

The Environmental Impacts of Agricultural Soil-NO_x Emissions on Ambient Air, O₃ and NO_x Levels: A Conceptual Model Framework

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Abstract: Attaining the ambient standard for tropospheric O₃ has been difficult despite efforts to reduce anthropogenic sources of the O₃ precursors including nitrogen oxides and volatile organic compounds. Nitrogen oxides in soil are produced primarily by microbial processes. This study proposes a conceptual model to determine the environmental impacts of agricultural soil-NO_x emissions on ambient air O₃ and NO_x levels. A conceptual framework of the methodology is given in this study. The study concludes that the methodology will offer significant contribution to the assessment of soil-NO_x emissions on ambient air O₃ and NO_x levels.

Key words: Tropospheric O₃, ambient air, agricultural soil, emissions, precursors

INTRODUCTION

Attaining the ambient standard for tropospheric O₃ has been difficult despite efforts to reduce anthropogenic sources of the O₃ precursors including nitrogen oxides (NO_x = NO + NO₂ nitric oxide and nitrogen dioxide) and Volatile Organic Compounds (VOC) (Hall and Matson, 1996). Until recently, NO_x emissions from biogenic sources in soils were not considered in simulations of air quality and emission reduction scenarios yet they may be significant, especially in agricultural regions where nitrogen fertilizers are applied (Hall and Matson, 1996). Nitrogen oxides in soil are produced primarily by microbial processes. Production and emissions from soils are controlled by suite of environmental variables including inorganic nitrogen availability water-filled pore space and soil temperature (Hall and Matson, 1996). Agricultural management practices such as fertilization and irrigation affect these environmental variables and thus have the potential to dramatically alter NO_x emissions from soil (Hall and Matson, 1996). Therefore, it is important to study the environmental impacts of agricultural soil-NO_x emissions on ambient air O₃ and NO_x levels.

Environmental context: NO_x plays a key role in almost all aspects of atmospheric chemistry. Emissions of NO_x (NO_x = NO + NO₂) are key factors in tropospheric O₃ production and affect the oxidative capacity of the atmosphere. Until recently, NO_x emissions from biogenic

sources in soils were not considered in simulations of air quality and emission reduction scenarios yet they may be significant. This study proposes a conceptual model to determine the environmental impacts of agricultural soil-NO_x emissions on ambient air O₃ and NO_x levels.

LITERATURE REVIEW

NO_x in the earth's atmosphere and soil: NO_x plays a key role in almost all aspects of atmospheric chemistry. Emissions of NO_x (NO_x = NO + NO₂) are key factors in tropospheric O₃ production and affect the oxidative capacity of the atmosphere (Hall and Matson, 1996). NO_x is important due to its role in the atmospheric reactive nitrogen cycle acidification of precipitation and regulation of the O₃ level of the atmosphere (Galbally *et al.*, 2008; Crutzen, 1979).

The major global sources of NO_x are fossil fuel combustion, biomass burning, soils and lightning (Galbally *et al.*, 2008; Penkett *et al.*, 2003). It has been suggested that ambient NO_x concentrations influence NO_x dynamics in the Soil System (Remde *et al.*, 1989, 1993; Johansson and Granat, 1984; Slemr and Seiler, 1984, 1991; Williams *et al.*, 1988; Kim *et al.*, 1994; Johansson, 1984; Galbally *et al.*, 1987; Aneja *et al.*, 1995; Wesley *et al.*, 1989; Delany *et al.*, 1986; Galbally and Roy, 1978; Kessel *et al.*, 1992). For example in many cases in which NO_x emissions have been measured using closed chambers, atmospheric concentrations build up linearly

and then level off (Hall and Maston, 1996). Although, the mechanisms are poorly understood, Johansson and Grant hypothesize that either (a) microbial NO_x production is inhibited by ambient NO concentrations or (b) microbial NO_x production is not influenced by ambient NO_x but concentrations within chambers level off because of increased NO_2 deposition to plants and soil (Johansson and Granat, 1984). An additional hypothesis is that NO consumption is stimulated when the concentration of NO exceeds the compensation concentration the NO mixing ratio at which production and consumption of NO are in balance (Remde *et al.*, 1993). When the compensation concentration for a given soil is reached or exceeded net NO flux between the soil and the atmosphere is zero or may be negative (flux into the soil) (Hall and Maston, 1996).

Sources of NO in the earth's soil: Soil is the naturally occurring unconsolidated or loose covering of broken particles and decaying matter on the surface of the earth capable of supporting life. Soil has three components: solid, liquid and gas. Soil is an important contributor to global biogeochemical cycles and acts as an open chemical and physical system subject to element losses and gains (Lovett *et al.*, 2002). The transformation of geological substrate into soil involves material input and output in widely varying proportions depending on the environment these losses and gains can occur simultaneously (Brantley *et al.*, 2007). Mineral weathering produces solutes that may be exported resulting in mass loss. Plants take up and recycle mineral components (e.g., K, Ca and Si) that may be subsequently removed by water or wind. Wind erosion selectively removes fine particles from the soil surface, resulting in local landscape deflation and addition elsewhere. As soil develops it may gain significant amounts of atmospheric Carbon (C) and Nitrogen (N) which are reduced by biological activity and incorporated as dead biomass. The C and N are present as soil organic matter and are reused by organisms and eventually leached into rivers and groundwater or released back into the atmosphere. The soil is one of the planet's most active regions of energy exchange particularly through the decomposition of organic materials. Overall the earth's soil is the biologically active zone where the atmosphere, water, sunlight and the earth's crust mix and interact.

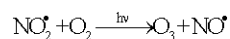
The natural production of NO_x in the soil is by microorganisms as a by product of nitrification and denitrification, two processes that convert nitrogen from one inorganic form to another and occur in many natural and agricultural ecosystems (Hall and Matson, 1996). Nitrification is the oxidation of ammonium (NH_4^+) to nitrite

(NO_2^-) and nitrate (NO_3^-) by a specialized group of bacteria that gain energy from the ammonium-oxidizing process (Chadwick *et al.*, 1998). Denitrification is a group of processes during which NO_3^- or NO_2^- is reduced to the gaseous nitrogen species, NO, N_2O or N_2 (Chadwick *et al.*, 1998). Denitrifying bacteria survive under anaerobic conditions by using NO_x as their electron acceptors in place of oxygen. In doing so they generate energy and reduced forms of nitrogen such as N_2O or N_2 . The general sequence of nitrogen species produced during denitrification is the following: $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$ (Hall and Matson, 1996).

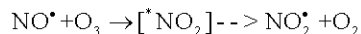
Recent estimates suggest that globally, microorganisms may release similar amounts of NO_x per year as combustion sources (20 Tg or NO-N) (Logan, 1983; Firestone and Davidson, 1989). The largest biogenic emissions of NO_x have been measured from systems that support rapid nitrogen cycling, high temperatures and/or seasonally low moisture including fertilized agriculture and seasonally dry tropical ecosystems. The various factors regulating NO_x emissions from soil are soil moisture, soil texture, nutrient availability, temperature, vegetation, ecosystem types, ambient atmospheric NO_x concentration and agricultural management (Hall and Matson, 1996).

O_3 and NO_x interrelationship: Tropospheric O_3 is a primary ingredient of photochemical smog the type of air pollution that is associated with sunlight-driven chemical reactions. The formation of O_3 results from complex interactions among nitrogen oxides (NO^* and NO_2^* with the sum denoted as NO_x) and Volatile Organic Compounds (VOC) and proceeds via a photochemical catalyzed reaction. The photochemical reactions that take place during O_3 formation are complex. Simply stated in the presence of sunlight, O_2 reacts with NO_x and VOCs to produce O_3 . The major reactions involved in the regulation of O_3 concentration in photochemical smog are summarized (Wilson, 2009).

NO_x , primarily produced by combustion engines (power plants, boilers, heaters, incinerators, trucks and automobiles) is a mixture of about 90% NO^* and 10% NO_2^* . In near UV sunlight ($\lambda < 430 \text{ nm}$) the NO_2^* reacts with O_2 to form O_3 and NO^* :



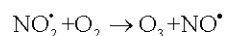
In a reverse process, NO^* slowly reacts with O_3 and destroys it even in the dark to make first an excited intermediate $^*\text{NO}_2$ which emits a photon and produced NO_2^* and O_2 :



In sunlight, VOCs which typically come from sources such as trees, gasoline, solvents and paint, recycle NO_x by reacting with NO^* to produce more NO_2^* , fueling the original reaction, resulting in further O_3 formed:



which leads to:



The environmental impacts of O_3 and NO_x are pollutants of concern because they are associated with extensive health effects. In humans, O_3 and NO_x are pulmonary irritants affecting the respiratory mucus membranes and other lung tissues, ultimately translating into respiratory dysfunction. As a gaseous pollutant its primary target tissue is the lung and breathing slightly elevated concentrations of O_3 and NO_x results in a range of respiratory symptoms. These include decreased lung function, airway inflammation, airway narrowing and hyper-reactivity, alterations of airway epithelial cell barrier function, altered mucociliary activity, pulmonary neutrophilia and activation of fibrogenic processes (USEPA, 1995; Cross *et al.*, 1998, 2001, 2002; Julliard, 1997; Frank-Piskorska and Piskorski, 2002; Churg and Brauer, 2000; Thron, 1996; Devouassoux and Brambilla, 2002; Handzel, 2000; Bromberg and Koren, 1995; Burnett *et al.*, 1999; Mikhailuts, 1980; Sharovsky *et al.*, 2004).

O_3 and NO_x can also affect both forest and agricultural crops. Ground-level O_3 can damage plants resulting in decrease of crop production and increased susceptibility to diseases. Ozone penetrates the leaves and needles of vegetation by way of the stomata and is then deposited on the water layer on the cells inside the leaves and forms free radicals and ions (e.g., HO_2 , $\bullet\text{HO}$, OH^- and O_2^-) which affect the cells (USEPA, 2006). Some agricultural crops such as tobacco and spinach are very sensitive to damage by O_3 while others are more resistant. Ecosystems such as forests are damaged by the same mechanism. NO_x forms acid rain contributes to global warming, hampers growth of plants and contributes to the haze air pollution in the national parks and wilderness areas (USEPA, 2006).

CONCEPTUAL MODEL FRAMEWORK

Until recently, NO_x emissions from biogenic sources in soils were not considered in simulations of air quality

and emission reduction scenarios yet they may be significant. Earlier studies have been performed to assess soil- NO_x emissions and the implications or effect on atmospheric chemistry (Hall and Matson, 1996). Studies using measurements from soil chambers in the field and laboratory experiments show that soil- NO_x emissions vary greatly with climate and edaphic conditions but are most strongly correlated with N-availability temperature and soil moisture making soil- NO_x dependent on regional temperature and precipitation patterns and fertilizer management practices (Hall and Matson, 1996). Soil- NO_x has been estimated on local, regional and global scales using process-based models, empirical models and by scaling field observations (Hall and Matson, 1996). Various models have included the hole-in-the-pipe model of Firestone and Davidson the NASA-CASA Model the DAYCENT Model, Berkeley-Dalhousie Soil NO_x Parameterization (BDSNP) and the TVA Soil NO_x Chamber Model (Davidson *et al.*, 2000; Hudman *et al.*, 2012; Parton *et al.*, 2001; Potter *et al.*, 1996; Valente and Thornton, 1993).

Proposed herein is a conceptual model framework that will be identified as the Agricultural Soil- NO_x /Atmospheric NO_x/O_3 Parameterization Model (Fig. 1). The conceptual model framework depicts the interrelationships of soil temperature/moisture and meteorological parameters, plants and microorganisms, soil NO_x emissions and ambient air, O_3 and NO_x levels on the overall analysis of the environmental impacts of agricultural soil NO_x emissions on ambient air, O_3 and NO_x levels.

Soil temperature, moisture, meteorological parameters, plants, microorganisms and ambient air, O_3 and NO_x levels

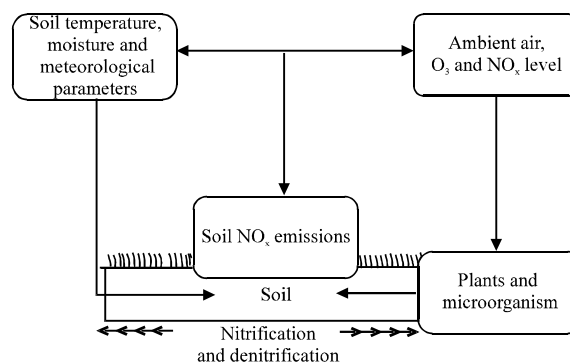


Fig. 1: Conceptual model framework: Agricultural Soil- NO_x /Atmospheric NO_x/O_3 Parameterization Model (— = direct impact). Soil temperature, moisture, meteorological parameters, plants, microorganisms and ambient air, O_3 and NO_x levels have a direct impact on soil NO_x emissions

have a direct impact on soil NO_x emissions. Having a direct impact means that variations in soil temperature, moisture content, wind direction and speed, humidity, types of plants grown, types of microorganisms, daily O₃ and NO_x levels can play a determinant role on soil NO_x emissions. It is expected that variations of soil NO_x emissions will exist on days when it is very warm, humidity is low and perhaps there is low wind speed and clear weather conditions versus a day when it is cold, humidity is high and there is high wind speed and poor weather conditions. Plants and microorganisms have various direct impacts on soil NO_x emissions. Plants take up and recycle mineral components (e.g., K, Ca, Si and N) that may be subsequently removed by water or wind which will ultimately directly impact soil NO_x emissions. As earlier stated, microorganisms play a direct role in the natural production of NO_x in the soil by serving as a by-product of nitrification and denitrification (Hall and Matson, 1996). Ambient air, O₃ and NO_x levels have a direct impact on soil NO_x emissions. It has been suggested that ambient NO_x concentrations influence NO_x dynamics in the Soil System (Remde *et al.*, 1989, 1993; Johansson and Granat, 1984; Slemr and Seiler, 1984, 1991; Williams *et al.*, 1988; Kim *et al.*, 1994; Johansson, 1984; Galbally *et al.*, 1987; Aneja *et al.*, 1995; Wesley *et al.*, 1989; Delany *et al.*, 1986; Galbally and Roy, 1978; Kessel *et al.*, 1992). For example, in many cases in which NO_x emissions have been measured using closed chambers, atmospheric concentrations build up linearly and then level off (Hall and Matson, 1996). Although, the mechanisms are poorly understood, Johansson and Grant hypothesize that microbial NO_x production which directly impacts soil NO_x emissions is inhibited by ambient NO concentrations (Johansson and Granat, 1984). It has been shown that ambient NO_x can damage the leaves of plants, decrease their ability to produce food (photosynthesis) and decrease their growth (USEPA, 1995). In addition to directly affecting plants, NO_x can directly impact meteorological conditions by producing acid rain and ultimately over fertilize sensitive ecosystems resulting in a range of harmful indirect effects on plants and soils changing in biodiversity, reduced tree growth, etc. (USEPA, 1995).

ANALYSIS OF CONCEPTUAL MODEL FRAMEWORK

Soil temperature/moisture and meteorological parameters: Currently, at Alabama Agricultural and Mechanical University (AAMU), the Department of Biological and Environmental Sciences (DBES), Center for Hydrology and Soil Climatology and Remote Sensing (HSCaRS) has established the Alabama Mesonet

(ALMNet) System (<http://wx.aamu.edu/ALMNet.php>). The ALMNet System is devoted to measuring meteorological as well as soil variable (i.e., air and soil temperature, soil moisture, wind speed, relative humidity, etc.). The ALMNet System has been in operation since, 2002. At each station, there exist soil moisture and temperature sensors that record soil moisture, temperature and salinity fluxes at five depth intervals from 5-100 cm. The soil-NO_x emissions monitoring chambers will be augmented with the existing ALMNet stations which are currently located across Alabama and southern Tennessee (21 across Alabama and 3 in southern Tennessee).

Assessing soil temperature/moisture and meteorological parameters is important because they have been found to play a significant role in soil-NO_x emissions. Earlier studies have shown that soils emit large quantities of NO_x at intermediate moisture levels, less under saturated or dry conditions (Anderson and Levine, 1987; Cardenas *et al.*, 1993; Colbourn *et al.*, 1987; Johansson and Granat, 1984; Johansson and Sanhueza, 1988; Keller and Reiners, 1994; Levine *et al.*, 1990; Matson *et al.*, 1996; Rondon *et al.*, 1993; Shepherd *et al.*, 1991; Slemr and Seiler, 1984, 1991; Stocker *et al.*, 1993; Thornton *et al.*, 1996; Thornton and Valente, 1996; Valente and Thornton, 1993; Williams and Fehsenfeld, 1991). Many studies have shown a positive relationship between soil temperature and NO_x emissions (Anderson and Levine, 1987; Johansson and Sanhueza, 1988; Shepherd *et al.*, 1991; Slemr and Seiler, 1984, 1991; Stocker *et al.*, 1993; Valente and Thornton, 1993; Williams and Fehsenfeld, 1991; Yamulki *et al.*, 1995; Williams *et al.*, 1988, 1987; Skiba *et al.*, 1992; Johansson, 1984; Bakwin *et al.*, 1992; Davidson *et al.*, 1993). Other studies have shown negative correlations with NO_x emissions (Aneja *et al.*, 1995). Overall, relationships have been shown between soil temperature/moisture and meteorological parameters and soil-NO_x emissions.

Plants and microorganisms: Plants and microorganisms have both indirect and direct effects on soil-NO_x emissions (Hall and Matson, 1996). Hall and Matson (1996) have shown that plants may affect soil-NO_x emissions indirectly by Hall and Matson (1996).

- Competing with microorganisms for soil ammonium and nitrate thus limiting nitrification and denitrification
- Altering microclimate at the soil surface (caused by canopy cover and evapotranspiration)
- Altering soil moisture, soil physical properties and pH

- Physically and chemically enhancing the habitats of microorganisms through the addition of carbon and nitrogen compounds to the soil system

Plants directly affect NO_x exchange between the ecosystem and the atmosphere through its ability to take up particulate and gaseous nitrogen compounds through stomata (Johansson, 1989).

As earlier stated, soil NO_x is produced by microorganisms as a by-product of nitrification and denitrification. Therefore, it is essential to assess the environmental impact of plants and microorganisms on agricultural soil- NO_x emissions on ambient air, O_3 and NO_x levels.

Soil NO_x emissions: The soil- NO_x emissions chamber is modeled after the Tennessee Valley Authority Soil- NO_x Chamber (Sharovsky *et al.*, 2004). It is a completely automated Closed-Chamber System (Sharovsky *et al.*, 2004). This Closed-Chamber System will cover 0.28 m^2 of soil area (Sharovsky *et al.*, 2004). The Closed-Chamber System is inserted into the soil to a depth of 10 cm and is equipped with air pressure so that the tops can be automatically raised and lowered onto the frame for a measurement (Sharovsky *et al.*, 2004). Consideration will be given to the effect on the measurement of withdrawing air from the chamber for sampling due to the fact that this is an operating closed-chamber system above the soil (Sharovsky *et al.*, 2004).

In studying soil- NO_x emissions one can assess the impact of land use on soil- NO_x emissions and create a database in order to assist in modeling the overall environmental impact of agricultural soil- NO_x emissions on ambient air, O_3 and NO_x levels.

Ambient air, O_3 and NO_x levels: NO_x plays a key role in almost all aspects of atmospheric chemistry. Emissions of NO_x are key factors in tropospheric O_3 production and affect the oxidative capacity of the atmosphere (Hall and Matson, 1996).

The ambient air monitoring station will measure NO_x/O_3 levels continuously. Ambient O_3 is NO_x -limited. Studying and measuring NO_x/O_3 levels in ambient air where soil- NO_x emissions might contribute significantly is important because NO_x/O_3 and the pollutant formed can be transported over long distances. This means that problems associated with NO_x/O_3 are not confined to areas where NO_x are emitted.

The analysis of the Agricultural Soil- NO_x /Atmospheric NO_x/O_3 Parameterization Model is shown in Fig. 2.

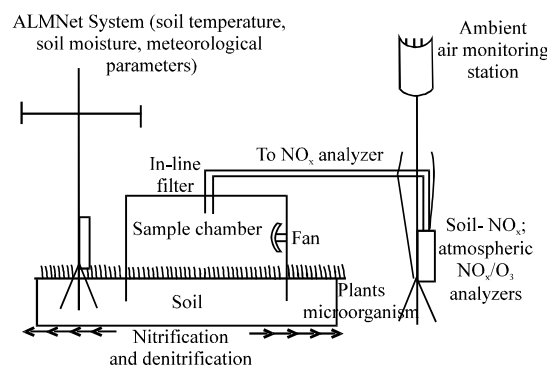


Fig. 2: Analysis of the Agricultural Soil- NO_x /Atmospheric NO_x/O_3 Parameterization Model. The conceptual model framework depicts the interrelationships of soil temperature/moisture and meteorological parameters (ALMNeT), plants and microorganisms, soil NO_x emissions and ambient air, O_3 and NO_x levels on the overall analysis of the environmental impacts of agricultural soil NO_x emissions on ambient air, O_3 and NO_x levels

CONCLUSION

There is an essential need to quantify soil- NO_x emissions and its role on O_3 and NO_x production in ambient air. This is essential due to the high concern of atmospheric pollutants and their effect on abiotic and biotic systems. The proposed Agricultural Soil- NO_x /Atmospheric NO_x/O_3 Parameterization Model will offer significant contribution to the assessment of soil- NO_x emissions on ambient air O_3 and NO_x levels. The contribution will ultimately lead to a regional and global awareness of the importance of implementing mitigation practices within the agricultural community which will lead to a decrease in soil- NO_x emissions and an overall improvement of ambient air with respect to O_3 and NO_x levels.

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