Air Quality Modelling & Assessment Unit (AQMAU)

Environment Agency

Proposed assessment method to include amines and degradation products in nutrient nitrogen deposition estimations at ecological sites

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Summary

Amines used in amine-based solvent scrubber techniques in carbon capture can be a large group of chemical substances. When these substances are released to ambient air, they may react with atmospheric radicals to form nitrosamines and nitramines. Amines, nitrosamines, and nitramines contain nitrogen in their chemical structure, thus have the potential to contribute to nutrification of habitats.

The Air Quality Modelling and Assessment Unit (AQMAU) proposes an interim framework to include amines and amine degradation products in nutrient nitrogen deposition estimations from air dispersion modelling. Our recommended methodology is based on the available evidence found by us and provided to us at the time of writing this document.

At the time of writing this document, the only commercially available modelling software to evaluate the potential impacts from amines atmospheric reaction products is the 'amines chemistry module' within ADMS. The module is based on established science considering published research on amines reaction mechanisms. Although the validation of the module is not possible at the moment, the ADMS air dispersion modelling algorithms are continually validated against real world situations, field campaigns and wind tunnel experiments. We do not endorse a specific modelling software and we acknowledge the level of uncertainty.

The purpose of this document is to set guidelines for applicants to make judgements on the assessment of nutrient nitrogen deposition impacts at ecological sites from these substances. The document includes a practical example of the framework, which consists of:

1. Identification of pollutants with nutrifying effect
2. Approaching potential screening ('business as usual' assessment)
3. Detailed assessment (use of available transformation and deposition models)

1 Introduction

1.1 Amines used in amine-based solvent scrubber techniques in carbon capture can be a large group of chemical substances. When these substances are released to ambient air, they may react with atmospheric radicals to form nitrosamines and nitramines.

1.2 In addition, amine degradation products such as nitrosamines can be directly released from the stack (i.e., directly released nitrosamines). Nitrosamines (either directly released or formed in ambient air) may or may not be stable in the atmosphere. There can be two potential sources of nitrosamines, such as N-nitrosodimethylamine (NDMA), oftentimes referred as 'direct' and 'indirect':

- 'indirect': NDMA formed in ambient air through chemical reaction of dimethylamine (DMA) with hydroxyl radical (OH).
- 'direct': NDMA directly emitted from the stack.

1.3 Amines, nitrosamines, and nitramines contain nitrogen in their chemical structure, thus have the potential to contribute to nutrification of habitats in addition to nitrogen dioxide (NO_2) and ammonia (NH_3).

1.4 The amines chemistry module incorporated in the Cambridge Environmental Research Consultants (CERC) Air Dispersion Modelling Software (ADMS) estimates the unreacted amines and transformed products concentrations at downwind locations of emitting sources, although validation is not possible at the moment.

- When the ADMS amines chemistry option is not used, concentrations are estimated using common transport and dispersion algorithms (i.e., 'business as usual' air dispersion modelling).
- When the ADMS amines chemistry option is used, concentrations are estimated incorporating atmospheric reaction mechanisms into the common dispersion and transport algorithms (i.e., 'amines modelling'). In ADMS, deposition cannot be modelled when the amines chemistry option is selected.

1.5 The order of magnitude of concentrations at ecological sites is case specific, mainly dependent on:

- The amine emission levels.
- The substance specific atmospheric transformation reactions (inputs to the ADMS amines chemistry module).
- The overall site-specific dispersion and transport case and location of receptors.

1.6 ADMS is the only commercially available modelling software to evaluate the potential impacts from amines atmospheric reaction products. The module is based on established science considering published research on amines reaction mechanisms. Although the validation of the module is not possible at the moment, the ADMS air dispersion modelling algorithms are continually validated against real world situations, field campaigns and wind tunnel experiments. We do not endorse a specific modelling software and we acknowledge the level of uncertainty.

1.7 The purpose of this document is to propose a method and set guidelines for applicants to make judgements to include amines and amine degradation products in nutrient nitrogen deposition estimations at ecological sites. This document includes an example of the framework. For context, it is recommended that this document is read alongside our Environment Agency modelling guidance[1] and the AQMAU recommendations document[2].

[1] Guidance: Environmental permitting: Air dispersion modelling reports. Available at https://www.gov.uk/guidance/environmental-permitting-air-dispersion-modelling-reports [Accessed in October 2023]
[2] AQMAU recommendations for the assessment and regulation of impacts to air quality from amine-based post-combustion carbon capture plants. AQMAU-C2025-RP01. November 2021. Available at AQMAU-C2025-RP01.pdf (ukccsrc.ac.uk).

2 AQMAU recommended process to estimate nutrient nitrogen deposition

A summary of the framework recommended by AQMAU is:

- Step 1: Identification of pollutants with nutrifying effect
- Step 2: Approaching potential screening
- Step 3: Detailed assessment

Step 1: Identification of pollutants with nutrifying effect

2.1 Identify the pollutants with nitrogen in their chemical structure, the amine(s') chemical reaction(s) and their molecular weight(s). In this case, the substances are:

- Directly emitted pollutants (direct) with nitrogen in their chemical structure: amines, nitrosamines, in addition to NO_2 and NH_3.
- Pollutants formed through atmospheric reactions (indirect) with nitrogen in their chemical structure: nitrosamines, nitramines.

2.2 Estimate the factors to convert dry deposition flux (µg/m^2/s) to nutrient nitrogen deposition (kg N/ha-y) using the nitrogen (N) available for deposition within the pollutant molecule (i.e., nitrogen atomic weight, 14, divided by the species molecular weight).

2.3 Assign a deposition velocity to each substance based on similarities in physicochemical behaviour to substances with known deposition velocities[3]. These judgements should be made per substance(s), also considering those formed through atmospheric chemical reaction(s). You may need to consult published research and chemical databases to justify your decision. If in doubt, use a conservative deposition velocity as a precautionary approach. If an alternative to a known/published deposition velocity is proposed, you will need to justify your choice.

Step 2: Approaching potential screening

2.4 Calculate the nutrient nitrogen Process Contributions (PCs) per pollutant with the assumption that emitted amines do not react and the directly emitted nitrosamines are stable (i.e., pollutants only transport and disperse 'business as usual' air dispersion modelling).

2.5 Evaluate how much each pollutant contributes to the total nutrient nitrogen deposition at the ecological receptor. Use these results, contour plots and air dispersion modelling knowledge to estimate the level of uncertainty in the total nutrient nitrogen PCs and judge whether you may need to carry out a detailed assessment using the available transformation and deposition models (i.e., Step 3).

Step 3: Detailed assessment

2.6 As deposition cannot be modelled in conjunction with amine chemistry in ADMS, the CERC ADMS 6 amines chemistry supplement[4] proposes the following method to estimate the deposition fluxes (µg/m^2/s), D:

$$D = C1 \cdot \left(\frac{D2}{C3}\right)$$

[3] AQTAG06 Technical guidance on detailed modelling approach for an appropriate assessment for emissions to air, March 2014 (Habitats Directive)
[4] ADMS 6 Amine chemistry. User Guide Supplement. Version 6.0. Cambridge Environmental Research Consultants Ltd. (CERC). March 2023

Where:

- C1 is the output concentration from run with the amines chemistry ON (Run 1)
- D2 is the output deposition flux from run with amines chemistry OFF and deposition ON (Run 2)
- C3 is the output concentration from run with amines chemistry OFF and deposition OFF (Run 3)

2.7 Following the AMDS amines chemistry supplement, add the deposition velocity in the pollutants palette (refer to point 2.3).

2.8 Carry out the suggested model runs and calculations to judge the significance of your results:

- Estimate the deposition fluxes, D, according to the equation presented above (refer to point 2.6). Then convert to kg N/ha-y to calculate the nutrient nitrogen deposition PCs.
- Evaluate the significance of your nutrient nitrogen deposition PCs against the critical loads at the ecological site (refer to point 2.5).

We note that there is also an aqueous amine scheme within ADMS 6 which includes an option to incorporate the absorption of amines (and their products) into any liquid water in the plume. Further information can be found in the CERC ADMS 6 Amine chemistry supplement.

3 Example of nutrient nitrogen calculations

3.1 An example of the recommended framework and calculation steps is presented in Table 2.

3.2 The emitted and formed substances to consider in the model and nutrient nitrogen deposition calculations are presented in Table 1. The emissions are amines MEA and DMA and nitrosamine NDMA, in addition to NO_X and NH_3. NDMA is directly emitted, and it is also formed from the reaction of DMA in ambient air.

3.3 In Step 3 of this example, the deposition flux (D) has been estimated for DMA and MEA only. Noting the comparatively small contribution of nitrosamines and nitramines in this example (in the order of ng/m^3), a conservative screening approach for calculating the nutrient nitrogen deposition has been used for these substances.

Table 1 – Emitted and formed substances in the example

Directly emitted ('direct')	Formed ('indirect')	Conceptual reaction
MEA	MEA-NO_2	MEA → MEA-NO_2
DMA	NDMA DMA-NO_2	DMA → NDMA DMA → DMA-NO_2
NDMA NO_X NH_3	- - -	- - -

Table 2 – Example of the calculation steps and recommended framework to include amines and degradation products in nutrient nitrogen deposition estimations at ecological sites

STEPS	PARAMETERS	UNITS	NO_2	NH_3	NDMA (emitted)	MEA	DMA	NDMA (formed)	MEA-NO_2 (formed)	DMA-NO_2 (formed)	
					nitrosamine	amine	amine	nitrosamine	nitramine	nitramine	
Identification	Molecular weight	g/mol	46	17	74	61	45	74	106	90	
	N in the molecule which is available for deposition	-	0.30	0.82	0.19	0.23	0.31	0.19	0.13	0.16	
	Conversion factor µg/m²/s to kg N/ha-y	-	96	260	60	72	98	60	42	49	
	Deposition velocity species approximation	-	NO_2	NH_3	Precautionary NH_3 deposition velocity assumed						
	Deposition velocity	m/s	0.003	0.03	0.03	0.03	0.03	0.03	0.03	0.03	[AQTAG06]
	Critical Load value (Clo)	**kg N/ha-y**	**10**	[APIS]							
Screening No amines model	PC (C3) - chemistry OFF, deposition OFF	µg/m³	0.12	0.08	4.16E-05	0.208	0.104	-	-	-	['business as usual' modelling]
	Nutrient Nitrogen deposition	kg N/ha-y	0.04	0.65	7.44E-06	0.45	0.31	-	-	-	
	PC % of critical load	%	**0.36%**	**6.48%**	**<0.001%**	**4.52%**	**3.06%**	**-**	**-**	**-**	
	Total Nutrient Nitrogen deposition PC/Clo (Screening)	**%**	**14.4%**								
Detailed Amines and deposition model	PC (C1) - chemistry ON, deposition OFF	µg/m³	-	-	-	0.195	0.099	1.06E-04	1.66E-04	4.50E-04	[amines modelling]
	Deposition flux (D2) - chemistry OFF, deposition ON	µg/m²/s	-	-	-	3.88E-03	1.94E-03	-	-	-	[deposition modelling]
	Calculated deposition flux (D) = C1*(D2/C3)	µg/m²/s	-	-	-	3.65E-03	1.84E-03	-	-	-	
	Nutrient Nitrogen deposition	kg N/ha-y	-	-	-	0.26	0.18	1.9E-04	2.07E-04	6.63E-04	
	PC % of critical load	%	-	-	-	**2.64%**	**1.80%**	**<0.002%**	**<0.002%**	**0.01%**	
	Nutrient Nitrogen deposition PC/Clo (Amines and degradation products)	%	**4.4%**								
	Total Nutrient Nitrogen deposition PC/Clo (Detailed)	**%**	**11.3%**								