N_2O EMISSIONS FROM ADIPIC ACID AND NITRIC ACID PRODUCTION

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This paper was written by Heike Mainhardt (ICF Incorporated) and reviewed by Dina Kruger (USEPA).

ABSTRACT

Nitrous oxide (N_2O) is generated as a by-product during the production of adipic acid and nitric acid. The main use for adipic acid is as a component of nylon-6/6; thus production trends are closely correlated with nylon consumption trends. Worldwide, there are very few adipic acid plants. The U.S. is a major producer with three companies in four locations accounting for approximately forty percent of world production. Other producing countries include Brazil, Canada, China, France, Germany, Italy, Japan, Korea, Singapore, Ukraine, and United Kingdom. Most of these countries have only one adipic acid plant. Nitric acid is used primarily to make synthetic commercial fertiliser. Worldwide, the number of nitric acid plants is somewhat uncertain. Estimates range from 255 to 600 plants (Choe et al., 1993; Bockman and Granli, 1994). In 1990, adipic acid production was the largest source of industrial N_2O emissions. As of 1999, industrial sources report that all major adipic acid producers have implemented N_2O abatement technologies (Reimer, 1999). As a result, nitric acid production is currently believed to be the largest industrial source of N_2O emissions.

The Revised 1996 *IPCC Guidelines for National Greenhouse Gas Inventories (IPCC Guidelines)* outline a straightforward method for estimating emissions from both adipic acid and nitric acid, in which an emission factor is multiplied by production data. Thus, the key factors regarding the accuracy of the estimate will be the quality of the emission factor and activity data used.

The accuracy and precision of N_2O emission factors are directly correlated with the number of samples and the frequency of sample collection. Countries have three broad options for obtaining emission factors: continuous monitoring, periodic sampling, and the use of default factors. The chosen approach will depend on the desired level of accuracy and resource availability, as well as plant-level characteristics such as the range of process variability and the state of technology (including N_2O abatement technology). The IPCC recommends using plant-specific emission factors where possible.

Continuous emission monitoring is the most accurate approach, because it can account for the variability in the overall process and directly capture the effects of control measures. It can be costly, however. The calculation of plant-specific emission factors can be an accurate alternative to continuous monitoring if based on periodic sampling under process conditions that are representative of routine operation. Ideally, plants should determine the frequency of their sampling programme by conducting very frequent monitoring for a period of time in order to determine the range of variability in the overall process. If periodic sampling is not feasible, the IPCC provides default emission factors for both adipic acid and nitric acid production. These default emission factors, which are currently used by most countries, introduce a large degree of uncertainty because they represent a relationship based on information from only a few plants.

Adipic acid and nitric acid production data are necessary to estimate N_2O emissions regardless of the selected estimation method. Countries should obtain plant-level data on an annual basis. Where such data are unavailable, it appears that some countries have used plant capacity information as a proxy. However, since these data do not represent actual annual production, they introduce uncertainty into the estimate. Producers may consider adipic acid and nitric acid production data proprietary. Thus, it may be necessary to ensure that these data are not released to the public, or to publish them in a way that ensures that individual plants are not identified.

Reporting of these sources is quite clear, compared to other industrial process gases, because the *IPCC Guidelines* call for adipic acid and nitric acid emissions to be reported individually.

Quality assurance and quality control activities should occur at several points in the emission estimation process. At the plant level, key elements should include internal quality control on plant level measurements and production data, documentation of data and methods for reviewers. The inventory agency must ensure the accuracy of plant submissions as well as the compiled inventory. The agency will also be responsible for providing documentation and reporting sufficient information to the United Nations Framework Convention on Climate Change (UNFCCC) Secretariat. One or more different types of external reviews and audits may also be appropriate.

1 INTRODUCTION

1.1 Nature, magnitude, and distribution of source

1.1.1 Overview of N_2O emissions

The main sources of industrial anthropogenic N_2O potential emissions are adipic acid and nitric acid production, each of which is discussed below.

Adipic acid is a white crystalline solid used primarily as the main constituent of nylon (nylon-6/6), representing about half of the nylon molecule. It is also used in the manufacture of some low-temperature synthetic lubricants, synthetic fibers, coatings, plastics, polyurethane resins, and plasticizers, and to give some imitation food products a "tangy" flavour. In 1990, adipic acid production was the largest source of industrial N_2O emissions. As of 1999, industrial sources report that all major adipic acid producers have implemented N_2O abatement technologies and, as a result, this source has been decreased substantially (Reimer, 1999). Adipic acid production also generates emissions of non-methane volatile organic compounds (NMVOCs), carbon monoxide (CO), and nitrogen oxides (NO_x).

Since the main use for adipic acid is as a component of nylon, adipic acid production trends are closely correlated with nylon consumption trends. Rising demand for engineering plastics has sparked expansion in existing adipic acid capacity in North America and Western Europe, as well as new facilities in the Asia-Pacific region. Global adipic acid production is expected to total nearly 2.7 million metric tons (6 billion pounds) in 2000 (CW, 1999) as compared to 1.8 million metric tons (4 billion pounds) in 1995 (CMR, 1998a; SRI, 1997). Economic drivers include new housing starts and nylon engineering resins in the automotive and electronics industries (CMR, 1998a).

Worldwide, there are very few adipic acid plants. The U.S. is a major producer with three companies in four locations accounting for approximately forty percent of world production. Other producing countries include Brazil, Canada, China, France, Germany, Italy, Japan, Korea, Singapore, Ukraine, and United Kingdom. Most of these countries have only one adipic acid plant except China (3), Germany (2), Japan (2), and U.S. (4) (SRI Consulting, 1998).

Although global adipic acid demand is expected to increase, N_2O emissions from this source are expected to continue to decrease substantially as they have since 1996. As reported by industrial sources, the decrease is a result of nearly all adipic acid producers' installation of N_2O abatement technologies. Overall, N_2O abatement is estimated to have improved from approximately 32% in 1990 to approximately 90% in 2000 (Reimer, 1999). Abatement technologies' current efficiency range is 90 to 99 percent reduction of N_2O emissions.

Nitric acid (HNO_3) is an inorganic compound used primarily to make synthetic commercial fertiliser. The raw material is also used for the production of adipic acid and explosives, metal etching, and in the processing of ferrous metals. Now that most adipic acid plants have implemented abatement technologies, nitric acid production is currently believed to be the largest industrial source of N_2O emissions.

Since the main use for nitric acid is as a component of fertiliser, nitric acid production trends are closely correlated with fertiliser consumption trends. Future trends in fertiliser production vary greatly depending on the region. In parts of Western Europe, the use of nitrogen-based fertilisers is decreasing due to concerns over nutrient run-off. Other regions, such as Asia, South America, and the Middle East are building up their nitrogen fertiliser production capacities (CMR, 1998b). In the U.S, fertiliser production is projected to increase by 4 percent by 2000 (FAO, 1998). Other factors to consider are government programmes, weather conditions and general economic growth. As a result of having many variables, it is very difficult to project future nitric acid production.

Worldwide, the number of nitric acid plants currently in operation is somewhat uncertain. Bockman and Granli (1994) report that there are approximately 500 to 600 nitric acid plants. While Choe et al. (1993) place the number at around 255 plants. This uncertainty may be due to the fact that nitric acid plants are often part of larger production facilities, such as fertiliser or explosive manufacturing. As a result, only a small volume of nitric acid is sold on the merchant market.

Nitrous oxide emissions from nitric acid production will be influenced by the degree to which emission control efforts are applied in both new and existing nitric acid plants. Since many nitric acid production facilities are between 20 and 30 years old (CMR, 1995), there appear to be opportunities to install or update emissions control technologies. However, it is unclear whether these improvements are actually taking place.

1.1.2 N_2O generation process

Table 1 summarizes factors that influence N_2O generation for adipic and nitric acid production. Both production processes are described in detail below.

TABLE 1

FACTORS THAT POTENTIALLY INFLUENCE N_2O GENERATION

Factor	Specific Examples/Description
Adipic Acid Production	
Oxidizing Agent	Nitric Acid Oxidation vs. Hydrogen Peroxide Oxidation (currently this is not a cost effective commercial option)
N_2O Abatement Technologies	Thermal destruction, catalytic destruction, recycle to adipic acid, and recycle to nitric acid. Technologies currently range from 90 to 99 percent N_20 emission reduction.
Abatement System Utility	The total reduction in N_2O emissions from abatement technology depends on the system's tility rate. Therefore, the technology's N_20 destruction factor should be multiplied by an abatement system utility factor in order to account for any down time of the emission abatement equipment (i.e., time the equipment is not operating).
Nitric Acid Production	
Type of Facility	Nitric acid plants are often part of a larger production facility, such as fertiliser or explosive manufacturing, which can cause significant operating variations between facilities. Emissions will vary substantially depending on the specific type of nitric acid plant (e.g., high pressure, medium pressure, double absorption; see Table 3).
Production Factors	Catalyst type, catalyst age, metal gauze type, and reactor operating conditions. In general, N_2O generation decreases with increasing gauze temperature, and increases with increasing inlet ammonia concentration (Choe et al., 1993).
N_2O Abatement Technologies	BASF N_2O Decomposition (catalytic destruction)[1], Norsk Hydro Agri (process integrated N_2O destruction), and thermal destruction.
NO_x Abatement Technologies	Nitric acid plants with NOx control measures impact N_2O emissions. Emission factors up to 19 kg N_2O/tonne nitric acid have been reported for plants not equipped with non-selective catalytic reduction (NSCR) technology (Choe et al., 1993). Choe et al. (1993) estimate that approximately 80% of nitric acid plants do not employ NSCR technology. Also, some nitric acid plants may recycle N_2O for use in other phases of the facility.
Abatement System Utility	Please see abatement system utility explanation above.

Manufacturing process of adipic acid: Adipic acid is a dicarboxylic acid manufactured by a two-stage process. The first stage of manufacturing usually involves the oxidation of cyclohexa[2] to form a cyclohexanone/cyclohexanol mixture. Generally, the second stage involves oxidizing this mixture with nitric acid to produce adipic acid. N_2O is generated as a by-product of the nitric acid oxidation stage, as illustrated below:

$$(CH_2)_5CO + (CH_2)_5CHOH + wHNO_3 \Rightarrow HOOOC(CH_2)_4COOH \text{ (Adipic Acid)} + xN_2O + yH_2O$$

Process emissions from the production of adipic acid will vary with the types of technologies and level of emissions controls employed by a facility. Recently, researchers at Nagoya University developed a new method for adipic acid production. The Nagoya process substitutes 30 percent aqueous hydrogen peroxide for nitric acid, producing adipic acid in over 90 percent yield and eliminating N_2O as a by-product (Sato, 1998). However, commercial application of this process will depend on finding cheaper ways to produce hydrogen peroxide.

A facility can employ a number of activities to control emissions. These activities include implementing thermal and catalytic destruction technologies, and recycling activities. Table 1 summarizes factors that influence N_2O generation from adipic acid production.

Manufacturing process of nitric acid: The production of nitric acid (HNO_3) generates nitrous oxide (N_2O) as a by-product of the high temperature catalytic oxidation of ammonia (NH_3).

[1] Currently unavailable to other nitric acid producers.

[2] Or sometimes cyclohexanone.

Nitric acid production involves three distinct chemical reactions:

$$4NH_3 + 5O_2 \Rightarrow 4NO + 6H_2O$$

$$2NO + O_2 \Rightarrow 2NO_2$$

$$3NO_2 + H_2O \Rightarrow 2HNO_3 + NO$$

Although nitrous oxide generation during the production of nitric acid is not well documented. The steps of nitrogen oxidation are considered to be potential sources of N_2O. Nitric oxide (NO), an intermediate in the production of nitric acid, readily decomposes to N_2O and nitrogen dioxide (NO_2) at high pressures for a temperature range of 30-50°C (Cotton and Wilkinson, 1988). Table 1 summarizes factors that influence N_2O generation from nitric acid production.

1.2 The current state of inventory methodologies

The *IPCC Guidelines* describe a simple method for estimating N_2O emissions from both adipic and nitric acid production, in which an emission factor is multiplied by production data to yield an emission estimate. The *IPCC Guidelines* encourage plant level measurement programmes, but provide default emission factors for both sources. Currently, most Parties appear to be using these default values as opposed to conducting monitoring programmes.

2 METHODOLOGICAL ISSUES

2.1 Selection of the estimation method

The *IPCC guidelines* outline a straightforward method for estimating emissions from both adipic acid and nitric acid, in which an emission factor is multiplied by production data. Thus, the key factor regarding the accuracy of the estimate will be the quality of the emission factor and the activity data used. Both of these are discussed below.

2.2 Emission factors

The accuracy and precision of N_2O emission factors are directly correlated with the number of samples and the frequency of sample collection. Generally, countries have three broad options for obtaining emission factors: continuous monitoring, periodic sampling and the use of default factors. The chosen approach will depend on the desired level of accuracy and resource availability, as well as plant-level characteristics such as the range of process variability and the state of technology. The IPCC recommends using plant-specific emission factors where possible, and notes that the small number of adipic acid plants per country should make it possible to obtain such data for this source. As a general rule, sampling and analysis should be undertaken when a plant makes any significant process changes that would affect the generation rate of N_2O.

2.2.1 Continuous emissions monitoring

Continuous emissions monitoring is the most accurate approach, because it can account for the variability in the overall process and can directly capture the effects of control measures. Continuous emissions monitoring can be performed using a gas chromatograph with an automated sampling system, appropriate detector (e.g., thermal conductivity), and a device to measure volumetric flowrate. Samples of the vented gas stream taken as frequently as every few minutes, and coupled with the volumetric flowrate, provide a direct measure of the mass emission rate.

This approach can be very accurate when quality assurance and quality control (QA/QC) procedures are performed. It will account for abatement technology variability and any other factors that affect emissions. The major shortcoming of this approach is that it can be expensive in terms of the installed capital cost of the equipment and the operating costs, especially costs associated with inspection, QA/QC, and maintenance of the equipment.

2.2.2 Periodic sampling and analysis

The calculation of a plant-specific emissions factor, which relates the mass rate of N_2O generation to the production rate of adipic acid or nitric acid (e.g., tonne of N_2O/tonne of adipic or nitric), can be an accurate alternative to continuous monitoring if it is based on periodic sampling. The sampling must be performed under process conditions that are representative of routine operation. If process changes are subsequently made that will affect the generation rate of N_2O, then sampling should be performed again to quantify emissions under the new conditions. Otherwise, scaling an emissions factor based on non-representative sampling over the period of a year will introduce error.

Ideally, plants should determine the frequency of their sampling programme by conducting continuous or very frequent monitoring for a period of time in order to determine the range of variability in the overall process. Such frequent monitoring should also be undertaken when new technologies (e.g., control measures) are employed, in order to determine the new range of variability and account for the common set-backs associated with the start-up phase of a new technology.

Periodic sampling and analysis are performed by taking samples of the vent stream in an appropriate container, such as glass flasks, flexible bag, or stainless steel canister, and transporting it to a laboratory for analysis of N_2O concentration. At the time the sample is taken, the volumetric flow rate is determined using an appropriate measuring device, such as a gas volume meter, pitot tube, rotameter, etc. The concentration multiplied by the flowrate provides a measure of the mass rate of N_2O, which can be applied to the rate of production of adipic acid or nitric acid for the whole year.

2.2.3 Default emission factors

If periodic sampling is not feasible, the IPCC provides default emission factors for both adipic acid and nitric acid production. These default emission factors, which are currently used by most countries, represent a relationship based on information from a few plants and laboratory experiments. Thus, the current default emission factors introduce a large degree of uncertainty in the emission estimates. The key to minimizing this uncertainty is sampling and analysis to determine an appropriate emission factor at each specific plant.

Adipic Acid Default Emission Factors

The current IPCC default emission factor for adipic acid is 300 kg of N_2O per tonne of product. This factor was developed based on experiments (Thiemens and Trogler 1991) that attempt to replicate the industrial process and, thereby, measure the reaction stoichiometry for N_2O production in the preparation of adipic acid. Reimer et al. (1992) support this factor as being representative of measured industrial rates. Furthermore, Japanese emissions have been measured at 264 kg of N_2O per tonne of product, which is consistent with this value (Japan Environment Agency, 1995).[3] However, because N_2O emissions are controlled in many adipic acid production facilities, the amount of N_2O that is actually released will depend on the level of controls in place at a specific plant. Where N_2O control technologies are in use, the *IPCC Guidelines* recommend the use of plant-specific data.

In addition to the *IPCC Guidelines'* current default emission factor for adipic acid production, Table 2 provides default values for abatement technology destruction and abatement system utilization.

Nitric Acid Default Emission Factors

Currently, N_2O emission estimates for nitric acid production are highly uncertain, due to a lack of information on manufacturing processes and emission controls. The IPCC default emission factor range of 2 to 9 kg of N_2O per tonne of nitric acid produced is correspondingly large. In addition, although there are not many known abatement technologies specifically directed at removing N_2O at nitric acid plants, existing control measures for other pollutants have impacts upon N_2O emissions. Table 3 shows the IPCC default factors for this source.

It is important to note that several documents give emission factors up to 19 kg N_2O/tonne nitric for plants not equipped with non-selective catalytic reduction (NSCR) technology (Choe et al., 1993; Olivier, 1996; Oonk, 1996.). Furthermore, Choe et al., estimate that approximately 80 percent of the nitric acid plants worldwide do not employ NSCR technology. Since most Parties appear to be using the IPCC default values (of 2-9 kg N_2O/tonne nitric) as opposed to conducting monitoring programmes; it seems the current estimates of N_2O emissions may be underestimated.

[3] With regards to the Japan Environment Agency value (264 kg N_2O/tonne adipic acid) provided in the Revised 1996 IPCC Guidelines, it is believed that this manufacturer uses oxidation of pure cycolhexanol (alcohol), instead of a ketone-alcohol mixture (Reimer, 1999). This is the only plant known to use this method.

TABLE 2 **DEFAULT FACTORS FOR ADIPIC ACID PRODUCTION**		
Production Process	**N_2O Generation Factor**	**Notes**
Nitric Acid Oxidation	300 kg/tonne adipic acid[1]	Uncertainty = ± 10% (based on expert judgement). The uncertainty represents a variability in N_2O generation due to differences in the composition of the cyclohexanone and cyclohexanol feedstock (i.e., ketone (K) and alcohol (A)) that are used by different manufacturers. Higher K content results in increased N_2O generation, whereas higher A content results in less N_2O generation (Reimer, 1999). An individual plant should be able to determine the production of N_2O (based on HNO_3 consumption) within 1%. The range of 300 kg ± 10% encompasses the variability from pure ketone to pure alcohol feedstocks, with most manufacturers somewhere in the middle.[2]
Abatement Technology	**N_2O Destruction Factor[3]**	**Notes (Uncertainty estimates are distinct from destruction factor ranges)**
Catalytic Destruction	90 – 95%	Uncertainty = ± 5% (based on expert judgement). Manufacturers known to employ this technology include: BASF (Scott, 1998), and DuPont (Reimer, 1999).
Thermal Destruction	98-99+%	Uncertainty = ± 5% (based on expert judgement). Manufacturers known to employ this technology include: Asahi, DuPont, Bayer, and Solutia (Scott, 1998).
Recycle to Nitric Acid	98-99+%	Uncertainty = ± 5% (based on expert judgement). Manufacturers known to employ this technology include: Alsachemie (Scott, 1998).
Recycle to Adipic Acid	90 – 98%	Uncertainty = ± 5% (based on expert judgement). Solutia will be implementing this technology around 2002. (Scott, 1998).
Abatement System	**Utilisation Factor[4]**	**Notes**
Catalytic Destruction	80-98%	Note that these default values are based on expert judgement and not industry supplied data or plant specific measurements. In the first 1-5 years of the abatement technology implementation, the utilization factor tends to be at the lower end of the range. Lower utility of the equipment typically results because of the need to learn how to operate the abatement system and because more maintenance problems occur during the initial phase. After 1-5 years, the operating experience improves and the utilization factor would tend to be at the high end of the range.
Thermal Destruction	95-99+%	See note above
Recycle to Nitric Acid	90-98+%	See note above
Recycle to Adipic Acid	80-98%	See note above

[1] Thiemans and Trogler, 1991.

[2] With regards to the Japan Environment Agency value (264 kg N_2O/tonne adipic acid) provided in the Revised 1996 IPCC Guidelines, it is believed that this manufacturer uses oxidation of pure cycolhexanol (alcohol), instead of a ketone-alcohol mixture (Reimer, 1999). This is the only plant known to use this method.

[3] The destruction factor (which represents the technology abatement efficiency) should be multiplied by an abatement system utility factor. NOTE: This range is not an uncertainty estimate.

[4] Reimer, Ron, 1999. Personal communication between Ron Reimer of DuPont, USA and Heike Mainhardt of ICF, Inc., USA. May 19, 1999.

TABLE 3

IPCC DEFAULT EMISSION FACTORS FOR N_2O FROM NITRIC ACID PRODUCTION

Country	Emission Factor kg N_2O/tonne nitric acid	Reference
USA	2-9[a]	Reimer et al., 1992
Norway - modern, integrated plant	<2	Norsk Hydro, 1996
- atmospheric pressure plant	4-5	Norsk Hydro, 1996
- medium pressure plant	6-7.5	Norsk Hydro, 1996
Japan	2.2-5.7	Japan Environment Agency, 1995

[a] Emission factors up to 19 kg N_2O/tonne nitric acid have been reported for plants not equipped with non-selective catalytic reduction technology (Choe et al., 1993; Olivier, 1996; Oonk, 1996.).

Furthermore, in addition to the *IPCC Guidelines'* current default emission factors for nitric acid production, Table 4 provides examples of when to apply specific default values. The table also provides default values for abatement technology destruction.

TABLE 4

DEFAULT FACTORS FOR NITRIC ACID PRODUCTION

Production Process	N_2O Generation Factor (kg N_2O/tonne HNO_3)	Notes
Canada • plants without NSCR[1]	8.5[2]	Based on an average emissions rate for plants of European design.
• plants using NSCR	<2[3]	The N_2O generation factor accounts for N_2O destruction by NSCR. Uncertainty = ± 10% (based on expert judgement).
USA • plants without NSCR	9.5[4]	An estimated 80% of HNO_3 plants do not use NSCR systems (Choe, et al., 1993).
• plants using NSCR	2	The N_2O generation factor accounts for N_2O destruction by NSCR. Industry indicates a range of 1.12 to 2.5 kg N_2O/tonne HNO_3, field experts have indicated that the lower end of the range is more accurate (Choe, et al., 1993; Collis, 1999). A factor of 2 was selected as a conservative default. An estimated 20% of HNO_3 plants use NSCR systems (Choe, et al., 1993). Uncertainty = ± 10% (based on expert judgement)
Norway • process-integrated N_2O destruction	<2[5]	Norsk Hydro developed a state of the art reactor design in which emissions of N_2O are reduced in a process-integrated manner. There is only one installation operational of this type (Oonk, 1999).
• atmospheric pressure plant (low pressure)	4-5[6]	
• medium pressure plant	6-7.5[7]	
Japan	2.2-5.7[8]	
Other Countries • European designed, dual pressure, double absorption plants	8 –10[9]	Emission factors up to 19 kg N_2O/tonne nitric acid have been reported for plants not equipped with NSCR technology (Choe et al., 1993; EFMA, 1994). Such a high emissions rate would most likely apply to only a few, outdated plants.

TABLE 4 (CONTINUED) DEFAULT FACTORS FOR NITRIC ACID PRODUCTION		
NO_x Abatement Technology	**N_2O Destruction Factor**	**Notes**
Non-Selective Catalytic Reduction (NSCR)	80 – 90 %	Uncertainty = ± 10% (based on expert judgement). NSCR is a typical tail gas treatment in the USA and Canada with less application in other parts of the world.
Selective Catalytic Reduction (SCR)	0%	SCR with Ammonia does not reduce N_2O (Johnson Matthey, 1991; Choe et al., 1993).
[1] Non-Selective Catalytic Reduction (NSCR) [2] Collis, 1999. [3] Collis, 1999. [4] Choe, et al., 1993.		[5] Norsk Hydro, 1996. [6] Norsk Hydro, 1996. [7] Norsk Hydro, 1996. [8] Japan Environment Agency, 1995. [9] Oonk, 1999.

2.3 Activity data

Adipic acid and nitric acid production data are necessary to estimate N_2O emissions regardless of the selected estimation method. Countries should obtain plant-level data on an annual basis so that they can apply plant-specific emission factors. Where plant-level production data are unavailable, it appears that some countries have used plant capacity information as a proxy (this is especially the case for adipic acid production). Since these data do not represent actual annual production, they introduce uncertainty into the estimate.

Producers may consider adipic acid and nitric acid production data proprietary. Thus, it may be necessary to ensure that these data are not released to the public, or to publish them in a way that ensures that individual plants are not identified.

2.4 Uncertainty

Parallel to the IPCC sector-specific workshops on *good practice guidance*, the IPCC is completing a programme of work on emissions inventory uncertainty. This work will result in recommendations to the UNFCCC on approaches to assessing and managing uncertainty. During the IPCC Inventory Experts Group Meeting in Paris (October 1998), technical experts in the uncertainty programme came up with a series of questions to be answered in the sector workshops. Specifically, the sector workshops should provide answers to these questions in the individual source context, to inform work of the uncertainty programme on establishing a general methodological approach. These questions are listed in the general background paper and should be answered during the workshop for these sources.

2.5 Completeness

A review of 42 national inventories submitted to the UNFCCC Secretariat indicated that 21 countries reported on N_2O emissions from industrial processes. However, only 11 countries reported N_2O emissions separately for adipic acid and nitric acid production, and all others reported emissions as an industrial aggregate. Thus, it is difficult to assess the completeness of current inventories.

Given that there are a relatively small number of adipic acid facilities in most producer countries, and that it should be possible to develop plant-specific emissions estimates, complete reporting of this source should be attainable. Complete reporting for nitric acid, however, will be more difficult given that there may be approximately 600 plants and only a small amount of the product is sold on the merchant market.

For both sources, reporting should include qualitative and quantitative information from each industrial plant including amount of adipic acid and nitric acid produced, relevant operating parameters (i.e., production process and abatement technologies), and associated N_2O emissions, subject to appropriate confidential business information concerns.

2.6 Other important issues

2.6.1 Emissions baselines

If measurements and sampling of N_2O emissions are not available for previous years, there will be a consistency problem in an emissions time series. This will inevitably be the case, for example, if a plant was producing adipic or nitric acid during a baseline year but shut down before a rigorous inventory measurement programme is implemented. The only alternative in this case is to apply emission factors developed from other plants to available historical production data, or production estimates based on operating capacity. It is important that the emission factors represent operating conditions in the baseline year as closely as possible. Nevertheless, emission estimates for these plants in these years will be uncertain, and little documentation will be available for verification.

3 REPORTING AND DOCUMENTATION

3.1 Current IPCC reporting guidelines

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

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

N_2O emissions from adipic acid and nitric acid production are reported individually in Table 2-1: Potential Emissions from Industrial Processes, which calls for entries for each source emissions totals of carbon dioxide, methane, nitrous oxide, precursor gases (NO_X, CO, NMVOCs, SO_2), HFCs, PFCs, and SF_6.

N_2O emissions from adipic acid and nitric acid production are reported in the *IPCC Guidelines* on pages 2.19 and 2.17 respectively.

3.2 Confidential business information

In most cases, detailed descriptions of how nitric acid and adipic acid producers determine N_2O emissions can be evaluated based on knowledge of the process chemistry; however, validation of the actual calculations may require access to confidential business information (CBI). For example, some U.S. producers have indicated that the following information is considered CBI at the company level, but not when aggregated for all companies:

- Adipic acid and nitric acid production levels, and
- N_2O emissions.

The issue of confidential business information may complicate the desire for clear and transparent national reporting. An alternative is to report on the number of plants and national level production. However, in cases where there is only one plant, plant-level production will equal national production.

4 INVENTORY QUALITY

4.1 Introduction

Inventory quality assurance and quality control (QA/QC) is a process integral to the development of a credible inventory. A well-developed and well-implemented quality assurance programme fosters confidence in the final inventory results regardless of the purpose and goal of the inventory. A successful quality assurance programme is two-fold requiring internal industrial plant level procedures and external review and audit activities. The internal QC activities are designed to ensure accuracy, documentation and transparency. The external review process is designed to minimise errors that occur in the preparation of emissions inventories, and reduce or eliminate potential inherent bias from any given facility. Figure 1 outlines the flow of information and processes followed at each step.

Figure 1 Inventory QA/QC process

Plant

Internal QC:	Plant-level measurement and calculations
Documentation:	Plant-level information provided to the government agency, and results of internal QC

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Government Agency

Review/QA:	Plant-level inputs
Internal QC:	Compilation of national inventory from plant-level data
Documentation:	Results of compilation and results of QA/QC
Reporting:	Official submission to UNFCCC

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External Review

External Review:	External audit, stakeholders, peer and public review of inventory results, external verification against other data etc.
Documentation:	Results of external review

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UNFCCC Secretariat

External Review:	Requires standard format and transparency – ensure consistency with other inventories and external data

4.2 Internal inventory QA/QC systems

4.2.1 Plant-level activities

Plant-Level Measurement and Sampling QC

The inventory QC procedures used at the industrial plant level will be determined in large part by plant personnel. There are, however, certain procedures common to monitoring programmes which should be specified:

- sample collection methods (including frequency, container type and preparation);
- sample stability (prior to analysis);
- written standard operating procedures for sampling and analysis;
- calibration procedures (number, frequency, standard chosen, acceptance criteria);
- limits for accuracy and precision;
- method to flag suspect data, and
- maintenance of records.

Plant-Level Production Data QC

Annual activity data are required to estimate N_2O emissions from industrial processes. Accurate production records should be available at the plant level.

Plant-Level Documentation

The emissions information necessary to allow a thorough analysis by the reviewing/auditing agency will include adipic acid and nitric acid production, and the basis for estimating the emissions for unit of product.

4.2.2 Inventory agency level activities

Inventory Agency Review (QA) of Plant-Level Information

Before accepting plant-level emissions data, the inventory agency should carry out an assessment of data quality and sampling procedures. This type of review requires close cooperation with plant owners to obtain enough information to verify the reported emissions, as discussed above. The assessment should include sample recalculations, an examination of the representation of the data and operating conditions, and identification of potential bias in the methodology and recommendations for improvement.

Inventory Agency QC on Compiling National Emissions

In addition to a thorough quality assessment of plant-level data discussed above, the inventory agency should ensure that the process of aggregating plant data to develop the national inventory undergoes quality control. This should include, among other things:

- cross-referencing aggregated adipic acid and nitric acid production statistics with national totals;
- back-calculating national emissions factors from aggregated emissions and production data;
- ensuring all plants are included, and
- comparison with industry trends to identify anomalies and patterns.

Inventory Agency Documentation on Compiling National Emissions

- For the N_2O emission inventories, a QA/QC management plan should address the specific items needed to perform audits and reviews. When each plant provides the estimates, the details should be documented at the plant level to account for differences in the procedures among plants. Examples of the types of information needed for documentation and external audit include:
- a detailed description of the inventory methodology;
- identification of the input parameters that are needed and how the input parameters are obtained (measured or estimated);
- frequency of the measurements and results of determinations of accuracy and precision for the measurements;
- an estimate or discussion of uncertainty and variability for input parameters that are estimated instead of measured, and
- when plants use a N_2O emission factor relationship derived from measurements at another industrial plant, local measurements should be taken to verify that the relationship is valid due to differences in plant operating conditions. Countries should provide information on the origin and basis of the factor, compare it with other published emission factors explaining any significant differences as well as attempting to place bounds on the uncertainty.

4.3 External inventory QA/QC systems

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

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

An audit of the documentation and calculations ensures that each number is traceable to its origin. Given that much of the information used in developing N_2O emission estimates may be proprietary, a third party audit that protects confidentiality may be a necessary type of review.

Expert (peer) review

A detailed peer review would be appropriate when a procedure for determining N_2O emissions is first adopted or revised; it would not be needed on an annual basis. Such a review is designed to ensure that the methodology accurately represents the plant's particular situation, is as rigorous as possible, and that the data and assumptions used reflect the best available information.

Stakeholder review

Review by adipic acid and nitric acid producing companies, industrial organizations and government can provide a forum for review of the methods used. This type of review would be of most value early in the inventory process when plant-specific details are shared, which can lead to ways for some companies to improve their methods to the levels achieved by the plants with the best methodology.

Public review

Some countries make their entire inventory available for public review and comment. This process may result in a range of comments and issues broader than those from other review processes. Confidential Business Information (CBI) issues should be considered when inventories are presented for public review.

5 CONCLUSIONS

Industrial nitrous oxide (N_2O) emissions are generated as a by-product during the production of adipic acid and nitric acid. In 1990, adipic acid production was the largest source of industrial N_2O emissions. However, as of 1999, industrial sources report that all major adipic acid producers have implemented N_2O abatement technologies (Reimer, 1999). As a result, nitric acid production is currently believed to be the largest industrial source of N_2O emissions.

The *IPCC Guidelines* recommend a straightforward method for estimating emissions from both adipic acid and nitric acid, in which an emission factor is multiplied by production data.

Given that N_2O emissions are controlled in many adipic acid production facilities, the amount of N_2O that is actually released will depend on the level of controls in place at a specific plant. To achieve the highest accuracy, the *IPCC Guidelines* recommend the use of plant-level N_2O emission generation and destruction factors developed from plant-specific measurement data. In the case of nitric acid production—with many more facilities than adipic acid and with a much greater variation among plant types—plant-specific data may be much more difficult to collect, and thus default factors may be needed more often.

Where adipic acid or nitric acid plant-level information is not available, IPCC default generation factors and destruction factors should be selected based on the plant types and abatement technologies implemented. Adipic acid and nitric acid production data are necessary to estimate N_2O emissions regardless of the selected estimation method.

Quality assurance and quality control activities should occur at several points in the emission estimation process. At the plant level, key elements should include internal quality control on plant level measurements and production data, and documentation of data and methods for reviewers. As a quality assurance check, a country that calculates emission estimates from plant level information (bottom-up approach) should compare those values with estimates produced from national statistics (top-down approach).

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