

# Protocol

## 2B5: N<sub>2</sub>O emissions during caprolactam production

IPCC Category:	2B5
NFR Code:	n.a.
NOSE Code:	n.a.
NACE Code 2008	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 methods and working processes for determining the emissions of laughing gas (N<sub>2</sub>O) that are released during the industrial production of caprolactam in the Netherlands (IPCC category 2B5). This concerns the SBI industrial code 201499.

Caprolactam is produced in the Netherlands as part of the production cycle for nylon materials, and is manufactured (since 1952) by only one company. This emission source is therefore responsible for the entire (100%) laughing gas emissions by the caprolactam industry in the Netherlands. The production capacity increased from 200 kton in 1990 to 250 kton in 2005.

Caprolactam is manufactured from raw materials such as phenol, ammonia, hydrogen, sulphur dioxide, ammonium nitrite and oleum. The company consists of a number of installations, several of which release N<sub>2</sub>O emissions, primarily the:

- HPO plant (Hyam Phosphate Oxime).
- HSO plant (Hyam Sulphate Oxime).
- Nitrite plant.

Both the HPO and HSO plants use cyclohexanon as one of the raw materials when preparing cyclohexanon-oxime. The oxime is processed into lactam in a so-called 'diversion', after the final product is formed via purification and concentration. A nitrite solution is produced in the nitrite plant, which then forms a raw material for the HSO.

Laughing gas is formed in two ways within the aforementioned processing plants:

1. When preparing the hyam, in the HPO and HSO.
2. As a result of the catalytic combustion of ammonia in the nitrite plant and HPO.

## **1.2 Significance and influences**

### **1.2.1 Contribution to total national emissions**

The N<sub>2</sub>O emissions from caprolactam production contribute less than 0.5% to the total annual greenhouse gas emissions in the Netherlands.

### **1.2.2 Developments that influence emissions**

At this point in time there are no measures available to limit laughing gas emissions. The caprolactam manufacturer is currently researching the effects and feasibility of several ideas aimed at reducing emissions.

## **2 METHOD, EMISSION FACTORS AND ACTIVITY DATA**

### **2.1 Calculation method**

The IPCC Good Practice Guidance (GPG, 2001) and the IPCC Revised Guidelines (IPCC, 1997) do not describe any method for defining emissions from caprolactam production. However, the IPCC GPG does mention this production as a source of N<sub>2</sub>O emissions (IPCC, 2001, p. 3.30).

Since 2003 the company has been implementing a monitoring programme for the HSO, HPO and the nitrite plant. The N<sub>2</sub>O emissions are measured at various emission points every year. Annual N<sub>2</sub>O emissions are determined by adding up these intermediate emission results.

If there is any change to the methods of monitoring these emissions, the company reports this in its corporate worksheet (see Appendix 1), as part of its obligation to provide data for the annual environmental report (AER/MJV). The company also submits the modified monitoring programme to the Competent Authority.

If laughing gas emissions change due to modifications to the plant or process conditions, then these emissions are measured again. This is important in order to obtain reliable annual emission results and to substantiate the annual emission reduction measures. The company reports modifications to the plant in its corporate worksheet (see Appendix 1).

Based on the recommendations by the Review (April 2007), in August 2007 the constant presumed N<sub>2</sub>O emissions for the period 1990-2002 were recalculated. This new calculation was implemented using a production-index range provided by the manufacturer (actual production figures are confidential) for the period 1990-2004 and the measured N<sub>2</sub>O emissions for 2003 and 2004.

### **2.2 Emission factors**

Not applicable

### 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	Report in annual environmental report (AER/MJV)	AER/MJV	Companies
AERs/MJVs	Validate AER/MJV	Validated AER/MJV	Competent Authority (Province)
Validated AER/MJV	Include in FO-I file	FO-I file	FO-I (Facilitary Organisation – Industry)
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

*Submitting data via AER/MJV*

The company reports emissions resulting from caprolactam production as part of its annual environmental report (AER/MJV), which is submitted to the Competent Authority for the plant in question, before 1 April in the year following the reporting year. The AER/MJV includes the total emissions monitored at the various emission points.

The methods used, (measurement) results and frequencies, calibration records, characteristics and (where applicable) the efficiency of the technologies used to reduce laughing gas, plus other important data or information are all recorded and updated regularly. The company is also required to estimate the reliability of these data. Confidential information is only made available to the Competent Authority, ENINA, and the review teams.

## 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 <sub>onz.</sub>	EF <sub>onz.</sub>	Uncertainty estimates <sub>tot</sub>
2B5	Caprolactam production	N <sub>2</sub> O	50	50	71

The uncertainty in annual N<sub>2</sub>O emissions from caprolactam production was estimated to be about 70% (based on uncertainties of 50% in activity data and 50% in the N<sub>2</sub>O 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 producers of caprolactam [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**

The first (indicative) N<sub>2</sub>O measurements for the caprolactam industry were taken during the period 1995-1996. Before this time not all sources of N<sub>2</sub>O emissions were monitored. The first reference value for 1990 is based on these initial measurements. A monitoring programme was started in 2003 that resulted in more reliable figures. In August 2007, N<sub>2</sub>O emissions for 1990-2002 were recalculated using measurements for 2003 and 2004, plus a production-index range for the period 1990-2002.

Appendix 1 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 Emission Registration (ER). 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**

The N<sub>2</sub>O monitoring programme was included in the permit in 2005. Since there is no standard, or norm, for N<sub>2</sub>O emission, inclusion in the permit is a voluntary matter. Both the competent authority and the industry itself see a need for a realistic European standard, although until now there have been no technical solutions found.

The company will set up a validation programme to determine the uncertainty of the emission definitions.

## **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**

Not applicable

## **6 REFERENCES AND ADDITIONAL INFORMATION**

### **6.1 References**

- 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
- 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**

Appendix 1: Worksheet for companies

## APPENDIX 1. WORKSHEET FOR COMPANIES

(NB: This worksheet will be included in the governmental part of the Annual Environmental Report)

### 1. General information

• <i>Source category:</i>	N <sub>2</sub> O during caprolactam production
• <i>Target group ER process:</i>	Industry
• <i>ER codes:</i>	RAP (reporting) code B034311 SBI 24142
• <i>IPCC category:</i>	n.a.
• <i>IPCC method:</i>	n.a.
• <i>Other emission reports:</i>	AER/MJV
• <i>Validity period of protocol:</i>	From 1 January 2005, re-evaluation no later than 2007
• <i>Reporting year :</i>	.....

### 2. Data for emissions monitoring

#### Installation information

Company name	
Location of the installation	
Contact person	
Telephone number	
E-mail address	
Coding of the installation	
Type of installation	

#### Emissions data

Data	Value
Emissions at various emission points	

(1) Describe any modifications made to the measurement and analysis method (confidential, not public). If changes have been made, the updated 'Measurement programme for laughing gas emissions from caprolactam' must also be submitted (see Appendix 2 of the Protocol N<sub>2</sub>O emissions for caprolactam production):

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(2) Describe any modifications made to the installation that effect N<sub>2</sub>O emissions (confidential, not public):

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