Environmental impacts of amines and their degradation products: Current status and knowledge gaps

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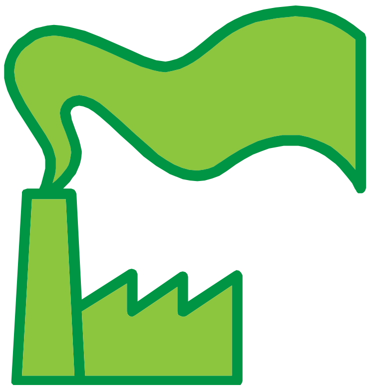
Three main focus areas for emissions



Emission profile and concentration

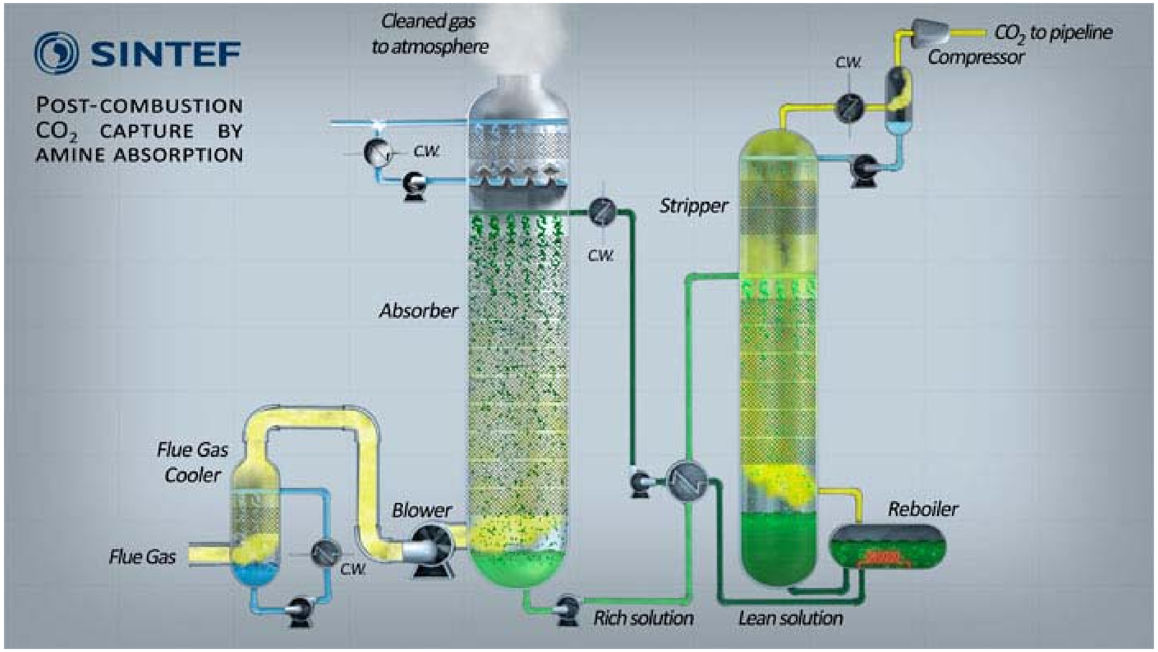
Atmospheric transport, processes and deposition

Terrestrial and aquatic transport, processes and exposure

These three processes ultimately determine who (people) or what (environment) is exposed to which chemicals and at which concentration

Capture plant emissions

- Most focus has been on the use of MEA
- An increasing number of studies are considering other solvent systems
- Computational chemistry and modelling used to predict MEA degradation products (and other amine solvents)



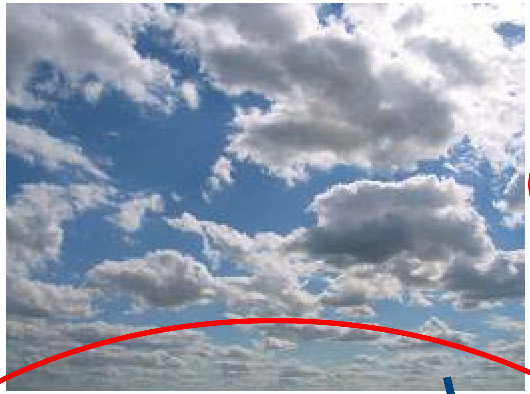
- Wide range of degradation products - ammonia, nitrosamines, nitramines, alkylamines, aldehydes and ketones[1]
- Compounds of most concern (e.g. nitrosamines) are formed in very small amounts or thought to form in very small amounts (e.g. nitramines)
- **There are currently no emission standards for CO_2 capture plants**

[1]Brakstad, O. G.; Silva, E. F. d.; Syversen, T. "Support on input to environmental discharges - Evaluation of degradation components," SINTEF, 2010.

Atmospheric transport and processes

Emission

Local or long distance transport[2]



Atmospheric processes[3]

- Photo-induced degradation
- Chemical degradation

Partitioning

Rain

Aerosols/particles

Wet deposition

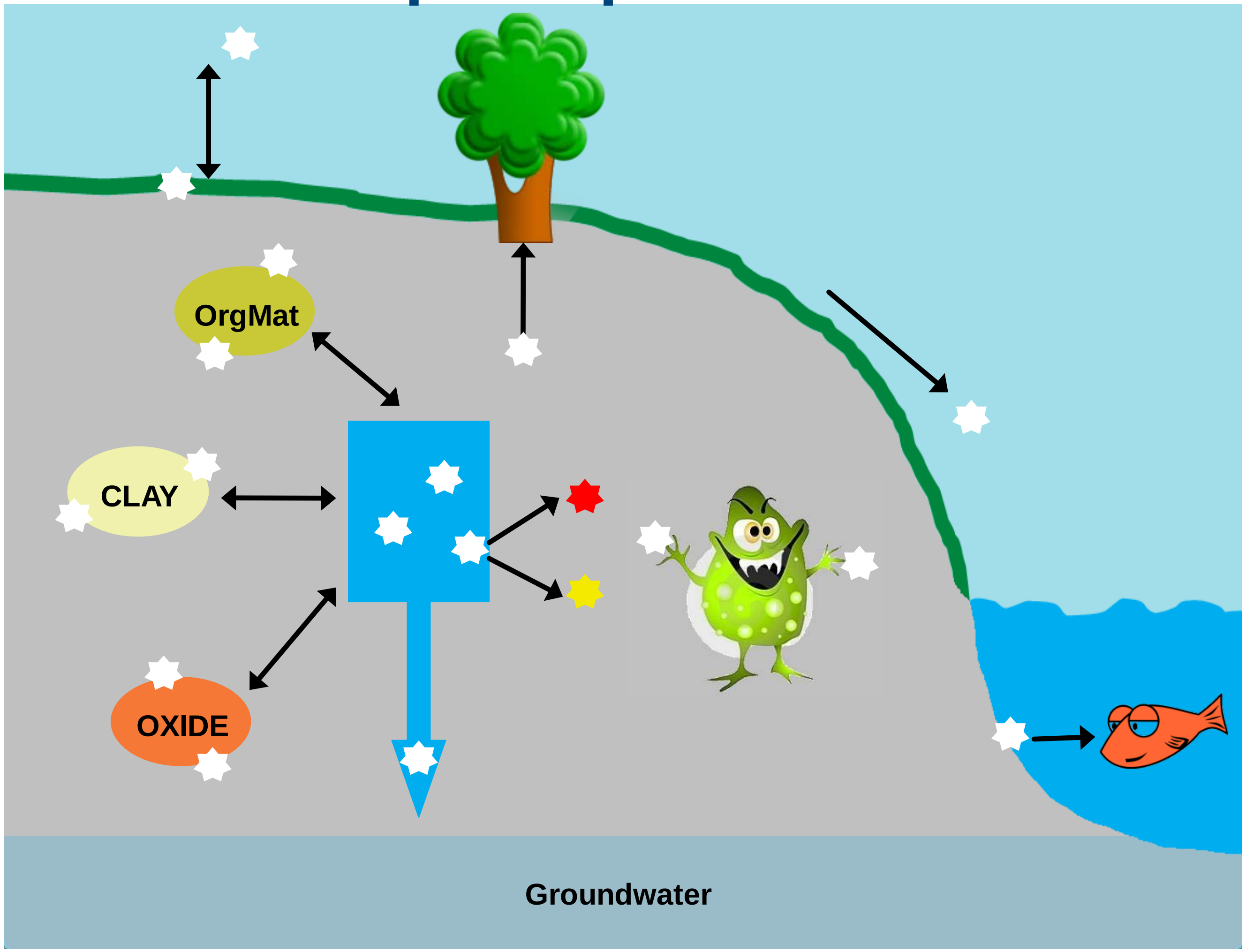
Dry deposition

[2]Berglen, T. F.; Tønnesen, D.; Dye, C.; Karl, M.; Knudsen, S.; Tarrasón, L. "CO2 Technology Centre Mongstad – updated air dispersion calculations. Update of OR 12/2008," Norwegian Institute for Air Research, 2010.

[3]Bråten, H. B.; Bunkan, A. J.; Bache-Andreassen, L.; Solimannejad, M.; Nielsen, C. J. "Final report on a theoretical study on the atmospheric degradation of selected amines," NILU, 2009

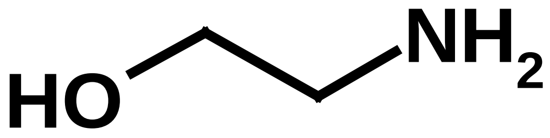
Terrestrial and aquatic processes

- Volatilisation
- Run-off
- Uptake
- Dissolution and transport
- Chemical reaction/hydrolysis
- Adsorption
- Biodegradation



Persistence and Exposure = *f* (volatilisation, run-off, leaching, chemical reaction, biodegradation, adsorption and uptake)

MEA as an example



Environment – MEA biodegradation & ecotox data

GROUP	Degradation product	Biodegradability (%)	[A]Ecotoxicity (EC_{50} or LC_{50}; mg/L)
Nitrosamines	N-nitroso-dimethylamine	Judged biodegrable	4 (phytoplankton)
	4-nitroso-morpholine	No data	75 (fish)
	N-nitroso-diethanolamine	No data	No data
	2-(methyl-nitrosoamino)-ethanol	No data	No data
Nitramines	Dimethylnitramine	No data	No data
Amines, amides, aldehydes, ketones	Methylamine	55-100	10 (fish)
	Dimethylamine	30-100	9 (phytoplankton)
	Ethylamine	98-100	10
	Diethanolamine (DEA)	93-97	2 (phytoplankton)
	N-(2-hydroxyethyl)-formamide (HEF)	No data	No data
	N-(2-hydroxy-ethyl)imidazole (HEI)	No data	No data
	2-methylaminoethanol	93	33 (Daphnia)
	1,2-Ethanediol or ethyleneglycol (EG)	56	18 (Daphnia)
Other compounds	Ammonia	Nitrification	0.024 (fish)
	Formaldehyde	90	0.30 (phytoplankton
	Acetaldehyde	80	31 (fish)
	Acetone	84-90	2840 (phytoplankton)
	Formamide	30-100	4600 (fish)

A) Highest ecotoxicity selected from 3 trophic levels

The quantity and quality of equivalent data available for other solvent types is usually less than for MEA

Terrestrial and aquatic processes

- **Most terrestrial and aquatic environment studies have focused on parent amines only, however:**
  - A recent study assessed the biodegradability and ecotoxicity of MEA degradation products using modelling and reported data[1]
  - All compounds with available data appeared to be biodegradable (30-100%), whilst ecotoxicity varied significantly
  - Experimental data is missing for many compounds and compound groups (e.g. nitrosamines and nitramines)
  - Some degradation products may persist in the environment due to low biodegradability, posing a possible risk if accumulated in aquatic systems (e.g. groundwater).

[1]Brakstad, O. G.; Silva, E. F. d.; Syversen, T. "Support on input to environmental discharges - Evaluation of degradation components," SINTEF, 2010.

Human health – MEA degradation products data

GROUP	Degradation product	Acute LD_{50} (mg/kg bw)	Long-term	Occupational exposure limits (OEL – mg/m³)
Nitrosamines	N-nitroso-dimethylamine	< 0.5 (inhalation)	CMR	0.001
	4-nitroso-morpholine	< 0.5 (inhalation)	CM(R)	0.001
	N-nitroso-diethanolamine	>2000 (oral)	CM(R)	0.001
	2-(methyl-nitrosoamino)- Ethanol	No data	CM(R)	---
Nitramines	Dimethylnitramine	300-2000 (oral)	(C)	---
Amines, amides, aldehydes, ketones	Methylamine	0.5-20 (inhalation)	M	0.13
	Dimethylamine	2-10 (inhalation)	S	3.5
	Ethylamine	50-300 (oral)	?	18
	Diethanolamine (DEA)	No data	?	---
	N-(2-hydroxyethyl)- Formamide (HEF)	No data	?	---
	N-(2-hydroxy-ethyl)imidazole (HEI)	300-2000 (oral)	?	---
	2-methylaminoethanol	300-2000 (oral)	?	9.4
	1,2-Ethanediol or ethyleneglycol (EG)	300-2000 (oral)	R	---
Other compounds	Ammonia	0.5-2 (inhalation)	(M)	18
	Formaldehyde	< 0.5 (inhalation)	CM(R)S	0.6
	Acetaldehyde	300-2000 (oral)	CMRS	45
	Acetone	Negligible	---	295
	Formamide	10-20	R	18

Acute toxicity
- LD_{50} is the concentration of a chemical which causes 50% mortality in a population

Long-term toxicity
- C – carcinogenicity
- M – mutagenicity
- R – reproduction toxicity
- S – sensitisation

Occupational exposure limits (OEL)
- OEL is exposure limits for healthy people
- OEL may vary from country to country
- OEL used here are the strictest available limits

Human health

- **Human health hazards are associated with several of the suggested degradation products for MEA, however:**
  - Data for many products are not available
  - Potential long-term effects associated with mutagenicity, genotoxicity/carcinogenicity and reproduction effects are documented for specific nitrosamines, volatile aldehydes and alkylamines
  - Indicates that nitrosamines may contribute to the health risk of the population, although their emission concentration is small[1]
  - The real risks cannot be estimated until the fate of these compounds has been determined
- **The quantity and quality of equivalent data available for other solvent types is usually less than for MEA**

How do we use this data???

RISK ANALYSIS!

- RA combines the toxicity and ecotoxicity information with the potential fate of the components in the environment
- RA identifies the concentrations people and the environment are exposed to
- Fate data (and therefore environmental concentrations) are difficult to predict............but we can use available models (e.g. QSAR and computational chemistry)
- Need to understand the limitations with using such modelling methods to generate predicted values

Case literature study

Nitrosamines – fate in the aquatic environment

EPISUITE – Soil adsorption and bioaccumulation (QSAR)

Nitrosamine	A)Soil adsorption (Koc)	B)Bioaccumulation (log Pow)
N-nitrosodiethanolamine	0.2242	-1.28
Nitrosopiperidine	12.04	0.7223
Nitrosodiethylamine	14.03	0.48
Nitrosodimethylamine	3.683	-0.57
Nitroso-N-methylethylamine	8.01	0.04
Nitrosomorpholine	3.528	-0.44
Nitroso-N-propylamine	43.03	1.36
Nitrosopyrrolidine	5.976	-0.19
Nitrosopiperazine	2.332	-1.49
Dinitrosopiperazine	2.332	-0.85

A) Compounds with Koc values of less than 500 indicate little or no adsorption to soils and are more mobile

B) Compounds with log Pow ≥ 3 are regarded as bioaccumulating

- Commercially available suite of nitrosamines (not necessarily amine degradation products)
- Nitrosamines have low soil/sediment adsorption coefficients and a low bioaccumulation potential
- Nitrosamines are therefore expected to follow the water flow through soil and surface runoff

EPISUITE – Biodegradation based on QSAR approaches

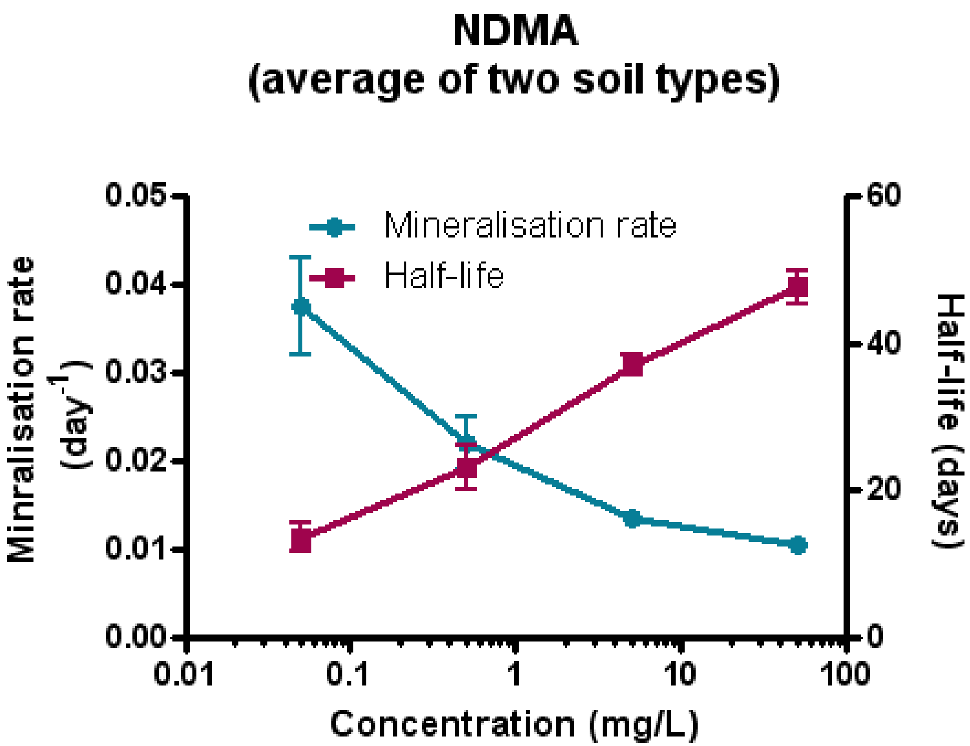
Nitrosamine	Biodegradation probability			
	[A] Primary	[A] Ultimate	[B] Anaerobic	[C] Ready biodegradable
N-nitrosodiethanolamine	3.93 (days)	2.84 (weeks)	1.21 (fast)	Yes
Nitrosopiperidine	3.70 (days-weeks)	2.56 (weeks-months)	0.24 (not fast)	No
Nitrosodiethylamine	3.72 (days-weeks)	2.59 (weeks-months)	0.73 (fast)	No
Nitrosodimethylamine	3.76 (days-weeks)	2.66 (weeks-months)	0.68 (fast)	No
Nitroso-N-methylethylamine	3.74 (days-weeks)	2.62 (weeks-months)	0.70 (fast)	No
Nitrosomorpholine	3.69 (days-weeks)	2.55 (weeks-months)	0.10 (not fast)	No
Nitroso-N-propylamine	3.68 (days-weeks)	2.53 (weeks-months)	0.78 (fast)	No
Nitrosopyrrolidine	3.72 (days-weeks)	2.59 (weeks-months)	0.36 (not fast)	No
Nitrosopiperazin	3.74 (days-weeks)	2.58 (weeks-months)	0.53 (fast)	No
Dinitrosopiperazine	3.68 (days-weeks)	2.11 (weeks-months)	0.36 (not fast)	No

[A] *5=hours; 4=days; 3=weeks; 2=months*

[B] *>0.5 = biodegradaes fast*

[C] *If the ultimate survey result is 'weeks' or faster (i.e. 'days' or 'days-weeks') the prediction is YES (ready biodegradable). If this condition is not satisfied, the prediction is NO (not readily biodegradable).*

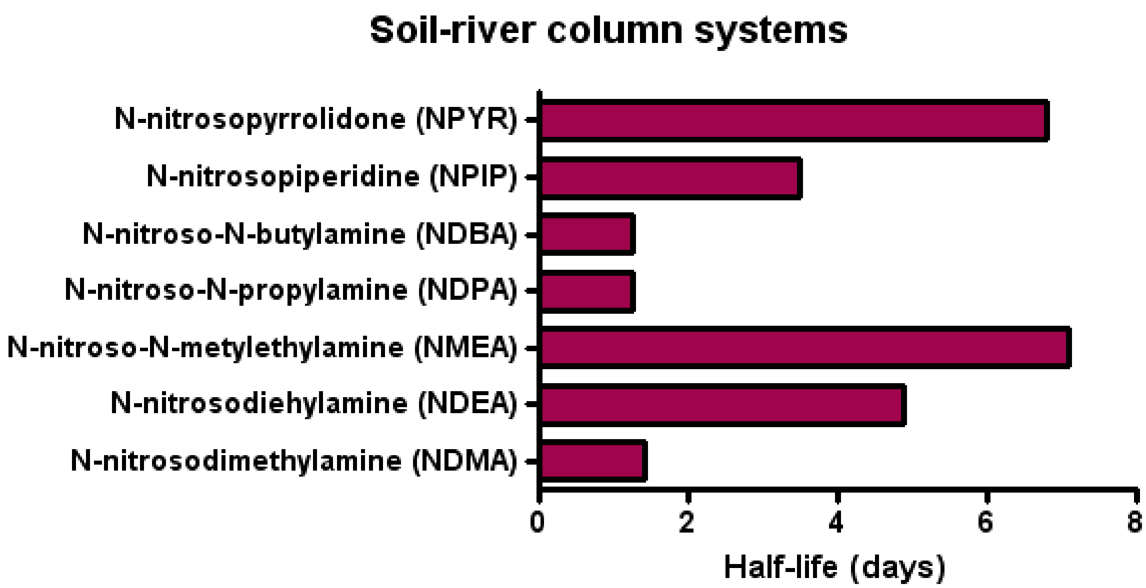
Concentration-dependent biodegradation of nitrosamines



From Gunnison et al., 2000

- Sub mg/L (ppm) concentrations of NDMA had half-lives of approximately 15 days
- These concentrations are still significantly above those expected in the environment, suggesting even shorter half-lives

Concentration-dependent biodegradation of nitrosamines



From Drewes et al., 2006

- Similar half-lives were obsevred for a range of nitrosamines studied at the same concentration

Non-biological degradation of nitrosamines in aquatic systems

- **Photodegradation is considered to be the most rapid (minutes) degradation process for nitrosamines present in the atmosphere**

- **Photodegradation half-lives of 7 nitrosamines in water under California midsummer conditions varied between 11 and 16 minutes**
  - 99 % removal of nitrosamines after one hour sunlight exposure

- **Photodegradation in aquatic systems is dependent on oxygen and pH levels**
  - Photodegradation rates higher in aerobic than in anaerobic environment and vary with pH

- **Hydrolysis: Nitrosamines are resistant to hydrolysis under acid and basic conditions**

Knowledge gaps

- **The composition and concentration of amines and degradation products present in the emissions from a PCCC plant:**
  - Chemical composition and concentration of MEA emissions not fully characterised in CO_2 capture plants
  - Individual assessment is required for other solvents and solvent mixtures

- **The atmospheric fate and transport of amines and their degradation products:**
  - Atmospheric degradation processes still relatively poorly understood
  - Atmospheric transport models allow dispersion of chemicals to be predicted but must be applied to specific cases (i.e. not general)
  - Deposition of amines and degradation products to soil and aquatic environments is difficult to predict

Knowledge gaps

- **The environmental fate of amines and their degradation products in terrestrial and aquatic systems:**
  - Environmental fate and effects studies require reliable emissions data and atmospheric dispersion and process data
  - Focus on biodegradation to date, but limited experimental data on hydrolysis and adsorption (+ other processes)
  - Suitable extraction and analytical chemical methods lacking for complex environmental samples, such as water and soil
  - QSAR approaches may not be very suitable for certain compound groups, and therefore must be improved with experimental data

- **The health effects of classes of compounds are relatively well understood from previous studies:**
  - Specific studies on long-term effects such as carcinogenicity and impaired reproduction have not been completed for nitrosamines, nitramines and other compounds

The way forward

- **Accurate emissions data (composition and concentration) from CO_2 capture plants is needed for a range of solvent types**

- **Assessment of exposure (no toxicity without exposure)**
  - Persistence in the environment (degradation processes)
  - Transport in the environment (identification of sinks)
  - Bioaccumulation (uptake and storage by organisms including humans)

- **Use available toxicity data to determine exposure limits for humans (where this data is not already available)**

- **Determine what the acceptable emissions levels are using risk assessment**

Evaluation should be undertaken at each step to identify if there is a need to continue with the processes

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