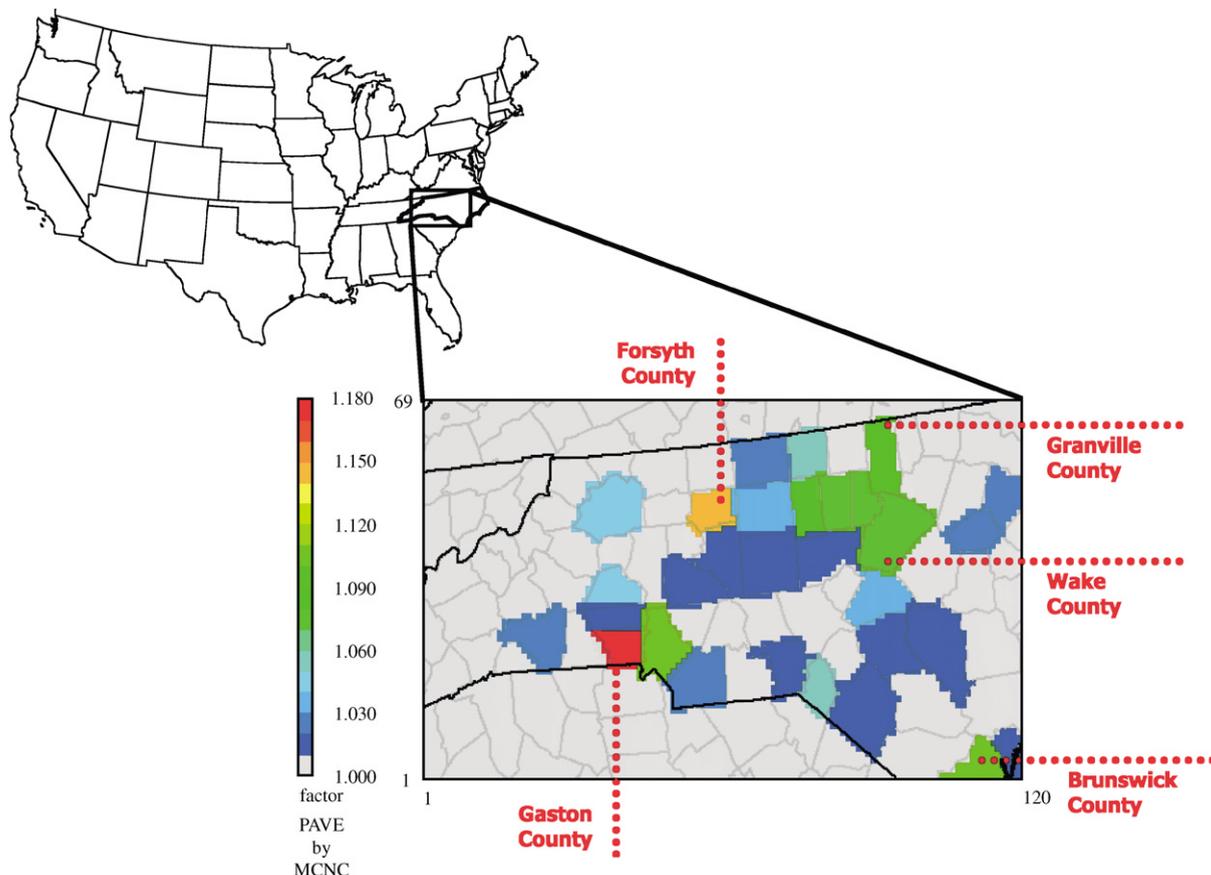


Fig. 1. Percent increase of NO resulting from including those acreages amended with municipal-waste biosolids in the current NO emissions inventory.

indicating ozone is being depleted. After sunrise (Fig. 2b), the same regions of maximum biosolid application continue to indicate the greatest ozone depletion, however the magnitudes begin to get smaller.

Interestingly, while the large urban centers (Charlotte, Raleigh, Winston-Salem) continue to indicate ozone depletion at 10:00 a.m., some of the more rural areas which also had high biosolid application rates are beginning to show modest increases in O_3 production. This relationship could confirm that some areas in North Carolina may be NO_x limited, meaning an increase in the NO_x emissions results in increased $[O_3]$. Throughout the afternoon hours (~11:00 a.m.–7:00 p.m.), no consistent changes in $[O_3]$ were observed on any of the modeled days. This same diurnal pattern of O_3 being consumed throughout the evening and then no changes being evident during the daylight hours was observed during all of the modeled days and can be explained by the combined effects of meteorology and chemistry.

It is well known that the mixed layer of the troposphere varies throughout the day. Typically, this

mixed layer will grow to its maximum in the afternoon (1–2 km) coinciding with the maximum daytime heating and will reach a minimum (1–100 m) in the evening/early morning hours (Stull, 1988). It is therefore expected that the greatest impact of any increased NO emissions would occur during the morning/evening hours when they are confined to the smallest mixing volume. Any increased emissions during the daytime would be rapidly diluted as the species mix through a significantly greater volume of the troposphere. The influence of chemistry also plays a significant role which is based on the following equation: $NO + O_3 \rightarrow NO_2 + O_2$. During daylight hours, NO_2 is photolyzed ($\lambda < 420$ nm) to eventually produce O_3 . However, during the evening, in the absence of photolytic activity, NO acts to remove O_3 throughout the night (Fourth Report of the Photochemical Oxidants Review Group, 1997). During the evening when the boundary layer is confined, and the biogenic NO source strength is increased as a result of the biosolids, ozone consumption is increased and most evident in the areas of greatest biosolid application, as shown in Fig. 2. However, as was shown

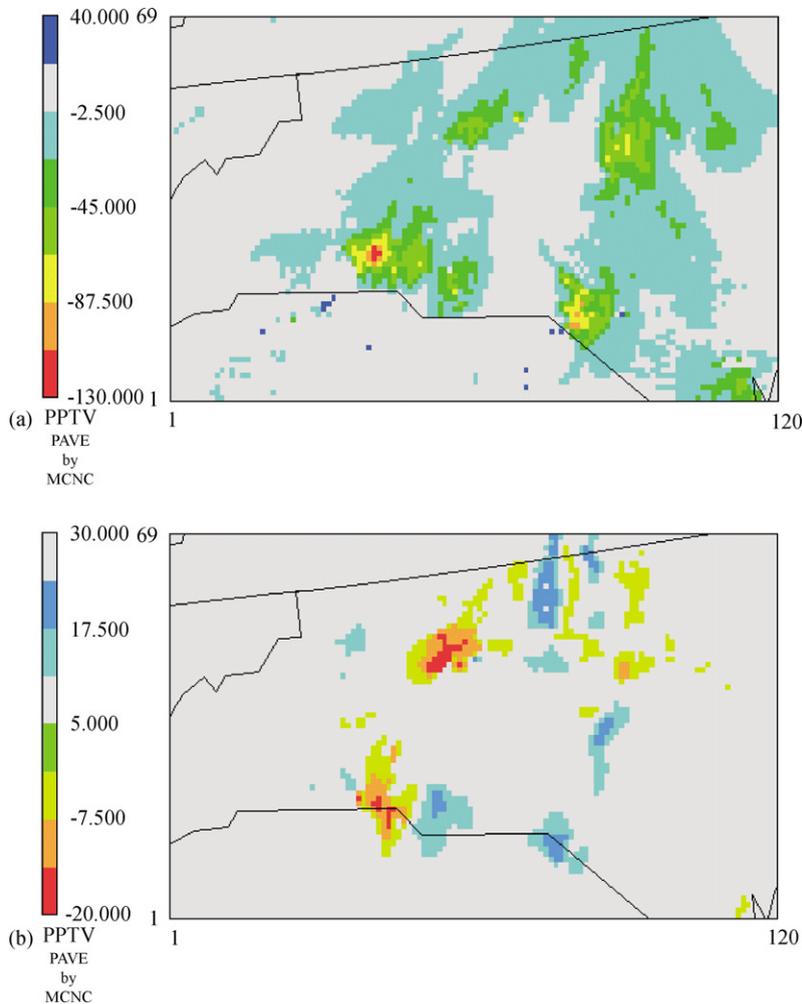


Fig. 2. Change in O_3 concentrations on Saturday, 29 June and Sunday, 30 June 1996 (modified case–base case) plotted at 4:00 a.m. (a) and 10:00 a.m. (b).

in Fig. 2b, there may be a few hours prior to the boundary layer reaching its maximum, and in regions which can be considered NO limited, that the increased NO results in slight increases of $[O_3]$.

It should be pointed out that all of the $\Delta[O_3]$ data presented in Fig. 2 are in units of pptV whereas ambient concentrations of O_3 during this same time period are typically on the order of 1–100 ppbV. At no time during the daylight hours does the $\Delta[O_3]$ approach the same order of magnitude as the ambient concentrations and is typically several orders of magnitude smaller indicating that during periods of greatest mixing the increase in NO has negligible consequences on overall ozone formation. The simulation with the overall greatest change in $[O_3]$ is plotted in Fig. 3 along with a time series of the data throughout a diurnal cycle. This relationship highlights that changes in daytime ozone concentrations (6:00 a.m.–6:00 p.m.) caused by the increased biogenic

NO emissions are almost non-existent and this is attributed to the diluting effect of the increased mixing volume. Any change at night consisted of ozone depletion, and was small ($<1\%$).

It is estimated that $\frac{1}{2}$ of the total cost of wastewater treatment is tied to disposal of the biosolids produced as a byproduct of the wastewater treatment process (Viessman and Hammer, 1993). Consequently, transporting distances will, in part, dictate where these biosolids are applied and evenly distributing the biosolids throughout the county may not be the most likely scenario. Therefore, in another scenario we have also analyzed the impact of concentrating the biosolids in only one area of the county. For example if a given county is known to apply biosolids to 500 ha, then in the model one grid cell in that county would receive all of these biosolids. Applying all biosolids in a concentrated region of the county produces more pronounced results.

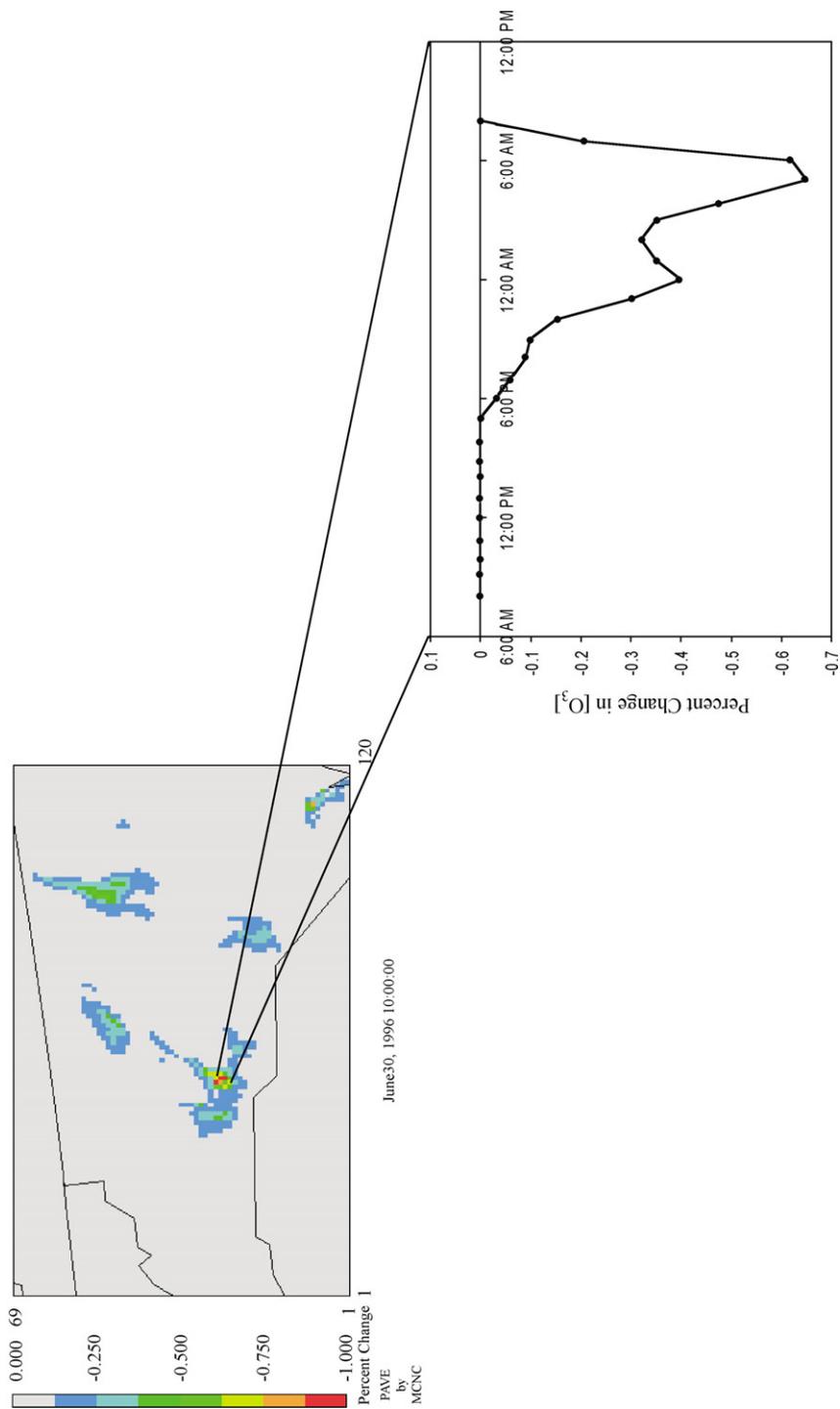


Fig. 3. Percent change of ozone (between the modified case and the base case) of ozone in the modeling domain. Time series plot represents the average percent change throughout the 24 hour period (8:00 a.m. Saturday–8:00 a.m. Sunday). Negative values indicate that ozone levels are lower in the modified case than in the base case.

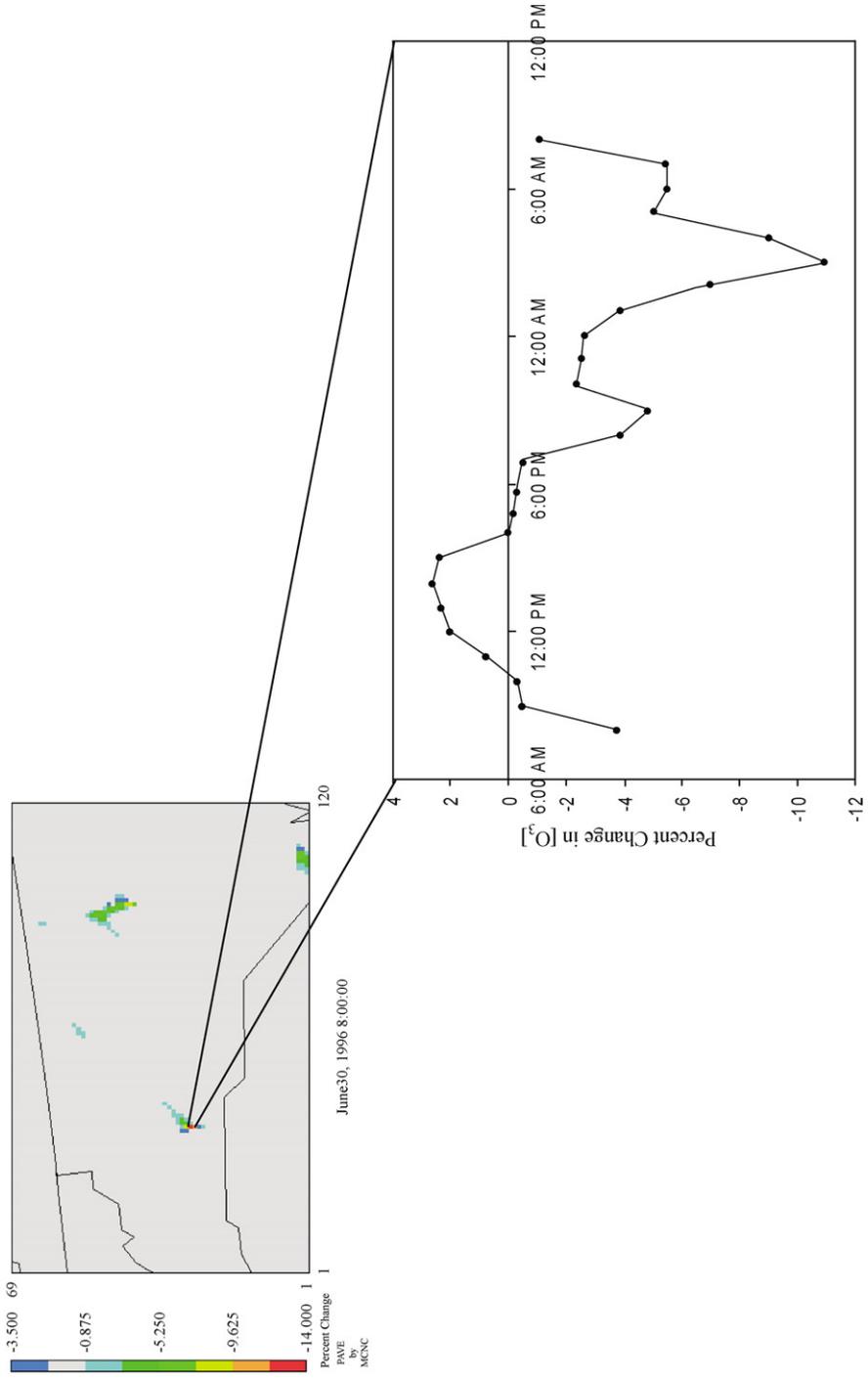


Fig. 4. Percent change of ozone (between the modified case and the base case) in the modeling domain with biosolids concentrated within the counties. Time series plot represents the average percent change throughout the 24 hour period (8:00 a.m. Saturday–8:00 a.m. Sunday). Negative values indicate that ozone levels are lower in the modified case than in the base case.

Fig. 4 shows the percentage change in $[O_3]$ and the corresponding time series of this change throughout a diurnal cycle at a Gaston County location. Like the other plots, the biggest change in $[O_3]$ occurs at night and consists of ozone depletion. Whereas the earlier method of evenly distributing the biosolids throughout the county resulted in changes of less than 1%, the concentrated biosolid areas now see ozone being depleted by as much as 11%. Further, for the first time, consistent trends of increased ozone production during afternoon hours were evident ($<3\%$).

In addition to O_3 production, as NO is oxidized it also gives rise to new compounds which are often grouped together in the family called NO_y . This family of odd-reactive nitrogen species consists of NO_x ($NO + NO_2$), nitric acid (HNO_3), nitrous acid ($HONO$), the nitrate radical (NO_3), dinitrogen pentoxide (N_2O_5), peroxy-nitric acid (HNO_4), peroxyacetyl nitrate (PAN) ($RC(O)OONO_2$), alkyl nitrates ($RONO_2$) and peroxy-alkyl nitrates ($ROONO_2$). Fig. 5 shows the percentage change in NO_y concentrations between the modified case and the base case where the biosolids have been evenly distributed throughout all grid cells in the county. Also included in Fig. 5 is the time series of the data with the greatest percentage change throughout a diurnal cycle which was observed to be in Brunswick County. Brunswick County is believed to have produced the largest change due to it being a relatively non-urban county with high-application rates of biosolids. Therefore, the effect of any increased NO as a result of the biosolid application is not diluted by anthropogenic sources as is believed to be the case in the more urban counties. As shown in the graph, any change in $[NO_y]$ during daylight hours was not evident and the maximum change throughout the evening was an increase in $[NO_y]$ of $\sim 2\%$. NO_y , which is a quasi-conserved quantity, is of significant atmospheric interest because through ratio analysis it is possible to examine the fate of the increased nitrogen and also to determine relative aging of an air mass (Roberts, 1995). During the nighttime, the increase in $[NO_y]$ observed in Fig. 5 can almost solely be attributed to the increased NO, as investigation of the changes in the ratios of all the individual species to NO_y resulted in changes of $<0.01\%$.

4. Conclusions and recommendations

Comparing the NO emissions inventory using an algorithm developed for this field site to results using the BEIS2 model revealed that, for this field site, the BEIS2 model would have underestimated NO emissions, on a yearly average, by a factor of 26. Applying this new observationally based model to the biosolid amended acreage data, a modified NO inventory was developed. It should be noted that the data used to produce this

revised inventory was from only one field site and has been extended to all soils throughout the model domain receiving the biosolids. Future studies should be conducted at other soils amended with biosolids to verify the relationships presented here. However, the exponential dependence of NO emissions on soil temperature has been consistently reported for various chemically fertilized soil and crop types and therefore provides some basis for this biosolid amended study to be extended to different soil and crop types throughout North Carolina (Thornton et al., 1997; Warneck, 2000). It should not be assumed, however that this temperature dependence can be extended to all temperatures, as temperatures outside the range of $15\text{--}35^\circ\text{C}$ are found to alter the often-cited exponential relationship (Sullivan et al., 1996).

The results of this research revealed that on a broad scale (entire model domain $\sim 132,000\text{ km}^2$), the contribution of NO from biosolid amended soils to the total biogenic emissions inventory in North Carolina is approximately 1%. It can be argued that when the entire model area is taken into consideration, biogenic NO emissions are $<5\%$ of the anthropogenic emissions, and therefore any modest increase in the biogenic source strength will likely have negligible consequences on tropospheric air quality. However, the majority of the anthropogenic emissions are concentrated in or around areas which contain large power plants or large urban centers. Consequently, in these industrial and urban areas, biogenics are a very small fraction of the total NO inventory. In the more remote/rural areas; however, biogenics can be as much as an order of magnitude larger than the anthropogenic NO emissions. Therefore, an underestimation of the biogenic NO in these remote regions could result in a significant bias in the emissions inventory for these areas.

Results from the model scenario (modified case–base case), where the biosolids were evenly distributed throughout the county grid cells revealed that any increased NO from biosolid amended soils produced $\Delta[O_3]$ several orders of magnitude smaller than background concentrations during daytime hours. During the late evening/early morning hours when the mixing volumes are at their smallest, $[O_3]$ were found to be reduced at most, by $<1\%$. During one particular episode, both ozone production and ozone depletion were observed during the same time period, possibly indicating that some of the more remote areas of North Carolina are NO_x limited. NO_y species showed slightly larger changes, although most of the increase could be attributed to the increased NO rather than to any of the oxidized products. In another approach, the biosolids were concentrated within the respective counties, in an attempt to account for the fact that $\frac{1}{2}$ of the total cost of wastewater treatment is estimated to be tied to disposal, and therefore wastewater treatment plants will likely

attempt to minimize transport distances (Viessman and Hammer, 1993). In this approach, ozone concentrations were found to be consumed by approximately 11% in the late evening/early morning hours and slight ozone production was observed during the afternoon (<3%).

Given that the production of biosolids will increase with population, there is a great likelihood that application rates will only get larger in the future. Significant NO emission datasets have been collected from agricultural soils amended with chemically derived fertilizers and as a result A factors (used in Eq. (1)) have been established for the vast majority of crop types. This study, which was conducted at only one field site, does demonstrate that biosolid application to agricultural soils can be ignored in terms of reactive nitrogen production on a regional scale. However, air quality modelers and those developing biogenic NO emission datasets should at least be aware of this potential source, especially when considering localized effects. Furthermore, additional soil and crop types amended with municipal waste biosolids should be investigated in order to gain more confidence in the A factors assigned to these land-use classes.

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References

- Barnett, K., 2000. North Carolina Department of Environment and Natural Resources, Division of Water Quality, non-discharge compliance/enforcement unit, Raleigh. Personal Communication.
- Birth, T.L., Geron, C.D., 1995. User's guide to the personal computer version of the biogenic emissions inventory system (PC-BEIS2). EPA-600/R-95-091.
- Fourth Report of the Photochemical Oxidants Review Group, 1997. Ozone in the United Kingdom, ISBN 1-870393-30-9.
- MCNC, 2001. <http://envpro.ncsc.org/NCDAQ/PGM/results;http://airchem.sph.unc.edu/DENR/index.htm>.
- Peirce, J.J., Aneja, V.P., 2000. Nitric oxide emissions from engineered soil systems. *Journal of Environmental Engineering, ASCE* 126 (3), 225–232.
- Roberts, J.M., 1995. Reactive odd-nitrogen (NO_y) in the atmosphere. In: Singh, H.B. (Ed.), *Composition, Chemistry, and Climate of the Atmosphere*. Van Nostrand Reinhold, New York, pp. 176–215.
- Roelle, P.A., Aneja, V.P., 2002. Nitric oxide emissions from soils amended with municipal-waste biosolids. *Atmospheric Environment* 36, 137–147.
- Roelle, P.A., Aneja, V.P., O'Connor, J., Robarge, W., Kim, D.S., Levine, J.S., 1999. Measurement of nitrogen oxide emissions from an agricultural soil with a dynamic chamber system. *Journal of Geophysical Research* 104, 1609–1619.
- Roelle, P.A., Baek, B.H., Aneja, S., Aneja, V.P., 2001. Nitric oxide emissions from biosolid amended soils. *Hydrological Science and Technology Journal* 17, 305–316.
- Stull, R.B., 1988. *An Introduction to Boundary Layer Meteorology*. Kluwer Academic Publishers, Boston, MA, pp. 2–26.
- Sullivan, L.J., Moore, T.C., Aneja, V.P., Robarge, W.P., 1996. Environmental variables controlling nitric oxide emissions from agricultural soils in the southeast United States. *Atmospheric Environment* 30, 3573–3582.
- Thornton, F.C., Pier, P.A., Valente, R.J., 1997. NO emissions from soils in the southeastern United States. *Journal of Geophysical Research* 102, 21189–21195.
- Viessman, W., Hammer, M.J., 1993. *Water Supply and Pollution Control*. HarperCollins, NY.
- Warneck, P., 2000. *Chemistry of the Natural Atmosphere*, 2nd Edition. Academic Press, Inc., New York, NY, pp. 511–517.
- Williams, E., Guenther, A., Fehsenfeld, F., 1992. An inventory of nitric oxide emissions from soils in the United States. *Journal of Geophysical Research* 97, 7511–7519.
- Yienger, J.J., Levy II, H., 1995. Empirical model of global soil-biogenic NO_x emissions. *Journal of Geophysical Research* 100, 11447–11464.