

Mechanisms, rates and assessment of N₂O in groundwater, riparian zones and rivers

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Keywords: nitrate, leaching, denitrification, nitrification, mitigation

ABSTRACT: Much of the fertilizer and manure nitrogen (N) that is applied to crop fields leaves the field in runoff and leaching to groundwater. This N is transformed as it moves across the landscape through riparian zones, rivers and estuaries and nitrous oxide (N₂O) is produced along the way. In this paper, we 1) discuss the mechanisms that lead to these "indirect" N₂O emissions, 2) describe the Intergovernmental Program on Climate Change (IPCC) methodology for assessing these emissions, 3) review the data in support of the methodology, 4) discuss implications for mitigation and 5) summarize with a case study for the nation of Denmark.

1 INTRODUCTION

Nitrous oxide (N₂O) is a "greenhouse" gas that influences radiative budget of the earth and contributes to stratospheric ozone destruction (Mooney et al. 1987, Prather et al. 1995). The concentration of N₂O in the atmosphere is increasing at a rate of 0.2 - 0.3% a year and is responsible for approximately 5% of the global enhanced greenhouse effect (Prather et al. 1995).

Under the terms of the United Nations Framework Convention on Climate Change (UNFCCC) and the Kyoto protocol, each nation is required to compile national emission inventories for radiatively active trace gases (CO₂, CH₄, N₂O). The Intergovernmental Program on Climate Change (IPCC) has developed protocols for quantifying N₂O emissions from industry, agriculture and natural ecosystems (IPCC 1997). The protocols for N₂O emissions from agriculture consider "direct" emissions from fertilized/manured crop fields as well as "indirect emissions." The indirect emission calculations attempt to account for N₂O production associated with transformations of the significant amount of the fertilizer nitrogen (N) that leaves crop fields in harvest, leaching and runoff or is transferred to the atmosphere (Mosier et al. 1996, 1998).

In this paper, we discuss the mechanisms and rates of N₂O emission associated with the N that leaves crop fields in leaching and runoff. The IPCC methodology for calculating indirect emissions is based on the idea that small amounts of N₂O are produced as agriculturally derived N moves through the landscape from fields to groundwater to streams to estuaries to the ocean. The validity of the methodology is hindered by the fact that the amounts of N moving across the landscape, and the emissions along the way, are poorly quantified. There is great interest in evaluating and improving the methodology because indirect emissions represent a significant fraction of the agricultural N₂O source. Moreover, there is potential for mitigation of indirect emissions because there are active efforts to control the movement of N across the landscape for water quality protection. Methods for controlling N movement could possibly be adapted to reduce N₂O emissions. In the sections that follow, we 1) discuss the mechanisms that lead to indirect N₂O emissions, 2) describe the IPCC methodology for assessing these emissions, 3) review the data in support of the

methodology, 4) discuss implications for mitigation and 5) summarize with a case study for the nation of Denmark.

2 MECHANISMS

It has long been known that a significant portion of the fertilizer and manure N that is applied to crop fields leaves the field in leaching and runoff. A general assumption is that roughly 50% of N applied is removed in harvest (Keeney and Follett 1991). Given that most agricultural soils are not accumulating organic matter (Paul and Clark 1996), the other 50% of applied N leaves by either hydrologic or gaseous pathways. In regions where precipitation exceeds evaporation, especially during the non-growing season, the dominant vector of N loss is hydrologic, primarily leaching of nitrate (NO_3^-). Nitrate is a drinking water pollutant and a prime cause of eutrophication in marine waters (Keeney 1986, Diaz 2001).

Once NO_3^- leaves crop fields it passes through the vadose (unsaturated) zone of the soil profile and into groundwater. While the potential for biological processing of NO_3^- in the subsurface is often thought to be low, many studies have found biological activity, including N_2O production in groundwater (Groffman et al. 1998). Groundwater-borne NO_3^- moves towards streams and is subject to processing in the near-stream (riparian) zone (Figure 1). In riparian zones, groundwater often approaches the soil surface where the potential for biological activity is much higher than in deeper aquifers. Once NO_3^- moves into streams, lakes estuaries and oceans, there is potential for biological processing in both the water column and sediments of these aquatic ecosystems.

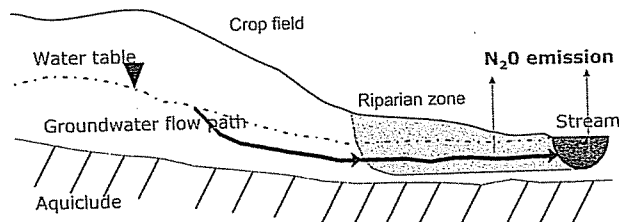


Figure 1. N flows through the landscape lead to indirect N_2O emissions from agriculture.

The dominant biological processes leading to N_2O production are denitrification and nitrification. Denitrification refers to the primarily anaerobic reduction of NO_3^- to nitrite (NO_2^-) and the N gases nitric oxide (NO), N_2O and dinitrogen (N_2). The yield of different gases is highly variable and is controlled by several environmental factors (e.g., oxygen, pH). Most of the denitrifying bacteria that have been studied are heterotrophic (use carbon as a source of energy), however there are some denitrifiers capable of deriving energy from the oxidation of inorganic compounds, e.g. pyrite (Hiscock et al. 1991). Denitrification is expected to be vigorous in wet, high C wetland soils and in the aerobic layers of aquatic sediments.

Nitrification refers to the oxidation of NH_4^+ to NO_2^- and NO_3^- by a specialized group of chemo-autotrophic bacteria that derive energy from these oxidations. N_2O is produced as a by-product of the oxidation of NH_4^+ (Davidson et al. 2001). The process is considered to be aerobic, but has been observed to occur under microaerophilic and anaerobic conditions (Firestone and Davidson 1989). Nitrification is expected to be vigorous in upland soils, the water column of lakes, streams and estuaries, and in aerobic layers of aquatic sediments.

3 IPCC METHODOLOGY FOR INDIRECT N_2O EMISSIONS FROM AGRICULTURE

The IPCC methodology for calculation of national emission inventories for agriculturally derived N_2O includes both direct and indirect emissions. Direct emissions from fertilized fields are assumed to be 1.25% of fertilizer and manure N applied to the field. Indirect emissions are:

$\text{N}_2\text{O}(\text{Indirect}) = \text{N}_2\text{O}(\text{G}) + \text{N}_2\text{O}(\text{L}) + \text{N}_2\text{O}(\text{S})$ where:

- $\text{N}_2\text{O}(\text{G}) =$ emissions associated with atmospheric deposition of agricultural N that has been transferred to the atmosphere.
- $\text{N}_2\text{O}(\text{S}) =$ emissions associated with human sewage.
- $\text{N}_2\text{O}(\text{L}) =$ emissions associated with the N that leaves crop fields in leaching and runoff.

$\text{N}_2\text{O}(\text{L}) = \text{NLEACH} * \text{EF5}$ where:

$\text{NLEACH} =$ the amount of N that leaves crop fields in leaching and runoff. This is assumed to be 30% of the fertilizer and manure N that is applied to crop fields.

$\text{EF5} =$ N_2O emission factor for N that leaves crop fields in leaching and runoff and is processed as it moves ultimately to the world ocean. This factor is assumed to be 2.5% and is partitioned as EF5-g (groundwater, 1.5%), EF5-r (rivers, 0.75%) and EF5-e (estuaries, 0.25%).

The indirect emissions represent 1/3 of total agricultural emissions and are dominated (75%) by those associated with leaching and runoff, which in turn is dominated (60%) by the emissions from groundwater. It is interesting to note that EF5 is the highest emission factor in the inventory methodology, higher even than the emission factor for direct emissions from fields. The uncertainty associated with indirect emissions is large and the dataset supporting EF5 is small (Nevison 2000).

The original formulation of EF5-g was based on the idea that some of the N_2O produced in surface soils is transported to groundwater with leaching water and eventually degasses to the atmosphere. The value of EF5 was derived from a small number of studies that reported $\text{N}_2\text{O}:\text{NO}_3^-$ ratios in agricultural drainage water. This formulation is problematic because it assumes that there is no biological processing of N and N_2O production between surface soils and streams (Groffman et al. 2000). Numerous studies of the vadose zone, groundwater and riparian zones have found active N processing and significant N_2O production along the pathway from fields to streams (Hill 1996, Lowrance 1998, Groffman et al. 1998, 2000). Degassing of surface-produced N_2O is likely important in areas with artificial drainage that greatly increases the speed, and reduces the biological processing, of water and N movement from fields to streams (Hack and Kaupenjohann 2002). Nevison (2000) reviewed the literature on groundwater degassing and suggested that the original value for EF5-g (0.015) was overestimated and should be reduced, possibly to as low as 0.001.

Values for EF5-r and EF5-e were based on the idea that N processing and N_2O production in rivers and estuaries are a function of NO_3^- inputs to these water bodies (Seitzinger and Kroeze 1998). The database in support of these factors is small. Moreover, factors such as water depth

and residence time may be more important controllers of NO_3^- processing and N_2O production in rivers than NO_3^- inputs (Cole and Caraco, 2000).

4 DATA IN SUPPORT OF THE IPCC METHODOLOGY

There are very few data available to validate the IPCC emission factors for N_2O emissions associated with leaching and runoff. This lack of data is in marked contrast to the emission factor for direct emissions, which is based on several hundred field studies (Bouwman 1996, Lagreid 2002). True validation of indirect emissions requires a combination data on N flows across the landscape with measurement of N_2O concentrations and fluxes. While hydrologic-based analysis of N flows in agricultural watersheds are relatively common, N_2O data are seldom collected in these studies. Evaluation of the methodology for indirect emissions is also complicated by the fact that these emissions are a spatially explicit phenomenon, involving the interaction of specific parcels of water with specific landscape features with different potential for N processing and N_2O production. It is difficult to incorporate spatially explicit phenomena into a methodology that is driven solely by the amount of N added.

Weller et al. (1996) presented data on N flows and N_2O emission from a small watershed in Maryland, USA with maize cropping in the upland and riparian forests at the interface between the fields and stream. N_2O production in the riparian forest was equal to 0.0065 kg N_2O per kg of NO_3^- input into the riparian forest, which is less than the IPCC value for EF5-g of 0.015.

We have produced estimates of riparian N_2O emission for an 850 km² watershed in Rhode Island that attempts to account for the spatially explicit nature of indirect emissions (Gold et al. 2002). The analysis considered variation in the amount of N that different riparian zones process by denitrification as well as variation in N_2O production during this denitrification (the $\text{N}_2\text{O}:\text{N}_2$ ratio). We accounted for variation in riparian denitrification using field data on riparian characteristics known to influence the ability of these areas to intercept and denitrify upland-derived NO_3^- (Rosenblatt et al. 2001). These characteristics were linked to soil characteristics (parent material, drainage class) that are included in new soils databases (SSURGO) available for many states in the U.S. (Soil Survey Staff 1997). Variation in $\text{N}_2\text{O}:\text{N}_2$ ratios was assessed with ¹⁵N-based field measurements at four riparian sites in the watershed. The analysis suggested that for the entire watershed, 0.014 kg N_2O were produced per kg of NO_3^- leached, a value very close to the IPCC value for EF5-g of 0.015.

Cole and Caraco (2001) assembled data on N_2O emissions from rivers and evaluated the assumption that these emissions are driven by NO_3^- inputs. They were able to assemble data from seven rivers and compared measured emissions with those derived from an emission-factor type model driven by NO_3^- input (Seitzinger and Kroeze 1998). The model tended to over-predict N_2O emissions, suggesting that river physical and/or biological characteristics may also need to be considered, along with NO_3^- inputs, as a driver of emissions.

There is a clear need for more data to evaluate the components of EF5. While the two riparian studies described above suggest that the values for EF5-g may be reasonable, the degassing-based formulation of this factor needs to be revised, and many more spatially explicit evaluations are needed to increase confidence in its validity. The analysis of N_2O emissions from rivers suggests that EF5-r may be an overestimate, but again, many more measurements are needed. More fundamentally, we need to consider if we need to make the methodology for computing indirect emissions spatially explicit to at least some degree. It is clear that there is great variation in the ability of groundwater, riparian zones, wetlands, rivers and estuaries to process agriculturally derived NO_3^- and produce N_2O . Incorporating this variation into the methodology may be critical for reducing the uncertainty associated with indirect emissions.

One efficient route to improving the database underlying the indirect emission calculations is to add N_2O measurements to existing hydrology-based studies of N flows in landscapes. For example, Steinheimer et al. (1998) presented data from 23 years of intensive monitoring of a 40 ha maize-dominated watershed in Iowa, USA. They determined that approximately 50% of the N ap-

pressed in the field due to multiple factor interactions and the effect of physical factors, e.g. diffusion, hydrologic flow path that are important in the field, but not in the laboratory (Blicher-Mathiesen and Hoffmann 1999). If we cannot control the ratio in landscape features that we are managing as NO_3^- sinks, we cannot use these features to mitigate indirect N_2O emissions.

6 INDIRECT EMISSION SCENARIOS FOR DENMARK

Data from the nation of Denmark are useful for illustrating the nature of indirect emissions and the potential for, and complexities of, options for mitigation of these emissions. An emission inventory for 1998 showed N input to crop fields (fertilizer plus manure) of 653 kt, which produces 196 kt of N leaching using the IPCC default leaching fraction of 30%. This application yields 8.2 kt of direct and 4.9 kt of indirect emissions of N_2O using the IPCC default factors of 1.25% and 2.5% for direct and indirect emissions respectively (Table 1).

Table 1. Nitrogen input, management and N_2O emission scenarios for Denmark using national input and leaching data for 1998 from Kyllingsbæk et al. (2001).

Scenario	N input -- kt --	N leached --- kt ---	Direct emissions ---- kt ----	Indirect emissions ---- kt ----	Total emissions ---- kt ----
Current	653	196	8.2	4.9	13.1
Reduce fertilizer input by 30%	457	137	5.7	3.4	9.1
Reduce leaching by 50%	653	98	8.2	2.4	10.6
Reduce leaching by 50%, but increase direct emissions by 50%.	653	98	12.3	2.4	14.7
Reduce indirect emissions by 50% by managing riparian zones.	653	196	8.2	2.4	10.6
Increase indirect emissions by 50% by managing riparian zones	653	196	8.2	7.4	15.5

These data allow us to explore the effect of different N management schemes on N_2O emissions. The most straightforward approach to N management is to reduce fertilizer input. A 30% reduction in input produces a 30% reduction in leaching losses and both direct and indirect emissions (Table 1, line 3). Reducing input is the only way to mitigate emissions in the current IPCC methodology. However, in some areas, reducing fertilizer input could result in unacceptable reductions in crop production. Moreover, in many areas, leaching is currently less than 30% and/or there are active efforts to reduce leaching to less than 30%. By the current methodology, a 50% reduction in leaching would yield a 50% reduction in indirect emissions and a significant reduction in total emissions (Table 1, line 3). However, the fate of N preserved by reducing leaching is unclear. If this N remains in the crop field, it can be cycled by plants and microorganisms with emission of N_2O . We must accept the possibility that reducing leaching could increase direct emissions from the field, resulting in an increase in total emissions, even though indirect emissions are reduced (Table 1, line 4). Research to determine the effect of leaching reductions on direct and indirect N_2O emissions should be a priority research topic and should be evaluated before the IPCC methodology is altered to allow for reduction of the 30% N leaching default value.

The data from Denmark also allow us to evaluate the possible effects of riparian zone management on indirect N_2O emissions. If we can develop clever ways to manage the $\text{N}_2\text{O}:\text{N}_2$ ratio during denitrification in these zones, there could be significant reductions in indirect emissions (Table 1,

we currently do not have a clever way to manage this ratio, it is quite important to manage riparian zones to prevent the movement of NO_3^- to coastal waters and to reduce N_2O emissions (Table 1, line 6).

For more data to evaluate the magnitude of indirect N_2O emissions and the reliability of the IPCC methodology for quantifying these emissions. Data on the landscape and the N_2O emissions associated with these flows are needed. We currently have active programs to assess the movement of water and N in many nations. Adding N_2O measurements to these programs would significantly reduce the uncertainty in the IPCC methodology for assess-

ing. To make the IPCC methodology for assessing indirect N_2O emissions more reliable and explicitly explicit. These emissions depend fundamentally on the interactions of NO_3^- -laden water interacting with specific landscape features and hydrology for transforming N and producing N_2O . In areas with well-developed groundwater, geology, soils and hydrology (e.g. SSURGO in the US) it is possible to markedly improve assessment of indirect N_2O emissions.

Managing indirect emissions is highly uncertain and somewhat controversial. There is great interest in managing N flows across the landscape for water quality and climate effects of this management on N_2O emissions is not clear. There is a need to evaluate the effects of water quality-based N management schemes on N_2O emissions (direct and indirect). There is potential for these schemes to reduce emissions. We need to develop techniques to manage the $\text{N}_2\text{O}:\text{N}_2$ ratio during denitrification.

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