Supporting information for:

Toward understanding amines and their degradation products from post-combustion CO$_2$ capture processes with aerosol mass spectrometry

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Contents

Information about chemicals ................................................................. 4
HR-ToF-AMS data analysis................................................................. 5
Lab-generated PCCC degradation samples ........................................ 6
Tables .............................................................................................. 8

Table S1. Analytical performance of the IC cation system .................... 8
Table S2. Analytical performance of the IC anion system ..................... 9
Table S3. List of compounds in Figure 2 analyzed for elemental ratios using EI mass spectra, including the chemical structure, name, molecular formula, molecular weight (M_w: g mol^{-1}), and the ratios calculated directly based on ion composition (O/C_{cal}, H/C_{cal} and N/C_{cal}). Compounds No.1-43 have been identified as degradation products of MEA, MDEA or PIP as summarized by Gouedard et al. Compounds marked with "**" indicates results from AMS measurements at the vaporizer temperature of 250 °C, others are results from NIST spectral analysis. ................................................................. 10

Table S4. Major degradation products identified in MEA degradation sample and proposed EI spectral signature ions ........................................................................................................ 14
Table S5. Major degradation products identified in MDEA degradation sample and proposed EI spectral signature ions .................................................................................................. 15
Table S6. Major degradation products identified in PIP degradation sample and proposed EI spectral signature ions .............................................................................................. 16
Table S7. Cross correlation coefficients (Pearson's r^2) between the mass spectra of the eight identified MDEA degradation products and the correlation coefficients of each product spectrum with the sample spectrum. Mass spectra of unit mass resolution (UMR) are used in these calculations. ..................................................................................................................... 17

Figures ............................................................................................ 18

Figure S1. Chromatographic responses and elution times of cation standard mixture which contains Li^+ (5 µg·L^{-1}), Na^+ (20 µg·L^{-1}), NH_4^+ (40 µg·L^{-1}), ethanolamine (100 µg·L^{-1}), methylamine (100 µg·L^{-1}), K^+ (20 µg·L^{-1}), diethanolamine (100 µg·L^{-1}), ethylamine (100 µg·L^{-1}), dimethylethanolamine (100 µg·L^{-1}), magnesium (20 µg·L^{-1}) and calcium (20 µg·L^{-1}) (upper panel); and anion standard mixture which contains fluoride (5 µg·L^{-1}), acetate (100 µg·L^{-1}), formate (100 µg·L^{-1}), glyoxylate (100 µg·L^{-1}), chloride (100 µg·L^{-1}), methanesulfonic acid (100 µg·L^{-1}), nitrite (100 µg·L^{-1}), bromide (100 µg·L^{-1}), nitrate (100 µg·L^{-1}), malate (100 µg·L^{-1}), and malonate (100 µg·L^{-1}) (upper panel); and anion standard mixture which contains fluoride (5 µg·L^{-1}), acetate (100 µg·L^{-1}), formate (100 µg·L^{-1}), glyoxylate (100 µg·L^{-1}), chloride (100 µg·L^{-1}), methanesulfonic acid (100 µg·L^{-1}), nitrite (100 µg·L^{-1}), bromide (100 µg·L^{-1}), nitrate (100 µg·L^{-1}), malate (100 µg·L^{-1}), and malonate (100 µg·L^{-1}) (lower panel).
1), sulfate (100 µg·L⁻¹), oxalate (100 µg·L⁻¹), phosphate (100 µg·L⁻¹) and maleate (100 µg·L⁻¹) (lower panel). For anions, there are two co-elutes, which are formate with glyoxylate, and oxalate with phosphate; since glyoxylate and phosphate are unlikely important ions in amine-based PCCC samples, these coelutes should not be a concern.  

Figure S2. High-resolution AMS spectra of MEA, MDEA, and PIP, measured at vaporizer temperatures of 250 °C (a-c) and 600 °C (d-f). The spectral peaks are colored by 9 different ion categories listed in (a); Marker "▲" indicates the molecular ion; NIST spectra (in UMR) are also plotted.  

Figure S3. For the 12 N-containing compounds measured by the HR-ToF-AMS at vaporizer temperatures of both 250 °C and 600 °C in this study: (a) Correlation coefficients (r²) of NIST spectra with AMS spectra (both in UMR); (b) Mass fractions of the molecular ions in the AMS spectra; (c) N/C ratios calculated from the AMS spectra measured at vaporizer temperature of 250 °C versus the real ratios (CI: confidence interval); (d) N/C ratios calculated from the AMS spectra measured at vaporizer temperature of 600 °C versus the real ratios (CI: confidence interval); (e) Comparisons between the N/C ratios calculated from the AMS spectra measured at vaporizer temperatures of 250 °C and 600 °C.  

Figure S4. AMS spectra (vaporizer temperature = 600°C) of pure MEA (a), MDEA (d), PIP (g) and sucrose (b,e,h), and 1:1 (mass ratio) mixtures of MEA/sucrose (c), MDEA/sucrose (f) and PIP/sucrose (i). The spectral peaks are colored by 9 different ion categories listed in (a); Note the amines were prepared in the chloride salts to ensure their mass ratios to sucrose in the particles analyzed by the AMS are consistent with the ratios designed in the solutions.  

Figure S5. Comparisons between deconvoluted mass ratios from AMS spectra (vaporizer temperature = 600 °C) with the real values. (a) MEA/sucrose, (b) MDEA/sucrose, and (c) PIP/sucrose. AMS spectra of the binary mixtures with different mass ratios of amine to sucrose were first obtained, and then each mixture spectrum was decomposed according to equation (1) in the main text, where i refers to the corresponding amine and sucrose, respectively.  

Figure S6. Raw AMS spectra of MEA-based, MDEA-based and PIP-based degradation samples measured at the AMS vaporizer temperatures of 250 °C (a-c) and 600 °C (d-f). Note that the H₂O⁺, HO⁺, O⁺ and CO⁺ signals are directly measured values. Elemental ratios for 250 °C spectra are calculated using the new factors obtained in Figure 2 of the main text, while ratios for 600 °C spectra are determined based on the factors reported in Aiken et al. The spectral peaks are colored by 9 different ion categories listed in (a).  

Figure S7. AMS spectra of MEA-based, MDEA-based and PIP-based degradation samples measured at the AMS vaporizer temperatures of 250 °C (a-c) and 600 °C (d-f), after removal of H₂O⁺, HO⁺, O⁺, and CO₂-related ions (based on fragmentation pattern for CO₂ in NIST). Elemental ratios for 250 °C spectra are calculated using the new factors obtained in Figure 2 of the main text, while ratios for 600 °C spectra are determined based on the factors reported in Aiken et al.
Figure S8. Differences between the AMS spectra measured at vaporizer temperatures of 250 °C and 600 °C for the degradation samples of (a) MEA, (b) MDEA, and (c) PIP (calculated from the spectra shown in Figure S7). The spectral peaks are colored by 9 different ion categories listed in (a). ................................................................. 25

Figure S9. AMS spectra of MEA-based, MDEA-based and PIP-based degradation products measured at the AMS oven temperatures of 250 °C (a-c) and 600 °C (d-f), after removal of parent amine signals (calculated from spectra shown in Figure S7). Elemental ratios for 250 °C spectra are calculated using the new factors obtained in Figure 2 of the main text, while ratios for 600 °C spectra used the factors reported in Aiken et al.20 The spectral peaks are colored by 9 different ion categories listed in (a). ...................................................................................... 26

Figure S10. ESI-MS spectra for the degradation samples of (a) MEA, (b) MDEA, and (c) PIP. (only major peaks are shown). The species identified in Tables S4-S6 are marked in the spectra. ...................................................................................................................................... 27

Figure S11. Comparisons of the MDEA degradation sample spectrum (Figure S7b) with the one reconstructed using the multivariate fitting algorithm (a), the scatter plot between the two (b), and (c-j) NIST spectra of the eight degradation products used in the fitting. .................... 28

References.......................................................................................................................................................... 29

**Information about chemicals**

Amino compounds, including ethanolamine (MEA), diethanolamine (DEAOH), triethanolamine (TEAOH), methyl diethanolamine (MDEA), piperazine (PIP), bis-2-hydroxypropylamine (BOHA), methylamine (MMA), dimethylamine (DMA), trimethylamine (TMA), and ethylamine (EA) (all >99% purity), were from Sigma-Aldrich. Ethanolamine hydrochloride (MEA·HCl, >98%) was from Sigma-Aldrich, the chloride salts of MDEA and PIP were prepared by neutralizing MDEA and PIP with HCl (37%, Sigma-Aldrich). Other chemicals include sucrose (>99%, Fisher Scientific), glycolic acid, glyoxylic acid, sodium acetate, methanesulfonic acid, malic acid, malonic acid, oxalic acid and maleic acid (all >99%, Sigma-Aldrich).
**HR-ToF-AMS data analysis**

The AMS data were processed using the standard toolkits SQUIRREL v1.51H and PIKA v1.10H, written in Igor Pro 6.22A (Wavemetrics, Portland, USA). The toolkits were downloaded from [http://cires.colorado.edu/jimenezgroup/ToFAMSResources/ToFSoftware/index.html](http://cires.colorado.edu/jimenezgroup/ToFAMSResources/ToFSoftware/index.html). The results reported in this manuscript were determined from analyzing the W mode spectra. All spectra were fitted up to $m/z = 190$.

Since argon was used for atomization, interference of air signal at $m/z$ 28 was negligible. The CO$^+$ signal was thus quantified directly from fitting the W-mode data using the Peak Integration by Key Analysis (PIKA) software instead of scaling against the CO$_2^+$ signal. In addition, since particles were likely fully dried prior to AMS analysis, the contributions of particle-bound water and water vapor to measured H$_2$O$^+$ signal were negligible. We thus determined the organic H$_2$O$^+$ signal as the difference between measured H$_2$O$^+$ signal and the inorganic H$_2$O$^+$ signal estimated according to the known fragmentation pattern of sulfate.$^1$

The PIKA software employs a peak-shape modified Gaussian fitting algorithm to deconvolve and quantify the signals of a user-defined array of ions.$^2$ Each ion is represented with a custom peak shape function derived based on analyzing known isolated ions in the background spectrum.$^2$ Choosing the right array of ions to fit is important for PIKA analysis of a raw mass spectrum to determine the ion composition of the sample. Given the fact that the degradation products are dependent on the precursor amines, the mass spectrum of each degradation sample was fitted using a custom ion list determined based on carefully examining the raw mass spectrum and the residual spectral signals to avoid over-fitting or under-fitting. But for a specific amine, the same ions were selected to fit the pure compound spectra regardless of the vaporizer temperature and were included in the ion list used for fitting the degradation products.

Generally speaking, the determination of the signal intensity of an ion that overlaps with ions of much larger signal intensities based on PIKA fitting tends to be uncertain. This is the reason that the quantification of N/C of organics in ambient aerosol could be associated with significant uncertainties since a large number of the N-containing ions have much lower signals compared to the overlapping hydrocarbon (i.e., C$_x$H$_y^+$) and oxygenated (C$_x$H$_y$O$_z^+$) ions. However, this is
not an issue for the current study because of the abundance of N-containing species in our samples. The N/C atomic ratios of the samples analyzed in this study varied between 0.15 – 0.3. As shown in Figure 3 in the manuscript, for almost all \(m/z\)'s larger than 20 amu, the dominant ions are the N-containing ones. We are therefore able to quantify the \(C_xH_yN_p^+\) and \(C_xH_yN_pO_z^+\) ions and determine the ion-speciated mass spectra and the N/C ratios of the degradation samples with little ambiguity.

**Lab-generated PCCC degradation samples**

The composition of flue gases from coal-fired power plants is dependent on the type of coal and design of the coal combustor\(^3\) and generally contains particulate matter (PM), gaseous component (such as \(N_2, O_2, CO, CO_2, SO_x\) and \(NO_x\)), organic compounds (likely including dioxin and furan), and trace metals or elements. A typical flue gas was found to contain 70–75% \(N_2\), 10–15% \(CO_2\), 8–10% \(H_2O\), and 3–4% \(O_2\).\(^4\) Due to the complexity of actual flue gas composition and flow rates, degradation processes under industrial conditions are relatively poorly understood and difficult to accurately simulate. In general, two types of degradations can occur in a PCCC plant:\(^5\) oxidative degradation in the absorber column (typically 40-50 °C at 1 atm), which is mainly caused by the presence of a large amount of \(O_2\) in the flue gas, and thermal degradation mainly occurring in the stripper column (typically 100-150 °C at slightly higher pressures, 1.5-2 atm). Presence of \(NO_x\) in the flue gas is of concern because reaction with amine solvents produces nitrosamines which are likely carcinogenic.

In this study, the degradation of amines started with 7M MEA, 7M MDEA, and 1.7M PIP. A mixture of air with ~200 ppm \(NO_2\) was used to mimic the major oxidation degradation conditions that likely occur in the actual PCCC absorber. The degradation lasted for 2-3 months to simulate the solvent conditions after many cycles in an actual PCCC plant. In addition, the temperature during degradation was kept at ~150 °C, this temperature also mimics the industrial condition in the PCCC stripper column, which could cause thermal degradation. Overall, different from many other studies that mainly focus on one type of degradation,\(^5\) our degradation samples are expected to contain both oxidative and thermal degradation products that are likely present in the actual PCCC facilities. This is verified in Tables S4-S6, which indeed show the
presence of both oxidative and thermal degradation products that were observed in previous lab studies or plant samples.
Table S1. Analytical performance of the IC cation system.

| Cations            | Retention time\(^1\) (min) | Response factor\(^2\) (µS·cm\(^-1\)/µg·L\(^{-1}\)) | MDL (µg·L\(^{-1}\))\(^3\) | Calibration curves | Correlation coeff. (r\(^2\))\(^5\) | % Reproducibility (RPD)\(^6\) |
|--------------------|----------------------------|---------------------------------|---------------------------|--------------------|-------------------------------|------------------------|
| Lithium (Li)       | 6.63                       | 0.01214                         | 1.0                       | 50                 | 50.00                         | 0.9993, 0.9993         | 4.70%                   |
| Sodium (Na)        | 7.93                       | 0.005315                        | 2.5                       | 200                | 80.00                         | 0.9677, 0.9629         | 1.55%                   |
| Ammonium (NH\(_4\)) | 8.71                       | 0.00491                         | 3.0                       | 400                | 133.33                        | 0.9940, 0.9937         | 19.59%                  |
| Ethanolamine (MEA) | 9.64                       | 0.001124                        | 3.8                       | 1000               | 266.67                        | 0.9997, 0.9999         | 12.16%                  |
| Methylamine (MMA)  | 10.18                      | 0.002275                        | 4.7                       | 1000               | 214.13                        | 0.9994, 0.9993         | 7.85%                   |
| Potassium (K)      | 10.81                      | 0.00207                         | 7.2                       | 200                | 27.78                         | 0.9960, 0.9923         | 10.31%                  |
| Diethanolamine (DEAOH) | 11.41                   | 0.000616                        | 15.1                      | 3000               | 198.68                        | 0.9999, 0.9999         | 5.07%                   |
| Ethylamine (EA)    | 11.79                      | 0.001172                        | 8.3                       | 2000               | 240.67                        | 0.9999, 0.9999         | 6.85%                   |
| Dimethylamine (DMA)| 13.53                      | 0.001323                        | 10.7                      | 2000               | 187.79                        | 0.9997, 0.9998         | 9.22%                   |
| Triethanolamine (TEAOH)| 14.62                | 0.000502                        | 12.3                      | 5000               | 406.50                        | 0.9998, 0.9999         | 8.03%                   |
| Methyl diethanolamine (MDEA) | 15.66            | 0.00121                         | 6.2                       | 1000               | 162.60                        | 0.9999, 0.9999         | 8.21%                   |
| bis(2-hydroxypropyl)amine (BOHA) | 17.11           | 0.000532                        | 4.9                       | 7000               | 1431.49                       | 0.9999, 0.9998         | 4.53%                   |
| Trimethylamine (TMA) | 23.27                      | 0.001069                        | 16.2                      | 4000               | 246.76                        | 1.0000, 0.9997         | 4.16%                   |
| Magnesium (Mg)     | 31.54                      | 0.00189                         | 17.5                      | 2000               | 11.43                         | 0.9895, 0.9795         | 10.85%                  |
| Calcium (Ca)       | 32.96                      | 0.000237                        | 155.0                     | 1000               | 6.45                          | 0.9733, 0.9695         | 11.07%                  |

\(^1\)The retention times for these species can vary in different runs due to small fluctuations of eluent composition and instrument responses, especially for Mg\(^{2+}\) and Ca\(^{2+}\). The retention times listed in the table were recorded for an experiment, at the eluent composition of 1.75 mM HNO\(_3\) + 0.75 mM DPA (dipicolinic acid) with a flow rate of 0.3 ml·min\(^{-1}\), and a standard mixture containing the following ions: Li\(^{+}\) (5 µg·L\(^{-1}\)), Na\(^{+}\) (20 µg·L\(^{-1}\)), NH\(_4\)\(^{+}\) (40 µg·L\(^{-1}\)), K\(^{+}\) (20 µg·L\(^{-1}\)), Mg\(^{2+}\) (20 µg·L\(^{-1}\)), Ca\(^{2+}\) (100 µg·L\(^{-1}\)), MMA, DMA, TMA, MEA, DEAOH, TEAOH, EA, BOHA (all 100 µg·L\(^{-1}\)) and MDEA (200 µg·L\(^{-1}\)).

\(^2\)Response factor is calculated as: Peak height (in µs·cm\(^{-1}\))/solute concentration (in µg·L\(^{-1}\)).

\(^3\)The method detection limit (MDL), which is also the limit of quantification (LOD), is the smallest measure that can be detected with reasonable certainty for a given analytical procedure. First, we injected the purified water for 3 times and determined the average peak height at the retention time of the target ion to be the blank signal (x\(_b\)). Secondly, we injected 7 times at a concentration which is close to the detection limits (for example, 10 µg L\(^{-1}\) for TEAOH) and determined the standard deviation (S) of the peak height for the 7 duplicates. The student t-value for 7 duplicates and 6 degrees of freedom with 1% probability level is ~3.14, so the detection limit is determined as: MDL = x\(_b\) + 3.14S.

\(^4\)Linearity was determined as: maximum concentration (in µg·L\(^{-1}\))/MDL (in µg·L\(^{-1}\)).

\(^5\)Correlation coefficient (r\(^2\)): Each calibration was repeated to check the reproducibility, so there are two correlation coefficients for each cation.

\(^6\)The reproducibility of the measurement was determined as the average relative percentage difference (RPD) of each point, RPD\(_i\) = |x\(_{i1}\)-x\(_{i2}\)|/(x\(_{i1}\)+x\(_{i2}\)/2)*100%, in the calibration curves.
Table S2. Analytical performance of the IC anion system.

| Anions             | Retention time\(^1\) (minutes) | Response factor\(^2\) (µS·cm\(^{-1}\)/µg·L\(^{-1}\)) | MDL (µg·L\(^{-1}\))\(^3\) | Calibration curves | Correlation coeff. (\(r^2\))\(^5\) |
|--------------------|---------------------------------|---------------------------------|-----------------|------------------|-------------------|
|                    |                                 |                                 |                  | Max. conc. (µg·L\(^{-1}\)) | Linearity\(^4\) |
| Fluoride           | 4.94                            | 0.00285                         | 10.2             | 400              | 39.22             | 0.9995           |
| Glycolate          | 5.44                            | 0.00022                         | 16.51            | 1000             | 60.57             | 0.9990           |
| Glyoxylate         | 5.82                            | 0.00019                         | 27.61            | 1000             | 36.22             | 0.9993           |
| Formate            | 5.82                            | 0.00045                         | 19.32            | 500              | 25.88             | 0.9998           |
| Acetate            | 6.2                             | 0.00019                         | 9.19             | 1000             | 108.81            | 0.9996           |
| Chloride           | 6.65                            | 0.0005                          | 13.06            | 600              | 45.94             | 0.9995           |
| Methanesulfonic acid| 7.52                           | 0.00017                         | 11.53            | 1000             | 86.73             | 0.9992           |
| Nitrite            | 7.95                            | 0.00026                         | 21.18            | 2000             | 94.43             | 0.9992           |
| Bromide            | 10.16                           | 0.00014                         | 5.22             | 2000             | 383.14            | 0.9999           |
| Nitrate            | 11.96                           | 0.00017                         | 17.07            | 2000             | 117.16            | 0.9999           |
| Malate             | 14.55                           | 6.0e-05                         | 27.81            | 1000             | 35.96             | 0.9991           |
| Malonate           | 16.23                           | 8.0e-05                         | 35.21            | 2000             | 56.80             | 0.9991           |
| Sulfate            | 17.79                           | 0.000173                        | 4.55             | 750              | 164.84            | 0.9990           |
| Oxalate            | 18.76                           | 0.00011                        | 21.54            | 2000             | 92.85             | 0.9998           |
| Phosphate          | 18.76                           | 1.33e-05                        | 99.02            | 3000             | 30.30             | 0.9905           |
| Maleate            | 21.03                           | 4.0e-05                         | 66.68            | 4000             | 59.99             | 0.9996           |

\(^1\)The retention times for these species can vary in different runs due to small fluctuations of eluent composition and instrument responses. The retention times listed in the table were recorded for an experiment, at the eluent composition of 5 mM Na\(_2\)CO\(_3\) + 0.3 mM NaOH with a flow rate of 0.8 ml·min\(^{-1}\), and a standard mixture containing the following ions: fluoride (5 µg·L\(^{-1}\)), chloride (30 µg·L\(^{-1}\)), phosphate (150 µg·L\(^{-1}\)), and nitrite, bromide, nitrate, sulfate, glycolate, glyoxylate, formate, acetate, methanesulfonic acid, malate, malonate, oxalate, and maleate (all 100 µg·L\(^{-1}\)).

\(^2,3,4,5\)Same as the note for Table S1.
Table S3. List of compounds in Figure 2 analyzed for elemental ratios using EI mass spectra, including the chemical structure, name, molecular formula, molecular weight ($M_w$: g mol$^{-1}$), and the ratios calculated directly based on ion composition (O/C<sub>cal</sub>, H/C<sub>cal</sub> and N/C<sub>cal</sub>). Compounds No.1-43 have been identified as degradation products of MEA, MDEA or PIP as summarized by Gouedard et al.$^5$; Compounds marked with "*" indicates results from AMS measurements at the vaporizer temperature of 250 °C, others are results from NIST spectral analysis.

| No. | Chemical structure | Name (abbreviation) | Formula | $M_w$ | O/C<sub>cal</sub> | H/C<sub>cal</sub> | N/C<sub>cal</sub> | Solvent |
|-----|-------------------|---------------------|---------|------|------------------|------------------|----------------|---------|
| 1*  | ![Dimethylamine](image) | Dimethylamine (DMA) | C$_2$H$_7$N | 45   | 0 | 2.711 | 0.547 | MDEA |
| 2   | ![Formamide](image) | Formamide | CH$_3$NO | 45   | 1.003 | 3.611 | 1.242 | MEA |
| 3   | ![Formic acid](image) | Formic acid | CH$_2$O$_2$ | 46   | 1.473 | 1.19 | 0 | MEA |
| 4   | ![Glyoxal](image) | Glyoxal | C$_2$H$_2$O$_2$ | 58   | 1.232 | 1.028 | 0 | MEA |
| 5*  | ![Trimethylamine](image) | Trimethylamine (TMA) | C$_3$H$_9$N | 59   | 0 | 2.589 | 0.368 | MDEA |
| 6   | ![Acetic acid](image) | Acetic acid | C$_2$H$_4$O$_2$ | 60   | 0.83 | 1.637 | 0 | MEA |
| 7   | ![Ethylenediamine](image) | Ethylenediamine (EDA) | C$_2$H$_8$N$_2$ | 60   | 0 | 3.276 | 0.954 | PIP |
| 8*  | ![Ethanolamine](image) | Ethanolamine (MEA) | C$_2$H$_7$NO | 61   | 0.189 | 3.476 | 0.768 | MEA |
| 9   | ![Ethylene glycol](image) | Ethylene glycol (EG) | C$_2$H$_6$O$_2$ | 62   | 0.827 | 2.801 | 0 | MDEA |
| 10  | ![N,N-dimethylethylamine](image) | N,N-dimethylethylamine (DMEA) | C$_4$H$_{11}$N | 73   | 0 | 2.575 | 0.358 | MDEA |
| 11* | ![Glycine](image) | Glycine | C$_2$H$_3$NO$_2$ | 75   | 0.446 | 3.363 | 0.859 | MEA |
| 12  | ![2-(Methylamino)ethanol](image) | 2-(Methylamino)ethanol (MAE) | C$_3$H$_9$NO | 75   | 0.093 | 2.648 | 0.435 | MEA |
| 13  | ![Glycolic acid](image) | Glycolic acid | C$_2$H$_4$O$_3$ | 76   | 1.072 | 2.642 | 0 | MDEA |
| 14  | ![Imidazolidin-2-one](image) | Imidazolidin-2-one (2-Imid) | C$_3$H$_8$N$_2$O | 86   | 0.142 | 2.464 | 0.661 | PIP |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
|   |   |   |   |   |   |
| 15* | Piperazine (PIP) | C\textsubscript{4}H\textsubscript{10}N\textsubscript{2} | 86 | 0 | 2.478 | 0.511 | PIP |
| 16 | Oxazolidin-2-one (OZD) | C\textsubscript{3}H\textsubscript{4}N\textsubscript{2}O \textsubscript{2} | 87 | 0.344 | 2.061 | 0.449 | MEA |
| 17 | Oxalamide | C\textsubscript{3}H\textsubscript{4}N\textsubscript{2}O | 88 | 1.096 | 2.818 | 1.211 | MEA |
| 18 | N,N-(dimethyl)ethanolamine (DMAE) | C\textsubscript{4}H\textsubscript{11}NO | 89 | 0.115 | 2.42 | 0.31 | MDEA |
| 19 | Oxalic acid | C\textsubscript{2}H\textsubscript{2}O\textsubscript{4} | 90 | 1.896 | 1.328 | 0 | MEA MDEA PIP |
| 20 | N-methylpiperazine (MPZ) | C\textsubscript{4}H\textsubscript{12}N\textsubscript{2} | 100 | 0 | 2.342 | 0.455 | PIP |
| 21 | N-methylmorpholine (MM) | C\textsubscript{5}H\textsubscript{11}NO | 101 | 0.203 | 1.962 | 0.223 | MDEA |
| 22 | N-(2-hydroxyethyl)acetamide (HEA) | C\textsubscript{4}H\textsubscript{12}N\textsubscript{2}O | 103 | 0.376 | 2.228 | 0.319 | MEA |
| 23 | N-(2-hydroxyethyl)ethylenediamine (HEEDA) | C\textsubscript{5}H\textsubscript{12}N\textsubscript{2}O | 104 | 0.136 | 2.766 | 0.586 | MEA |
| 24 | Diethanolamine (DEAOH) | C\textsubscript{4}H\textsubscript{11}NO \textsubscript{2} | 105 | 0.291 | 2.445 | 0.352 | MDEA |
| 25 | N-(2-hydroxethyl)imidazole (HEI) | C\textsubscript{4}H\textsubscript{8}N\textsubscript{2}O | 112 | 0.213 | 1.587 | 0.434 | MEA |
| 26 | N,N-dimethylpiperazine (DMP) | C\textsubscript{6}H\textsubscript{14}N\textsubscript{2} | 114 | 0 | 2.289 | 0.395 | MDEA PIP |
| 27 | N-ethylpiperazine (EPZ) | C\textsubscript{6}H\textsubscript{14}N\textsubscript{2} | 114 | 0 | 2.311 | 0.35 | PIP |
| 28 | N-formylpiperazine (FPZ) | C\textsubscript{5}H\textsubscript{10}N\textsubscript{2}O | 114 | 0.168 | 1.938 | 0.445 | PIP |

S11
|   | ![Chemical Structure](image) | Name                          | Molecular Formula | Molecular Weight | pKa                        | Water Solubility | Solvent  
|---|-------------------------------|-------------------------------|-------------------|-------------------|----------------|----------------|----------|
| 29 | ![Chemical Structure](image) | Methyl diethanolamine (MDEA)  | C<sub>9</sub>H<sub>13</sub>NO<sub>2</sub> | 119               | 0.253 | 2.745 | 0.326 | MDEA |
| 30 | ![Chemical Structure](image) | N-(2-hydroxyethyl)-N<sub>1</sub>'-methyl piperazine (HMP) | C<sub>9</sub>H<sub>15</sub>N<sub>3</sub> | 129               | 0  | 2.25 | 0.601 | PIP |
| 31 | ![Chemical Structure](image) | N-(2-hydroxyethyl)piperazine (HEP) | C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>O | 130               | 0.118 | 2.014 | 0.394 | PIP |
| 32 | ![Chemical Structure](image) | N-(2-hydroxyethyl)imidazolidin-2-one (HEIA) | C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> | 130               | 0.264 | 1.79 | 0.441 | MEA |
| 33 | ![Chemical Structure](image) | N-(2-hydroxyethyl)oxazolidin-2-one (HEOD) | C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>O | 131               | 0.49  | 1.497 | 0.289 | MDEA |
| 34 | ![Chemical Structure](image) | N-glycylglycine | C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub> | 132               | 0.351 | 2.188 | 0.62  | MEA |
| 35 | ![Chemical Structure](image) | N-(2-hydroxyethyl)succinimide | C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub> | 143               | 0.374 | 1.416 | 0.253 | MEA |
| 36 | ![Chemical Structure](image) | N-(2-hydroxyethyl)-N<sub>1</sub>'-methylpiperazine (HMP) | C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O | 144               | 0.061 | 2.079 | 0.322 | MDEA |
| 37 | ![Chemical Structure](image) | N,N,N<sub>1</sub> ',N<sub>1</sub>'-trimethyl-N,N<sub>1</sub> '-(2-hydroxyethyl)ethylenediamine | C<sub>13</sub>H<sub>18</sub>N<sub>2</sub> | 146               | 0.131 | 2.479 | 0.282 | MDEA |
| 38 | ![Chemical Structure](image) | N,N<sub>1</sub> ',bis-(2-hydroxyethyl)urea | C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub> | 148               | 0.702 | 2.878 | 0.457 | MEA |
| 39 | ![Chemical Structure](image) | Triethanolamine (TEAOH) | C<sub>9</sub>H<sub>15</sub>NO<sub>3</sub> | 149               | 0.286 | 2.261 | 0.265 | MDEA |
| 40 | ![Chemical Structure](image) | N-(carboxymethyl)diethanolamine (bicine) | C<sub>13</sub>H<sub>13</sub>NO<sub>4</sub> | 163               | 0.371 | 1.978 | 0.246 | MDEA |
| 41 | ![Chemical Structure](image) | N,N<sub>1</sub> ',bis-(2-hydroxyethyl)piperazine (BHEP) | C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> | 174               | 0.13  | 2.013 | 0.3  | MDEA |
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 42 | N,N'-bis(2-hydroxyethyl)oxalam ide (BHEOX) | C₆H₁₂N₂O₄ | 176 | 0.429 | 2.001 | 0.367 | MEA |
| 43 | N,N,N',N'-Tetrakis(2-hydroxyethyl)ethylenediamine | C₁₀H₂₄N₂O₄ | 236 | 0.33 | 2.348 | 0.233 | MDEA |
| 44* | H₃C—NH₂ | Methylamine (MA) | CH₅N | 31 | 0 | 3.253 | 1.067 | Other |
| 45* | H₃C—NH₂ | Ethylamine (EA) | C₂H₇N | 45 | 0 | 2.861 | 0.803 | Other |
| 46* | H₃C—NH—CH₃ | Diethylamine (DEA) | C₄H₁₁N | 73 | 0 | 2.643 | 0.418 | Other |
| 47* | H₃C—N—CH₃ | Triethylamine (TEA) | C₆H₁₅N | 101 | 0 | 2.488 | 0.351 | Other |
| 48* | H₅N | Pyrazole (PRZ) | C₅H₄N₂ | 68 | 0 | 1.897 | 0.675 | Other |
| 49* | H₅N=N=CH₃ | 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide (DMPED) | C₈H₁₇N₃ | 155 | 0 | 2.596 | 0.391 | Other |
| EI mass spectral signature ions | Parent compound | Exact mass of parent compound | Chemical structure of parent compound | References |
|-------------------------------|----------------|------------------|-------------------------------------|------------|
| C<sub>3</sub>H<sub>3</sub>NO<sub>2</sub> | Glycine | 75.0320 | ![Glycine structure](image) | 6,7 |
| C<sub>4</sub>H<sub>8</sub>NO<sup>+</sup> | 2-(Methylamino)ethanol (MAE) | 75.0684 | ![MAE structure](image) | 6,7 |
| C<sub>3</sub>H<sub>5</sub>NO<sub>2</sub> | Oxazolidin-2-one (OZD) | 87.0320 | ![OZD structure](image) | 10,14 |
| C<sub>3</sub>H<sub>5</sub>NO<sup>+</sup> | (2-Hydroxyethyl)formamide | 89.0477 | ![Fm structure](image) | 11,14 |
| C<sub>4</sub>H<sub>11</sub>NO<sub>2</sub> | Diethanolamine | 105.0790 | ![DEA structure](image) | This work |
| C<sub>4</sub>H<sub>9</sub>NO<sup>+</sup> | N-(2-hydroxethyl)imidazole (HEI) | 112.0637 | ![HEI structure](image) | 13,15 |
| C<sub>4</sub>H<sub>7</sub>NO<sub>2</sub> | 2-Hydroxy-N-(2-hydroxyethyl)acetamide (HHEA) | 119.0582 | ![HHEA structure](image) | 13,15 |
| C<sub>5</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> | N-(2-hydroxyethyl)imidazolidin-2-one (HEIA) | 130.0742 | ![HEIA structure](image) | 9,10,12,13,15,16 |
| C<sub>5</sub>H<sub>11</sub>NO<sup>+</sup>, C<sub>4</sub>H<sub>8</sub>NO<sup>+</sup>, C<sub>3</sub>H<sub>5</sub>NO<sup>+</sup> | N-(2-Hydroxyethyl)lactamide | 133.0739 | ![Lactamide structure](image) | This work |
| C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> | N-(2-hydroxyethyl)piperazin-3-one (HEPO) | 144.0899 | ![HEPO structure](image) | 13,14 |
| C<sub>5</sub>H<sub>12</sub>N<sub>2</sub> | N,N'-bis-(2-hydroxyethyl)urea | 148.0848 | ![Urea structure](image) | 8,9,11 |
| C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub> | N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide (HEHEAA) | 162.1004 | ![HEHEAA structure](image) | 13,15 |
| C<sub>5</sub>H<sub>11</sub>NO<sub>3</sub> | N,N’-bis(2-hydroxyethyl)oxalamide (BHEOX) | 176.0798 | ![BHEOX structure](image) | 13,14 |
Table S5. Major degradation products identified in MDEA degradation sample and proposed EI spectral signature ions

| EI mass spectral signature ions | Parent compound                  | Exact mass of parent compound | Chemical structure of parent compound | References |
|--------------------------------|----------------------------------|------------------------------|---------------------------------------|------------|
| C₃H₇N⁺                         | Azetidine (AZ)                   | 57.0578                      |                                       | This work  |
|                                |                                  |                              |                                       |            |
| C₃H₈NO⁺                        | 2-(Methylamino)ethanol (MAE)     | 75.0684                      |                                       |            |
|                                |                                  |                              |                                       |            |
| C₄H₁₁NO⁺                       | N,N-(dimethyl)ethanolamine (DMAE)| 89.0841                      |                                       |            |
|                                |                                  |                              |                                       |            |
| C₄H₁₁NO⁺, C₆H₁₂NO⁺             | N-methylmorpholine (MM)          | 101.0841                     |                                       |            |
|                                |                                  |                              |                                       |            |
| C₅H₁₁NO₂⁺                      | Diethanolamine (DEAOH)           | 105.0790                     |                                       |            |
|                                |                                  |                              |                                       |            |
| C₅H₁₂NO₂⁺                      | Ethyldiethanolamine (EDEA)       | 133.1103                     |                                       | This work  |
|                                |                                  |                              |                                       |            |
| C₅H₁₂NO₂⁺                      | Triethanolamine (TEAOH)          | 149.1052                     |                                       |            |
|                                |                                  |                              |                                       |            |
| C₆H₁₀NO₃⁺, C₆H₁₂NO⁺            | N-(carboxymethyl)diethanolamine (bicine) | 163.0845 |                                       |            |

References:
11, 12
Table S6. Major degradation products identified in PIP degradation sample and proposed EI spectral signature ions

| EI mass spectral signature ions | Parent compound                  | Exact mass of parent compound | Chemical Structure of parent compound | References |
|---------------------------------|----------------------------------|------------------------------|--------------------------------------|------------|
| $\text{C}_3\text{H}_6\text{N}_2\text{O}^+$ | Imidazolidin-2-one               | 86.0480                      | ![Chemical Structure](image1)         |            |
| $\text{C}_4\text{H}_8\text{N}_2\text{O}^+$, $\text{C}_3\text{H}_7\text{N}_2^+$ | Piperazinone                     | 100.0637                     | ![Chemical Structure](image2)         | This work  |
| $\text{C}_3\text{H}_12\text{N}_2^+$ | N-methylpiperazine (MPZ)         | 100.1000                     | ![Chemical Structure](image3)         |            |
| $\text{C}_5\text{H}_{10}\text{N}_2\text{O}^+$, $\text{C}_3\text{H}_6\text{NO}^+$ | N-formylpiperazine (FPZ)         | 114.0793                     | ![Chemical Structure](image4)         |            |
| 1-Methyl-2-Piperazinone         |                                 |                              |                                      |            |
| 3-Methyl-2-piperazinone         |                                 |                              |                                      |            |
| $\text{C}_6\text{H}_{12}\text{N}_2\text{O}^+$ | 1,4-Dimethyl-2-Piperazinone     | 128.0950                     | ![Chemical Structure](image5)         | This work  |
| 1,3-Dimethylpiperazin-2-one     |                                 |                              |                                      |            |
|                                  |                                  |                              |                                      |            |
Table S7. Cross correlation coefficients (Pearson's r²) between the mass spectra of the eight identified MDEA degradation products and the correlation coefficients of each product spectrum with the sample spectrum. Mass spectra of unit mass resolution (UMR) are used in these calculations.

| Products | AZ     | MM     | DEAOH  | EDEA   | TEAOH  | Bicine | MAE    | DMAE   | Sample |
|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| AZ       | -      |        |        |        |        |        |        |        |        |
| MM       | 0.002  | -      |        |        |        |        |        |        |        |
| DEAOH    | 0.05   | 0.003  | -      |        |        |        |        |        |        |
| EDEA     | 0.01   | 0.003  | 0.029  | -      |        |        |        |        |        |
| TEAOH    | 0.003  | 0.001  | 0.298  | 0.013  | -      |        |        |        |        |
| Bicine   | 0.02   | 0.148  | 0.180  | 0.027  | 0.148  | -      |        |        |        |
| MAE      | 0.00   | 0.015  | 0.004  | 0.001  | 0.006  | 0.052  | -      |        |        |
| DMAE     | 0.06   | 0.001  | 0.056  | 0.135  | 0.014  | 0.011  | 0.002  | -      |        |
| Sample   | 0.29   | 0.124  | 0.261  | 0.117  | 0.126  | 0.347  | 0.385  | 0.135  | -      |
Figures

Figure S1. Chromatographic responses and elution times of cation standard mixture which contains Li$^+$ (5 µg·L$^{-1}$), Na$^+$ (20 µg·L$^{-1}$), NH$_4$$^+$ (40 µg·L$^{-1}$), ethanolamine (100 µg·L$^{-1}$), methylamine (100 µg·L$^{-1}$), K$^+$ (20 µg·L$^{-1}$), diethanolamine (100 µg·L$^{-1}$), ethylamine (100 µg·L$^{-1}$), dimethylamine (100 µg·L$^{-1}$), triethanolamine (100 µg·L$^{-1}$), methyldiethanolamine (200 µg·L$^{-1}$), bis(2-hydroxypropyl)amine (100 µg·L$^{-1}$), trimethylamine (100 µg·L$^{-1}$), Mg$^{2+}$ (20 µg·L$^{-1}$) and Ca$^{2+}$ (100 µg·L$^{-1}$) (upper panel); and anion standard mixture which contains fluoride (5 µg·L$^{-1}$), glycolate (100 µg·L$^{-1}$), formate (100 µg·L$^{-1}$), glyoxylate (100 µg·L$^{-1}$), acetate (100 µg·L$^{-1}$), chloride (30 µg·L$^{-1}$), methanesulfonic acid (100 µg·L$^{-1}$), nitrite (100 µg·L$^{-1}$), bromide (100 µg·L$^{-1}$), nitrate (100 µg·L$^{-1}$), malate (100 µg·L$^{-1}$), malonate (100 µg·L$^{-1}$), sulfate (100 µg·L$^{-1}$), oxalate (100 µg·L$^{-1}$), phosphate (100 µg·L$^{-1}$) and maleate (100 µg·L$^{-1}$) (lower panel). For anions, there are two co-elutes, which are formate with glyoxylate, and oxalate with phosphate; since glyoxylate and phosphate are unlikely important ions in amine-based PCCC samples, these coelutes should not be a concern.
Figure S2. High-resolution AMS spectra of MEA, MDEA, and PIP, measured at vaporizer temperatures of 250 °C (a-c) and 600 °C (d-f). The spectral peaks are colored by 9 different ion categories listed in (a); Marker "▲" indicates the molecular ion; NIST spectra (in UMR) are also plotted.
Figure S3. For the 12 N-containing compounds measured by the HR-ToF-AMS at vaporizer temperatures of both 250 °C and 600 °C in this study: (a) Correlation coefficients ($r^2$) of NIST spectra with AMS spectra (both in UMR); (b) Mass fractions of the molecular ions in the AMS spectra; (c) N/C ratios calculated from the AMS spectra measured at vaporizer temperature of 250 °C versus the real ratios (CI: confidence interval); (d) N/C ratios calculated from the AMS spectra measured at vaporizer temperature of 600 °C versus the real ratios (CI: confidence interval); (e) Comparisons between the N/C ratios calculated from the AMS spectra measured at vaporizer temperatures of 250 °C and 600 °C.
Figure S4. AMS spectra (vaporizer temperature = 600°C) of pure MEA (a), MDEA (d), PIP (g) and sucrose (b,e,h), and 1:1 (mass ratio) mixtures of MEA/sucrose (c), MDEA/sucrose (f) and PIP/sucrose (i). The spectral peaks are colored by 9 different ion categories listed in (a); Note the amines were prepared in the chloride salts to ensure their mass ratios to sucrose in the particles analyzed by the AMS are consistent with the ratios designed in the solutions.
Figure S5. Comparisons between deconvoluted mass ratios from AMS spectra (vaporizer temperature = 600 °C) with the real values. (a) MEA/sucrose, (b) MDEA/sucrose, and (c) PIP/sucrose. AMS spectra of the binary mixtures with different mass ratios of amine to sucrose were first obtained, and then each mixture spectrum was decomposed according to equation (1) in the main text, where $i$ refers to the corresponding amine and sucrose, respectively.
Figure S6. Raw AMS spectra of MEA-based, MDEA-based and PIP-based degradation samples measured at the AMS vaporizer temperatures of 250 °C (a-c) and 600 °C (d-f). Note that the H2O⁺, HO⁺, O⁺ and CO⁺ signals are directly measured values. Elemental ratios for 250 °C spectra are calculated using the new factors obtained in Figure 2 of the main text, while ratios for 600 °C spectra are determined based on the factors reported in Aiken et al. The spectral peaks are colored by 9 different ion categories listed in (a).
Figure S7. AMS spectra of MEA-based, MDEA-based and PIP-based degradation samples measured at the AMS vaporizer temperatures of 250 °C (a-c) and 600 °C (d-f), after removal of H2O+, HO+, O+, and CO2-related ions (based on fragmentation pattern for CO2 in NIST). Elemental ratios for 250 °C spectra are calculated using the new factors obtained in Figure 2 of the main text, while ratios for 600 °C spectra are determined based on the factors reported in Aiken et al.20 The spectral peaks are colored by 9 different ion categories listed in (a).
Figure S8. Differences between the AMS spectra measured at vaporizer temperatures of 250 °C and 600 °C for the degradation samples of (a) MEA, (b) MDEA, and (c) PIP (calculated from the spectra shown in Figure S7). The spectral peaks are colored by 9 different ion categories listed in (a).

- (a) MEA degradation sample (250 °C vs. 600 °C: $r^2 = 0.554$)
- (b) MDEA degradation sample (250 °C vs. 600 °C: $r^2 = 0.560$)
- (c) PIP degradation sample (250 °C vs. 600 °C: $r^2 = 0.966$)

Chemical species: $C_xH_y^+$, $C_xH_yO_1^+$, $C_xH_yO_{z(>1)}^+$, $C_xH_yN_{p(>1)}^+$, $C_xH_yNO_{1}^+$, $C_xH_yN_{p(>1)}O_{z(>1)}^+$, $H_3O^+$, $NO_2^+$, $NH_4^+$
Figure S9. AMS spectra of MEA-based, MDEA-based and PIP-based degradation products measured at the AMS oven temperatures of 250 °C (a-c) and 600 °C (d-f), after removal of parent amine signals (calculated from spectra shown in Figure S7). Elemental ratios for 250 °C spectra are calculated using the new factors obtained in Figure 2 of the main text, while ratios for 600 °C spectra used the factors reported in Aiken et al. The spectral peaks are colored by 9 different ion categories listed in (a).
Figure S10. ESI-MS spectra for the degradation samples of (a) MEA, (b) MDEA, and (c) PIP. (only major peaks are shown). The species identified in Tables S4-S6 are marked in the spectra.
Figure S11. Comparisons of the MDEA degradation sample spectrum (Figure S7b) with the one reconstructed using the multivariate fitting algorithm (a), the scatter plot between the two (b), and (c-j) NIST spectra of the eight degradation products used in the fitting.
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