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Supplementary information is given in the Appendix under analogous headings, e.g. A1 in the Appendix corresponds to Section 1 in the main body of this chapter.

1 Overview

Ammonia (NH₃) emissions lead to the acidification and eutrophication of natural ecosystems. Ammonia may also form secondary particulate matter (PM). Nitric oxide (NO) and non-methane volatile organic compounds (NMVOCs) play a role in the formation of ozone, which near the surface of the Earth can have an adverse effect on human health and plant growth. Particulate emissions also have an adverse impact on human health.

This chapter describes methods to estimate the emissions of NH₃, NO, NMVOCs and PM from crop production and agricultural soils. This includes both from land to which nitrogen (N)-containing fertilisers are applied and soils cultivated for crop production and grasslands, which are not given N-fertiliser.

Although losses of NH₃ from N-fertilisers applied to grass grazed by livestock are difficult to distinguish from subsequent NH₃ emissions from urine patches produced by grazing animals, those two emissions are calculated separately. Emissions following application of fertiliser-N and sewage sludge are calculated in this chapter. However, those emissions following application of livestock manures to land and from excreta deposited on fields by grazing animals are calculated in Chapter 4.B Animal husbandry and manure management. This is because the methodology developed to calculate NH₃ emissions from animal husbandry treat those emissions as part of a chain of events so that we may estimate the impacts of any factors that affect NH₃ emissions at one stage of manure management on subsequent NH₃ emissions (see Appendix A1 of Chapter 4.B Animal husbandry and manure management). Nevertheless, grazing emissions have to be reported in NFR category 4.D.2.c Persistent organic pollutants should be reported under 4G Agriculture other; as yet, no robust methodology has been developed.

We currently consider that there is insufficient evidence to justify discriminating between different crops when estimating emissions of NH₃, even though there is some evidence that NH₃ emissions from rice fields are significantly different to NH₃ emissions from the other crops. Emissions from unfertilised crops, with the exception of legumes, are usually considered to be negligible.

Crop production and agricultural soils typically contribute *ca.* 10 % of the total source strength for European emissions of NH₃ (the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC), 1994) and NO (Skiba et al., 1997), albeit the contribution varies widely among EU Member States. Emissions of gaseous N species from crop production and agricultural soils are generally related closely to the amount of fertiliser-N applied. Further information on NO is provided in Appendix A2.1.

Crop production and agricultural soils are currently estimated to emit < 1 % of total NMVOC emissions, and therefore do not yet require a methodology for calculation. 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.

Particulate matter emitted to the atmosphere is defined according to size or size distribution. In different conventions, fractions are reported from total dust down to the ultra-fine particles (see definitions in Appendix A4). Emissions from tillage land are currently estimated to account for *ca.* 10 % of agricultural PM₁₀ emissions, and as a first estimate between 1 and 4 % of total national PM emissions.

Emissions from movement of agricultural vehicles on unpaved roads, from the consumption of fuels and emissions due to the input of pesticides are not included here. Pollen and wind-blown

particles from cultivated soils not arising directly from field operations are considered as natural emissions. Further information on PM is provided in Appendix A4.1.

Table 1-1 Contributions of emissions of gases from livestock excreta and fertiliser application only: 2005 estimates from <http://webdab.emep.in> for EU-27

	NH ₃ ¹	NO _x	NMVOC	PM _{2.5}	PM ₁₀	TSP ²
Total Gg a ⁻¹	3 554	9 776	8 288	1 234	1 930	3 453
Crop production and agricultural soils Gg a ⁻¹	745	0	28	0	0	0
Crop production and agricultural soils %	21.0	0.0	0.3	0.0	0.0	0.0

Notes:

1. The estimate of NH₃ emissions includes those from grazing which while reported under 4.D, Crop production and agricultural soils, are calculated in chapter 4.B, Animal husbandry and manure management.
2. TSP = total suspended particles.

2 Description of sources

There are four main sources of emissions from crop production and agricultural soils:

- fertiliser application (NH₃)
- soil microbial processes (NO)
- crop processes (NH₃ and NMVOCs)
- soil cultivation and crop harvesting (PM).

2.1 Process description

2.1.1 Ammonia

Ammonia volatilization occurs when NH₃ in solution is exposed to the atmosphere. The extent to which NH₃ is emitted depends on the chemical composition of the solution (including the concentration of NH₃), the temperature of the solution (He et al., 1999), the surface area exposed to the atmosphere and the resistance to NH₃ transport in the atmosphere.

Although N-fertilisers are normally applied as solids, there is usually sufficient moisture in the soil or air for the fertiliser to dissolve. High pH favours the volatilization of NH₃ from many N fertilisers, so where the soil is acidic (pH values less than *ca.* 7), volatilization will tend to be small. In contrast, where the soil is alkaline, the potential for volatilization will be larger. However, the strong interaction between the fertiliser and the soil may override the effects of initial soil pH, so the volatilization depends on both the type of soil and the type of fertiliser. Direct emissions of NH₃ only occur from fertilisers containing N as ammonium (NH₄⁺) or where, as for urea, the fertiliser is rapidly decomposed into NH₄⁺. Those fertilisers containing N only as nitrate (NO₃⁻) are not direct sources of NH₃ but may increase NH₃ emissions via the crop foliage.

Emissions of NH₃ from crops mainly occur due to the increase in the concentration of N in the leaves of crops following the addition of fertiliser-N. The emission of NH₃ from crops is a complex process as it is influenced by both the concentration of NH₃ in the air and environmental conditions.

For further details see Appendix A1.2.1.1.

2.1.2 Nitric oxide

In agricultural soils, 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; Venterea et al., 2005). Nitrification is the process by which micro-organisms oxidize $\text{NH}_4^+\text{-N}$ to $\text{NO}_3^-\text{-N}$. The main determinants of NO production in crop production and agricultural soils are mineral N concentration, temperature, soil carbon concentration and soil moisture.

Increased nitrification is likely to occur following application of fertilisers containing NH_4^+ , soil cultivation and incorporation of crop residues (Aneja et al., 1997). Activities such as tillage and incorporation are considered to increase NO emissions by a factor of 4 (Skiba et al., 1997; Skiba and Ball, 2002; Civerolo and Dickerson, 1998), for periods of between one and three weeks.

2.1.3 NMVOCs

Emissions from crops may arise to attract pollinating insects, eliminate waste products or as a means of losing surplus energy. Ethene emission has been observed to increase when plants are under stress. As with forest NMVOC emissions, biogenic emissions from grasslands consist of a wide variety of species, including isoprene, monoterpenes, (α -pinene, limonene, etc.), and 'other' volatile organic compounds (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. Factors that can influence the emission of NMVOCs include temperature and light intensity, plant growth stage, water stress, air pollution and senescence.

2.1.4 PM

The main sources of PM emissions are soil cultivation and crop harvesting, which together account for > 80 % of total PM_{10} emissions from tillage land. These emissions originate at the sites where the tractors and other machinery operate and are thought to consist of a mixture of organic fragments from the crop and soil mineral and organic matter. There is considerable settling of dust close to the sources and washing out of fine particles by large particles. Field operations may also lead to re-suspension of dust already settled (re-entrainment). Emissions of PM are dependent on climatic conditions.

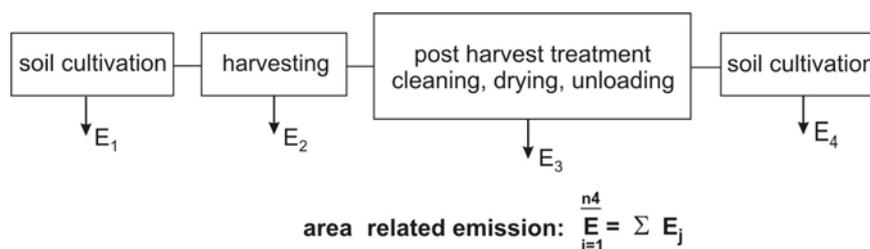


Figure 2-1 Process scheme for PM emissions from crop production and agricultural soils

2.2 Emissions

2.2.1 Ammonia

General reviews and estimates of NH_3 from fertilisers have been provided by Asman (1992), ECETOC (1994), Sutton et al. (1995b), Schjørring and Mattsson (2001) and Harrison and Webb (2001). These reviews have concluded that NH_3 emissions from urea are the most variable, ranging from 6 to 47 % of applied N, and are very dependent on factors such as soil type, weather conditions and application rates. In contrast, reported emissions from ammonium nitrate (AN) (and calcium AN, CAN) were much smaller, never exceeding 4 % of applied N. There are fewer studies of other fertilisers such as ammonium sulphate (AS) and di-ammonium phosphate (DAP). Variations in emissions result from differences in soil type and time of application. In general, it is considered that emissions from other fertilisers are less than those from urea, with the exception of AS and DAP on calcareous or otherwise alkaline soils. Results of field experiments reviewed by Harrison and Webb (2001) showed that emissions from urea ammonium nitrate (UAN) solutions were intermediate between those from urea and AN granules, but it is difficult to make firm conclusions on the effect of application in solution *per se*.

Van der Weerden and Jarvis (1997) and subsequently Harrison and Webb (2001) reviewed data from field measurements of NH_3 loss following application of N fertilisers to grassland and arable land, and concluded that NH_3 losses from N fertilisers are greater by a factor of 2 on grassland. However, subsequent measurements have failed to show such a large difference (Bouwman et al. 2002b; Misselbrook personal communication), and different EFs when N fertilisers are applied to arable or grassland are no longer considered appropriate.

Losses of NH_3 following applications of N-fertiliser 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_3 losses of up to 50 % of urea-N applied, and up to 60 % of AS-N. More recent studies of NH_3 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. A review by Patel et al. (1989) concluded that earlier studies using chambers had overestimated NH_3 losses in the field.

The evidence for direct emissions from, and uptake by, plant foliage is also good (Whitehead and Lockyer, 1989; Schjørring and Mattsson, 2001; Sutton et al., 1993). Although estimates of the component emissions from crop foliage have been made (Denmead et al., 1978; Nemitz et al., 2000), it is often difficult to separate the direct fertiliser and plant emissions in practice, since both are a function of fertiliser-N supply, and in many experiments total emissions were measured. Crop emissions appear to be rather small on an area basis; for example, Harrison (personal communication) found emissions of 1–2 kg ha^{-1} N early in the season. This means that it is difficult to obtain accurate estimates of crop emissions and the data are currently considered too uncertain to establish separate default EFs for this source. In the Tier 1 and 2 methodologies described here, the EFs used include direct emission from the fertiliser and the emission from foliage that occurs immediately following application. The only exception is the emission from cultivated legumes; here, a separate, tentative default EF is provided.

A further emission may occur from cereal crops during grain-filling or if the crop becomes diseased. However, there are currently insufficient data to justify establishing a default EF. If users have sufficient information to estimate emissions from crops, this would be considered a Tier 3 approach. In which case, users would also need to amend the EFs for fertilisers, otherwise there will be an element of double-counting.

Asman (1992) concluded that sewage sludge is a source of NH₃ emissions, but that emissions are very uncertain and not very important.

Further information on NH₃ is provided in Appendix A1.

2.2.2 Nitric oxide

A review of a global dataset of NO measurements from 189 agricultural fields, but biased toward industrialised countries, has shown that NO emissions are well related to the amount of N applied. Broadcasting fertiliser-N results in greater NO emissions than incorporating fertiliser-N or applying it as solution. Soils with organic C contents of > 3 % have significantly greater NO emissions than soils with < 3 % organic C, and good drainage, coarse texture and neutral pH promote NO emissions. Fertiliser and crop type do not appear to significantly influence NO emissions (Bouwman et al., 2002; Stehfest and Bouwman, 2006).

Stehfest and Bouwman (2006) suggested that for Europe, 1.2 % of N applied on cropland and fertilised grassland is reemitted as NO (manure application included). Freibauer and Kaltschmitt (2000) had earlier suggested 1.0 % of applied N be used as the EF. An EF of 0.66% was recently used to estimate emissions from upland soils in Asia (Yan et al., 2003). Bouwman et al. (2002) reported means of 0.5 % for animal manures and 1 % for fertiliser-N, albeit there was no significant difference in those means.

For further details see Appendix A2.

2.2.3 NMVOCs

Hewitt and Street (1992) concluded that only *ca.* 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. However, based on these limited data, a preliminary estimate of the order of magnitude of crop emissions may be made.

Emissions of NMVOCs from plants have usually been associated with woodlands, which predominantly emit isoprene and terpenes (König et al., 1995). 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.

Progress in quantification of OVOC from European vegetation has been made (König et al., 1995), although many more measurement data will be required before reliable attempts to inventory specific OVOC can be made.

Further information on how the methodology was developed is provided in Appendix A3.

2.2.4 PM

Emissions from crop production arise from soil cultivation and harvesting, of which harvesting is the predominant source. Source strength depends on crop, soil type, cultivation method, and weather conditions before and while working. Total dust emissions contain only small proportions of PM₁₀ and PM_{2.5}.

2.3 Controls

2.3.1 Ammonia

Ensuring that applications of N-fertiliser are no greater than are needed for optimum crop yield, by making full allowance for the N supplied by crop residues, organic manures, previous N-fertiliser applications, and mineralization of soil N, can lead to reductions of all N emissions including those of NH₃ and NO. Fertiliser application should also be timed to match crop demand.

Ammonia emissions from urea can be reduced by compliance with the United Nations Economic Commission for Europe (UNECE) Framework Advisory Code of Good Agricultural Practice for Reducing Ammonia Emissions

(<http://www.unece.org/env/documents/2001/eb/wg5/eb.air.wg.5.2001.7.e.pdf>) and related guidelines, for example by rapid incorporation of urea immediately after application. However, the majority of fertiliser-N is applied to growing crops of cereals or grass, where incorporation is seldom a practical option. Addition of a urease inhibitor has been reported to significantly improve the performance of urea, so that dry matter production and N uptake were almost the same as those with CAN (e.g. Watson et al., 1998). Nevertheless, it may be more cost-effective to choose an alternative N-fertiliser if the climate, soil and crop conditions are unfavourable for urea. This can reduce the NH₃ emission by up to 90 %, depending on the substituting fertiliser and on climatic and soil conditions.

Ammonia emissions may also be reduced by placing the fertiliser granule into the soil at the same depth as the seed (ca. 7–8 cm). This will only be applicable for crops sown in the spring (apart from grass reseeds in autumn). Following placement of fertilisers into the soil, NH₃ emissions have been estimated to be negligible (assuming that N supply is dimensioned correctly). Deep placement of fertiliser granules is a common technology and has been used for many years in Finland (Aura, 1967). Incorporation of fertiliser-N prior to rice planting, or delaying application until panicle initiation, have been shown to reduce NH₃ emissions from rice fields (Humphreys et al., 1988). These are already standard practices in the USA (Bacon et al., 1988). Simultaneous fertiliser application and soil cultivation could be adopted for reasons other than the desire to reduce NH₃ emissions (e.g. reduced labour demand).

Application of fertiliser-N when the weather is cool and moist or directly prior to probable rainfall will reduce NH₃ emissions. In general, increasing N use efficiency by proper timing and matching of fertilisation to crop demands will reduce all N fertiliser use, which will lead not only to reduced NH₃ emission, but losses of N₂O, NO and NO₃⁻ leaching will also be reduced. As NH₃ emissions are strongly a function of N supply, another potential control is to use cultivars or crop species which require less N.

It should be noted that few of these changes have so far been applied by countries as measures to limit NH₃ emissions, and further work would be required to provide a detailed evaluation of all these possibilities. If these techniques are adopted, it is important to consider wider implications than at the field scale. For example, if a technique decreases the yield of feed crops on a livestock farm, the farmer may respond by importing more feed. This could negate the reductions achieved and lead to other adverse side-effects.

2.3.2 NO

No potential controls have been proposed for NO emissions from fertilised crops, but the topic is discussed in Appendix A2.

2.3.3 NMVOCs

No potential controls have been proposed for NMVOC emissions from fertilised crops.

2.3.4 PM

No potential controls have been proposed for PM emissions from tillage operations. Emissions can be reduced during harvesting by encapsulating the source of emissions/by the use of dust separators.

3 Methods

3.1 Choice of method

Figure 3-1 provides the decision tree for this source category. Starting from the top left, it guides the user towards the most applicable approach.

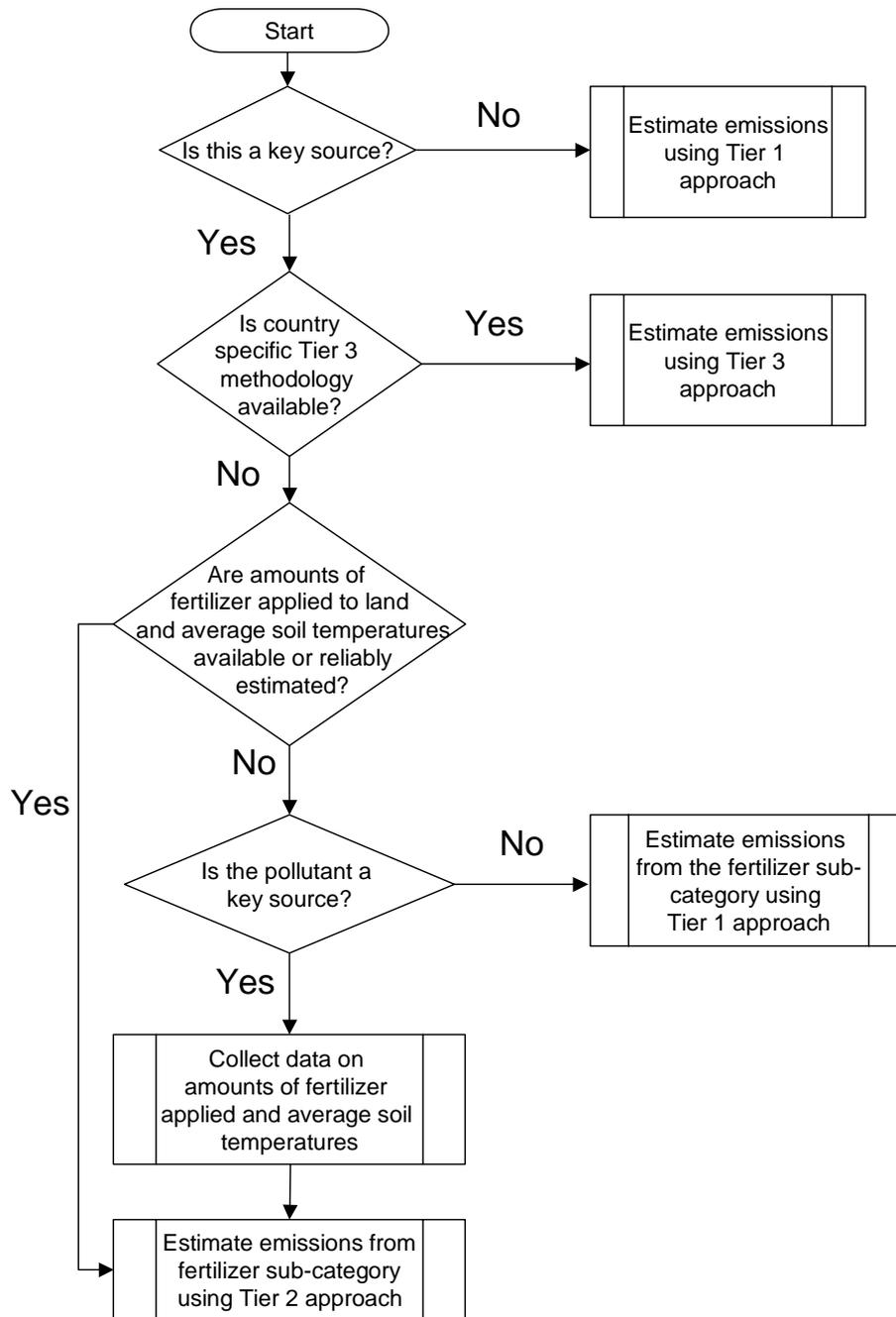


Figure 3-1 Decision tree for source category 4.D Crop production and agricultural soils

3.2 Tier 1 default approach

3.2.1 Algorithm

The Tier 1 approach for NH₃ and NO emissions from crop production and agricultural soils uses the general equation

$$E_{\text{pollutant}} = AR_{\text{fertiliser_applied}} \cdot EF_{\text{pollutant}} \quad (1)$$

where:

$$E_{\text{pollutant}} = \text{amount of pollutant emitted (kg a}^{-1}\text{),}$$

$$AR_{\text{fertiliser_applied}} = \text{amount of N applied (kg a}^{-1}\text{),}$$

$$EF_{\text{pollutant}} = \text{EF of pollutant (kg kg}^{-1}\text{).}$$

This equation is applied at the national level, using annual national total fertiliser nitrogen use.

The Tier 1 approach and for NMVOC and PM emissions from crop production and agricultural soils uses the general equation

$$E_{\text{pollutant}} = AR_{\text{area}} \cdot EF_{\text{pollutant}} \quad (2)$$

where:

$$E_{\text{pollutant}} = \text{amount of pollutant emitted (kg a}^{-1}\text{),}$$

$$AR_{\text{area}} = \text{area covered by crop (ha),}$$

$$EF_{\text{pollutant}} = \text{EF of pollutant (kg ha}^{-1} \text{ a}^{-1}\text{).}$$

It is important to note that the PM emissions calculated here are intended to reflect the amounts found immediately adjacent to the field operations. A substantial proportion of this emission will normally be deposited within a short distance of the location at which it is generated.

3.2.2 Default emission factors

The Tier 1 default NH₃ EF has been derived as a mean of default EFs for individual N fertilisers weighted according to their use in the EU-27 in 2006/7. More information on the key equations and assumptions behind these defaults can be found in Appendices A1–A4.

Table 3-1 Tier 1 emission factors for source category 4.D crop production and agricultural soils

Tier 1 default emission factors					
	Code	Name			
NFR Source Category	4D	Agricultural Soils			
Fuel	NA				
Not estimated	NO _x , CO, SO _x , Pb, Cd, Hg, As, Cr, Cu, Ni, Se, Zn, Aldrin, Chlordane, Chlordecone, Dieldrin, Endrin, Heptachlor, Heptabromo-biphenyl, Mirex, Toxaphene, HCH, DDT, PCB, PCDD/F, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, Total 4 PAHs, HCB, PCP, SCCP				
Not applicable	TSP				
Pollutant	Value	Unit	95% confidence interval		Reference
			Lower	Upper	
NMVOC	5.95539E-09	kg kg ⁻¹ fertilizer-N applied	1.92E-10	8.51E-08	Steinbrecher et al (2008)
NH ₃	0.084	kg kg ⁻¹ fertilizer-N applied	0.06	0.10	Harrison & Webb (2001)
PM ₁₀	1.56	kg/ha	0.78	7.8	van der Hoek & Hinz (2007)
PM _{2.5}	0.06	kg/ha	0.03	0.3	van der Hoek & Hinz (2007)
NO	0.026	kg kg ⁻¹ fertilizer-N applied	0.005	0.104	Steinbrecher et al (2008)

Note:

* NH₃ range of emission factors due to temperature range. Lower value refers to average spring soil temperatures below 6 °C, default 6–13 °C and upper above 13 °C.

The NO emission factor was calculated from data for Europe in Table 6 of Stehfest and Bouwman (2006), as the weighted average of the emission factors for cropland and grassland. See Appendix A3 for details of how the EF for NMVOCs was derived. The values for PM do not include emissions from fertiliser, pesticides or from grassland, e.g. hay making. These emissions

are mainly from combine harvesting and soil cultivation. In Appendix A4, further information is provided on estimates of PM emissions. In the absence of specific data with which to produce EFs following the application of sewage sludge, as a first approximation the EFs for animal manure application reported in Chapter 4.B, Animal husbandry and manure management, may be used. It is suggested that for liquid sludge the EF for pig slurry (0.40, Table 3–5) be used, while for solid sludge the EF for solid pig manure (0.81, Table 3–5) be used. Both EFs are expressed as proportion of total ammoniacal N (TAN) in the manures applied and reported in kg NH₃-N.

3.2.3 Activity data

Information is required on the annual consumption national of total N-fertiliser. Annual fertiliser consumption data may be collected from official country statistics, often recorded as fertiliser sales and/or as domestic production and imports. If country-specific data are not available, data from the International Fertiliser Industry Association (IFIA, 2002) on total fertiliser use by type and by crop, or from the Food and Agriculture Organisation of the United Nations (FAO, <http://faostat.fao.org/>) on mineral fertiliser consumption, can be used. The amounts and types of sewage sludge applied to land will also need to be known. To calculate emissions of NO data is also needed on additions of N in manures and excreta. Methods to estimate emissions of NO following manure application and from excreta deposited during grazing are provided in Chapter 4.B, Animal husbandry and manure management.

3.3 Tier 2 technology-specific approach

3.3.1 Algorithm

3.3.1.1 Ammonia

Noting the interdependence of direct fertiliser emissions and subsequent emissions from foliage and decomposing residues from fertilised vegetation, the emissions are treated here as a single integrated term. These are estimated as proportional losses of the fertiliser-N use for each of the main fertiliser categories. Emissions from unfertilised crops are considered to be zero.

A simple calculation routine is provided to estimate an EF for each major type of fertiliser-N, according to the mean spring air temperature (t_s , °C). Spring is defined as beginning when the accumulated day degrees above 0 °C since 1 January have reached 400 °C (Tsum = 400 °C) and ending three months later. The justification for this is well established, as crop emissions are known to be larger in warmer climates (Fenn and Hossner, 1985; He et al., 1999).

Step 1 is to partition the total area to which N fertiliser is applied into a number of climatic regions, according to mean spring air temperature. The temperature range within each region should not exceed 7 °C. For example, if the mean spring air temperature varies between 2 °C and 15 °C, the total area could be partitioned into the following regions; $t_s \leq 6$ °C, > 6 °C, ≤ 13 °C, > 13 °C.

Step 2 is to use the model in Table 3–2 to estimate emissions from each type of N fertiliser in each of the regions. The emission from each fertiliser type for each region is calculated as the product of the mass of fertiliser of that type applied in the region and the EF for that fertiliser type in that region. Emissions of NH₃ from fertilisers applied to grass cut for hay or silage may be calculated using the same factors as for arable and other crops. In addition, the effect of calcareous soils is included through use of a multiplier on the basis of values for different areas.

$$E_{fert_NH3} = \sum_{i=1}^I \sum_{j=1}^J \left(m_{fert_i_j} \cdot EF_{i_j} \cdot (1 - p_{alk_j} \cdot (1 - c_i)) \right) \quad (3)$$

where:

E_{fert_NH3}	=	emission flux (kg a ⁻¹ NH ₃),
$m_{fert_i_j}$	=	mass of fertiliser-N applied as type i in the jth region (kg a ⁻¹ , N),
EF_{i_j}	=	EF for fertiliser type i in region j (kg NH ₃ (kg N) ⁻¹),
p_{alk_j}	=	proportion of the ith region where soil pH>7.0,
c_i	=	soil pH multiplier for fertiliser type i.

Step 3 is to calculate the ammonia emission from pasture grazed by livestock (E_{graz_NH3} ; kg a⁻¹ NH₃):

$$E_{graz_NH3} = E_{graz} \cdot 17/14 \quad (4)$$

where

E_{graz} (kg a⁻¹, NH₃-N) is calculated in Step 14 of the Tier 2 methodology of calculating ammonia emission from Chapter 4.B, Animal husbandry and manure management.

Step 4 is to calculate the total ammonia emission from soil (E_{NH3} ; kg a⁻¹ NH₃):

$$E_{NH3} = E_{fert_NH3} + E_{graz_NH3} \quad (5)$$

There is no Tier 2 approach for sewage sludge applications.

3.3.1.2 Nitric oxide

No Tier 2 methodology available; use Tier 1, but see Appendix A2 for discussion of proposed approaches.

3.3.1.3 NMVOCs

No Tier 2 methodology available; use Tier 1.

3.3.1.4 PM

Emissions should be calculated by multiplying the cultivated area of each crop by an EF and by the number of times the emitting practice is carried out.

$$E_{PM} = \sum_{i=1}^I \sum_{n=0}^{N_{i_k}} EF_{PM_i_k} \cdot A_i \cdot n \quad (6)$$

where

E_{PM}	=	emission of PM ₁₀ or PM _{2.5} from the ith crop in kg a ⁻¹ ,
I	=	number of crops grown,
A_i	=	annual cropped area of the ith crop in ha,
N_{i_k}	=	number of times the kth operation is performed on the ith crop, in a ⁻¹ ,
$EF_{PM_i_k}$	=	EF for the kth operation of the ith crop, in kg ha ⁻¹ .

The default values of the EF are shown in Tables 3–3 to 3–6.

It is important to note that the PM emissions calculated here are intended to reflect the amounts found immediately adjacent to the field operations. A substantial proportion of this emission will normally be deposited within a short distance of the location at which it is generated.

3.3.2 Technology-specific emission factors

3.3.2.1 Ammonia

For ease of reference, the NH₃ EF are summarized below in a single table.

Table 3-2 Emission factors for total NH₃ emissions from soils due to N fertiliser volatilization and foliar emissions for various climatological regions with adjustments for emissions on soils of pH > 7.0. Values are kg NH₃ volatilized per kg fertiliser-N applied and the mean spring temperature t_s (in °C). Derived from van der Weerden and Jarvis (1997) and expert judgement

Fertiliser type	EF _i	Multiplier c
Ammonium sulphate	= 0.0107 + 0.0006 t_s	¹⁾ 10
Ammonium nitrate	= 0.0080 + 0.0001 t_s	1
Calcium ammonium nitrate	= 0.0080 + 0.0001 t_s	1
Anhydrous ammonia	= 0.0127 + 0.0012 t_s	4
Urea	= 0.1067 + 0.0035 t_s	1
Nitrogen solutions	= 0.0481 + 0.0025 t_s	1
Ammonium phosphates	= 0.0107 + 0.0006 t_s	¹⁾ 10
Other NK and NPK	= 0.0080 + 0.0001 t_s	1

Note

¹⁾ The multipliers are used when these fertilisers are applied to soils with pH > 7.0 (Harrison and Webb, 2001).

3.3.2.2 Nitric oxide

No method is currently available.

3.3.2.3 NMVOCs

No method is currently available.

3.3.2.4 PM

Dry climate conditions = mediterranean climate, wet climate conditions = all other climates

Table 3-3 Tier 2 EFs for agricultural crop operations, in kg ha⁻¹ PM₁₀, wet climate conditions

Crop	K				
	I	1	2	3	4
Wheat	1	0.25	0.49	0.19	0.56
Rye	2	0.25	0.37	0.16	0.37
Barley	3	0.25	0.41	0.16	0.43
Oat	4	0.25	0.62	0.25	0.66
Other arable	5	0.25	NA	NA	NA
Grass	6	0.25	0.25	0	0

Note: grass includes hay making only.

Table 3–4 Tier 2 EFs for agricultural crop operations, in kg ha⁻¹ PM₁₀, dry climate conditions

Crop	Soil cultivation		Harvesting		Cleaning	Drying
	I	1	2	3		
Wheat	1	2.25	2.45	0.19	0	
Rye	2	2.25	1.85	0.16	0	
Barley	3	2.25	2.05	0.16	0	
Oat	4	2.25	3.10	0.25	0	
Other arable	5	2.25	NA	NA	NA	
Grass	6	2.25	1.25	0	0	

Note: grass includes hay making only.

Table 3–5 Tier 2 EFs for agricultural crop operations, in kg ha⁻¹ PM_{2.5}, wet climate conditions

Crop	Soil cultivation		Harvesting		Cleaning	Drying
	I	1	2	3		
Wheat	1	0.015	0.02	0.009	0.168	
Rye	2	0.015	0.015	0.008	0.111	
Barley	3	0.015	0.016	0.008	0.129	
Oat	4	0.015	0.025	0.0125	0.198	
Other arable	5	0.015	NA	NA	NA	
Grass	6	0.015	0.01	0	0	

Note: grass includes hay making only.

Table 3–6 Tier 2 EFs for agricultural crop operations, in kg ha⁻¹ PM_{2.5}, dry climate conditions

Crop	Soil cultivation		Harvesting		Cleaning	Drying
	I	1	2	3		
Wheat	1	0.12	0.098	0.0095	0	
Rye	2	0.12	0.074	0.008	0	
Barley	3	0.12	0.082	0.008	0	
Oat	4	0.12	0.125	0.0125	0	
Other arable	5	0.12	NA	NA	NA	
Grass	6	0.12	0.05	0	0	

Note: grass includes haymaking only.

Source of default EFs - Van der Hoek and Hinz (2007).

3.3.3 Activity data

Information is required on the annual national consumption of the N-fertiliser types shown in Table 3–2. Annual fertiliser consumption data may be collected from official country statistics, often recorded as fertiliser sales and/or as domestic production and imports. If country-specific data are not available, data from the International Fertiliser Industry Association (IFIA, 2002) on total fertiliser use by type and by crop, or from the Food and Agriculture Organisation of the United Nations (FAO, <http://faostat.fao.org/>) on mineral fertiliser consumption, can be used. Fertiliser use also needs to be disaggregated by fertiliser type and climatic region for major crops. In addition, if ammonium sulphate or diammonium phosphate are significant sources, then

information will be needed on the amounts of those fertilisers applied to soils of < and > pH 7.0. It should be noted that most data sources (including FAO) might limit reporting to agricultural N uses, although applications may also occur on forest land, settlements, or other lands. This unaccounted N is likely to account for a small proportion of the overall emissions. However, it is recommended that countries seek out this additional information whenever possible.

Where spatially disaggregated inventories of fertilised culture emissions are required (see subsection 4.7 of the present chapter), information on the spatial distribution of different crop types and average N-fertiliser inputs to each crop type may be used. In the absence of data on the use of different fertilisers for crop types, the average N-fertiliser inputs to crops may be combined with the average NH₃ EF for a country estimated: total NH₃ emission/total N-fertiliser consumption.

3.4 Tier 3 emission modelling and use of facility data

3.4.1 Algorithm

Tier 3 methodologies are those that result in more accurate estimates of emissions than would be achieved using the Tier 2 methodology. This could include the use of alternative EFs, based on local measurement, the use of more detailed activity data and EFs or the use of process-based models. Users are encouraged to use Tier 3 methodologies wherever possible. If measures are taken to reduce emissions, such as those mentioned in subsection 2.4 above, it may be necessary to use a Tier 3 methodology to gain acceptance of the effect on emissions. For example, immediate incorporation of mineral fertiliser would reduce direct emissions, so the EF for the relevant type of fertiliser would require modification. In contrast, reducing fertiliser use by balancing fertiliser applications to crop requirements would not require a Tier 3 approach, since the effect would be adequately reflected by the change in the activity data.

For estimating NH₃ emissions using Tier 3 methodology, process-based models are useful because in appropriate forms they can relate the soil and environmental variables responsible for NH₃ emissions to the size of those emissions. These relationships may then be used to predict emissions from whole countries or regions for which experimental measurements are impracticable. Models should only be used after validation by representative experimental measurements.

An example of a simple process-based model for estimating NH₃ emissions from fertiliser applications to agricultural land is provided by Misselbrook et al. (2004). This has been incorporated into the UK NARSES model and used for construction of the UK NH₃ emission inventory. Important influencing variables which are included in this model are type of N fertiliser, soil pH, land use, application rate, rainfall and temperature. Each fertiliser type is associated with a maximum potential emission (EF_{max}), which is modified by functions relating to the other variables (soil pH, land use, etc.,) to give an EF for a given scenario:

$$EF = EF_{\max} \cdot RF_{\text{soilpH}} \cdot RF_{\text{landuse}} \cdot RF_{\text{rate}} \cdot RF_{\text{rainfall}} \cdot RF_{\text{temperature}} \quad (7)$$

where

RF is the reduction factor, expressed as a proportion, associated with the variable.

Process-based modelling could also be used to estimate emissions from legumes and unfertilised pastures. A Tier 3 methodology for NH₃ emission from legumes could include alternative, empirically-derived values of the N fixation rate or EF used in equation 3.

3.4.2 Activity data

Data will typically be required on type of N fertiliser applied, soil pH, land use, application rate, rainfall and temperature. Activity data for model input can be gathered from country-specific databases, trade associations (preferred) or, where these data are unavailable, can be found in different international databases: International Food Policy Research Institute (IFPRI) and International Soil Reference and Information Centre (ISRIC) in Wageningen, Netherlands (www.isric.org); EUROSTAT (<http://epp.eurostat.ec.europa.eu>); CAPRI database (www.agp.uni-bonn.de/agpo/rsrch/capri/capri_e.htm).

4 Data quality

4.1 Completeness

All nitrogenous fertilisers and all cropped land should be included. See Appendices A3.4.1 and A4.4.1 for NMVOC and PM.

4.2 Avoiding double counting with other sectors

Caution is required to account for the possible double counting of fertiliser/foiar emissions from grazed grassland, noted in subsection 2.1.1. 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 soil emission should also be taken.

4.3 Verification

There are no direct methods to evaluate total inventory estimates of NH₃ 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 NH₃ fluxes over a range of crop types in different climates.

Emissions of NO, NMVOC and PM cannot be verified except by field studies of emissions from example situations.

4.4 Developing a consistent time series and recalculation

Ideally, the same method is used throughout the entire time series. However, the detail and disaggregation of emissions estimates from this source category may improve over time. In cases where some historic data are missing, it may be necessary to derive the data using other references or data sets. Estimates of the proportions of N fertilisers applied to soils of pH > 7.0 may need to be derived based on expert judgment. Interannual changes in EF are not expected unless mitigation measures are undertaken. These factors should be changed only with the proper justification and documentation. If updated defaults for any of these variables become available through future research, inventory agencies must recalculate their historical emissions. It is important that the methods used reflect the results of action taken to reduce emissions and the methods and results are thoroughly documented. If policy measures are implemented such that activity data are affected directly (e.g., increased efficiency of fertiliser use resulting in a decrease in fertiliser consumption), the effect of the policy measures on emissions will be transparent, assuming the activity data is carefully documented. In cases where policy measures have an

indirect effect on activity data or EF (e.g., a change to the timing of fertiliser-N application), inventory input data should reflect these effects. The inventory text should thoroughly explain the effect of the policies on the input data.

4.5 Uncertainty assessment

The main uncertainty lies in the generalization of EF, 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 $\pm 50\%$.

The relative 95 %-confidence interval for the NO emission estimates may be regarded as from -80 % to +406 % as given by Stehfest and Bouwman (2006), thus overall uncertainty may be considered to be a factor of four. See also Appendix A2.4.5.

For NMVOCs, the uncertainty in the emission potential of plant species accounts for about half of the overall uncertainty of a factor of four for, e.g. an annual emission inventory of Great Britain (Stewart et al., 2003). See also Appendix A3.4.5.

No uncertainty can be given for the first estimates of PM, but will be probably in the range of one order of magnitude depending on the high variations of EFs and activity data.

4.5.1 Activity data uncertainties

Application of fertiliser-N may be estimated with an accuracy of $\pm 10\%$; other factors such as returns of N in manures may be estimated to within $\pm 25\%$. With respect to national data on crop areas, an uncertainty of $< 5\%$ is assumed, with a normal distribution.

4.6 Inventory quality assurance/quality control QA/QC

Guidance on the checks of the emission estimates that should be undertaken by the persons preparing the inventory are given in the General Guidance Chapter 6, Inventory management. Some issues of particular relevance are given here.

Review of emission factors

The inventory compiler should review the default EFs and document the rationale for selecting specific values. If using country-specific factors, the inventory compiler should compare them with the default EFs reported here. Also, if accessible, relate to country-specific EFs used by other countries with comparable circumstances. Differences among country-specific factors and default or other country factors should be explained and documented.

Review of any direct measurements

If using factors based on direct measurements, the inventory compiler should review the measurements to ensure that they are representative of the actual range of environmental and management conditions, and interannual climatic variability, and were developed according to recognised standards (IAEA, 1992). The QA/QC protocol in effect at the sites should also be reviewed and the resulting estimates compared between sites and with default-based estimates.

Activity data check

The inventory compiler should compare country-specific data on mineral fertiliser consumption with fertiliser usage data from the IFA and mineral fertiliser consumption estimates from the FAO. National crop production statistics should be compared with FAO crop production statistics.

4.7 Gridding

Emissions due to N-fertiliser application may be spatially- as well as temporally-disaggregated using census data on the distribution of different crops and the application data statistics, together with mean fertiliser-N inputs to those crops, and climatic information as outlined in Appendices A1.4.7 and A2.4.7.

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

Specific yield is one factor which may influence PM emissions during harvesting. More important are climatic conditions and soil composition in the particular cereal-growing regions. This is important because there are large regional differences in plant production depending on the properties of soil and climate and the requirements of the end user.

4.8 Reporting and documentation

General guidance on reporting and documentation is given in the General Guidance Chapter 6, Inventory management.

The main supplementary documentation required for applying the estimates in this chapter are details of national N-fertiliser consumption. The approximate timing of soil cultivation, including crop residue incorporation, will also be useful. 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.

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See in particular: Asman (1992), Bouwman (1996), ECETOC (1994), Holtan-Hartwig and Bøckman (1994), Intergovernmental Panel on Climate Change (IPPC)/ Organisation for Economic Co-operation and Development (OECD) (1995), Skiba et al. (1997), Sutton et al. (1995b), and Harrison and Webb (2001).

6 Point of enquiry

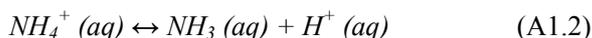
Enquiries concerning this chapter should be directed to the relevant leader(s) of the Task Force on Emission Inventories and Projection's expert panel on Agriculture and Nature. Please refer to the TFEIP website (tfeip-secretariat.org/) for the contact details of the current expert panel leaders.

Appendix A1 Ammonia

A1.2 Description of sources

A1.2.1 Process description

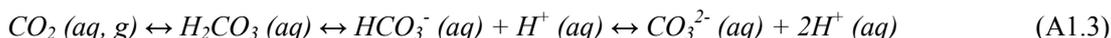
Ammonia volatilization is a physic-chemical process which results from the equilibrium (described by Henry's law) between gaseous phase NH_3 and NH_3 in solution (equation A1.1), NH_3 in solution is in turn maintained by the equilibrium between ammonium (NH_4^+) and NH_3 (equation A1.2):



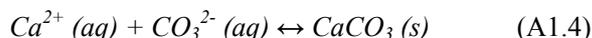
High pH (i.e. low $[\text{H}^+ (aq)]$) favours the right-hand side of equation (A1.2), resulting in a greater concentration of NH_3 in solution and also, therefore, in the gaseous phase. Thus, where the soil is buffered at pH values less than *ca.* 7, the dominant form of ammoniacal-N (NH_x) will be NH_4^+ and the potential for volatilization will be small. In contrast, where the soil is buffered at higher pH values, the dominant form of NH_x will be NH_3 and the potential for volatilization will be large, although other chemical equilibriums may serve to increase or decrease this.

While NH_3 emissions tend to increase with soil pH, there is a strong interaction between the fertiliser and the soil solution which may (e.g. for urea) override the effects of initial soil pH through hydrolysis and precipitation reactions. Important in this regard is the effect of the soil cation exchange capacity (CEC); large soil CEC (more specifically, high NH_4^+ retention) tends to reduce NH_3 volatilization potential by reducing the concentration of NH_4^+ in the soil solution by adsorption of NH_4^+ on the exchange sites.

The ambient soil pH results in the establishment of bicarbonate-carbonate equilibrium with dissolved carbon dioxide (CO_2):



In acid soils, this equilibrium lies to the left, so that the concentration of free carbonate (CO_3^{2-}) ions is negligible. However, in alkaline (calcareous) soils, the CaCO_3 solubility equilibrium also becomes important:



It is apparent that the addition of soluble Ca^{2+} will move this equilibrium (A1.4) to the right, reducing the concentration of CO_3^{2-} in solution, thus generating additional H^+ ions (i.e. reducing the pH) via equilibrium (A1.3). Further, the addition of any other ion which forms sparingly soluble salts with Ca^{2+} (e.g. sulphate) will act in the opposite manner by reducing $[\text{Ca}^{2+}]$ and hence increasing $[\text{CO}_3^{2-}]$ (A1.4). This will move equilibrium (A1.3) to the right and reduce $[\text{H}^+]$ (i.e. increase pH).

Meteorological conditions and time of application in relation to crop canopy development (Holtan-Hartwig and Bøckmann, 1994; Générumont, 1996) also have an influence. Emissions of NH_3 increase with increasing temperature and wind speed. Emissions may be reduced if significant rainfall occurs during the main volatilization period, essentially in the 10 days after fertiliser application (Misselbrook et al., 2004).

The timescale over which the emission estimates are made is important to note. Fertiliser emissions are largest in the days after fertiliser application, but in some instances (e.g. urea applied in dry conditions resulting in a slow hydrolysis), fertiliser emission may proceed for over a month after application (Sutton et al., 1995a). For background emissions (other than initial fertiliser losses) during the plant growing period, most of the emission occurs indirectly from the foliage. The direct emissions of NH_3 that have been measured from crops have been attributed to enrichment of the apoplast with NH_4^+ following addition of fertiliser-N (Sutton et al., 1995a). However, as well as being influenced by air concentration and environmental conditions, both emission and deposition occur on diurnal cycles.

Foliar emissions are expected to be larger from annual cereal crops than from fertilised 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. The limited experimental work (Whitehead and Lockyer, 1989) found only emission from grass foliage with a large N content where much N-fertiliser had been applied, and was restricted to laboratory measurements which may overestimate emission. Measurements have also indicated significant NH_3 emissions from decomposing brassica leaves, especially after cutting (Sutton et al., 2001; Husted et al., 2000).

A1.1.2 Additional justification of methodologies and emission factors

Ammonia

Direct emission following fertiliser-N application is the most understood source of NH_3 emissions from crop production and agricultural soils. Emissions take place from the soil surface layer and decrease as the NH_4^+ ions are absorbed onto soil colloids or nitrified. Hence, fertiliser-N that is immediately incorporated into the soil will not be a source of NH_3 .

The main factors controlling NH_3 volatilization are the type of N-fertiliser applied, the rate of hydrolysis for urea fertiliser, and changes in soil pH following application for all fertilisers (Whitehead and Raistrick, 1993; ECETOC, 1994; Harrison and Webb, 2001). When N is applied to soils in the form of urea it is rapidly hydrolyzed by the extracellular enzyme urease (which is ubiquitous in soils) to ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) and the NH_4^+ ions provide the main source of NH_3 . In addition, hydrolysis of urea releases CO_2 , which increases pH and favours NH_3 volatilization (equation A1.2). While NH_3 losses from AS and di-ammonium phosphate (DAP) have been found to increase markedly with increasing pH (e.g. Whitehead and Raistrick, 1993), NH_3 loss from urea is less dependent on initial soil pH, due to the pH increase immediately around the fertiliser granule to *ca.* 9.2 from urea hydrolysis (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-fertilisers, NH_3 loss from urea did not increase consistently with pH, and was not greater on a calcareous soil (Whitehead and Raistrick, 1993). This was considered due to differences in cation exchange capacity (CEC). Whitehead and Raistrick (1993) also found losses of NH_3 from cattle urine were no greater on calcareous than on non-calcareous soils. The best correlation with NH_3 loss was with CEC. Gezgin and Bayrakli (1995) measured NH_3 losses from urea, AS and AN on calcareous soils in Turkey. Losses from AS (*ca.* 16 %) and AN (*ca.* 5 %) were greater than those measured on non-calcareous soils by Sommer and Jensen (1994), which were < 5 % and < 2 % respectively. However losses from urea at *ca.* 8 % were less

than those measured by Sommer and Jensen (1994). Nevertheless a greater EF for urea in Group 1 countries is justified by the greater temperatures. Application to calcareous soils will, however, increase NH_3 losses from AS (Fleisher et al., 1987). Other fertilisers, such as AN, are more neutral in pH and produce much smaller emissions. These are often difficult to distinguish in measurements from plant-atmosphere fluxes.

Recent results from Japan (Hayashi et al., 2006) suggest large losses usually reported from paddy fields may be a consequence of high temperatures and not directly applicable to production in more temperate regions. Furthermore, an application rate also affects an EF for urea; 21 % with a rate of 30 kg N ha^{-1} at panicle formation and reduced to 0.5 % with a rate of 10 kg N ha^{-1} at heading, in which the rice plants effect on net exchange was included (Hayashi et al., 2008). In consideration of the reduced emissions from application at panicle initiation and the practice of applying much of the fertiliser-N at that stage, an EF of 22 % for urea was recently proposed by Yan et al. (2003). The same EF was used for AS.

Measured data on NH_3 fluxes over legume crops are sparse. Dabney and Bouldin (1985) measured significant diurnal variation in emissions from a growing alfalfa crop with an average daily emission equivalent to $1.2 \text{ kg ha}^{-1} \cdot \text{a}^{-1} \text{ NH}_3\text{-N}$, but an annual nightly deposition of $1.6 \text{ kg ha}^{-1} \cdot \text{a}^{-1} \text{ NH}_3\text{-N}$. However, losses during the three 10-day periods following the three cuts of hay averaged $3.8 \text{ g ha}^{-1} \cdot \text{h}^{-1}$ for 24-h-day⁻¹, or *ca.* $2.3 \text{ kg ha}^{-1} \cdot \text{a}^{-1} \text{ NH}_3\text{-N}$ from an alfalfa crop. Harper et al. (1989) reported fluxes ranging from -0.4 (deposition) to $0.4 \text{ g ha}^{-1} \cdot \text{h}^{-1}$, with net depositions of $0.4\text{--}3.1 \text{ kg ha}^{-1} \cdot \text{a}^{-1}$ to soybeans. Lemon and van Houtte (1980) measured both emissions of $3 \text{ g ha}^{-1} \cdot \text{h}^{-1} \text{ NH}_3$ from soybeans and $0.36 \text{ mg ha}^{-1} \cdot \text{h}^{-1} \text{ NH}_3$ from the top leaves of the alfalfa, and deposition fluxes over soybeans, the balance depending upon the ambient concentration at the top of the canopy. These data indicate that, while the impact of such emissions on annual net emissions might be small, they may have a substantial impact on temporal variability at both the seasonal and diurnal scales.

Appendix A2 Nitric oxide

A2.1 Overview

Soils and crops are considered to be a net sink for most NO_x (NO + NO₂) compounds. However, NO may be released from soils during nitrification and denitrification following N application and mineralization 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., 2001). At the global scale recent estimates consider that NO_x emission from soils could represent more than 40 % of NO_x emission (Davidson and Kinglerlee, 1997; Penner et al., 1993) and up to 65 % for the USA (Hall et al., 1996).

A2.2 Description of sources

A2.2.1 Process description

In plant production and agricultural soils, where pH is likely to be maintained above 5.0, nitrification is considered to be the dominant pathway of NO emission. Nitric oxide is also a substrate and product of denitrification, but it is only very rarely emitted as a consequence of denitrification in European soils. See Ludwig et al (2001) for further details.

A2.2.2 Emissions

Data on NO emissions in relation to fertiliser-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 fertiliser-N. Based on almost the same dataset Skiba et al. (1997) showed that NO losses ranged from 0.003 to 11 % of applied fertiliser-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 fertiliser induced NO emission of 0.7 %. Earlier, an EF of 1.0 % of applied N was suggested by Freibauer and Kaltschmitt (2000).

A2.2.3 Controls

In temperate climates, NO emissions are considered to be predominantly a consequence of nitrification. Hence, substitution of AN for urea to reduce NH₃ emissions, may also give some reduction in NO emissions, the results from Slemr and Seiler (1984) are consistent with this hypothesis. Nevertheless, these conclusions can only be tentative as there are insufficient data to discriminate between fertiliser-N sources (Skiba et al., 1997). Chu et al. (2006) reported that the use of controlled-release urea fertiliser could reduce emissions of NO.

A2.3 Methods

A2.3.1 Tier 2 Technology Specific Approach

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

$$E_{\text{NO}} = \alpha \cdot e^{\zeta \cdot t_s} \quad (\text{A2.1})$$

where:

E_{NO} = emission flux ($\text{ng m}^{-2} \text{s}^{-1}$ NO-N),

α = experimentally derived constant for the land use types of grasslands and pasture, forests and urban trees, and the individual agricultural categories ($\text{ng m}^{-2} \text{s}^{-1}$ NO-N),

ζ = factor ($\zeta = 0.071 \text{ K}^{-1}$),

t_s = soil temperature ($^{\circ}\text{C}$).

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

$$\ln E_{NO} = -0.82 + 0.354 \ln N_{input} + 0.0036 (-WFPS^2 + 80 WFPS - 1593) \quad (\text{A2.1})$$

where

E_{NO} = emission flux ($\text{kg ha}^{-1} \cdot \text{a}^{-1}$ N),

N_{input} = input of N to soil by fertiliser, animal excreta, N deposition ($\text{kg ha}^{-1} \cdot \text{a}^{-1}$ 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.

Based on a statistical analysis of a wide range of published experimental data, Stehfest and Bouwman (2006) produced the following model for the emission of NO (E_{NO}):

$$\ln(E_{NO}) = \text{const} + c_{\text{climate}} + c_{\text{soilN}} + c_{\text{Nrate}} \quad (\text{A2.2})$$

Where c_{climate} , c_{soilN} and c_{Nrate} are constants describing the effect of climate, soil N and the rate of N fertiliser application respectively. The 'const' term relates to the empirical constant found in the analysis, plus the effect of the length of the trials from which the data were collated. This model seems suitable for use as a Tier 2 methodology but further consideration of the availability of activity data.

An improvement of estimates of NO emissions from soils may be achieved by use of detailed mechanistic models, which allow simultaneous calculations of production, consumption and emission of NO from soils with regard to all processes involved.

A2.4 Data quality

A2.4.5 Uncertainty assessment

Less information is available on factors determining losses of NO from soils (N input, soil temperature and soil moisture, soil texture, soil carbon). Long-term intensive field experiments are not currently sufficient to provide a good degree of certainty in the estimate. Data available suggest that the EF for NO is broadly similar to the EF for N_2O (Bouwman et al., 2002; Stehfest and Bouwman, 2006).

A2.4.7 Gridding and temporal disaggregation

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_4^+ -based N-fertilisers, 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., 2004). In common with NH_3 , NO emissions may vary greatly in space and time from year to year, depending upon weather conditions, and fertiliser input.

Appendix A3 NMVOCs

A3.2 Description of sources

A3.2.1 Emissions

Hewitt and Street (1992) concluded that trees are the main emitters of non-methane hydrocarbons (NMHCs). Other plants, including crops, were insignificant sources in comparison. However, although NMVOC emissions from plant production and agricultural soils are smaller than from woodlands, they may not be entirely negligible (Simpson et al., 1999). König et al., (1995) noted that in earlier studies NMHCs had been regarded as the major component of VOC emissions. However, König et al. (1995) 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.

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.

As with forest NMVOC emissions, biogenic emissions from grasslands consist of a wide variety of species, including isoprene, monoterpenes, (α -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 (König et al., 1995), although many more measurement data will be required before reliable attempts to inventory specific OVOC can be made.

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).

Justification of methodologies and emission factors

The sparse information on NMVOC emissions does not allow for the construction of a Tier 2 methodology. However, Dämmgen et al. (2008) 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 Tier 1 methodology. The EFs include partial EFs for isoprene, terpenes, alcohols, aldehydes, ketones, ethers and other organic compounds and their contribution to overall emissions.

The use of the following equation and data is recommended for Northern and Central Europe:

$$E_{\text{NMVOC}_{\text{crop}}} = \sum A_i \cdot m_{\text{D}_i} \cdot t_i \cdot \text{EF}_i \cdot \beta \quad (\text{A3.1})$$

where

$E_{\text{NMVOC}_{\text{crop}}}$	NMVOC emission flux from cropped areas (kg a^{-1} NMVOC),
A_i	area covered by crop _{<i>i</i>} (ha a^{-1}),
m_{D_i}	mean dry matter of crop _{<i>i</i>} ($\text{kg ha}^{-1} \cdot \text{a}^{-1}$),
t_i	fraction of year during which crop _{<i>i</i>} is emitting (in a^{-1}),
EF_i	emission factor for crop <i>i</i> (kg kg^{-1} NMVOC),
β	mass units conversion ($\beta = \text{kg kg}^{-1}$).

with

$$EF_{\text{NMVOC-C}_{i,k}} = EF_{\text{NMVOC}_{i,k}} / f_{\text{NMVOC}_k} \quad (\text{A3.2})$$

where

$EF_{\text{NMVOC}_i, k}$ NMVOC-C emission factor for crop i and aggregated species k (in kg kg^{-1} NMVOC-C),
conversion factor NMVOC-C to NMVOC for aggregated species k (in kg kg^{-1}).

For further information consult Dämmgen et al. (2007) and the literature cited therein.

Table A3-1 NMVOC EFs $EF_{\text{NMVOC-C}, i}$ for agricultural crops, in kg kg^{-1} NMVOC, and fraction of year, during which crops emit, in a^{-1}

Crop	Isoprene	terpenes	alcohols	aldehydes	ketones	ethers and others	Fraction of year emitting
Cereals			$8.0 \cdot 10^{-10}$	$2.8 \cdot 10^{-9}$	$2.2 \cdot 10^{-9}$	$5.1 \cdot 10^{-9}$	0.3
Oilseed rape		$7.5 \cdot 10^{-8}$	$5.2 \cdot 10^{-8}$	$1.1 \cdot 10^{-9}$		$6.4 \cdot 10^{-8}$	0.3
Grass	$2 \cdot 10^{-10}$	$6.4 \cdot 10^{-8}$	$7.5 \cdot 10^{-10}$	$1.3 \cdot 10^{-9}$		$1.8 \cdot 10^{-9}$	0.5

NMVOC-C EF can be converted to NMVOC EF once the speciation is known. In Table A3–2, alcohols, aldehydes and ketones as well as ethers and others have to be disaggregated. For alcohols, aldehydes and ketones we made use of the default NMVOC split provided in Steinbrecher et al. (2008) for oxy-VOCs. In Helmig et al. (1999), one compound was identified for ‘ethers and others’ that was analyzed for a grass species (cis-3-hexenyl acetate). It occurs in roughly the same concentration ratio terpenes to ester as given by König et al. (1995). The derivation of the conversion factors can be traced in Table A3–2.

The conversion factor $f_{\text{NMVOC}, k}$ for aggregated species is calculated from the percentage abundance a_j of a species j within a group of species (alcohols, aldehydes, etc.) and the ratio of the molecular mass M_j and the carbon content of the single species $X_{C, j}$.

$$f_{\text{NMVOC}_k} = (1/100) \cdot \sum a_j \cdot M_j / X_{C, j} \quad (\text{A3.3})$$

Table A3-2 Conversion of NMVOC-C EFs to NMVOC EFs

Group of compounds	Constituents	Relative abundance a_j	Composition	Molecular mass M_j g mol^{-1}	Individual mass conversion factor $M_j / X_{C, j}$ kg kg^{-1}	Aggregated mass conversion factor f_{NMVOC_k} kg kg^{-1}
isoprene			C_5H_8	68.13	1.1355	1.1355
terpenes			$\text{C}_{10}\text{H}_{16}$	136.24	1.1353	1.1353
alcohols	methanol	84.51	CH_4O	32.04	2.6700	2.5537
	ethanol	15.49	$\text{C}_2\text{H}_6\text{O}$	46.07	1.9196	
aldehydes	formaldehyde	47.83	CH_2O	30.03	2.5025	2.1545
	acetaldehyd	52.17	$\text{C}_2\text{H}_4\text{O}$	44.05	1.8354	
ketones	acetone		$\text{C}_3\text{H}_6\text{O}$	58.08	1.6133	1.6133
ethers and others	cis-3-hexenyl acetate		$\text{C}_8\text{H}_{14}\text{O}_2$	142.2	1.4813	1.4813

The values used for calculating the Tier 1 emission factors are those used by Dämmgen et al. (2008).

A3.4 Data quality

A3.4.1 Completeness

The small number of measurements of NMVOC emissions from agricultural vegetation is a considerable weakness. It is unknown whether emissions are related to fertiliser-N inputs.

A3.4.5 Uncertainty Assessment

A3.4.5.1 Emission factor uncertainties

Biogenic VOC emissions for the UK were summarized by Hewitt and Street (1992). These ranged from 38–211 Gg a⁻¹ total NMVOCs. Emissions from woodlands were estimated to be 72 % of total biogenic emissions by Anastasi et al. (1991). Thus between *ca.* 10 and 59 Gg a⁻¹ appear to be of agricultural origin. In their incomplete analysis Hobbs et al. (2004) calculated *ca.* 5 t a⁻¹ from agricultural crops. This compares with the Corinair 94 estimate of only 2 Gg a⁻¹ for SNAP Code 1001, Cultures with fertilisers, NFR 4.D.1, 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.

A3.4.5.2 Activity data uncertainties

Hewitt and Street (1992) concluded that only *ca.* 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.

With respect to national data on crop areas, an uncertainty of < 5 % is assumed, with a normal distribution.

Appendix A4 Particulate matter

A4.1 Overview

Definitions of PM₁₀, PM_{2.5} and TSP

There are different definitions for particle fractions, but all of them define penetration curves by particle size fractions into the lungs. The US Environmental Protection Agency (USEPA) defined PM₁₀ and PM_{2.5} for environmental purposes, while ISO gives health related definitions.

Figure A4–1 shows these different curves. Differences are obvious for PM₁₀ and the thoracic fraction which corresponds with it by the same cut off at 10 μm . PM₁₀ do not consider particles larger than 15 μm while thoracic reaches up to 40 μm .

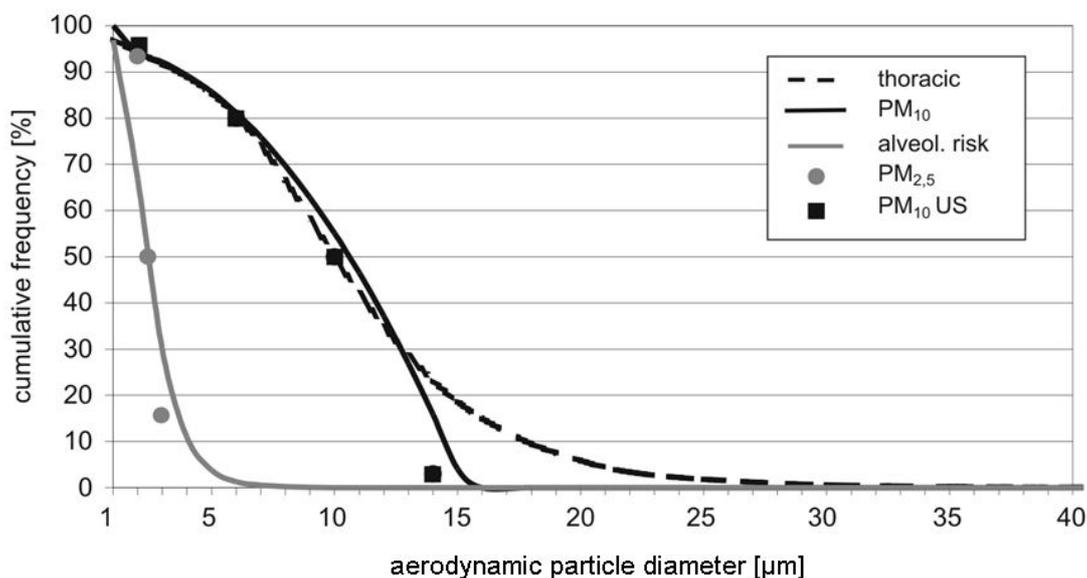


Figure A1–1 Sampling criteria for inhalable, thoracic and respirable particles expressed as percentage of TSP.

Curves describe virtual particle separators simulating the corresponding parts of the breathing tract. They are characterized by their shape and by the 50 % value of separation and penetration the so-called cut off diameter. Samplers with the same cut off diameters but different shaped penetration curves will collect different fractions of PM. This must be considered for PM₁₀ and thoracic fraction if the emissions include a high portion of particles with size between 15 μm and 40 μm . Practical measuring equipment will often follow the ISO definition.

Definitions for PM_{2.5} and the respirable fraction (risk group) are consistent.

TSP means total suspended particles and it is mainly used in ambient air for sizes below 57 μm .

For emission site, TSP means more or less total dust considering all sizes up to the largest particles which size depends on the origin of the dust.

Dust particles should be limited to sizes not larger than 500 μm (aerodynamic diameter).

A4.2 Description of sources

Emissions of PM vary according to the following:

- type of crop;
- the physical properties of the particles;
- origin of the particles: soil, plant, machinery;
- meteorological conditions of soil and/or produce before and during the operation (wind speed, temperature, rain fall, humidity);
- type of operation;
- parameters of the machinery (working speed, working capacity, working surface).

A4.3 Methods

A4.3.1 Tier 1 default approach

The EFs for PM₁₀ and PM_{2.5} can be determined directly by measurements using pre-separators which realize the aerodynamic definitions by the flow properties. These measurements can be used directly for comparison or balancing. Another way is to calculate the pEFs from the total size distribution of the total dust emissions. For this it is necessary to know the sizing system which may influence the result. A third way which has been done in the past is to calculate PM_x as share of TSP. To get comparable results the definition and measuring procedure for TSP must be known. Takai et al. (1998) introduced a sampler for the inhalable part of dust to be total dust (TSP). These samplers have a cut diameter (50 % separation) at 100 µm.

A literature review reported different ways to create EFs for arable farming.

Direct measurements of the primary PM emissions from the use of cultivation implements. From these, machinery-related estimates of the potential strength of a source and field-related EF may be calculated.

Indirect estimation of source strength using concentration measurements carried out using machinery placed in the driver's cab and layer- or plume-based models of the treated area to establish a relationship with a balance volume or a volume flow rate concerned.

Measurements of PM concentrations at the border of a field fitted to an inverse computing model of dispersion.

The following PM₁₀ EFs were reported:

Combine harvesting:

- 4.1–6.9 kg ha⁻¹, parameter cereal, cereals humidity during harvesting (Batel, 1976);
- 3.3–5.8 kg ha⁻¹ (WRAP, 2006).

Due to the settling effect of coarse particles, it was assumed that only a part of the primary emitted PM₁₀ leaves the field to comprise the field EF. Two situations have been considered: one with 50 % of the original PM₁₀ emissions leaving the field and one with 10 % leaving the field.

Soil cultivation:

- 0.1 kg ha⁻¹, The Regional Air Pollution INformation and Simulation (RAINS);
- 0.06-0.3 kg ha⁻¹ (Wathes et al., 2002);
- 0.28-0.48 kg ha⁻¹ (Hinz, 2002).

Assumptions based on both models are not consistent with measured values and lead to overestimates of EF. Corrections gave an averaged field emission factor of 0.25 kg ha ha⁻¹ as given in the matrix:

- 4.2 kg ha⁻¹ U.S. NEI method;
- 5.2 kg ha⁻¹ U.S. CARB method.

Measurements from California are much larger. The reason will be the climatic and soil conditions with higher temperature and lower humidity. This intention will be supported by measurements done in Brandenburg, Germany under the 2006 conditions — hot and dry and emission values one order of magnitude higher than in former years.

Table A4-1 EFs for PM₁₀, PM_{2.5} and PM₁ for field operations

	PM ₁₀ kg ha ⁻¹	PM _{2.5} kg ha ⁻¹	PM ₁ kg ha ⁻¹
Harrowing	0.82	0.29	<1
Discing	1.37	0.12	0.03
Cultivating	1.86	0.06	0.02
Ploughing	1.20	0.05	0.01

Source: EFs for soil operations (Oettl et al., 2005).

Source strength is computed using the inverse Lagrangian dispersion model aided by concentration measurements using particle counter. This is a first approach to calculation with some uncertainties in the model but also in measurements.

A4.3.2 Default emission factors

Emissions should be calculated by multiplying the cultivated area of each crop by an EF and by the number of times the emitting practice is carried out.

$$E_{10} = \sum_{i=1}^n EF_{10} \cdot A \cdot n \quad (\text{A4.1})$$

where

E ₁₀	emission of PM ₁₀ in kg a ⁻¹ ,
A	annual cropped area in ha,
n	number of times emitting practice is carried out, in n a ⁻¹ ,
EF ₁₀	EF in kg ha ⁻¹ .

Emission factors that have been calculated in terms of the mass of PM emitted per unit mass of crop harvested can be converted to the area related factors by the averaged annual yield:

$$EF_{10} = EF_{10m} \cdot Y \quad (\text{A4.2})$$

where

EF _{10m}	emission factor in kg kg ⁻¹ ,
Y	averaged annual grain yield in t ha ⁻¹ ,

Table A4-2 PM emission factors EF_{PM} for agricultural crop operations, in $kg\ ha^{-1}\ PM$. (van der Hoek and Hinz, 2007)

Crop	Soil cultivation	Harvesting	Cleaning	Drying
Wheat	0.25	4.9	0.19	0.56
Rye	0.25	3.7	0.16	0.37
Barley	0.25	4.1	0.16	0.43
Oat	0.25	6.2	0.25	0.66

The measured values are of emissions from the immediate surroundings of the tractors and harvesting machinery in the field.

Further information about PM emissions can be found in Hinz and Funk (2007) and Hinz and Tamoschat-Depolt (2007).

A4.4 Data quality

A4.4.1 Completeness

The small number of measurements of PM emissions from agricultural activities is a considerable weakness.

Appendix A5 Summary of updates

Table A5-1 Summary of updates to calculation methodologies and EFs made during the 2009 revision of this chapter

Emission	Tier 1		Tier 2	
	Methodology	EFs	Methodology	EFs
NH ₃	Updated	Updated	Updated	Updated
NO	Not updated	Updated	NA	NA
NMVOC	Updated	Updated	NA	NA
PM	Updated	Updated	Updated	Updated

NA, not applicable

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