Amine-based Carbon Capture Secondary Emissions - A Study of the Regulatory Landscape

Rafay Anwar[a,*],Esther Praise Avor[a], Colin Campbell[a], Shannon Timmons[a]

[a]*The International CCS Knowledge Centre, 198-10 Research Drive, Regina, SK, S4S 7J7 Canada*

Abstract

This paper provides insight into the present status of environmental and regulatory requirements for potential secondary emissions produced by amine-based CCS systems. The paper reviews the path to permitting secondary emissions taken by two major CCS projects in development: the Humber Zero project in the United Kingdom (UK) and Project Tundra in the United States of America (USA) with a focus on nitrosamines. By discussing the approach taken by various jurisdictions and highlighting the industrial best practices already in place for the management of secondary emissions, this paper aims to demonstrate the importance of transparency and knowledge sharing in achieving collective success for the global CCS industry.

Keywords: CCS; absorber emissions; secondary emissions; amines; nitrosamines; environmental permit; Humber Zero; Project Tundra

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1. Introduction

Carbon capture and storage (CCS) is expected to play a significant role in helping reduce greenhouse gas emissions (GHGs), particularly from heavy industrial operations [1]. Presently, amine-based capture systems, having a Technology Readiness of 9, are the most mature technology for capturing carbon dioxide (CO_2) from flue gas streams from power plants, cement, steel, and other industrial processes. CCS facilities are highly effective at removing large amounts of CO_2 from industrial flue gas streams and, by design, also significantly reduce the emissions of other common industrial pollutants such as SO_2, NO_x and particulate matter ($PM_{2.5}$ and PM_{10}) [2] that would otherwise be emitted to the atmosphere.

Amines are a widely used class of chemicals and are commonly used in the production of several industrial products including dyes, drugs, epoxy resins, detergents, cosmetics, and agricultural chemicals. They are also used as solvents in the absorption process of amine-based carbon capture facilities. The absorption of CO_2 occurs in the absorber tower. With the majority of CO_2 removed, the remaining gas leaves the absorber via a vent at the top. Flue gas impurities such as NO_x, SO_x, etc., may react with the amine solvent forming degradation products resulting in low levels of secondary emissions released at the absorber vent to the atmosphere. The amount and composition of these emissions is dependent on flue gas conditions, the technology and amines being used, and operating conditions of the upstream process and capture facility. In addition to the components mentioned above, secondary emission profiles may also include small amounts of amine and their nitrosamines that form in the absorber.

Regulations exist across jurisdictions for managing the emissions of common industrial pollutants. This includes guidelines provided by the US Environment Protection Agency (EPA) and the UK Environment Agency. To illustrate this, the International CCS Knowledge Centre reviewed the pathway to permitting for secondary emissions taken by two major CCS projects in development: Humber Zero in the UK and Project Tundra in the US [3], [4]. This review focused on how the permitting process handles the potential for nitrosamine emissions. Several commonalities were observed between the two jurisdictions (e.g. both processes require the completion of a dispersion model). Differences observed were noted to be driven by the methodology prescribed by the regulator. In both instances, project developers

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* Corresponding author. Email address: ranwar@ccsknowledge.com

used the existing regulatory framework in their jurisdiction which provides guidelines for limiting common industrial emissions including emissions of commonly occurring nitrosamines. For both projects, the current dispersion modelling predicts levels of nitrosamines below the limits established by each project's jurisdiction.

Further evaluation of secondary emission profiles is an ongoing engineering process that project developers are carrying out in collaboration with their technology licensors. During this time, a conservative approach to design rooted in global best practices will be necessary along with greater transparency and knowledge sharing by technology licensors. It is also noted that potential for nitrosamine production is not specific to CCS they are already present in the human environment including through processed foods, tobacco products, cosmetics, and impurities present in pharmaceuticals [5]. Therefore, recommended limits for common nitrosamines exist in many jurisdictions as detailed in the next section of this paper. Additionally, the measurement of very low amounts of some components is a challenge. As CCS develops globally, it is expected that improvements in technology will help close this gap.

Nomenclature

AERMET	Meteorological data preprocessor for AERMOD
AERMOD	American Meteorological Society/Environmental Protection Agency Regulatory Model
ACGIH	American Conference of Governmental Industrial Hygienists
CEMS	Continuous Emission Monitoring System
ILO	International Labor Organization
NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
WHO	World Health Organization

2. Literature Review

This section reviews existing regulations concerning secondary emissions from amine-based CO_2 capture. It focuses on amines and their degradation products (nitrosamines, nitramines, aldehydes), with additional, high-level information provided on other compounds expected to be present in secondary emissions.

2.1. Amines

Several proprietary amines are being considered for CO_2 capture. However, as limited public data is available on proprietary amines, this review focuses on the most common, non-proprietary amines with existing exposure limits:

- **MEA (Monoethanolamine):** Widely used in various industries, MEA is biodegradable with an 11-hour photo transformation half-life. Exposure limits vary across jurisdictions (Table 1). Notably, the UK, as of September 2021, lacked regulatory standards for MEA but proposed a recommended environmental assessment level (EAL) of 0.1 mg/m^3 (24-hour mean) and 0.4 mg/m^3 (1-hour mean) [6].
- **DEA (Diethanolamine):** Used similarly to MEA, DEA is considered less irritating but slightly more acutely toxic than MEA. While not a genotoxin, DEA has shown potential carcinogenicity when tested on mice [7]. Limits are primarily established for long-term exposure (Table 2).
- **MDEA (Methyl diethanolamine):** A tertiary amine with irritant properties, MDEA exhibits high selectivity for H_2S in gas sweetening [8]. Currently, globally established exposure limits for MDEA are in development. However, Norway recommends a maximum outdoor air concentration of 120 µg/m^3 based on reproductive toxicity studies in rats [7].
- **Piperazine:** Primarily used in pharmaceuticals and gas washers, piperazine exposure is linked to occupational asthma. The Norwegian Institute of Public Health (NIPH) advises a maximum public exposure limit of 5 µg/m^3

[7]. The European Chemical Agency (ECHA) also classifies piperazine as a suspected reproductive toxicant, and a skin and respiratory sensitizer [9]. While the Canadian government considers current piperazine levels safe, they acknowledge potential concerns with increased usage [9]. Notably, piperazine is used in low concentrations in amine blends for CO_2 capture due to its tendency to form precipitates at higher concentrations [10], [11]. Workplace exposure limits for piperazine are provided in Table 3.

Table 1. MEA-workplace exposure limits for different territories

Territory	Workplace Exposure Limit				Reference
	Long-term Exposure limit (8-hr TWA)		Short-term exposure limit (15 minutes)		
	ppm	mg/m^3	ppm	mg/m^3	
Australia	3	7.5	6	15	[12]
Ontario	3	-	6	-	[13]
Alberta	3	7.5	6	15	[14]
European Commission (EC)	1	2.5	3	7.6	[15]
Mexico	3	-	6	-	[16]
OSHA	3	6	-	-	[17]
NIOSH	3	8	6	15	[17]
ACGIH	3	8	6	15	[17], [18]

Table 2. DEA-workplace exposure limits for different territories

Territory	Workplace Exposure Limit				Reference
	Long-term Exposure limit (8-hr TWA)		Short-term exposure limit (15 minutes)		
	ppm	mg/m^3	ppm	mg/m^3	
Australia	3	13	-	-	[12]
NIOSH	3	15	-	-	[19]
ACGIH	0.2[a]	1[a]	-	-	[19], [20]
Ontario	-	1[a]	-	-	[13]
Alberta	-	2	-	-	[14]
EC/ILO/WHO	-	1	-	-	[21]

[a] Inhalable fraction and vapour (IFV). This is an endnote established by ACGIH and it is used when a substance exerts sufficient vapor pressure such that it may be present in both particle and vapor phase, with each contributing a significant portion of the dose at the TLV-TWA concentration. The ratio of the Saturated vapor concentration (SVC) to the threshold limit value-time weighted avaerage (TLV-TWA) is considered when assigning the IFV. The SVC values are determined for pure substances, typically at or near room temperature where the substance has sufficient time to reach an equilibrium between the partition of the aerosol and vapor phase. The IFV endnote is used for sbustances with an SVC/TLV ratio between 0.1 and 10 [22].

Table 3. Piperazine – workplace exposure limits for different territories

Territory	Workplace Exposure Limit				Reference
	Long-term Exposure limit (8-hr TWA)		Short-term exposure limit (15 minutes)		
	ppm	mg/m^3	ppm	mg/m^3	
EC/UK	-	0.1	-	0.3	[23], [24]
Ontario	0.03[a]	-	-	-	[13]
Australia	0.03	0.1	0.09	0.3	[25]
ACGIH	0.03[a]	-	-	-	[26]

2.2. Degradation Products

- **Nitrosamines/Nitramines:** Amine-based CO_2 capture secondary emissions may contain nitrosamines and nitramines from reactions between the amine and NO_x in flue gas or the atmosphere. NDMA and NDEA are two frequently studied nitrosamines, with NDMA being the most extensively studied nitrosamine. The NIPH recommends using NDMA emission limits as a conservative approach for new CCS facilities. However, a refined risk evaluation considering the potency of different nitrosamines is suggested when total nitrosamine levels exceed NDMA limits [7]. Cancer slope factors (CSF) for various nitrosamines and risk estimates for NDMA are provided in Table 4 and Table 5, respectively.
- **Aldehydes:** Formaldehyde and acetaldehyde, identified as carcinogenic and mutagenic, may be emitted from amine-based CO_2 capture, primarily MEA systems. Formaldehyde is also known to catalyze nitrosamine formation [27].
- **VOCs (Volatile Organic Compounds):** Commonly measured VOCs like benzene, toluene, ethylbenzene, and xylene (BTEX) pose health risks, particularly with prolonged exposure. Benzene is classified as a human carcinogen by the US EPA [28].

In the majority of jurisdictions there are well established exposure limits for various aldehydes, VOCs, and other compounds such as ammonia, ketones, amides, and hydrocarbons.

Table 4. Relative carcinogenic potencies of different nitrosamines [7]

Substance	CAS No.	Oral CSF (mg/kg bw/day) -1
N-Nitrosodiethanolamine (NDELA)	1116-54-7	2.8
N-Nitrosodi-n-butylamine (NDBA)	924-16-3	5.4
N-Nitrosomorpholine (NMOR)	59-89-2	-
N-Nitroso-di-n-propylamine (NDPA)	621-64-7	7
N-Nitrosomethylethylamine (NMEA)	10595-95-6	22
N-Nitrosopiperidine (NPIP)	100-75-4	37.5
N-Nitrosodimethylamine (NDMA)	62-75-9	51
N-Nitrosodiethylamine (NDEA)	55-18-5	150

Table 5. Risk estimates for NDMA in air in different jurisdictions

Territory	Risk Level	Limit, $\mu g/m^3$	Reference
Norway	Below 10^{-5}	0.0003	[29]
USA	10^{-5}	0.0007	[30]
	10^{-6}	0.00007	[30]
Canada	10^{-5}	0.003	[29]
	10^{-6}	0.0003	[29]
WHO	10^{-5}	0.003	[29]
	10^{-6}	0.0003	[29]
UK	10^{-6}	0.0002	[6]

3. Case Studies

This section provides insights into the approach to regulatory permitting of absorber secondary emissions that is being followed by the developers of two prominent, large-scale amine-based CCS projects. Both projects are at the stage where they are carrying out assessments of their expected secondary emissions to fulfil regulatory requirements in their regions. The first of these is the Humber Zero Project in Immingham, UK, which will capture CO_2 from flue gas emitted by an existing natural gas fired power plant and a refinery [3]. The second is Project Tundra in North Dakota, USA, which aims to capture CO_2 from the flue gas of an existing coal fired power station [4]. Both projects plan to implement amine-based post combustion carbon capture. While the industrial processes are different, as are the selected amine solvent suppliers, there are commonalities in the list of components expected to be found the secondary emission profiles. This includes NO_x, SO_2, CO, particulate matter, volatile organic compounds (VOCs), amines and nitrosamines.

While limits for common nitrosamines exist in both the UK and US, strict regulation of the relatively low levels of these compounds that may be present in amine-based CCS secondary emission profiles, poses some challenges. Modelling their behaviour once they have been released out of the absorber vent and finding reliable methods and equipment for measuring their concentration are two such challenges.

3.1. Humber Zero Project

The Humber region is the UK's largest industrial emitter of CO_2 In its first phase, the Humber Zero Project (HZP) will capture emissions from two major industrial emitters: VPI's Immingham power plant and Phillips 66 Limited's refinery. Up to 3.3 million tonnes/year of CO_2 is planned to be captured at VPI Immingham alone, from two existing gas turbines and two existing auxiliary boilers. After capture, compressed CO_2 will be transported for storage in depleted gas fields in the North Sea. HZP is proceeding through the engineering phase and has selected Shell's CANSOLV technology to capture CO_2.

3.1.1. Applicable Regulations

In the UK, outdoor air quality standards are regulated by the Air Quality Standards Regulations 2010, the Air Quality Standards (Wales) Regulations 2010, the Air Quality Standards (Northern Ireland) 2010, and the Air Quality Standards (Scotland) Regulations 2010. These regulations set limits for common air pollutants such as NO_x, SO_2, CO and PM_{10} and $PM_{2.5}$. However, they do not address other potential components of secondary emissions from amine-based carbon capture such as amines and nitrosamines. The UK's Environment Agency carried out a risk assessment (last updated in September 2021), including a comprehensive consultation, to determine environmental assessment levels (EAL) for components not addressed by the existing regulatory framework [31]. An EAL is defined as the limit below which a substance does not pose a significant adverse impact on human health. Recognizing the increasing need for regulations tailored to potential emissions from amine-based carbon capture facilities, the Environment Agency's risk assessment included a review of MEA and NDMA.

The addition of carbon capture capability to the existing power production facility required the project developer to apply to the UK's Environment Agency for a variation to the existing environmental permit for the facility. As part of this submission, the developer completed an Air Impact Assessment [3] in December 2023. This assessment focuses on the developments to be completed at VPI's Immingham facility.

3.1.2. Background Concentrations

The project developer was required to demonstrate that secondary emissions from their project would not exceed the established limits for any regulated components in air. The developer used air quality sample data available from various local and national databases to establish baselines for common pollutants expected in the secondary emissions stream. However, background information was not available for amines and their potential nitrosamines.

3.1.3. Identifying Potential Nitrosamines in Secondary Emissions

The expected emissions of nitrosamines from the absorber stack were provided by Shell CANSOLV based on a proprietary emissions model. This model accounts for both vapor phase and liquid entrainment of amines and nitrosamines leaving the absorber vent. The proposed solvent consists of three amines. The respective nitrosamines formed from these amines are named in the project developers air impact assessment document and are provided in Table 6 below. Amine 3 is reported to be a tertiary amine that is not expected to form stable nitrosamines and therefore its associated nitrosamine (N-amine 3) is not included in the emissions analysis.

Table 6. CANSOLV DC-103 potential nitrosamines produced due to degradation (Humber Zero Project) [3]

Component	Chemical Name	CAS Number
N-Amine 1	4-Nitroso-1-piperazineethanol	48121-20-6
N-Amine 2	1-nitrosopiperazine	5632-47-3
N-Amine 3		

The combined annual average emissions of N-Amine 1 & 2 at the absorber stack are expected to be 1.3 $\mu g/m^3$.

3.1.4. Determining Applicable Limits

The risk assessment carried out by the UK Environment Agency included a review of limits for MEA and NDMA to address the growing need for CCS specific ambient air quality limits. This resulted in a new long term EAL for NDMA at 0.2 ng/m^3 annual average with an Estimated Lifetime Cancer Risk (ELCR) of 1 in 1,000,000 (refer to Table 5 for data from other jurisdictions). No short term EAL was defined as NDMA is understood to have adverse impacts on human health as a result of chronic exposure. Additional details on the derivation of this EAL were provided including reference to the work of other jurisdictions in establishing NDMA limits (last updated: September 2021) [6].

NDMA is the most widely studied nitrosamine. This is in part due to NDMA's relatively higher potential for adverse impact on human health compared to other nitrosamines [32]. Based on this the Environment Agency chose to establish an EAL for NDMA [6]. Other than for NDMA, there is limited information on other nitrosamines regarding the toxicological impacts of long-term, low-level exposure via ambient air. Therefore, the Environment Agency has recommended using the NDMA EAL as a proxy for limiting overall nitrosamines emissions from an amine-based carbon capture facility [3]. The next step for the project developer was to carry out dispersion modelling to determine the expected total nitrosamine concentration in air once the capture facility is operational. If the EAL could be exceeded the regulator would require the project developer to take further steps in collaboration with the agency to determine the most cost-effective manner to reduce the expected emission rate.

3.1.5. Dispersion Modelling

Per the HZP Air Impact Assessment, Amine 3 is a minor component of the CANSOLV solvent. This amine also has much lower volatility and being a tertiary amine, is not expected to form stable nitrosamines. As a result, Amine 3 was not included in the dispersion model. Amines 1 and 2 were grouped together for assessment of impact via dispersion modelling.

The Humberside Airport, which is less than 10 km away from the proposed location, was selected to provide the meteorological input for this model. Meteorological data over a five-year period from 2017 to 2021 was used for the model. Along with meteorological data, all relevant terrain and building data were inputted into the model.

The Atmospheric Dispersion Modeling System (ADMS) was used to carry out this assessment. An amine chemistry module has been developed for use with ADMS by Cambridge Environmental Research Consultants (CERC). This allows the rate of amine degradation to be considered as well as the potential reactions of amines with other components of the flue gas and the atmosphere. This capability within the model is critical for accurate assessment of impact as nitrosamine formation is also expected to occur as a result of emitted amines reacting in the atmosphere.

Given the complexity of reactions involving amines and their nitrosamines, a significant amount of amine specific data was input into the module. Shell CANSOLV provided this reaction rate data based on laboratory studies and other sources. Despite this, the project developer has noted several limitations and assumptions when using dispersion modelling to determine the concentration of nitrosamines in air. Therefore, where possible, a conservative approach was adopted when building the model.

The expected average annual emission rate at the stack for each component was used as an input to the dispersion model. The results showed that, at any of the receptor sites considered as part of the dispersion model, the highest total nitrosamine (i.e., N-Amine 1 and 2 combined) concentration is expected to be no more than 0.195 ng/m^3. This is below the NDMA EAL of 0.2 ng/m^3 (annual mean) set by the UK Environment Agency. The project developer notes that the available data shows N-Amine 1 and 2 as having lower mutagenic and carcinogenic potency than NDMA. Hence, using the NDMA EAL as a proxy represents a conservative approach [3]. Further toxicological work will be completed as the project progresses.

3.2. Project Tundra

The state of North Dakota produces energy from a number of sources including coal. The Milton R. Young coal fired power plant, which is owned by the Minnkota Power Cooperative, is located in Oliver County, North Dakota, USA. Project Tundra aims to capture up to 4 million tonnes/year of CO_2 from the flue gas produced by this power plant. The CO_2 will be sequestered at a permitted site close to the capture facility. Project Tundra has chosen Mitsubishi Heavy Industries (MHI) as the technology licensor for the carbon capture process.

3.2.1. Applicable Regulations

Project Tundra is moving through the permitting process and recently received an air permit to construct. As part of the application process the developer provided details on the expected amine plant absorber emissions. The application was submitted to the North Dakota Department of Environmental Quality (NDDEQ) in June 2023 [4]. NDDEQ is aligned with the requirements of the federal Clean Air Act which regulates the emissions of Hazardous Air Pollutants (HAPs).

A key requirement for developers of new stationary sources of emissions is to limit the emission of any single HAP to less than 10 tons/year and the emission of total HAPs to less than 25 tons/year. In the case of Project Tundra, the expected emissions of acetaldehyde exceed the limit for a single HAP and also contribute to the project’s expected total emissions exceeding the limit for total HAPs. In this case, the EPA requires the application of strict controls known as maximum achievable control technology (MACT) to minimize the potential for these secondary emissions. The developer presented options for changing the absorber design to reduce the potential emission of acetaldehyde in support of their application and the proposal was accepted by NDDEQ.

When the developer submitted their application for an air permit in June 2023, the Policy for the Control of Hazardous Air Pollutant Emissions in North Dakota (Air Toxics Policy) was in effect. The Air Toxics Policy required the developer to further analyze the potential for producing HAPs that could have carcinogenic and other toxicological impacts on human health. In this manner, despite the very low concentration of potential nitrosamines in the secondary emissions, the developer was required to address their potential impact using dispersion modelling.

3.2.2. Background Concentrations

The baseline concentrations for HAPs were based on dispersion modelling guidelines provided by NDDEQ. As with HZP, these values were for major HAPs, (or 'criteria pollutants' as defined by the EPA) including SO_2, NO_2, CO and particulate matter ($PM_{2.5}$ and PM_{10}) and not for amines and their nitrosamines.

3.2.3. Identifying Potential Nitrosamines in Secondary Emissions

MHI provided expected emissions of HAPs based on proprietary information using the composition of the flue gas from the existing plant as an input to their process. Only the nitrosamines noted by MHI are listed in Table 7 below.

Table 7. MHI potential nitrosamines produced due to degradation (Project Tundra)

Chemical Name	CAS Number
N-nitrosodiethylamine (NDEA)	55-18-5
Nitrosodimethylamine (NDMA)	62-75-9
N'-Nitrosomorpholine (NMOR)	59-89-2

The annual average total nitrosamine emissions have the potential to be up to 0.084 tons/year, based on short-term hourly emissions at 8,760 hours per year. The application did not provide a concentration in air at the stack.

3.2.4. Determining Applicable Limits

The Clean Air Act HAP list (2013) includes NDMA and NMOR but not NDEA, whereas the list of pollutants included in the Air Toxics Policy includes all three nitrosamines. However, the EPA provides their latest information on human health assessments relating to environmental chemicals via their Integrated Risk Information System (IRIS). For example, the US EPA limits for NDMA provided in Table 5 of this paper are sourced from IRIS.

The information provided on IRIS includes ambient air concentration limits for HAPs. However, per the Air Toxics Policy, and in contrast to the process followed in the UK, the limit for individual HAPs were not used directly to determine risk. The methodology used is described further in the next section.

3.2.5. Dispersion Modelling

The Air Toxics Policy provides a three tier procedure for determining the potential risk posed by the presence of HAPs in an emissions stream. Project Tundra completed the Tier 3 steps using hourly meteorological data from 2017 to 2021 collected for Beulah, ND, with additional information provided from the Bismarck airport weather station. An AERMOD dispersion model was used as recommended by the Air Toxics Policy. Pre-processing of meteorological data was completed using AERMET with consideration given to seasonal variability in the vegetative landscape. The Air Toxics Policy directs where receptors should be modelled.

The model was run based on the expected annual average emissions of HAPs at the absorber vent stack. The results showed the highest total combined nitrosamine concentration at any receptor to be 0.0505 ng/m^3. However, unlike HZP, the Air Toxics Policy does not prescribe using the limit for NDMA (or any other nitrosamine) to determine if total nitrosamine concentration after dispersion modelling is acceptable. Instead, a unit risk factor (in $m^3/\mu g$) is provided for each pollutant listed in the policy including NDMA, NDEA and NMOR (for these components, risk factors provided by the Air Toxics Policy match those provided by the EPA on IRIS). Following the methodology laid out in the Air Toxics Policy, the highest, after dispersion, modelled concentration ($\mu g/m^3$) of each known or potential carcinogen was multiplied by its corresponding unit risk factor to provide a dimensionless value referred to as the maximum individual carcinogenic risk (MICR). The MICR values for all known or possible carcinogens potentially present in the secondary emission stream were totaled. Per the policy, a combined MICR value of 1×10^{-5} was used as the threshold. This is defined as the increased potential for one additional case of cancer occurring in a population of 100,000 through chronic exposure to a HAP, or combination of HAPs, in ambient air, over a 70-year period. In the case of Project Tundra, the combined MICR was found to be 1.02×10^{-6} indicating that the project is expected to meet regulatory requirements. As this approach combines the MICR of a number of individual components, it is seen as a conservative approach to managing the concentration of potentially carcinogenic secondary emissions in air.

4. Key Insights

4.1. Carbon Capture Industry's Reliance on Existing Regulations

Section 3 provided an overview of how two key large-scale amine-based carbon capture projects are managing the permitting of secondary emissions. While there are several commonalities and some key differences between the two approaches, both projects are working within the bounds of the applicable regulatory framework as it stands today. This aligns with the work the Knowledge Centre has done with clients across heavy emitting industries where we have found project developers relying on the existing regulatory frameworks when defining the limits on potential secondary emissions. While both the regions we investigated as part of this review have some form of regulatory requirement to manage potential secondary emissions from carbon capture projects, these regulations may not necessarily be directly tailored towards the carbon capture industry.

In the case of Project Tundra, the permit to construct has been provided with the focus being on the requirement to use MACT to reduce emissions of individual and total HAPs. Using the regulator's handling of nitrosamines as a way to extend this analysis, it is noted that, whereas the Clean Air Act HAP list does include nitrosamines, it is highly unlikely that either of these species will be emitted at levels (10 tons/y or more) that would trigger the need for MACT [33]. Hence, under the requirements of MACT standards alone project developers may not be motivated to consider nitrosamines (and other low concentration HAPs). For Project Tundra, this gap is closed by the Air Toxics Policy which requires a dispersion model to be executed to assess the risk of potentially carcinogenic HAPs despite their comparatively low emission rates. However, while the air permit provided to Project Tundra does require measurement and monitoring of 'criteria pollutants', it is unclear if the project will be required to verify nitrosamine concentrations at the absorber vent once the project is operational. That said, the NDDEQ does have the authority to request testing of emissions at any source under its jurisdiction and must be notified if any emission control technology or measurement instruments face operational issues. It is expected that both developers will follow best practices once the facility is operational and implement a regular and reliable sampling program at their absorber vent to measure the concentration and flowrate of all components of secondary emissions. This information will be necessary not just for regulatory compliance but for increasing the understanding and knowledge in this area of the carbon capture industry, and ensuring projects are operating safely.

Determining the appropriate regulatory pathway for obtaining secondary emissions permits may pose a challenge depending on the jurisdiction. Developers may find they need to determine all regulatory requirements that apply to their project and then aim to comply with the strictest requirements. In this way they can confirm that less stringent regulatory requirements have been met. This review also revealed that the pace of regulatory development may be relatively slow when compared to CCS project timelines. Again, best practice for project developers would be to collaborate with their technology partners to understand the potential secondary emissions from their project as fully and as early as possible and guide project development to align with the anticipated direction of regulatory development.

4.2. Existing Industrial Landscape

A discussion on the potential impact of secondary emissions from carbon capture projects would be incomplete without touching on emissions from existing industrial and public activities. For ease of discussion, focusing again on nitrosamines, Section 5.2 of Health Canada's 2011 guideline on NDMA in drinking water provides data on samples of ambient air taken in outdoor industrial and urban locations as well as indoor locations contaminated with tobacco smoke [34]. These measurements were taken on a short-term basis. Longer term sampling would be necessary to determine the annual average for NDMA concentration in ambient air at each of these locations. While in some instances the concentration of NDMA in samples was below detection limits, in other instances the measured concentration of NDMA was found to be orders of magnitude greater than the proposed limits in the UK, Norway or US. This was true for an outdoor sample taken close to a chemical factory and an indoor space contaminated by tobacco smoke. This indicates that significant other sources of nitrosamines are already present in our environment and that CCS project developers are working to meet strict limits for these components in a proactive manner.

With reference to HZP, emissions parameters for the two existing gas turbines and two existing auxiliary boilers are provided in Table 4-1 of the Air Impact Assessment report. The combined release rate for NO_x on an annual basis is reported as 79.6 g/s. The annual release rate for SO_2 is reported as 5.8 g/s. After the installation of carbon capture, the release rate from the absorber stacks is expected to be 39.8 g/s for NO_x and 2.9g/s for SO_2. Therefore, on the basis of mass of pollutants emitted, HZP is expected to reduce the amount of NO_x and SO_2 emitted by approximately 50%.

These are just two examples that demonstrate the net benefit that carbon capture stands to provide to society. In addition to reducing the impacts of climate change, despite the potential for secondary emissions, it is expected that carbon capture projects will provide further benefits by meeting existing and evolving standards for air quality.

4.3. The Evolution of Measurement Technology

The Health Canada guideline noted that the detection limit for NDMA in air was in the range of 0.003 - 0.005 $\mu g/m^3$ or 3 - 5 ng/m^3 [33]. Measurement technology continues to improve, however, with limits as low as 0.2 to 0.7 ng/m^3 (UK EA and US EPA, respectively), developers are unlikely to be able to verify the predictions of their dispersion models by physically sampling at receptor sites. It is expected that measurements at the absorber vent will be monitored to ensure they remain below the concentrations input into dispersion models executed during the engineering phase.

However, even at the absorber stack, accurate measurement of secondary emissions remains a challenge that industry is actively working on. During their consultation on defining new limits for air emissions, the UK Environment Agency received a question about the ability of existing technology to accurately measure at the levels being proposed. Their response to this query was: "***To date no certified CEMS for amine monitoring from carbon capture plant has been developed. This is in part because there has been no commercial reason for them to be developed and then certified. The same applies to periodic monitoring. We believe that stack monitoring companies do have the ability to carry out required monitoring but there will be some development necessary to refine measurement methods***." [31]. It is a positive sign that the UK regulator has demonstrated awareness of the limitations of existing sampling and measurement techniques. Maintenance of an open dialogue with key industry players is welcomed as a strategy for expediting development in this area of carbon capture.

4.4. The Value of Knowledge Sharing

As noted in this paper some potential components of secondary emissions are being further studied by industry. It is recommended that, as developers mature their designs and facilities go into operation, plentiful and reliable data be made available from these facilities to help guide the industry as a whole. For example, the technology licensors for both HZP and Tundra have used their current flue gas parameters in tandem with their previous operating experience, pilot plant experience, and in-house simulations to determine expected secondary emissions at the absorber stack. Regular and accurate measurement will help confirm these modelled values. This process also has the potential to provide invaluable insight into whether secondary emission profiles change over longer periods of operation with factors such as variable weather conditions, amine degradation, and potentially because of external emissions from sources such as other industrial or urban activity in the region. Finally, greater volumes of real-world data on secondary emissions will help to improve confidence in the results of dispersion models.

As the CCS landscape evolves, technology licensors will likely need to share information about their products. Shell CANSOLV has provided significant information about their technology to the HZP project developer in order for them to fulfill regulatory requirements in the UK. The developer has also noted that further toxicological analysis of their solvent and its degradation products will be completed as the project progresses. Similarly, MHI has provided information on potential secondary emissions from their absorber in support of the Project Tundra air permit to construct application. Ultimately, beyond the permitting process, all large-scale carbon capture facilities will benefit from the installation of appropriately designed and selected emissions monitoring equipment as well as the use of regular carbon capture specific sample collection, testing and reporting. As noted earlier, this is an area of ongoing development.

In some cases, the regulatory process may direct the project developer to propose controls to manage secondary emissions by identifying existing control technologies that are being successfully used at similar facilities. In the permit application for Project Tundra, the developer notes that there are a limited number of carbon capture projects deployed on coal fired power plants. This necessitated a case-by-case process for determining appropriate MACT to manage potential secondary emissions. This again demonstrates the essential need for open sharing of data and lessons from capture facilities in the near and long-term future. Whereas the regulator will need to provide the pathway for industry to obtain permits in the first instance, sharing of data and the ability to derive insights from this data will be critical to the process of refinement. This will ensure the global CCS industry moves in the right direction to manage secondary emissions.

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