Project number 327341
ACT – Accelerating CCS Technologies

Regulatory framework for sustainable and cost-efficient amine emission control

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Background (1)

- Several studies on amine emission and environmental effect have been conducted.
  - *E.g.,* a large number of studies from Norwegian funded projects on emissions are available online: https://gassnova.no/en/uncategorized-en/studies-focusing-on-amine-components

- Emission of amines and amine degradation compounds is still a challenge:
  - lack of data
  - quantitative documentation
  - predictive models for the emissions
- Limits the pace of regulatory developments
- Limits the drive towards development of process design for efficient amine emission control

Background (2)

- SCOPE will provide:
  - Critical data
  - Methodologies
  - Tools

  essential for plant owners and regulators engaged in managing emissions and permitting processes

SCOPE – Sustainable OPEration of post-combustion Capture plants

Building upon ACT 1: ALIGN-CCUS and ACT2: LAUNCH: Follow the continuous path of the treated gas from source to recipient and ensure a sustainable and environmentally safe operation of the capture plant

Flue gas impurities and pre-treatment, impact of load and fuel variations

Emissions control and mitigation, minimizing aerosol emissons

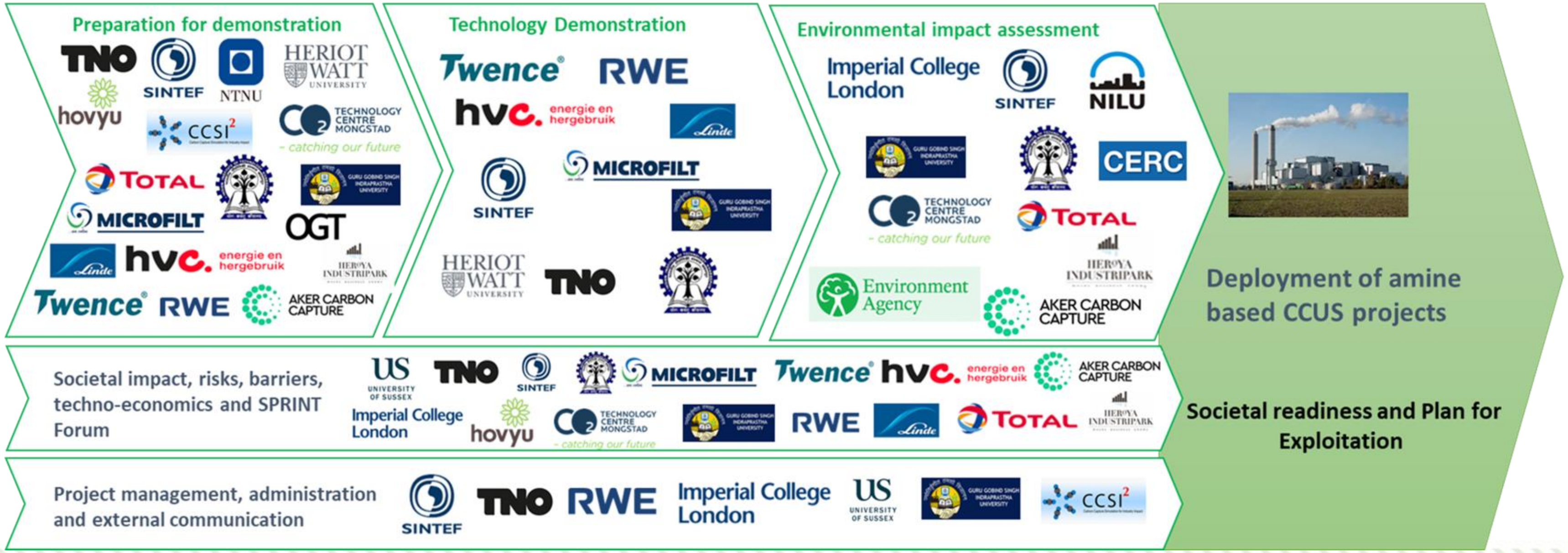
Emissions monitoring and measurements of component and whole effluent

Atmospheric chemistry and dispersion modeling

Biodegradation, Ecotoxicity, Environmental effect concentrations

SCOPE – is accelerating the decarbonisation of industry

- **Objective:** ensure that emission reductions in amine-based CCUS are technically feasible, cost-efficient, and robust enough to mitigate environmental risks and gain public acceptance
- **Collaboration**: Interdisciplinary group of experts from academia, research, technology providers and end-users of the technology



Accelerating CCS Technologies

Timeline:
01.10.2021-30.09.2024

Budget: € 6 M
Funding from ACT
€ 3.7 M

Partners:
24 (19 from Norway, The Netherlands, UK, and Germany, 2 from USA and 3 from India)

7 AFFORDABLE AND CLEAN ENERGY

13 CLIMATE ACTION

How shall we determine what is acceptable capture plant emission?

- Possible to bring capture plant emissions down to meet regulatory requirements, but improved emission-control might be costly
- Approach in SCOPE:
    1. Determine acceptable levels of emitted compounds in the environment (most important: nitrosamines, nitramines, amines, ammonia and aldehydes)
    2. Based on 1., determine acceptable plant emissions
- Requires insight into a number of topics:
    1. Detailed insight into stack emissions
    2. Atmospheric dispersion and atmospheric chemistry
    3. Fate of chemicals in the environment
    4. Determination of acceptable concentrations in the environment

Activities in SCOPE so far

1. Conducting test campaigns with focus on emission and emission control in different pilots and develops models important for design of mitigation options
2. Improving dispersion models to better predict the atmospheric chemistry for the emitted compounds and how these are spread out
3. Reviewing status related to fate of emission and explore how seasonal variations impact the fate of emission
4. Reviewing knowledge related to determining realistic levels not influencing the human health and based on this a human health hazard assessment strategy will be determined for development of risk assessment practices

SCOPE test facilities: small pilots to larger demonstration plants

Tiller CO_2 Lab (SINTEF IND), NO

Biomass or propane incineration: 30-40 kg CO_2/h
Solvent: CESAR1 (blend of AMP and PZ)
Flue gas: CO_2 11 vol.-%, O_2 4 vol.-%
Focus in SCOPE: Emission monitoring

Alkmaar (HVC), NL

Waste-to-energy plant 540 kg CO_2/h
Solvent: MDEA/Piperazine blend
Flue gas: CO_2 11.3 vol.-% (dry), O_2 4.1 vol.-% (dry),
Focus in SCOPE: Emission mitigation, effect of particles in the flue gas on emission

Niederaussem (RWE), DE

Lignite-fired power plant: 300 kg CO_2/h
Solvent: CESAR1 (blend of AMP and PZ)
Flue gas: CO_2 15.2 vol.-%, O_2 5.0 vol.-%
Focus in SCOPE: Long-term test campaigns and various emission mitigation tools

Tuticorin site, India

Alkali Chemicals and Fertilizers: 7.5 t CO_2/h
Solvent: CDRmax (Proprietary solvent of Carbon Clean Ltd)
Flue gas: CO_2 ~ 12 vol.-%, O_2 8 vol.-%
Focus in SCOPE: Emission measurement

Hengelo (Twence), NL

Waste-to-energy plant 500 kg CO_2/h
Solvent: 30% MEA,
Flue gas: CO_2 9.5 vol.-%, O_2 8.3 vol.-%,
Focus in SCOPE: Emission mitigation, effect of particles in the flue gas on emission

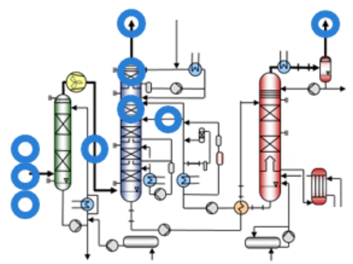
Mongstad (TCM), NO

Flue gas from CHP and cracker: 10 t CO_2/h
Solvent: CESAR1 (blend of AMP and PZ)
Focus in SCOPE: Results from previous campaigns for comparison and emission limits

1. Highlights from piloting (1)

Demonstration of emission management technologies and validated models to predict volatile & aerosol-based emissions

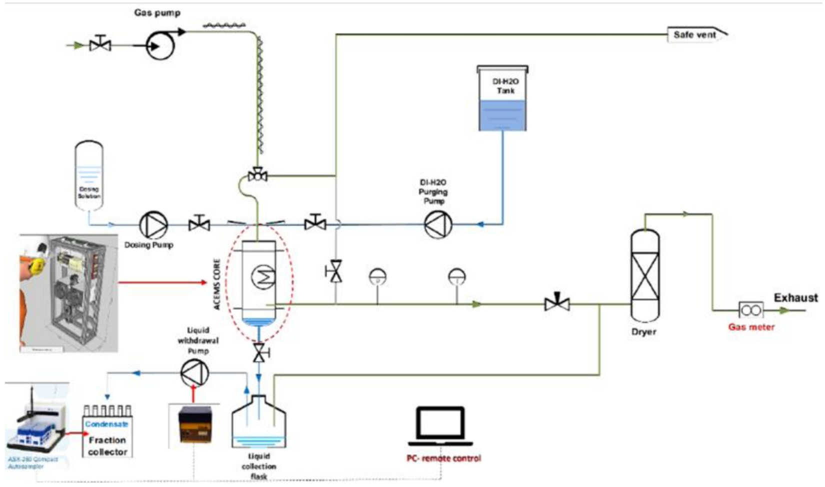
- Reliable process and performance data from until now 7 test campaigns with >20 configurations of emission mitigation technologies
- Investigation of the emission dependency
  - ✓ solvent (MEA, CESAR1, MDEA/PZ)
  - ✓ solvent aging (1,000 – 30,000 h without exchange of solvent inventory) (Session 4B)
  - ✓ flue gas properties (content of CO_2, O_2, trace components, particle number concentration and particle size distribution)
  - ✓ capture rate (90%-98%)
  - ✓ plant operation (stationary and dynamic behaviour)



- Water wash
- Acid wash
- Double water wash
- Flue gas pre-treatment
- Wet Electrostatic Precipitator (WESP)
- Dry bed (OASE aerozone)
- Brownian Demister
- Lean loading tuning
- CO_2 quality monitoring

1. Highlights from piloting (2)

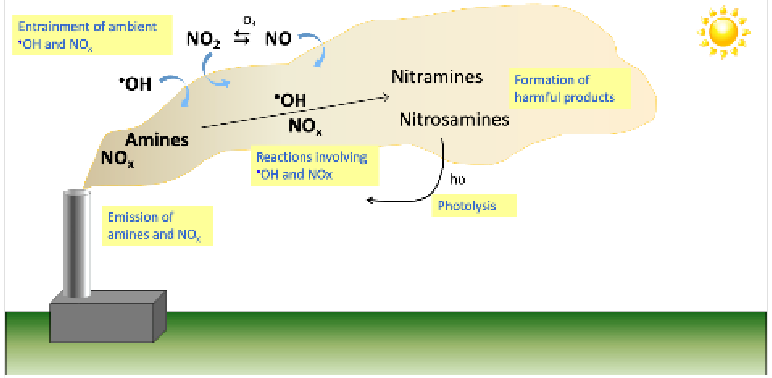
- Emission modelling ongoing with validation from test campaigns at different locations (Session 8A)
- Case studies being developed in an advanced techno-economical framework for cost estimation of emission mitigation options
- ACEMS online monitoring tool upgraded and ready for testing (Session 4B)



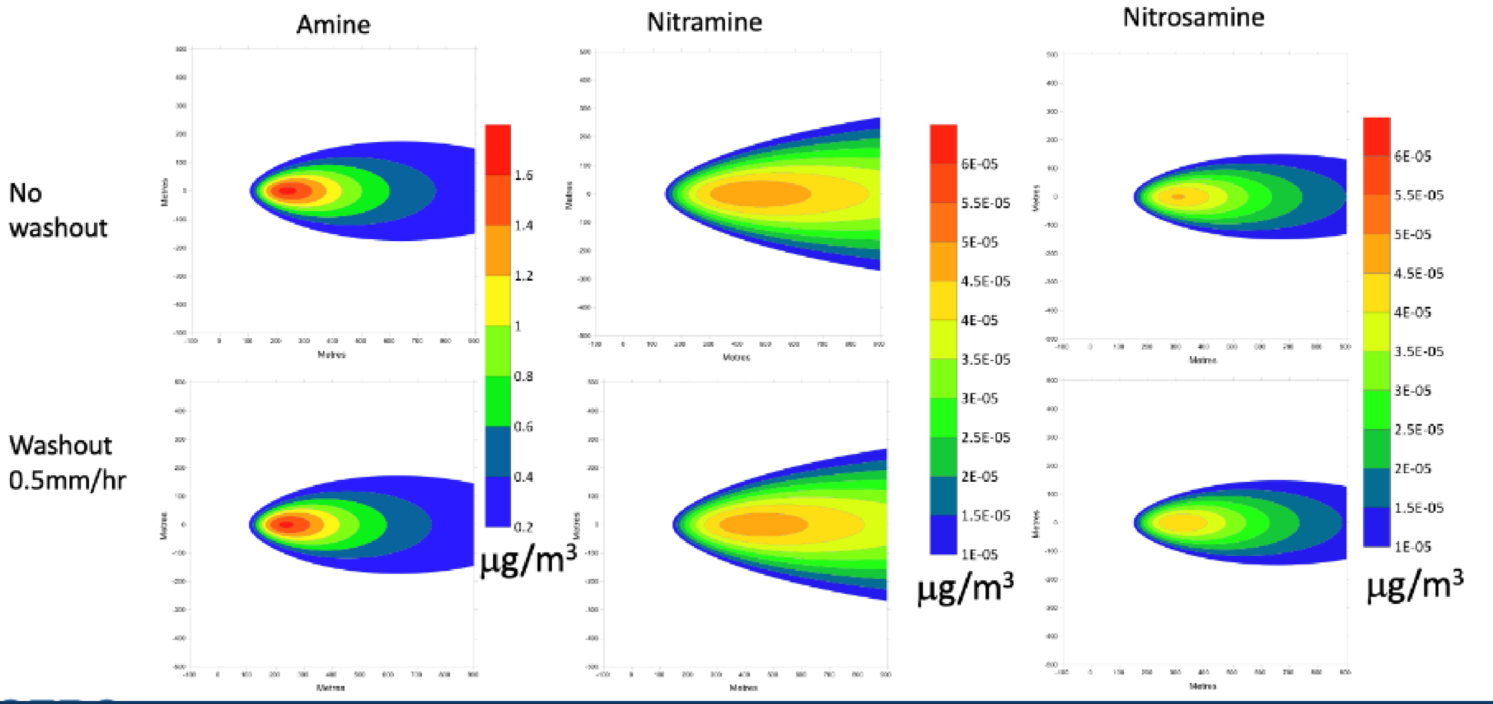
ACEMS setup

2. Highlights from dispersion and atmospheric chemistry modelling (1)

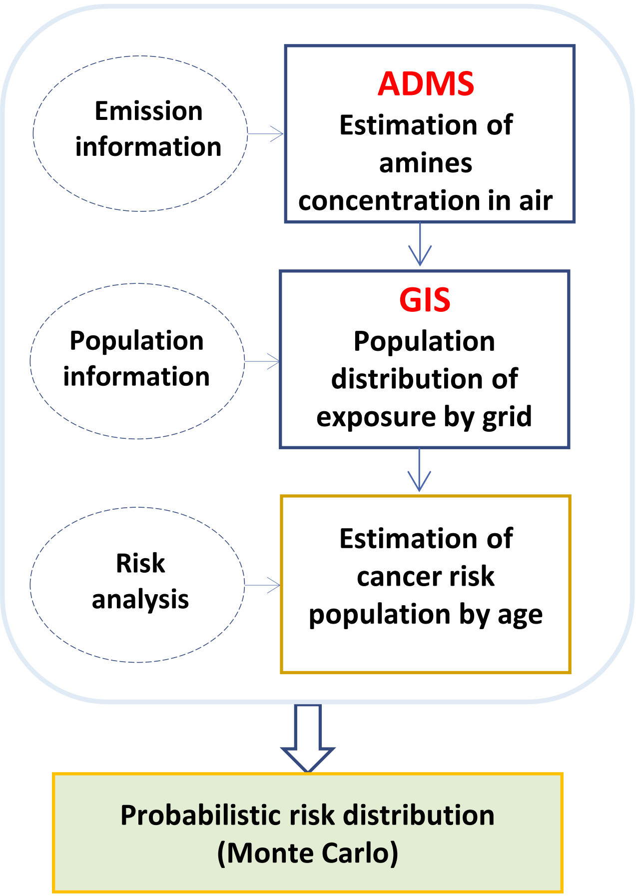
- ADMS code modifed:
  - Improve versatility in modelling
  - Reduce the need for post-processing of separate runs
  - allow interaction between species
  - consider amine uptake into liquid water which can reduce peak nitramine and nitrosamine concentrations.

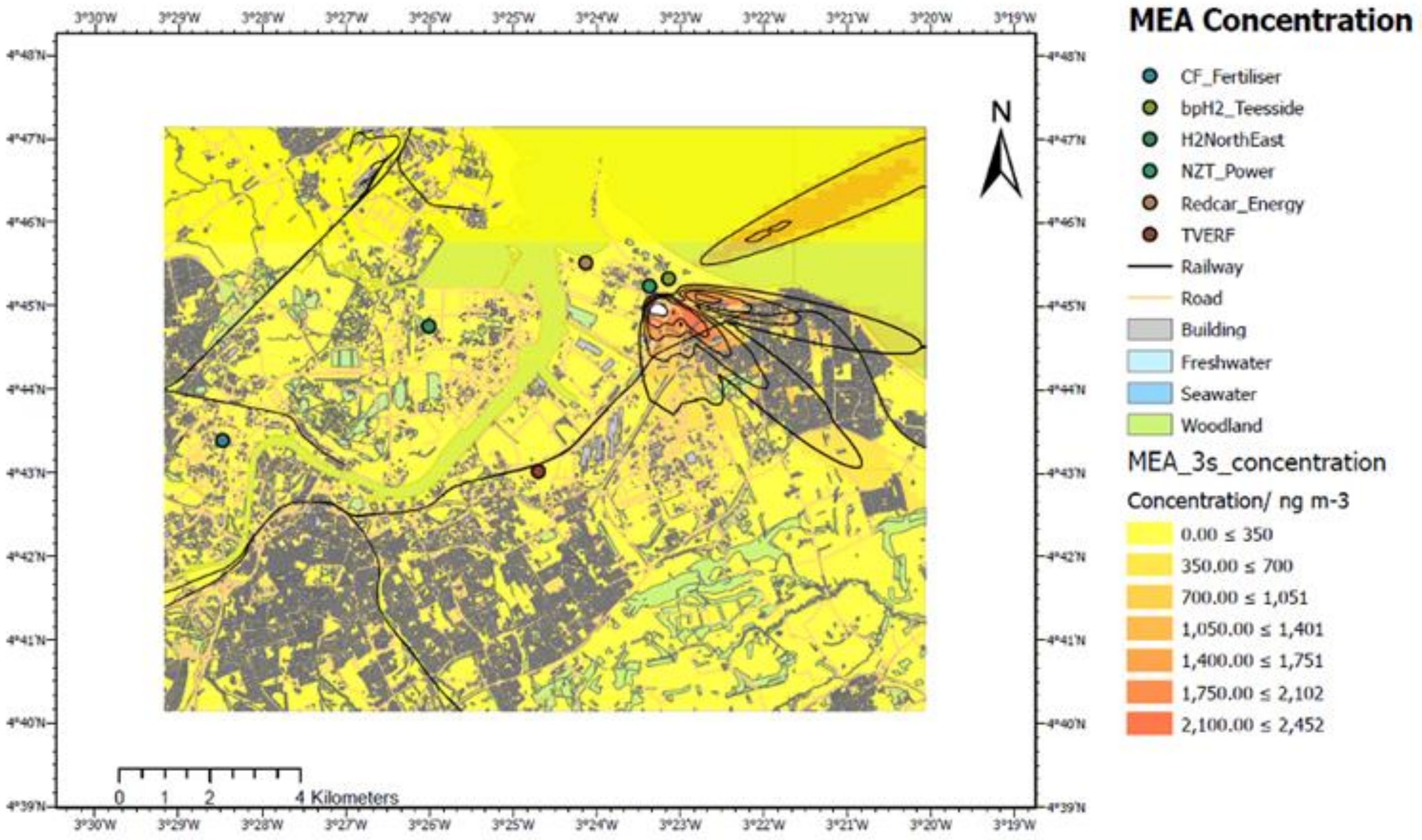


Example output of ground level concentrations for a test case



2. Highlights from dispersion modelling and atmospheric chemistry case studies (2)





Atmospheric ground-level concentrations varying as a function of distance from emitting PCC facilities UK case study (single facility and multiple facility studies)

3. Highlights from environmental effect and risk assessment

- Available and reliable data on toxicity effects for several amines and degradation products on freshwater fish, invertebrates, algae and bacteria collected and assessed.
  - nitrosamines are relatively more acutely toxic to phytoplankton than to invertebrates and fish. Ecotoxicities in the order algae > herbivores (Daphnia) > fish.
- More information:

  Public report: "D3.1 PNECs and degradation data for amine and degradation products" available on the SCOPE web-site:

  https://www.scope-act.org/project-deliverables
- Lack of comprehensive and systematic studies on impacts of the amines and degradation products on various types of living organisms and ecosystems

Chronic toxicity effects of some amines on freshwater fish.

Compound	Fish	Toxicological Endpoint	mg l^{-1} (mg kg^{-1})	Reference
Amines				
MDEA	Carp (Cyprinidae)	Decrease in egg hatching - LOEC	0.5	Bieniarz et al., 1996
PIPA	Aholehole (*Kuhlia sandvicensis*)	Behavioural changes (schooling) - NOEC	20	Hiatt et al., 1953
Nitrosamine				
NDMA	Rainbow trout (*Oncorhynchus mykiss*)	52-week exposure – presence of hepatocellular carcinomas - LOEC	*200	Grieco et al., 1978
Nitramines				
CL-20	Fathead minnow (*Pimephales promelas*)	Growth IC50	0.2-2.0	Hayley et al., 2003; 2007
RDX	Fathead minnow (*Pimephales promelas*)	Growth effects - early development (LOEC)	5.8	Bentley et al., 1977
		Survival chronic exposure (LOEC)	4.9-6.3	Bentley et al., 1977
	Zebra fish (*Danio rerio*)	Effects on body weight after 4 weeks (LOEC)	1	Mukhi & Patiño, 2008

4. Highlights from Human Health Hazard Assessment (1)

- Literature and CO_2 capture related documentation on human health and toxicology for amines and degradation products reviewed and compiled
- Focus on airborne exposure and exposure through drinking water, quantifying potential health risks following acute and chronic exposure
- Majority of the nitrosamines (NSA) are classified possibly carcinogenic or probably carcinogenic to humans.
  - Nitramines (NA) are considered as highly toxic, but less potent as mutagens and carcinogens than their corresponding nitrosamines.
  - Both were found to have severe eye and skin irritation and corrosion potential, depending upon the exposure concentration.
  - Seasonal variation in temperature and sunlight was found to influence both the NSA and NA concentrations.
  - NSA shown to be photolytically degraded
    - During winter the effect of photodegradation is reduced due to weaker sunlight radiation (shorter days and lower temperatures)
    - This variation should be accounted for in any monitoring program

4. Highlights from Human Health Hazard Assessment (2)

- Special attention needs to be paid to sensitive populations (*e.g.,* infants and children);
  - Important to apply age-dependent adjustment factors to estimate lifetime cancer risk
- TD50* has been suggested by the CPDB** to estimate the theoretical excess cancer risk (1:100,000 or 1:1,000,000).
  - ➢ TD50 evaluations are based on animal experiments and thus assessment factors must account for the differences between animals and humans

**TD50: the median Toxic Dose of a drug or toxin is the dose at which toxicity occurs in 50% of cases*

***CPDB: Carcinogenic Potency Database*

TD50 values from the Carcinogenic Potency Database for available Nitrosamines and Nitramines.

Agent	TD50 (mg kg^{-1} day^{-1}) rat	TD50 (mg kg^{-1} day^{-1}) sensitive species (tissue)	TD50 (mg kg^{-1} day^{-1}) other species
NMPEA	0.00998	0.00788, rat (gastrointestinal)	
NDEA	0.026	0.05, rat (liver) 0.026, rat (oesophagus)	0.00725, cynomolgus; 0.012 bush babies
NMEA	0.053		
NDMA	0.096	0.04 rat (liver) 0.06, rat (liver)	0.189, mouse
NDELA	3.17	0.19 rat (liver)	
NMOR	0.109	0.127 rat (liver)	3.57 hamster
NMPA	0.142		0.034 rat
NDPA	0.186		0.012 rhesus (liver)
NDBA	0.691		1.09 mouse (liver)
NPYR	0.799		1.7 rat (liver) 0.697 mouse
NPIP	1.43	1.31 rat (oesophagus)	1.3 mouse
NPZ	8.78		
NNK	0.0999	0.182 rat (lung)	
NNN	0.096		10.8 (hamster)
NNM	0.109		
DNP	3.6		
MNNG	0.803	0.284 rat (pylorus)	2.03 mouse
NMBA	0.982		
NTMA	17.4		
NDTMA	0.54		

4. Highlights from Human Health Hazard Assessment (3)

- More information:

  Public report: “D3.3 Human Health hazard assessment strategy for amine emissions around PCC facilities” available on the SCOPE web-site:

  https://www.scope-act.org/project-deliverables

- Conclusion so far: continuing efforts in toxicity assessment studies are needed to derive realistic levels that are protective of the human health.

Acknowledgements

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