Climate MRV for Africa – Phase 2
Development of National GHG Inventory
Chemical Industry: Nitirc Acid Production

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Project of the European Commission DG Clima Action

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IPPC 2006 IPPU – Chemical Industries – Nitric Acid

Introduction to Nitric Acid: Uses

- Approximately **80 %** of nitric acid is used as intermediate in the production of nitrogenous **fertilizers**. The remaining **20 %** is used in the production of **explosives** or as intermediates for **polymers**.

Source: U.S. Bureau of Labor Statistics, (2013), Growing demand for fertilizer keeps prices high

Introduction to Nitric Acid: Production

- **Nitric acid** (HNO_3) is an extremely **important** chemical used in the **manufacture** of fertilisers and explosives.
- During its production, **N_2O** gas is emitted to the atmosphere.

Source: Cosale Projecto, Nitric Acid

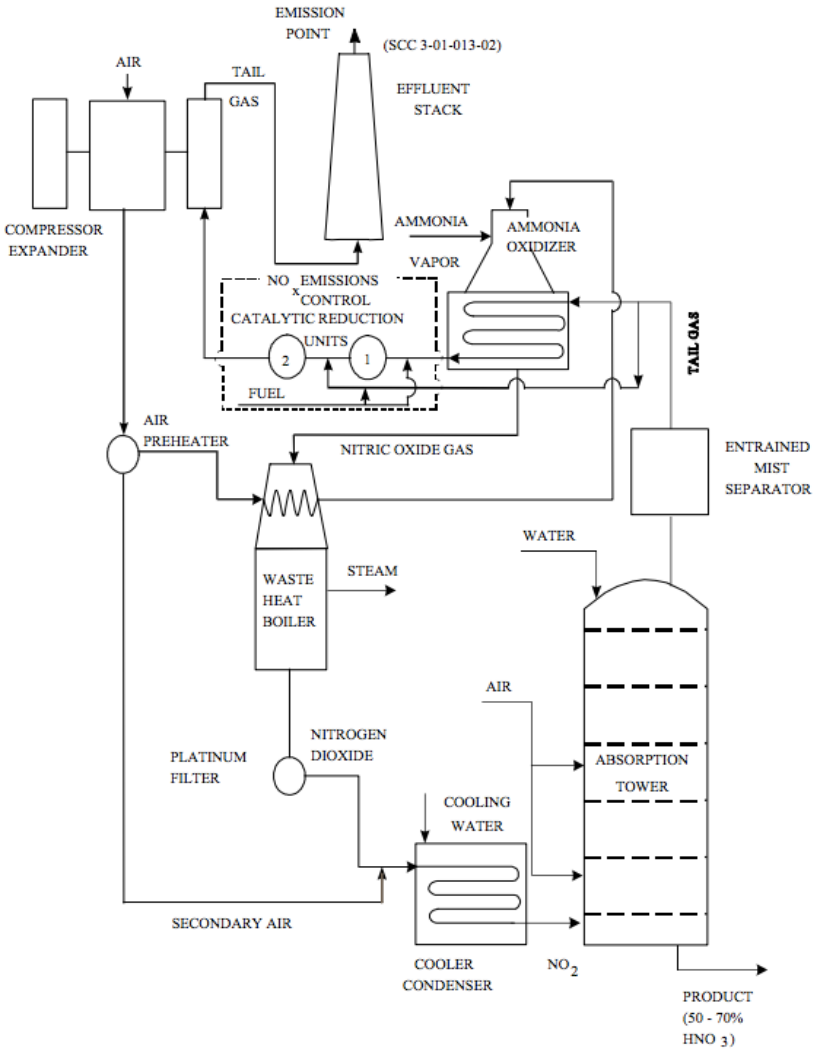
Emissions Sources from Nitric Acid Production

- **Nitric Acid Production:** manufactured by the high-temperature catalytic oxidation of ammonia.
- ***Ammonia oxidation*** is the source of N_2O emissions from nitric acid production, as an **unintended** byproduct of the main reactions among NH_3, O_2 and H_2O.

$$2\ NH_3 + 2O_2 \rightarrow N_2O + 3\ H_2O$$

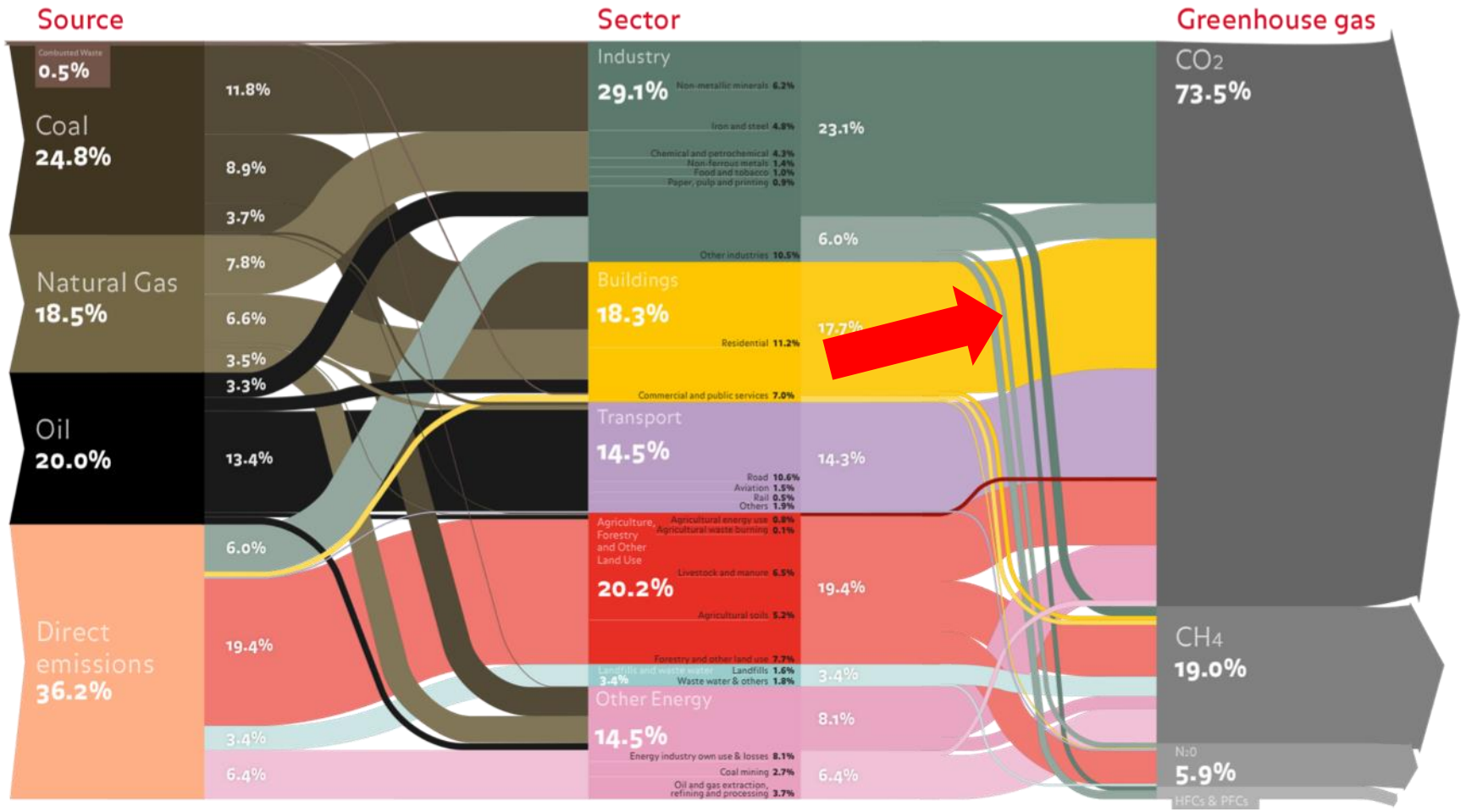
$$2\ NH_3 + 8NO \rightarrow 5\ N_2O + 3\ H_2O$$

$$4\ NH_3 + 4NO + 3\ O_2 \rightarrow 4\ N_2O + 6\ H_2O$$



Source: **Available and emerging technologies for reducing greenhouse gas emissions from the nitric acid production industry, 2010.**

Nitric Acid Production and Global GHG Emissions



Source: ASN Bank and Ecofys (2016), update to the WRI 2000 figure, using 2012 data

Total N_2O emission worldwide (2012) 3,058 Mt $CO_{2\ EQ}$

N_2O Abatement Methods in Nitric Acid Production

- **Primary abatement**: prevents formation of N_2O (at ammonia burner, catalyst)
- **Secondary abatement**: removes N_2O immediately downstream of the ammonia oxidation catalyst
- **Tertiary and Quaternary abatement**: treats tail-gas to destroy N_2O, at different points in the tail-gas stream

N_2O Abatement Methods in Nitric Acid Production

TABLE 3.2
N_2O ABATEMENT APPROACHES AND ABATEMENT MEASURES

Abatement approaches	Abatement measures
Primary abatement	• Optimal oxidation process • Modification of platinum-rhodium gauzes • Oxide-based combustion catalysts
Secondary abatement	• Homogeneous decomposition in the burner • Catalytic decomposition in the burner (process gas catalytic decomposition) • Catalytic decomposition downstream of the burner (before the absorption column)
Tertiary abatement	• Thermal decomposition • Non-selective catalytic reduction (NSCR) • Tail-gas catalytic decomposition • Selective catalytic reduction (SCR)
Quaternary abatement	• Non-selective catalytic reduction (NSCR) • Catalytic decomposition • Selective catalytic reduction (SCR)

Source: Adapted from Perez-Ramirez *et al.* (2003).

Source: IPCC 2006 Vol. 3, Ch. 3, Table 3.2

N_2O Abatement Methods in Nitric Acid Production (1)

- Modified catalytic gauze

Source: Heraeus

N_2O Abatement Methods in Nitric Acid Production (2)

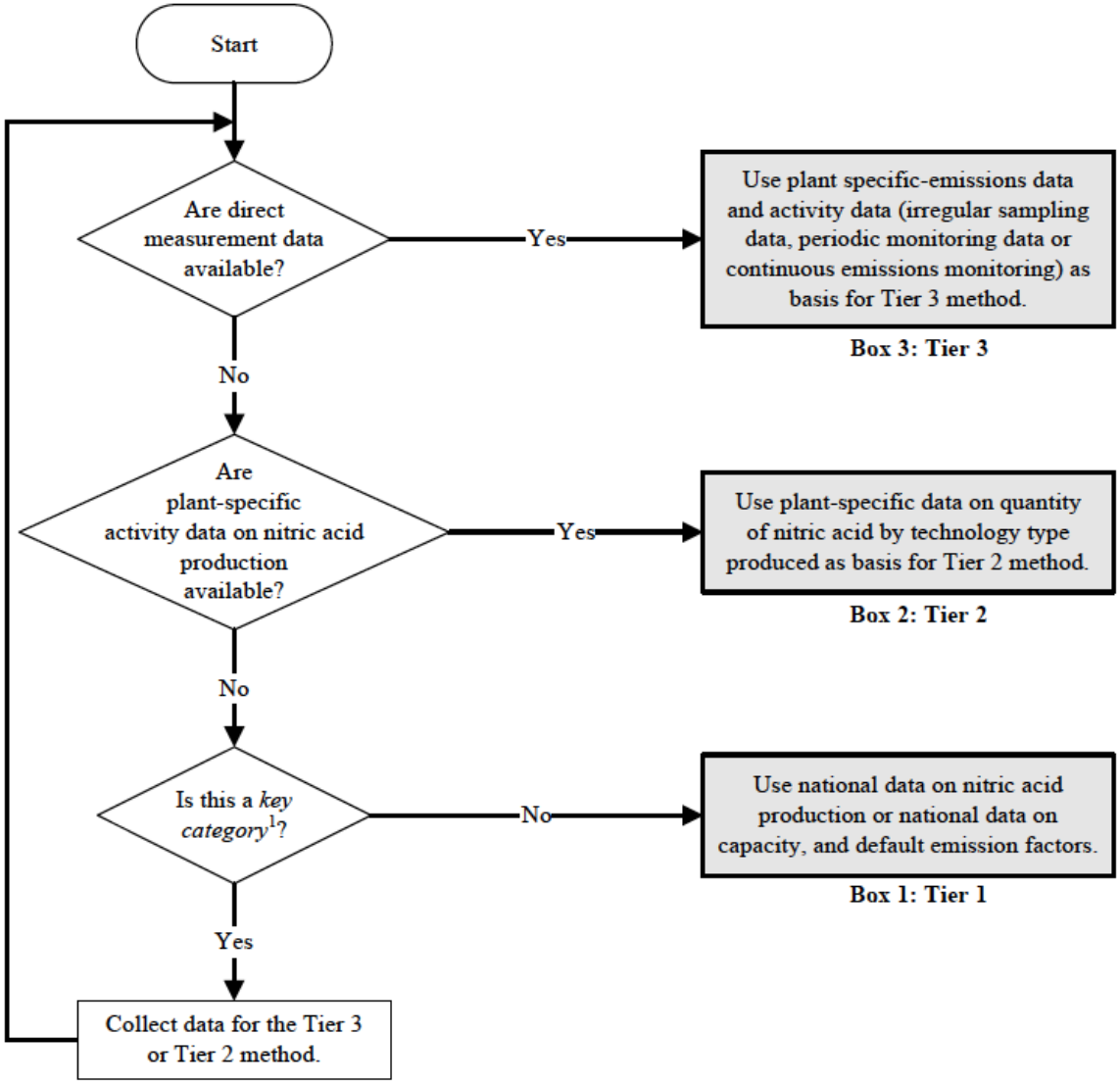
- Selective catalytic reduction

Source: Climeco

Emissions Potential for the Category

- Medium pressure plants have a default emission factor of 7 kilograms of N_2O per tonne of nitric acid.
  - ***Plants with extensive abatement measures can achieve as little as 2 kilograms of N_2O per tonne of nitric acid***
- 1 million tonnes of nitric acid leads to 7,000 tN_2O of direct emissions (2,170,000 tCO_2e)

Decision Tree for N_2O Emissions



Source: IPCC 2006 Vol. 3, Ch. 3, Fig. 3.2

Nitric Acid Production
Tier 1 Method

IPCC 2006: Tier 1 Method

Emissions are estimated as follows:

EQUATION 3.5
N_2O EMISSIONS FROM NITRIC ACID PRODUCTION – TIER 1

$$E_{N2O} = EF \bullet NAP$$

Where:

E_{N2O} = N_2O emissions, kg

EF = N_2O emission factor (default), kg N_2O/tonne nitric acid produced

NAP = nitric acid production, tonnes

Source: IPCC 2006 Vol. 3, Ch. 3, Eq. 3.5

- When applying the Tier 1 method it is good practice to:
  - Assume that there is no abatement of N_2O emissions.
  - Use the highest default emission factor based on technology type.

Tier 1 Emission Factors

TABLE 3.3
DEFAULT FACTORS FOR NITRIC ACID PRODUCTION

Production Process	N_2O Emission Factor (relating to 100 percent pure acid)
Plants with NSCR[a] (all processes)	2 kg N_2O/tonne nitric acid ±10%
Plants with process-integrated or tailgas N_2O destruction	2.5 kg N_2O/tonne nitric acid ±10%
Atmospheric pressure plants (low pressure)	5 kg N_2O/tonne nitric acid ±10%
Medium pressure combustion plants	7 kg N_2O/tonne nitric acid ±20%
High pressure plants	9 kg N_2O/tonne nitric acid ±40%

[a]Non-Selective Catalytic Reduction (NSCR).
Source: van Balken (2005).

Source: IPCC 2006 Vol. 3, Ch. 3, Table. 3.3

Tier 1 Activity Data

- ***NAP*:** National production of nitric acid (tonnes), in 100% HNO_3 equivalent (***good practice***).
- If not available, information on production capacity can be used, however a big proportion of the national nitric acid production may be omitted.
- It is good practice to multiply the total national production capacity by a capacity utilization factor of 80 percent ± 10 percent (i.e., a range of 70-90 percent).

Nitric Acid Production
Tier 2 Method

IPCC 2006: Tier 2 Method

EQUATION 3.6
N_2O EMISSIONS FROM NITRIC ACID PRODUCTION – TIER 2

$$E_{N2O} = \sum_{i,j} \left[EF_i \bullet NAP_i \bullet \left(1 - DF_j \bullet ASUF_j\right) \right]$$

Where:

E_{N2O} = emissions of N_2O, kg

EF_i = N_2O emission factor for technology type *i*, kg N_2O/tonne nitric acid produced

NAP_i = nitric acid production from technology type *i*, tonnes

DF_j = destruction factor for abatement technology type *j*, fraction

$ASUF_j$ = abatement system utilisation factor for abatement technology type *j*, fraction

Source: IPCC 2006 Vol. 3, Ch. 3, Eq. 3.6

In Tier 2 method, the plant-level production data and default emission factors are disaggregated by technology type.

Tier 2 Method Emission Factor

- There are variations in the N_2O generation factor among plant types, therefore, plant-level factors may applied for nitric acid N_2O emissions estimates.
- If plant-level factors are not available, **it is good practice to use default factors according to type and use as well as an appropriate N_2O generation factor.**
- **When applying Tier 2:**
  - Verify the abatement technology is installed at individual plants and operated throughout the year, and
  - Consider the time the abatement equipment is not operating.

Tier 2 Activity Data & Sources

- Requires plant-level production data disaggregated by technology and abatement system type.
- Gather activity (production) data with the same level of detail as the generation and destruction data.
- Typical plant-level production data is assumed to have an uncertainty of ±2 percent due to the economic value of having accurate information.

Nitric Acid Production
Tier 3 Method

IPCC 2006: Tier 3 Method

- Emissions can be derived using the same equation as for Tier 2, however:
- The Tier 3 emission estimate is based on real measurements data (e.g. CEMS – Continuous Emissions Monitoring System).
  - The Plant-level production data is disaggregated by technology type, and
  - Plant level emission factors obtained from direct measurement of emissions (periodic, or sampling)
- *CEMS: Gives the concentration of N_2O for a specific interval*
  - *high costs are the main disadvantage of CEMS*

Source: IPCC 2006 Vol. 3, Ch. 1, Eq. 2.3

IPCC 2006: Tier 3 Method

It is considered **good practice to:**

- Conduct sampling and analysis whenever the plant makes significant process changes or to ensure operating conditions.
- Plant operator should verify the correct operation of the destruction technologies.
- Emissions should be based on the *exit* stream. Any abatement efficiency should be provided only for information purposes, not used to calculate emissions.

Tier 3 Activity Data & Sources

- Plant-level production data disaggregated by technology and abatement system type are required.
- Gather activity (production) data with the same level of detail as the generation and destruction data.
- When estimates are based on CEM, it is recommended to collect and report production data to ensure that changes in variables that influence emissions can be monitored over time.
- Typical plant-level production data is assumed to have an uncertainty of ±2 percent due to the economic value of having accurate information.

Nitric Acid Production Emissions QA/QC

QA/QC for Nitric Acid Emissions

- **Recommendation 1**: When bottom-up data are applied (using data from individual nitric acid plants), make a comparison with the results of the top-down method (using national production data).
- **Recommendation 2**: Inventory compilers should archive sufficient information to allow making historical comparisons.
- **Recommendation 3:** Compare plant-based factors to the IPCC default factors and explain the differences.
- **Recommendation 4**: When plant-level N_2O measurements are available, check that internationally recognized, standard methods were used. Otherwise, re-evaluate the use of these emissions data and reconsider the uncertainty estimates for the QA/QC results.

Considerations for Reporting

- **It is *good practice* to document & archive all data needed to generate the emissions estimates**
- **Some specific documentation for the report:**
  - Description of the method used;
  - Number of nitric acid plants;
  - Emission factors;
  - Production data;
  - Production capacity;
  - Number of plants using abatement technology;
  - Type of abatement technology, destruction efficiency, and utilization;
  - Any other assumptions.

Thank you!

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