# INDIRECT N<sub>2</sub>O EMISSIONS FROM AGRICULTURE

#### ACKNOWLEDGEMENTS

This paper was written by Cindy Nevison with the support of ICF Kaiser Incorporated. Cindy Nevison. would like to thank Peter Groffman, Sybil Seitzinger, Carolien Kroeze, Martin Schmid, Jeff Smith, and all members of the Wageningen expert subgroup on indirect  $N_2O$  emissions for their helpful comments.

#### ABSTRACT

Agricultural perturbations to the global nitrogen cycle, directly and indirectly, lead to enhanced biogenic production of nitrous oxide (N<sub>2</sub>O). Direct pathways include microbial nitrification and denitrification of fertiliser and manure nitrogen that remains in agricultural soils or animal waste management systems. Indirect pathways involve nitrogen that is removed from agricultural soils and animal waste management systems via volatilisation, leaching, runoff, or harvest of crop biomass. Like their direct counterparts, the long-term fate of agricultural nitrogen also eventually provides substrate for microbial nitrification and denitrification, with associated N<sub>2</sub>O production. According to the *Revised 1996 National Greenhouse Gas Inventories (IPCC Guidelines,)* and Mosier et al., 1998), indirect N<sub>2</sub>O emissions account for one third of the total global agricultural N<sub>2</sub>O source and approximately two thirds of the uncertainty in the total source. Indirect emissions include small contributions from human sewage and volatilised nitrogen, but are derived predominantly from nitrogen lost through leaching and surface runoff. Because of their importance in defining both the magnitude and the uncertainty of the agricultural N<sub>2</sub>O source, leaching/runoff emissions deserve high priority in any consideration of "good practice" in the IPCC methodology.

Three major areas of uncertainty in estimating leaching-related  $N_2O$  emissions are identified in this report. Firstly, the entire amount of fertiliser and manure, including that assumed to be volatilised and burned as fuel is subject to a default leaching fraction of 0.3. Secondly, under current practices, this default leaching fraction is commonly used by all countries, despite large variations within individual watersheds and agricultural systems. Finally, the  $N_2O$  emission factor assigned to leached nitrogen is estimated from a 3-step derivation which tracks the leached fraction through groundwater, rivers and estuaries, and broadly assumes some microbial  $N_2O$ production at each step on the basis of limited information. The groundwater step, which currently accounts for 60 percent of leaching-related  $N_2O$  emissions, is particularly problematic. In re-evaluating leaching/runoffrelated  $N_2O$  emissions, all of these areas of uncertainty should be addressed.

The volatilisation  $N_2O$  source in theory is meant to represent the fraction of fertiliser and manure that volatilises to  $NO_x$  and  $NH_3$  soon after application/deposition and subsequently redeposited on nearby soil, providing substrate for nitrification and denitrification. In practice, the current methodology formulation is fairly insensitive to assumptions about the volatilised fraction of fertiliser and manure. This is true because the direct and volatised  $N_2O$  emission factors are essentially the same (0.0125 and 0.01, respectively). Thus a re-evaluation of the default volatilisation fractions probably is not a first priority in refining the methodology. One question with respect to the volatilisation source might be, whether the distinction between 0.0125 and 0.01 is meaningful and is meant to be so.

Unlike leached and volatilised nitrogen, which are intricately linked to the direct and animal emissions methodologies, sewage nitrogen is estimated from independent activity data. The independence of the sewage nitrogen calculation is both a strength and a weakness of the current methodology. While cross-checks based on independent inputs are useful for validation purposes, one of the original goals of the methodology was to track agricultural nitrogen from "cradle to grave" in an internally consistent manner. Future refinement of the methodology might involve consistently linking harvested crop biomass to the long-term fate of sewage nitrogen, food waste, animal fodder and manure.

Quality assurance (QA) and quality control (QC) activities should encourage the collection of more countryspecific information to estimate the various fates of agricultural nitrogen and its associated  $N_2O$  emission factors. Because these data are sparse and likely to remain so in the near future, QA/QC efforts should also consider independent methods for validating methodology estimates. Two independent methods include the approach of Seitzinger and Kroeze (1998) for estimating nitrogen loading to rivers, and semi-empirical gas transfer calculations, in which  $N_2O$  flux from estuaries is estimated based on observed surface supersaturation of  $N_2O$ and modelled gas-transfer coefficients. When compared to the methodology estimates, the former would be useful for validating the estimated amount of leached nitrogen and the latter would be useful for validating  $N_2O$  emissions from estuaries. Gas-transfer calculations are probably best performed by an expert group rather than by individual Parties.

The methodology is based on widely available fertiliser, livestock population, human population and protein consumption activity data that are reported on a country-by-country basis to the United Nations Food and Agricultural Organization (FAO). The FAO data contain their own inherent uncertainties, and the inventory agency should ensure the accuracy of these inputs as well as the compiled inventory. The greatest uncertainty, however, in the indirect  $N_2O$  emissions estimate more likely stems from the methodology's detailed, multi-step assumptions about the fate of agricultural nitrogen and associated  $N_2O$  emission factors. In the case of Parties replacing default partitioning factors with country-specific information with respect to the fate of agricultural nitrogen, care must be taken that internal consistency of the methodology is maintained. Because of the complex logic of the methodology, the potential for omitting or double-counting some sources of  $N_2O$  production is significant.

Currently, insufficient information exists to evaluate the success of individual Parties in using the IPCC indirect emissions methodology. This is due, to a large extent, to the inadequacy of the reporting table in the *IPCC Guidelines*. Direct and most indirect emissions from the agricultural sector are lumped into one line called "Agricultural Soils." This label is a misnomer with respect to indirect emissions, since approximately 85 percent is estimated to come from groundwater, rivers, and estuaries. Some additional indirect agricultural  $N_2O$  emissions are reported in different sectors, including energy, waste, and land-use change. The dispersal of the indirect source among various sectors again illustrates the need for care in maintaining the methodology's internal consistency and for communication between inventory preparers.

## **1 INTRODUCTION**

## 1.1 Nature, magnitude, and distribution of source

#### 1.1.1 Overview of N<sub>2</sub>O emissions

Atmospheric  $N_2O$  is increasing at a rate of 0.2-0.3 percent/yr. This suggests an anthropogenic  $N_2O$  source about 50 percent as large as the natural microbial source from soils and oceans. Enhanced microbial  $N_2O$  production associated with agricultural perturbations to the nitrogen cycle accounts for an estimated 75 percent of this anthropogenic source. Biomass burning, which is closely tied to agriculture, supplies another ~7 percent, and direct industrial  $N_2O$  production contributes the remainder (IPCC, 1997). Natural and agricultural  $N_2O$  sources are not always easy to separate. Both are microbial in nature, and agricultural  $N_2O$  production to some extent has supplanted natural  $N_2O$  production (Mosier et al., 1998). The 1997 estimate based on the IPCC Phase II methodology suggests that, out of a total agricultural source of 6.3 Tg N/yr, 0.9 Tg N/yr overlaps with/replaces natural  $N_2O$  production in soils and oceans.

#### **1.1.2** Need for an indirect N<sub>2</sub>O emissions category

Estimates of the agricultural  $N_2O$  source in the early 1990s were based on global extrapolations of  $N_2O$  emission factors measured in fertilized fields. Because these measurements captured mainly direct short-term  $N_2O$  emissions, the resulting global estimates were often relatively small, ranging from 0.01 to 2.2, with mean values generally less than 1 Tg N/yr [*Eichner*, 1990; IPCC, 1990; *Matthews*, 1994]. These estimates suggested that fertiliser might be a modest or even relatively small source of the observed atmospheric  $N_2O$  increase. Increasingly, however, researchers began noticing elevated concentrations of dissolved  $N_2O$  in drainage ditches, groundwater, rivers and estuaries contaminated by agricultural and sewage nitrogen, leading many to suggest that indirect  $N_2O$  emissions associated with agriculture may be just as important as direct emissions (Dowdell et al., 1979; Ronen et al., 1988; Minami and Oshawa, 1990; Seitzinger and Kroeze, 1998). With this new perspective, recent  $N_2O$  inventories, which consider both short and long term fates of indirect agricultural nitrogen, have concluded strongly that agriculture is the dominant contributor to the anthropogenic  $N_2O$  source (IPCC, 1997).

#### **1.1.3** N<sub>2</sub>O production processes

 $N_2O$  production occurs primarily via microbial nitrification and denitrification. Nitrification is the aerobic oxidation of ammonium to nitrate, a process, which commonly accompanies the release (mineralization) of ammonium from organic matter during decomposition and contributes to the internal recycling of nutrient nitrogen. Denitrification is the anaerobic reduction of nitrate to molecular dinitrogen gas, a process, which accounts for the major loss of fixed nitrogen from soils and oceans. Nitrous oxide is an obligate intermediate in denitrification, and often comprises 5 percent or more of the denitrification end product in soils. N<sub>2</sub>O is also produced during nitrification, although by a less well understood mechanism. In normal oxygenated environments, N<sub>2</sub>O generally accounts for <1 percent of the nitrification end product in soils. The fractional N<sub>2</sub>O yield has been extensively studied in soil environments. It depends on a large number of variables including organic carbon availability, O<sub>2</sub> partial pressure, soil moisture content, pH, and temperature (Bouwman et al., 1993). Because of these multiple variables, the average soil N<sub>2</sub>O yield is still highly uncertain, especially from denitrification.

Most indirect agricultural  $N_2O$  production likely occurs in aquatic environments such as groundwater, rivers and estuaries, where much of the nitrogen lost from agricultural land through leaching, runoff, crop harvest and human consumption ultimately ends up. Measurements of fractional  $N_2O$  yields are sparse in aquatic environments, although the yields appear to be governed by many of the same variables described for soils. In rivers and estuaries,  $N_2O$  may be produced by nitrifiers and denitrifiers both in bottom sediments and in the water column. Commonly, a uniform yield of 0.5 percent for both nitrification and denitrification has been assumed for such environments (Mosier et al., 1998; Seitzinger and Kroeze, 1998).

#### **1.2** The current state of inventory methodologies

The *IPCC Guidelines* describe a comprehensive method, using widely available input data, which attempts to account for all  $N_2O$  emissions, both direct and indirect, associated with agriculture. The *IPCC Guidelines* encourage country-specific measurement programmes, particularly for tropical and developing countries, but provide default emission factors. Given the many detailed steps of the methodology, most Parties appear to be using the default values. The multi-step detail, however, is important for understanding the logic behind the methodology and as a starting point for revision and improvement.

The *IPCC Guidelines* divide the agricultural N<sub>2</sub>O source into 3 categories: direct emissions from agricultural land, emissions from animal waste management systems, and indirect emissions associated with N that is volatilised, leached, removed in biomass, or otherwise exported from agricultural land. Each of these 3 categories is estimated to contribute one third each to the total estimated agricultural source. Indirect emissions, however, account for a disproportionate share (approximately two thirds) of the uncertainty in the total source (Table 1), in which uncertainty is quantified mainly according to the range in the estimated N<sub>2</sub>O emission factors (see discussion below of EF4 and EF5). Thus, defining *good practice* for estimating indirect N<sub>2</sub>O emissions will go a long way toward narrowing the uncertainty in the total agricultural N<sub>2</sub>O emissions inventory.

Та	ble 1		
GLOBAL N <sub>2</sub> O emissions calculated with the IPCC Guidelines (Tg N y-1)			
Direct soil emissions			
• subtotal	2.1 (0.4-3.8)		
Animal production			
• subtotal	2.1 (0.6-3.1)		
Indirect emissions			
• atmospheric deposition	0.3 (0.06-0.6)		
nitrogen leaching and runoff	1.6 (0.13-7.7)		
• human sewage	0.2 (0.04-2.6)		
• subtotal	2.1 (0.23-11.9)		
Total	6.3 (1.2-17.9)		
*values in parentheses indicate estimate range which is derived from	n the emission factor ranges.		

The indirect emissions category consists in theory of 5 different sources:

- (i) Volatilisation and subsequent atmospheric deposition of NH<sub>3</sub> and NOx (N<sub>2</sub>O (G))
- (ii) Nitrogen leaching and runoff (N<sub>2</sub>O (L))
- (iii) Human consumption of crops followed by municipal sewage treatment (N<sub>2</sub>O(S))
- (iv) Formation of N<sub>2</sub>O in the atmosphere from NH<sub>3</sub>
- (v) Food processing.

In practice, sources D and E are not included in the methodology due to lack of information. Total indirect emissions are calculated as,

## $\label{eq:equation1} \begin{array}{l} \textbf{EQUATION 1} \\ \textbf{N_2O INDIRECT} = \textbf{N_2O}(G) + \textbf{N_2O}(L) + \textbf{N_2O}(S) \end{array}$

Of the 3 contributing sources,  $N_2O(L)$  accounts for over 75 percent of estimated indirect emissions, as shown in Table 1. In the methodology,  $N_2O(G)$  and  $N_2O(L)$  are closely linked to and dependent on assumptions about the fate of fertiliser and manure, while  $N_2O(S)$  is calculated from independent activity data.

## 2 METHODOLOGICAL ISSUES

## 2.1 Selection of the estimation method

The *IPCC Guidelines* outline a method for estimating indirect  $N_2O$  emissions from agricultural based on widely available fertiliser, crop production, human population, and livestock population and management data reported to the FAO. The guidelines involve factors which partition agricultural nitrogen into different various fates, such as leaching, removal from the field in crop biomass, and volatilisation, and which assign  $N_2O$  emission factors to each fate. Hereafter, these are referred to as partitioning factors and emission factors, respectively. Among 34 countries reporting greenhouse gas emissions from agricultural soils before August, 1998, 12 used the simpler 1995 IPCC Methodology, 7 used the *IPCC Guidelines* described below with default factors, 7 used country-specific factors, 2 used a mix of methods, and 6 provided no information about which method they used (Table 1, UNFCCC 1998/7). Note that the United Nations Framework Convention on Climate Change (UNFCCC) report did not partition agricultural soils by greenhouse gas (although presumably  $N_2O$  is the dominant component), nor did it partition  $N_2O$  methodology is unclear.

### 2.2 Science and logic behind factors and equations

## 2.2.1 Volatilisation and subsequent atmospheric deposition of NH<sub>3</sub> and NO<sub>x</sub>

 $N_2O(G)$  accounts for manure and fertiliser nitrogen that volatilises as  $NO_x$  or  $NH_3$  soon after application to soil, but subsequently redeposits on soil, providing nitrogen substrate for nitrifiers and denitrifiers. Model and measurement studies indeed suggest that most volatilised agricultural nitrogen simply redeposits on nearby soil.

#### EQUATION 2 $N_2O(G) = (NFERT \bullet FRACGASF + NEX \bullet FRACGASM) \bullet EF4$

Where:

FRACGASF:	partitioning factor for the fraction of synthetic fertiliser N applied to soils that volatilises as $NH_3$ and $NO_x$ (Default = 0.1)
FRACGASM:	partitioning factor for the fraction of livestock N excretion that volatilises as $NH_3$ and $NO_x.$ (Default = 0.2)
NFERT:	synthetic fertiliser use in country from Food and Agriculture Organisation (FAO) data (kg $N\!/yr)$
NEX:	amount of N excreted by livestock (kg N/yr). Calculated from FAO livestock populations and N excretion/animal data (Mosier et al., 1998)

EF4: emission factor for atmospheric deposition

Default partitioning factors assume 10 percent (FRACGASF) of synthetic fertiliser nitrogen and 20 percent (FRACGASM) of manure nitrogen are volatilised. The higher value assumed for manure reflects the greater likelihood of  $NH_3$  volatilisation from urea. The volatilised fractions are then assumed to redeposit and are assigned an emission factor EF4 of 0.01, on the basis of a limited number of studies of N deposition on soils (Bowden et al., 1991; Brumme and Beese, 1992) (see Table 2). (Note, these were generally forest soils receiving nitrogen deposition generated by energy use and industrial activities.) The default value of EF4 is very similar to EF1 =0.0125, the direct emission factor from agricultural land. EF1 was derived from a linear regression analysis of a much more extensive body of available  $N_2O$  measurements from fertilized fields (Bouwman, 1996).

Interestingly, if no volatilisation of fertiliser and manure nitrogen were assumed, this nitrogen would be subject to the very similar direct emission factor EF1 rather than EF4. The uncertainty in total agricultural N<sub>2</sub>O emissions therefore appears fairly insensitive to FRACGASF and FRACGASM, barring revisions in and divergence of the values of EF1 and EF4. Total emissions would, in fact, be completely insensitive, if EF1 were simply rounded off to 1 rather than set at 1.25. (Question: Is 3-significant-figure precision justified for a parameter that has a  $\pm$  80 percent uncertainty). One area for future improvement might involve evaluating whether the distinction between EF1 and EF4 is meaningful and intended or an artefact of the increased precision of EF1. Perhaps EF4 should simply be set equal to EF1, assuming a large fraction of volatilised agricultural nitrogen redeposits on nearby agricultural land rather than forest soil. A second area for future improvement might involve accounting for microbial N<sub>2</sub>O emissions associated with other sources of atmospheric NO<sub>x</sub> and NH<sub>3</sub> deposition, such as fossil fuel combustion. Such emissions should be assigned to the country which originates rather than receives the volatile nitrogen, as is currently done for agricultural NO<sub>x</sub> and NH<sub>3</sub>.

		TABLE 2			
SUMMARY OF DEFAULT EMISSION FACTORS RELEVANT TO INDIRECT $N_2O$ emissions					
Factor	Description	kg N <sub>2</sub> O-N/kg N input	Derivation		
EF1	direct emissions	0.0125	Linear regression of large number of measurements from agricultural soils (Bouwman, 1996)		
		(0.0025-0.0225)			
EF4	volatilisation/deposition emissions	0.01 (0.002-0.02)	estimated from small number of measurements from forests (Mosier et al., 1998)		
EF5	leaching/runoff emissions	0.025 (0.002-0.12)	estimated from 3-step derivation tracking leached nitrogen through groundwater, rivers, and estuaries (Mosier et al., 1998)		
EF6	sewage emissions	0.01 (0.002-0.12)	Same as EF5, but assuming no groundwater phase		

#### 2.2.2 Nitrogen leaching and runoff

 $N_2O(L)$  represents  $N_2O$  production by nitrification and denitrification of agricultural nitrogen that is lost from the field through leaching and runoff into groundwater, drainage ditches, rivers, and finally estuaries.

#### EQUATION 3 NLEACH = (NFERT + NEX) • FRACLEACH $N_2O(L) = NLEACH • EF5$

Where:

FRACLEACH: partitioning factor for the fraction of fertiliser and manure N applied to soils that is lost through leaching and runoff. Default = 0.3 (0.1-0.8)

EF5: emission factor for leaching/runoff

EF5-g (groundwater = 0.015)+EF5-r (rivers = 0.0075)+EF5-e (estuaries= 0.0025)

Note that all fertiliser and animal waste (i.e., NFERT + NEX), even that assumed to be volatilised or burned, is multiplied by FRACLEACH.

 $N_2O$  (L) is by far the major component of  $N_2OINDIRECT$  and is one of the major sources of uncertainty in the entire agricultural  $N_2O$  emissions estimate (Table 1). Hence, narrowing the uncertainty in the agricultural  $N_2O$  source requires careful re-evaluation of the assumptions used to derive  $N_2O(L)$  and consideration of independent methods that might be used to validate the  $N_2O(L)$  estimate. The uncertainties in  $N_2O(L)$  are threefold. They involve uncertainties in the nitrogen inputs, NFERT+NEX, in the partitioning factor FRACLEACH, and in the  $N_2O$  emission factor EF5. The entire nitrogen input from fertiliser and manure is multiplied by FRACLEACH. In contrast, in the direct emissions calculation, NFERT and NEX are scaled down by various partitioning factors

before multiplication by EF1. The true amount of nitrogen subject to leaching is uncertain, since the value of FRACLEACH derived for agriculture may not be appropriate for all fates of N. For example, a large fraction of the nitrogen content of animal waste burned as biofuel may be pyrodenitrified to atmospheric  $N_2$  (Crutzen and Andreae, 1990).

#### 2.2.2.1 FRACLEACH

In contrast to FRACGASF and FRACGASM, the total agricultural N<sub>2</sub>O emission estimate is highly sensitive to the assumed fraction (FRACLEACH) of synthetic fertiliser and manure lost to leaching and runoff. This sensitivity results from the fact that the emission factor EF5 =0.025 associated with leached nitrogen is twice as large as the direct emission factor EF1 =0.0125 from agricultural fields. Indeed, Monte Carlo simulations confirm that FRACLEACH is one of the major uncertainties in the total N<sub>2</sub>O estimate (Mosier et al. 1998). (Note, the sensitivity of the methodology to FRACLEACH may decrease if EF5 is lowered -see discussion below).

In known cases in which country-specific values of FRACLEACH have been used, lower values of 0.15-0.2 have been substituted for the current default of 0.3, leading to lower total agricultural N<sub>2</sub>O emissions (M. Schmid, Switzerland, private communication; R. Pipatti, Finland, private communication; K Rypdal, Norway, private communication, E. Rasmussen, Denmark, private communication, S. Jarvis, U.K., private communication; J. Smith, U.S.A., private communication; UNFCCC/SPSTA/1998/7 (for New Zealand)). While these country-specific values may well be based on good science and extensive measurements, in only one case (Switzerland) was sufficient documentation provided for this author, acting as an independent reviewer, to evaluate the appropriateness of the country-specific value (M. Schmid, private communication).

The Swiss value was based on a compilation of N leaching values (in kg N/ha/y) for various crops measured in Switzerland by lysimeters located just below the main rooting zone (Prasuhn and Braun, 1994). For each crop, a somewhat subjective average leaching value was taken and multiplied by the area (in ha) covered by that crop to calculate the total N leached. This sum was then divided by the total N input to agriculture from fertiliser, sludge, compost, and animal waste, yielding a value of 0.2 for FRACLEACH (although one could easily have chosen different averages to yield a FRACLEACH of 0.3). By way of validation, the averages of Prasuhn and Braun were used to estimate N loading in various Swiss rivers. These estimated N loadings generally compared well to observed N loadings, although the measured loadings were subject to large uncertainties. A further uncertainty in the comparison was that the N leaching inputs were reduced by 15-25 percent to account for reductions in N concentration that had been observed to occur between the root zone and groundwater from grassland and arable land through which cultivated fields drain. However, these reductions may not account for further N removal that occurs in the riparian zone between groundwater and rivers (Groffman et al., 1999). The Swiss example, which was by far the most thoroughly described FRACLEACH calculation available to this author, suggests the need for caution and clear guidelines before accepting country-specific values of FRACLEACH.

The current FRACLEACH default of 0.3 was based largely on the general knowledge of the expert group that met in Geneva in 1995, and the range of 0.1-0.8 was justified on the basis of the global-scale modelling study of N loading in rivers by Seitzinger and Kroeze, 1998. Otherwise, this default is not documented in Mosier et al., 1998. To critically examine the current default, I reviewed 6 specific case studies in which the inputs and outputs of agricultural N were explicitly measured at the watershed level over a number of years and a mass balance for N was constructed (Keeney and DeLuca, 1993; Randall and Iragavarapu, 1995; Weed and Kamwar, 1996; David et al., 1997; Randall et al., 1997; Steinheimer et al., 1998). (All these studies took place in the Midwestern U.S., generally in maize and/or soybean fields underlain by drainage tiles, which have been shown to increase leaching to rivers.) In these studies, the inorganic nitrogen loading in nearby rivers was typically equivalent about 20 percent of N inputs. Some variation was found between till and no-till systems and between crop types (deep rooted crops tended to reduce leaching loss), but by far the most significant factor determining interannual variability in leaching loss was precipitation. Low leaching and accumulation of inorganic soil N tended to occur during dry years, followed by large leaching losses in subsequent wet years. In one study, the fraction of N inputs leached ranged from 3-70 percent, depending on interannual variability in rainfall (Weed and Kanwar, 1996).

While the above discussion might suggest a value of 0.2 for FRACLEACH, a few cautionary notes are in order. First, these mass balance studies were somewhat inconsistent in their definition of N inputs and outputs. Some studies considered N<sub>2</sub> fixation and mineralization of crop residue as explicit inputs, while others ignored N<sub>2</sub> fixation and assumed that mineralization of last year's crop residue was simply balanced by uptake of N into the current crop stover. Moreover, lumping maize and soybean (an N<sub>2</sub> fixer) together, results in a larger crop uptake efficiency (>60 percent) for N inputs than the efficiency (<50 percent) that would be calculated if maize were considered separately (NRC, 1993; David et al. 1997).

Secondly, several studies found that  $NO_3^-$  concentrations in rivers were not necessarily correlated over time with fertiliser and animal waste inputs to nearby fields. These studies concluded, rather, that cultivation and tillage of soil, with or without fertiliser input, may enhance the rate of soil organic N mineralization, leading to large leaching losses (Keeney and DeLuca, 1993; David et al., 1997). Note that the IPCC currently does not consider this enhanced-mineralization source of leached N. Third, while ~20 percent of N inputs tended to end up in rivers, often, an additional ~30-40 percent of N inputs was unaccounted for (Keeney and DeLuca, 1993; Randall and Iragavarapu, 1995; David et al., 1997; Steinheimer et al., 1998). A variety of fates were suggested for this "missing" N, including denitrification, volatilisation to NH<sub>3</sub> or other reactive N gases (including through plant leaves), leaching into groundwater, and loss in the riparian zone. Note that these latter two fates would fall under the IPCC definition of NLEACH, and would imply that FRACLEACH should be greater than 0.<sub>2</sub>. Finally, the above studies do not consider organic N, which may constitute a significant fraction of total leached N (Seitzinger and Kroeze, 1998). Since FRACLEACH in theory encompasses total inorganic + organic N, studies that consider only inorganic N may underestimate the true amount of N leaching.

#### 2.2.2.2 EF5

The derivation of EF5, the leached nitrogen  $N_2O$  emission factor, involves a multi-step set of assumptions of nitrification and denitrification in groundwater and rivers and subsequent (de)nitrification in estuaries. The logic runs as follows: All of NLEACH enters groundwater or drainage ditches, where a fraction EF5-g =0.015 (0.003-0.06) is lost to  $N_2O$  within one year. EF5-g is based on a compilation of observed  $N_2O/NO_3^-$  ratios in groundwater and drainage ditches (Mosier et al., 1998). All of NLEACH then continues into rivers, where all is nitrified once during river transport and half is denitrified, i.e., lost to the atmosphere, by denitrification in river sediments. An  $N_2O$  yield of 0.005 is assumed for both nitrification and denitrification, resulting in a river  $N_2O$  emission factor EF5-r of 0.0075. The surviving half of NLEACH ultimately flows into estuaries, where half is nitrified and half is denitrified. Again, (de)nitrification  $N_2O$  yields are both assumed to be 0.005, resulting in an estuary  $N_2O$  emission factor EF5-e of 0.0025.

The assumption of 0.015kgN<sub>2</sub>O/kgN for EF5-g is based on literature search of 6 studies, in which the ratio of N<sub>2</sub>O/NO<sub>3</sub><sup>-</sup> in groundwater was found to range typically from 0.007 to 0.02 (Mosier et al., 1998 and references therein). The ratio in ditch water was found to be generally lower, i.e., 0.003 or less. This author's own review of 4 out of 6 of the cited papers and one other paper (see Table 3) shows lower yields of .0002-.0044 (groundwater) and 0.0005-0.01 (drainage ditches) and no strong difference between groundwater and drainage ditches (Dowdell et al., 1979; Ronen et al., 1988; Minami and Oshawa, 1990; Ueda and Ogura, 1991; Muehlherr and Hiscock, 1997). On the basis of Table 3, a value of 0.001 (0.0002-0.01) seems more appropriate for EF5-g than 0.015.

The observed  $N_2O/NO_3^-$  ratio in groundwater should be distinguished from that in the ocean. In ocean depth profiles,  $N_2O$ ,  $NO_3^-$  and  $O_2$  utilization are highly correlated, suggesting  $N_2O$  production associated with aerobic mineralization and nitrification (Yohinari, 1976; Cohen and Gordon, 1979). In groundwater, however,  $N_2O$  generally is not well correlated to  $O_2$  utilization (Ueda and Ogura, 1991), implying that the observed  $N_2O/NO_3^-$  ratio cannot be interpreted as the  $N_2O$  yield of in situ nitrification, as has been done in ocean analyses. In fact, Ronen et al. 1988 conclude that most  $NO_3^-$  in groundwater is not produced in situ. Despite this caveat, the observed  $N_2O/NO_3^-$  ratio in groundwater currently may be the best available parameter for linking  $N_2O$  to leached N.

		TABLE 3			
SUMMARY OF DEFAULT EMISSION FACTORS RELEVANT TO INDIRECT $N_2O$ emissions					
Referenc	<b>Study Location</b>	N <sub>2</sub> O/NO <sub>3</sub> <sup>-</sup>	Contaminants	Comments	
Drainage Ditches					
Dowdell et al. 1979	England	0.01 (month after fertilization) 0.01-0.001 (other months	Fertiliser	N <sub>2</sub> O shown as bars, NO <sub>3</sub> as curves on a very hard-to-read log scale graph	
Minami and Oshawa, 1990	Japan	0.0005-0.001	Fertiliser		
Groundwater					
Ronen et al., 1988	Israel	0.002-0.003	Fertiliser and Sewage, extremely contaminated	ratio of 0.06 cited in Mosier et al., 1998 is actually ratio of observed N <sub>2</sub> O:estimated NO <sub>3</sub> produced in situ	
Ueda and Ogura, 1991	Japan	0.0002-0.0044	Sewage	13 wells < 0.001	
				3 wells > 0.001	
Muelherr and Hiscock, 1997	England	0.0005-0.0025	Fertiliser	I assumed NO <sub>3</sub> is reported as mg NO <sub>3</sub> /L, as written. If actually mg N/L, then ratio is 0.0001-0.0006	

There may have been some confusion in the interpretation of Ronen et al. (1988), on the source of the highest cited groundwater  $N_2O/NO_3^-$  ratio of 0.06. Ronen et al. estimated the rate of in situ mineralization/nitrification based on organic C input to the aquifer, and then took the ratio of observed  $N_2O$  to the estimated fraction of  $NO_3^-$  produced in situ. The  $N_2O/in$  situ  $NO_3^-$  ratio is considerably higher than the actual observed  $N_2O/total NO_3^-$  ratio, which was only 0.002-0.003, even in the very contaminated aquifers they studied.

The derivation of EF5 in the IPCC Phase II methodology was a courageous first attempt to estimate the potential  $N_2O$  production associated with leached agricultural nitrogen. Each step of the 3-step derivation involves rough generalizations and assumptions based on limited information. One assumption that bears particular scrutiny is that all of NLEACH experiences a groundwater or drainage ditch phase, sufficient for 0.015kg  $N_2O$  -N/kg NLEACH to be converted to  $N_2O$ . Note that EF5-g accounts for 60 percent of the magnitude of EF5. All of NLEACH is assumed to survive the groundwater phase and subsequently to enter rivers. In other words, all  $N_2O$  observed in groundwater and agricultural drainage ditches is assumed to be produced by nitrification. However, Minami and Oshawa (1990) found that  $N_2O$  in drainage ditch water may have been derived partly from sediment denitrification, and Groffman et al., 1999 suggest that significant additional N losses may occur in the riparian zone between groundwater and rivers. Furthermore, the assumption of annual turnover of nitrogen in groundwater neglects deep aquifers, which may act mainly as a long-term sink for leached N.

EF5, as described above, in which groundwater is treated as a chimney which emits 60 percent of the  $N_2O$  associated with leached N, may be conceptually inconsistent with FRACLEACH, as derived from the mass balance studies described in Section 2.2.2.1. These studies generally quantify the fraction of leached N by dividing N loading in rivers by agricultural inputs. Often, a large fraction of leached N appears to be channelled more or less directly to rivers, bypassing the groundwater phase. When groundwater is considered in these mass balance studies, it is often mentioned mainly as a sink for the 30 percent or more of agricultural N inputs that otherwise cannot be accounted for. To be more conceptually consistent with FRACLEACH, the IPCC methodology should consider defining emission factors which distinguish between water-borne agricultural N that flows directly into rivers versus drains through groundwater and riparian zones. In the latter case, the amount of NLEACH should be reduced to account for N removal that occurs before the river stage. This discussion suggests that a uniform EF5 may not be appropriate for all leached agricultural N and may create the misleading impression that leaching-related N<sub>2</sub>O emissions occur primarily from groundwater. For example,

Seitzinger and Kroeze's estimated emission (primarily anthropogenic) of ~2 Tg N<sub>2</sub>O-N/yr from rivers, estuaries, and coastal areas, might be extrapolated on the basis of the current EF5 to suggest an additional 3 Tg N<sub>2</sub>O-N/yr from groundwater. This would be difficult to reconcile with the current understanding of the N<sub>2</sub>O source and the constraints imposed by the observed atmospheric increase (see discussion in Section 2.7).

## 2.2.3 Human consumption of crops followed by municipal sewage treatment

 $N_2O$  emissions associated with human sewage are reported under the Waste Sector rather than the Agricultural Sector (*IPCC Guidelines:* Reporting Instructions, Tables 4 and 6). However, human sewage ultimately is derived from agricultural nitrogen. Accordingly, the scientific basis for sewage  $N_2O$  emissions was developed by the agricultural working group and is discussed briefly below. The methodology does not consider direct  $N_2O$  emissions from sewage treatment plants. This decision was based on three studies that measured fairly negligible  $N_2O$  emissions from operating wastewater treatment facilities (Hemond and Duran 1989; Czepiel et al. 1995; Velthof and Oenema 1993). The methodology does consider crop nitrogen that ends up as human sewage in rivers and estuaries, where it provides substrate for nitrification and denitrification. Unlike the leached and volatilised fractions of fertiliser and manure nitrogen used to calculated  $N_2O(L)$  and  $N_2O(G)$ , microbial  $N_2O$  production associated with human sewage is calculated from activity data that are independent of the direct and animal emissions calculations. Sewage nitrogen is estimated based on protein consumption per capita multiplied by human population, with an assumed 16 percent N by weight of protein.

EQUATION 4 NSEWAGE = PROTEIN • FRACNPR • NRPEOPLE  $N_2O(S) = NSEWAGE • EF6$ 

Where:

EF6:	emission factor for sewage nitrogen
FRACNPR:	0.16kg N/kg of protein
NRPEOPLE:	human population from FAO data
PROTEIN:	annual per capita protein consumption from FAO data (kg/person/yr)

The N<sub>2</sub>O yield (EF6) of sewage nitrogen is based on a subset of the same assumptions that go into determining the leaching and runoff N<sub>2</sub>O yield. The main difference is that sewage N is assumed to be discharged directly to rivers, bypassing the groundwater phase, thus reducing EF6 to 0.01 versus 0.025 for EF5. The sewage N<sub>2</sub>O source is a fairly minor (~10 percent) contributor to total indirect emissions. Questions: Is the assumption of no groundwater phase universally applicable? In some countries, might not some portion of sewage effluent end up in groundwater, e.g., via septic tanks (Ronen et al., 1988; Ueda and Ogura, 1991). Second, could the estimate of NSEWAGE somehow be linked to the crop N biomass assumptions used to calculate direct N<sub>2</sub>O emissions, thus helping to validate and ensure internal consistency within the methodology (see further discussion under Completeness, section 2.6). Finally, should the methodology consider removal of nitrogen in wastewater treatment?

#### 2.3 Default versus country-specific factors

The accuracy and precision of  $N_2O$  emission factors are correlated to the number of samples and the frequency of sample collection. Because of limited sampling, even on a global scale, countries often use default factors that are based largely on studies of temperate agriculture. Emissions factors for  $N_2O$  in aquatic systems are particularly sparse in tropical regions. In terms of temporal variability, measurement of  $N_2O$  dissolved in agricultural drainage ditches and groundwater is especially important soon after fertiliser application, since concentrations may change by a factor of 10 or more over an annual cycle (Dowdell et al., 1979). Although regional, seasonal, and crop-specific emission factors are desirable, the large range of agricultural systems in most countries and the difficulty of establishing continuous or periodic monitoring programmes may be prohibitive to obtaining such data. Among the 34 countries that reported greenhouse gas emissions from agricultural soils, 13 used default emission factors, 9 used country-specific factors, 3 used a mix, and 9 provided no information about which factors were used (Table 2, UNFCCC 1998/7). Again, agricultural soils are not partitioned in the UNFCCC report by greenhouse gas or by direct versus indirect emissions and the relevance of these statistics to indirect  $N_2O$  emission factors is unclear.

In addition to  $N_2O$  emission factors, the methodology contains a number of nitrogen partitioning factors, including FRACLEACH, FRACGASM, and FRACGASF. As discussed earlier, total agricultural  $N_2O$  emissions are relatively insensitive to the assumed volatilisation fractions, but highly sensitive to the fraction of nitrogen assumed leached from agricultural soils and animal waste management systems. The UNFCCC 1998/7 report does not provide detailed information about whether default or country-specific partitioning factors are currently being used. New Zealand was cited as one Party, which used a country-specific leaching factor of 0.15, which is only half as large as the default factor of 0.3.

## 2.4 Activity data

Current activity data used to calculate indirect N<sub>2</sub>O emissions include commercial synthetic fertiliser consumption, livestock and poultry populations, data on animal waste management, crop production, partitioned into regular and nitrogen-fixing crops, grazing animal wastes, human population, and per capita protein consumption. The above inputs are generally available from UN/FAO yearbooks. Additional activity data that may be useful for estimating the leaching partitioning factor include data on river discharge and water runoff (Caraco and Cole, 1998). Factors used to convert activity data into parameters needed in the methodology include N excrement/animal/year and C/N ratios for regular and nitrogen-fixing crops. Note that the "Field Burning of Agricultural Residues" sector of the *IPCC Guidelines* Workbook provides C/N ratios for a more detailed partitioning of crops (Table 4-15). This is a duplication of effort/inconsistency that should be corrected in future versions of the workbook.

The FAO data, particularly the data on synthetic fertiliser production and consumption, are probably one of the most reliable aspects of the methodology. The choice of single year versus 3-year average FAO input data does not appear especially critical. The United States reported a < 5 percent difference in estimated agricultural N<sub>2</sub>O emissions between these 2 different types of activity data (Table 10, UNFCCC 1998/7).

## 2.5 Uncertainty

All 34 Parties reporting to the UNFCCC indicated "low" confidence in their estimates of N<sub>2</sub>O emissions from agricultural soils. "Low" confidence indicates an uncertainty of 50 to > 100 percent (UNFCCC 1998/7). Indirect N<sub>2</sub>O emissions are not specifically discussed in the UNFCCC report, but generally they account for the majority ( $\sim$ 2/3) of the uncertainty in the 1996 estimated global agricultural N<sub>2</sub>O source. High uncertainty is to a large extent inherent to biogenic processes like microbial N<sub>2</sub>O production.

### 2.6 Completeness

A review of 34 national inventories submitted to the UNFCCC indicates that 85% of countries reported on  $N_2O$  emissions from agricultural soils (Table 18, UNFCCC 1998/7). However, since indirect  $N_2O$  emissions are not specifically listed, the completeness of reporting in current inventories is difficult to assess. In terms of the completeness of the methodology itself in accounting for all agricultural  $N_2O$  emissions, several additional sources, which were considered but ultimately omitted from the 1996 methodology, should be discussed. (The counterpart to completeness, redundancy or double-counting, is also considered here.)

#### 2.6.1 Formation of N<sub>2</sub>O from NH<sub>3</sub> in the atmosphere

Dentener and Crutzen (1994) proposed that oxidation of  $HN_3$  and subsequent reaction of the intermediate  $NH_2$  radical with  $NO_2$  could lead to a production of  $0.6\pm0.3$  Tg  $N_2O$  -N/yr. They parameterised natural  $HN_3$  emissions from vegetation using a highly uncertain  $NH_3$  canopy compensation point (the atmospheric concentration above which plants assimilate and below which they emit  $HN_3$ ). Without considering this compensation point,  $N_2O$  production was reduced by 55 percent. Other sources of  $HN_3$  in the tropics include animal waste decomposition (both from wild and domestic animals), fertiliser application and biomass burning emissions. About half of the atmospheric  $N_2O$  production may be associated with agricultural nitrogen, amounting to about 0.25 Tg  $N_2O$  - N/yr-1. Due to the high uncertainty of this estimate (ca. 100 percent), this source was not included in the 1997 IPCC  $N_2O$  emissions inventory. Recent calculations suggest that this hypothetical source may have been overestimated (Dentener, private communication) and confirm that it should not be included in the inventory at this time.

### 2.6.2 Food processing (and other fates)

This category currently is not included in the methodology due to lack of information. The category was intended to encompass the potentially significant fraction of the harvested crop that is not consumed by people, but that may eventually lead to  $N_2O$  production, e.g., as landfill, compost, fuel for biomass burning, or fodder for livestock. The default recommendation is that 45 percent of the crop is harvested.  $N_2O$  production associated with the mineralization of the 55 percent remaining on the field is treated in the direct emissions calculation.  $N_2O$  emissions associated with the 45 percent harvested are partially accounted for through category C (sewage), (although these emissions are based on independent human population and protein consumption data and are therefore not cross-linked to the assumed crop fate.) Future refinement of the methodology may require establishing internal consistency within these different emissions categories associated with the long-term fate of crop biomass removed from the field.

Since indirect N<sub>2</sub>O emissions from agriculture are treated by a number of different sectors (Agriculture, Energy, Waste, Land-Use Change), inventory experts should take care to communicate with each other among these sectors, especially when substituting country-specific partitioning factors for default values. In part, this need for caution results from the conceptual incompleteness of the current methodology in tracking nitrogen from "cradle to grave." One example of a possible redundancy lies in the calculation of direct N<sub>2</sub>O emissions associated with mineralization of crop residue. Currently, the methodology assumes that 45 percent of total crop biomass is harvested and 55 percent, minus the 0-25 percent burned, is mineralised in the field. N<sub>2</sub>O emissions due to biomass burning estimate are handled by the Land-Use Change sector rather than the Agricultural sector. In some countries, a significant fraction of unburned crop residue may be fed to livestock. Since livestock manure is treated as an external nitrogen input, estimates of  $N_2O$  from manure and mineralization of crop residue may involve some double counting. Although this example is a fairly minor source of uncertainty (~5 percent of direct emissions), it illustrates the desirability of developing a more complete and unified accounting of agricultural nitrogen in future versions of the methodology (see Figure 1). Note that animal manure, in contrast to synthetic N fertiliser (which is manufactured industrially from atmospheric N<sub>2</sub>), is derived in part from harvested (e.g., corn, soybeans) and unharvested (e.g., rice straw) crop nitrogen and therefore is not a true external input to the system.

### 2.7 Consistency with atmospheric increase

The IPCC 1997 agricultural N<sub>2</sub>O source is estimated at 6.3 (1.2-17.9) Tg N/yr. Even without the additional 1.3 (0.7-1.8) Tg N/yr industrial and 0.5 (0.2-1.0) Tg N/yr biomass burning source, the mean and upper range of the agricultural estimate significantly exceed the observed atmospheric N<sub>2</sub>O increase of 3.9 (3.1-4.7) Tg N/yr. The N<sub>2</sub>O stratospheric sink has likely increased by 1-2 Tg N/yr due to the increased atmospheric burden of N<sub>2</sub>O. However, even with this adjustment, the 1997 IPCC total N<sub>2</sub>O source is difficult to reconcile with the observed atmospheric increase, which is one of the best and most precisely measured constraints available on the N<sub>2</sub>O budget (A. Khalil, International Workshop on the Atmospheric N<sub>2</sub>O Budget, Tsukuba, Japan, 1999.). The consistency of the agricultural N<sub>2</sub>O source estimate with the overall global N<sub>2</sub>O budget probably deserves more detailed discussion than it has been granted so far.

## **3 REPORTING AND DOCUMENTATION**

## 3.1 Current IPCC reporting guidelines

The *IPCC Guidelines: Reporting Instructions* are used to guide countries in the preparation and submissions of annual greenhouse gas emissions inventories to the UNFCCC. The Guidelines establish:

- Standard tables, definitions, units, and time intervals for reporting all types of emissions;
- Necessary documentation to enable comparison of national inventories, including worksheets, major assumptions, methodological descriptions, and enough data to allow a third party to reconstruct the inventory from national activity data and assumptions, and
- An uncertainty assessment.

Step by step directions for calculating indirect  $N_2O$  emissions from volatilisation and leaching are given in Workbook Section 4.6, steps 6-8, of the *IPCC Guidelines*. Directions for calculating indirect  $N_2O$  emissions from field burning of agricultural residue are given in section 4.5. Directions for calculating indirect  $N_2O$ 

emissions from sewage and biofuel burning of manure are presented in the Waste and Energy sections, respectively.

Indirect N<sub>2</sub>O emissions from volatilisation and leaching are reported in Table 4 of the Reporting Instructions of the *IPCC Guidelines*. (Sewage N<sub>2</sub>O emissions are reported separately in Table 6.) Unfortunately, direct emissions and indirect emissions in Table 4 are lumped into one line labeled "Agricultural Soils." This consolidation of the reported source hinders transparency and analysis of national emissions inventory reports (UNFCCC/SBSTA/1998/7). Furthermore, it is a misnomer with respect to indirect N<sub>2</sub>O emissions, since ~85% of these emissions is estimated to occur from aquatic systems rather than soils.

## 4 INVENTORY QUALITY

#### 4.1 Introduction

Inventory quality assurance and quality control (QA/QC) is a process integral to the development of a credible inventory. A well-developed and well-implemented quality assurance programme fosters confidence in the final inventory results regardless of the purpose and goal of the inventory. A successful quality assurance programme is two-fold requiring agricultural producer/government level procedures and external review and audit activities. The internal QC activities are designed to ensure accuracy, documentation, and transparency. The external review process is designed to minimize errors that occur in the preparation of emissions inventories, and reduce or eliminate potential inherent bias.

#### 4.2 Internal inventory quality assurance systems

#### Inventory agency review (QA) of agricultural inputs

Before accepting fertiliser consumption, crop production, and livestock population and production data, the inventory agency should carry out an assessment of data quality and auditing procedures. This type of review requires cooperation with agricultural producers and suppliers to obtain enough information to verify the reported emissions, as discussed above. The assessment should include identification of potential bias in the methodology and recommendations for improvement.

#### Inventory agency QC on compiling national emissions

In addition to a thorough quality assessment of the standard input data discussed above, the inventory agency should investigate additional country-specific information which could be used to replace default emissions factors or to provide independent cross-checks on the  $N_2O$  emissions estimated by the default methodology. This information would include, among other things:

- Fraction of nitrogen applied as synthetic and organic fertiliser lost to leaching;
- Dissolved N<sub>2</sub>O concentration in groundwater, rivers and estuaries contaminated by human and agricultural waste;
- Correlations between N<sub>2</sub>O, NO<sub>3</sub><sup>-</sup> and or O<sub>2</sub> in above areas;
- Fraction of sewage and agricultural waste discharged directly to rivers and estuaries, versus allowed to infiltrate groundwater;
- Turnover time of groundwater in contaminated aquifers, and
- River runoff rates.

#### 4.3 External inventory quality assurance systems

External QA activities include a planned system of review and audit procedures conducted by personnel not actively involved in the inventory development process. The key concept is independent, objective review to assess the effectiveness of the internal QC programme, the quality of the inventory, and to reduce or eliminate any inherent bias in the inventory processes. Several types of external reviews, or audits, may be appropriate for  $N_2O$  emission inventories.

#### Third party audit by an accredited organization, expert, independent third party

An audit of the documentation and calculations ensures that each number is traceable to its origin. Most of the information used in estimating indirect  $N_2O$  emissions from agriculture is generally available worldwide through the United Nations Food and Agricultural Organization (FAO) yearbooks.

#### Expert (peer) review

A detailed peer review would be appropriate when a procedure for determining  $N_2O$  emissions is first adopted or revised. Such a review generally would not be needed on an annual basis. However, to ensure that the methodology is as rigorous as possible, and that the data and assumptions used reflect the best available information, default factors and emission factors should be revisited as needed if significant restructuring occurs in a Party's agricultural system (e.g., changes in fertilization practices, irrigation, sewage management, livestock production systems, etc.).

Given the large uncertainties in both FRACLEACH and EF5 discussed in section 2.2.2, one of the best ways to build more confidence into the estimate of  $N_2O$  (L) might be to cross-check the methodology against independent calculations. One possible cross-check is the method of Seitzinger and Kroeze (1998), who describe a formula for estimating the amount of dissolved inorganic nitrogen that is exported by rivers as a function of fertiliser use, human population, atmospheric N deposition, and water runoff, which can be validated to some extent by empirical data. Seitzinger and Kroeze (1998) have shown that this formula is practical for global-scale analysis on a watershed basis. However, it cannot be used to calculate N leaching from agriculture on a national scale without modifications to the model. Moreover, this method does not provide an independent estimate of fractional  $N_2O$  yields, although it perhaps can help narrow the uncertainty in FRACLEACH, since it involves a validation of model N loading in rivers against measured values.

A second possible cross-check on predicted  $N_2O$  emissions from estuaries is the semi-empirical gas-transfer method (Nevison et al. 1995; Bange et al., 1996), in which measured surface  $N_2O$  supersaturation in coastal regions are multiplied by gas transfer factors to estimate flux to the atmosphere. The latter calculation is global by nature, and is probably best performed by an expert group rather than by individual Parties.

As an example of the cross-check, the IPCC methodology predicts that only 10% (EF5-e/EF5) of leaching emissions occurs from estuaries. Using Seitzinger and Kroeze's (1998) estimate that 75% of N loading to estuaries is anthropogenic, Bange et al.'s estimate of 2.3-3.6 Tg N<sub>2</sub>O -N/yr from estuaries, would imply that a total of 17-20 Tg N<sub>2</sub>O -N/yr is emitted from leaching-related sources! The Bange et al. estimate clearly appears too high, but a higher resolution semi-empirical gas-transfer calculation focused on estuaries could help clarify the leaching source and validate the IPCC methodology estimate.

#### Stakeholder review

Review by government and private agricultural organizations can provide a useful check on the methodology assumptions and default parameters. In some cases, sensitive issues concerning food production/security may be involved. Confidentially with respect to private businesses is probably not a major concern.

#### Public review

Some countries make their entire inventory available for public review and comment. This process may result in a range of comments and issues broader than those from other review processes.

#### REFERENCES

- Bange, H.W., S. Rapsomanikis, and M.O. Andreae. 1996. Nitrous oxide in coastal waters. Global Biogeochemical Cycles 10, 197-207.
- Bouwman, A.F., Fung, I., Matthews, E., and John, J. 1993. Global analysis of the potential for N<sub>2</sub>O production in natural soils, *Global Biogeochem. Cycles*, 7, 557-597.
- Bouwman, A.F. 1996. Direct emission of nitrous oxide from agricultural soils. *Nutrient Cycling in* Agroecosystems 46, 53-70.
- Bowden, W.B., and Bormann, F.H. 1991. Transport and loss of nitrous oxide in soil water after forest clearing, *Science*, 233, 867.
- Brumme, R. and Beese, F. 1992. Effects of liming and nitrogen fertilization on emission of CO<sub>2</sub> and N<sub>2</sub>O from a temperate forest. *J. Geophys. Res.* 97, 12851-12858.
- Caraco, N.F. and Cole, J.J., 1998, Human impact on aquatic nitrogen loads: A regional scale study using large river basins, *Ambio*, in press.
- Cohen, Y. and L.I. Gordon, Nitrous oxide production in the ocean, J. Geophys. Res., 84, 347-353, 1979.
- Crutzen, P.J. and Andreae, M.O. 1990. Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles. *Science 250*, 1669-1677.
- Czepiel, P. Crill, P. and Harriss, R. 1994. Nitrous oxide emissions from municipal wastewater treatment. *Environ. Sci. Techno. 29(9)*, 2352-2356.
- David, M.B., L.E. Gentry, D.A. Kovacic, and K.M. Smith, 1997. Nitrogen balance in and export from an agricultural watershed. *J. Environ. Qual.* 26, 1038-1048.
- Dentener, F.J. and P.J. Crutzen. 1994. A three-dimensional model of the global ammonia cycle. J. Atmos. Chem. 19, 331-369.
- Dowdell, R.J., J.R. Burford, and R. Crees. 1979. Losses of nitrous oxide dissolved in drainage water from agricultural land. *Nature*. 278:342-343.FAO. 1990a. Fertiliser Yearbook. Volume 39. FAO statistics series No. 95. FAO, Rome.
- Eichner, M.J., 1990, Nitrous oxide emissions from fertilized soils: Summary of available data, J. Environ. Qual., 19, 272-280.
- Food and Agricultural Organization (FAO) of the United Nations, 1947-1996: FAO Production Yearbook, FAO Stat. Ser., Rome, Italy, 1996
- Food and Agricultural Organization (FAO) of the United Nations, 1947-1996: FAO Fertiliser Yearbook, FAO Stat. Ser., Rome, Italy, 1996
- Groffman, P. et al. 1999. Nitrous oxide production in riparian zones. In preparation for submission to the Chemosphere special section on the International Workshop on the N<sub>2</sub>O Budget, Tsukuba, Japan.
- Hemond, H.F., and Duran, A.P. 1989. Fluxes of N<sub>2</sub>O at the seiment-water and water-atmosphere boundaries of a nitrogen -rich river. *Water Res*, 25, 839-846.
- IPCC. 1997. (Intergovernmental Panel on Climate Change/Organization for Economic Cooperation and Development). *Guidelines for National Greenhouse Gas Inventories*. OECD/OCDE, Paris.
- Keeney, D.R. and T.H. DeLuca. 1993. Des Moines river nitrate in relation to watershed agricultural practices: 1945 versus 1980s. J. Environ. Qual. 22, 267-272.
- Matthews, E., 1994. Nitrogenous fertilisers: Global distribution of consumption and associated emissions of nitrous oxide and ammonia, *Global Biogeochem. Cycles*, *8*, 411-439.
- Minami, K. and S. Fukushi. 1984. Methods for measuring N<sub>2</sub>O flux from water surface and N<sub>2</sub>O dissolved in water from agricultural land. *Soil Sci. Plant Nutr. 30*, 495-502.
- Minami, K. and A. Ohsawa. 1990. *Emission of nitrous oxide dissolved in drainage water from agricultural land. In: A.F. Bouwman (ed.). Soils and the greenhouse effect.* John Wiley & Sons, New York. p. 503-509.
- Mosier, A.R., J.M. Duxbury, J.R. Freney, O. Heinemeyer, and K. Minami. 1996. Nitrous oxide emissions from agricultrual fields: Assessment, measurement and mitigation. *Plant and Soil 181*:, 95-108.
- Mosier A., C. Kroeze, C. Nevison, O. Oenema, S. Seitzinger, and O. van Cleemput, Closing the global atmospheric N<sub>2</sub>O budget: Nitrous oxide emissions through the agricultural nitrogen cycle, *Nutrient Cycling in Agroecosystems*, *52*, 225-248, 1998.

- Muehlherr, I.H., and K.M. Hiscock. 1997. A preliminary assessment of nitrous oxide in Chalk groundwater in Cambridgeshire, U.K. *Applied Geochem.* 12, 797-802.
- National Research Council (NRC). 1993. Soil and Water Quality: An Agenda for Agriculture. National Academy Press, Washington, D.C.
- Nevison, C.D., Weiss, R.F., and Erickson III, D.J.: 1995, Global oceanic nitrous oxide emissions, J. Geo. Res. 100, 15,809-15,820.
- Owens, N.J.P. 1986. Estuarine nitrification: a naturally occurring fluidized bed reaction? *Estuarine Coastal and Shelf Science 33*, 31-44.
- Prasuhn, V. and M. Braun. 1994. Abschätzung der Phosphor- und Stickstoffverluste aus diffusen Quelle in die Gewässer des Kantons Bern. Schriftenreihe der FAC 18. Liebefeld-Bern.
- Randall, G.W., D.R. Huggins, M.P. Russelle, D.J. Fuchs, W.W. Nelson, and J.L. Anderson. 1997. Nitrate losses through subsurface tile drainage in conservation reserve program, alfalfa, and row crop systems. J. Environ. Qual. 26, 1240-1247, 1997.
- Randall, G.W. and T.K. Iragavarapu. 1995. Impact of long-term tillage systems for continuous corn on nitrate leaching to tile drainage. *J. Environ. Qual.* 24, 360-366.
- Ronen, D., M. Margaritz and E. Alman. 1988. Contaminated aquifers are a forgotten component of the global N<sub>2</sub>O budget. *Nature*. 335, 57-59.
- Schimel, D.S., Parton, W.J., Adamsen, F.J., Woodmansee, R.G., Senft, R.L., and Stillwell, M.A. 1986. The Role of Cattle in the Volatile Loss of Nitrogen from a Shortgrass Steppe, *Biogeochemistry 2*, 39-52.
- Seitzinger S.P. and C. Kroeze. 1998. Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems. *Global Biogeochem. Cycles.* 12, 93-113, 1998.
- Steinheimer, T.R., K.D. Scoggin, and L.A. Kramer. 1998. Agricultural chemical movement through a field-size watershed in Iowa: Surface hydrology and nitrate losses in discharge. *Environ. Sci. and Tech.* 32, 1048-1058.
- Ueda, S., N. Ogura and E. Wada. 1991. Nitrogen stable isotope ratio of groundwater N<sub>2</sub>O. *Geophys. Res. Lett.* 18(8), 1449-1452.
- Ueda, S., N. Ogura and T. Yoshinari 1993. Accumulation of nitrous oxide in aerobic groundwaters. *Wat. Res.* 27(12), 1787-1792.
- United Nations Framework Convention on Climate Change (UNFCCC), UNFCCC/SBSTA/1998/7 (www.unfccc.de, official documents, SBSTA), Methodological Issues: Methodological Issues Identified while processing 2nd National Communications: Greenhouse Gas Emissions Note by the Secretariat, UNFCC/SBSTA 1998.
- Velthof, G.L. and Oenema, O. 1993. Orienterende lachgasemissiemetingen in RWZI's. NMI-Report 93.263. Wageningen. 6p.
- Weed, D.A.J. and R.S. Kanwar. 1996. Nitrate and water present in and flowing from root-zone soil. J. Environ. Qual. 25, 709-719.
- Yoshinari, T. Nitrous Oxide in the Sea. 1976 Mar. Chem., 4, 189-202.

## QUESTIONS FOR PAPER ON DIRECT N<sub>2</sub>O EMISSIONS AND WORKSHOP DISCUSSIONS

Some of these may infringe on the direct and animal emissions categories, but since these are intricately related to indirect emissions (i.e., a reduction in direct emissions often means an increase in indirect emissions), they deserve mention here.

- 1) While N<sub>2</sub>ODIRECT uses the reduced inputs FSN and FAW, the entire synthetic fertiliser (NFERT) and animal (NEX) nitrogen inputs are subject to 30 percent (default) leaching. In calculating N<sub>2</sub>O(L), should FSN=NFERT (1-FRACGASF) be used instead of NFERT? And should FAW = (NEX  $\bullet$  (1-(FRACFUEL + FRACGRAZ + FRACGASM))) be used instead of NEX? These substitutions reduce N<sub>2</sub>O(L) to 0.9 rather than 1.6 Tg N<sub>2</sub>O-N/yr. (Furthermore, should not FAW be calculated rather as FAW = NEX  $\bullet$  (1-FRACGASM)(1-FRACFUEL-FRACGRAZ)?) In theory, FRACGAS(F,M) represents immediate volatization of NHx and NOx after deposition. It seems like double counting to assume that the volatized fractions (the entire amounts of which are subject to EF4) can also be leached.
- 2) Can the observed N<sub>2</sub>O/NO<sub>3</sub><sup>-</sup> ratio in groundwater be translated directly into an N<sub>2</sub>O emission factor? This is an important question because EF5-g accounts for 60 percent of the leaching emission factor, and is a principal reason why EF5 is so much larger than the other emission factors (and consequently, why the methodology is highly sensitive to the assumed leached fraction). If not, is there a better approach for determining EF5?
- 3) What sort of independent methods can be used to validate the standard methodology estimates?
- 4) The methodology is admittedly complex and the logic may appear convoluted to inventory experts who do not understand its basis. Parties are encouraged to substitute country-specific factors for default factors. However, could these substitutions lead to problems of omission or double-counting if experts do not understand the logic of the methodology? For example, if a country uses a large value of FRACBURN to reduce its direct N<sub>2</sub>O emissions associated with mineralization, it must be careful to account for the increased biomass-burning N<sub>2</sub>O emissions.
- 5) The example of sewage nitrogen being calculated from human population and protein consumption, rather than linked to crop harvest, illustrates the lack of complete internal consistency of nitrogen tracking within the methodology and as well as the difficulties of accounting for N<sub>2</sub>O emissions under separate categories of agricultural, waste, and energy-related emissions. Can the methodology be revised to meet its original goal of a complete "cradle to grave" accounting of nitrogen? Would this help eliminate confusion and overlap?
- 6) Is such a complex approach really necessary or justified? Does it all come out in the wash anyway (for example, the methodology is fairly insensitive to assumptions about volatilised fractions of fertiliser and manure)?
- 7) Does the increased precision of EF1 (0.0125) versus EF4 (0.01) have an unintended and artificial impact on the total agricultural emissions estimate, or does the higher value of EF1 reflect a meaningful distinction?