Protocol
2B2: N_2O emissions resulting from the production of nitric acid

IPCC Category:	2B2
NFR Code:	n.a.
NOSE Code:	n.a.
NACE Code	2015 en 201499

FOREWORD
Under the Kyoto Protocol, the Netherlands is required to set up and maintain a national system to monitor its greenhouse gas emissions. One of the elements of this system is a transparent and verifiable description of the methods and processes used in this monitoring system. These methods must meet international guideline criteria, which have been defined by the United Nations (UN) and the European Union (EU).

The Netherlands meets the aforementioned requirement, for example, by defining a series of Monitoring Protocols, which describe the methods and work processes used to determine greenhouse gas emissions and the amounts of carbon sinks available. Protocols have been written for about 40 greenhouse gas sources or sinks. This document describes the protocol for one of these sources or sinks.

The protocols have been compiled in close collaboration with experts from various sectors of society in the Netherlands, particularly experts from the Emissions Registration (ER). The ER is a collaborative group that includes institutions such as CBS, WUR, RIVM and PBL. Until 31 December 2009 this was coordinated by PBL (Planbureau for the Leefomgeving, or the Netherlands Environmental Assessment Agency), but on 1 January 2010 this coordination task was taken over by RIVM (the Netherlands institute for public health and the environment). Other institutions that have contributed to the protocols include NL Agency; Ministry of Agriculture, Nature and Food Quality; and the Ministry of VROM (Housing, Spatial Planning and the Environment).

1 SCOPE AND SIGNIFICANCE OF EMISSION SOURCES/ACTIVITIES

1.1 Scope and definition
This protocol describes the method and working processes for determining the emissions of laughing gas (N_2O) that are released during the industrial production of nitric acid in the Netherlands (IPCC category 2B2). This concerns the SBI codes 2015 (two production locations) and 201400 (a single production location).

The production of caprolactam also forms an important industrial source of N_2O emissions in the Netherlands, but the monitoring of these emissions is described in a separate protocol.

In the Netherlands, nitric acid is used in the production of fertilisers (e.g. lime ammonia nitric acid). Up to the end of 2000 there were three companies manufacturing this product in seven factories throughout the Netherlands. However, one of these companies ceased production in 2000, so there are currently only two companies using six production locations. These emission sources are entirely (100%) responsible for the N_2O emissions from nitric acid production in the Netherlands.

Nitric acid production starts by converting (combusting) ammonia (NH_3) with air into nitrogen monoxide (NO), under the influence of a platinum alloy catalyst. This continues with further oxidation into nitrogen dioxide (NO_2) and absorption in water, thus producing nitric acid (HNO_3).

N_2O is created as an undesirable by-product during the catalytic oxidation of ammonia with oxygen. The amount of N_2O formed primarily depends on the temperature and the time spent in the reactor, because N_2O is unstable at high temperatures (850-950°C). In most nitric acid plants the process gases are cooled after combustion, with heat-recovery techniques being used to recover the heat released. The reactor time at high temperatures (850-950°C) is therefore relatively short (Infomil, Novem 2001).

Since the platinum alloy catalyst becomes less efficient over time, the amount of N_2O produced fluctuates continually. These platinum alloys are very active when new (i.e. little N_2O produced), but this efficiency is gradually reduced as they become worn, so that the amount of N_2O increases and the platinum alloys will eventually need to be replaced (production stop).

1.2 Significance and influences

1.2.1 Contribution to total national emissions

The N_2O emissions from nitric acid production contribute a few percent to the Netherlands annual greenhouse gas emissions.

1.2.2 Developments that infuence emissions

In theory there are several ways of limiting the amount of N_2O that is formed as an undesirable by-product:

(1) Primary measures: measures that limit the formation of N_2O during catalytic conversion, e.g.
 (a) optimising conventional platinum-based catalytic converters, or
 (b) using alternative catalytic converters.

(2) Secondary measures: these are measures that can be taken in the process gas flow originating from the oxidation catalytic converter up to the absorption towers, e.g.
 (a) thermic decomposition of N_2O by enlarging the reaction chamber, or
 (b) catalytic dissection of N_2O at high temperatures (850-900°C).

(3) Tertiary measures: measures that can be taken between the absorption towers and the expansion chamber, e.g.
 (a) catalytic dissection of N_2O at temperatures of 400-450°C, or
 (b) selective catalytic reduction (SCR) of N_2O with propane or methane as reagents, possibly combined with the reduction of NO_x, or
 (c) non-selective catalytic reduction (NSCR) of NO_x (with simultaneous N_2O reduction).

(4) End of pipe measures (post-switched techniques). The techniques described under point 3 (particularly a and b) can also be implemented after the expansion turbine.

Most of these technologies will result in a high reduction (around 80-90%), with the exception of 1a, where the reduction is only around 30% (Infomil, Novem, 2001).

Many of the aforementioned measures are still being developed and are therefore not yet available on a commercial scale. One of the production companies has not yet taken any measures in the Netherlands. However, the concern is currently developing and demonstrating technologies in order to limit N_2O emissions. In 2000, another company optimised its platinum-based catalytic converter alloys and is also currently developing technologies to reduce N_2O emissions. The plant that ceased production in 2000 uses an NSCR system.

2 METHOD, EMISSION FACTORS AND ACTIVITY DATA

2.1 Calculation method

The way in which N_2O emissions by the nitric acid industry in the Netherlands are calculated is based on the following formula:

*N_2O emissions [kg/year] = Specific emission factor [kg N_2O/ton nitric acid] * Production [ton nitric acid/year] * [1 – (N_2O Destruction factor * Corporate time factor)]*

The production of nitric acid is expressed in ton HNO_3 100%.

The aforementioned formula is applied per plant, using the plant-specific measurement data. The sum of the emissions from the various plants equals the total national N_2O emissions by the nitric acid industry.

However, it should be noted that the aforementioned calculation is based on measurement data from the (cleaned) exit gas flow. The effects of the N_2O emission-reduction measures, plus the corporate time factor, are therefore included in the specific emission factor for N_2O. Data concerning the efficiency of N_2O emission-reducing measures are therefore not included in the calculation, but are certainly used for information purposes. The aforementioned formula can thus be simplified to:

*N_2O emissions [kg/year] = Specific emission factor [kg N_2O/ton nitric acid] * Production [ton nitric acid/year]*

This conforms to the required method for specifying N_2O emissions from nitric acid production as per Box 4, as described in the IPCC GPG § 3.2.1 (IPCC, 2001, p. 3.31 etc.). Plant-specific emission factors are used.

2.2 Emission factors

The manufacturer determines the specific emission factor per plant by multiplying the following elements (apart from any conversion factors that may be required):

- Concentration of N_2O in the exhaust gas from the plant [mg N_2O/Nm^3];
- Specific flow factor [Nm^3/ton nitric acid].

The specific emission factor is calculated as follows:

$$EF_{specific} = C_{N2O} * F_{p \rightarrow a} * F_{v \rightarrow m}$$

C_{N_2O}: average N_2O emissions in the exhaust gas (ppm)
$Fp_{\rightarrow}a$: conversion factor from nitric acid production to exhaust gas flow (Nm^3/ton acid)
$Fv_{\rightarrow}m$: conversion factor from volume to mass (ton/Nm^3 gas)

The annual N_2O emissions can then be calculated by multiplying the specific emission factor by the annual nitric acid production. An example calculation can be found in Appendix 1.

The specific emission factor for each plant is considered confidential information. The manner in which this is calculated is reported and archived by the manufacturer.

The N_2O concentration in the plant's exhaust gas increases during a normal production schedule (i.e. the period between replacing the platinum alloy catalyst). In order to determine the actual N_2O concentration, a measurement is taken every 2-3 weeks from the exhaust gas flow of the plant, during these normal production runs. At least 10 concentration measurements are taken over the course of each production run. The trend line is used to establish the average concentration throughout the production period.

Modifications to the plant or the process conditions that are important to the N_2O emissions require the emission factor to be redefined. This is important in substantiating the emissions reduction achieved through new techniques. Factors that can influence the emission factor are primarily:

- Changes to the reactor temperature
- Changes to the type and structure of the ammonia oxidation catalytic converter
- Changes to the NH_3 content in the input mix
- Installation of specific reduction measures

Changes in the intensity have no influence on the specific emission factor.

Accessibility of measurement data
Under the framework of the N_2O nitric acid working group from the ROB programme (reduction of other GHGs), the sector has indicated that N_2O measurements should be made available to ENINA, in order to improve the international reports on greenhouse gases. Measurement data are available from the 1990s onwards, though accuracy is limited. The emissions data from companies before this date are based on estimates according to the size of the production.

The year 1990 is used as a reference year for the nitric acid industry. Measurement data can therefore not be used to achieve a consistent range from 1990 to 1995. Since the variation lies primarily in the size of the production and not in the technology (there have been no important technical changes over the last 10 years), pre-1990 emissions are calculated by extrapolating data.

2.3 Activity data
Not applicable

3 WORKING PROCESSES

Process for estimating (t-1)
If preliminary figures are required at any point, the following process is used to estimate the figure for t-1. The preliminary data for the work package leader are calculated by extrapolating them from the previous years' figures, based on prognoses for the developments in the most important activity data (taken from CBS (Statistics Netherlands) or other statistical sources).

INPUT	PROCESS	OUTPUT	BY WHOM
Preliminary data work package leader (t-1)	Include t-1 data in ER database	ER-db with (t-1) data	Work package leader
ER-db with (t-1) data	Check emission figures: compare with previous years (trend), modify if required and document everything	ER-db (t-1) with any modified figures	Task force

Process for final determination of (t-2)
The final emission figures (as described in this protocol) are calculated using the following process.

INPUT	PROCESS	OUTPUT	BY WHOM
Internal corporate emission figures	Reporting in annual environmental report (MJV)	Annual environmental report (MJV)	Companies
MJVs	Validating MJV	Validated MJV	Competent authority (Province)
Validated MJV	Included in FOI file	FOI file	FOI
FOI file	Checking emission figures: - Comparing MJVs with MJVs from previous years (trend) If non-substantiated deviations in MJV text found, contact the Province and/or Company→ If necessary modify emission figures and document everything.	Final data Work package leader (t-2)	Work package leader
Final data Work package leader (t-2)	Include (t-2) data in ER database	ER-db with (t-2) data	Work package leader
ER-db with (t-2) data	Check, and trend analysis of air emissions: explain deviations or modify figures	Final defined emission figures (t-2)	Task forces and PBL experts

Supplying data via the MJV
Companies are required to report their emissions, per plant, as part of their annual environment report (MJV), differentiating between confidential and non-confidential data. This must be submitted (before 1 April of the year following the reporting year) to the competent authority for the particular plant.

The methods used, measurement results and frequencies, calibration records, characteristics and possibly the efficiency of the technologies used to reduce N_2O emissions, plus other important information or data, are all recorded and updated for each company. Companies can also make a substantiated estimate concerning the reliability of their data, if there is sufficient reason for doing so, e.g. a particular deviation. Confidential data concerning the technologies used remain within the company, which updates these figures regularly. These confidential data are only made available to the review teams of the competent authority/ENINA (air emissions from energy, industry and waste disposal).

4 UNCERTAINTY AND QUALITY

4.1 Estimating uncertainties

A Tier-1 uncertainty analysis is implemented every year before the NIR is submitted by the ER, based on the greenhouse gas inventory and in compliance with IPCC guidelines. The assumptions used and the results thereof are described in a background report to the NIR. In addition to this, where included in the QA/QC programme for the relevant period, extra analyses are implemented regularly in specific situations, which include any updating of the Tier-2 uncertainty analyses. The Tier-2 uncertainty assessment was last updated in 2006. This assessment showed that a Tier-1 uncertainty assessment is sufficiently reliable and that Tier-2 uncertainty assessments need only be implemented at periodic intervals of around 5 years, unless a major change in an important source is sufficient to require earlier reassessment.

- Source-specific uncertainty

The uncertainty estimate-totaal concerns the root of the sum of uncertainty in the data sources used (AD_{onz}) in the square and the uncertainty of the emission factor (EF_{onz}) in the square. The extent of the total uncertainty is here primarily determined by the greatest AD or EF uncertainty.

$$\text{Uncertainty estimate}_{\text{total}} = \sqrt{EF_{onz.}^{\;2} + AD_{onz.}^{\;2}}$$

The uncertainty estimates concerning the data sources (AD) and emission factors (EF) used, and the total uncertainty estimate, are listed in the following table.

IPCC	Category	Gas	AD $_{onz.}$	EF $_{onz.}$	Uncertainty estimates $_{tot}$
2B2	Nitric acid production	N_2O	10	50	51

The uncertainty in N_2O emissions from nitric acid was estimated to be about 50%, resulting from an uncertainty in activity data of 10% and 50% in the N_2O emission factor. Uncertainty estimates were based on expert judgements, since no accurate information was available for assessing the uncertainties in the emissions reported by the nitric acid producer [Olivier et al, 2009].

4.2 Quality assurance and quality control (QA/QC)

The ER work package leaders check that:

1. the basic data are well documented and adopted (check for typing errors, use of the correct unit sizes and correct conversion);
2. the calculations have been implemented correctly;
3. assumptions are consistent, also whether specific parameters (e.g. activity data) are used consistently;
4. complete and consistent data sets have been supplied.

Any actions that result from these checks are noted on an ‘action list’. Before defining the data, supervisors check whether the relevant actions on this list, plus the QC checks, have all been completed. Defining the data is carried out by the WEM (working group on emissions monitoring), and confirmed in writing via an e-mail from the institute representatives to the ER project leader at PBL.

The work package leaders fill out a new documentation sheet when adding new data. For reasons of efficiency a minimum level has been set for obligatory documentation, i.e. 5% changes at target group level, and 0.5% at levels concerning the national total. These documentation sheets form part of the trend analysis, as well as the eventual definition of the data set.

The ER work package leaders communicate by e-mail regarding these QC checks, results and actions. They send a printed copy to the ER secretary, who keeps a logbook and compiles these e-mails into an ‘action list’. This shows explicitly that the required checks and corrections have been carried out.

4.3 Verification

In order to check the quality of the emission figures for the sources in this protocol, general QA/QC procedures have been followed that are in line with the IPCC guidelines. These are described further in the QAQC programme used by the National System, and the annual working plans published by the ER.

- Sector-specific QC

No additional specific verification procedures are implemented for the sources defined in this protocol.

4.4 Possibilities for improvement compared to the current calculation method

4.4.1 History

Appendix 2 describes how the emission figures are calculated, up to and including the year 2000. Appendix 3 includes a worksheet for companies. After a successful pilot in 2005 the worksheet has been added to the government section of the Annual Environment Report (MJV). The worksheet turned out to be usable for de validation of the Annual Environment Report by the Competent authority and for the determination of the annual emissions by PBL (Netherlands Environmental Assessment Agency). Concerning the procedure to be followed, it has been decided that the complete forms are kept by the companies in their own administration and are made available to the Competent authorities of reviewers, whenever asked.

4.4.2 Future

There is currently no unambiguous information concerning the uncertainty of the calculation methods. This needs to be further substantiated.

5 REMAINING ASPECTS

5.1 Point source criteria

Not applicable

5.2 Substance profiles

Not applicable

5.3 Regionalisation
Not applicable

5.4 Time-based variations in source strength
The N_2O concentrations in the exhaust gas of the plant increase during normal production runs (i.e. the period between replacement of the platinum alloy catalysts). See Section 7.

6 REFERENCES AND ADDITIONAL INFORMATION

6.1 References

- Infomil and Novem, Reduction of nitrous oxide (N2O) in the nitric acid industry, Den Haag/Utrecht, The Netherlands, October 2001.
- IPCC, 1997: Revised 1996 IPCC Guidelines for National Greenhouse Gas Emission Inventories, Three volumes: Reference Manual, Reporting Guidelines and Workbook. IPCC/OECD/IEA. IPCC WG1 Technical Support Unit, Hadley Centre, Meteorological Office, Bracknell, UK
- IPCC, 2001: Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories, IPCC-TSU NGGIP, Japan
- Mertens, P.R, Munnichs, N. Aanzet tot N2O meetprotocol (background to N2O measurement protocol); memo dated 17 May 2001.
- NIR 2005: Greenhouse Gas Emissions in the Netherlands, National Inventory Report 2005, RIVM report 773201009 / 2005
- Olivier J.G.J., L.J. Brandes and R.A.B. te Molder, 2009 (in print) Uncertainty in the Netherlands' greenhouse gas emissions inventory: Estimate of annual and trend uncertainty for Dutch sources of greenhouse gas emissions using the IPCC Tier 1 approach, PBL-Report 500080013, Bilthoven
- UNFCCC, 2004, Guidelines for the preparation of national communications by Parties included in Annex I to the convention, Part I: UNFCCC reporting guidelines on annual inventories, UNFCCC/SBSTA/2004/8, 3 September 2004

6.2 Additional information
Appendices:
1. Background to N_2O measurement protocol for companies; memo dated 17 May 2001
2. Description of the monitoring method, up to and including the year 2000
3. Worksheet for companies

APPENDIX 1: MEMO BACKGROUND TO N_2O PROTOCOL

MEMO

To	:	J. van Damme; Th. Huurdeman
From	:	P.R. Mertens, N. Munnichs
Date	:	17 May 2001
Concerning	:	Background to N2O measurement protocol
Cc	:	R. Coster

Some time ago the working group for N_2O in the nitric acid industry agreed that we need to decide how N_2O emissions from the nitric acid industry can best be determined.

During the discussions held at that time, the nitric acid industry indicated that they would not like to see emissions being defined according to N_2O concentrations in the exhaust gases, and then multiplying this by the flow rate. These companies preferred that N_2O emissions be defined per plant, based on the amount of nitric acid produced (in tons N). N_2O emissions could be determined by multiplying these plant-based parameters by the amounts of nitric acid produced.

This preference was based on the consideration that the accuracy with which the exhaust gas rate could be determined was considerably less than the number of tons nitric acid production. Based on discussions with both the production and instrumentation staff, I conclude that this would be acceptable. The annual production can be determined (to 1% accuracy) from the stocks of raw materials, while the inaccuracy in the flow rate (which only measures that particular point in time in a turbulent gas flow) would be more than 10%.

One of the companies has gathered an extensive set of data for both its nitric acid plants. This shows that, as expected, the N_2O concentrations in the exhaust gas increase in a fairly linear line the longer the catalyst is used. This therefore means that, in order to achieve a reliable definition of the emission factor per plant, more measurements would need to be carried out during a complete (but primarily representative) production run. After analysis of the available data it is possible to conclude that, in order to achieve sufficient accuracy, at least seven (but preferably more) measurements would need to be taken throughout a production run. A trend analysis could then be used to determine the average N_2O emissions per production run for that particular plant, with an accuracy of over ±5%.

The plant parameter required to translate this representative N_2O concentration into an annual emission level, is the factor that shows the relationship between the production and the exhaust gas flow rate. For a nitric acid plant based on the ‘dual pressure’ concept, this is 3200 Nm^3 per ton of nitric acid (based on 100% concentration). This parameter depends on the conversion efficiency of ammonia and the amount of O_2 in the exhaust gas. Under normal circumstances this figures represents an accuracy of over 2%.

CALCULATION EXAMPLE

C_{N_2O} : (average N_2O emission); for this plant = 1393 ppm

$Fp \rightarrow a$: (conversion factor from nitric acid production to exhaust gas rate) = 3165 Nm^3/ton acid

$Fv \rightarrow m$: (conversion factor from volume to mass) = $1.964*10^{-3}$ ton/Nm^3 gas

P : the annual nitric acid production = 181,233 ton (100%)

The annual N_2O emissions can then be calculated using the following formula:

$$E_{N_2O} = C_{N_2O} * F_{p \rightarrow a} * F_{v \rightarrow m} * P = 1570\, ton N_2O$$

APPENDIX 2: DESCRIPTION OF MONITORING METHODS UP TO AND INCLUDING THE YEAR 2000

Up to and including the year 2000 there were three companies producing nitric acid in the Netherlands. One of these companies ceased production at its Pernis plant in 1999, and in 2000 at its Rozenburg plant, so that there were then only two companies left, with three production locations and six plants. N_2O is emitted during the production process. The amount emitted is measured by all three companies on a regular basis[1]. The N_2O concentration varies according to production circumstances. Until 1997 (Kyoto Protocol) the emission figures were only important to the companies themselves. However, after Kyoto, N_2O emissions became a hot item for the Dutch and European climate policy, and these measurements are particularly important for external reports. To date this measurement data has been voluntarily reported under the framework of the Corporate Environmental Plan (CEP) by one of the companies, and compulsorily by one of the other companies under the framework of the environmental permits. The third company reports N_2O emissions at corporate level and thus not for its individual nitric acid production.

Up to and including 2000 the annual N_2O emissions were therefore calculated within the Netherlands Emissions Registration system. This is based on aggregated emission factors and production volumes of nitric acid (production index via CBS). The method is as follows:

N_2O emissions (kton) = emission factor (kg N_2O/ton HNO_3) * production (kton HNO_3) * 10^{-3}

A study commissioned in 1995 by VROM, where N_2O process emissions were measured at nitric acid plants in the Netherlands, showed that the Dutch N_2O emissions from nitric acid plants amounted to 24-29 ktons. Using this as a basis, the emission factor was determined as 9.0 kg N_2O per ton nitric acid. It was assumed that there were no NSCR techniques (non-selective catalytic reduction techniques) used in the Netherlands (Spakman et al., 1997).

However, under the framework of the N_2O nitric acid working group from the ROB programme (established in August 2000), it was concluded that this assumption was incorrect, because one of the companies did use NSCR techniques. The N_2O emissions for the nitric acid industry were therefore defined at an excessively high level (in the Netherlands Emissions Register) for many years.

Literature

- Spakman et al., 1997. Methode voor de berekening van broeikasgasemissies (method of calculating greenhouse gas emissions). VROM. Emissieregistratie 37. Den Haag.

[1] The amount of laughing gas formed fluctuates because the reactivity of the platinum alloy catalysts drop as they become worn. When they are new they are very active (forming very little laughing gas), but they gradually become less efficient (whereby the laughing gas increases) until they eventually need to be replaced (production stop)

APPENDIX 3: WORKSHEET FOR COMPANIES

(NB: One worksheet should be used per plant and included in the government section of the Annual Environmental Report)

1. General information

- *Source category:* N_2O from nitric acid production
- *Target group ER* process: Industry
- *ER codes:* RAPcode 8900903 SBI ……..(*2415 or 24142)*
- *IPCC category:* Table 2(I) Sectoral report for industrial processes B. (Chemical industry 2. Nitric acid production)
- *IPCC method:* Box 4, IPCC Good Practice Guidance Chapter 3.2
- *Other emission reports:* MJV
- *Validity of protocol:* From 1 January 2004, re-evaluation in 2007 at the latest
- *Reporting year:* ……………………..

2. Data concerning emission monitoring

Plant information

Company name	
Location of the plant	
Contact person	
Telephone number	
E-mail	
Coding for the plant	
Type of plant: • Single pressure plant (Medium or High pressure) • Dual pressure plant (Medium/High or Atmospheric/Medium pressure)	

Emissions data

Data	Value	Qualification
Specific emission factor [kg N_2O/ton nitric acid]		Confidential, not public (1)
Production [ton nitric acid/year]		Confidential, not public
Calculated annual emission freight in N_2O [kg N_2O/year]		Public
Reduction measure (type, e.g. NSCR, SCR, catalytic decomposition)		Confidential, not public
Estimated destruction factor of the reduction measure [%]		Confidential, not public
Corporate time factor of the reduction measure [%] (percentage of the company time at the plant where the reduction measure was used)		Confidential, not public

(1) Reference to the report in which the emission factor was determined and where this can be viewed (confidential, not public):
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(2) Specification of any changes to the plant that may effect the N_2O emissions (confidential, not public):
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