

<b>SNAP CODES :</b>	<b>100101</b>
	<b>100102</b>
	<b>100103</b>
	<b>100104</b>
	<b>100105</b>

<b>SOURCE ACTIVITY TITLE :</b>	<b>CULTURES WITH FERTILIZERS</b>
	<b>(Fertilized Agricultural Land)</b>
	<i>Permanent crops</i>
	<i>Arable land crops</i>
	<i>Rice fields</i>
	<i>Market gardening</i>
	<i>Grassland</i>

<b>NOSE CODES:</b>	<b>110.01.01</b>
	<b>110.01.02</b>
	<b>110.01.03</b>
	<b>110.01.04</b>
	<b>110.01.05</b>

<b>NFR CODES :</b>	<b>4D1</b>
	<b>4C</b>

## 1 ACTIVITIES INCLUDED

This chapter considers the emissions of ammonia (NH<sub>3</sub>), nitrous oxide (N<sub>2</sub>O), other oxides of nitrogen (NO<sub>x</sub>), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and non-methane volatile organic compounds (NMVOCs) from agricultural soils to which nitrogen (N)-containing fertilizers are applied. For NH<sub>3</sub>, emissions following application of animal manures to land are considered in SNAP code 100900, Manure Management Regarding Nitrogen Compounds. Although losses of NH<sub>3</sub> from N-fertilizers applied to grass grazed by livestock are difficult to distinguish from subsequent NH<sub>3</sub> emissions from urine patches produced by grazing animals, emissions are calculated separately; the calculation results are then compiled in this chapter. Ammonia emissions from grazed grassland due to decomposition of animal excreta applied to land are calculated in SNAP Code 100900, nitrous oxide losses after application are covered in this chapter. Persistent Organic Pollutants are dealt with separately under SNAP code 100600, Use of Pesticides.

This chapter is a development of chapter ag100100 (EMEP/CORINAIR 1999), which replaced its earlier version (EEA 1996).

The chapter is comprised of the following sub-codes

100101	Permanent crops
100102	Arable land crops
100103	Rice fields
100104	Market gardening

100105 Grassland

Sub-code 100106, Fallows, is not included, as N-fertilizer will not be applied to such land. In most cases there is insufficient evidence to discriminate between the sub-codes when estimating emissions. However there is some evidence that NH<sub>3</sub> emissions from grassland and rice fields are significantly different to NH<sub>3</sub> emissions from the other sub-codes. Separate NH<sub>3</sub> emission factors are therefore used for 100103 and 100105. Also separate emission factors are used for CH<sub>4</sub> in 100103 versus the other land use categories.

## 2 CONTRIBUTIONS TO TOTAL EMISSIONS

Fertilized agricultural land typically contributes approximately one tenth of the total source strength for European emissions of NH<sub>3</sub> (ECETOC, 1994; Bouwmann *et al.*, 1997) and NO (Skiba *et al.*, 1997), more than one third of N<sub>2</sub>O (Mosier *et al.*, 1998), and about 1 % of CO<sub>2</sub> (Freibauer 2002). On national level, the contribution varies widely among EU member states. Emissions of gaseous N species from fertilized agricultural land are generally related closely to the amount and, in some cases, the type of fertilizer-N applied.

The major source of NH<sub>3</sub> in Europe is volatilization from livestock excreta. 10 - 20 % of agricultural NH<sub>3</sub> emissions have been estimated to derive from the volatilization of N-fertilizers and from fertilized crops (Asman, 1992; ECETOC, 1994). This range may be compared with the estimate of the CORINAIR 94 inventory (ETCAE, 1997) shown in Table 2.1. CORINAIR estimated a contribution of *c.* 5 % to the total which is probably an underestimate compared with more recent numbers. The non-agricultural sources make only a marginal contribution to the total emission of NH<sub>3</sub> (Sutton *et al.*, 2000).

**Table 2.1: Relative contribution of cultures with fertilizers to total emissions in EU15 and accession states (25 countries) in 1995 (in %)**

Source-activity	NO <sub>x</sub>	NMVOC	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O	NH <sub>3</sub>
SNAP-code 100100						
Cultures with Fertilizers	4.0	0.4	0.2	1.2	30	5.3
Reference	Freibauer 2002, extended	ETCAE, 1997	Freibauer 2002, extended	Freibauer 2002, extended	Freibauer 2002, extended	ETCAE, 1997

Freibauer (2002) estimated that, via soil processes, fertilizers and crops contributed *c.* 42 % of N<sub>2</sub>O emissions on a European scale, including application of animal manures (30 % of total nitrogen fertilizer applied). Soils and crops are considered to be a net sink for most NO<sub>x</sub> (NO + NO<sub>2</sub>) compounds. However, NO may be released from soils during nitrification and denitrification following N application and mineralisation of incorporated crop residues and soil organic matter. Estimates of NO emissions are very uncertain, but soils may contribute *c.* 4 - 8 % of total European emissions. On a hot summer day this fraction may increase to values > 27 % (Stohl *et al.*, 1996, Butterbach-Bahl *et al.*, 2002).

A net carbon dioxide flux from agriculture (not regarding tractors and other machinery (see SNAP 0806, Other Mobile Sources, Agriculture) originates from land use changes and from the degradation of soil organic matter. The latter is of particular importance when organic soils are used as croplands.

In agriculture, methane is produced by anaerobic bacterial fermentation of organic matter in the presence of water. The three major sources are enteric fermentation (see SNAP 100400), manure management (see SNAP 100500) and wet rice production. Well aerated agricultural soils are a minor sink for methane, which is oxidized by methanotrophic bacteria. A mean consumption rate of about  $0.5 \text{ kg ha}^{-1} \text{ a}^{-1} \text{ CH}_4$  can be assumed for well aerated European agricultural soils (Freibauer, 2002). Even for countries with a low fraction of the surface covered with rice fields or wetlands – which are strong sources for atmospheric  $\text{CH}_4$  –, agricultural soils can be a net sink for methane (Roger *et al.*, 1999).

NMVOCs from this SNAP Code represent < 1 % of current total emission estimates, and do not therefore require a methodology for calculation yet. However, given current uncertainties over the magnitude of NMVOC emissions from agricultural crops, some information is given in this chapter, in order to provide background information and a tool to estimate the order of magnitude of these emissions as well as to highlight current uncertainties.

### 3 GENERAL

#### 3.1 Description

##### 3.1.1 Ammonia

The best information on  $\text{NH}_3$  emissions from cultures with fertilizers concerns the direct emissions following fertilizer-N application. The evidence for direct emissions from, and uptake by, plant foliage is also good (Schjørring and Mattsson, 2001), though estimates of net emissions are much more uncertain. Although estimates of the component emissions from crop foliage have been made (Denmead *et al.*, 1983; Nemitz *et al.*, 2000), it is often difficult to separate the direct fertilizer and plant emissions in practice, since both are a function of fertilizer-N supply, and in many experiments total emissions were measured. General reviews and estimates of  $\text{NH}_3$  from these sources have been provided by Asman (1992), ECETOC (1994), Sutton *et al.* (1995b) and Schjørring and Mattsson (2001).

Emissions of  $\text{NH}_3$  from mineral fertilizers depend on the type of N-fertilizer applied, soil type (especially soil pH), meteorological conditions and time of application in relation to crop canopy development (Holtan-Hartwig and Bøckmann, 1994; Générmont, 1996). In particular, the type of N-fertilizer applied has a great effect on the magnitude of emissions (Whitehead and Raistrick, 1990; ECETOC, 1994). Emissions are largest from urea fertilizer because urea hydrolysis in the soil releases  $\text{CO}_2$ , which creates a pH increase and favours  $\text{NH}_3$  volatilization. These emissions can be reduced significantly by use of urease and nitrification inhibitors (e.g. Gioacchini *et al.*, 2001, and literature cited therein). Emissions from ammonium sulphate (AS) may also be large, but these are very dependent on soil pH, with larger emissions from calcareous soils. Other fertilizers, such as ammonium nitrate (AN), are more neutral in pH and produce much smaller emissions. These are often difficult to distinguish in

measurements from plant-atmosphere fluxes. Fertilizers containing only nitrate ( $\text{NO}_3^-$ ) will not emit  $\text{NH}_3$  directly, but may increase  $\text{NH}_3$  emissions by the crop foliage.

Depending on the interpretation of results, emissions from growing vegetation and from decomposing grass herbage may be treated as an additional emission, or they may be included together with fertilizer emissions as a single emission factor. The time scale over which the emission estimates are made is important to note. Fertilizer emissions are largest in the days after fertilizer application, but in some instances (e.g. urea applied in dry conditions resulting in a slow hydrolysis), fertilizer emission may proceed for over a month after application (Sutton *et al.*, 1995a). For background emissions (other than initial fertilizer losses) during the plant growing period, most of the emission occurs indirectly from the foliage. However, as well as being influenced by air concentration and environmental conditions, both emission and deposition occur on diurnal cycles. It has been suggested that for some arable ecosystems, on an annual basis, foliar emission may balance dry deposition to the same vegetation (Sutton *et al.*, 1995a; Schjørring and Mattsson, 2001). Foliar emissions are expected to be larger from annual cereal crops than from fertilized agricultural grassland, since much of the emission may occur during the grain ripening and vegetation senescence phase (Schjørring, 1991). In contrast, where agricultural grassland, or other crops, are cut and left in the field for extended periods, decomposition may result in emissions of similar magnitude. Emissions from this source are extremely uncertain, and probably vary greatly from year to year depending on environmental conditions and success of harvests.

Emissions of  $\text{NH}_3$  from grazed grassland have been shown to increase with increasing fertilizer-N application (Jarvis *et al.*, 1989; Bussink, 1992). Moreover the proportion of  $\text{NH}_3$  emitted increases with increasing fertilizer-N.

Particularly large emissions (c. 30 % of N applied), have been measured following application of urea and ammonium sulphate (AS) to flooded rice fields.

The estimates of  $\text{NH}_3$  emission from decomposing crop residues are also extremely uncertain, and emissions from this source are likely to be very variable. The limited experimental work (Whitehead and Lockyer, 1989) found only emission from grass foliage with a high N content where much N-fertilizer had been applied, and was restricted to laboratory measurements which may overestimate emission. Recent measurements have also indicated significant  $\text{NH}_3$  emissions from decomposing brassica leaves, especially after cutting (Sutton *et al.*, 2000; Husted *et al.*, 2000).

### 3.1.2 Nitrous Oxide

In soil,  $\text{N}_2\text{O}$  is produced predominantly by two microbial processes, nitrification, i.e. the oxidation of ammonium ( $\text{NH}_4^+$ ) to nitrate ( $\text{NO}_3^-$ ) and denitrification, i.e. the reduction of  $\text{NO}_3^-$  to gaseous forms of N, ultimately  $\text{N}_2\text{O}$  and  $\text{N}_2$ . The rate of  $\text{N}_2\text{O}$  production is primarily dependent on the availability of mineral N in the soil (e.g. Granli and Bøckman, 1994; Bouwman, 1996) and on the microbial characteristics of the soil, some soils promoting denitrification until  $\text{N}_2$  and some other producing a large fraction of  $\text{N}_2\text{O}$  (Hénault *et al.*, 1998). Maximum  $\text{N}_2\text{O}$  emissions are generally observed within 2 to 3 weeks of N-fertilizer application. The magnitude of the emissions depend on the rate and form of fertilizer applied, the crop type and the soil temperature and soil moisture content. Application of N-fertilizer to, or incorpo-

ration of N-rich crop residues into, moisture-retentive soils produces greater N<sub>2</sub>O emissions than application to free-draining soils (Skiba *et al.*, 1992). Repeated changes in soil moisture status and re-wetting of dry soil promote episodic high N<sub>2</sub>O emission rates (Flessa *et al.*, 1995). Application to or incorporation into warm soils is also likely to lead to greater emissions than from soils which are cold. However, recent studies showed, that the largest N<sub>2</sub>O emissions occur during thawing of frozen soils (Müller *et al.*, 1997), and the total emissions between November and February were 50% of the total annual flux (Kaiser *et al.*, 1997). Rapid crop growth, and demand for NO<sub>3</sub><sup>-</sup>-N, will reduce N<sub>2</sub>O emissions by reducing the pool of mineral N available for denitrification (Yamulki *et al.*, 1995). Increased exudation of C from plants may also increase denitrification.

At the present stage of knowledge, too few data are available to derive emission factors for different fertilizers or soil types from existing data (Bouwman, 1996; Hénault *et al.*, 1998). In contrast, different emission factors have been estimated according to the type of crop in Scotland (Skiba *et al.*, 1997; Dobbie *et al.*, 1999), with larger emission factor for grassland, sugar beet, potato and horticultural crops and smaller for cereals. However, this has not yet been confirmed under different conditions and cannot be included in the general methodology at the present stage. Therefore, the IPCC method (IPCC/OECD, 1997) defines one single method for all types of N input and all crops. Furthermore, it must be taken into account, that annual emissions may vary significantly between different years due to differences in weather conditions, as was shown e.g. for a grassland site in the UK where annual emissions varied over 20-fold over 8 years (Smith and Dobbie, 2002).

Following the IPCC Methodology (IPCC/OECD 1997), N<sub>2</sub>O emissions from agricultural soils may be calculated as the sum of direct soil emission following N inputs to agricultural fields, either from mineral or organic sources, direct emissions from cultivation of histosols, direct emission from excreta deposition of grazing animals and indirect emission following atmospheric deposition of NH<sub>3</sub> and NO<sub>x</sub> in natural ecosystems like e.g. forests or leaching and runoff.

Emissions from animal waste management and manure spreading are included in SNAP Code 100900, Manure Management.

Direct emissions from cultures with fertilizers include emissions which are induced by N input (mineral and organic fertilizer, excretal N deposited during grazing, biological N fixation and crop residues). Emissions from plants have been observed (Gründmann *et al.*, 1993) but they are considered as marginal. In addition, cultivation of organic soils (histosols) is regarded as a direct source of N<sub>2</sub>O. The magnitude of direct N<sub>2</sub>O emissions varies with a range of soil and environmental factors. These soil and environmental factors also influence the magnitude of indirect N<sub>2</sub>O emissions following atmospheric deposition of NH<sub>3</sub> and NO<sub>x</sub>. The magnitude of the so called indirect emissions from e.g. forest ecosystems, is significant, since – due to chronically high atmospheric N-deposition – most forest ecosystems in Central Europe are N-saturated and have been shown to emit N<sub>2</sub>O in a range of 0.2 – 5.0 kg N<sub>2</sub>O-N ha<sup>-1</sup> a<sup>-1</sup> (Brumme and Beese, 1992; Butterbach-Bahl *et al.*, 1997a, 2001; Papen and Butterbach-Bahl, 1999).

### 3.1.3 Nitric Oxide

Nitric oxide (NO) is also a substrate and product of denitrification, but it is only very rarely as a consequence of denitrification in European soils. In cultures with fertilizers, where pH is likely to be maintained above 5.0, nitrification is considered to be the dominant pathway of NO emission (Remde and Conrad 1991; Skiba *et al.* 1997). Recent estimates consider that NO<sub>x</sub> emission from soils could represent more than 40 % of NO<sub>x</sub> emission at global scale (Davidson and Kinglerlee, 1997; IGAC, 2000) and more than 10% for some European countries (Skiba *et al.*, 1997; Stohl *et al.*, 1996, Butterbach-Bahl *et al.*, 2002). Emissions resulting from fertilizer use could represent 40 % of soils emissions at global scale (IGAC, 2000) and up to 65 % for USA (Hall *et al.*, 1996).

The main determinants of NO production in agricultural soils are mineral N concentration (Skiba *et al.*, 1997), temperature and soil moisture (Yamulki *et al.*, 1995; Williams *et al.*, 1992). This is increased by N-fertilizer application, excretal N deposited during grazing, crop residue incorporation and cultivation.

Activities such as tillage and incorporation were considered to increase NO emissions by a factor of 2 to 7 (Skiba *et al.*, 1997, 2002). Thus a knowledge of the N concentration and mineralisation rate of crop residues could provide an estimate of soil NH<sub>4</sub><sup>+</sup> on which to base an emission estimate. A knowledge of soil N content could also allow an estimate to be made of NO emissions following cultivation. The magnitude of indirect emissions of NO from soils of natural ecosystems like forests can be very high due to increased atmospheric N-deposition. Gasche and Papen (1999) showed, that NO-emissions from a spruce forest site in Bavaria were in a range of 5 - 7 kg NO-N ha<sup>-1</sup> a<sup>-1</sup>. Using a process-oriented model for regionalization Butterbach-Bahl *et al.* (2001) calculated that on annual basis NO-emissions from forest soils of Bavaria contributed less than 2 % to the total regional NO<sub>x</sub> burden, whereas this figure was less than 8 % during summer.

### 3.1.4 Carbon Dioxide

Land use change leads to changes in the carbon stocks in vegetation and soil. The quantification of these changes requires long-term studies on carbon budgets and long term documentation of the kind of land use changes. The change from high soil organic carbon (SOC) to low SOC is a process that is faster by factor 5 than the sequestration process taking place when a soil accumulates carbon. Improved land management (for example measures that aim at carbon sequestration) can increase SOC. Here it is important to realise that increase of the soil organic carbon level (C-sequestration) takes a period of 50 - 100 a. Decrease in SOC (decomposition) due to any disturbance of the soil will take place within 10 a.

According to the IPCC Methodology (IPCC/OECD 1997), at minimum, the following processes of land use change have to be considered for cultures with fertilizers:

- conversion of woodland to grassland and cropland <sup>1</sup>,
- conversion of grassland to cropland and *vice versa*, and

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<sup>1</sup> Woodland has a complete or near-complete canopy, whereas forests are considered to be fairly open areas with some trees, but also grassland and heath land.

- other land use change activities. These include the drainage of wetlands and cultivation of organic soils. Such activities represent a significant source of CO<sub>2</sub> in many, especially in Northern European countries. Since no default methodology was recommended, these emissions are rarely reported in national inventories although this neglect can lead to an underestimation of national emissions of CO<sub>2</sub>-equivalents by up to 10 % (Kasimir Klemedtsson *et al.*, 1997).

The oxidation of peat in drained organic soils also occurs on histosols that have been under cultivation for many years. Subsidence associated with the loss of organic matter leads to a further drainage of the soil, which in turn enhances peat oxidation. The IPCC Methodology considers N<sub>2</sub>O emissions on histosols (section 3.1.2) in the agriculture chapter, but addresses the concomitant CO<sub>2</sub> release in the chapter on land use change and forestry.

The management of agricultural land also affects its carbon balance through tillage, crop residues and organic amendments, which can lead to either CO<sub>2</sub> removals or release.

### 3.1.5 Methane

Both methanogenesis and CH<sub>4</sub> oxidation occur both sequentially and concurrently in soils. Heavy wetting or flooding cuts off the soil's oxygen supply, which may lead to anaerobic fermentation of organic matter and concomitant CH<sub>4</sub> formation. As CH<sub>4</sub> is produced by strictly anaerobic *Archaea*, CH<sub>4</sub> production can take place in micro-habitats only, where oxygen diffusion is inhibited by high water content, and where all oxygen and other electron acceptors (such as the oxides of iron and sulfur) have already been consumed by other bacterial processes. The last step in carbon degradation in soils is CH<sub>4</sub> production from the substrates acetic acid or the gases CO<sub>2</sub> and H<sub>2</sub>. On the other hand, most of the methanotrophic bacteria (which belong to the *Eubacteria*) are limited to oxygen-rich environments. But soils which consume CH<sub>4</sub> more efficiently are those in which methanogenic conditions have occurred (see e.g. Roger *et al.*, 1999). Emission data of CH<sub>4</sub> from soils with heterogenic water saturation, in space or in time, are therefore always mixtures of the two components stated above: anaerobic CH<sub>4</sub> production and aerobic CH<sub>4</sub> consumption (Conrad, 1996).

Fertilized and cultivated soils consume CH<sub>4</sub> at rates of 40 % or less of those in undisturbed forest soils as a result of complex short-term and long-term adverse effects of soil disturbance, shift in microbial species diversity and ammonium inhibition of methanotrophic activity (Hütsch, 2001).

### 3.1.6 Non-Methane Volatile Organic Compounds

Volatile Organic Compounds (VOCs) are all organic hydrocarbons and their derivatives. It has been customary to differentiate between methane and non-methane volatile organic compounds (NMVOCs). VOCs can produce photochemical oxidants and secondary particles, in particular by reaction with nitrogen oxides.

Three categories of sources may be distinguished:

- activities that emit NMVOCs by combustion or evaporation;
- land clearing, including burning;
- biogenic processes.

The primary sources in the agricultural sector are:

- burning stubble and other plant wastes;
- the use of organic solvents in pesticide production;
- anaerobic degradation of livestock feed and animal excreta.
- biogenic emissions of oxygenated VOCs

These 4 major sources are dealt with elsewhere. Stubble burning in SNAP Code 100300, emissions from burning other crop residues in SNAP Code 090700 (Open Burning of Agricultural Wastes) and emissions from pesticides in SNAP Code 100600. Emissions from livestock manure are included in SNAP Code 100500, Manure Management Regarding Carbon Compounds.

The emission of some NMVOCs may be of benefit to plants, e.g. to attract pollinating insects, while others may be waste products or a means of losing surplus energy (Hewitt and Street 1992). Ethene emission has been observed to increase when plants are under stress. Factors that can influence the emission of NMVOCs include temperature and light intensity, plant growth stage, water stress, air pollution and senescence (Hewitt and Street 1992). Emissions of NMVOCs from plants have usually been associated with woodlands, which predominantly emit isoprenes and terpenes (König *et al.*, 1996). Hewitt and Street (1992) took qualitative measurements of the major grass and crop species in the UK (except for barley, *Hordeum vulgare*). The only crop species producing any significant emissions was Blackcurrant (*Ribes nigrum*). However these workers cautioned against classifying plants as ‘non-emitters’ on the basis of limited measurements, as plant growth stage had been shown to be an important factor in emission. The role of the soil as a source or sink of VOCs requires investigation. Although NMVOCs emissions from cultures with fertilizers are smaller than from forests, they may not be entirely negligible (Simpson, 1999).

Hewitt and Street (1992) concluded that trees are the main emitters of non-methane hydrocarbons (NMHCs). Other plants, and crops are negligible in comparison. König *et al.*, (1996) noted that in earlier studies NMHCs had been regarded as the major component of VOC emissions. However, König *et al.* (1996) found oxygenated VOCs to be the major VOC emissions from cereals. In that study emissions were not invariably greater from trees than from agricultural crops.

### 3.2 Definitions

*Animal Manures.* Animal excreta deposited in houses and on yards, collected, either with bedding or without, to be applied to land.

*Livestock excreta.* Livestock excreta deposited at any time, including while grazing.



*Fertilized agricultural grassland.* Grassland, to be used for either cutting grass or conservation, grazing or both, to which synthetic N-fertilizers have been applied.

*Crop residues.* The unharvested parts of crops that are left on the field and ultimately incorporated into the soil.

### 3.3 Controls

#### 3.3.1 Ammonia

Emissions of NH<sub>3</sub> from crops (including emission from the applied fertilizer and from the plant *via* stomata) have not generally been seen as a major option for control, primarily because the emissions from animal husbandry are much larger and therefore provide greater scope for reducing total emissions.

However, there may be potential for reducing crop emissions by switching from urea to other N-fertilizers. Urea has been considered to contribute approximately 50 % of the fertilizer emissions in western Europe (ECETOC, 1994) because of its wide use and greater NH<sub>3</sub> volatilization rate. A potentially effective control of fertilizer emissions would, therefore, be to use alternative N-fertilizers with smaller NH<sub>3</sub> emissions. A further possibility is to add urease regulators/inhibitors to urea fertilizer which are expected to reduce emissions. Costs of these measures would include the differential price of more expensive fertilizers or of inhibitors.

As NH<sub>3</sub> emissions are strongly a function of N supply, another potential control is to use cultivars or crop species which require less N. Use of less N-demanding species and cultivars will generally reduce total produce yields, the costing of which may be difficult because of the close link to produce supply and market values. However, it may be appropriate to consider reduction in fertilizer-N inputs where these have an additional benefit for other environmental effects, such as reducing NO<sub>3</sub><sup>-</sup> leaching.

Emissions may also be reduced by placing the fertilizer granule into the soil at the same depth as the seed (*c.* 7 - 8 cm). This will only be applicable for crops sown in the spring (apart from grass reseeds in autumn). When urea is used care needs to be taken to ensure the fertilizer is not placed so close to the seed that germination is inhibited. The NH<sub>3</sub> emissions from placement of fertilizers have been estimated to be negligible (assuming that N supply is dimensioned correctly). Deep placement of fertilizer granules is a common technology and has been used for many years in Finland (Aura, 1967).

Application of fertilizer-N when the meteorological conditions are cool and moist or directly prior to probable rainfall will reduce NH<sub>3</sub> emissions. In general, increasing nitrogen use efficiency by proper timing of fertilization and matching crop demands will reduce all N fertilizer use, NH<sub>3</sub>, N<sub>2</sub>O, NO emissions and nitrate leaching.

Incorporation of fertilizer-N prior to rice planting, or delaying application until panicle initiation, have been shown to reduce NH<sub>3</sub> emissions from rice fields (Humphreys *et al.*, 1988). These are already standard practices in the USA (Bacon *et al.*, 1988). Freney *et al.* (1988) warned that measures to reduce NH<sub>3</sub> emissions from rice cultivation may not reduce total N losses in soils with large nitrification or denitrification rates.

Reducing fertilizer-N applications to grassland may be effective in reducing NH<sub>3</sub> emissions per unit area. However, this will reduce milk yield and live weight gain, unless extra forage is made available. The provision of such extra forages may increase NH<sub>3</sub> losses, either at grazing or in buildings, by increasing excretal returns.

It should be noted that few of these changes have so far been applied by countries as measures to limit NH<sub>3</sub> emissions, and further work would be required to provide a detailed evaluation of all these possibilities.

### 3.3.2 Nitrous Oxide

Since emission of N<sub>2</sub>O is a consequence of nitrification as well as denitrification (e.g. Klemedtsson *et al.*, 1988; Arcara *et al.*, 1990), the greatest potential for reducing N<sub>2</sub>O emissions will come from reducing mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) concentrations in soils. This may be done most simply by reducing inputs of fertilizer-N. As stated in section 3.3.1, such a measure will have a significant cost if it reduces crop yields. However, some scope may remain for better matching of N-fertilizer to crop requirement. This may be done by avoiding N applications in excess of the economic optimum. Such applications are sometimes made as an insurance against under-fertilizing. To reduce the likelihood of excessive N fertilization care should be taken, when deciding N-fertilizer applications, to make full allowance for N available in the soil from previous crop residues, organic manure applications and mineralisation of soil organic matter. Careful timing of fertilizer-N application may also reduce N<sub>2</sub>O emissions. Crops and soil microbes may be regarded as being in direct competition for the mineral N in soil (Recous *et al.*, 1988). If large amounts of N-fertilizer are applied to the soil at times when plant growth is limited, and when soil moisture and temperature are favourable, denitrifying and nitrifying bacteria may use the mineral N as a substrate. However, if the N-fertilizer is applied to an actively-growing crop, much of it (especially NO<sub>3</sub><sup>-</sup>) may be taken up quickly by the crop, and removed from sites of bacterial activity. Timing of fertilizer-N application to coincide with crop demand is already recommended in many countries to reduce NO<sub>3</sub><sup>-</sup> leaching. Preliminary results from a UK study (S Ellis, pers. comm.) suggest this strategy may also be effective in reducing N<sub>2</sub>O emissions. For grasslands, adjusting the type of fertilizer to meteorological conditions and avoiding the simultaneous application of organic N fertilizers and nitrate may reduce N<sub>2</sub>O emissions by up to 50 % (Clayton *et al.*, 1997).

The effect of fertilizer type on the emission of N<sub>2</sub>O is inconclusive (Hénault *et al.*, 1998), and is therefore not included in the IPCC methodology. However, some studies suggest, that fertilizer - induced emissions of N<sub>2</sub>O may be greater with the use of anhydrous ammonia and organic N fertilizers (Bouwman, 1996). More recently Dobby and Smith (2002) reported that N<sub>2</sub>O emissions from fertilized grasslands can be reduced by applying urea rather than ammonium nitrate based fertilizers.

Timing the incorporation of crop residues, to avoid incorporating when soils are poorly aerated, may also give some reduction in N<sub>2</sub>O emissions (Flessa and Beese, 1995). The relative importance of nitrification and denitrification need to be defined, if correct soil management is to be applied. Mitigation options to reduce N<sub>2</sub>O emissions from agricultural soils are further discussed by Mosier *et al.* (1998).

### 3.3.3 Nitric Oxide

Since, in temperate climates, NO emissions are considered to be predominantly a consequence of nitrification, the use of urea fertilizer may produce larger NO emissions than equivalent amounts of N applied as ammonium nitrate (AN) or any nitrate-based fertilizer. While at present there is insufficient data to discriminate between fertilizer-N sources (Skiba *et al.*, 1997), the substitution of AN for urea to reduce NH<sub>3</sub> and N<sub>2</sub>O emissions, may also give some reduction in NO emissions.

Currently the only other possible option is to ensure that applications of N-fertilizer are no greater than is needed for optimum crop yield, by making full allowance for the N supplied by crop residues, organic manures, previous N-fertilizer applications, and mineralisation of soil N. Fertilizer application should also be timed to match crop demand.

### 3.3.4 Carbon Dioxide

Soil carbon stocks accumulate by a surplus of input of organic material over decomposition. Any disturbance of the soil system, e.g. by ploughing, drainage, and conversion of forest or grassland to cropland will increase the decomposition rate and hence lead to the release of CO<sub>2</sub>. This effect is particularly pronounced in farmed peatlands.

Carbon sequestration in agricultural soils may be encouraged by promoting organic input on arable land instead of grassland (crop residues, cover crops, FYM, compost, sewage sludge), permanent revegetation of arable set-aside land (e.g. afforestation) or extensification of arable production by introduction of perennial components, biofuel production with short-rotation coppice plantations and perennial grasses on arable set-aside land, organic farming, zero tillage vs conservation tillage, and the promotion of a permanently shallow water table in farmed peatland (Freibauer *et al.*, 2002).

### 3.3.5 Methane

Methane is mainly emitted from paddy rice fields (SNAP-code 100103). The emission rate depends on the different water regimes, the length of the growth season, and the duration of flooding (continuous, intermittent, or not flooded). Fertilization and the addition of organic material, as well as the aerenchyma of the specific rice cultivars affect the CH<sub>4</sub> emissions (Heyer 1994; Butterbach-Bahl *et al.*, 1997b; Roger *et al.*, 1999).

Most agricultural soils take up CH<sub>4</sub>. The uptake rate depends basically on land use, soil texture and soil aeration, and is reduced by nitrogen availability. In general, CH<sub>4</sub> oxidation rates in agricultural soils is roughly a fifth of native soils. Ammonium inhibition of CH<sub>4</sub> oxidation seems one of the reasons for this decline in oxidation capacity. There is only limited scope for enhancing CH<sub>4</sub> oxidation in agricultural soils by conservation tillage and increased application of organic amendments while it takes decades until the CH<sub>4</sub> oxidation in soil recovers from disturbance (Priemé *et al.*, 1997).

### 3.3.6 Volatile Organic Compounds

No potential controls have been proposed for VOC emissions from fertilized crops.

## 4 SIMPLER METHODOLOGY

## 4.1 Ammonia

### 4.1.1 Application of Mineral Fertilizer

Noting the interdependence of direct fertilizer emissions and subsequent emissions from foliage and decomposing material of fertilized vegetation, the emissions are treated here as a single integrated term. These are estimated as % losses of the fertilizer-N use for each of the main fertilizer categories. In the simpler methodology the % N emissions factors are taken to be the same for all countries. Soil type and climate are expected to affect emissions and an approach is given in the detailed methodology (section 5) to account for this.

The emission factors for the simple methodology are provided in Table 4.1. These are based largely on the estimates of Asman (1992), ECETOC (1994) and Sutton *et al.* (1995b). The combined fertilizer-plant emission factors are smaller than the totals of ECETOC (1994), since in the original estimates of ECETOC their emissions factors referred to just fertilizer losses, while they provided an additional emission from indirect foliar emissions (not shown in Table 4.1). In contrast the estimates here are larger than the estimates of Sutton *et al.* (1995b). It should be noted that the estimates published by Buijsman *et al.* (1987) are now considered to be out of date and to overestimate NH<sub>3</sub> emissions.

**Table 4.1: Simpler methodology estimates of total NH<sub>3</sub> emissions from cultures due to fertilizer volatilization, foliar emissions and decomposing vegetation (second column). The estimates are compared with other literature values.**

**Values are kg NH<sub>3</sub>-N volatilized per kg of N in fertilizers applied.**

Fertilizer type	Present simpler methodology to apply	Asman (1992) (Europe)	ECETOC (1994) Group II European countries)	Sutton <i>et al.</i> (1995) (UK)
Estimates from	fertilizer and plants	fertilizer	fertilizer	Fertilizer and plants
Ammonium sulphate	0.08	0.08	0.10	-
Ammonium nitrate	0.02	0.02	0.02	0.01
Calcium ammonium nitrate	0.02	0.02	0.02	0.01
Anhydrous ammonia	0.04	0.01	0.04	-
Urea	0.15	0.15	0.15	0.10
Nitrogen solution (mixed urea and ammonium nitrate)	0.08	-	0.08	-
Combined ammonium phosphates (generally di-ammonium phosphate)	0.05	0.04	0.05	-
Mono-ammonium phosphate	0.02			
Di-ammonium phosphate	0.05			
Other complex NK, NPK fert	0.02	0.02 - 0.04	0.02	0.025

To calculate NH<sub>3</sub> emissions from fertilized cultures in a country, the use of each fertilizer type (expressed as mass of fertilizer-N used per year), is multiplied by the appropriate emission factor, and the emissions for the different fertilizer types summed. More detailed spreadsheets for this calculation are provided in the detailed methodology (see section 5). Emissions of NH<sub>3</sub>-N from fertilizers applied to grass cut for hay or silage may be calculated using the same factors as for arable and other crops. Separate emission factors are used for NH<sub>3</sub> emission from grazed grassland.

### 4.1.2 Grazed Grassland

To estimate NH<sub>3</sub> emissions from grazed grassland, Pain *et al.* (1997) proposed a function of the form

$$E_{\text{NH}_3} = c + dN \quad (1)$$

which subsequently was applied to a variety of experimental data sets in Misselbrook *et al.* (2001).

with	$E_{\text{NH}_3}$	NH <sub>3</sub> emitted (kg a <sup>-1</sup> NH <sub>3</sub> )
	$c$	-0.51 kg a <sup>-1</sup> NH <sub>3</sub>
	$d$	0.0742 kg (kg N) <sup>-1</sup> NH <sub>3</sub>
	$N$	N excreted (kg a <sup>-1</sup> N)

to estimate NH<sub>3</sub> emissions from grassland grazed by cattle. Thus, a mean emission factor of 7.5 % of the N excreted is recommended.

No distinction is made between emissions from cattle and sheep excreta. Equation (1) was derived almost entirely from measurements of NH<sub>3</sub> emissions in Northwest Europe. The relationship may not give accurate estimates of emissions from grazing in drier, or warmer climates.

For the amount of N excreted see tables provided in SNAP 100900, Manure Management Regarding Nitrogen Compounds.

## 4.2 Nitrous Oxide

The methodology used here follows the approach taken by IPCC/OECD (1997) in order to maintain consistency between the different emission inventories. Emissions arising from animal housing and manure storage are dealt with in SNAP Code 100900, Manure Management Regarding Nitrogen Compounds. Emissions arising from biological nitrogen fixation are dealt with in SNAP Code 100200, Cultures without Fertilizers.

The IPCC methodology for the assessment of N<sub>2</sub>O emissions from cultures with fertilizers requires the following input data:

1. Total synthetic fertilizer-N applied
2. Total N content of fertilized crop residues and excreta from grazing animals returned to the soil.
3. Area of organic soils (histosols) cultivated in the country.
4. Estimate of atmospheric emission of NH<sub>3</sub> and NO<sub>x</sub>.
5. Estimate of N lost from soils by leaching and runoff.

These input data can be estimated from FAO data (see IPCC/OECD 1997), see Table 4.2.

The amount of excreta returned to the soil can be derived from figures calculated in SNAP 100900. The atmospheric emission of NH<sub>3</sub> and/or NO is obtained from this chapter as well as

from SNAP 100200 (Cultures without Fertilizers: legumes, grazing animals) and SNAP 100900 (Manure Management Regarding Nitrogen Compounds).

**Table 4.2: Summary of IPCC source categories (IPCC Guidelines for National Greenhouse Gas Inventories, Volume 2: Workbook, 1997) to be reported as CORINAIR sub-sectors for agriculture.**

CORINAIR SUB-SECTOR (SNAP code)	IPCC N <sub>2</sub> O SOURCE (IPCC WORKBOOK WORKSHEET)
Cultures with/without Fertilizers (100100, 100200)	<ul style="list-style-type: none"> <li>- Direct soil emission due to N-inputs including manure (4-5, sheet 1 )</li> <li>- Direct soil emissions due to histosol cultivation (4-5, sheet 2)</li> <li>- Direct soil emissions from grazing animals; pasture, range &amp; paddock (4-5, sheet 3)</li> <li>- Indirect emissions due NH<sub>3</sub> and NO<sub>x</sub> emissions/deposition from synthetic fertilizer use and grazing animals (4-5, sheet 4, excluding animal waste used as fertilizer)</li> <li>- Indirect emissions due N leaching/runoff from synthetic fertilizer use and grazing animals (4-5, sheet 5, excluding animal waste used as fertilizer)</li> </ul>

Total N<sub>2</sub>O emission may be calculated as:

$$E_{N_2O-N} = E_{N_2O, \text{direct}} + E_{N_2O, \text{indirect}}$$

Within this SNAP, direct emissions comprise the emissions from (mineral) fertilizer application, application of manures as fertilizers and from farmed organic soils:

$$E_{N_2O-N, \text{direct}} = EF_{\text{fert}} \cdot m_{\text{fert}} + EF_{\text{hist}} \cdot A_{\text{hist}} \quad (2)$$

where	$E_{N_2O-N, \text{direct}}$	emission flux of N <sub>2</sub> O directly emitted from soils (Mg a <sup>-1</sup> N <sub>2</sub> O)
	$EF_{\text{fert}}$	emission factor for emissions from fertilizers (mineral fertilizer and animal manures) ( $EF_{\text{fert}} = 0.0125 \text{ kg kg}^{-1} \text{ N}$ )
	$m_{\text{fert}}$	amount of N applied with mineral fertilizer and animal manures spread (Mg a <sup>-1</sup> N)
	$EF_{\text{hist}}$	emissions factor for emissions from cultivated organic soils ( $EF_{\text{hist}} = 8 \text{ kg ha}^{-1} \text{ a}^{-1} \text{ N}$ )
	$A_{\text{hist}}$	area of histosols (ha)

‘Net’ inputs of animal manure N applied can be obtained from SNAP 100900 as the amount of N excreted ( $m_{\text{excr}}$ ), the N content of straw ( $m_{\text{straw}}$ ) and the amount of NH<sub>3</sub>-N, N<sub>2</sub>O-N and N<sub>2</sub>-N emitted ( $E_{\text{NH}_3\text{-N}}$ ,  $E_{\text{N}_2\text{O-N}}$ ,  $E_{\text{N}_2\text{-N}}$ ):

$$m_{\text{aw}} = (m_{\text{excr}} + m_{\text{straw}}) - (E_{\text{NH}_3\text{-N}} + E_{\text{N}_2\text{O-N}} + E_{\text{N}_2\text{-N}}) \quad (3)$$

The IPCC guidelines are modified here in order to reach consistency with the NH<sub>3</sub> methodology.

Emissions from crop residues, excreta from grazing animals and from biological N fixation as well as indirect emissions are dealt with in SNAP 100200, Cultures without Fertilizers.

### 4.3 Nitric Oxide

Current data on NO emissions in relation to fertilizer-N use were reviewed by Yienger and Levy (1995) and were updated by Skiba *et al.*, (1997). Yienger and Levy (1995) calculated an arithmetic mean emission of 2.5 % loss of fertilizer-N. Based on almost the same dataset Skiba *et al.* (1997) showed that NO losses ranged from 0.003 to 11% of applied fertilizer-N with a geometric mean emission of 0.3 %. More recently Bouwman *et al.* (2002) used the Residual Maximum Likelihood (REML) technique to calculate from 99 studies of NO emissions a global mean fertilizer induced NO emission of 0.7%. 1 % of applied N was suggested by Freibauer and Kaltschmitt (2000).

It is recommended to use the emission factor 0.7 % of NO-N related to the input of mineral fertilizer N.

### 4.4 Carbon Dioxide

Carbon dioxide emitted as a consequence of land management and land use change depends strongly on the conditions and direction of change, soil properties, and land management. No simple methodology is suggested.

The IPCC methodology suggests the following emission factors for CO<sub>2</sub> released from farmed organic soils: croplands 3.7 Mg ha<sup>-1</sup> a<sup>-1</sup> CO<sub>2</sub> and pastures 1 Mg ha<sup>-1</sup> a<sup>-1</sup> CO<sub>2</sub> (IPCC/OECD 1997 Workbook, Chapter 5.6). However, recent measurements in Europe (e.g. Kasimir Klemetsson *et al.*, 1997) suggest higher emission rates. Therefore, emission factors of 15 ± 5 Mg ha<sup>-1</sup> a<sup>-1</sup> CO<sub>2</sub> for arable crops and 10 ± 5 Mg ha<sup>-1</sup> a<sup>-1</sup> CO<sub>2</sub> for grasslands are recommended (Freibauer and Kaltschmitt, 2000). These emission factors result from the mineralisation of peat and hence reflect the background emissions in farmed organic soils without fertilization. The emission factors used for and (cereals and row crops), respectively. They suit for farming of organic soils, not for the conversion of peat soils to farmed soils. The uncertainty in the emission factors can be greatly reduced by further long-term measurements.

### 4.5 Methane

In Europe, most rice paddies are continuously flooded. Methane emissions can be calculated by a simplification of the IPCC Methodology, assuming a uniform water regime. Methane emissions depend on the average air temperature during the growing season, the season length and the area harvested.

$$E_{\text{CH}_4} = EF_{\text{CH}_4} \cdot (A_{\text{rice}} \cdot t_{\text{rice}}) \quad (4)$$

with	$E_{\text{CH}_4}$	emission flux (Gg a <sup>-1</sup> )
	$EF_{\text{CH}_4}$	emission factor (Gg ha <sup>-1</sup> d <sup>-1</sup> ), representative of the water regime and temperature conditions in a country
	$A$	area harvested per year (ha)
	$t$	length of season (d)

So far, there is no standard methodology to assess CH<sub>4</sub> consumption in agricultural soils. The CH<sub>4</sub> sink on agricultural soils is estimated at  $0.5 \pm 0.5 \text{ kg ha}^{-1} \text{ a}^{-1}$  CH<sub>4</sub> (Freibauer and Kaltschmitt 2000). This emission factor relies on a set of 66 long-term measurements in Europe and agrees well with the log-mean oxidation rate of  $-0.65 \text{ kg ha}^{-1} \text{ a}^{-1}$  CH<sub>4</sub> of agricultural soils in Northern Europe given by (Smith *et al.*, 2000).

#### 4.6 Non-methane Volatile Organic Compounds

The sparse information about emissions of non-methane volatile organic compounds (NMVOCs) does not allow for the construction of a simpler methodology. However, Hobbs *et al.* (2003) have compiled the data presently available. They can be used to provide information of the order of magnitude of NMVOC emissions from agriculture as a first estimate. The use of the following equation and data is recommended for Northern and Central Europe:

$$E_{\text{NMVOC}} = \sum A_i \cdot m_{\text{D},i} \cdot t_i \cdot EF_i \quad (5)$$

with	$E_{\text{NMVOC}}$	emission flux ( $\text{Mg a}^{-1}$ NMVOC)
	$A_i$	area covered by crop <sub><i>i</i></sub> (ha)
	$m_{\text{D},i}$	mean dry matter of crop <sub><i>i</i></sub> ( $\text{Mg ha}^{-1}$ )
	$t_i$	fraction of year during which crop <sub><i>i</i></sub> is emitting
	$EF_i$	emission factor ( $\text{kg kg}^{-1}$ NMVOC)



**Table 4.2: Summary of default emission factors for NMVOC emissions from cultures with fertilizer**

Crop type	$m_D$ Mg ha <sup>-1</sup>	$T$ a a <sup>-1</sup>	$EF$ kg kg <sup>-1</sup> h <sup>-1</sup> NMVOC
Temperate grassland	2	0.5	$1.0 \cdot 10^{-8}$
Wheat	2	0.3	$1.1 \cdot 10^{-8}$
Oil seed rape	2	0.3	$2.0 \cdot 10^{-7}$

For further information consult Hobbs *et al.* (2003) and the literature cited therein.

An approach for estimating the emissions from grassland and crop is given in Chapter 110400, Natural Grassland. If the method given in Chapter 110400 is used, emissions from fertilized agricultural land must be reported under Chapter 100100.

## 5 DETAILED METHODOLOGY

### 5.1 Ammonia

#### 5.1.1 Emissions from Crops and Cut Grassland

To provide a more detailed methodology it is desirable to distinguish between the different climates and soil types for different countries or regions. The justification for this is well established, as crop emissions are known to be larger in warmer climates (Fenn and Hossner, 1985), while soil emissions (direct fertilizer losses) generally increase at higher soil pH (e.g. Whitehead and Raistrick, 1990). Given the need to generalize, only a broad scale approach is possible to apply these known differences in inventories. A first attempt has been applied by ECETOC (1994). Based on findings reported or collated by Misselbrook *et al.* (2000) and Harrison and Webb (2001), Sutton *et al.* (2000, 2001, 2002) a detailed approach should consider both mean temperatures for the most important period of fertilizer application (March to May) as well as soil pH.

Three climatological regions are to be distinguished according to their mean spring air temperatures  $t_s$ :

$$\begin{aligned} \text{Region A} & \quad t_s > 13 \text{ }^\circ\text{C} \\ \text{Region B} & \quad 6 \text{ }^\circ\text{C} < t_s < 13 \text{ }^\circ\text{C} \\ \text{Region C} & \quad t_s < 6 \text{ }^\circ\text{C} \end{aligned}$$

In addition, the effect of calcareous soils would be considered through use of a multiplier on the basis of values for different areas.

The national or regional inventory should then be calculated as the sum of emissions from each fertilizer type for each region:

$$E_{\text{NH}_3} = \sum m_{\text{fert}, i, A} \cdot EF_{i, A} \cdot c_i + \sum m_{\text{fert}, i, B} \cdot EF_{i, B} \cdot c_i + \sum m_{\text{fert}, i, C} \cdot EF_{i, C} \cdot c_i \quad (6)$$

with	$E_{\text{NH}_3}$	emission flux ( $\text{Mg a}^{-1} \text{NH}_3\text{-N}$ )
	$m_{\text{fert}, i, A}$	mass of fertilizer N applied as type i in region A ( $\text{Mg a}^{-1} \text{N}$ )
	$EF_{i, A}$	emission factor for fertilizer type i in region A ( $\text{kg kg}^{-1} \text{N}$ )
	$c_i$	multiplier reflecting soil pH

**Table 5.1: Detailed methodology emission factors for total  $\text{NH}_3$  emissions from soils due to N fertilizer volatilization and foliar emissions for various climatological regions. Values are  $\text{kg NH}_3\text{-N}$  volatilized per  $\text{kg fertilizer-N}$  applied**

Fertilizer type	Region A $EF_A$	Region B $EF_B$	Region C $EF_C$	Multiplier c	Comment
Ammonium sulphate	0.025	0.020	0.015	10	<sup>1)</sup>
Ammonium nitrate	0.020	0.015	0.010	1	
Calcium ammonium nitrate	0.020	0.015	0.010	1	
Anhydrous ammonia	0.04	0.03	0.02	4	
Urea	0.20	0.17	0.15	1	
Nitrogen solutions	0.11	0.09	0.07	1	<sup>2)</sup>
Ammonium phosphates	0.025	0.020	0.015	10	<sup>1)</sup>
Other NK and NPK	0.020	0.015	0.010	1	<sup>3)</sup>
Nitrate only (e.g. $\text{KNO}_3$ )	0.007	0.005	0.005	1	

<sup>1)</sup> Note very strong pH effect supported by measurements and chemical principles (Harrison and Webb, 2001)

<sup>2)</sup> saturated solution of urea and ammonium nitrate

<sup>3)</sup> for fertilizers largely based on ammonium nitrate

With respect of urea, a greater  $\text{NH}_3$  loss on calcareous soils may not be justified. While  $\text{NH}_3$  losses from AS and AN have been found to increase markedly with increasing pH (e.g. Whitehead and Raistrick, 1990; Gosse *et al.*, 1999),  $\text{NH}_3$  loss from urea is less dependent on initial soil pH, since hydrolysis of urea will increase pH immediately around the fertilizer granule to *c.* 9.2 (Fenn, 1988). Moreover reaction with calcium ions reduces the volatilization potential of  $(\text{NH}_4)_2\text{CO}_3$  produced by urea hydrolysis (Fenn and Hossner, 1985). In contrast to other N-fertilizers,  $\text{NH}_3$  loss from urea did not increase consistently with pH, and was not greater on a calcareous soil (Whitehead and Raistrick, 1990). This was considered due to differences in cation exchange capacity (CEC). Whitehead and Raistrick (1993) also found losses of  $\text{NH}_3$  from cattle urine were no greater on calcareous than on non-calcareous soils. The best correlation with  $\text{NH}_3$  loss was with CEC. Gezgin and Bayrakli (1995) measured  $\text{NH}_3$  losses from urea, AS and AN on calcareous soils in Turkey. Losses from AS (*c.* 16 %) and AN (*c.* 5 %) were greater than those measured on non-calcareous soils by Somner and Jensen (1994), which were < 5 % and < 2 % respectively. However losses from urea at *c.* 8 % were less than those measured by Sommer and Jensen (1994). Nevertheless a greater emission factor for urea in Group 1 countries is justified by the greater temperatures. The large proportion of calcareous soils will however increase  $\text{NH}_3$  losses from AS (Fleisher *et al.*, 1987).

Van der Weerden and Jarvis (1997) and subsequently Harrison and Webb (2001) reviewed data from field measurements in Regions B and C of  $\text{NH}_3$  loss following application of N fertilizers to grassland and arable land. They concluded that  $\text{NH}_3$  losses from urea are greater by a factor of 2 on grassland. This greater potential for  $\text{NH}_3$  loss had been attributed to greater urease activity in grassland soils by O'Toole and Morgan (1985).

It is obvious that the effects on emission factors of grassland vs arable land application exceed the climatological differentiation. Therefore, it seems justified to replace the emission factors given in Table 5.1 by separate emission factors for grassland and arable land according to Table 5.2, if the respective activity data are available.

**Table 5.2: Detailed methodology emission factors for total NH<sub>3</sub> emissions from arable and grassland soils due to N fertilizer volatilization and foliar emissions for regions B and C. Values are kg NH<sub>3</sub>-N per kg fertilizer-N applied.**

Fertilizer type	Grassland $EF_{A,B,gr}$	Arable land $EF_{A,B,ar}$
Ammonium nitrate	0.016	0.006
Calcium ammonium nitrate	0.016	0.006
Urea	0.23	0.115
Nitrogen solutions	0.12	0.06
Other NK and NPK	0.016	0.006

### 5.1.2 Emissions from Grazed Grassland

The method for calculating NH<sub>3</sub> emissions from grazed grassland is given in Section 4.1. No detailed methodology has been established.

### 5.1.3 Emissions from Rice Fields

Losses of NH<sub>3</sub> following applications of N-fertilizer to flooded rice soils are considered to be potentially greater than from other cropping systems (Fenn and Hossner 1985). Vlek and Crasswell (1979) measured NH<sub>3</sub> losses of up to 50 % of urea-N applied, and up to 60% of AS-N. More recent studies of NH<sub>3</sub> emissions following urea application to flooded soils, have measured losses in the range *c.* 8 - 56 % of urea-N, with a median loss of 30 %. Many of these studies used micrometeorological techniques. Patel *et al.* (1989), in a review, concluded that earlier studies using chambers, had overestimated NH<sub>3</sub> losses in the field.

A loss coefficient of 0.30 kg NH<sub>3</sub>-N per kg urea-N applied should therefore be used to calculate NH<sub>3</sub> emissions from flooded rice fields.

As noted above, application of fertilizer-N to flooded rice fields is not standard practice in all countries. When application is either to the soil before flooding, or when the crop is at panicle initiation, losses will be significantly less. In such cases, emissions should be calculated using the coefficients given in Table 4.1.

No data was found on NH<sub>3</sub> losses following AN application to rice fields. In the absence of more specific data, emissions should be calculated from Table 4.1. Fillerey and De Datta (1987), found NH<sub>3</sub>-N losses of 37 % from AS applied to flooded rice fields. We propose using the same loss coefficients for AS as for urea, when estimating NH<sub>3</sub> losses from rice field.

## 5.2 Nitrous Oxide

### 5.2.1 Nitrous Oxide – Improved Methodology

Climate, weather and soil conditions exhibit a similarly important control on N<sub>2</sub>O emissions from agricultural soils as management and fertilization. Against this background, improved methodologies were developed on the basis of multivariate regression analysis (Europe: Freibauer and Kaltschmitt, 2002; UK: Sozanska *et al.*, 2002).

Freibauer and Kaltschmitt (2002) reviewed European data of long-term field measurements and derived and applied statistical equations for annual N<sub>2</sub>O fluxes (Freibauer 2002):

- Mineral arable soils in the temperate oceanic and Mediterranean climate (without pronounced frost in winter):

$$E_{\text{N}_2\text{O}} = \alpha + \beta \cdot m_{\text{fert}} + \gamma \cdot \rho_{\text{C}} + \delta \cdot \rho_{\text{sand}} \quad (7)$$

with	$E_{\text{N}_2\text{O}}$	emission flux of N <sub>2</sub> O (Mg ha <sup>-1</sup> a <sup>-1</sup> N <sub>2</sub> O)
	$\alpha_1$	constant ( $\alpha_1 = 0.6 \text{ kg ha}^{-1} \text{ a}^{-1} \text{ N}_2\text{O}$ )
	$\beta_1$	factor ( $\beta_1 = 0.002 \text{ kg kg}^{-1}$ )
	$m_{\text{fert}}$	amount of fertilizer N applied (kg ha <sup>-1</sup> a <sup>-1</sup> N)
	$\gamma_2$	factor ( $\gamma_1 = 12.7 \text{ kg g}^{-1} \text{ ha}^{-1} \text{ N}_2\text{O}$ )
	$\rho_{\text{C}}$	organic carbon content in topsoil (g kg <sup>-1</sup> of soil weight in A horizon)
	$\delta_1$	factor ( $\delta_1 = -0.24 \text{ kg g}^{-1} \text{ ha}^{-1} \text{ N}_2\text{O}$ )
	$\rho_{\text{sand}}$	sand content in topsoil (kg kg <sup>-1</sup> of soil weight in A horizon)

- Mineral arable soils in the pre-alpine, alpine and sub-boreal climate regions (with severe frost and regular snow cover):

$$E_{\text{N}_2\text{O}} = \alpha_2 + \beta_2 \cdot m_{\text{fert}} + \varepsilon_2 \cdot \rho_{\text{N}} \quad (8)$$

with	$E_{\text{N}_2\text{O}}$	emission flux of N <sub>2</sub> O (Mg ha <sup>-1</sup> a <sup>-1</sup> N <sub>2</sub> O)
	$\alpha_2$	constant ( $\alpha_2 = -1.3 \text{ kg ha}^{-1} \text{ a}^{-1} \text{ N}_2\text{O}$ )
	$\beta_2$	factor ( $\beta_2 = 0.03 \text{ kg kg}^{-1}$ )
	$m_{\text{fert}}$	amount of fertilizer N applied (kg ha <sup>-1</sup> a <sup>-1</sup> N)
	$\varepsilon_2$	factor ( $\varepsilon_2 = 280 \text{ kg g}^{-1} \text{ ha}^{-1} \text{ N}_2\text{O}$ )
	$\rho_{\text{C}}$	total nitrogen content in topsoil (g kg <sup>-1</sup> of soil weight in A horizon)

- Mineral grassland soils in the temperate and sub-boreal climate regions:

$$E_{\text{N}_2\text{O}} = \alpha_3 + \beta_3 \cdot m_{\text{fert}} \quad (9)$$

with	$E_{\text{N}_2\text{O}}$	emission flux of N <sub>2</sub> O (Mg ha <sup>-1</sup> a <sup>-1</sup> N <sub>2</sub> O)
	$\alpha_3$	constant ( $\alpha_3 = 2.4 \text{ kg ha}^{-1} \text{ a}^{-1} \text{ N}_2\text{O}$ )
	$\beta_2$	factor ( $\beta_2 = 0.015 \text{ kg kg}^{-1}$ )
	$m_{\text{fert}}$	amount of fertilizer N applied (kg ha <sup>-1</sup> a <sup>-1</sup> N)

- Farmed organic soils (grassland and cereal crops):

$$E_{\text{N}_2\text{O}} = 7 \text{ (6-9) kg ha}^{-1} \text{ a}^{-1} \text{ N}_2\text{O-N} \quad (10)$$

- Farmed organic soils (vegetables and root crops):

$$E_{\text{N}_2\text{O}} = 20 \text{ (10-30) kg ha}^{-1} \text{ a}^{-1} \text{ N}_2\text{O-N} \quad (11)$$

It should be noted that the emission factors for organic soils do not fit the factor given by the IPCC Guidelines.

### 5.2.2 Nitrous Oxide – Detailed Methodology

N-trace gas emissions from soils are the result of different microbial and physico-chemical processes, i.e. mainly of nitrification and denitrification for NO and N<sub>2</sub>O and chemo-denitrification at soil pH-values < 5.0 for NO, occurring simultaneously in the soil. The magnitude of processes involved in N-trace gas production is strongly controlled by other biotic processes (e.g. mineralization, plant N-uptake) or by abiotic factors like e.g. temperature, soil moisture or fertilization and N-deposition, which do change substantially on spatial and temporal scales. Therefore, significant improvements of current estimates of N-trace gas fluxes from soils may only be achieved, if mechanistic models are developed and used, which are able to predict N-trace gas emissions based on the processes involved in N-trace gas production/ consumption and emission (Butterbach-Bahl *et al.*, 2001). Such mechanistic models have currently been developed, e.g. DNDC (e.g. Li *et al.*, 1992, 2000) and CENTURY (e.g. Parton *et al.*, 1996) and have already been applied at a regional scale for calculations of N-trace gas emission inventories (Brown *et al.*, 2002; Butterbach-Bahl *et al.*, 2002).

For a detailed regression orientated approach see Sozanka *et al.* (2002).

### 5.3 Nitric Oxide

A more detailed methodology, based on the soil temperature and the land use type has been developed by Williams *et al.* (1992).

$$E_{\text{NO}} = \alpha \cdot e^{\zeta \cdot t_s} \quad (12)$$

where $E_{\text{NO}}$	emission flux (ng m <sup>-2</sup> s <sup>-1</sup> NO-N)
$\alpha$	experimentally derived constant for the land use types of grasslands and pasture, forests and urban trees, and the individual agricultural categories (SNAP code 11, Table 8.1)
$\zeta$	factor ( $\zeta = 0.071 \text{ K}^{-1}$ )
$t_s$	soil temperature (°C)

To improve this approach, N input and soil moisture contents (Meixner, 1994) need to be included in the equation. Furthermore, also the soil pH is crucial determinant, since NO can be produced at soil-pH < 4.0 also by chemo-denitrification. A multiple regression approach was

developed by Sozanska (1999, see Skiba *et al.*, 2001). Soil NO emissions were calculated from the N input and the water filled pore space of the soil

$$\ln E_{\text{NO}} = -0.82 + 0.354 \ln N_{\text{input}} + 0.0036 (-WFPS^2 + 80 WFPS - 1593) \quad (13)$$

where	$E_{\text{NO}}$	emission flux (kg N ha <sup>-1</sup> y <sup>-1</sup> )
	$N_{\text{input}}$	input of N to soil by fertilizer, animal excreta, N deposition (kg ha <sup>-1</sup> a <sup>-1</sup> N)
	$WFPS$	water filled pore space (%)

The Williams approach produces much greater estimates of NO emission than are given by the simpler methodology, whereas Sozanska's multiple regression model produces much smaller estimates than the simple methodology. The authors conclude that due to the lack of data it is not appropriate to use either methodology at this stage.

As mentioned already for N<sub>2</sub>O, an improvement of estimates of NO emissions from soils may only be achieved by use of detailed mechanistic models, which allow to calculate simultaneously production, consumption and emission of NO from soils with regard to all processes involved.

#### 5.4 Carbon Dioxide

No detailed methodology is suggested.

#### 5.5 Methane

No detailed methodology is suggested.

At least with regard to CH<sub>4</sub>-emissions from rice paddy fields progress has been achieved by using mechanistic models in order to calculate CH<sub>4</sub>-emission from a plot up to a regional scale (van Bodegom *et al.*, 2001; Segers and Kengen, 1998; Denier van der Gon *et al.*, 2000).

#### 5.6 Non-methane Volatile Organic Compounds

A detailed methodology is not available.

### 6 RELEVANT ACTIVITY STATISTICS

Information is required on the annual consumption of major N-fertilizer types by each country. In principle, this may be obtained from IFA (2002) as well as from national agricultural censuses. Information may also be required on the amounts and N concentrations of crop residues returned to the soil. This may be obtained from statistics on crop production. The amounts of N deposited by animals while grazing are given in SNAP Code 100900, Manure Management Regarding Nitrogen Compounds. The area of organic soils (histosols) under cultivation is also useful. Finally information is needed on emissions of NH<sub>3</sub> and NO<sub>x</sub>.

Where spatially disaggregated inventories of fertilized culture emissions are required (section 12), information on the spatial distribution of different crop types and average N-fertilizer

inputs to each crop type may be used. In the absence of data on the use of different fertilizers for crop types, the average N-fertilizer inputs to crops may be combined with the average  $\text{NH}_3$  emission factor for a country estimated according to Tables 6.1, 6.2 and 6.3 as: Total  $\text{NH}_3/\text{N}_2\text{O}/\text{NO}$  emission/total N-fertilizer consumption. All the activity statistics required are summarized in Table 6.4.

For the improved methodology for  $\text{N}_2\text{O}$  emission, additional information on soil texture, top-soil organic carbon and total nitrogen content is required.

**Table 6.1: Spreadsheet for calculating  $\text{NH}_3$  emissions from grassland and arable land with fertilizers according to either the simpler or the detailed methodologies**

Group of country (for detailed methodology)			
Column	A	B	C
Fertilizer type	N emission factors (from Table 4.1 or 5.1) $\text{kg NH}_3\text{-N per kg N applied a}^{-1}$	Fertilizer use $\text{kg N a}^{-1}$ (see section 6)	Ammonia emissions $\text{kg NH}_3 \text{ a}^{-1}$ ( $A \cdot B \cdot 17/14$ )
Ammonium sulphate			
Ammonium nitrate			
Calcium ammonium nitrate			
Anhydrous ammonia			
Urea			
Mono-ammonium phosphate			
Di-ammonium phosphate			
Other complex NK, NPK fertilizers			
Nitrogen solution (mixed urea and ammonium nitrate)			
Total ammonia emissions in $\text{kg NH}_3$ per year			

**Table 6.2: Spreadsheet for calculating nitrous oxide emissions from cultures with fertilizers according to either the simpler methodology or the more complex methodology**

	A	B	
N input	N emission factor $\text{kg N}_2\text{O-N per kg 'net' N applied}$	N input in $\text{kg a}^{-1} \text{ N}$	$\text{N}_2\text{O}$ emission in $\text{kg N}_2\text{O a}^{-1}$ ( $A \cdot B \cdot 44/28$ )
Fertilizer- N	0.0125		
Crop residues N	0.0125		
Excretal- N deposited during grazing	0.020		
	$\text{kg ha}^{-1}$	Area (ha)	
Cultivation of histosols	5		

**Table 6.3: Spreadsheet for calculating nitric oxide emissions from cultures with fertilizers according to the simple methodology**

	A	B	
N input	NO emission factor kg NO-N per kg N applied	Fertilizer-N use in kg N a <sup>-1</sup>	Nitric oxide emission kg NO a <sup>-1</sup>
			(A · B · 30/14)
Fertilizer-N	0.007		

**Table 6.4: Summary of activity statistics which may be required for the simple and detailed methodologies.**

Activity Statistic		Source
Synthetic Fertilizer-N use	By type of fertilizer for arable and grassland	IFA or national statistics
Amount and N concentration of fertilized crop residues	By crop type	FAO, See IPCC/OECD (1997)
Amount and N concentration of animal excreta deposited during grazing	By livestock type	SNAP Code 100900, Manure Management Regarding Nitrogen Compounds
Area of cultivated histosols		FAO, See IPCC/OECD (1997)
Topsoil sand, organic carbon and total nitrogen contents	For arable soils	Combined soil / land use map

Spreadsheets for calculations of emissions according to improved or detailed methodologies can be found at The UNECE Task Force on Emission Inventories and Projections homepage (<http://www.aeat.co.uk/netcen/airqual/TFEI/unece.htm>, Supplementary Technical Information)

## 7 POINT SOURCE CRITERIA

Ammonia, N<sub>2</sub>O, NO, CH<sub>4</sub> and VOC emissions from cultures with fertilizers should be treated as area sources.

## 8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The emission factors for NH<sub>3</sub>, N<sub>2</sub>O and NO losses from cultures with fertilizers, are treated as kg of N per kg N applied as fertilizer or, in the case of crop residues incorporated into the soil, and excretal-N deposited during grazing, of the N returned in these forms. Emissions of CH<sub>4</sub> and of CO<sub>2</sub> and N<sub>2</sub>O from farmed organic soils are given per hectare and year. Full details of calculations are provided in sections 5 and 6.



## 9 SPECIES PROFILES

### 9.1 Volatile Organic Compounds

As with forest NMVOC emissions, biogenic emissions from grasslands consist of a wide variety of species, including isoprene, monoterpenes, ( $\alpha$ -pinene, limonene, etc.), and 'other' VOC. The 'other' VOC (OVOC) species consist of a large number of oxygenated compounds (alcohols, aldehydes, etc.), and have proven difficult to quantify in atmospheric samples. Progress in quantification of OVOC from European vegetation has been made recently (König *et al.*, 1995). although many more measurement data will be required before reliable attempts to inventory specific OVOC can be made.

## 10 UNCERTAINTY ESTIMATES

### 10.1 Ammonia

Although the processes governing the emission of NH<sub>3</sub> from fertilizers and crops are reasonably well understood, the interactions of many biological, chemical and environmental factors make quantitative estimates of emission rather uncertain. Key uncertainties that require further attention include:

- The extent of the temperature effect is in principle quite clearly based on physico-chemical principles. However, it is noted that warm conditions tend to be more drying due to a larger vapour pressure deficit.
- There is no effect of soil pH on emissions from ammonium nitrate and calcium ammonium nitrate in practice for emissions from grassland, as the results of GRAMINAE suggest. However, there may be some effect of pH for bare soils.
- The emission rate from anhydrous ammonia is considered to be particularly uncertain. Anhydrous ammonia is normally applied under pressure by deep injection into arable soils. Basic thermodynamics would suggest that there is a clear effect of both temperature and soil pH.
- Experimental data show that the vegetation mediated NH<sub>3</sub> emissions from fertilized cultures may be extremely variable depending on climate conditions. In principle, larger emissions are expected in warm conditions. However, Schjørring *et al.* (1991) found that under cool wet summer conditions with poor growth, grainfilling of cereals was less effective than in warm summer conditions, and this coupled with higher ammonia emissions.
- Comparative measurements of NH<sub>3</sub> emissions from urea as contrasted to ammonium nitrate almost always show much larger rates of NH<sub>3</sub> emission. However, the actual rate is extremely variable, with lowest emissions in very wet and cold conditions ( e.g. 2 % volatilization, measured by Nemitz *et al.*, 2001). Some moisture is necessary for urea hydrolysis, so the largest emissions are likely to occur in warm drying conditions where application is made onto a soil following rain (Harrison and Webb, 2001). The values are based on an average of measurements for grassland and arable soils, where emissions from the latter are half those on grassland due to frequent incorporation of urea into arable soils (Misselbrook *et al.*, 2000).

The main uncertainty lies in the generalization of emissions factors, rather than the areas of crops under cultivation which is probably accurate in most countries to better than  $\pm 10\%$ . Overall emissions are probably no better than  $\pm 50\%$ .

## 10.2 Nitrous Oxide

The processes controlling the emission of  $N_2O$  from soils are reasonably well understood. Their interactions, and the partitioning between nitrification and denitrification, and hence estimates of emission, have started to be accurately modelled in mechanistic models such as DNDC, PnET-N-DNDC and CENTURY. Application of fertilizer-N, in most countries, can probably be estimated to within  $\pm 10\%$ . However the magnitude of crop residues, and their N contents are only likely to be accurate to within  $\pm 25\%$ . Wet deposition of N may be estimated to  $\pm 20\%$ , but dry deposition of  $NH_3$  to no more than  $\pm 50\%$  (UKRGIAN 1994). Most importantly fertilizer-N induced  $N_2O$  emissions can be estimated with a certainty of a factor of 9 (range 0.25 - 2.25 % of N inputs; Bouwman, 1996). The importance of winter time  $N_2O$  emissions caused by freezing and thawing has only recently been discovered and has not been included in the IPCC methodology. This will create a further large uncertainty. There will be even greater uncertainty with regard to indirect emissions of  $N_2O$  since there are fewer measurements available of  $N_2O$  formation from atmospheric deposition, or leached N. Recent reviews suggest that the indirect  $N_2O$  emissions from leaching and runoff tend to be overestimated (Nevison 2000; Groffman *et al.*, 2000).

For typical soil conditions and fertilization rates under common agricultural practice in Europe and mean flux rates, the regression models of the improved methodology for  $N_2O$  have a mean standard error of 40 to 50 % (equation 7), 30 % (8) and 70 to 100 % (9).

## 10.3 Nitric Oxide

Although much less information is available on factors determining losses of NO from soils (N input, soil temperature and soil moisture), data, especially long-term intensive field experiments are not available to provide a good degree of certainty in the estimate. While application of fertilizer-N may be estimated with an accuracy of  $\pm 10\%$ , other factors such as returns of N in crop residues and soil N contents may be estimated to within  $\pm 25\%$ . However, the greatest uncertainty is over emission factors. Using data from essentially the same body of published work, Yienger and Levy (1995) and Skiba *et al.* (1997) arrived at mean emission factors almost an order of magnitude different, suggesting an uncertainty of a factor of 10.

## 10.3 Carbon Dioxide

## 10.4 Methane

The uncertainty in the soil  $CH_4$  sink is 100 %. The uncertainty with regard to  $CH_4$  emissions from rice paddy fields is still significant, since the magnitude of emissions is strongly affected by environmental parameters like e.g. temperature, soil properties and by field management (fertilization, drainage, cultivar). Thus, the estimates may show an error of 50 - 100 %.

## 10.5 Non-methane Volatile Organic Compounds

Biogenic VOC emissions for the UK were summarized by Hewitt and Street (1992). These ranged from 38-211 Gg a<sup>-1</sup> total NMVOCs. Emissions from woodlands were estimated to be 72 % of total biogenic emissions by Anastasi *et al.* (1991). Thus between *c.* 10 and 59 Gg a<sup>-1</sup> appear to be of agricultural origin. In their incomplete analysis Hobbs *et al.* (2003) calculated *c.* 5 Mg a<sup>-1</sup> from agricultural plants. This compares with the CORINAIR 94 estimate of only 2 Gg a<sup>-1</sup> for SNAP Code 100100 or < 2 % of emission from agriculture and forestry. Thus the range of emissions may be uncertain by a factor of 30. However the estimate for agriculture by Anastasi *et al.* (1991) was recognised as likely to be too large.

Hewitt and Street (1992) concluded that only *c.* 700 plant species, mainly from North America, had been investigated as isoprene or monoterpene emitters. Few of these were agricultural crops, and quantitative data was available for only a few species. Many measurements had been made at temperatures higher than those prevailing in North and West Europe.

## 11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

### 11.1 Ammonia

A major criticism of the present simpler estimates is their reliance on simple fixed (%) emission factors, given in relation to amounts of N applied. A first attempt to account for broad scale differences between countries (based on climate and soil type) has been included here (detailed methodology) but it is very much an empirical interpretation of the available data. Soil pH and temperature need to be included in the methodology with first priority. This could be realised by deriving functions as a synthesis of existing literature or from mechanistic modelling. More work needs to be done in the development of mechanistic process-based models for predicting NH<sub>3</sub> emissions from N-fertilizers and the foliage of fertilized crops, which take into account the known physico-chemical equilibria as well as interactions with biological processes to predict net fluxes. Such models are under development (Rachpal-Singh and Nye, 1993; van der Molen *et al.*, 1990; Génarmont and Cellier, 1997). They could be used to derive different functions in order to account for the effects of different environmental factors (temperature, rain, pH, ...). It is well established that NH<sub>3</sub> may be exchanged with the soil surface and with leaves via stomata and cuticular absorption/desorption as well as with decomposing leaves, and future work needs to quantify the interactions and exchange cycles between these different components (Sutton *et al.*, 2000). Studies of NH<sub>3</sub> emissions from grazed grassland have largely been carried out in Northwest Europe. Data is needed on emissions in warmer and drier climates. For grazed grasslands, more measured data are generally needed.

The current estimates are limited to net emission of NH<sub>3</sub> over the year, and as such integrate both periods of emission from cultures and deposition to them on both diurnal and seasonal scales. Further work is needed in quantifying the temporal variability in emissions as well as the integration of emitting surfaces and depositing surfaces for development of atmospheric models.

## 11.2 Nitrous Oxide

Current estimates of N<sub>2</sub>O emissions are also limited by the use of fixed emission factors. More work needs to be done in the development of process-based models that will allow greater discrimination to be made between soils with different moisture regimes, and between areas of different climate. Process-based models should run on daily time steps in order to capture the variability of N<sub>2</sub>O emission rates and of their controlling factors. Such models could be used to refine and adjust emission factors and to monitor N<sub>2</sub>O reduction measures (Brown *et al.*, 2002, Butterbach-Bahl *et al.*, 2002). Emissions of N<sub>2</sub>O per kg fertilizer-N applied, have been shown to be greater from grasslands, particularly from grazed grasslands, than from arable crops (Velthof *et al.*, 1996). This is caused by a combination of: soil compaction caused by the grazing animals; localised very high N and C inputs from animal excreta; and in cooler climates grasslands tend to be located on the wetter soils, less suitable for arable crop production. In addition the question of differentiating between fertilizer-N sources needs to be addressed.

Estimates of indirect emissions of N<sub>2</sub>O are dependent on accurate estimates of NH<sub>3</sub> and N<sub>2</sub>O emissions and N leaching and runoff. As long as uncertainties in these estimates are large, then so too will be estimates of indirect N<sub>2</sub>O emissions. Losses of N by leaching and run off are not necessarily directly proportional to N inputs, but depend on crop, soil, climate, etc.. It would be useful therefore to be more specific in this regard. Also integrated studies on watershed level are needed in order to quantify the relation between N input on the agricultural area and N<sub>2</sub>O emissions in surface waters downstream.

## 11.3 Nitric oxide

Reliance on a simple fixed (%) emission factor in relation to the amount of N-fertilizer applied is the major weakness. No account is taken of potentially large differences between climatic regimes. Nor is any account taken of the potential contribution from non-fertilizer sources of N, and from the mineralisation (and hence nitrification) of N already present in soils. There are not enough data available to discuss the effect of grazing on NO emissions, but the localised very high N and C inputs caused by animal excreta are likely to stimulate NO production. Again, NO emissions should be linked with N input, soil and climatic conditions by using process-based models. The mechanistic models DNDC and CENTURY have been extended to cover NO emissions.

## 11.4 Carbon Dioxide

## 11.5 Methane

The CH<sub>4</sub> sink in agricultural soils is small, so the large uncertainty does not introduce a large error in the national inventories. Therefore, no major need for improvement is seen at present stage.

## 11.6 Non-methane Volatile Organic Compounds

Lack of measurements of NMVOC emissions from agricultural vegetation is a considerable weakness. It is unknown whether emissions are related to fertilizer-N inputs.

## 12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

### 12.1 Ammonia

The simplest approach to spatially disaggregate the emissions from cultures with fertilizers is to scale these by the distribution of total arable and fertilized grassland. In a more detailed approach census data on the distribution of different crop types may be combined with characteristic fertilizer inputs to each crop type, together with the overall fertilizer emissions factor estimated from Table 4.2. Where the average N-fertilizer application to crops is derived from similar national data as the fertilizer consumption, there should be a reasonable agreement between the mapped and national total emission. However, caution is required and spatially disaggregated estimates may need to be corrected.

Caution is also required to account for the possible double counting of fertilizer/foliar emissions from grazed grassland, noted in the detailed methodology (section 5).

Where only the distribution of total grassland is available, estimates would need to be made of the fraction that is grazed, while account of the temporal overlap of grazing and culture emission should also be taken.

### 12.2 Nitrous Oxide

Direct emissions may be spatially disaggregated using census data on the distribution of different crops together with mean fertilizer-N inputs to those crops. Data on the distribution of organic soils (histosols) and on soil moisture regimes in mineral soils may also be included to improve spatial disaggregation.

Information on climatic variations (temperature and rainfall) within the country should be included. At present no standard model to do this is available, but some biogeochemical models such as DNDC (Li *et al.*, 1992) and CENTURY (Parton *et al.*, 2001) can be readily adjusted to European conditions, are being adjusted, or have already been (Brown *et al.*, 2002; Butterbach-Bahl *et al.*, 2002). Dividing the country/region into 3 to 4 climatic and soil groups and slightly modifying the IPCC methodology, by increasing and reducing the various emission factors for the individual regions, or by using simple linear regression models may be a step forward.

Indirect emissions may also be spatially disaggregated if spatial data is available for N deposition and also for N leaching and runoff.

Due to the long atmospheric lifetime of N<sub>2</sub>O, spatial resolution is not really needed.

### 12.3 Nitric Oxide

Emissions due to N-fertilizer application may be spatially disaggregated using census data on the distribution of different crops, together with mean fertilizer-N inputs to those crops, and climatic information as outlined in section 12.2.

### 12.4 Carbon Dioxide

## 12.5 Methane

The location of rice paddies is available from land use surveys. Within agricultural soils, the sink strength for CH<sub>4</sub> is small enough that no significant error is introduced to emission/removal maps if agricultural land is treated in a uniform way, even though the relative spatial variability in the CH<sub>4</sub> sink is large.

## 12.6 Volatile Organic Compounds

In the absence of specific data for VOC emissions from different agricultural crops, there appears to be little scope at present for spatially disaggregating VOC emissions.

# 13 TEMPORAL DISAGGREGATION CRITERIA

## 13.1 Ammonia

As noted in section 11, little information is available to generalize on temporally disaggregating NH<sub>3</sub> emissions from fertilizers and crops. Most of the direct emission from N-fertilizer occurs within a month of application and, for some countries, agricultural statistics and knowledge from common agricultural practice may be available on the timing of these applications. Further crop emissions may occur particularly during senescence of crop plants, and may account for *c.* 1 - 3 kg ha<sup>-1</sup> NH<sub>3</sub> emission (Schjørring and Mattsson, 2001). A major uncertainty with fertilizer, foliar, grazing and decomposing vegetation emissions, is that losses are expected to vary greatly from year to year depending on agricultural and environmental conditions.

## 13.2 Nitrous Oxide

Most of the direct emission from fertilizer-N occurs within a few weeks of application (Bouwman, 1996), and during freeze-thaw events in spring. Statistics on the timing of fertilizer-N application should be available, for some countries at least. Some data may also be available on the timing of crop residue incorporation. However, until process-based models have been developed and validated it will not be possible to take account of fluxes of N<sub>2</sub>O emission that take place when soil mineral N concentrations, soil water regimes and soil temperature combine to produce favourable conditions for N<sub>2</sub>O production by denitrification and nitrification.

As for NH<sub>3</sub>, losses may vary greatly from year to year, depending upon weather conditions.

## 13.3 Nitric Oxide

Losses of NO take place mainly as a consequence of nitrification and in acid soils as a consequence of chemo-denitrification. Peaks in NO emission are therefore likely following application of NH<sub>4</sub><sup>+</sup>-based N-fertilizers, incorporation of crop residues and tillage of soils. Data on all these should be available, for some countries at least. At present, however there are insufficient data on NO emissions to quantify these effects. Ultimately, as the mechanisms of NO production become better understood, climatic data may also be utilised to assess when soil and weather conditions are favourable for nitrification, and hence NO production (Butterbach-Bahl *et al.*, 2002). In common with NH<sub>3</sub> and N<sub>2</sub>O, emissions may vary greatly from year to year, depending upon weather conditions.

### **13.4 Carbon Dioxide**

### **13.5 Methane**

Both methanogenesis and CH<sub>4</sub> oxidation show clear seasonal trends in dependence of soil temperature and soil aeration status.

### **13.6 Volatile Organic Compounds**

Emissions of VOCs are likely to differ according to crop type, crop growth stage, soil type, cultivation and weather conditions. Some temporal disaggregation may be possible, if seasonal variations in emissions by non-agricultural plants, can be assumed to be valid for fertilized crops.

## **14 ADDITIONAL COMMENTS**

Where more detailed methodologies than those described here are used by countries, a detailed description should be given of the methodology used, and comparison made with the results of the methodology described here. Efforts to establish integrated models to quantify emissions from agricultural land should be undertaken, coupling soil, climatic and process information with GIS methods.

## **15 SUPPLEMENTARY DOCUMENTS**

The main supplementary documentation required for applying the estimates in this chapter are details of national N-fertilizer consumption and areas of fertilized grassland that are grazed. In addition estimates of the amounts and N concentrations of crop residues returned to the soil, together with the area of cultivated organic soils (histosols) will be required. The approximate timing of soil cultivation, including crop residue incorporation will also be useful. Finally information on deposition of NH<sub>3</sub> and NO<sub>x</sub>, together with estimates of N leaching and runoff are needed. Where disaggregated estimates are to be made, details on N application rates to crops and spatially disaggregated crop distribution are needed.

The use of temperature and soil pH dependent data presupposes knowledge and documentation of regional spring air temperatures and soil pH distribution.

## **16 VERIFICATION PROCEDURES**

There are no direct methods to evaluate total inventory estimates of NH<sub>3</sub> emissions from croplands, and verification is dependent on laboratory and micrometeorological field studies of emissions from example situations. In particular, many studies have focused on laboratory measurements and there is a need to provide long-term field measurements using micrometeorological techniques to estimate NH<sub>3</sub> fluxes over a range of crop types in different climates.

Emissions of N<sub>2</sub>O, NO and VOCs cannot be verified except by field studies of emissions from example situations. There is a need to obtain long-term field measurements to estimate fluxes over a range of crop types and climates.

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## 19 RELEASE VERSION, DATE AND SOURCE

Version: 4.0

Date: February 2003

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