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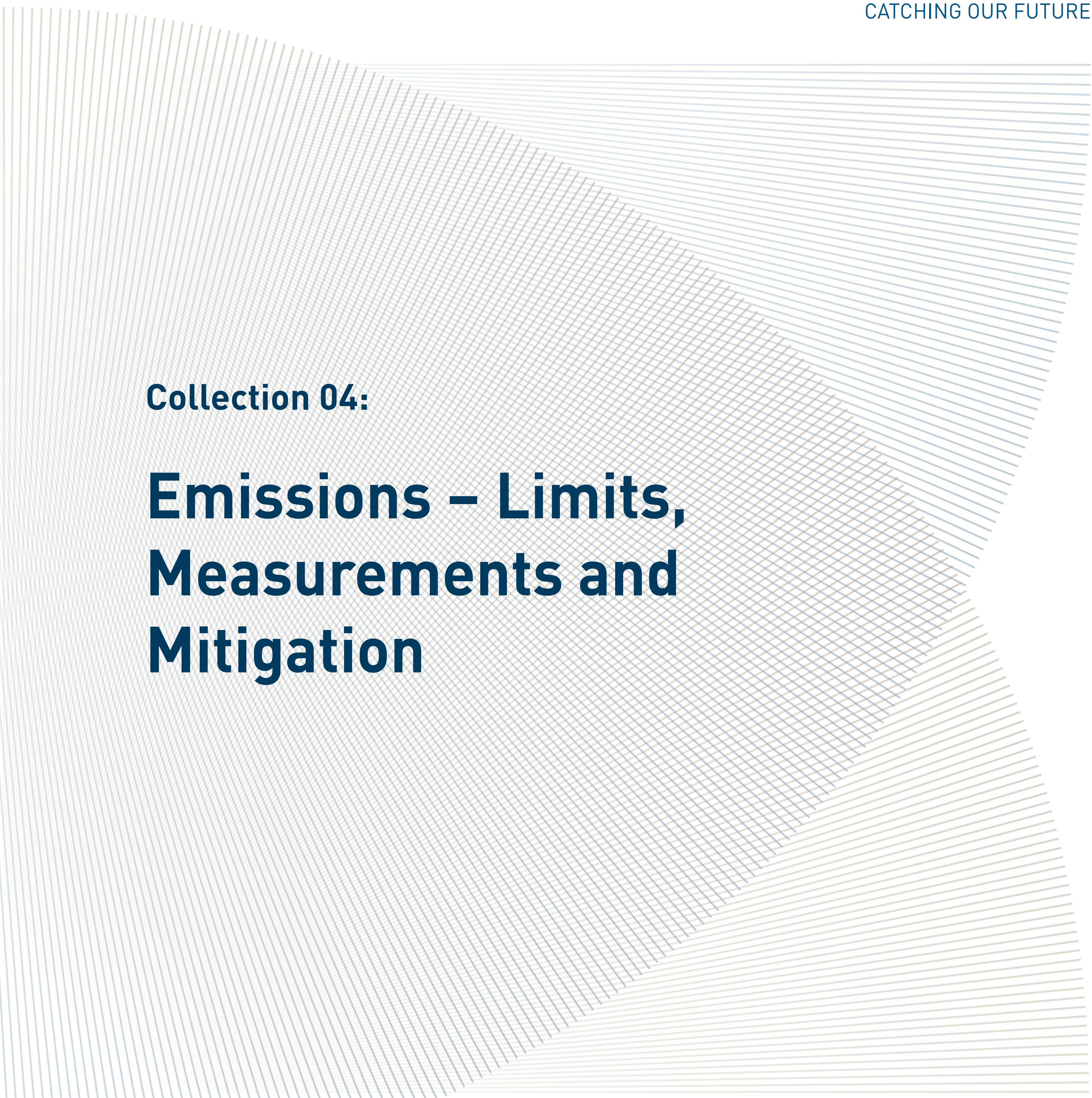

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04

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(2021)

15th International Conference on Greenhouse Gas Control Technologies, GHGT-15

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Atmospheric emissions of amino-methyl-propanol, piperazine and their degradation products during the 2019-20 ALIGN-CCUS campaign at the Technology Centre Mongstad

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Abstract

In the frame of the 2019-20 ALIGN-CCUS campaign, the amine plant at the Technology Centre Mongstad (TCM) was operated with the CESAR 1 solvent, i.e. an aqueous solution of 2-amino-2-methylpropan-1-ol (AMP) and piperazine (PZ), for removing carbon dioxide from the flue gas of Equinor's combined cycle gas turbine plant. An online Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-TOF-MS) was used for quantifying atmospheric emissions of AMP and PZ, as well as emissions of amine degradation products and solvent impurities. Mean and median AMP levels emitted to the atmosphere over an operational period of 13 weeks were 562 and 377 ppb, respectively. PZ emissions to the atmosphere were much lower, with mean and median levels being 6.0 and 0.4 ppb, respectively. Three small carbonyl species (formaldehyde, acetaldehyde, acetone) were emitted at levels of tens to hundreds of ppb. Nitrogen-containing degradation products and impurities of solvent amines with mean emission levels >1 ppb included the following compounds: monomethylamine (MMA), formamide (FA), morpholine (MOR), 4,4-dimethyloxazolidine (DMO), 2-methyl-2-(methylamino)propan-1-ol (MeAMP), 4-acetylmorpholine (AMOR) and a compound with a molecular sum formula of $C_8H_{14}N_2$, which we tentatively assigned to an alkylated imidazole or pyrazole. Low (<5 ppm) emissions of AMP were associated with a low flue gas temperature (<38 °C) and large temperature gradient between the two water wash sections.

Keywords: Amines; 2-amino-2-methyl-1-propanol (AMP); Piperazine (PZ); PTR-MS; TCM; Carbon Capture

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1. Introduction

Amine-based post-combustion carbon capture (PCCC) is the technologically most mature solution for removing carbon dioxide (CO_2) from a flue gas stream. The reduction in CO_2 emissions comes, however, at the expense of amine emissions to the atmosphere. Atmospheric oxidation processes may partially transform the emitted amines into nitrosamines and nitramines [1], which are substances with known carcinogenic or potential carcinogenic properties. Since it is not possible to monitor and surveil nitrosamines and nitramines at ambient sub-ng/m³ levels, exposure to nitrosamines and nitramines is usually calculated taking into account dispersion and atmospheric processing of emitted amines. A key input parameter to such calculations is the emission rate of solvent amines and of smaller amines formed during solvent degradation. Amine emission data are thus of pivotal importance for ensuring an environmentally safe operation of an amine-based PCCC plant. A recent review by Scottish Environment Protection Agency [2] concludes that there is limited open source data available on amine emissions to the atmosphere and that most available data is based on capture solvents such as monoethanolamine (MEA) that are not necessarily representative of the mix of solvents used in state-of-the-art PCCC plants.

Nomenclature

ALIGN	Accelerating Low CarboN Industrial Growth
CCUS	Carbon Capture Utilization and Storage
TCM	Technology Centre Mongstad
PCCC	Post-combustion carbon capture
CCGT	Combined cycle gas turbine
PTR-TOF-MS	Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry
WW	Water wash
CO_2	Carbon dioxide
AMP	2-amino-2-methyl-1-propanol
PZ	Piperazine
MEA	Monoethanolamine
MMA	Mmonomethylamine
FA	Formamide
MOR	Morpholine
DMO	4,4-dimethyloxazolidine
MeAMP	2-methyl-2-(methylamino)propan-1-ol
AMOR	4-acetylmorpholine

The Technology Centre Mongstad (TCM) (www.tcmda.com) in Norway is one of the world's leading facilities for testing and improving CO_2 capture technologies. TCM's tasks also include the assessment of amine emissions to the atmosphere and the development of emission reduction strategies. Only few results from the emission measurements have, however, hitherto been disclosed. This is because detailed emission data would reveal the chemical composition of the solvent, which is, in most cases, confidential business information. Therefore, only MEA emission data are currently available in the open literature [3, 4].

ALIGN-CCUS (Accelerating Low CarboN Industrial Growth through Carbon Capture Utilisation and Storage) is a project financed through the first ERA-NET Co-fund ACT program funded by nine European countries and the European Union Horizon 2020 program. The ALIGN consortium includes 31 partners from industry, research and academia and has considerable involvement of industrial companies and an enterprise organization. The ALIGN-CCUS project aims at accelerating the transition of current industry and power sectors into a future of continued economic activity and low-carbon emissions, in which carbon capture, utilization and storage (CCUS) plays an essential role. For optimizing and reducing costs of PCCC, the ALIGN consortium has implemented test programs at four different pilot plants and testing facilities including TCM, the SINTEF pilot rig at Tiller/Trondheim in Norway, RWE's Coal Innovation Centre at Niederaussem in Germany, and the Pilot-scale Advanced CO_2 Capture Technology

(PACT) facilities in Sheffield in the United Kingdom. TCM's contribution to the ALIGN-CCUS project is aimed at bridging knowledge gaps as well as reducing HSE, technical and financial risks of technology upscaling.

In the 2019-20 ALIGN-CCUS campaign at TCM, flue gas from Equinor's combined cycle gas turbine (CCGT) plant in Mongstad was treated with the aqueous 2-amino-2-methylpropan-1-ol (AMP) / piperazine (PZ) (CESAR 1) solvent. The CESAR 1 solvent was selected due to its lower energy consumption and higher stability as compared to MEA. Among the topics of the study were emission control and monitoring as well as solvent consumption. The main goal of the campaign was to demonstrate that this advanced amine solvent can be used at a large scale and with a real flue gas.

Results from the ALIGN-CCUS project are in the open domain, and we are herein reporting, for the first time, atmospheric emission data of AMP, PZ and their degradation products.

2. Method

The ALIGN-CCUS 2019-2020 campaign was carried out at TCM from September 12, 2019 to January 10, 2020. Flue gas from Equinor's CCGT plant in Mongstad was treated in TCM's amine plant operating with the CESAR 1 solvent. The chemical-analytical set-up to measure atmospheric emissions of amines, amine impurities and amine degradation products is described in detail in a companion paper [5]. Herein, we only use the data collected with an online Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-TOF-MS) [3]. The calibration of AMP and PZ is also described in the companion paper. Formaldehyde, acetaldehyde and acetone as well as acetonitrile were calibrated using a dynamically diluted calibration gas standard (Apel-Riemer Environmental, Inc., Miami, FL, U.S.A.). All other compounds are reported as acetone-equivalents, i.e. the acetone response factor was used for signal quantification. Reported volume mixing ratios have an accuracy of ±10% for calibrated compounds, and ±50% for compounds reported as acetone-equivalents.

3. Results and discussion

3.1. Atmospheric emissions of AMP and PZ

Figure 1 shows the distribution of AMP and PZ volume mixing ratios, respectively, as measured during the 2019-2020 ALIGN-CCUS campaign at TCM. Mean and median AMP levels emitted were 562 and 377 ppb, respectively. PZ emissions were much lower, with mean and median levels being 6.0 and 0.4 ppb, respectively. The mean value is significantly higher than the median value because of sporadic PZ bursts. No experimental data are available in the open literature to compare our data with. Kolderup et al. [6] carried out modeling simulations and estimated total AMP and PZ emissions in the 0.55 – 30 ppm range. The AMP levels observed in this study were similar to MEA levels found in previous work at TCM [7, 4, 8]. Notably, AMP emissions were typically three orders of magnitude higher than PZ emissions. Khakharia et al. [9] reported an AMP-to-PZ emission ratio of 26, while Mertens et al. [10] found two orders of magnitude higher AMP emissions as compared to PZ. This discrepancy cannot be explained by the AMP-to-PZ-ratio in the solvents (3 M AMP and 1.8 M PZ in the Mertens et al. study [10]; 3.6 M AMP and 0.9 M PZ in the Khakharia et al. study [9]; 3 M kg^{-1} AMP and 1.5 M kg^{-1} PZ in the CESAR 1 solvent). The low PZ emission levels observed during the ALIGN-CCUS campaign can be explained by a low entrainment rate of PZ into the gas phase and/or more efficient scrubbing of PZ in the water wash sections.

3.2. Atmospheric emissions of amine degradation products and impurities

10 amine degradation products and 1 solvent impurity were emitted to the atmosphere with a mean and median volume mixing ratio above 1 ppb during the ALIGN-CCUS 2019-2020 campaign (Figure 2). Three small carbonyl species (formaldehyde, acetaldehyde, acetone) were emitted at levels of tens to hundreds of ppb, with acetone reaching the highest levels. It was observed previously [12, 13] that acetone is a major decomposition product of an aqueous AMP/PZ blend. Seven of the remaining species that were emitted to the atmosphere included one nitrogen atom: monomethylamine (MMA), formamide (FA), morpholine (MOR), 4,4-dimethyloxazolidine (DMO), 2-methyl-2-(methylamino)propan-1-ol (MeAMP), and 4-acetylmorpholine (AMOR). The remaining compound has a molecular

sum formula of $C_8H_{14}N_2$, which we tentatively assign to an alkylated imidazole or pyrazole. Notably, MMA was emitted at a mean level of almost 20 ppb. Wang [12] expected MMA to be formed from AMP degradation but did not detect it. Wang [12] also observed the formation of formamide when exposing AMP to UV radiation. MeAMP is a common impurity of AMP and DMO has been observed as a decomposition compound in the liquid phase [12]. But so far, they have not been reported as being released to the atmosphere. MOR, AMOR and $C_8H_{14}N_2$ have not been reported previously. It is also noteworthy that 1-nitrosopiperazine was detected in the emitted flue gas. A tentative quantification puts emission levels well below 1 ppb, but more calibration work is needed for quantifying nitrosamines.

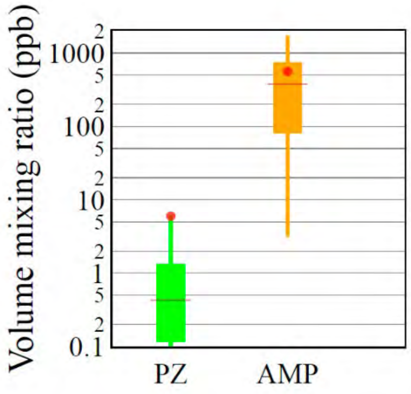

Fig. 1. Distribution of volume mixing ratios of PZ and AMP emitted to the atmosphere when flue gas from Equinor's CCGT plant in Mongstad was scrubbed of CO_2 in TCM's amine plant operating with the CESAR 1 solvent. Boxes represent 25th and 75th percentiles, the horizontal line is the median, the dot is the mean, and whiskers represent 5th and 95th percentiles.

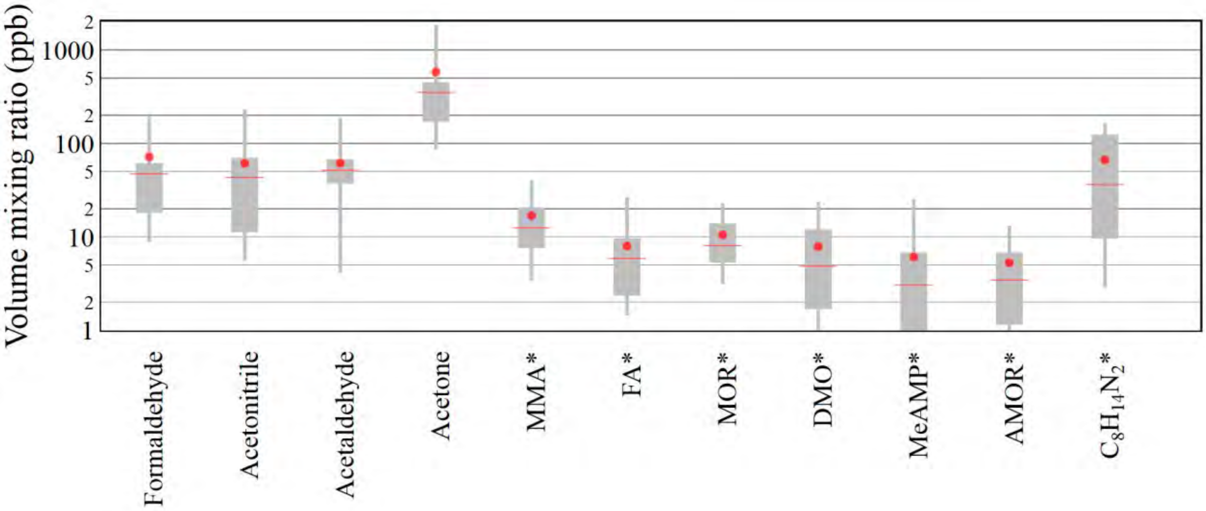

Fig. 2. Distribution of the 10 amine degradation products and 1 solvent impurity (MeAMP) that were emitted to the atmosphere with a mean level > 1 ppb. Boxes represent 25th and 75th percentiles, the horizontal line is the median, the dot is the mean, and whiskers represent 5th and 9^5th percentiles. Compounds marked with an asterisk (*) are reported as in acetone-equivalent mixing ratios (see text).

3.3. Impact of the operational parameters of the plant

The operating parameters of the amine plant obviously influence the level of emissions. Mertens et al. [10] found that emissions depend upon the flue gas temperature and the temperature gradient over the water wash (WW) section. Our initial analysis thus focused on the effect of these two parameters on atmospheric emissions. Figure 3 (upper panel) shows that high (>5 ppm) AMP emissions were associated with high (>38 °C) flue gas temperatures. Figure 3 (lower panel) on the other hand shows that high AMP emissions only occurred when the temperature gradient between the two WW sections was low. Emissions of PZ and degradation products exhibited similar trends. More details will be disclosed in a forthcoming paper.

Our findings are thus in agreement with the observations by Mertens et al. [10], and this information may be used to mitigate emissions from amine plants. Previous work [9, 11] has, however, also shown that other parameters such as solvent temperature, pH and CO_2 content significantly impact atmospheric emissions. The effect of additional parameters will be investigated in future work.

Finally, we would like to point out that the results shown here were obtained when the amine plant was operated with flue gas from the CCGT plant. This flue gas has a low acidic content, which prevents the formation of aerosol particles ("mist") in the absorber column. Currently ongoing studies indicate that emission profile changes significantly when the amine plant runs on the other flue gas available at TCM, which is from the Residue Fluid Catalytic Cracker (RFCC). The results from these ongoing studies will be presented in future work.

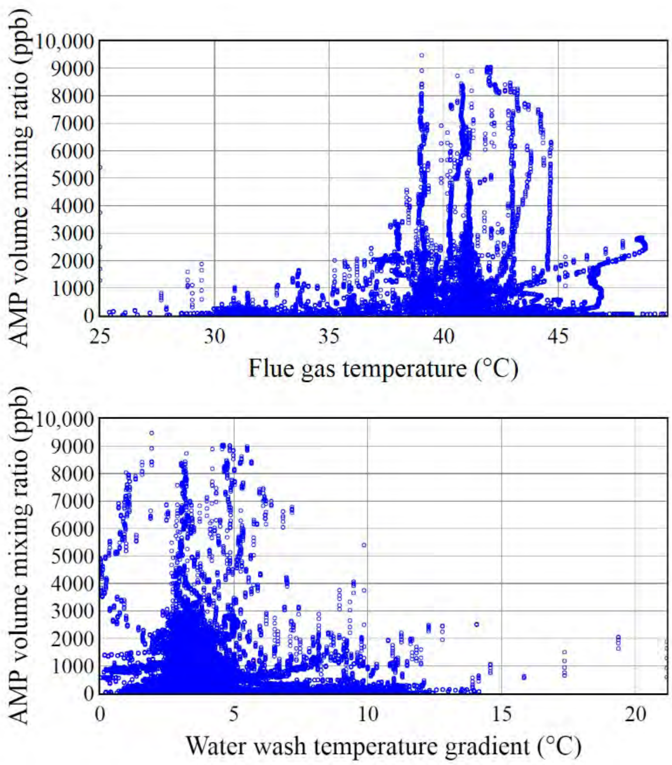

Fig. 3. Scatter plots of AMP emissions versus flue gas temperature (upper panel) and AMP emissions versus the temperature gradient over the water wash sections (lower panel). Data associated with flue gas temperatures below 25 °C were not included in the analysis. Such low temperatures only occur during the plant warm-up and not during regular plant operation.

Conclusions

We herein report, for the first time, the levels of AMP and PZ as well as of their degradation products that are emitted into the atmosphere from a PCCC plant, which was operated on the CESAR 1 solvent. Significant emissions of AMP and of two small reactive carbonyls (formaldehyde, acetaldehyde) will need to be considered in any atmospheric impact assessment study, while minor emissions of other degradation products (in particular of 1-nitrosopiperazine) warrant further investigations. We also characterized the impact of specific plant parameters on emissions and found that high (>5 ppm) AMP emissions were associated with a high flue gas temperature (>38 °C) and small temperature gradient between the two water wash sections. A more in-depth analysis of the collected data will allow us to give recommendations for mitigating emissions from amine-based PCCC plants operating on the advanced CESAR 1 solvent.

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Best practices for the measurement of 2-amino-2-methyl-1-propanol, piperazine and their degradation products in amine plant emissions

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Best practices for the measurement of 2-amino-2-methyl-1-propanol, piperazine and their degradation products in amine plant emissions

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Abstract

We herein present the chemical-analytical setup used to measure atmospheric emissions of amines and amine degradation products from an amine-based post-combustion carbon capture plant. The emission measurements were carried out at the Technology Centre Mongstad (TCM) in Norway, in the frame of the ALIGN-CCUS campaign from September 2019 to January 2020, when the amine plant was operated with the CESAR 1 solvent. This advanced solvent is an aqueous solution of 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ). Four chemical-analytical techniques were deployed for characterizing emission of AMP, PZ and their degradation products: online Fourier Transform Infrared (FTIR) Spectroscopy, online Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS), online Proton-Transfer-Reaction Quadrupole Mass Spectrometry (PTR-QMS), as well as manual impinger sampling followed by offline Ion Chromatography Mass Spectrometry (IC-MS) analysis. AMP was detected by all four methods, with the results being in reasonably good agreement. PZ was detected by PTR-TOF-MS, PTR-QMS and IC-MS, but because of the low emission levels (single-digit ppb) the latter two methods suffered from a positive bias (due to an interfering compound) and a large measurement uncertainty, respectively. 17 amine degradation products were only detected by the PTR-ToF-MS analyzer. We present exemplary results from the emission measurements carried out during the ALIGN-CCUS 2019-2020 campaign and share some of the lessons learned from this exercise.

Keywords: amines; 2-amino-2-methyl-1-propanol (AMP); piperazine (PZ); PTR-MS; TCM.

Introduction

Amine-based post-combustion carbon capture (PCCC) is the technologically most mature solution for removing carbon dioxide (CO_2) from a flue gas stream. The reduction in CO_2 emissions does, however, come at the expense of amine emissions to the atmosphere [1]. Atmospheric oxidation processes may partially transform the emitted amines

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into nitrosamines and nitramines [2], which are substances with known carcinogenic or potential carcinogenic properties. Based on a conservative risk analysis, inhalation exposure to the sum of PCCC-derived nitrosamines and nitramines should be kept below an annual average concentration of only 0.3 ng m^{-3} [3] for the general public. Since it is not possible to monitor such low concentrations in the atmosphere, exposure to nitrosamines and nitramines is calculated taking into account emission rates of amines, as well as the dispersion and atmospheric processing of emitted amines. Amine emission rates need to be measured, but their low concentrations (typically 0.1-10 ppm) and the high humidity levels in the treated flue gas make this a challenging analytical effort.

Nomenclature

ALIGN	Accelerating Low CarboN Industrial Growth
CCUS	Carbon Capture Utilization and Storage
TCM	Technology Centre Mongstad
PCCC	Post-combustion carbon capture
CCGT	Combined cycle gas turbine
PTR-TOF-MS	Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry
PTR-QMS	Proton-Transfer-Reaction Quadrupole Mass Spectrometry
FTIR	Fourier Transform Infrared
IC-MS	Ion Chromatography Mass Spectrometry
VP	Vaporizer
HF	Heated filter
PCR	Principal component regression
SS	Stainless steel
PTFE	Polytetrafluoroethylene
CO_2	Carbon dioxide
AMP	2-amino-2-methyl-1-propanol
PZ	Piperazine
MEA	Monoethanolamine

The Technology Centre Mongstad (TCM) (www.tcmda.com) in Norway is one of the world's leading facilities for testing and improving CO_2 capture technologies. TCM's tasks also include the validation and optimization of emission sampling and measurement techniques. TCM has put considerable efforts into the characterization of atmospheric emissions and nowadays routinely monitors amines in the absorber effluent stream using a variety of analytical methods [4]. These include online Fourier Transform Infrared (FTIR) Spectroscopy, online Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS) [5], online Proton-Transfer-Reaction Quadrupole Mass Spectrometry (PTR-QMS) [6], as well as manual impinger sampling followed by offline Ion Chromatography Mass Spectrometry (IC-MS) analysis [4]. While amine emission data are routinely reported to the authorities, only few results have hitherto been publicly disclosed because the solvent composition is, in most cases, confidential.

ALIGN-CCUS (Accelerating Low CarboN Industrial Growth through Carbon Capture Utilisation and Storage) is a project financed through the first ERA-NET Co-fund ACT program funded by nine European countries and the European Union Horizon 2020 program. The ALIGN consortium includes 31 partners from industry, research and academia and has considerable involvement of industrial companies and an enterprise organization. The ALIGN-CCUS project aims at accelerating the transition of current industry and power sectors into a future of continued economic activity and low-carbon emissions, in which carbon capture, utilization and storage (CCUS) plays an essential role. For optimizing and reducing costs of PCCC, the ALIGN consortium has implemented test programs at four different pilot plants and testing facilities including TCM, the SINTEF pilot rig at Tiller/Trondheim in Norway, RWE's Coal Innovation Centre at Niederaussem in Germany, and the Pilot-scale Advanced CO_2 Capture Technology (PACT) facilities in Sheffield in the United Kingdom. TCM's contribution to the ALIGN-CCUS project is aimed at bridging knowledge gaps as well as reducing HSE, technical and financial risks of technology upscaling.

In the ALIGN-CCUS 2019-2020 campaign at TCM, flue gas from Equinor's combined cycle gas turbine (CCGT) plant in Mongstad was treated with the aqueous 2-amino-2-methyl-1-propanol (AMP) / piperazine (PZ) (CESAR 1) aqueous solvent. The CESAR 1 solvent was selected due to its lower energy consumption and higher stability as compared to monoethanolamine (MEA). Its promising characteristics have made CESAR 1 the new benchmark IEAGHG amine solvent. Emission control and monitoring as well as solvent consumption were among the study topics of the ALIGN-CCUS 2019-2020 campaign. The main goal of the campaign was to demonstrate that this advanced amine solvent can be used at a large scale and with a real flue gas. Results from the ALIGN-CCUS project are in the open domain, thus offering the opportunity to show, for the first time, qualitative and quantitative results on the measurement of AMP and PZ in the absorber effluent. Emission data will be presented in a companion paper.

In this work, we will present the chemical-analytical methods used for carrying out the emission measurements during the ALIGN-CCUS 2019-2020 campaign and present some of the results along with the lessons learned from this exercise.

Methods

2.1. Overview of the campaign and overall system description

The ALIGN-CCUS campaign at TCM was conducted from September 12th 2019 to January 10th 2020. As already stated above, flue gas from a CCGT plant was treated with the CESAR 1 solvent. Figure 1 is a sketch of the analytical set-up used for emission monitoring. Table 1 gives an overview of the analytical methods used for emission monitoring, their time of deployment, the measurement frequency and the compounds measured.

Table 1. Overview of the analytical methods used for emission monitoring, their time of deployment, the measurement frequency and the compounds measured.

Type	Instrument	Start	End	Time step	Compounds measured
Online	PTR-TOF-MS	12-09-2019	10-01-2020	1 min	AMP, PZ + 17 degradation products
	PTR-QMS	12-09-2019	10-01-2020	1 min	AMP (+PZ, positive bias due to interfering compound)
	FTIR	12-09-2019	10-01-2019	5 min	AMP
Offline	Impinger/IC-MS	13-09-2019	19-12-2019	12 samples	AMP (+ PZ, not quantified due to high uncertainty)

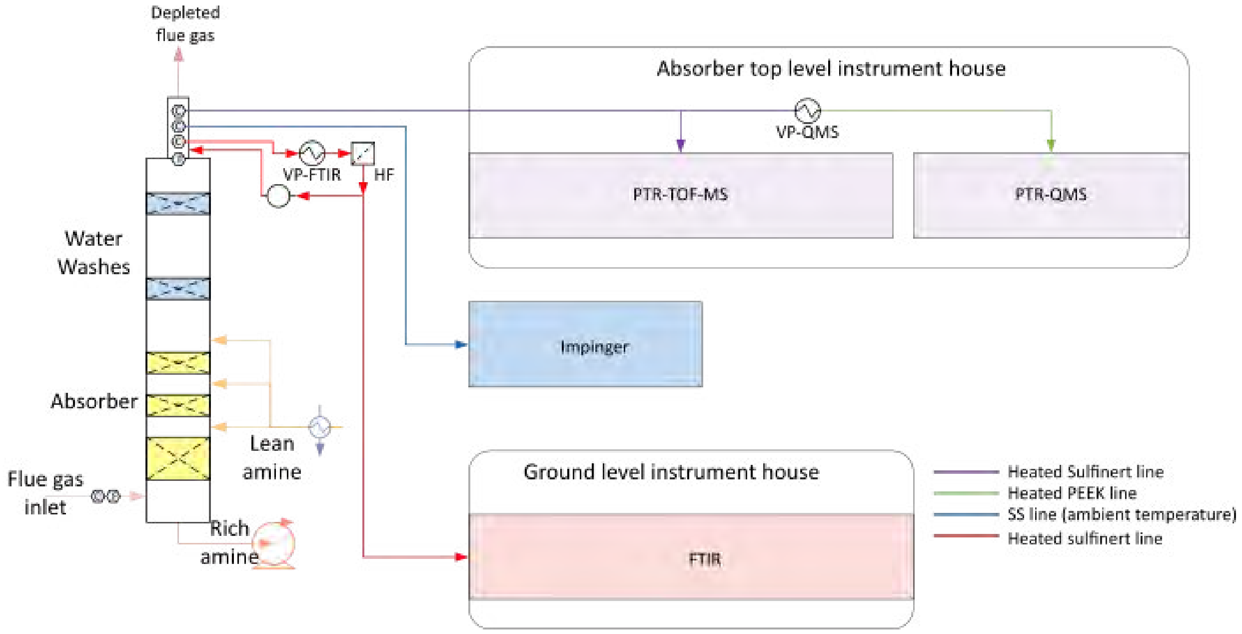

Fig. 1. Process flow diagram of emission sampling of absorber outlet. (VP: vaporizer)

2.2. Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)

PTR-MS is a well-established technique for monitoring organic trace gases online (*i.e.*, without sample pre-treatment), at a typical measurement frequency of 1 Hz and down to ppt levels [7]. In PTR-MS, the gas to be analyzed is introduced into a low-pressure reaction cell wherein organic molecules are softly ionized via gas-phase proton transfer reactions with H_3O^+ ions [8]. The protonated analyte molecules are detected in a quadrupole mass spectrometer (QMS) or a time-of-flight mass spectrometer (TOF-MS). [5] have described the use of PTR-MS for monitoring amines in the treated flue gas emanating from an amine-based PCCC plant. For the work presented herein, we used two different PTR-MS instruments, a PTR-TOF-MS analyzer (model PTR-TOF 8000; Ionicon Analytik, Innsbruck, Austria) and a PTR-QMS instrument (model QMS 300; Ionicon Analytik, Innsbruck, Austria). The latter is a cheaper and easier to use instrument version, which was conceived for industrial monitoring purposes. Both instruments were placed in an analyzer house on top of the absorption tower, and connected to the stack via a ~10 m long heated (120 °C) sampling line made of SilcoNert2000®/Sulfinert. The subsampling line of the PTR-QMS instrument included a vaporizer (VP-QMS) for evaporating potential mist particles. The operating parameters of both PTR-MS instruments were as follow: drift tube pressure 2 mbar, drift tube temperature 120 °C, drift tube voltage 500 V. The resulting reduced electric field strength (E/N) was ~150 Td (1 Td = 10^{-17} V.cm^2).

Both PTR-MS instruments were calibrated for AMP and PZ using a HovaCAL® calibration gas generator (model 312-MF; IAS GmbH, Oberursel, Germany). A quantitative aqueous amine solution (AMP, PZ) was prepared by TCM's analytical laboratory. This solution was evaporated at 180 °C in the HovaPOR evaporator (IAS GmbH, Oberursel, Germany) under a pure nitrogen atmosphere. By increasing the calibration solution flow into the evaporator, the humidity increases in the resulting calibration gas. This allowed us to study the response of the two PTR-MS instruments at different humidity levels.

2.3. Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR instrument (Analect 5000; Schneider Electric) was located in the analyzer house at the bottom of the absorption tower. It was connected to the stack via a 100 m long sampling line made of SilcoNert2000®/Sulfinert. The flue gas was extracted from the stack at a fixed flow rate using a fast flow loop system mimicking isokinetic conditions [9]. The fast flow loop system included a vaporizer (VP-FTIR) for evaporating potential mist particles and a heated filter (HF). The temperatures of these units were adjusted to minimize the thermal degradation of analytes. The FTIR instrument was calibrated using the same HovaCAL® calibration gas generator as described above. Principal component regression (PCR) models were used for extracting CO_2, H_2O, NO, NO_2, SO_2, NH_3, acetaldehyde, formaldehyde, AMP and PZ from the FTIR spectra.

2.4. Impinger sampling followed by Ion Chromatography Mass Spectrometry (IC-MS) analysis

Samples were extracted isokinetically and collected in a standard impinger sampling train including a condensation flask, a filter flask and three absorption flasks. Typical sampling times were 1-2 hours. The samples were analyzed in TCM's laboratory using a Dionex Integrion HPIC System (model ICS-5000, Thermo Fisher Scientific) which included an IonPac CS19 column and an IonPac CG19 guard column.

Results and Discussion

3.1. Measurement of AMP emissions and encountered difficulties

The only compound detected by all four measurement techniques was AMP. The results obtained with the four methods were in good agreement. As shown in Figure 2, the distribution of the measured AMP volume mixing ratios was very similar, with the PTR-TOF-MS, the PTR-QMS and the FTIR instrument measuring median AMP levels of 433, 400 and 388 ppb, respectively. Mean measured AMP levels were 592, 549 and 503 ppb, respectively. Figure 3 shows an exemplary time series of AMP as recorded over a period of ten days. Two impinger samples were collected during this period. The measurements are again in good agreement, the only major discrepancy being the systematically lower levels measured by the FTIR instrument during periods with enhanced emissions. Table 2 shows a systematic comparison for all data collected during twelve impinger sampling periods, with sample collection times ranging from 42 to 136 minutes. The overall agreement was good, even though in some case large discrepancies were observed. It is not clear why the level of agreement varied between the samples. Future work is needed for addressing this issue.

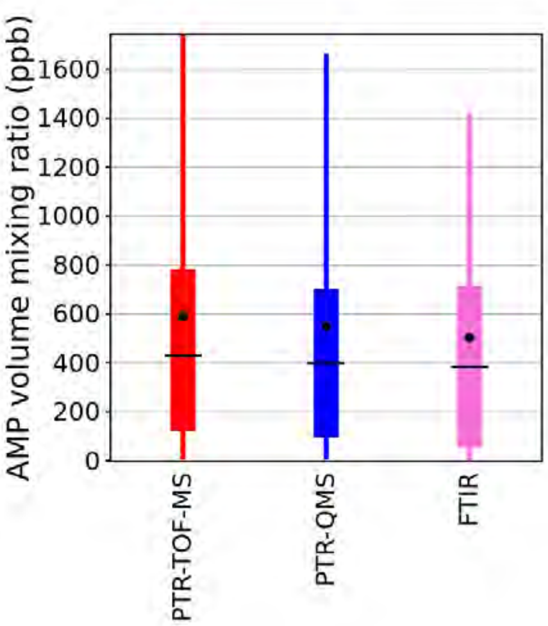

Fig. 2. Distribution of AMP volume mixing ratios as measured in the emitted flue gas by the PTR-TOF-MS, PTR-QMS and FTIR instruments, respectively, over the duration of the whole 2019-2020 ALIGN-CCUS campaign. Boxes represent 25th and 75th percentiles, the black line is the median, and the black dot is the mean. Whiskers represent 5th and 95th percentiles.

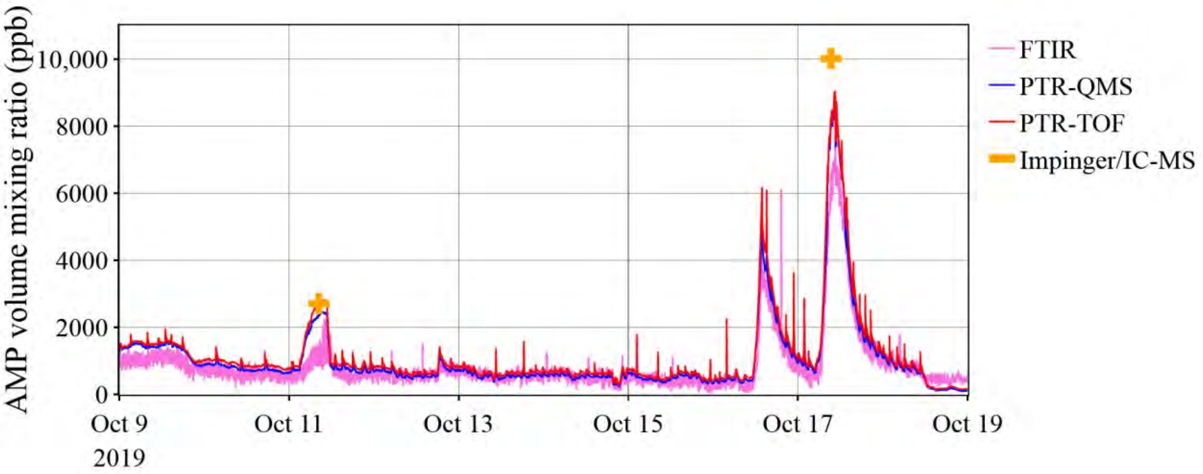

Fig. 3. Exemplary time series of AMP volume mixing ratios as measured in the emitted flue gas by the PTR-TOF-MS, PTR-QMS and FTIR instruments, respectively, in the period from October 9 to October 19, 2019. Also included are the two discrete measurement points obtained via impinger sampling followed by IC-MS analysis.

Table 2. AMP mixing ratios as measured by all four measurement techniques during the impinger sampling periods. Standard deviations are given in brackets.

		AMP (ppb)			
Date	Sampling time (min)	PTR-TOF-MS	PTR-QMS	FTIR	Impinger/IC-MS
2019-09-13	120	470 (33)	416 (26)	18 (21)	740
2019-09-18	60	1009 (25)	1043 (41)	0 (0)	1270
2019-09-24	60	1449 (28)	1271 (12)	521 (131)	1660
2019-09-26	72	1073 (93)	1049 (50)	1042 (107)	1140
2019-10-01	60	1892 (27)	1814 (30)	1393 (150)	2680
2019-10-11	114	2708 (73)	2356 (63)	1209 (263)	2710
2019-10-17	60	8027 (280)	7939 (286)	6113 (452)	10010
2019-10-22	137	495 (37)	461 (37)	103 (55)	950
2019-10-29	128	37 (1)	39 (8)	258 (69)	588
2019-12-11	136	447 (15)	339 (16)	150 (112)	831
2019-12-19	68	30 (3)	12 (1)	14 (19)	110
2019-12-19	42	3893 (462)	3242 (359)	2423 (512)	9200

A number of problems and difficulties were observed for all of the measurement methods used during the ALIGN-CCUS campaign. A forthcoming paper will address these issues in more detail and only a brief outline is given here.

The FTIR analyzer was sampling through a 100 m long sampling line. Long sampling lines are known to require long conditioning times for amines, meaning that peak levels were dampened and thus underestimated. In addition, we found that a stainless steel (SS) line originally connected to the FTIR instrument was corroded. The SS line was replaced with a sampling line made of polytetrafluoroethylene (PTFE) during the campaign. AMP degrades when in contact with a hot SS surface. It was thus important to reduce the temperature of the vaporizer (see Figure 1) to a level at which no AMP decomposition is observed. Finally, it should be noted that the AMP concentrations in the treated flue gas were close to the detection limit of the FTIR instrument, which made the measurements with this instrument less accurate.

The response of PTR-MS instrument to amines usually does not depend on the humidity of the sample matrix. This was not the case for AMP. The response of the PTR-QMS and the PTR-TOF-MS instruments varied by a factor of 5 between dry and humid conditions. For obtaining accurate results, it was essential to calibrate both instruments over the full range of humidity levels observed in the flue gas stack. Also, the reduction, processing and analysis of the PTR-TOF-MS data was highly complex and time-consuming and required a full time engagement of an expert scientist.

Impinger sampling followed by ICMS analysis is time consuming and laborious. Only 12 samples were thus collected and analysed over a period of the whole campaign. In addition, the measurement uncertainty was high at low ppb levels. Only AMP (typically >100 ppb) was thus quantitatively reported from the IC-MS analysis.

Finally, it should be noted, that during the ALIGN-CCUS campaign no mist was observed in the treated flue gas. Measurement problems that occurred in the presence of mist will be presented in a separate study.

3.2. Measurement of PZ

PZ was only present at low ppb levels in the treated flue gas, meaning that only the PTR-TOF-MS instrument was able to quantitatively detect it. PZ also exhibited a humidity-dependent response. It was thus necessary to carry out a humidity-dependent calibration of the PTR-TOF-MS instrument. The PTR-QMS instrument also detected an ion signal at *m/z* 87, which corresponds to protonated PZ. An intercomparison with the PTR-TOF-MS data revealed that a second peak at *m/z* 87 (which can only be resolved by the PTR-TOF-MS and not by the PTR-QMS) becomes quantitatively relevant at low ppb levels. Since these were typical emission levels during the ALIGN-CCUS 2019-2020 campaign at TCM, it was not possible to quantitatively measure PZ with the PTR-QMS instrument. Impinger sampling followed by offline Ion Chromatography Mass Spectrometry (IC-MS) analysis suffered from a high measurement uncertainty at low ppb levels, meaning that not quantitative PZ data were reported during the ALIGN-CCUS 2019-2020 campaign.

3.3. Measurement of solvent degradation products

The PTR-TOF-MS analyzer also detected a series of solvent degradation products. The high mass accuracy (typically <10 ppm) of the measurement combined with an isotopic pattern analysis allowed us to identify the elemental composition (i.e., the molecular sum formula) of the decomposition products. Table 3 lists the *m/z* of the main signals detected in the flue gas, the assigned molecular sum formula and the name of the compound that we assigned (or tentatively assigned) to this signal based on previous work specified in the fourth column. An identification of compounds with a higher degree of confidence warrants complementary analyses by GC-MS or LC-MS.

Table 3. Main *m/z* signals detected by the PTR-TOF-MS instrument in the flue gas that was emitted to the atmosphere when the amine plant was operated with the CESAR 1 solvent. The molecular sum formula was assigned unambiguously; the assignment to a specific chemical substance was based on chemical plausibility and literature data specified in the "References" column. Assignments marked with an asterisk are tentative.

m/z	**Molecular sum formula**	**Assignments**	**References**
87.092	$C_4H_{10}N_2$	Piperazine	
90.092	$C_4H_{11}NO$	2-Amino-2-methyl-1-propanol	
31.021	CH_2O	Formaldehyde	[10]
42.034	C_2H_3N	Acetonitrile	-
45.033	C_2H_4O	Acetaldehyde	[11]
59.049	C_3H_6O	Acetone	[10]
32.050	CH_5N	Methylamine	[11]
46.029	CH_3NO	Formamide	[10]
88.077	C_4H_9NO	Morpholine*	[4]
101.171	$C_2H_8N_2O$	2-Oxopiperazine	[10]
101.108	$C_5H_{12}N_2$	Methylpiperazine	[10]
102.092	$C_5H_{11}NO$	4,4-Dimethyloxazolidine	[10]
104.107	$C_5H_{13}NO$	2-Methyl-2-(methylamino)propan-1-ol*	-
115.088	$C_5H_{10}N_2O$	1-Formylpiperazine	[10]
116.071	$C_5H_9NO_2$	4,4-Dimethyl-1,3-oxazolidine-2-one	[10]
116.082	$C_4H_9N_3O$	1-Nitrosopiperazine	[10]
129.102	$C_6H_{12}N_2O$	1-Acetylpiperazine*	-
130.086	$C_6H_{11}NO_2$	4-Acetylmorpholine*	-
139.122	$C_8H_{14}N_2$	Alkylated imidazole* or pyrazole*	-

Conclusions

Amine-based PCCC plants emit a variety of organic chemicals into the atmosphere. Treatment of CCGT flue gas with the CESAR 1 solvent generates ppb-to-ppm levels of AMP in the emission stream. Our study has shown that such emissions can be measured with sophisticated chemical-analytical techniques (PTR-TOF-MS; impinger sampling/IC-MS) but also with less demanding methods that are suitable for routine industrial monitoring purposes (PTR-QMS, FT-IR). Special care must be taken to avoid losses (due to adsorption and/or thermal decomposition of AMP) in the inlet system and to calibrate the online analyzers. Only the PTR-ToF-MS instrument was capable of detecting PZ at low ppb levels, which were typical emission levels during the ALIGN-CCUS campaign. The PTR-TOF-MS analyser is also capable of detecting amine degradation products, 17 of which were observed at significant levels in the flue gas after treatment with the CESAR 1 solvent. The unambiguous identification of these degradation products would, however, require complementary analyses using highly specific offline GC/LC-MS^n methods.

While it seems unfeasible to make similar chemical-analytical efforts for emission characterization at each amine-based PCCC plant, TCM and its partners provide the know-how and infrastructure to characterize the emission profile of new solvents.

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A compact and easy-to-use mass spectrometer for online monitoring of amines in the flue gas of a post-combustion carbon capture plant

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ABSTRACT

We herein report on the adaptation and deployment of a compact and easy-to-use mass spectrometer for online monitoring of amines in industrial flue gas at ppb to ppm levels. The use of ammonia as a source gas in proton-transfer-reaction mass spectrometry (PTR-MS) greatly simplifies the detection of amines, making it possible to use a low-end commercial instrument version (PTR-QMS 300) for the measurements. We characterized the analytical performance of the instrument (sensitivity, limit of detection, precision, matrix effects) for nine solvent amines (monoethanolamine, dimethylaminoethanol, aminomethylpropanol, methyldiethanolamine, diglycolamine, piperazine, aminoethylpiperazine, methylpiperazine, N-(2-hydroxyethyl)piperazine) and three degradation amines (methylamine, dimethylamine, trimethylamine). The new analyzer was tested and validated in side-by-side measurements with established emission monitoring techniques at the Technology Centre Mongstad (TCM) in Norway. After validation, the instrument was permanently installed on top of the absorber tower to deliver real-time amine emission data to the plant information management system.

Futher information: https://www.sciencedirect.com/science/article/abs/pii/S1750583618304122?via%3Dihub

The Technology Centre Mongstad (TCM) (www.tcmda.com) in

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Ambient Measurements of Amines by PTR-QiTOF: Instrument Performance Assessment and Results from Field Measurements in the Vicinity of TCM, Mongstad

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Abstract

A PTR-QiTOF instrument was deployed in the field in the vicinity of the CO_2 Technology Center Mongstad (TCM) for measuring amines in ambient air. The observed single-to-double-digit pptv levels of dimethylamine (DMA) and trimethylamine (TMA) are comparable to natural background values reported in the literature for these species. No indication was found that these small alkylamines stem from industrial activities at Mongstad. Monoethanolamine (MEA) was observed at single-digit pptv levels, but further analytical work is needed to validate measurements at such low concentrations. No indication was found that small enhancements in ambient MEA levels were caused by emissions from TCM. No other industrial amines (2-amino-2-methylpropanol, diethylamine and piperazine) were detected in ambient air. According to the current state of knowledge, the observed levels of amines pose no harm to human health or the environment.

Keywords: amines, post-combustion CO_2 capture, PTR-MS, baseline measurements

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1. Introduction

Amine-based capture of carbon dioxide (CO_2) results in the release of trace amounts of amines to the atmosphere. While amines are nowadays routinely monitored in stack gas, the detection of amines under highly diluted atmospheric conditions remains an analytical challenge [1]. Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) has been successfully used for on-line monitoring of amines in stack gas [2,3] and in atmosphere simulation chambers [4,5,6]. Recently, the ultra-sensitive proton-transfer-reaction quadrupole ion guide time-of-flight mass spectrometer (PTR-QiToF-MS) has become available [7], which is capable of detecting trace gases at single-digit pptv levels (1 pptv = 1 pmol mol^{-1} = 10^{-12} v/v). In the present study, we have used this novel analytical tool for carrying out exploratory measurements of amines in ambient air in the vicinity of the CO_2 Technology Center Mongstad (TCM).

2. Methods

Ambient air measurements were carried out at Sunsbø (60°46'10.1"N, 5°09'08.6"E), Sande (60°50'56.6"N, 5°00'21.0"E) and Mongstad West (60°48'45.7"N, 5°00'43.4"E) from Aug 6 - 28, Aug 28 - Sept 10 and Sept 10 – 25, 2015, respectively. The geographic location of the three measurement sites and of TCM is shown in Figure 1.

Fig. 1. Geographical map showing the locations of the measurement sites at Sunsbø, Sande and Mongstad West and of the Technology Center Mongstad (TCM).

PTR-MS is an on-line chemical ionization (CI) technique for atmospheric trace gases that has been routinely deployed in atmospheric chemistry field studies over the past decade [8]. Only recently, the ultra-sensitive PTR-QiTOF-MS instrument version has become available which detects gaseous analytes at single-digit pptv-levels [7].

We operated the PTR-QiTOF instrument in the routine mode of operation recommended by the manufacturer (H_3O^+ CI; drift tube pressure 3.8 mbar, drift tube temperature 60 °C, reduced electric field strength 120 Td with 1 Td = 10^{-17} V cm^2). Mass spectra were recorded in the *m/z* 15 to *m/z* 510 range, but only selected signals corresponding to protonated methylamine, dimethylamine (DMA) and ethylamine, trimethylamine (TMA), monoethanolamine (MEA), 2-amino-2-methylpropanol (AMP), diethylamine and piperazine, respectively, were analyzed in detail. The list of target amines was taken from a previous study [1]. The PTR-TOF Data Analyzer v4.44 was used for data analysis [9]. 2-minute and 1-hour averages were generated from the data output.

An optimized inlet system was used for minimizing inlet losses of amines. Ambient air was sampled at a flow rate of 12 liters per minute trough a passivated stainless steel tube (material: SilcoNert® 2000, outer diameter: 6.35

mm, length: 115 cm, temperature: 60 °C). The PTR-QiTOF instrument sub-sampled a flow of 0.5 liters per minute through a heated capillary (material: PEEK, outer diameter: 1.59 mm, temperature: 60 °C). No evidence for inlet losses was found when ambient air was spiked with known amounts of DMA and TMA at pptv levels.

Amine-free air generated from compressed and catalytically cleaned (Pt/Pd at 325 °C) ambient air was periodically (every 12 hours for 30 minutes) fed to the inlet system for instrumental background determination.

Instrumental response factors for DMA, TMA and MEA were calculated from ion-molecule reaction kinetics using the molecular properties reported previously [4,5,6]. The estimated accuracy of the reported volume mixing ratios is ±20% for volume mixing ratios above 10 pptv.

TCM is part of a large industrial complex (refinery, power plant, oil terminal) at Mongstad which is located in a pristine coastal environment. Oil and gas tracers were used for distinguishing between periods when the outflow from the Mongstad complex was advected to the sampling sites and periods when natural background air was sampled. TCM was in operation during the ambient air measurement campaign, with MEA being used for CO_2 capture.

3. Results

AMP, diethylamine and piperazine were not detected at levels above 10 pptv in the recorded mass spectra. It was not possible to measure these species at single-digit pptv levels due to mass spectral interferences. The PTR-QiTOF instrument, in its routine mode of operation, was not capable of detecting methylamine. The abundant O_2^+ signals distorted the mass spectrum in the region where methylamine is detected.

The hourly average time series of DMA, TMA and MEA are shown in Figures 2a, 2b and 2c, respectively. The color-coded data points identify the time periods when the outflow from the Mongstad industrial complex was advected to the sampling site.

DMA was observed at single-digit pptv levels, which is at or close to the instrumental detection limit. The detection of amines at such low concentrations is an analytical challenge and all single-digit pptv data reported herein should be taken with caution. More analytical validation work is needed in this concentration regime. The 2-minute average data show episodic short-term enhancements in the 10 to 22 pptv range at all three measurement sites. These enhancements were found both in natural background air and in the outflow from the Mongstad complex.

TMA levels were typically close to zero, with the exception of an episode lasting from Sept 1 to 12 when hourly average volume mixing ratios up to 49 pptv were recorded. Enhanced levels of TMA were observed at the Sande and the Mongstad West site, both in natural background air and in the outflow from the industrial site.

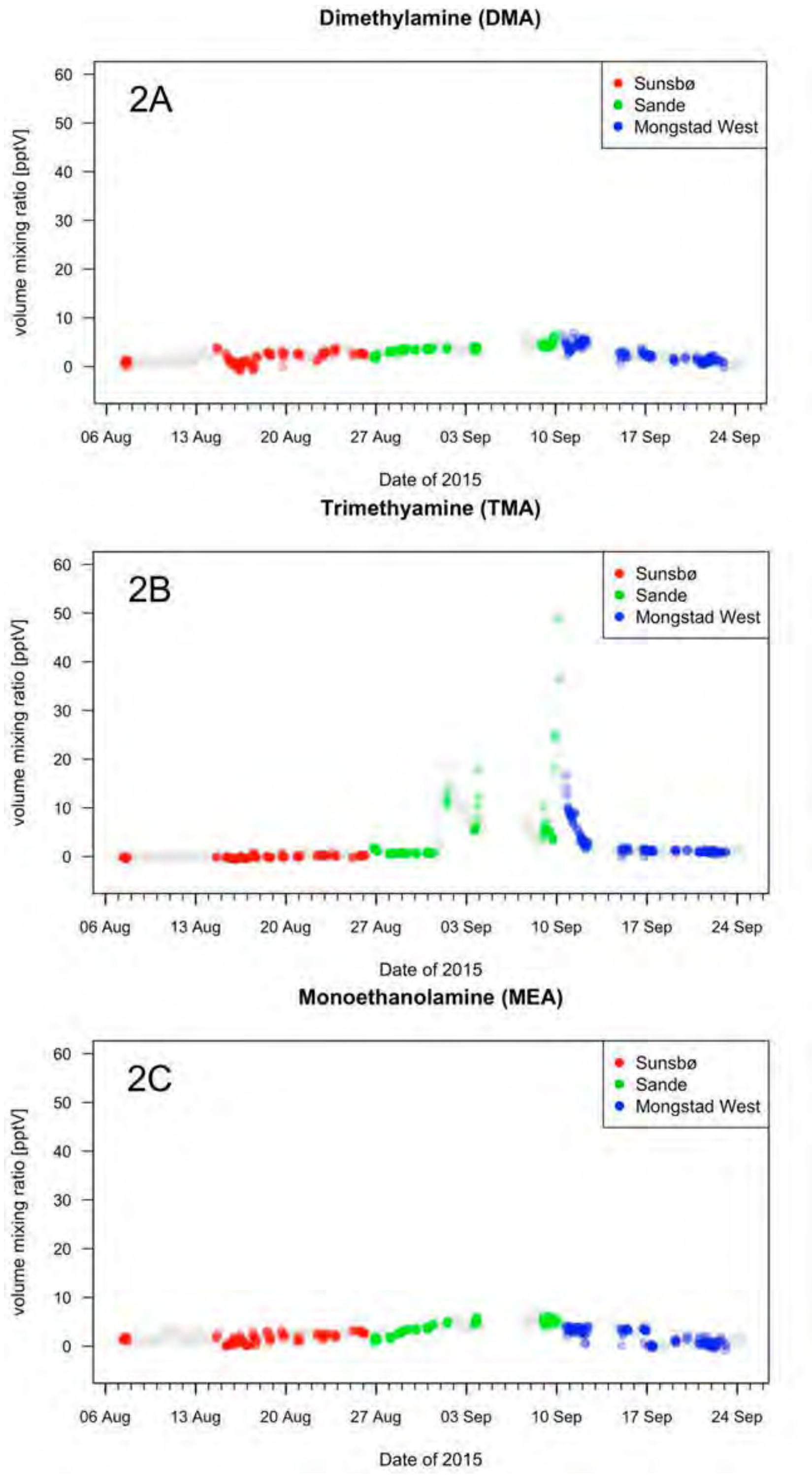
MEA levels were also in the single-digit pptv range. Yet again, these concentrations should be interpreted with caution. A 1-2 pptv enhancement was observed in the period from Aug 31 to Sept 10, both in natural background air and in the Mongstad outflow. This comes as a surprise as MEA is not believed to have natural sources. Further research is warranted to confirm these findings and exclude potential signal interferences for MEA.

The time series data indicate that amine levels were not enhanced in the Mongstad outflow as compared to natural background conditions. This is also reflected in the overall statistical analysis summarized in Table 1.

4. Discussion and Conclusions

A PTR-QiTOF instrument was successfully deployed in the field for the first time to measure amines in ambient air. The observed single-to-double-digit pptv levels of DMA and TMA are comparable to coastal background values reported in the literature for these species [10]. No indication was found that these small alkylamines stem from industrial activities at Mongstad. According to the current state of knowledge, the observed levels of alkylamines pose no direct or indirect harm to human health or the environment.

TCM was operating on MEA during the ambient measurements. Single-digit pptv levels of MEA were observed in ambient air, but no indications were found that these small enhancements were caused by emissions from TCM. Further analytical work is, however, needed to validate MEA measurements at such low concentrations. No other industrial amines (AMP, diethylamine and piperazine) were detected.



Dimethylamine (DMA)

Trimethyamine (TMA)

Monoethanolamine (MEA)

Fig. 2. Hourly average time series of DMA, TMA and MEA amine as measured at Sunsbø, Sande and Mongstad West in August and September of 2015. The color-coded data points identify the time periods when the Mongstad outflow was advected to the sampling sites.

Table 1. Average mixing ratios (in pptv) of DMA, TMA and MEA as observed at the Sunsbø, Sande and Mongstad West sites, respectively, when the Mongstad plume was advected and under natural background conditions. No statistically significant enhancement of amines was found in the outflow from the Mongstad industrial complex as compared to natural background conditions.

	DMA		TMA		MEA	
	TCM	baseline	TCM	baseline	TCM	baseline
Sunsbø	1.2 ± 1.8	1.6 ± 1.9	0.5 ± 0.6	0.5 ± 0.7	0.2 ± 1.9	0.5 ± 1.9
Sande	3.3 ± 1.9	3.4 ± 1.7	5.2 ± 7.9	5.7 ± 7.1	2.4 ± 2.2	2.5 ± 1.8
Mongstad west	0.9 ± 2.1	0.6 ± 1.8	0.7 ± 1.1	1.0 ± 1.1	0.1 ± 2.1	0.5 ± 2.2

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Emission results of amine plant operations from MEA testing at the CO_2 Technology Centre Mongstad

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Abstract

Extensive atmospheric emission monitoring has been conducted at the CO_2 Technology Centre Mongstad (TCM DA) during amine based post-combustion CO_2 capture. The TCM DA amine plant was operated with an aqueous monoethanolamine (MEA) solvent system, treating flue gas from a combined heat and power (CHP) plant. Emission monitoring was conducted by a Fourier Transform Infrared (FTIR) Spectroscopy analyzer, a Proton Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS) analyzer, and manual isokinetic sampling followed by off-line analysis in the laboratory.

Atmospheric emissions of MEA were very low throughout the entire campaign, ranging from a few to a few hundred parts per billion (ppb, 1 ppb = 10^{-9} v/v). Atmospheric emissions of MEA amine based degradation products such as nitrosamines and nitramines were below detectable levels. Atmospheric emissions of ammonia (NH_3) were in the low ppm range. Methylamine was emitted at low ppb range.

Absorber wash water sections were found to effectively reduce atmospheric emissions from amine based solvent system.

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Keywords: MEA, monoethanolamine, atmospheric emission, nitrosamine, nitramine, amine degradation products

1. Introduction

The CO_2 Technology Centre Mongstad (TCM DA) has in collaboration with partners undertaken several months test using the non-proprietary aqueous monoethanolamine (2-aminoethanol, MEA) solvent system at 30 wt% and 40 wt% in an attempt to characterize the performance and atmospheric emissions from such operations [1,2,3]. The operations were carried out at a considerably large scale of about 50.000 Sm^3/h of flue gas supply flow rates from a combined heat and power (CHP) plant, as described elsewhere [1,2,3]. In the CHP plant, the natural gas is combusted in a gas turbine and the flue gas content and characteristics are similar to those of a combined cycle gas turbine (CCGT) power plant. TCM DA has made significant investment in equipment and instrumentation for monitoring of stack emissions. Continuous efforts are being done to improve sampling methods, sampling lines and the instrumental analysis.

Quantitative emission data from a representative CO_2 capture plant is one remaining knowledge gap in the assessment of health and environmental risks posed by the amine-based post combustion capture (PCC) technology [4]. A health risk analysis for the emissions to air from the amine plant TCM DA was recently published [5]. The emission permit granted to TCM DA by the Norwegian Environmental Agency (Miljødirektoratet) in November 2011 regulates the emission levels for solvent amines, alkylamines, aldehydes and ammonia [6]. It also sets requirements for online monitoring and how to calculate the nitrosamine and nitramine environmental concentrations by a dispersion calculation method. The air and drinking water concentrations of 0.3 ng/m^3 and 4 ng/L respectively were associated with negligible excess risk level for cancer (10^{-6}) after lifelong exposure to nitrosodimethylamine (NDMA). Since all amines that are emitted to air from the absorber stack may undergo photo-oxidation in the atmosphere and be converted to nitramines or nitrosamines they will contribute to the environmental concentrations as calculated by the dispersion simulation method. In the granted permit the total sum of nitrosamines and nitramines must be below the given limits. Therefore both amine emissions and direct emissions of nitrosamines and nitramines will contribute to the total environmental budget of the harmful compounds.

Although sampling and analysis of flue gases in general are well known, the wet flue gas containing solvent amine, amine degradation products and other trace components give many sampling and analytical challenges. Very limited standard methods are established for such a task. Several studies were undertaken by international experts for the, now terminated, Carbon Capture Plant Mongstad (CCM) project, and much of the work is available for the public [7]. The CCM project developed a toolbox for qualifying amine based solvent technologies, consisting of the steps liquid sampling, isokinetic gas sampling, sample preservation and sample logistics, sample work-up and analytical procedures, atmospheric chemistry including dry and wet deposition, dispersion modelling including local Mongstad weather conditions, toxicology assessment of major degradation products as nitramines and nitrosamines, solvent degradation rig and test protocol for solvent stress testing as well as process emission reducing technologies. The analytical measurement chain was essential in the toolbox and it is also the basis for the current work.

This work is part of a continuous effort of gaining better understanding of the performance potential of the non-proprietary aqueous MEA solvent system, conducted by TCM DA and its affiliates and owners, in order to test, verify, and demonstrate CO_2 capture technologies [1, 2, 3]. The purpose of the current work is to provide results which quantify the amounts and the compositions of atmospheric emissions sampled and analyzed during amine plant operations treating CHP flue gases. A thorough overview and discussion of available equipment and instrumentation for monitoring of stack emissions will be given. The results are believed to provide realistic emission figures for emission monitoring and control for any future large scale carbon capture and storage (CCS) project due to the considerable size of the TCM DA amine plant.

2. Instrument and analysis

A description of the TCM DA amine plant is given elsewhere [1,2,3].

2.1 Overall system description and instrument position

Removing CO_2 from flue gas by using post-combustion amine based CO_2 capture reduces the emission of greenhouse gases to the atmosphere, but inevitably causes some emissions of amines and amine related degradation products to the atmosphere. Thus, qualitative and quantitative analysis of the emitted components is very important, but this task is far from trivial. For practical purposes, analytical instruments are preferably placed at ground level, but in that case a long sampling line (often >50 m) is required to direct the treated flue gas from the top of the absorber into the apparatus at ground level. This sample line has to be heated to well above the dew point of the gas to avoid condensation and possibly unwanted adsorption and/or reaction of emitted components.

TCM DA applies different measurement techniques to monitor and quantify the amounts and concentrations of emitted compounds. Some of the analyzer techniques currently applied on a permanent basis are;

- Fourier Transform Infrared (FTIR) Spectroscopy
- Proton Transfer Reaction Time of Flight Mass Spectrometry (PTR-TOF-MS)
- Manual isokinetic sampling technique with impingers and subsequent off-line laboratory analysis (carried out by TCM DA, Statoil CP Laboratory, SINTEF and Ramboll)

Online gas phase concentration measurements are also performed at ground level (via a sample line) using a Fourier Transform Infra-Red (FTIR) Spectroscopy instrument and a Proton Transfer Reaction – Time of Flight – Mass Spectrometry (PTR-TOF-MS) device. This online equipment is placed in an analyzer house at ground level. At the absorber top, isokinetic sampling is performed on a regular basis. There is an analyzer house and a shelter on the top of the amine absorber where all the equipment is located, as seen in Figure 1.

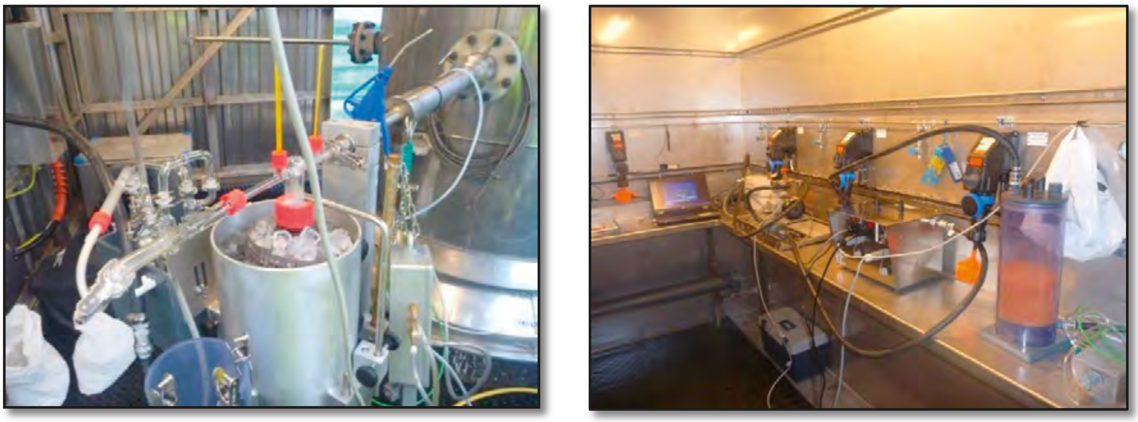


Figure 1: Emission sampling set-up on the top of the amine absorber. Stack configuration (left) and sampling control from analyzer house (right)

Extracted gas is sampled from the stack through an impinger train containing absorption liquids. By onsite measurement of the gas flow and laboratory analysis of the impinger liquids, the gas phase concentration of different components can be determined. The measurement system is shown schematically in Figure 2 and the techniques are further explained in the sections below.

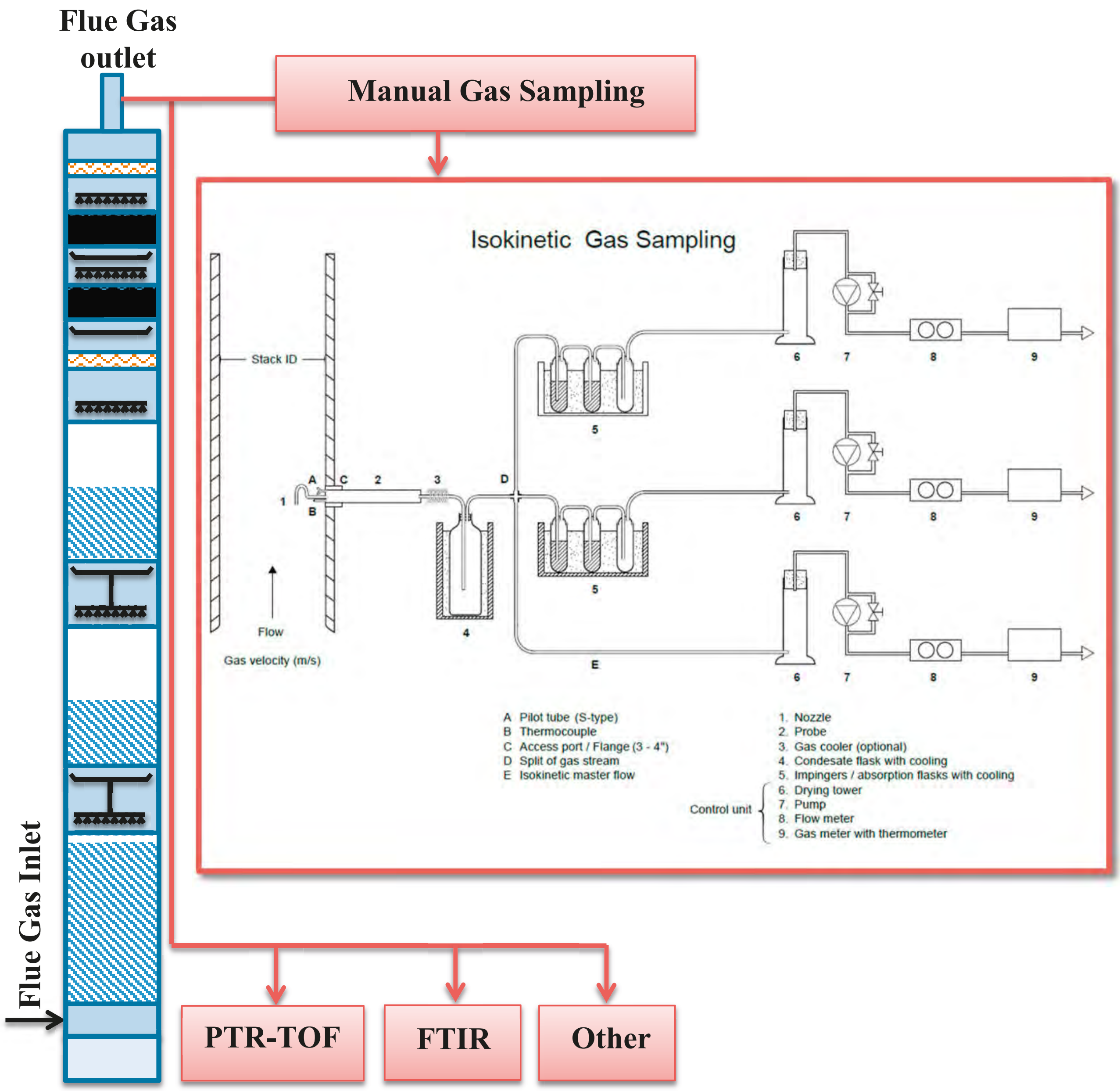


Figure 2: Schematic drawing of the emission monitoring set-up at the TCM DA amine plant

2.2 Sampling lines

The sampling line bundle installed at TCM DA is 101 meters long. It consists of 3 separate lines made from the following materials, respectively:

- PFA Teflon®
- Electro-polished stainless steel
- Sulfinert®-treated passivated stainless steel

All lines can be heated to 140 °C. Sample transfer via a heated sampling line has several benefits over placing the equipment at the top of the absorber:

- Easy access to the analyzer for maintenance and calibration and to utilities such as power, gas supplies, etc.
- Increased physical space for the analyzer
- Safer operations

Some negative aspects are however:

- Delayed analyzer response
- Potential degradation reactions and adsorption effects in the sampling line

Potential sample line effects are rarely reported in open literature. It is generally accepted is that the sample path should be kept as short as possible, and that the line temperature should be well above the dew point. However, increasing the temperature too much may lead to unwanted decomposition, to potential formation of nitrosamines, and to other sampling artefacts. Switch between different sample lines should be avoided due to memory effects. The effects of different sample lines were investigated by Cents et al [8].

2.3 FTIR analyzer

The FTIR model Anafin 2000 is employed at TCM DA to measure standard gas phase components (CO_2, water, NO_x, SO_x) as well as amines, aldehydes and ammonia. The analyzer operates at wave numbers between 500 and 7000 cm^{-1}, with a resolution of 2 cm^{-1}. The path length is 7 meters. The detection limit for amines, aldehydes and ammonia is on the order of 1 ppmv. According to the discharge permit from the Norwegian Environmental Agency (Miljødirektoratet), TCM DA is allowed to emit 6 ppmv of total amines as a daily average [6]. For this purpose, the detection limit of the FTIR instrument is satisfactory.

The FTIR is connected via heated sampling lines to sampling probes at the absorber inlet (downstream DCC), absorber outlet and desorber overhead condenser outlet. An automatic stream selector makes it possible to program the plant's control system to alternate between the different measuring locations as desired. The FTIR is calibrated for a list of standard flue gas pollutants, including CO_2, SO_2, NH_3, etc., as well as solvent amines and some volatile degradation products e.g. aldehydes. The instrument is not set up for measuring alkyl amines, nitrosamines and nitramines.

The FTIR technique has the advantage that the sample is measured without any preconditioning, hence reducing the risk for analytical artefacts. To avoid water condensation, the FTIR gas cell is heated to 85°C and the sampling lines are heated to 120°C. Target compounds contained in mist or droplets are likely to be evaporated at these temperatures. The FTIR monitor thus measures the total content of analytes in the flue gas. A draw-back of the FTIR technique is the interference from water vapor which results in a relatively high detection limit. The experience is that NH_3 and amines can be detected down to 1 ppm levels. This is also in accordance with earlier measurements of gaseous emissions in post combustion carbon capture [9, 10].

2.4 PTR-TOF-MS analyzer

The PTR-TOF-MS (model PTR-TOF 8000) used is manufactured by Ionicon Analytik (Innsbruck, Austria). The PTR technique has been widely used for environmental volatile compound measurements for over a decade. Its measurement principle is based on soft ionization, via proton transfer, followed by high mass resolution mass spectrometric analysis. At TCM DA, the PTR-TOF-MS instrument subsamples from the main sample line through a heated (100-130°C) Siltek inlet line. The sample flow is diluted by a factor of 10 to 20 with bottled synthetic (zero) air, to avoid ion signal titration caused by high ammonia levels. The PTR-TOF-MS is able to measure amines, ammonia, aldehydes, ketones, carboxylic acids, nitramines and nitrosamines which are all important target compounds in amine based CO_2 capture. The analytical setup at Mongstad is described in recent publications by Zhu et al. [11, 12].

2.5 Manual gas emission sampling

The analytical value chain applied for manual gas emission sampling and analysis is schematically shown in Figure 3. This value chain governs the measurement and is described in details below.

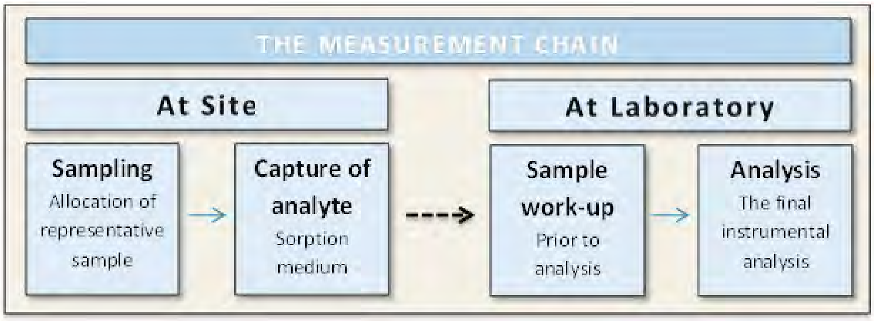


Figure 3: Schematic drawing of the emission measurement value chain

Sampling. The TCM DA stack is designed to achieve flow conditions suitable for isokinetic flue gas sampling as specified in the standard EN 15259:2007. The stack is insulated to minimize condensation. Sampling nozzles are located at a level 2 meters below the stack exit. A sampling system from Paul Goethe GmbH in Germany is used for allocation of a gas emission sample. The equipment is operated from an associated control unit (iTES). The special sampling equipment configuration is assembled for amine emissions based on experiences from the CCM project [7]. Isokinetic gas sampling principles are used to secure representative sampling from a ducted gas stream where two-phase conditions (particles or droplets with diameter > 1 μm) are present or may occur. From an amine absorber the presence of droplets in the flue gas has to be considered, hence isokinetic gas sampling is an assurance for representative samples.

Capture of analyte. The double tube sampling probe was cooled with pressurized air in order to start condensation of the extracted gas sample stream. Typical amine emission analytes are captured by two principles, condensation and liquid absorption. It is experienced that the main sampling step is condensation. The condensate flask is kept cool in an ice bath and has a size and design to maximize the condensation capacity. In this way the gas is dried and further downstream split to subsequent impinger trains or solid adsorbents. It is further experienced that only for the most volatile components like NH_3, small alkyl amines and aldehydes the second trap based on stepwise liquid absorption or solid phase adsorption is significant. In case of mist formation in the absorber, submicron aerosols will enter the sampling train. It is known that aerosols potentially can have limited retention through liquid sampling systems. In order to improve the capture of aerosols, a high capacity condensation step is followed by jet-impinger flasks to force agglomeration. However mist is normally not associated with the CHP flue gas.

The condensates were preserved with sulfamic acid at site directly after sampling to avoid potential nitrosation of secondary amines [7]. Ammonia and the different amines were absorbed in 0.05 M sulphuric acid, the aldehydes and ketones were adsorbed on DNPH cartridges (Sep-Pak DNPH-Silica Long Body Cartridges, Waters). For nitrosamines and nitramines 10 g/L sulfamic acid solutions were used as second sampling step.

Sample work-up. Samples were brought to TCM laboratory and immediately cooled or frozen for storage until analysis. As a principle the condensate sample was prepared for analysis first and subsequent absorbent solutions were prepared and analyzed secondly, with various experimental techniques (Table 1). This often includes extensive laboratory work.

Analysis. Expected degradation and emission products from a MEA based solvent system, were assessed from a recent study using the solvent degradation rig for stress testing of MEA [13]. The target analytes for the current work is given in Table 1. These compounds cover the requirements set forth by the Miljødirektoratet in the emission permit.

Table 1. TCM DA sampling and analysis configuration and principle for different parameters / component groups

Parameters/ component groups	Sampling	Analysis
Amines (solvent)	Condensate + 2x 0,05M sulphuric acid impingers + empty flask	LC MS QQQ
Amines (alkyl)	Condensate + 2x 0,05M sulphuric acid impingers + empty flask	UPLC-MS/MS (Ramboll [7])
Ammonia	Condensate + 2x 0,05M sulphuric acid impingers + empty flask	Cation chromatography, IC-ECD
Aldehydes	Condensate + 2x DNPH cartridges	LS MS QQQ
Nitrosamines* (Specific, generic and TONO)	Condensate + 2x 10 g sulfamic acid impingers + empty flask	See * (Ramboll [7])
Nitramines	Condensate + 2x 10 g sulfamic acid impingers + empty flask	UPLC-MS/MS or GC-HRMS (Ramboll [7])
pH**	-	pH-paper [7]
Nitrite (NO_3^-)**	-	Anion chromatography, IC-ECD [7]

*Specific; CLLE extraction followed by UPLC-MS/MS or GC-HRMS . Generic; LLE followed by analysis on GC-HRMS. TONO; Quench of soluted nitrite followed by break of N-NO bond in a reaction chamber. Total NO released from the N-nitroso groups detected by chemiluminscence analyzer.
**For sample preservation and work-up.

Amines, nitrosamines, and aldehydes were analyzed using an LC MS-MS QQQ (Agilent). The condensate from the first impinger was analyzed directly on the LC MS, the acidic impinger solutions were diluted before analysis. Ammonia was analyzed on an ion chromatograph (IC).

2.6 Additional analyzer techniques: Voice200 and PTR-QMS

TCM DA also tested a Voice200 analyzer from SYFT Technologies and a PTR-QMS 300 analyzer from Ionicon. These instruments operate on the same measurement principle as the PTR-TOF-MS but include cheaper and less specific quadrupole mass analyzers. Results from both analyzers compared well with the PTR-TOF-MS data. The results are not presented in this paper.

3. Results and Discussions

3.1 Analysis of Solvent samples

Solvent degradation processes were monitored during the course of the entire MEA campaign. The solvent amine, ammonia, and some degradation products were analyzed by TCM DA and Statoil CP laboratories. Alkyl amines, aldehydes, ketone, generic nitrosamines, solvent specific nitrosamines and nitramines were analyzed by Ramboll and SINTEF laboratories.

The concentration of the solvent amine was observed to remain stable over the extended period of the campaign indicating reasonable degradation rates of the solvent amine. The main degradation products of MEA were found to be amides, amino acids and other amines. Heat stable salts were also measured through the entire campaign, anions (OA, GA, FA, NO_3^-) by IC and total heat stable salts (HSS) by ion exchange and titration. Figure 4 displays the evolution of various degradation products and heat stable salts in the solvent. The components and amounts found were expected from an aqueous based MEA solvent system [9].

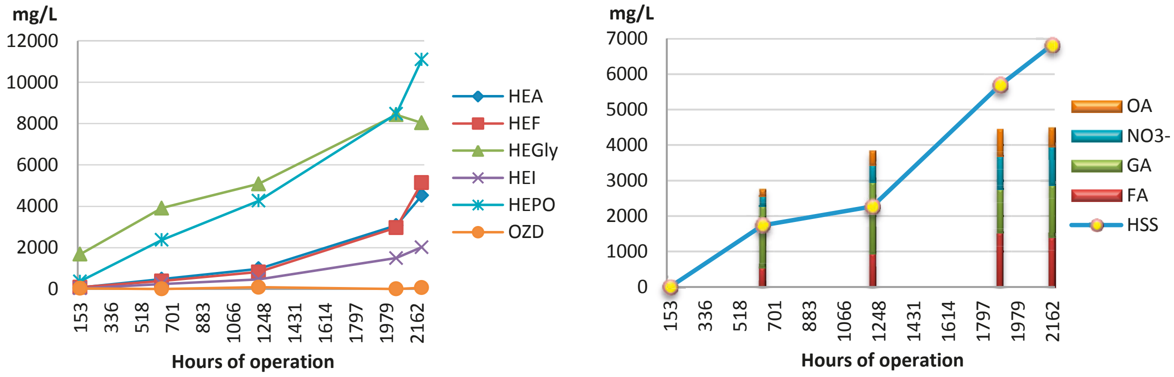


Figure 4: Results from some major degradation components (left figure) and heat stable salt formations (right figure) in the aqueous MEA solvent system during treatment of CHP flue gas

Two solvent specific nitrosamines, N-nitrosodiethanolamine (NDELA) and N-nitroso-2-hydroxyethyl-glycine (Nitroso-HeGly), were detected in the solvent as the degradation process progressed (Figure 5). The total concentrations of nitrosamines (TONO) were measured to be 797 µmol/L.

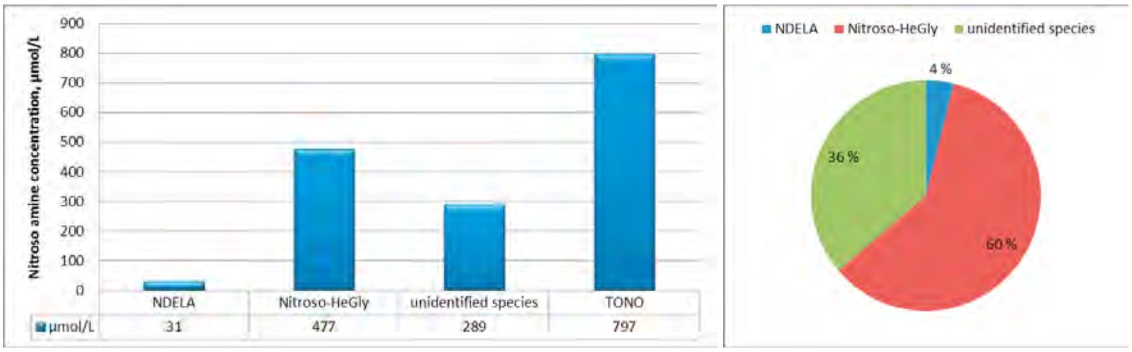


Figure 5: Results from degradation of solvent amine MEA (04.02.2014) [13]

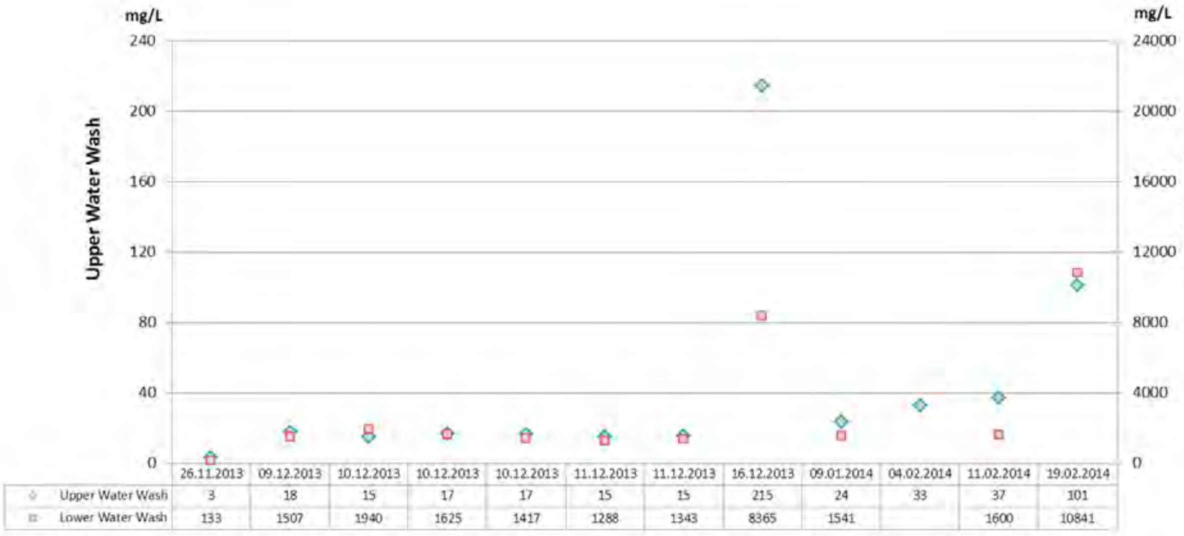
Since MEA is a primary amine it is not expected to form a stable nitrosamine. The identified compounds are thus formed from secondary amines occurring as impurities in the solvent or being formed during the degradation reactions. As is shown in Figure 5, there are still some unidentified nitrosamines in the used solvent sample. These nitrosamines are formed from high molecular weight amines and have low volatility. Only in the first water wash stage low quantities of nitrosamines were found (see below).

The solvent specific nitramine (MEA-NO_2) was detected at a concentration of approximately 2 mg/L (Table 3).

3.2 Analysis of wash water samples

MEA was periodically measured in the wash water from both water wash sections. The wash water sections are specifically designed to physically absorb gaseous and entrained aqueous MEA before the depleted flue gas is emitted to atmosphere. Figure 6 shows that the liquid phase concentration in the first wash water section (Lower wash water – right y-axis) was about 100 times higher than the upper section (Upper Water Wash – left y-axis). The results from 16/12-2013 show higher results, the temperature in the flue gas was 47°C and this will give higher MEA concentrations. Going from 30 to 40 wt% MEA in the solvent, will also give higher MEA concentrations in the water wash sections and this is measured at 19/2-2014, where the solvent MEA concentration was 40 wt%. Methylamine and minor amounts of ethylamine were also found in water wash samples, as presented in Table 3.

Figure 6 clearly demonstrates the effectiveness of two water wash sections.



	26.11.2013	09.12.2013	10.12.2013	10.12.2013	10.12.2013	11.12.2013	11.12.2013	16.12.2013	09.01.2014	04.02.2014	11.02.2014	19.02.2014
◇ Upper Water Wash	3	18	15	17	17	15	15	215	24	33	37	101
□ Lower Water Wash	133	1507	1940	1625	1417	1288	1343	8365	1541		1600	10841

Figure 6: MEA concentrations in wash water 1 and 2.

The concentration of alkylamines, nitrosamines and nitramines in wash water samples are given in Tables 2 and 3. TONO were above detection limit only in the first water wash section, in one of two samples. This clearly indicates that nitrosamine volatility is low and that nitrosamines escaping from the solvent are efficiently captured in the first water wash section. No generic or solvent specific nitramines were found in either of the wash water sections.

Methylamine and minor amounts of ethylamine were found in low concentrations (µg/L) and it is seen that the water wash also has effect of these volatile compounds. No generic or solvent specific nitramines were found in either of the wash water sections.

Table 2. TONO (Total nitrosamines) measurement, measured by Ramboll (flue gas, wash water) and Sintef (lean MEA).

Date	Sample	TONO, µmol/L	Operational Conditions
11.02.2014	Wash water 2	<0.05	30 wt% MEA
11.02.2014	Wash water 1	0.13	30 wt% MEA
04.02.2014	Lean MEA	797	30 wt% MEA

Table 3. Degradation components in solvent and wash water measured by Ramboll

Compound	Unit	Wash water 1 11.02.2014	Wash water 2 11.02.2014	Lean MEA 04.02.2014
Methylamine (MA)	µg/L	3700	1600	-
Dimethylamine (DEA)	µg/L	<50	<500	-
Ethylamine (EA)	µg/L	270	<500	-
Diethylamine (DiEA)	µg/L	<50	<50	-
Ethylmethylamine (EMA)	µg/L	<100	<1000	-
MEA	mg/L	1600	37	-
DEA	mg/L	<0.05	<0.5	-
Morpholine	mg/L	5.8	<1	-
MEA-NO2	µg/L	<1	<1	2120
Dimethylnitramine	µg/L	<0.2	<0.2	<2
Diethylnitramine	µg/L	<0.4	<0.4	<4
NDMA	µg/L	<0.1	<0.1	<1
NMEA	µg/L	<0.1	<0.1	<1
NDEA	µg/L	<0.1	<0.1	<1
NDPA	µg/L	<0.1	<0.1	<1
NPYR	µg/L	<0.1	<0.1	<1
NMOR	µg/L	<0.2	<0.2	<2
NPIP	µg/L	<0.1	<0.1	<1
NDBA	µg/L	<0.1	<0.1	<1
NDELA	µg/L	<1	<1	4200

3.3 Analysis of gas emission samples

Thirteen manual isokinetic sampling emission campaigns were conducted during the MEA-campaign. All emission samples were collected by TCM DA, except one which was performed by FORCE Technology. The amine plant operating conditions and detailed emission results are given in Tables 4 to 6. All nitrosamine and nitramine emissions were below detection limits. Emissions of alkyl amines were limited and only methylamine is quantified in the low ppb range. Possible emission of unknown compounds has been investigated via PTR-TOF-MS. A list of identified or tentatively identified compounds is given in Table 7. No alkylamines, nitrosamines and nitramines were detected by PTR-TOF-MS.

Table 4. List of emission measurements during the MEA campaign

Date and time	Start	Stop	Flue Gas volume, m^3/h	Temp. gas out, °C	Operational Conditions	Operational hours*
26.11.2013	09:14	11:14	58.000	46	30 wt% MEA	50
09.12.2013	10:33	12:33	50.000	25	30 wt% MEA	350
09.12.2013	13:33	15:33	50.000	25	30 wt% MEA	350
16.12.2013	10:38	12:38	47.000	43	30 wt% MEA	500
08.01.2014	12:11	14:11	49.000	25	30 wt% MEA	1000
08.01.2014	14:35	16:53	49.000	25	30 wt% MEA	1000
08.01.2014	17:12	19:12	49.000	25	30 wt% MEA	1000
09.01.2014	10:20	12:20	49.000	25	30 wt% MEA	1030
09.01.2014	12:40	14:40	49.000	25	30 wt% MEA	1030
27.01.2014	12:25	14:25	61.000	25	30 wt% MEA	1260
04.02.2014	11:53	13:53	62.000	27	30 wt% MEA	1390
11.02.2014	08:15	10:15	49.000	26	30 wt% MEA	1540
14.02.2014	10:50	12:50	62.000	25	40 wt% MEA	1600

* Operating hours counted as hours with CO_2 capture

Table 5. Result from isokinetic gas emission measurements during the MEA campaign

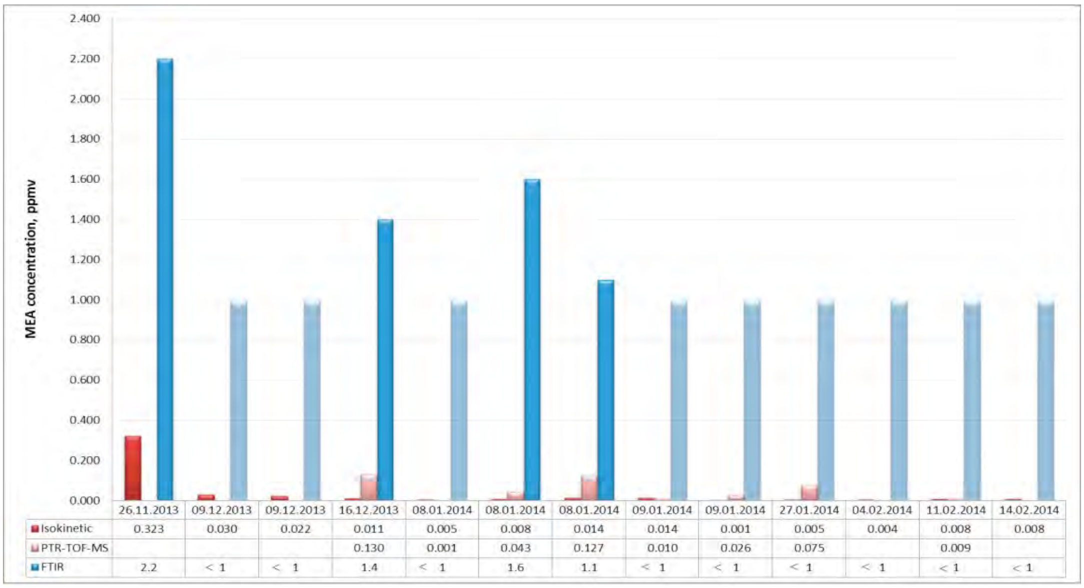
Date	MEA, $\mu g/m^3$	MEA, ppmv	NH_3, $\mu g/m^3$	NH_3, ppmv	Formaldehyde, $\mu g/m^3$	Formaldehyde, ppmv	Acetaldehyd, $\mu g/m^3$	Acetaldehyd, ppmv
26.11.2013	848	0.323	6413	8.3	-	-	-	-
09.12.2013	78	0.030	4907	6.3	-	-	-	-
09.12.2013	59	0.022	5242	6.8	-	-	-	-
16.12.2013	29	0.011	8907	11.5	-	-	-	-
08.01.2014	14	0.005	6336	8.2	-	-	-	-
08.01.2014	21	0.008	9611	12.4	-	-	-	-
08.01.2014	36	0.014	6452	8.3	-	-	-	-
09.01.2014	38	0.014	6729	8.7	-	-	-	-
09.01.2014	3.5	0.001	6806	8.8	-	-	-	-
27.01.2014	14	0.005	-	-	3.1	0.002	18.1	0.009
04.02.2014	12	0.004	-	-	4.4	0.003	31.7	0.017
11.02.2014	21	0.008	-	-	4.3	0.003	31.7	0.016
14.02.2014	22	0.008	10031	13	-	-	-	-

Figure 6 and Figure 7 display atmospheric emission results of MEA and NH_3 from absorber outlet over the entire campaign. Figure 6 display emission results from the FTIR and PTR-TOF-MS analyzer in comparison with results from manual isokinetic sampling and analysis. The MEA FTIR results are not considered to be reliable in the low ppm range, since they are below/around the detection limit. The first measurement (performed on the 26th of November) showed emissions above 300 ppb. The reason for the higher amine emission in the first measurement is related to amine plant operating conditions. The NH_3 emissions were reasonably low and as expected for MEA.

According to TCM DA experience the aldehyde concentrations were varying from low ppbv to several hundred ppbv during operations. Results found in this campaign and earlier campaigns are in agreement, and they are confirmed by third party. The FTIR is not measuring aldehydes below 1 ppm, but PTR TOF gives a good agreement to results found by isokinetic sampling and analysis, see tables 7 and 8. The PTR TOF is a good candidate for a reliable online analyzer of aldehydes in the ppb range.

Comparison of emission results from three sampling and analysis methods is somewhat tricky as there are some fundamental differences like; sampling point, sample extraction principles and sample transfer to the collecting or detection units. In this case manual samples are collected on the top of absorber using isokinetic extraction principles while the online methods are extracted non-isokinetic and switched in through a 101 meter long sampling line. Hence a comparison of MEA emission data can reflect differences in the sampling configuration. The analytical differences are first of all related to instrumental detection limits. Taking sampling and analytical differences into account the comparison of results is summarized and illustrated in figure 6. It is clear that the FTIR data is affected by high detection limit and by then increased uncertainty for this low ppm to ppb-level. Results from manual sampling and online PTR-TOF-MS are first of all according to both methods reported in a low concentration level (0,001 – 0,3 ppmv). The variation between the two data sets is significant and in general manual sampling reflects lower values than online PTR-TOF-MS results. Based on TCM-experience it is likely that the different sampling set-up explain this. TCM has experienced during this MEA campaign, that switch between different sampling points and long heated sampling lines are challenging and need to be tested more and further optimized to secure stable and representative gas composition.

The manual isokinetic sampling and analysis is considered to be a reference method for TCM DA. Isokinetic sampling and analysis is verified by two independent third party companies (during earlier campaigns by Kema/SGS and FORCE, and in this MEA campaign by FORCE).



	26.11.2013	09.12.2013	09.12.2013	16.12.2013	08.01.2014	08.01.2014	08.01.2014	09.01.2014	09.01.2014	27.01.2014	04.02.2014	11.02.2014	14.02.2014
■ Isokinetic	0.323	0.030	0.022	0.011	0.005	0.008	0.014	0.014	0.001	0.005	0.004	0.008	0.008
■ PTR-TOF-MS				0.130	0.001	0.043	0.127	0.010	0.026	0.075		0.009	
■ FTIR	2.2	< 1	< 1	1.4	< 1	1.6	1.1	< 1	< 1	< 1	< 1	< 1	< 1

Figure 6: MEA emissions determined by different analyzer techniques during the campaign. Results on the FTIR below detection limit (<1 ppmv) are colored lighter blue.

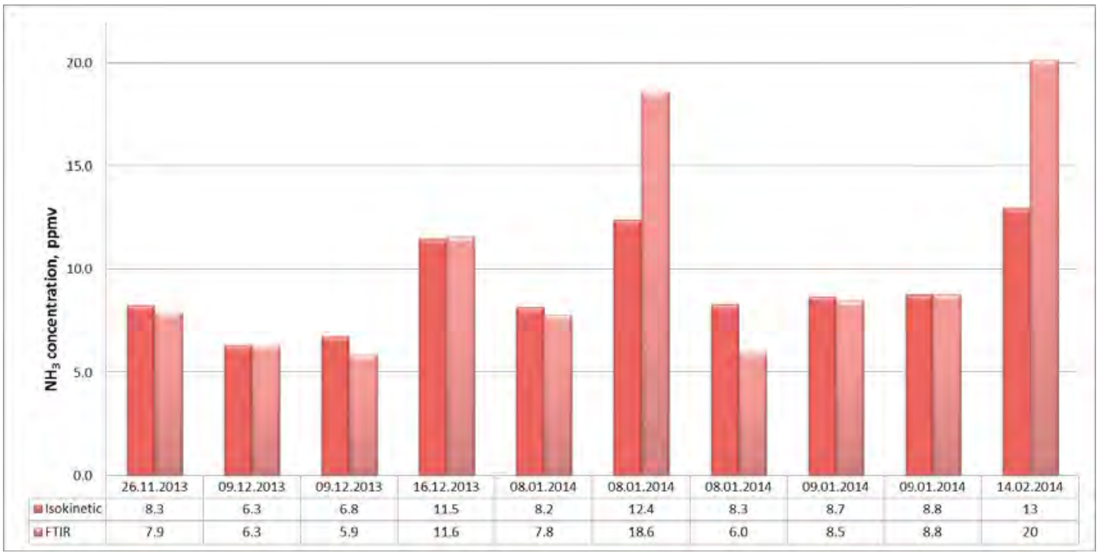


Figure 7: NH_3 emissions determined by different analyzer techniques during the campaign

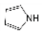
Table 6. Degradation components in Flue gas out of absorber from isokinetic gas emission measurements.

Compound	04.02.2014 µg/m^3	04.02.2014 ppbv	10.02.2014 µg/m^3	10.02.2014 ppbv
Methylamine	2.6	2	3.6	3
Dimethylamine	<1.1	<1	<1.1	<1
Ethylamine	<1.1	<1	<1.1	<1
Diethylamine	<1.1	<0.3	<1.1	<0.3
Ethylmethylamine	<2.2	<1	<2.1	<1
MEA	13	5	17	6
DEA	<1.1	<0.2	<1.1	<0.2
Morpholine	<2.2	<1	<2.1	<1
MEA-NO2	<0.01	<0.002	<0.01	<0.002
Dimethylnitramine	<0.002	<0.0006	<0.002	<0.0006
Diethylnitramine	<0.004	<0.001	<0.004	<0.001
NDMA	<0.001	<0.0003	0.001	0.0004
NMEA	<0.001	<0.0003	<0.001	<0.0003
NDEA	<0.001	<0.0002	<0.001	<0.0003
NDPA	<0.001	<0.0002	<0.001	<0.0002
NPYR	<0.001	<0.3	<0.001	<0.3
NMOR	<0.002	<0.0004	<0.002	<0.0004
NPIP	<0.001	<0.0002	<0.001	<0.0002
NDBA	<0.001	<0.0002	<0.001	<0.0002
NDELA	<0.01	<0.002	<0.01	<0.002
TONO*	<0.2	<0.04	<0.2	<0.04

*Converted from molar to mass basis, using M_w 130 g/mol

PTR-TOF-MS was also used for screening of potential other emissions. A list of identified or tentatively identified compounds is given in Table 7. It is noted that PTR-TOF-MS did not detect any emissions of alkylamines, nitrosamines or nitramines.

Table 7. Results from PTR-TOF-MS measurements on 11.02.2014, 08:15-10:15. Estimated uncertainty in measurements is ±20%.

Name	Formula	ppbv	Structure	m/z
2-aminoethanol	$H_2NCH_2CH_2OH$	8.9		62.060
Ammonia	NH_3	18265.7		18.034
Formaldehyde	HCHO	43.1		31.018
Acetaldehyde	CH_3CHO	454.9		45.033
Acetone	$(CH_3)_2CO$	88.2		59.049
Aceticacid	CH_3COOH	12		61.028
Formamide*	$CHONH_2$	13		46.028
Acetamide*	NH_2CH_2CHO	14.1		60.044
Methane,nitro*	CH_3NO_2	19.8		62.024
Ethane,nitro*	$CH_3CH_2NO_2$	0.8		73.039
Pyrrole*	C_4H_4NH	5.2		68.049
Pyrazine*	$C_4H_4N_2$	107.1		81.044
Pyrazinemethyl*	$C_4H_3N_2CH_3$	23.2		95.060
Pyrazinedimethyl*	$C_4H_2N_2(CH_3)_2$	7.1		109.079

* Tentative interpretation based on chemical formula, temporal profile or possible chemical pathway of formation.

3.4 Third party gas emission measurement

One third-party emission measurement was done on January 6. FORCE Technology carried out isokinetic sampling onto a solid sorbent (Thermosorb/N) in combination with condensate collection in an impinger. The condensate was analyzed separately. Analysis of collected samples was done by Isconlab GmbH. The results show that all nitrosamine and nitramine emissions were below detection limits.

Table 8. Results from third part measurement on 6th of January, done by FORCE Technology

Compound	µg/m^3
Total nitramine	<0.2
Total nitrosamine	<0.08
NDMA (N-nitrosodimethylamine)	<0.08
Formaldehyde	<70
Acetaldehyde	310

4. Conclusion

Extensive atmospheric emission monitoring has been conducted at the CO_2 Technology Centre Mongstad (TCM DA) during amine based post-combustion CO_2 capture. The TCM DA amine plant was operated with the aqueous MEA solvent system treating flue gas from a combined heat and power plant (CHP). Emission monitoring was conducted by a Fourier Transform Infrared (FTIR) Spectrometry analyzer, a Proton Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS) analyzer, and manual isokinetic sampling followed by off-line analysis in the laboratory.

Atmospheric emissions of monoethanolamine (MEA) were very low throughout the complete campaign, and determined to be in the parts per billion (ppb) range. Atmospheric emissions of MEA amine based degradation products such as nitrosamines and nitramines were below detectable levels. Atmospheric emissions of ammonia (NH_3) were in the low ppm range, and alkyl amines in the low ppb range.

Absorber wash water sections were found to effectively reduce possible atmospheric emissions from amine based solvent system.

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Appendix A. Abbreviations

AA	Acetic acid
CLLE	Continuous Liquid Liquid Extraction
DCC	Direct Contact Cooler
DiEA	Diethylamine
DMA	Dimetylamine
DMNA	N-nitro-N-methyl-methanamine
DMO	4,4-dimethyl-2-oxazolidinone
EA	Ethylamine
FA	Formic acid
GA	Glycolic acid
GC-HRMS	Gas Chromatography-High Resolution Mass Spectrometry
HEA	N-(2-hydroxyethyl) acetamide
HEF	N-(2-hydroxyethyl)formamide
HeGly	N-(2-hydroxyethyl)glycine
HEI	N-(2-hydroxyethyl)imidazole
HEIA	N-(2-hydroxyethyl)imidazolidinone
HEPO	4-(2-hydroxyethyl)piperazin-2-one
HSS	Heat Stable Salt
IC-ECD	Ion Chromatography-Electric Conductivity Detection
LC MS QQQ	Liquid Chromatography Mass Spectrometry Triple Quadrupole
LLE	Liquid Liquid Extraction
MA	Methylamine

NDBA	N-Nitrosodi-n-butylamine
NDEA	N-Nitrosodiethylamine
NDMA	N-methyl,N-nitroso-methanamine
NDPA	N-Nitrosodi-n-propylamine
NMEA	N-Nitrosomethylethylamine
NO2-MEA	2-(Nitroamino)ethanol
NO-HeGly	N-Nitroso(2-hydroxyethyl)glycine
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyrollidine
OA	Oxalic acid
TONO	Total Nitroso amines
UPLC-MS/MS	Ultra Performance Liquid Chromatography – Mass Spectrometry / Mass Spectrometry

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Health risk analysis for emissions to air from CO_2 Technology Centre Mongstad

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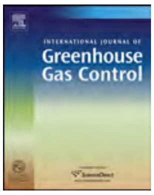

Health risk analysis for emissions to air from CO_2 Technology Centre Mongstad

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ABSTRACT

A health risk analysis for the emissions to air from the CO_2 Technology Centre Mongstad (TCM) has been executed. TCM is the world's largest facility for testing and improving technologies for CO_2 capture, and is located at the West coast of Norway. The risk analysis was an important fundament for the application for an emission permit for the amine based post-combustion CO_2 capture unit. The highest risk was assessed to be the exposure of the population to uncertain concentrations of nitrosamines and nitramines in air and drinking water. Nitrosamines and nitramines are groups of possible degradation products formed from amines. The components within these two groups have variable degrees of carcinogenicity. Nitrosamines are formed from amines in the CO_2 capture process and in the atmosphere, while nitramines are assumed to form only in the atmosphere. The risk was analyzed by comparing the sum of concentrations of nitrosamines and nitramines in air and fresh water with recently available guidelines. The concentrations were obtained by modelling atmospheric chemistry, dispersion, deposition by precipitation and degradation in fresh water with novel methods that were developed during the application process. Moreover, the nitrosamine and nitramine concentrations were measured in air and fresh water lakes prior to start-up as a baseline. TCM's conclusion was that the risk was acceptable. The Norwegian Climate and Pollution Agency granted TCM a permit in November 2011.

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Real-Time Monitoring of Emissions from Monoethanolamine-Based Industrial Scale Carbon Capture Facilities

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Real-Time Monitoring of Emissions from Monoethanolamine-Based Industrial Scale Carbon Capture Facilities

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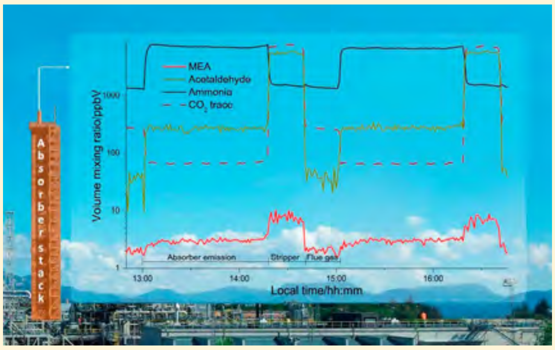
S *Supporting Information*



ABSTRACT: We demonstrate the capabilities and properties of using Proton Transfer Reaction time-of-flight mass spectrometry (PTR-ToF-MS) to real-time monitor gaseous emissions from industrial scale amine-based carbon capture processes. The benchmark monoethanolamine (MEA) was used as an example of amines needing to be monitored from carbon capture facilities, and to describe how the measurements may be influenced by potentially interfering species in CO_2 absorber stack discharges. On the basis of known or expected emission compositions, we investigated the PTR-ToF-MS MEA response as a function of sample flow humidity, ammonia, and CO_2 abundances, and show that all can exhibit interferences, thus making accurate amine measurements difficult. This warrants a proper sample pretreatment, and we show an example using a dilution with bottled zero air of 1:20 to 1:10 to monitor stack gas concentrations at the CO_2 Technology Center Mongstad (TCM), Norway. Observed emissions included many expected chemical species, dominantly ammonia and acetaldehyde, but also two new species previously not reported but emitted in significant quantities. With respect to concerns regarding amine emissions, we show that accurate amine quantifications in the presence of water vapor, ammonia, and CO_2 become feasible after proper sample dilution, thus making PTR-ToF-MS a viable technique to monitor future carbon capture facility emissions, without conventional laborious sample pretreatment.

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Establishment of Knowledge base for Emission Regulation for the CO_2 Technology Centre Mongstad

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Establishment of Knowledge base for Emission Regulation for the CO_2 Technology Centre Mongstad

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Abstract

The CO_2 Technology Centre Mongstad (TCM) is currently regarded as the world's largest CO_2 capture technology test centre at 100 000 ton/year of CO_2 capture capacity. The main aim of the project was to play an important role in the establishment of proven and cost efficient CCS (CO_2 capture and storage) value chains. At first two technologies are tested, namely and amine plant (designed by Aker Clean Carbon) and a chilled ammonia plant (designed by Alstom) which is fed with two different flue gas sources. The latter will, by normal composition as well as CO_2 recycle design, allow for a large band of CO_2 concentrations available to the various technologies. In principle, the two flue gas sources along with the recycle steam will allow to simulate flue gasses from both gas- as well as coal fired applications.

The work presented here aims to discuss and introduce the interaction between the Norwegian Climate- and Pollution Agency (Klif) and TCM. The importance of these activities are highlighted by the challenges faced to ensure safe emissions levels in order to allocate the emissions and discharge permit and subsequent regulatory measures associated with this permit. Large uncertainties regarding worst case assumptions for emissions from the TCM amine plant had to be addressed in order to deduce safe levels for amine degradation products, like nitrosamine and nitramines. The latter are known carcinogens with variable carcinogenic properties. Thus, a two-folded approach was taken by firstly addressing the knowledge gap towards amine degradation products and their respective impact on health and environment. Secondly, close cooperation with Klif was required to establish relevant regulation for the CO_2 capture facility.

In November 2011, an emission and discharge permit for TCM was approved by Klif. Regulatory levels for amines, ammonia, aldehydes and other flue-gas related species were depicted in the permit, both on immediate concentration levels as well as permitted annual levels and wider environment deposition

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concentrations. The paper concludes by looking at the first set of measured emissions parameters from the amine plant at TCM and considers the results in relation with the initial risk assessments associated with the permit.

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Keywords: Emissions regulations; nitrosamine; nitramine; post combustion; CO_2 capture demonstration

1. Introduction

Nomenclature

ACC	Aker Clean Carbon (now known as Aker Solutions)
ADA	Atmospheric Degradation of Amines
CAP	Chilled Ammonia Process
CCS	CO_2 Capture and Storage
CCM	CO_2 Capture Mongstad (the full scale project)
CHP	Combined Heat and Power plant
CLIMIT	Programme for Power Generation with Carbon Capture and Storage
COSMO	Previously called LM (non-hydrostatic and compressible meteorological model)
FTIR	Fourier Transform Infrared Spectroscopy
IfT	Leibniz Institute for Tropospheric Research
Klif	Norwegian Climate- and Pollution Agency
LC-MS	Liquid chromatography-mass spectrometry
MUSCAT	Multi-scale Chemistry Aerosol Transport
NILU	Norwegian Institute for Air Research
NIPH	Norwegian Institute for Public Health
NIVA	Norwegian Institute for Water Research
PTR-TOF	Proton Transfer Reactor Time-of-Flight Mass Spectrometer
RFCC	Residue Fluid Catalytic Cracker
TCM	CO_2 Technology Centre Mongstad
UiO	University of Oslo

CO_2 Technology Centre Mongstad (TCM), situated in Norway, currently stands as the largest facility for testing and improving CO_2 capture technologies. TCM aims of playing an important role in establishing proven and cost efficient CCS value chains. Hence, the activities at TCM are focussed on progressing technology development by testing and improving CO_2 capture technologies.

TCM is a company owned by Gassnova (the Norwegian state), Statoil, Norske Shell and Sasol. Initially two technologies will be tested, namely: an amine plant and a chilled ammonia plant. These two technologies will both be tested on two separate flue gas sources. The first source is off-gas from the residue fluid catalytic cracker (RFCC) at the Mongstad Refinery, and the second will be exhaust gas originating from the combined heat and power plant (CHP) at Mongstad. The two plants are designed to jointly capture *ca* 100 000 tons per year of CO_2. The work presented here aims to introduce and discuss the interaction between the Norwegian Climate- and Pollution Agency (Klif) and TCM in the challenging period when safe emissions levels from TCM were being established and an emissions discharge permit for the TCM facility was thereafter granted by Klif. This paper continues the discussion on emissions raised in an earlier paper on TCM [1].

2. Emissions and discharge permit application

TCM applied for an emissions and discharge permit from Klif in September 2010. At the time of submission of the application, large uncertainties existed for the worst case scenario for emissions from the TCM amine plant. The highest level of uncertainty was related to the possible impacts that amine degradation products, like nitrosamine and nitramines, could have on the public health in close vicinity (<50 km) from the facility.

Nitrosamine and nitramines are partly formed through the degradation of amines within the process itself and partly through the atmospheric reaction involving OH- radicals. Both of these component groups may consist of a wide range of species dependant on the mother amine and the reaction conditions, and some of their resulting nitrosamines and nitramines are known to have carcinogenic effects. For this reason, TCM placed a lot of emphasis on establishing a transparent risk analysis, which includes allowable risk limits relevant to these components. The knowledge base on the toxicology of nitramines is even less than for nitrosamines, but literature and studies to date indicate that nitramines are less carcinogenic than nitrosamines [3].

Focus at TCM during the year following the submission of the permit was on reducing the technical knowledge gap of these degradation components, while the regulating authorities in parallel tasked themselves to establish regulation and limitations levels. The technical knowledge gap was addressed by close interaction with programs like CLIMIT as well as the CCM project, dually by considering and defining the formation of nitrosamine and nitramine species during day and night operation as well as describing the exposure effect of these components to the immediate and wider areas around the TCM facility. The impact and risk of these components were investigated based on both human exposures to air, as well as possible negative effects by potential changes in drinking water quality.

A large number of acknowledged research facilities and institutes were engaged by TCM to address and assess various parts in the amine degradation products knowledge gap. The findings of the various studies have been/will be published by the different institutions as well as by Klif [2]. Therefore this paper will not reiterate these results, but rather describe the events and specific interaction that took place between the regulator (Klif) and TCM following the submission of the emissions and discharge permit application in September 2010. The application, supporting documentation and the resulting permit describe the first risk analysis from amine emissions. De Koeijer et al [11] presents the results on which the health risk analysis was based in greater detail. The main intention is experience transfer to other

CO_2-testing and full scale endeavours that in the future are applying for an emission and discharge permit and/or other regulation activities.

2.1. Initial amine degradation product knowledge base

The initial permit application was lodged while acknowledging that a large knowledge gap existed in terms of the impact of amine slip to air and the consequences of this to the direct and indirect environment. The standing knowledge base at that time was the intermediate results from the ADA (atmospheric degradation of amines) research campaign headed by the University of Oslo [4]. The latter was focused at identifying the gas phase photochemical degradation products of amine in the atmosphere, quantifying the products from photo-oxidation of amines, verification and updating of existing atmospheric photo-oxidation schemes as well as assessing aerosol formation during gas phase degradation of amines in air. In parallel to the ADA campaign, preliminary dispersion models developed by NILU indicated that significant levels of amine degradation products may be deposited close within the vicinity of the TCM process boundaries [5].

Subsequently, the knowledge at the time directed towards possible health impacts of amines and their degradation products, but no specified guideline values for nitrosamines and nitramines existed. The Norwegian Institute for Public Health (NIPH) was therefore approached to assess and recommend regulatory values for nitrosamines and nitramines as a first step towards discharge permissions for the TCM facility.

2.2. Studies aimed at closing the knowledge gap

An all encompassing research campaign was launched in order to address the prevailing knowledge gap associated with possible emissions from TCM. Three major areas were targeted: firstly, the atmospheric chemistry and dispersion of amines and their degradation products. Secondly, the fate of nitrosamines in water by means of biodegradation was investigated and the final activity was to establish baseline assessments in air, water and soil. During the selection process emphasis was placed in utilising well established and recognised institutions for these studies.

Main findings from the campaigns indicated that nitrosamine and nitramines are partly formed through the degradation of amines within the process itself and partly through the atmospheric reaction involving OH- radicals [4]. Formation of nitrosamines and nitramine species are highly dependent on the mother amine and reaction conditions. The various nitrosamine and nitramine component groups are known to vary in carcinogenic properties and thus a comprehensive dispersion model was compiled in order to assess the worst case and likely case concentrations for these species in ambient air and deposition in fresh water [11]. Emphases during the studies were placed on reducing the uncertainty while re-assessing assumptions made in the first dispersion modelling work. Furthermore, investigations were also launched into possible emissions levels of nitrosamines and nitramines species from other industrial plants and deducing whether or not these components are being regulated elsewhere [12].

In March 2011 the NIPH published guideline values for nitrosamine and nitramine species by stating that these component groups must not exceed 0.3 ng/m^3 for air concentrations and 4 ng/l for fresh water sources or drinking water when considering a 1 in 10^{-6} cancer risk for lifetime exposure [2]. Initial “worst case” assumptions for the dispersion model indicated that these guideline values will not be exceeded and thus more emphasis was placed in refining the atmospheric chemistry assumptions while introducing possible environmental degradation of these species through biodegradation studies. The purpose of the "worst case" study was to include worst estimates on the different aspects of formation and transformation, while a more likely parameter update was launched in order to include new findings and thus calculating the most likely impact involving air and water quality. The latter was further referred to as the "likely case", which in turn resulted in the following main conclusions [6]:

- Air concentrations of nitrosamines and nitramines (as a sum) are expected to be lower by a ratio of 3 to 5 when compared to the NIPH guidelines.
- Water concentrations of nitrosamine and nitramines (as a sum) are expected to be lower by a ratio of 16 to 22 when compared to the NIPH guidelines.

The likely case dispersion model included findings from other parallel studies by considering the reduction of nitrosamines in water by means of photolysis (3 weeks life-time) and possibly biodegradation (half-life of 40 to 400 days) [7]. Biodegradation reduction of nitramines of 33% over 28 days was also included [8].

Baseline assessments showed detectable amounts of neither nitrosamines nor nitramines [9]. The baseline study paired with the theoretical deposition of nitrosamine and nitramines in air and water therefore strengthened the position that the activities of TCM will not exceed the NIPH guidelines and is thus unlikely to be responsible for any detrimental health or environmental effects.

3. Updated information to Klif and public participation

All updated information was presented to Klif during the first and second quarters of 2011, including the final reports to all of the studies launched since the original emissions and discharge permit submission. During the processing time of the information by Klif, TCM embarked on a community information program in which several meetings were held with various community stakeholders as well inviting any interested parties to the TCM site. It was the first emissions and discharge permit of its kind and therefore public understanding of the risks and implications was deemed crucial if the application was to be successful – not only for the operation at TCM, but it was clear that the way was being paved in which future CCS projects will be governed in Norway and possibly the most of Europe. An open public hearing was also held in the second quarter of 2011 in which both Klif and municipal representatives participated, along with nearly 50 other interested parties. This, along with close communication with the Lindås and Austrheim municipalities, a general understanding towards the risks and acceptance towards the mitigation activities by TCM was received.

4. Final permit approval and conditions

More than a year after the initial application, the final emissions and discharge permit was allocated to TCM in November 2011, with the regulatory levels relevant to air emissions presented in Table 1.

Table 1. Regulatory levels for air emissions according to the TCM emissions and discharge permit [2]

Emissions component	Emitter	Limits[1] (concentration)	Limits[2] (extended period)
Ammonia (NH_3)	CAP	15 ppmv[3]	6 t/yr
Ammonia (NH_3)	Amine plant	33 ppmv[4]	6 t/yr
Total amines	Amine plant	6 ppmv	2.8 t/yr
Primary amines	Amine plant		2.8 t/yr
Secondary amines	Amine plant		0.8 t/yr

Tertiary amines	Amine plant	0.4 t/yr
Aldehydes	Amine plant	3 t/yr

[1] As an average for 90 % of operating time

[2] Annual accumulative limits

[3] In short intervals malfunctions can give concentration of NH_3 up to 250 ppmv

[4] The sum of primary, secondary and tertiary amines shall not exceed the total amount of amines. Maximum term limits will not exceed the values for the individual groups of amines in the table above.

The permission as shown in Table 1 is independent of solvent used. In order to obtain this independence in solvent, the amines were grouped in primary, secondary and tertiary amines based on the risk of each group towards nitrosamines and nitramines formation. The variability of these groups within different solvent compositions will require new evaluations and risk assessments before being introduced to the TCM plant [2].

Further to direct air emissions at source, restrictions are imposed on concentration levels calculated for fresh water and dispersed air for nitrosamines and nitramines. The permit states that emissions from TCM shall not lead to that the calculated concentration of the sum of nitrosamines and nitramines exceed 0.3 ng/m^3 for air concentrations and 4 ng/l for fresh water sources or drinking water [2]. These guidelines were derived from direct recommendations as published by the NIPH [3].

Apart from air regulations, the emissions and discharge permit covers all areas of environmental concern. This includes liquid discharges, solid wastes, noise and others. All of the individual regulated areas will not be discussed here as it is regarded as well known areas and have been established by the various governing authorities world-wide.

5. Ongoing and updating studies

In an effort to continuously update the knowledge base at TCM, which in turn will benefit future full scale projects, some study areas have been selected to be updated past the allocation of the permit. The first is an updated dispersion model conducted with IfT (Leibniz Institute for Tropospheric Research) and the other is the biodegradation of nitramines.

The updated dispersion model that is being developed by the team at IfT is aimed at providing the following improvements to the current model:

- The model will be based on COSMO-MUSCAT and thus improved meteorology will be used in the base model [10].
- The model will include the atmospheric chemistry of amines and thus present the true theoretical yields of amine degradation products to the wider environment.
- The model will provide a more detailed tool which will enable the evaluation of other solvents and will not be restricted to MEA (mono-ethanol amine) solvents.

The theoretical yields of nitrosamine and nitramines in the ADA study showed that more nitramines than nitrosamines will possibly be formed [4]. And prior biodegradation studies also indicated that nitramines are more readily biodegradable then their nitrosamine counterparts [8]. These two indications therefore led to the establishment of biodegradation studies with SINTEF on ethanolnitramine (MEA-NO_2), dimethylnitramine (DMNA), N-nitropiperazine (PZ-NO_2), methylnitramine (MNA), 2-methyl-2-(nitroamino)-1-propanol (AMP-NO_2), diethylnitramine (DENA) and methylethylnitramine (MENA). The selection of these components are believed to cover a broad range of future solvents that may be tested at

TCM. The results from these studies will in turn also be included in the updated dispersion model developed by IfT.

6. Environmental follow up program, latest results and conclusion

The TCM emissions and discharge permit, as outlined by Klif, entails an extensive environmental follow-up and monitoring plan. Monthly and annual reports have to be compiled in which all discharges and possible environmental impacts are clearly identified and quantified. The main aspects of the ongoing environmental follow-up and monitoring plan are:

- Terrestrial and fresh water surveys close to the TCM boundary fence. A background survey was completed by NIVA and bi-annual surveillance will be conducted during operation [13].
- Noise modelling and surveillance (these activities are done in conjunction with the refinery at Mongstad).
- A comprehensive air monitoring program will be followed in which air quality will be measured with online instruments (FTIR), third party measurements (PTR-TOF-MS with UiO) as well as manual isokinetic sampling conducted in-house (analysed through LC-MS).

During July 2012 the amine plant was started up, which allowed for initial environmental monitoring during August 2012. Considering the fact that this was the first month of operation on MEA solvent, very promising results were gathered with respects to amine emissions. Firstly, very low levels of amines were detected at the bottom of the 101m sample line by the on-line FTIR (less than 1ppm) as well as the PTR-TOF-MS (less than 100 ppb). The FTIR set-up typically allows for accuracy of 1ppm and is thus in line with the much more accurate PTR-TOF-MS which is connected to the same sample line as the FTIR. Secondly, the isokinetic sampling campaigns at the absorber exhaust have shown to exhibit the same low levels of MEA once analysed through LC-MS (less than 0.1ppm). At this early stage the first results serve as a confirmation that the initial risk assessments for TCM DA are realistic and translates that the NIPH levels are not likely to be exceeded for this solvent. It is important to note, however, that these results are not representative enough to be conclusive due to process variation, but it serves as a very promising first indication.

The main ambitions for TCM at conception were to test, verify and demonstrate CO_2 capture technologies while reducing costs, technical, environmental and financial risks. The ground made in terms of establishing the emissions and discharge permit with the Norwegian regulator was the first step in achieving these ambitions in environmental terms. The methodology, interaction and end result gained here will more than likely set the trend for new projects of similar stance throughout Europe and the rest of the world. Other than breaking ground in terms of regulation, the activities resulting from the work presented here also achieved an increase in global understanding in amine chemistry, amine degradation products and their respective environmental impact which is not restricted to CCS based projects alone.

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Health and environmental impact of amine based post combustion CO_2 capture

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Abstract

A post-combustion amine based CO_2 capture plant is associated with minor release of amine and amine degradation products to the atmosphere along with the treated flue gas. The possible health and environmental effect of this have been investigated extensively through the Norwegian CLIMIT-program, the CO_2 Technology Centre Mongstad (TCM) and the planning of a full scale capture plant at Mongstad (CCM). Based on flue gas from a combined cycle gas power plant, the capacity of TCM's amine plant and CCM are 25 000 and 1 000 000 t/yr CO_2, respectively. Special attention has been given to nitrosamines and nitramines and the investigations have provided new knowledge on their formation, degradation and dispersion, going from the capture plant towards the end point in the nature. The initiatives and programmes have also included means of emission reduction as well as refining of measurements techniques. Computer models for dispersion calculation and evaluation of maximum level of components in air and drinking water are important and are part of the environmental permit for TCM. Up to now, this new knowledge has significantly reduced the risk perception for the release of amine and amine degradation products to the atmosphere.

Kewords: CO_2 capture; amine; emmision to air; health and environmental impact; demonstration; nitrosamine; nitramine

1. Introduction

The possible health and environmental impact of amines and amine degradation products being released to the atmosphere has received a lot of attention in Norway and a substantial amount of research has been carried out. The majority of the investigations has been financed from the Norwegian CLIMIT-program (co-founded with industry) and through the planning of the amine based CO_2 capture plants at

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the CO_2 Technology Centre Mongstad (TCM) and the full scale plant at Mongstad (CCM). These programs and initiatives are all sponsored by the Norwegian state. This comprehensive work has provided a better understanding of the various issues of amine release to the atmosphere and up to now this new knowledge has significantly reduced the risk perception.

The investigations have been initiated in order to obtain a knowledge base enabling a risk assessment of environment and human exposure to amines and their possible degradation products. The studies include chemistry and degradation of amines in the capture plant, emission to air and emission reduction technologies, atmospheric degradation of amines and environmental fate studies. Thus the whole chain from the capture plant to the final end point is covered. Up to now this has resulted in 55 projects executed by international as well as Norwegian institutes. The total budget exceeds 20 million euro, and the programs are in progress. The CCM activities are part of the qualification of amine technology and have the largest budget, followed by the CLIMIT-program and TCM. CLIMIT is supporting RD&D for CO_2 capture, transport and storage, and has since 2008 also built up a special research portfolio on impact of amine uses. TCM's engagement is mainly linked to their application for a discharge permit. Impact of amine uses has also been investigated by others, but the current Norwegian initiatives are the largest and most comprehensive.

2. Investigations

An assessment from 2008 [1], based on available literature data, indicated that amine emission from capturing 1 million tons of CO_2 per year from a combined cycle gas power plant could imply a health and environmental risk. One important observation was that relevant experimental data was scarce. The possible routes of atmospheric degradation of emitted amine into nitrosamines and nitramines is an important part of an assessment, and by 2012 there are strong evidences that all major knowledge gaps in the relevant atmospheric chemistry are closed. This is the result of a focused effort on atmospheric chemistry through a series of comprehensive experimental- and theoretical investigations of amines and their degradation products. The amine chemistry in the capture plant itself has also been investigated and the degradation routes and conditions for provoking formation of substances such as nitrosamines are found. This knowledge is part of the activities for qualifying amines for CCM at Mongstad. Means of reducing emission from the absorber to the atmosphere are developed and tested. The stability of the nitrosamines and nitramines in the environment is an additional important parameter. Experimental investigations show that nitrosamines decompose more easily than nitramines in the environment and this is important for assessing the final concentration in air and drinking water. Overview of the activities can be found elsewhere [2,3,4].

2.1. Capture plant process

In an amine based capture plant the specific amine used as well as operational conditions determine candidates for emission to air. Flue gas degradation of monoethanolamine (MEA) as a function of O_2, NO_X and temperature has been studied by Fostås et al [5]. They used a laboratory sized absorber column in combination with post treatment of solvent in an autoclave and found the amine diethanolamine (DEA) and the corresponding nitrosamine, nitrosodiethanolamine (NDLA), as well as traces of nitrosodimethylamine (NDMA), nitrosomorpholine (NMOR) and methylamine (MMA). Their methodology has been brought forward in the technology qualification amine program for CCM.

Each of the participating vendors in the qualification program for CCM will get access to a lab rig in order to test process degradation of amines according to a test protocol which have been developed by Sintef [6]. The lab rig is a compact portable unit simulating the absorber/desorber process of a normal

CO_2 capture plant. The solvent is in this rig tested through extra high level of O_2 and NO_X in the exhaust gas and with extra high temperature in the desorber column. During the first test run by Sintef using MEA, nitrosamines were as expected, detected. By the end of 2012 four technology vendors, Mitsubishi Heavy Industries, LTD., Siemens AG, Aker Clean Carbon and Huaneng-CERI Powerspan Joint Venture will have completed this phase of the qualification program.

It is foreseen that further measures to reduce emissions from amine capture plants may be required. Amines and degradation products are expected to be found both in the gas phase and in droplet carry over from the absorber. Thus emission reduction technologies applicable for removing both gaseous components and droplets are of interest. The following technologies were ranked according to applicability and maturity [7]:

- An extra water wash section on top of the absorber
- High efficiency demisters and filters
- Acid wash in the final washing section on the absorber top
- UV treatment of lean amine, wash water or gaseous outlet

The least mature technologies have been investigated by e.g. Knuutila, Svendsen and Asif [8] who investigated UV treatment of MEA, DEA and wash water and Knudsen et al [9] who have addressed acid wash and also developed a new concept for reducing mist out of the absorber. The initiatives show that amine emission from gas power based capture in the order of ppb (parts-per-billion) is feasible.

Through the work on measuring amine and amine transformation products, sampling and analytical methods are being developed to be able to both identify and quantify nitrosamines and nitramines in process liquids and in emissions. This includes the construction of a sampling train including isokinetic sampling, sample handling, preservation, storage and transport [10] and the following analytical methods: a total nitrosamine analysis, a screening method for nitrosamines based on chemiluminescence, a quantitative method for analysis of both individual and groups of nitrosamines based on GC-MS [11] and a quantitative method for analysis of 5 nitramines based on LC-MS [12]. As more specific nitramines are being known and synthesized, analytical methods for a larger set of nitramines are expected to evolve. The total nitrosamine [13] analysis has very low detection limit and is suited for quantifying the unknown nitrosamines in the solvent and in emission samples. Online measurements by use of PTR-ToF-MS instruments have been used in a series of projects on atmospheric degradation, see next section, and will now be used at TCM for quantitative measurements of emissions from the CO_2 absorber unit as well as wider field measurements [14]. This instrument has limit of detection of 0.1 ppb for amines, nitrosamines and nitramines.

2.2. Atmospheric formation, destruction and dispersion

The first assessment with worst case estimates for Mongstad [1] was based on available literature data. There was e.g. no data for transformation of MEA in the atmosphere and a 2% conversion to nitrosamines was adapted from literature data on triethylamine [1]. The assessment was also based on a simplified modeling approach that e.g. assumed instantaneous conversion of amines at stack exit and no further degradation of harmful components in relation to their environmental fate. The assessment showed that amine emission from capturing 1 million tons of CO_2 per year from a combined cycle gas power plant could cause a risk to humans and the environment.

The study showed that there was little experimental data on atmospheric transformation of amines relevant for CO_2 capture as well as few data on further degradation and lifetime of the formed harmful components. In 2009 University of Oslo started their Atmospheric Degradation of Amine (ADA) program that included experimental investigations in the European Photo Reactor, EUPHORE in Valencia, Spain. The program (2009 to 2011) has investigated and quantified the potential for forming nitrosamines and nitramines of eight amines: MEA, methyl-, dimetyl-, trimethyl-, ethyl-, diethyl, triethyl-amine and piperazine [15,16]. The various components were identified and quantified by offline analysis and adsorbents as well as by online FT-IR and PTR-ToF-MS measurements. The photolysis of nitrosamines and atmospheric lifetime of nitramines were also part of the program. By use of QSAR (Quantitative structure–activity relationship) models this comprehensive set of data provides input for theoretical modeling of other amines relevant for CO_2 capture.

Other findings were that primary amines will not form nitrosamines, however, nitramines might form from primary amines both in process and in atmosphere. The potency to form nitrosamines and nitramines has been found to be increasing in the following row for primary < secondary < tertiary amines respectively. Volatile alkylamines can also form from the alkanolamines used in the capture process and be released to atmosphere where further transition to nitrosamines and nitramines could occur [15,16].

Atmospheric transformation, destruction and dispersion has been further investigated and applied through the environmental permit for TCM and as part of CCM's technology qualification amine program. The environmental permit for TCM, see Maree et al [17], includes limits for both the emission to air at absorber exit and the calculated yearly average of sum of nitrosamines and nitramines in the nature. These values shall not exceed 0.3 ng/m^3 and 4 ng/litre for air and drinking water, respectively. This is according to recommendations from Norwegian Institute of Public Health (NIPH) [18] and based on the toxicity of the nitrosamine NDMA. The concentrations in air and drinking water are obtained by modelling atmospheric chemistry, dispersion, deposition by precipitation and degradation in fresh water with methods that were employed by Norwegian Institute for Air Research (NILU) [19,20]. The risk levels as depicted by the NIPH guidelines for nitrosamines and nitramines decreased as the NILU model developed [21]. The first sets of assumptions to the model were largely conservative in which the chemistry was assumed to happen instantaneously with no degradation of species once they are formed. These set of results were dubbed the 'worst case' study, but with growing knowledge on the chemistry mechanisms as well as degradation of nitrosamine and nitramine species a more 'likely case' study was developed [19,20]. The latter showed a significant decrease in risk and which showed that the process will conform to NIPH guideline quality criteria as presented in Table 1.

Table 1. Risk level comparison of nitrosamine and nitramine concentrations (sum) with update in dispersion model assumptions at TCM, adapted from [21]. Two flue gas sources: CHP with 3.5 % CO_2 from a combined cycle gas power plant and RFCC with 13 % CO_2 from the residue fluid catalytic cracker.

Dispersion model case	NIPH guideline value	CHP	RFCC
Air - likely case (ng/m^3)	0.3	0.0022	0.0017
Water - likely case (ng/l)	4	0.023	0.027
Air - worst case (ng/m^3)	0.3	0.009	0.008
Water - worst case (ng/l)	4	0.52	0.63

The 'likely case' model and values, as presented in Table 1, accounted for degradation of nitramines and nitrosamines in both air and fresh water. Results from biodegradation studies conducted by SINTEF [22] on the nitrosamines NDELA, NDMA and nitrosopiperazine (NPz) showed significant biodegradation of these species. Nitramines, on the other hand, exhibited significant lower biodegradability [21].

CCM did during 2011 continue the study on atmospheric chemistry of amines and closed knowledge gaps related to both daytime and nighttime specific amine, nitrosamine and nitramine chemistry as well as chemistry in the aqueous phase in the atmosphere. Table 2 indicates what has been studied and what has been found less important pathway not necessary to pursue when chemistry models were to be put up and introduced in dispersion models.

Table 2. Reaction pathways of amines, nitrosamines and nitramines studied

Nitrosamine/Nitramine chemistry	Gas Phase	Aqueous Phase
Formation, Daytime	Amine +OH	None important
Formation , Nighttime	Amine+NO_3	None important
Destruction, Daytime	Nitrosamine+hν	None important
Destruction, Nighttime	None important	None important

For the most important reaction pathways all necessary data to decide reaction rates and quantities has been found through experiments and tests with the generic amines [15,16]. In this way reaction schemes with corresponding data can be included in dispersion models to enable simultaneous dispersion and chemical reaction of amines and the corresponding nitrosamines and nitramines in the atmosphere. Table 2 also shows that reactions in the aqueous phase were not found to be of importance neither for the formation or destruction of nitrosamines and nitramines. On the other hand the high solubility of capture type amines will pull the amines out of the gas phase reaction conditions in relation to degradation and they will not undergo reactions in the aqueous phase. As such partitioning of amines to the aqueous phase in the atmosphere will constitute an important loss process for capture related amines [16].

Cambridge Environmental Research Consultants (CERC) and DNV have in parallel developed two different dispersion models, ADMS- an advanced steady state gaussian plume model capable of treating simplified chemistry schemes – and Calpuff – a modified gaussian puff model with several chemistry schemes included. By introducing chemistry in dispersion models it has been shown that the maximum ambient air concentration of sum nitrosamines/nitramines can be reduced by a factor of 10 relative to the assumption of instant formation at the outlet of the stack. Simultaneous dispersion and chemical transformation is thus considerably slowing down the formation rate of nitrosamines and nitramines [23,24]. At TCM Leibniz Institute for Tropospheric Research (IfT) has been engaged to further develop dispersion modeling by use of the COSMO-MUSCAT model. NILU is currently introducing amine chemistry into WRF-Chem (Weather Research and Forecasting – Chemistry) in a CLIMIT project. Thus, several approaches for dispersion modeling with amine chemistry are currently developed in parallel.

2.3. Deposition, exposure and toxicity

Most amines and amino acids used in carbon capture are highly soluble in water. The same is expected for the corresponding nitrosamines and nitramines [25]. It is thus expected that these will dissolve in rain and fog droplets and ultimately be precipitated and end up in surface water, rivers and lakes.

The baseline studies conducted by the Norwegian Institute for Water Research (NIVA) and NILU were not able to show detectable amounts of nitramines or nitrosamines in the environment surrounding TCM at Mongstad. The surveillance activities did, however, detect amines in air, soil, moss and water [26,27]. Table 3 summarises the detection of a selection of amines in air, soil, moss and fresh water. Continuous monitoring in air, aquatic and terrestrial environments surrounding the TCM plant will be conducted on a 2 yearly basis.

Table 3. Detection of amines in air, soil, moss and fresh water as part of the baseline surveys by NIVA and NILU [26,27]. "D" refers to levels at or below detection limits that are 0.01 ng/m^3 for air, 1 ng/g for soil and moss and 10 ng/g for water. "S" refers to significant levels detected

Amine	Air	Soil	Moss	Fresh water
Methylamine	S	S	S	S
Ethylamine	D	D	D	D
Dimethylamine	S	S	S	S
Diethylamine	S	D	D	D
MEA	D	S	S	S
2-Amino-2-methylpropanol	D	D	S	D
Piperazine	D	D	D	D

Literature reviews have revealed that approximately 90% of the about 300 nitrosamines tested have shown carcinogenic effects in bioassays or laboratory animals [18]. A genotoxic mechanism has been confirmed which implies a non-threshold approach in the risk assessment. Existing data on 23 nitrosamines which might form during carbon capture has been reviewed and IARC (International Agency for Research on Cancer) has classified 2 of them as probably carcinogenic to humans and 7 of them as possibly carcinogenic to humans. There is considerably less data on nitramines but they are suspected carcinogenic. None are however classified by IARC. Animal carcinogenicity studies have been carried out for two nitramines: methylnitramine and dimethylnitramine. These results indicate that dimethylnitramine is to be considered at least 6 times less toxic than the corresponding nitrosamine, NDMA.

Due to the very limited amount of toxicity data available on nitramines a toxicity test campaign has been initiated [12]. The following five were investigated: dimethyl-, methyl-, MEA-, AMP- and piperazine-nitramine. Included in the test were acute toxicity, cytotoxicity, skin and eye corrosion, sensitization as well as genotoxicity in three different assays. Overall, the results showed very low toxicity levels. However, three out of the five tested positive on genotoxicity. The next step is to get a more quantitative evaluation of selected nitramines and rank them in relation to nitrosamines. This can give input to a more refined and less conservative toxicity evaluation than the one of today were all nitrosamines and nitramines are added and weighted equally toxic as one of the most toxic nitrosamines (NDMA).

2.4. Framework for qualifying amines for CO_2 capture

The knowledge gathered through the above explained studies, methods, models and procedures, will constitute a scientific framework for qualifying amines for use in CO_2 capture processes. This framework or toolbox is already in operation through CCM for Mongstad site.

3. Conclusion

The comprehensive investigations reported above have greatly reduced the uncertainty about health and environmental risks resulting from amine-based CO_2 capture. Valuable new know-how on amine technology, of high scientific and technical quality, has been generated and new sensitive methods for sampling and analysis of solvent and emissions have been developed. Atmospheric fate of emissions has been studied with regard to dispersion, transformation and degradation, and main knowledge gaps have been closed. The potential toxicity (carcinogenicity) of amine degradation products has been reviewed and tested. Finally, CCM's technology qualification program for amines is established as a valuable toolbox and the program is currently in operation with participation of four vendors.

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