Derivation of Environmental Assessment Levels for Carbon Capture

Draft Report: Third Update to v0.3

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EXECUTIVE SUMMARY

Mitsubishi Heavy Industries (MHI) are supporting multiple companies in the deployment of Carbon Capture and Storage (CCS) technology in the UK. The Environment Agency for England (EAE) is the statutory regulator for the Environmental Permitting process in England.

The EAE have stated that as part of the Permitting process, the Air Quality Impact Assessment (AQIA) undertaken in support of the Permit application must assess the potential impacts of all emissions from the CCS plant.

MHI CCS technology uses an amine-based solvent to preferentially strip CO_2 from the exhaust gases. The remaining exhaust gases are then released to atmosphere along with chemicals entrained from the solvent. The amine solvent contains chemicals that are reactive. These form degradation products through reactions with trace pollutants in the exhaust gases, notably nitrogen dioxide and nitric oxide, and further react once released into the atmosphere. The EAE require that both the entrained and degradation chemicals are identified, and the potential impacts assessed within the AQIA.

In order to undertake the AQIA the emissions must be modelled using dispersion modelling. The results of the modelling are then compared to Environmental Assessment Levels (EALs), these being the maximum concentrations of a chemical in ambient air at which harm is negligible. However, the EAE have published a limited suite of chemicals, and many do not have published EALs. The EAE have instructed industry to derive EALs for these chemicals and provide a justification for their use.

MHI reviewed the list of chemicals and focussed on those identified as being emitted during trials at the Technology Centre Mongstad and by pilot testing. Of note is that the nitramines and nitrosamines are grouped and compared to a common EAL, and therefore do not require separate EALs. MHI followed the EAE guidance, and a position paper provided by the Carbon Capture and Storage Association (CCSA), on how to derive EALs, and the hierarchy of information. Following this methodology MHI derived EALs for the chemicals identified. MHI also provided a data pedigree to indicate the robustness of the EAL and therefore the potential risk of the EAL changing.

1. INTRODUCTION

Mitsubishi Heavy Industries (MHI) Carbon Capture and Storage (CCS) system utilises amine-based solvent to preferentially strip CO2 from exhaust gases. This process results in the emission to atmosphere of a multiple chemicals both directly entrained and due to degradation in the solvent and subsequent atmospheric reactions.

The Environment Agency for England (EAE) require that the potential impacts of these chemicals are assessed in the Air Quality Impact Assessment (AQIA) that is required as part of the Permit application. A key element of the AQIA is the Environmental Assessment Levels (EALs), these being the maximum concentrations in ambient air at which potential harm to humans is negligible.

The suite of EALs published by the EAE is limited, and many of the chemicals that are released from MHIs CCS process do not have EALs. Drax engaged MHI to derive EALs for MHIs CCS process. This report sets out the derived EALs, provides methodology for the derivation and a 'pedigree' to provide an indication of certainty in the derived EAL.

2. BACKGROUND

2.1 OVERVIEW

MHI CCS technology uses an amine-based solvent to preferentially strip CO2 from the exhaust gases. The remaining exhaust gases are then released to atmosphere with trace amounts of entrained chemicals from the amine solvent. The amine solvent contains chemicals that are reactive. These form degradation products through reactions with trace pollutants in the exhaust gases, notably nitrogen dioxide and nitric oxide, and further react once released into the atmosphere. The EAE require that both the entrained and degradation chemicals are identified, quantified and the potential impacts assessed within the AQIA.

In order to undertake the AQIA the emissions must be modelled using dispersion modelling. The results of the modelling are then compared to EALs. However, the suite of EALs is limited. Whilst the EAE are deriving EALs for seven of the most common chemicals used in amine solvents, there are several additional chemicals which are emitted from the MHI process for which EALs are not published. The EAE have instructed industry to derive EALs for these chemicals and provide a justification for their use.

2.2 CCSA POSITION PAPER

The Carbon Capture and Storage Association (CCSA), in conjunction with a range of industry members and UK regulators have produced a position statement on the hierarchy for deriving EALs[1].

1. Use of EALs published by the Environment Agency, SEPA, NRW or NIEA;

2. Use of an EAL published by recognised international agency, including USEPA, Agency for Toxic Substances and Disease Registry (ATSDR), World Health Organisation, International Agency for Research on Cancer, other national environmental agencies;

3. Using an EAL derived from published occupational health data (i.e. EH40, MSDSs, scientific literature etc.) using the Environment Agency 2012 derivation methodology;

4. Use of an EAL derived from primary collected toxicology data provided by a carbon capture technology licensor;

5. Read across of toxicology data from appropriate surrogate species based on and health end points;

6. Use of appropriate surrogate species based on chemical structure similarities and properties

The CCSA hierarchy has been followed when deriving the EALs, and a ‘data pedigree’ assigned. This has been done to provide MHI with an understanding of the strength of the derived EAL and the risk of the EAL changing in the future, which could impact on the ability of project to be Permitted.

[1] CCSA (Sept 2023) Environmental Assessment Levels and Disclosure of Amine Species - CCSA position paper

2.3 READ ACROSS METHOD

Where there are no EALs and no occupational exposure limits or standards, the 'read across' method is used based on a comparison (or read across) of the base toxicology data.

This method uses the principle of 'read across'. This is where a chemical without an EAL is compared to one that does have an EAL by means of referring back to the underlying toxicology profile for the chemical of interest. The following are noted on the 'read across' method:

- Requires the toxicology effect to be similar, for example acute irritation
- Requires the toxicology data to be similar, for example based on exposure in rats through the same pathway to allow like for like comparison
- Requires data to be comparable, LD50 or No Observable Acute Exposure Limit (NOAEL)

The EAE have published a number of EALs which have been used for the purposes of the assessment. These are summarised in Table 3.1.

In the case of absence of any toxicological data for the chemical of interest the OECD Toolbox was used to generate profiles for key toxicological effects: mutagenicity, carcinogenicity, reproductive toxicity, and irritation/corrosion. Where the profiles thus generated, and structures were deemed similar it was considered appropriate to read-across.

2.4 MHI DERIVATION OF RELEASED CHEMICALS

The following steps were undertaken to derive a list of chemicals for which EALs are required:

- MHI calculated all of the possible entrained and degradation chemicals that could be released. This resulted in a list of several hundred chemicals.
- MHI undertook testing of the amine solvent at Technology Centre Mongstad (TCM) and through pilot testing. During these tests measurements of emitted chemicals were undertaken to identify which chemicals are actually present in potentially detectable quantities and quantify these.
- MHI reviewed the list and noted that of the chemicals identified, 8 are Nitrosamines and two are Nitramines. EAE guidance states that in the case of nitramines and nitrosamines (N-amines) these should be summed and compared to the EAEs EAL for Nitrosodimethylamine (NDMA). This negates the need for separate EALs for all of the N-amine species to be derived.

This process produced a final list of chemicals. Deriving EALs for those chemicals that are actually detected is considered to be pragmatic in order to keep the list to a sensible length and noting that many of the chemicals that could theoretically be produced will not be present.

3. SUMMARY OF DERIVED EALS

The EALs derived are summarised in Table 3.1, reprised from Table 2.2 of the Air Emission Risk Assessment provided as Appendix B of the Schedule 5 Part 1 response submitted on 29 November 2024. The method used for derivation of each EAL is then detailed in Section 4. Note that the EALs differ in averaging period depending on whether risk is acute, chronic or both.

TABLE 3.1 DERIVED EALS

Emission	Long Term AQAL		Short Term AQAL		Origin
	Standard ($\mu g/m^3$)	Averaging Period (permitted exceedances per year)	Standard ($\mu g/m^3$)	Averaging Period (permitted exceedances per year)	
Combustion Emissions (BECCS and non-BECCS sources)					
Nitrogen Dioxide	40	Annual	200	Hourly (18)	Air Quality Standards Regulations 2010
Sulphur Dioxide	125	Daily (3)	266 350	15min (35) Hourly (24)	Air Quality (England) Regulations 2000 (as amended) Air Quality Standards Regulations 2010
Ammonia	180	Annual	2500	Hourly	Non-statutory EAL, derived by Environment Agency
Hydrogen Chloride			750	Hourly	Non-statutory EAL, derived by Environment Agency
Hydrogen Fluoride	16	Monthly	160	Hourly	Non-statutory EAL, derived by Environment Agency
Particulate Matter (as PM_{10})	40	Annual	50	Daily (35)	Air Quality Standards Regulations 2010
Particulate Matter (as $PM_{2.5}$)	20	Annual			Air Quality Standards Regulations 2010

Emission	Long Term AQAL		Short Term AQAL		Origin
	Standard (µg/m^3)	Averaging Period (permitted exceedances per year)	Standard (µg/m^3)	Averaging Period (permitted exceedances per year)	
Emissions Introduced by Carbon Capture Plant (BECCS only)					
Acetaldehyde	370	Annual	9200	Hourly	Non-statutory EAL, derived by Environment Agency
Formaldehyde	5	Annual	100	30min	Non-statutory EAL, derived by Environment Agency
Ammonia	180	Annual	2500	Hourly	Non-statutory EAL, derived by Environment Agency
Ethylamine	22	Annual	2800	Hourly	Non-statutory EAL, derived by MHI
Methylamine	15	Annual	1900	Hourly	Non-statutory EAL, derived by MHI
Monoethanolamine	100	24-Hour	400	Hourly	Non-statutory EAL, derived by Environment Agency
Diethanolamine	3	24-Hour	-	-	Non-statutory EAL, derived by Environment Agency
Diethylamine	33	24-Hour	330	Hourly	Non-statutory EAL, derived by Environment Agency[†]
Dimethylamine	22	Annual	2800	Hourly	Non-statutory EAL, derived by MHI
Ethyl ethanolamine	50	Annual	300	Hourly	Non-statutory EAL, derived by MHI
Ethyl methylamine	250	Annual	-	-	Non-statutory EAL, derived by MHI
N-Dimethylethylenediamine	104	Daily	417	Hourly	Non-statutory EAL, derived by MHI
Piperazine	15	24-Hour	-	-	Non-statutory EAL, derived by Environment Agency[§]

Emission	Long Term AQAL		Short Term AQAL		Origin
	Standard ($\mu g/m^3$)	Averaging Period (permitted exceedances per year)	Standard ($\mu g/m^3$)	Averaging Period (permitted exceedances per year)	
Ethyl diethanolamine	440	Annual	-	-	Non-statutory EAL, derived by MHI
N-(2-hydroxyethyl) acetamide	0.085	Annual	-	-	Non-statutory EAL, derived by MHI
N-(2-hydroxyethyl) formamide	86	Annual	-	-	Non-statutory EAL, derived by MHI
N-Nitrosomethylethylamine	0.0002	Annual	-	-	Non-statutory EAL, derived by Environment Agency‡
N-Ethyl-N-(2-hydroxyethyl) nitrosamine	0.0002	Annual	-	-	Non-statutory EAL, derived by Environment Agency‡
N-Nitrosodimethylamine	0.0002	Annual	-	-	Non-statutory EAL, derived by Environment Agency
1-Nitrosopiperazine	0.0002	Annual	-	-	Non-statutory EAL, derived by Environment Agency‡
N-Nitrosodiethylamine	0.0002	Annual	-	-	Non-statutory EAL, derived by Environment Agency‡
N-Nitrosodiethanolamine	0.0002	Annual	-	-	Non-statutory EAL, derived by Environment Agency‡
N-Nitrosomorpholine	0.005	Annual	0.037	24-Hour	Non-statutory EAL, derived by Environment Agency†
1,4-Dinitrosopiperazine	0.0002	Annual	-	-	Non-statutory EAL, derived by Environment Agency‡
2-(Ethylnitroamino) ethanol	0.0002	Annual	-	-	Non-statutory EAL, derived by Environment Agency‡
1-Nitropiperazine	0.0002	Annual	-	-	Non-statutory EAL, derived by Environment Agency‡
Pollutants formed by degradation of amines in ambient air					

Emission	Long Term AQAL		Short Term AQAL		Origin
	Standard (µg/m^3)	Averaging Period (permitted exceedances per year)	Standard (µg/m^3)	Averaging Period (permitted exceedances per year)	
Nitrosamines	0.0002	Annual			Non-statutory EAL, derived by Environment Agency[‡]
Nitramines	0.0002	Annual			Non-statutory EAL, derived by Environment Agency[‡]

[†] These EAL are subject to finalisation by EA, followed by public consultation

[§] This EAL is subject to public consultation

[‡] This is set at the EAL for Nitrosodimethylamine

Ammonia included both as a combustion related emission and as introduced by the carbon capture plant

4. DETAILED DERIVATION OF EALS: OVERVIEW

The detailed derivation of the EALs in Table 3.1, other than those provided by the EAE, are set out in this section. For some EALs the derivation is straightforward as the EAL is directly published in a peer reviewed resource. For others there is a requirement to apply a derivation method to calculate the EAL. For completeness, the method, data source and derived EALs are set out for each chemical. Following the CCSA position paper hierarchy, the following sources were consulted when deriving the EALs in order of preference:

- EALs from other international bodies
    - o United States Environmental Protection Agency (USEPA) Chronic Dose-Response Values[2]
    - o USEPA Acute Dose-Response Values[3]
    - o Agency for Toxic Substances and Disease Registry (ATSDR) Toxic Substances Portal[4]
    - o New York State DAR-1 Guidelines for the Evaluation and Control of Ambient Air Contaminants[5]
- EALs derived from Occupational Health Standards
    - o DNEL values derived from REACH [6]

United Kingdom Health and Safety Executive EH40 Workplace Exposure Limits[7]

- o Occupational Safety and Health Administration: Permissible Exposure Limits –Annotated Tables[8]
- EALs derived from toxicology data
    - o Where used, specific sources are indicated

In the case of the EALs derived from toxicology data, these values can be uncertain. There are no derived EALs and instead these are based on limited toxicology data, in this case the LD_{50} (rat) or read-across. This is a crude metric for understanding the potential impacts and further work is recommended to strengthen these EALs.

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[2] USEPA (accessed December 2023) Prioritized Chronic Dose-Response Values https://www.epa.gov/system/files/documents/2021-09/chronicfinaloutput_9_29_2021-12-46-18-pm_0.pdf

[3] USEPA (Accessed December 2023) Acute Dose-Response Values for Screening Risk Assessments table2.pdf (epa.gov)

[4] Agency for Toxic Substances and Disease Registry (Accessed December 2023) Toxic Substances Portal https://wwwn.cdc.gov/TSP/index.aspx

[5] New York State DAR-1 Guidelines for the Evaluation and Control of Ambient Air Contaminants (accessed December 2023) https://extapps.dec.ny.gov/docs/air_pdf/dar1.pdf

[6] European Chemicals Agency (accessed May 2024) Search for REACH registrations https://echa.europa.eu/mt/information-on-chemicals

[7] United Kingdom Health and Safety Executive (accessed December 2023) EH40 Workplace Exposure Limits https://www.hse.gov.uk/pubns/priced/eh40.pdf

[8] Occupational Safety and Health Administration (Accessed December 2023) Permissible Exposure Limits – Annotated Tables https://www.osha.gov/annotated-pels/table-z-1

5. DETAILED DERIVATION OF EALS: PHASE 1

5.1 METHYLAMINE

The review for Methylamine identified:

TABLE 5.1 METHYLAMINE

Data Source	Data available
EAE EAL	No
USEPA Chronic Dose-Response Values	No
USEPA Acute Dose-Response Values	No
ATSDR	No
New York DAR-1 Guidelines	Yes
EH40	No review required
OSHA Exposure Limits	No review required
Toxicology data	No review required

The New York DAR guideline values for Methylamine are:

- 1-hour 1900µg/m^3
- Annual mean 15µg/m^3

As these are public health-based limits, these can be used directly, and no further derivation is needed.

5.2 ETHYLAMINE

The review for Ethylamine identified:

TABLE 5.2 ETHYLAMINE

Data Source	Data available
EAE EAL	No
USEPA Chronic Dose-Response Values	No
USEPA Acute Dose-Response Values	No
ATSDR	No
New York DAR-1 Guidelines	Yes
EH40	No review required
OSHA Exposure Limits	No review required
Toxicology data	No review required

The New York DAR guideline values for Ethylamine are:

- 1 hour 2,800µg/m^3
- Annual mean 22µg/m^3

As these are public health-based limits, these can be used directly, and no further derivation is needed.

5.3 DIMETHYLAMINE

The review for Dimethylamine identified:

TABLE 5.3 DIMETHYLAMINE

Data Source	Data available
EAE EAL	No
USEPA Chronic Dose-Response Values	No
USEPA Acute Dose-Response Values	No
ATSDR	No
New York DAR-1 Guidelines	Yes
EH40	No review required
OSHA Exposure Limits	No review required
Toxicology data	No review required

The New York DAR guideline values for Dimethylamine are:

- 1 hour 2,800µg/m^3
- Annual mean 22µg/m^3

As these are public health-based limits, these can be used directly, and no further derivation is needed.

5.4 N,N-DIMETHYLETHYLENEDIAMINE

The review for N,N-Dimethylethylenediamine identified:

TABLE 5.4 N,N-DIMETHYLETHYLENEDIAMINE

Data Source	Data available
EAE EAL	No
USEPA Chronic Dose-Response Values	No
USEPA Acute Dose-Response Values	No
ATSDR	No
New York DAR-1 Guidelines	No
EH40	No
OSHA Exposure Limits	No
Toxicology data	Yes

As there are no EALs for N,N-Dimethylethylenediamine and no occupational standards EALs are derived using the read across method detailed in Section 2.3.

Review of Material Safety Data Sheets for monoethanolamine and N,N-imethylethylenediamine identified that:

- The toxic effect is the same, this being acute irritation
- Both have an LD50 for oral exposure of rats
- There are no toxicology outcomes present for N,N-dimethylethylenediamine that are not present for monoethanolamine (mutagenic, carcinogenic or teratogenic effects)

As such, the read across method was deemed appropriate as a comparison of monoethanolamine to N,N-dimethylethylenediamine. The method was applied as follows:

- EALs for monoethanolamine:
  - o 1-hour 400µg/m^3
  - o 24-hour 100µg/m^3
- LD50 rat, oral monoethanolamine: 1089mg/kg
- LD50 rat, oral N,N-dimethylethylenediamine: 1135mg/kg
- Derived conversion factor: 1.04

Derived EALs for N,N-dimethylethylenediamine

- o 1-hour 417µg/m^3
- o 24-hour 104µg/m^3

6. DETAILED DERIVATION OF EALS: PHASE 2

6.1 N-(2-HYDROXYETHYL)ACETAMIDE

The review for N-(2-hydroxyethyl)acetamide identified:

TABLE 6.1 N-(2-HYDROXYETHYL)ACETAMIDE

Data Source	Data available
EAE EAL	No
USEPA Chronic Dose-Response Values	No
USEPA Acute Dose-Response Values	No
ATSDR	No
New York DAR-1 Guidelines	No
EH40	No
OSHA Exposure Limits	No
Toxicology data	Yes

As there are no EALs for N-(2-hydroxyethyl)acetamide and no occupational standards, EALs are derived using read-across to acetamide using the OECD Toolbox profile to assess toxicological reactivity.

OECD Toolbox profiles are similar. A DART profiler present for acetamide is not present for N-(2-hydroxyethyl)acetamide therefore read-across to acetamide is considered a worst-case scenario. N-(2-hydroxyethyl)acetamide gives a negative result in the reverse bacterial mutation assay and an oral LD50 of 22880 mg/kg bw in mouse is noted.

Both structures have a similar molecular weight and are acetamides. New York DAR guideline value for acetamide is:

- o Annual mean 0.05 µg/m^3

- Molecular weight acetamide: 59
- Molecular weight N-(2-hydroxyethyl)acetamide: 103
- Conversion factor: 1.7
- Converted DAR for N-(2-hydroxyethyl)acetamide

  o Annual mean 0.085 µg/m^3

6.2 N-(2-HYDROXYETHYL)FORMAMIDE

The review for N-(2-hydroxyethyl)formamide identified:

TABLE 6.2 N-(2-HYDROXYETHYL)FORMAMIDE

Data Source	Data available
EAE EAL	No
USEPA Chronic Dose-Response Values	No
USEPA Acute Dose-Response Values	No
ATSDR	No
New York DAR-1 Guidelines	No
EH40	No
OSHA Exposure Limits	No
Toxicology data	Yes

As there are no EALs for N-(2-hydroxyethyl)formamide and no occupational standards, EALs are derived using read-across to formamide using the OECD Toolbox profile to assess toxicological reactivity.

The OECD Toolbox profiles were similar. A DART profiler for formamide is not present for N-(2-hydroxyethyl)formamide therefore read-across to acetamide is considered a worst-case scenario. Both structures have a similar molecular weight and are formamides. New York DAR guideline value for formamide is:

  - Long term 43 µg/m^3

- Molecular weight formamide: 45
- Molecular weight N-(2-hydroxyethyl)formamide: 89
- Conversion factor: 2
- Converted DAR for N-(2-hydroxyethyl)formamide

  - Annual mean 86 µg/m^3

6.3 ETHYLMETHYLAMINE

The review for Ethylmethylamine identified:

TABLE 6.3 ETHYLMETHYLAMINE

Data Source	Data available
EAE EAL	No
USEPA Chronic Dose-Response Values	No
USEPA Acute Dose-Response Values	No
ATSDR	No
New York DAR-1 Guidelines	No
EH40	No
OSHA Exposure Limits	No
Toxicology data	Yes

As there are no EALs for ethylmethylamine and no occupational standards, EALs are derived using read-across to dimethylamine using the OECD Toolbox profile to assess toxicological reactivity.

The OECD Toolbox profiles were similar for both chemicals. Both structures are secondary amines and have a similar molecular weight. It is noted that read-across to diethylamine could also be similarly justified but dimethylamine was chosen as the worst-case scenario as it has a slightly lower New York DAR guideline value. The New York DAR guideline values for Dimethylamine are:

- o 1-hour 2800µg/m^3
- o Annual mean 22µg/m^3

- Molecular weight dimethylamine: 45
- Molecular weight ethylmethylamine: 59
- Conversion factor: 1.3
- Converted DAR for ethylmethylamine
  - o 1 hour 3,640µg/m^3
  - o Annual mean 28.6µg/m^3

6.4 ETHYL ETHANOLAMINE

The review for Ethyl ethanolamine identified:

TABLE 6.4 ETHYL ETHANOLAMINE

Data Source	Data available
EAE EAL	No
USEPA Chronic Dose-Response Values	No
USEPA Acute Dose-Response Values	No
ATSDR	No
New York DAR-1 Guidelines	No
EH40	No
OSHA Exposure Limits	No
Toxicology data	Yes

The published REACH DNELs for ethyl ethanolamine are:

- Long term 50µg/m^3
- Short term 300µg/m^3

As these are public health-based limits, they can be used directly, and no further derivation is needed.

6.5 ETHYL DIETHANOLAMINE

The review for Ethyl ethanolamine identified:

TABLE 6.5 ETHYL DIETHANOLAMINE

Data Source	Data available
EAE EAL	No
USEPA Chronic Dose-Response Values	No
USEPA Acute Dose-Response Values	No
ATSDR	No
New York DAR-1 Guidelines	No
EH40	No
OSHA Exposure Limits	No
Toxicology data	Yes

As there are no EALs for ethyl diethanolamine and no occupational standards, EALs are derived using read-across to methyl diethanolamine using the OECD Toolbox profile to assess toxicological reactivity.

The OECD Toolbox profiles were similar for both chemicals. Both structures are tertiary amines and have a similar molecular weight. The REACH DNEL for methyl diethanolamine is:

Long term 400µg/m^3

- Molecular weight methyl diethanolamine: 119
- Molecular weight ethyl diethanolamine: 133
- Conversion factor: 1.1
- Converted DNEL for ethyl diethanolamine

    o Long term 440µg/m^3

As this is a public health-based limit, it can be used directly, and no further derivation is needed.