Supplementary Information

Mitigating matrix effects in oil and gas wastewater analysis:

LC-MS/MS method for ethanolamines

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This Supplementary Information (SI) contains 4 texts, 23 figures, and 7 tables that support SPE-LC/MS method development. The document is organized as follows: the texts begin on page 2, the figures on page 11, and the tables on page 27.

Text S1. Method Description, Reagents and Materials

The goal of this study is to develop a robust method for the quantification of ethanolamines in oil and gas produced waters. The method utilizes solid-phase extraction (SPE) and LC-ESI-MS as discussed in the main text and detailed in Text S4. Prior to SPE, produced water samples were adjusted to pH 11 (using 0.1 M NaOH, prepared from pellets, Sigma Aldrich), confirmed with a pH meter (Hannah Instruments, calibrated daily) and filtered through pre-combusted glass fiber filters (Whatman GF/F) enclosed in a microsyringe filter holder (25 mm, Luer-Lok, stainless steel, Millipore). Multiple isotopic standards (i.e., one per compound namely monoethanolamine (1,1,2,2-D_4; D_4-MEA, 98%), diethanolamine (ethylene-D_8; D_8-DEA, 98%), *N*-methyldiethanolamine (diethyl- $^{13}C_4$; $^{13}C_4$-MDEA, 99%), *N*-ethyldiethanolamine (diethanol-$^{13}C_4$; $^{13}C_4$-EDEA, 98%), triethanolamine ($^{13}C_6$; $^{13}C_6$-TEA, 97%), Cambridge Isotopes, MA, USA) were spiked to 10-mL filtered samples. Ethanolamines were then extracted using Visiprep™ SPE Vacuum Manifold, Supelco), through 1 g Bondesil PPL polymeric sorbents (125 µm, Agilent, USA) packed in pre-combusted glass cartridges (glass SPE Tube with PTFE frit, 20 µm porosity, Sigma Aldrich). The SPE cartridges were sequentially preconditioned using 6 mL of methanol (Fisher Scientific, Optima LCMS grade) and 6 mL of ultrapure water (18.2 MΩ.cm, TOC< 5 ppb water, MilliQ water system). The sample (6 mL, pH 11) was then loaded onto the cartridge at 1 mL/min, after which the cartridges were washed with 15 mL ultrapure water and then dried under vacuum for 15 min (room temperature). The cartridges were eluted with 6 mL 2% formic acid (Fisher Scientific, Optima LCMS) in 90/10 methanol/water into pre-combusted glass VOC vials. The extracts were then analyzed using an 1290 Infinity II liquid chromatography system (Agilent, USA) equipped with an Acclaim Trinity P1 column (2.1 x 100 mm, 3 µm, Thermo Scientific USA). The target compounds were separated via isocratic elution (90% acetonitrile (Fisher Scientific, Optima LCMS grade); 10% 50 mM ammonium formate (pH 3.7, Sigma-Aldrich, ≥99.995%) at a flow rate of 0.5 mL/min (analysis time = 7 min) and injection volume of 10 µL. Mass spectrometry was performed using an Agilent 6495 iFunnel triple quadrupole system in positive ESI mode, and spectral data were acquired by multiple reaction monitoring. The concentrations of ethanolamines were calculated using the relative response of the target ethanolamine to its isotopic internal standard. The following standards (Sigma-Aldrich) were used for each target ethanolamine: Monoethanolamine (MEA, ≥99.5%), Diethanolamine (DEA, ≥99.5%), *N*-Methyldiethanolamine (MDEA, ≥99%), *N*-Ethyldiethanolamine (EDEA, 98%), Triethanolamine (TEA, ≥99%). All

glassware used for sample preparation and analysis were pre-combusted in a muffle furnace at 450 °C for 8 hours.

Text S2. Produced Water Sample Composition

The produced water samples (PW-Mar) had variable characteristics (Table S2). The samples had a distinct 'rotten egg' smell due to hydrogen sulfide (S^{2-} = 26 – 82 mg/L) formed during hydrocarbon generation and/or bacterial sulfate reduction under anaerobic conditions. The H_2S detection is supported by the high concentrations of acetate (39 – 63 mg/L), a common substrate for aerobic biodegradation. In addition to small organic acids, DRO (nC$_{10}$-nC$_{28}$ or "C10-C28", Fig. S1) were detected at 5.3 – 7.9 mg/L; these concentrations are three orders of magnitude greater than those found in some fracking impacted-groundwaters but not uncommon for flowback and produced waters. The samples all maintained near neutral pH with a high buffering capacity and carbonate content of 942 – 1353 mg/L. Consistent with other brines from oil and gas production, salinity in the samples was elevated (8110 – 18100 mg/L as NaCl and >100 mg/L bromide), where PW1 was the saltiest sample, followed by PW2, PW3, and PW4. The variable matrix composition of the samples is useful for illuminating the differences in degrees of ion suppression that can occur during LC/MS analysis

Text S3. Fragmentation of Ethanolamines with ESI

Proposed fragmentation reactions resulting in the observed product ions are shown in Figure S4.[3] With collision induced dissociation, all ethanolamines were prone to lose H_2O. MS^2 analysis of $[TEA+H]^+$ (m/z 150) shows that loss of H_2O is the first step to form $[(C_2H_4)N(C_2H_4OH)_2]^+$ at m/z 132, followed by elimination of C_2H_3OH to form $[(C_2H_4)NH(C_2H_4OH)]^+$ at m/z 88. This product ion subsequently undergoes elimination of another H_2O to produce $[(C_2H_4)N(C_2H_4)]^+$ at m/z 70. Protonated EDEA and MDEA also fragment by successive elimination of H_2O and C_2H_3OH (via cleavage with H rearrangement). MS^2 analysis of DEA (m/z 106) also shows that it undergoes elimination of H_2O to form $[(C_2H_4)NH(C_2H_4OH)]^+$ at m/z 88, followed by a loss of second H_2O forming $[(C_2H_4)N(C_2H_4)]^+$ at m/z 70. These product ions are identical to those formed from TEA, which suggests potential overlap from in-source fragmentation when TEA and DEA lack adequate chromatographic separation. False-positive detection of DEA from fragmentation of TEA

standards are illustrated in Figure S4b. Our method precludes this type of interference, as DEA and TEA did not co-elute and had retention times of 4.6 min and 3.3 min, respectively. Finally, $[MEA+H]^+$ (m/z 62) undergoes elimination of H_2O to form $[C_2H_2NH_2]^+$ (m/z 44) and can also fragment into $[C_2H_2OH]^+$ (m/z 45) from loss of NH_3 via inductive cleavage.[4]

Text S4. Step-by-step procedure for laboratory personnel

1. BATCH PREPARATION

a. Ethanolamine standards

i. Primary ethanolamine stock solutions in methanol (1000 mg/L)

Weigh 0.1 g of each ethanolamine standard into a single, 100-mL volumetric flask. Dilute to mark with methanol, mix well, and store in freezer. Record actual mass measured and calculate the actual concentration of stock solution.

ii. Working ethanolamine stock solution (1.0 mg/L ethanolamine standard mix)

Into a 25-mL volumetric flask, add a small volume of LCMS water, then transfer 25 µL of each of the primary stock ethanolamine solution into the flask. Make up to 25 mL volume with LCMS water, mix well, and transfer to a 40-mL VOC vial. Store this solution in freezer. This solution is routinely replaced every 2 months or earlier if it fails quality control.

b. Ethanolamine isotopic surrogate standards

i. Primary isotopically labelled ethanolamine stock solutions (1000 mg/L)

Measure out 0.01 g of each isotopic standard into 10-mL volumetric flask and fill to mark with methanol. Mix well. Record actual mass measured and calculate the actual concentration of the stock solution.

ii. Working isotopically labelled ethanolamine stock solution (1.0 mg/L surrogate standard mix)

Into a 25-mL volumetric flask, add a small amount of LCMS water, and then transfer 25 µL of each of the primary stock isotopically labelled ethanolamine solutions into the flask.

Make up to 25 mL volume with LCMS water and transfer to 40-mL VOC vial. Store this solution in freezer. This solution is routinely replaced every 2 months or earlier if it fails quality control.

c. Calibration standards

A calibration curve is run with every worklist. Prepare calibration standards in 25 mL LCMS water in glass volumetric flasks according to the range of concentrations expected in the samples. Use appropriate clean glass microsyringes for solution transfer. The table below gives a linear response at 1 – 40 µg/L ethanolamines with constant 10 µg/L surrogate standard concentration.

Volumes of working stock standard solutions needed to prepare calibration standards

STD concentration (µg/L)	Volume of 1 mg/L ethanolamine standard mix to add (µL)	Volume of 1 mg/L surrogate standard mix to add (µL)	Total final volume (mL)
0	0	250	25
1	25	250	25
5	125	250	25
10	250	250	25
15	375	250	25
20	500	250	25
40	1000	250	25

d. Blanks

i. Laboratory fortified sample

In a 10-mL volumetric flask, add 150 µL of 1.0 mg/L ethanolamine standard mix (MEA, DEA, MDEA, EDEA, and TEA) and dilute to mark with 10 mL LCMS water giving a final concentration of 15 µg/L. This is used to determine recovery during the SPE procedure.

ii. Laboratory reagent blank sample

Prepare a solution of 10 mL LCMS water. This is used to assess possible contamination.

iii. Matrix spike sample

Using a representative of the samples (10 mL) to be analysed (e.g., water collected in the field), spike 150 µL of the 1.0 mg/L ethanolamine standard mix (MEA, DEA, MDEA, EDEA, and TEA) to have a final concentration of 15 µg/L. Lower spike level (e.g., 2 µg/L) can also be used to validate the method at low and high concentrations. If standard addition exceeds the calibration range due to ethanolamines originally present in the sample, take another sample aliquot, make the necessary dilution, and spike the ethanolamine standard mix to have a total concentration that is within the calibration range.

2. CONTAINER PREPARATION, SAMPLE COLLECTION, AND STORAGE

All glassware used for sample collection and analysis must be pre-combusted in a muffle furnace at 450 °C for 8 hours. Combusted glassware is stored covered with pre-combusted aluminum foil until use. Note that good oxygen access is important during combustion, so foil covers must be secured after the combustion.

Samples (250 mL) should be collected without headspace in 250-mL amber bottles with Teflon lids. Prior to collecting the samples, open the sampling tap for about a minute or long enough to ensure flushing of "dead volume" in the collection system. Note that a pH or temperature monitor can help determine when one is seeing water from the source as opposed to water that has been stored in a tank. Rinse the bottles with water samples 3 times before filling them up to the brim. Gloves must be worn when handling effluent bottles. Wear a facemask to protect yourself against volatile organic compounds.

After collection, place the sample bottles in new Ziplock bags and transport them to the laboratory with ice packs. Samples designed as field blanks (e.g., LCMS-grade water collected in the field following similar procedures as the samples) should also accompany each shipment. Once in the lab, split the samples into two separate, 250-mL, pre-combusted amber bottles and freeze them until use. Samples are stable for at least 30 days.

3. SAMPLE PREPARATION

a. Measure 40 mL of sample into 40-mL VOC vial. Adjust pH to 11 to increase recovery during SPE using 2 M NaOH (e.g., by adding few drops via Pasteur pipet, mixing, and checking the pH). Check the pH of the solution by transferring 2 drops of the solution to a pH paper or transfer an aliquot for pH measurement via a pH electrode. Prepare another 40 mL as duplicate following the same procedure.

b. Using a clean, 50-mL glass syringe and pre-combusted glass microfiber filter, filter each sample and receive the filtrate into clean VOC vials. A new filter should be used for each sample. Clean syringe and filter assembly between each filtration by sonicating the filter assembly and syringe in acetone for 3 minutes followed by solvent rinsing with 3 volumes each of hexane, dichloromethane, acetone, methanol, and water.

c. Transfer 10 mL aliquot of the filtered sample into another VOC vial and spike each sample (including laboratory fortified and matrix spike samples) and blanks with 100 µL of 1.0 mg/L surrogate standard mix (D_4-MEA, D_8-DEA, $^{13}C_4$-MDEA, $^{13}C_4$-EDEA, and $^{13}C_6$-TEA) giving a final surrogate standard concentration of 10 µg/L.

d. Solid phase extraction

i. Prepare the SPE columns. Using clean forceps, insert PTFE frits to empty pre-combusted glass SPE tubes to serve as base support for the sorbent. Measure 1.0 g of Agilent Bondesil PPL sorbent and carefully transfer to the SPE tube. Add the top frit to compress and pack the column.

ii. Set up the vacuum manifold. Line up SPE columns labelled corresponding to the sample name. Make sure that the manifold and the Teflon solvent guide needles are clean by rinsing with acetone, methanol, and water prior to use.

iii. Condition SPE columns. Apply vacuum to have a flow rate of approximately 2 mL/min using the following solvents:
   - 2×3 mL methanol, SPE column must go to dryness. Use clean glass measuring pipets for solution transfer.
   - 2×3 mL ultrapure water. **DO NOT** allow column to go to dryness. Turn tap off with about 1 mL water layer visible above the top frit.

iv. Apply 2×3 mL sample to SPE column (i.e., adding into the water layer). Control the vacuum so the loading rate should be approximately 1 mL/min. Check samples frequently to ensure samples pass through the column dropwise.

v. Once all the samples are through the SPE column, add 5×3 mL of ultrapure water into each SPE column to remove salts (flow rate = 2 mL/min).

vi. Open the valves and let the columns dry under vacuum for 15 min.

vii. Elution of ethanolamines (**NOTE:** Elution must be done in a fume hood.)
   1. Prepare 100 mL elution solvent (2% formic acid in 90/10 methanol/LCMS water)
   2. Label VOC vials corresponding to each sample extract
   3. Remove the manifold cover (with columns intact) and insert clean VOC vials inside the glass basin. Align these vials to the column as these will receive the eluate, which now contains the ethanolamine analytes.
   4. Close the SPE manifold and add 2×3 mL eluent at a rate of 1 mL/min. Check that each eluate is being transferred to the designated VOC vial.

viii. Transfer the samples using combusted Pasteur pipets into 2-mL amber glass vials for analysis by LC-MS. Store in the laboratory freezer if not analyzed immediately.

4. LIQUID CHROMATOGRAPHY – MASS SPECTROMETRYANALYSIS

a. LC mobile phase preparation

Mobile phase A:

i. 250 mL of 1 M of ammonium formate stock solution: Weigh 15.8 g of ammonium formate into a 250 mL-volumetric flask. Dissolve with LCMS water and fill to the mark.

ii. 500 mL of 50 mM ammonium formate: Transfer 25 mL of 1 M ammonium formate stock solution to 500 mL-volumetric flask and fill to volume with LCMS water. Adjust pH to 3.7 using LCMS grade formic acid.

Mobile phase B: 100% LCMS grade acetonitrile

NOTE: DO NOT "top up" old mobile phases due to possible microbial growth. Dispose contents and clean mobile phase bottles by rinsing with the following solvent sequence as recommended by Agilent: isopropanol → methanol → LCMS water → methanol → LCMS water → mobile phase. Rinse the bottle with new mobile phase 3 times before completely filling up with mobile phase. Purge each pump and mobile phase line in the LC for 2 minutes before starting a worklist.

b. LC conditions. The conditions for liquid chromatography are listed below.

Conditions for liquid chromatography

Parameter	Description
Column	Acclaim Trinity P1 (2.1 x 100 mm, 3 µm)
Mobile phase	Isocratic, 90% acetonitrile; 10% 50 mM ammonium formate, pH 3.7
Injection volume, µL	10 (draw speed = 100 µL/min; eject speed = 400 µL/min; wait time after draw = 1.2 s)
Flow rate, mL/min	0.5
Column temperature, °C	20
Needle wash	Multiwash: Water (10 s) → Isopropanol (10 s) → 90/10 acetonitrile/water (10 s)

c. MS conditions

i. **Ion source.** Check tune MS every use and autotune every 2-3 months or every time the MS is turned off. Source conditions for mass spectrometry are detailed below. The values presented were obtained after performing source optimization during method development. Source optimization was done in the following order: drying gas temperature → sheath gas heater → nebulizer, capillary, nozzle, ion funnel (simultaneously).

Conditions for Mass Spectrometry

Parameter	Value
Capillary	2000 V
Ion funnel	150 V (high pressure RF) 50 V (low pressure RF)
Nebulizer	50 psi
Nozzle	0 V
Sheath gas heater	330 °C
Sheath gas flow	11 L/min
Drying gas temperature	150 °C
Drying gas flow	18 L/min

Scan segments. Acquisition is done using multiple reaction monitoring (MRM) in positive ESI mode. The precursor and product ions for ethanolamine analysis are listed in Table 1 (main text). Product ions were determined during method development and were the most abundant ions during fragmentation at specific collision energies.

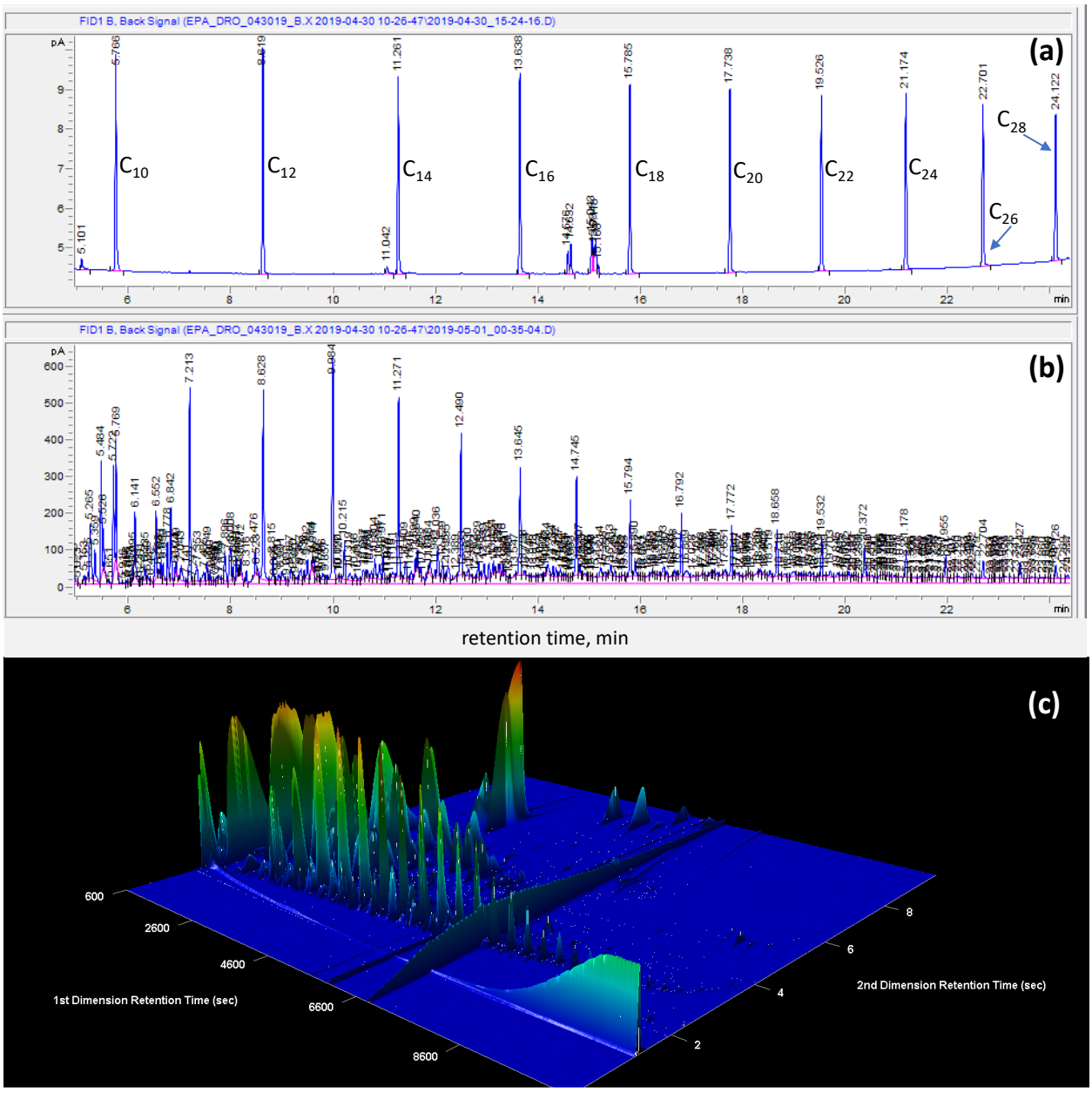

Figure S1. Gas chromatograms (1D and 2D) showing diesel range organic compounds extracted from produced water samples. (a) 500 µg/L DRO standard; (b) extract of PW2-Mar sample obtained via liquid-liquid extraction using dichloromethane; (c) GCxGC profile of PW4-Mar extract showing abundance of volatile organic compounds. Each peak corresponds to a compound separated by vapor pressure (1st dimension) and polarity (2nd dimension).

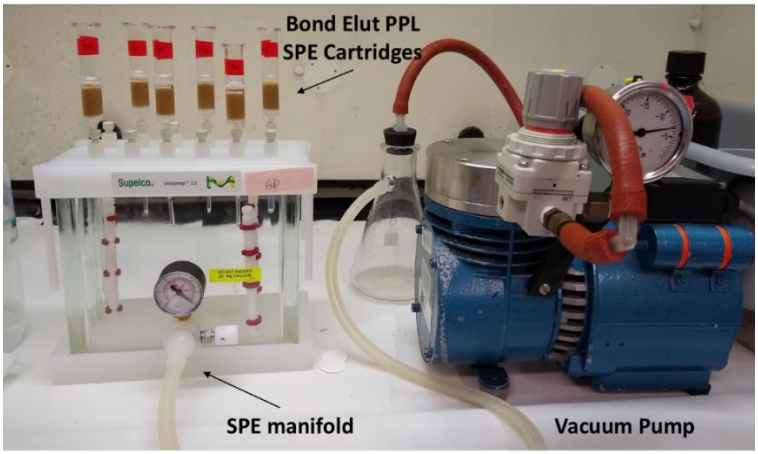

Figure S2. SPE extraction manifold for sample clean-up. SPE set-up shows the packed Agilent PPL columns, manifold connected to a solvent trap flask, and vacuum pump

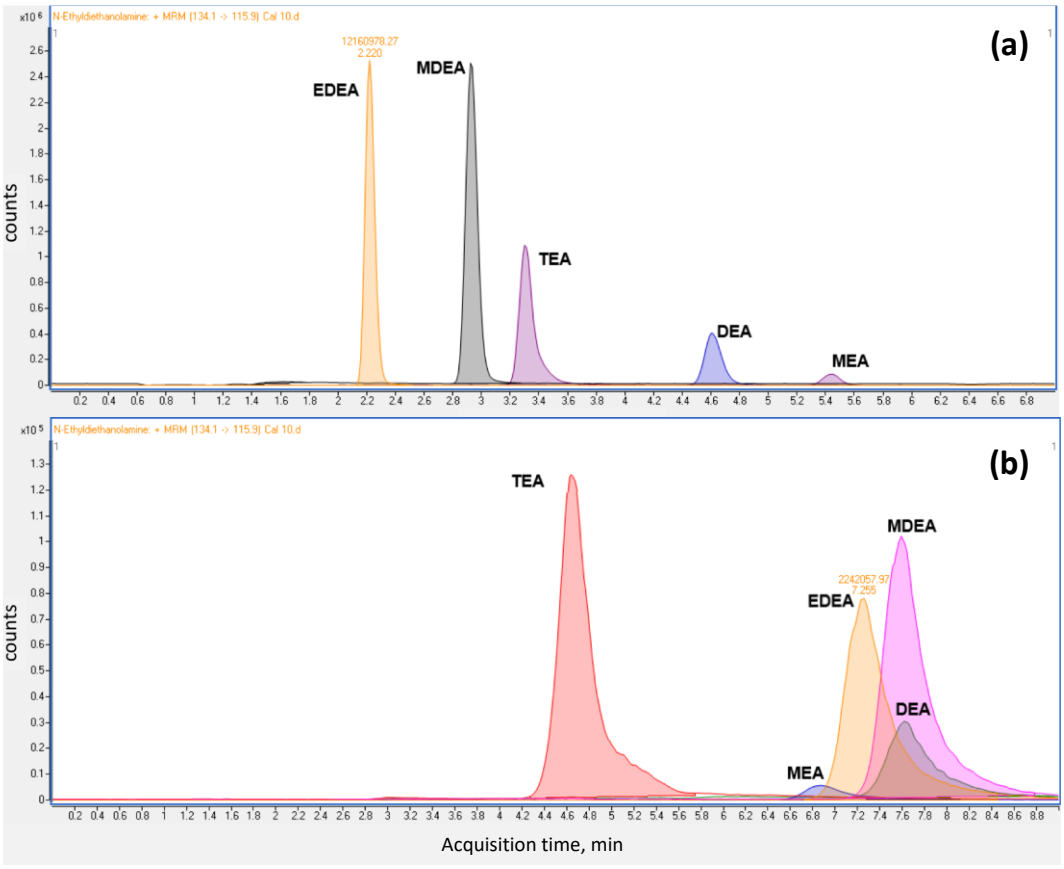

Figure S3. Overlaid target ion traces (isotopically labelled target ion traces not shown for clarity) of a 10 μg/L standard using (a) Acclaim Trinity P1 column showing good peak resolution and (b) Waters Atlantis HILIC column showing poor chromatographic separation of ethanolamines. The x-axis is time (min) and y-axis is counts/signal intensities. Distinct colors correspond to peak areas integrated to quantify ethanolamines.

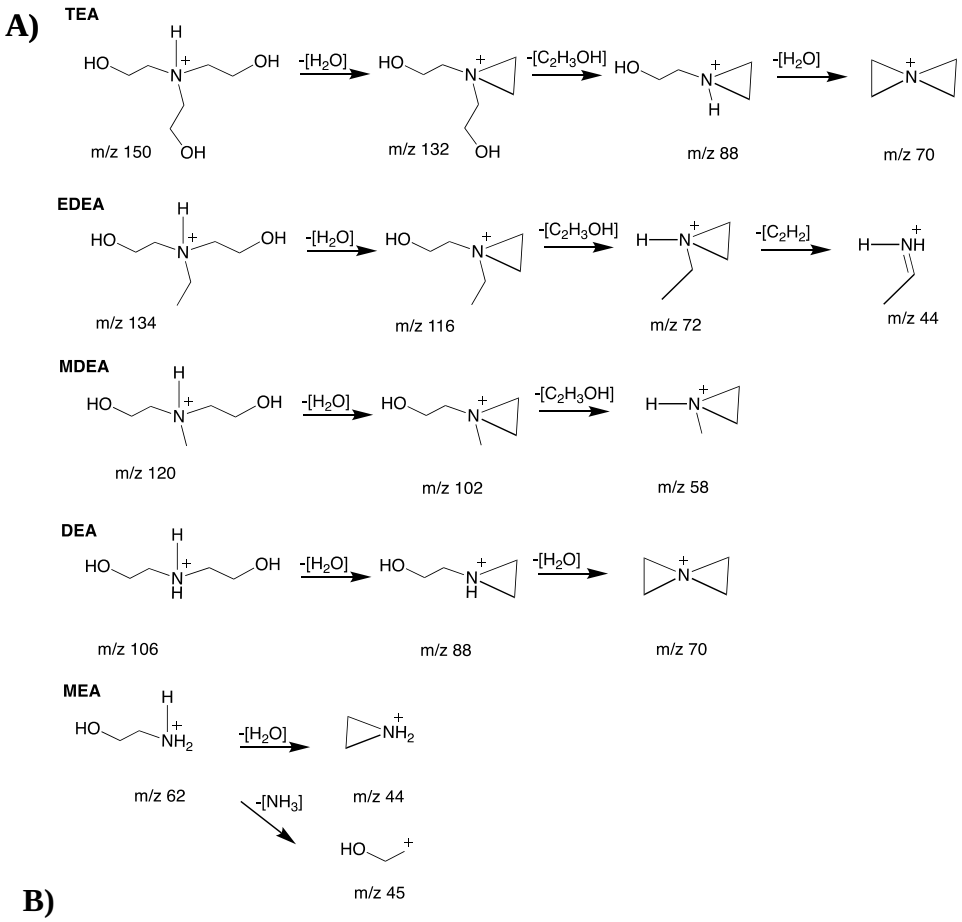

Figure S4. Fragmentation of ethanolamines. A) Proposed ESI+ fragmentation reaction for ethanolamines. References noted in above text. B) In-source fragmentation of TEA that forms product ions of DEA (e.g., m/z 70). This chromatogram employed a 20 µg/L ethanolamine standard. The inset shows a direct relationship of the peak area of TEA-derived DEA (t_R = 3.3 min) with TEA concentration. This interference associated with in-source fragmentation was avoided in the MIT-Acclaim method by ensuring good chromatographic separation of TEA and DEA.

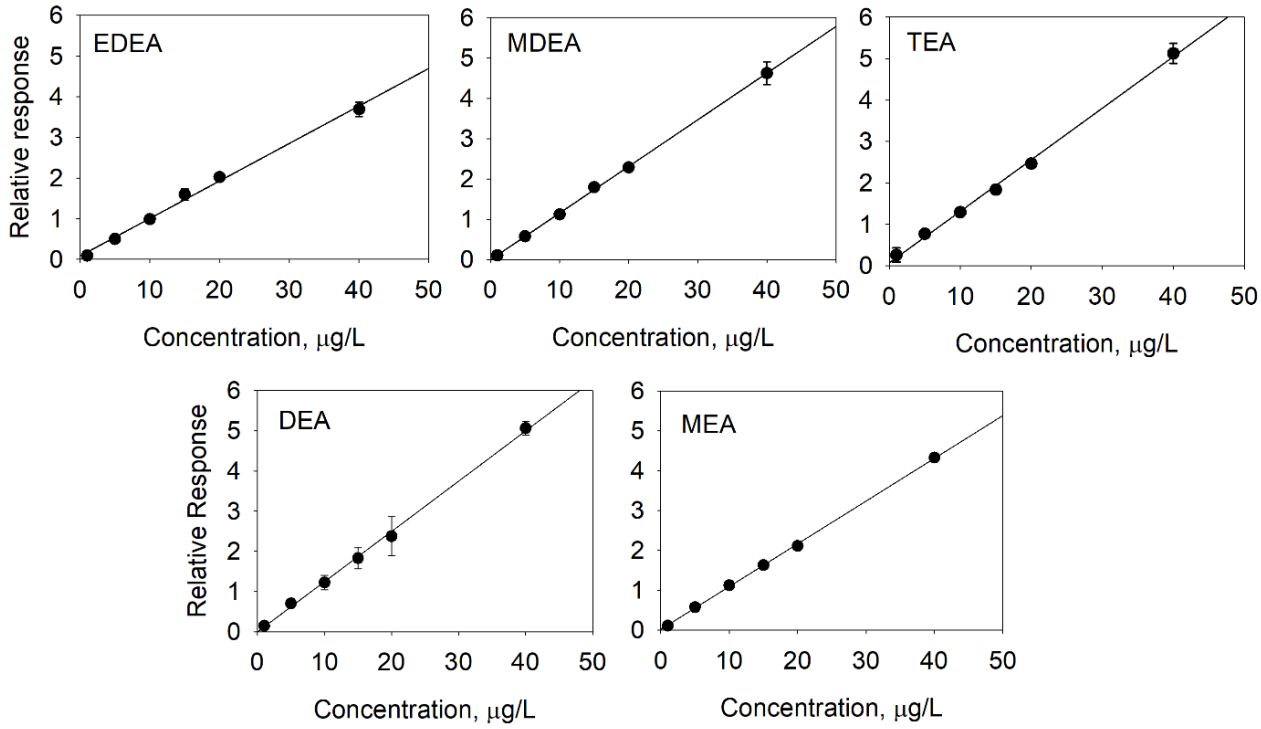

Figure S5. Representative linear calibration curves for EDEA, MDEA, TEA, DEA, and MEA (n=3). The x-axis represents ethanolamine concentration (µg/L), and y-axis is the response of the analyte relative to the internal standard (area analyte/area internal standard). R^2 for all plots > 0.990.

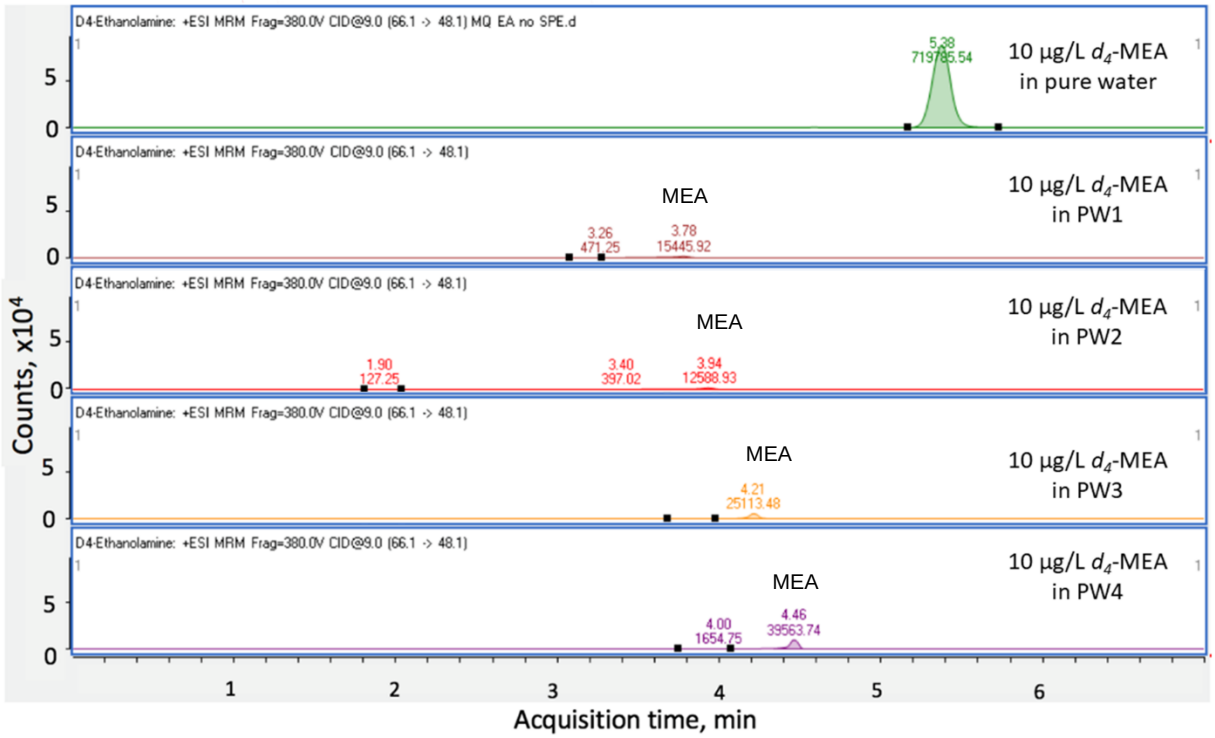

Figure S6. d_4-MEA (10 µg/L) signal in pure water and produced water samples showing effect of ion suppression from matrix components

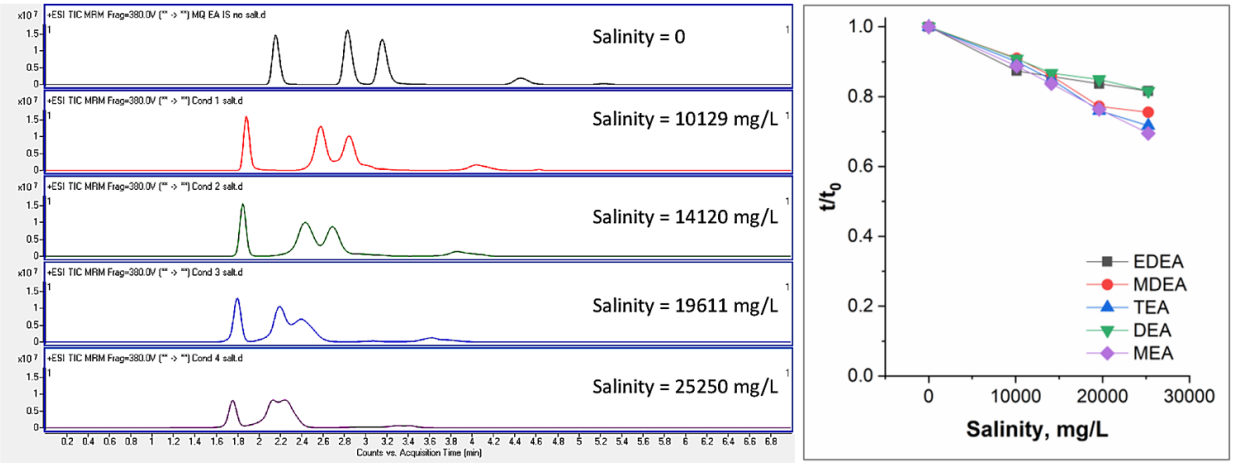

Figure S7. Effect of salinity on retention times of ethanolamines using Acclaim Trinity P1 column. t/t_0 corresponds to ratio of retention times with and without salt interference. X-axis in the chromatogram is time (min) and y-axis is counts/signal intensities in the left figure.

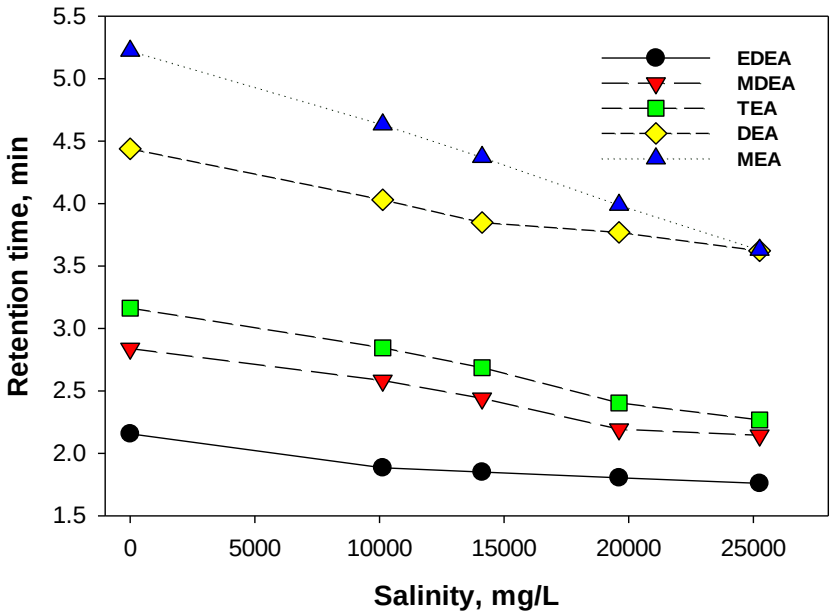

Figure. S8. Ethanolamine retention time shifts with increasing salinity. Evaluated from a 15 μg/L ethanolamine mixture spiked in brine solutions.

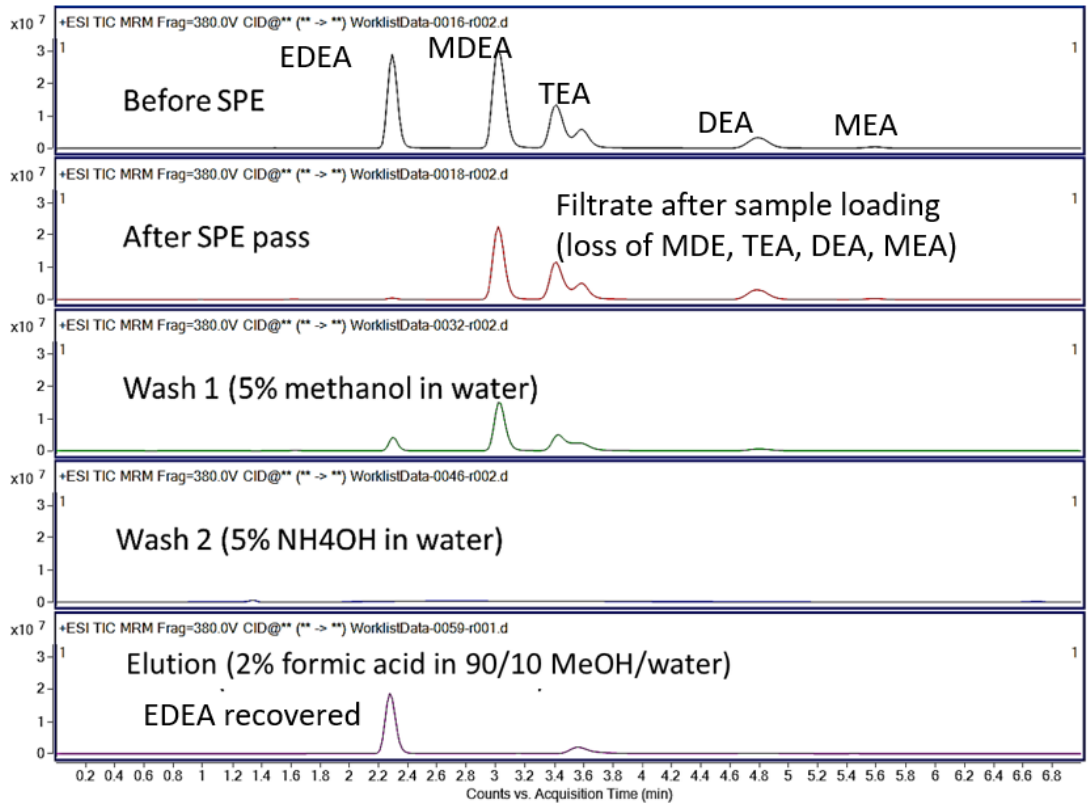

Figure S9. EDEA retention using Oasis HLB cartridge. (a) Improved SPE recovery of EDEA (10 μg/L) with increasing pH. The red line corresponds to calculated fraction of deprotonated EDEA (pKa_{EDEA} = 8.74); (b) Total ion chromatograms of ethanolamines at different stage of SPE using Oasis HLB. 'After SPE pass' chromatograms show losses of ethanolamines due to poor adsorption to SPE material. Only EDEA was recovered with this cartridge. X-axis is time (min) and y-axis is counts/signal intensities in the right figure. Procedure (following manufacturer's recommendation): The cartridges were conditioned with 10 mL methanol and equilibrated with 10 mL LCMS water prior to sample loading (10 mL) at 1 mL/min. The cartridges were dried for 5 min and washed with 5% methanol in water and 5% ammonium hydroxide in MeOH/water, and compounds were eluted with 10 mL 2% formic acid in MeOH/water.

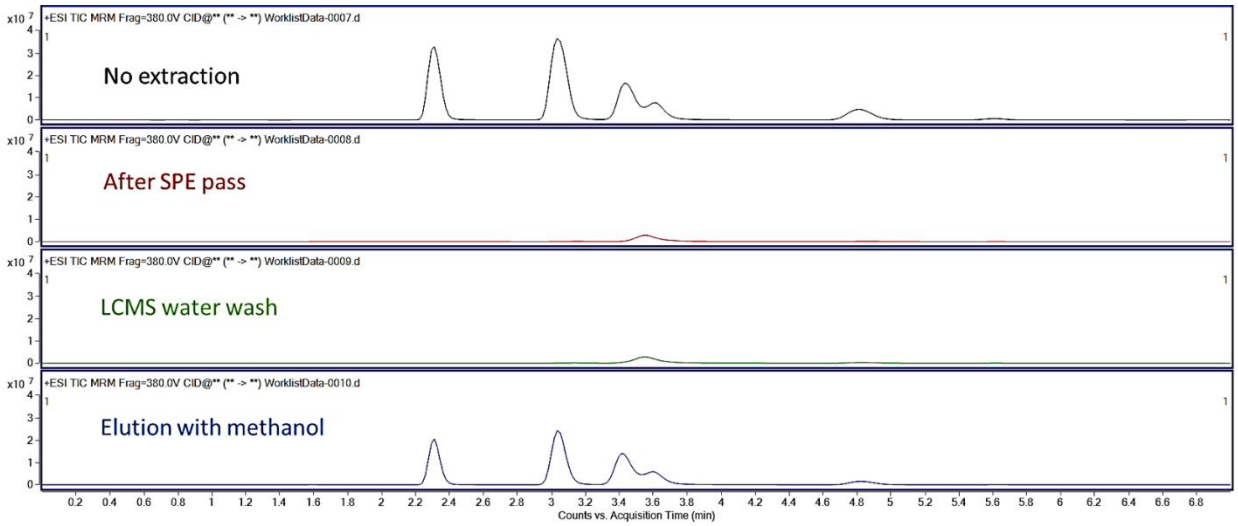

Figure S10. MRM total ion chromatograms of ethanolamines at different stage of SPE using Agilent PPL cartridge. Elution with methanol shows recovery of ethanolamines. X-axis is time (min) and y-axis is counts/signal intensities

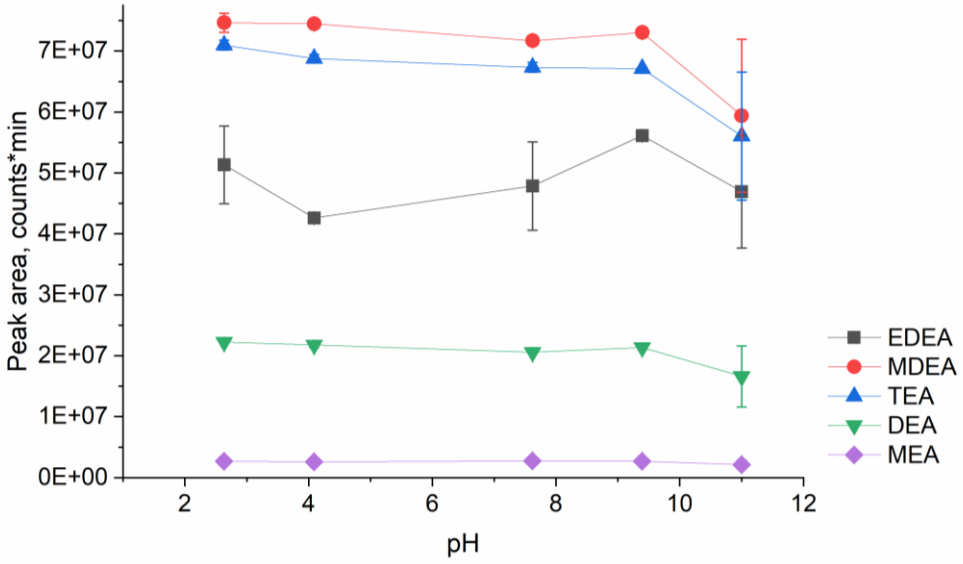

Figure S11. Stability of response at various solution pH. Each ethanolamine was present at 20 μg/L in pure water. pH was adjusted using 0.01 M HCl and 0.01 M NaOH. Note that lines are only included to guide the eyes.

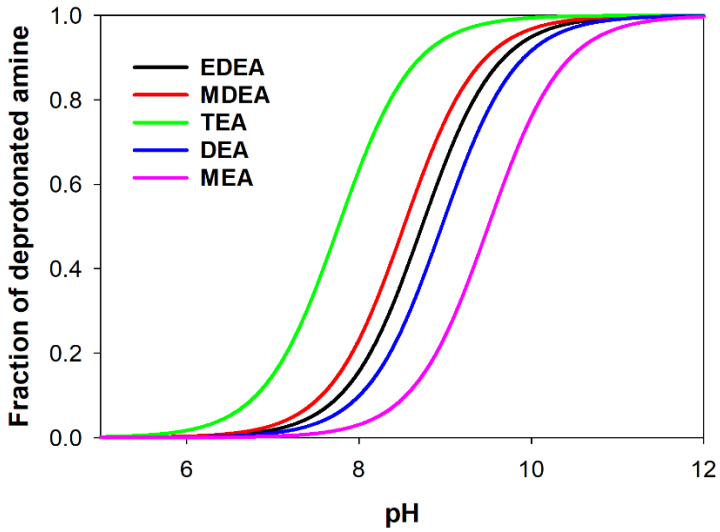

Figure S12. Ethanolamine species fractionation as a function of pH. At pH 11, ethanolamines exist predominantly in their deprotonated form (>97%). pKa values[5]: EDEA (8.73), MDEA (8.52), TEA (7.76), DEA (8.96), MEA (9.50).

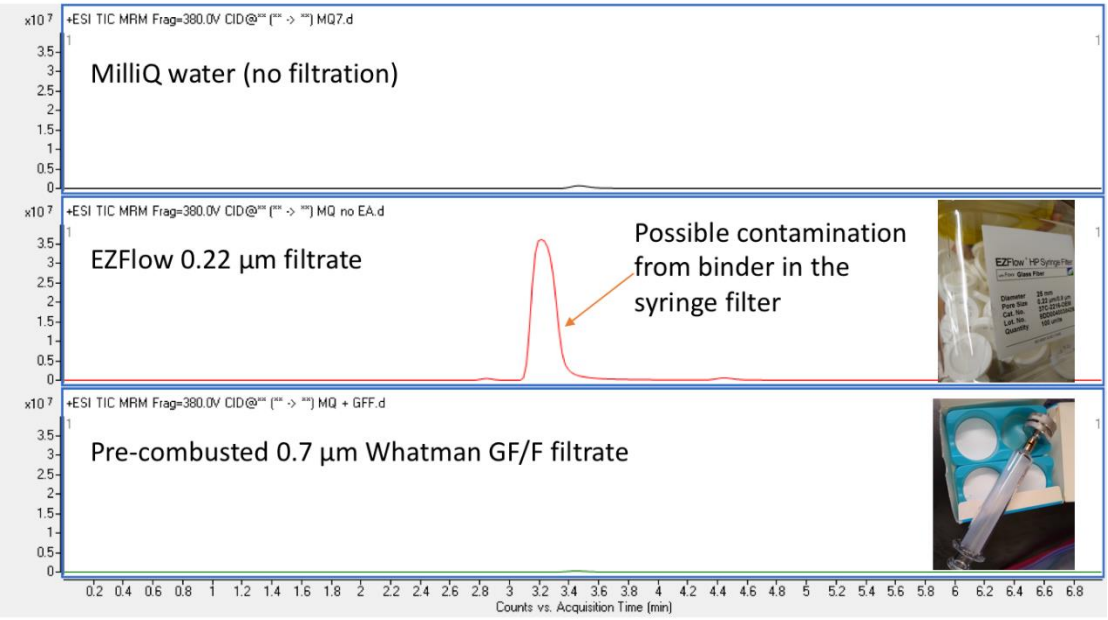

Figure S13. Absence of contaminant peak in filtrate using plastic pre-combusted glass fiber filters, unlike in plastic syringe filters (EZ Flow HP Syringe filters). The x-axis is time (min) and y-axis is counts/signal intensities for a total ion chromatogram.

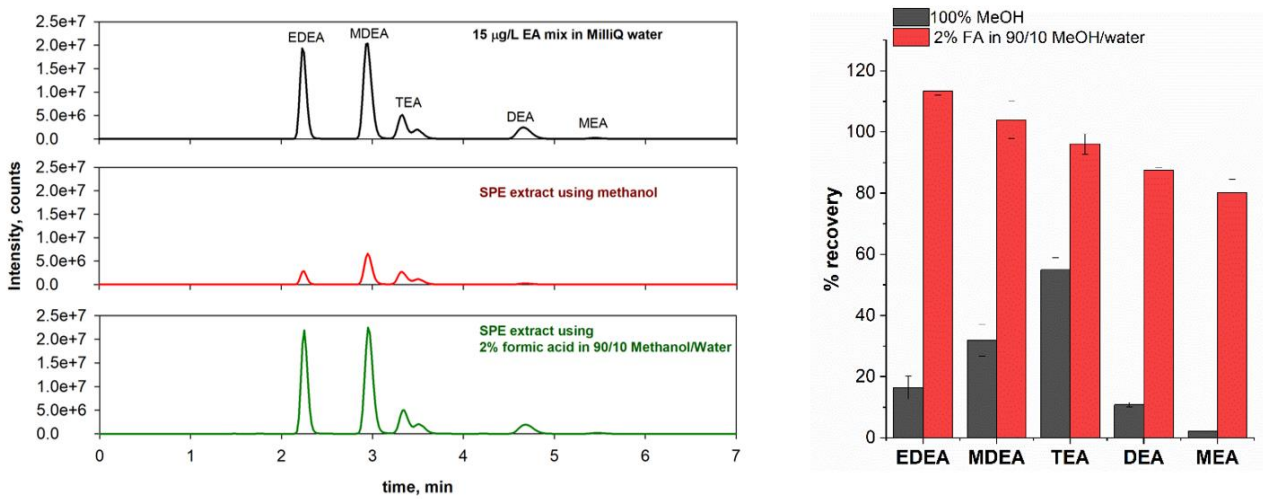

Figure S14. Enhancement of ethanolamine recoveries using 2% formic acid in 90/10 methanol/water eluent compared to methanol only.

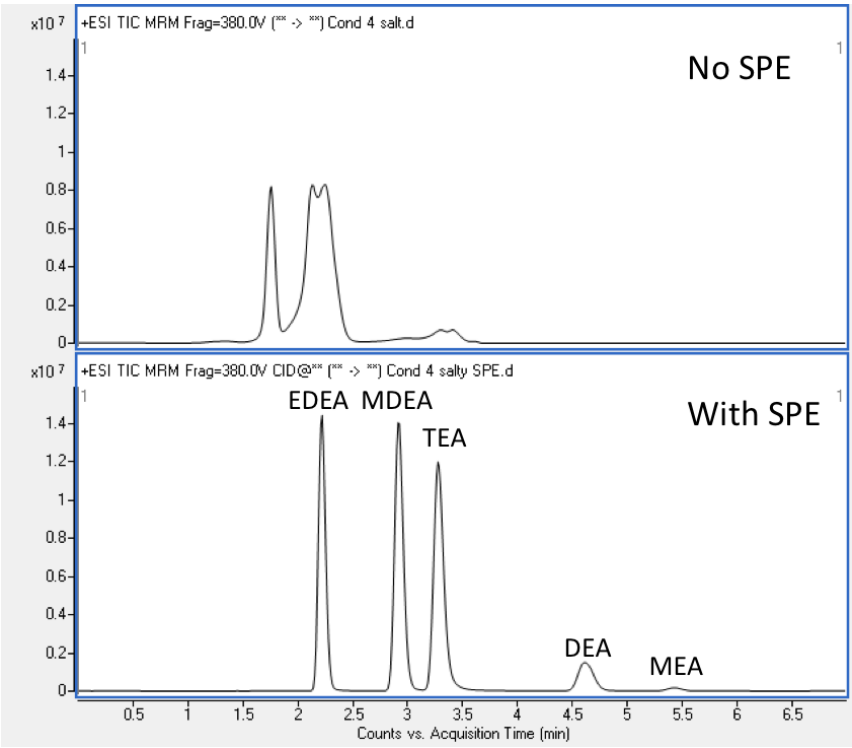

Figure S15. The total ion chromatogram (TIC) of ethanolamines (15 µg/L) in synthetic brine fluid (salinity of 25250 mg/L) showing improved method sensitivity and peak resolution using the proposed SPE procedure. The x-axis is time (min) and y-axis is counts/signal intensities.

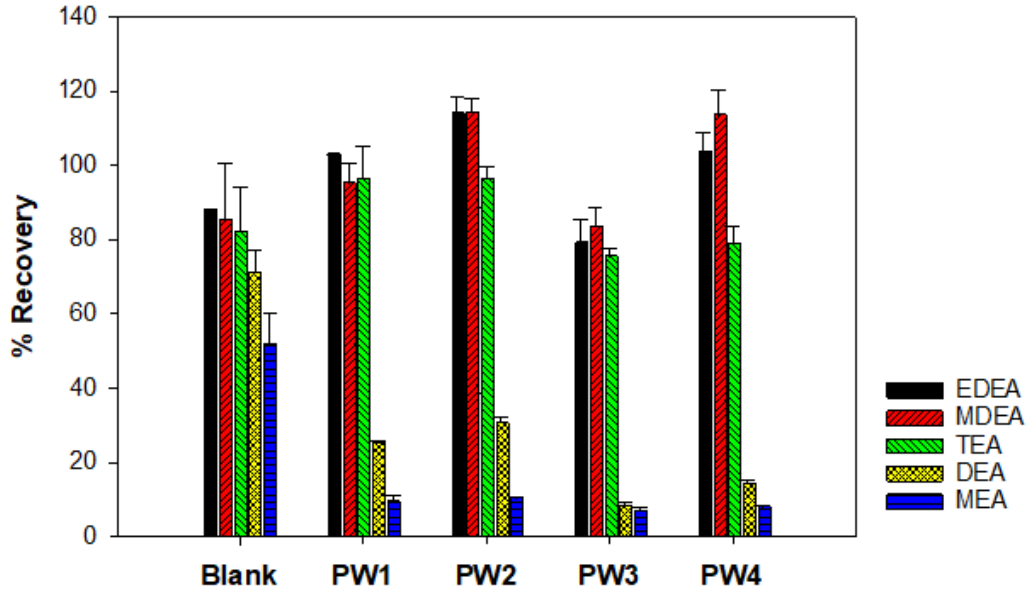

Figure S16. Varying recoveries of each ethanolamine isotopic standards (10 μg/L) measured in SPE extracts of blank- and matrix-spiked samples collected in March 2019. These effects occur after the majority of salts are removed from the samples (post-SPE) but where organic compounds remain.

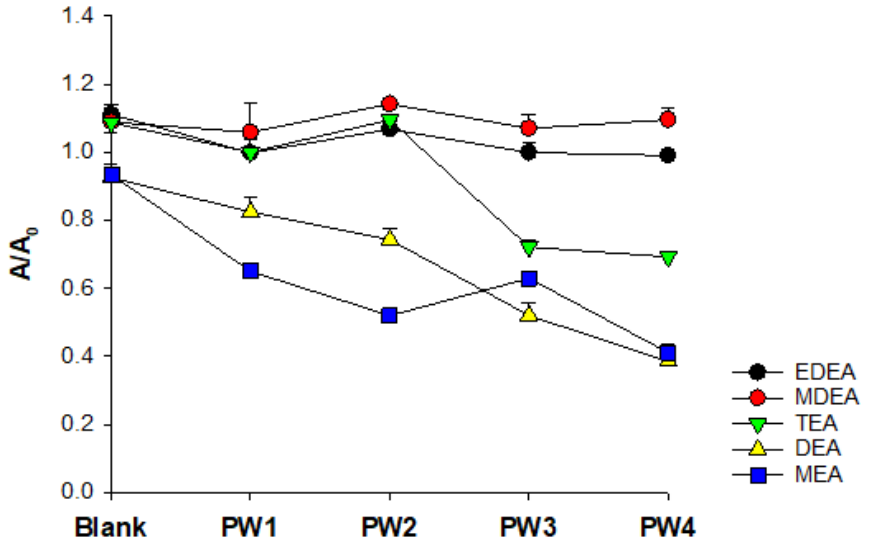

Figure S17. Ion suppression caused by co-extracted organic matter from produced water samples. A_0 is the area of labelled ethanolamines measured after adding 10 μg/L isotopic standards in the SPE extract of the blank solution. A is the area of labelled ethanolamines that were spiked to the SPE extract of the sample matrix.

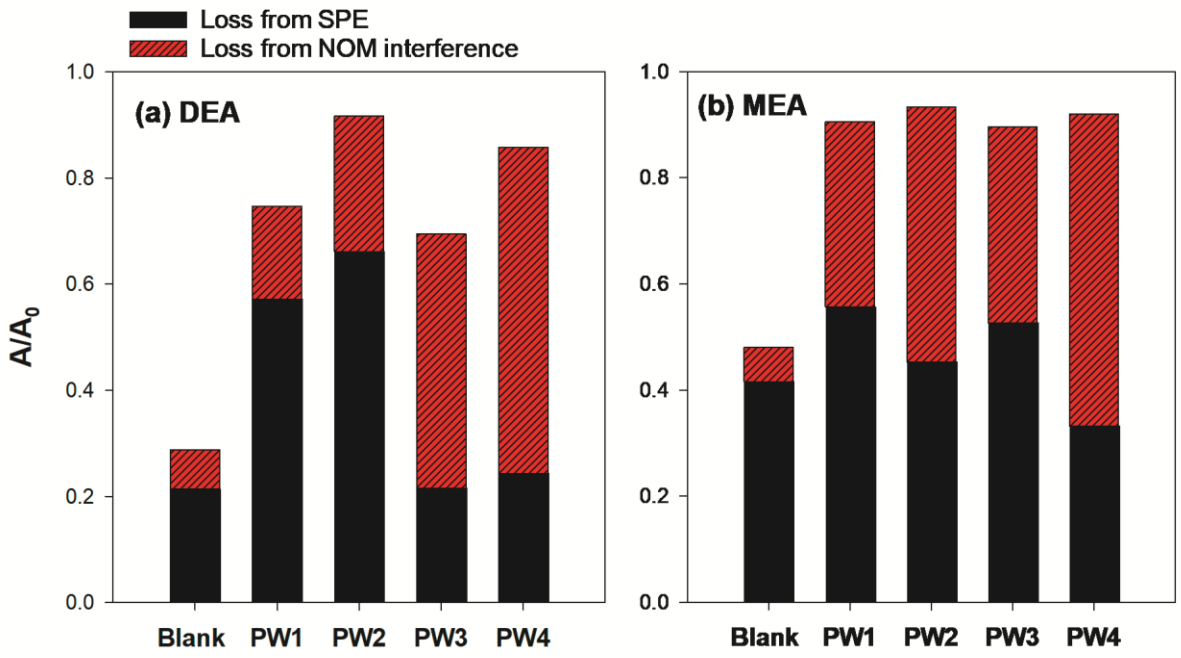

Figure S18. Contribution of ion suppression from eluted organic matter and losses during the SPE procedure on recovery of DEA and MEA. Total loss of recovery = losses from ion suppression by organic matter + losses from SPE procedure. Total loss was calculated from the recovery of spiked isotopic standard from beginning to end of the extraction procedure. Losses from ion suppression by organic matter was calculated from the recovery of isotopic standards spiked into the desalted, organic matter-containing SPE extracts.

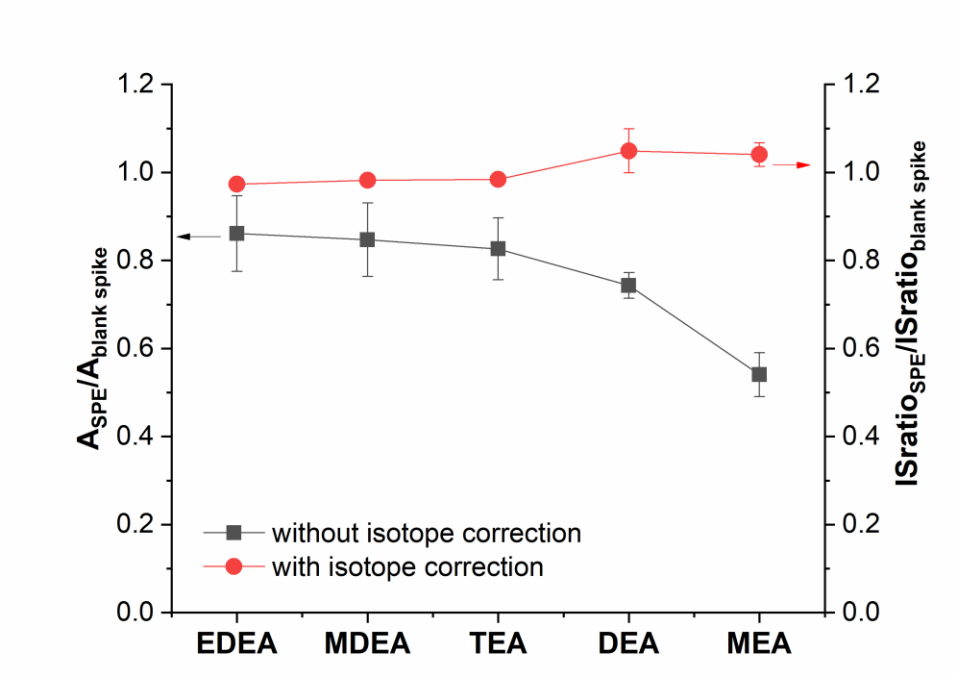

Figure S19. Interference correction using multiple isotopic ethanolamine standards. Black boxes correspond to area ratio of unlabelled ethanolamines without isotope correction showing significant decreased response for DEA and MEA. Red boxes are corrected data points through use of internal standard response ratios normalized to the ratio of the blank spike. Blank spike refers to a solution of 15 μg/L ethanolamine mixture and 10 μg/L labelled ethanolamines in ultrapure water. Error bars are standard errors (n=3).

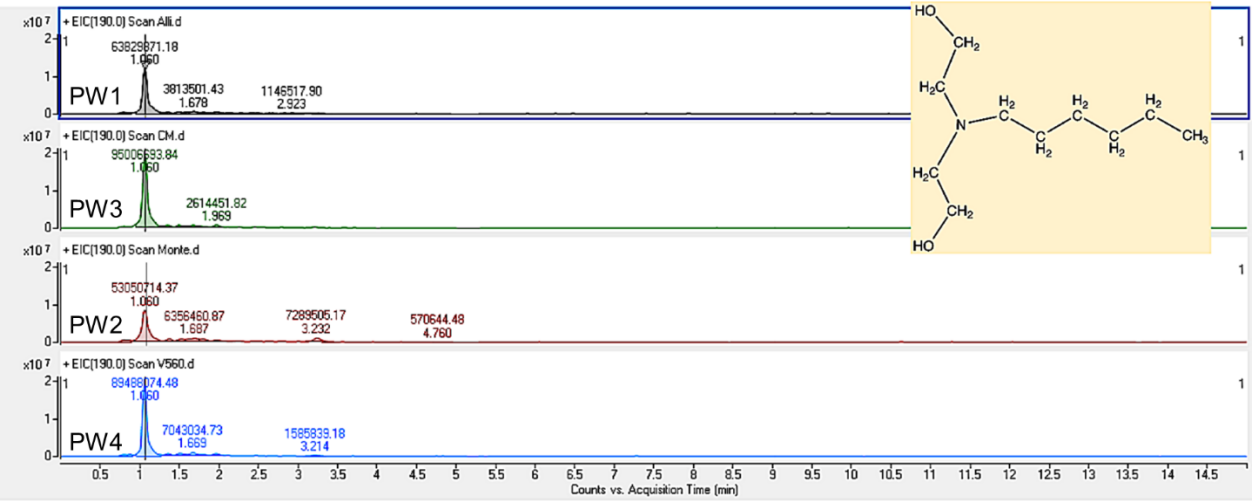

Figure S20. Extracted ion chromatograms for m/z 190 observed from SPE extracts of produced water samples. Inset figure is a proposed structure of *N*-hexyldiethanolamine that can be converted into diethanolamine after microbially-mediated cleavage of the N-C bond of the hexyl chain.

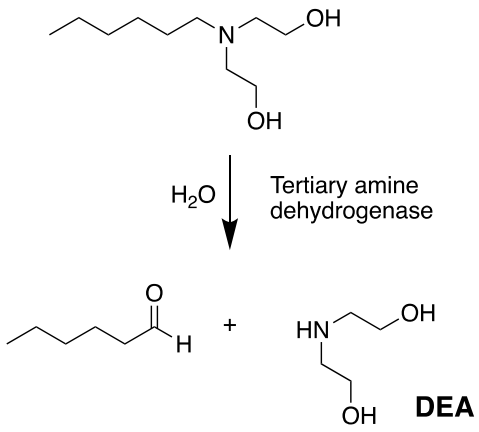

Figure S21. Biodegradation pathway for *N*-hexyldiethanolamine catalyzed by a tertiary amine dehydrogenase that may lead to diethanolamine formation.

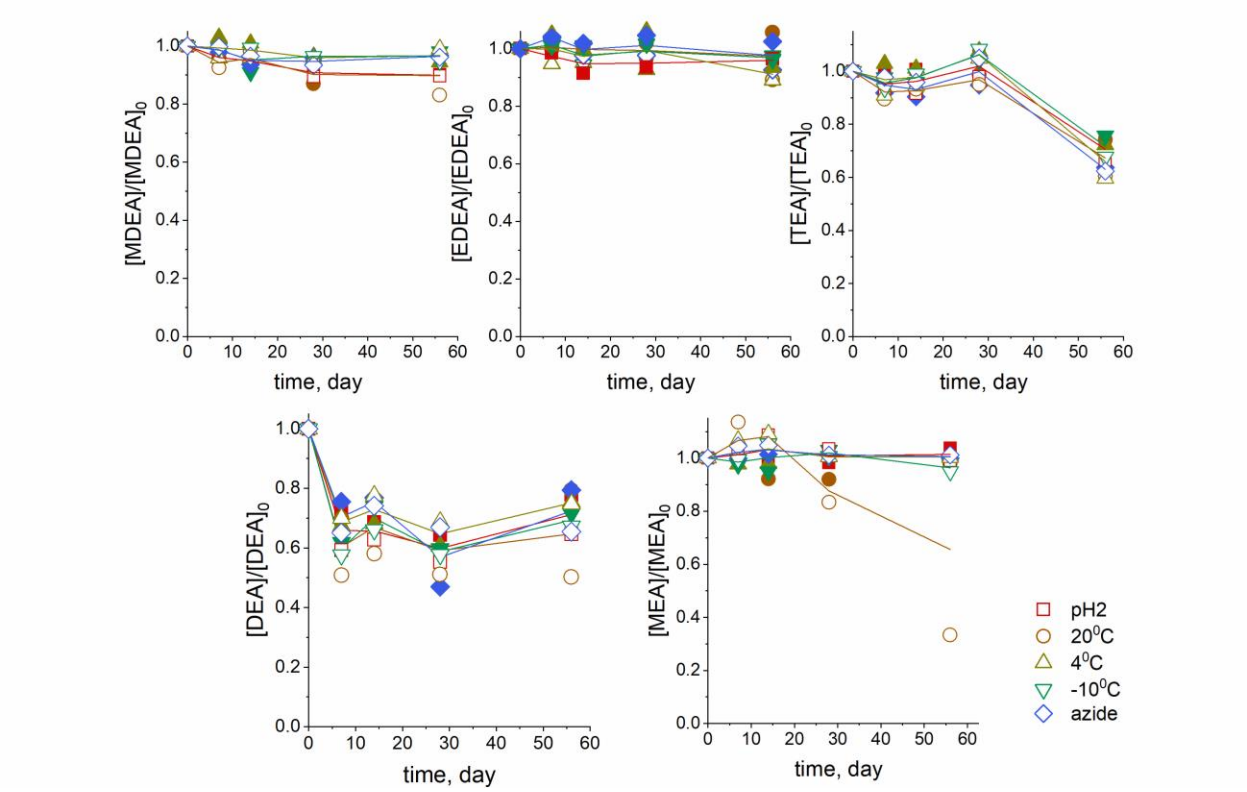

Figure S22. Stability of ethanolamines in produced waters using various sample preservation procedures (e.g., acidification at pH 2, storage at room temperature (20^{0}C), refrigerator (4^{0}C), and freezer (-10^{0}C), and addition of sodium azide (133 mg/L)). Solid symbols are data for PW1 samples while open symbols are data for PW2 samples. The lines correspond to the average of results from PW1 and PW2 samples. Experiments were done in dark conditions. Each sample was spiked with 20 µg/L ethanolamines and 10 µg/L isotopic standards. Samples were analysed after 4-fold dilution.

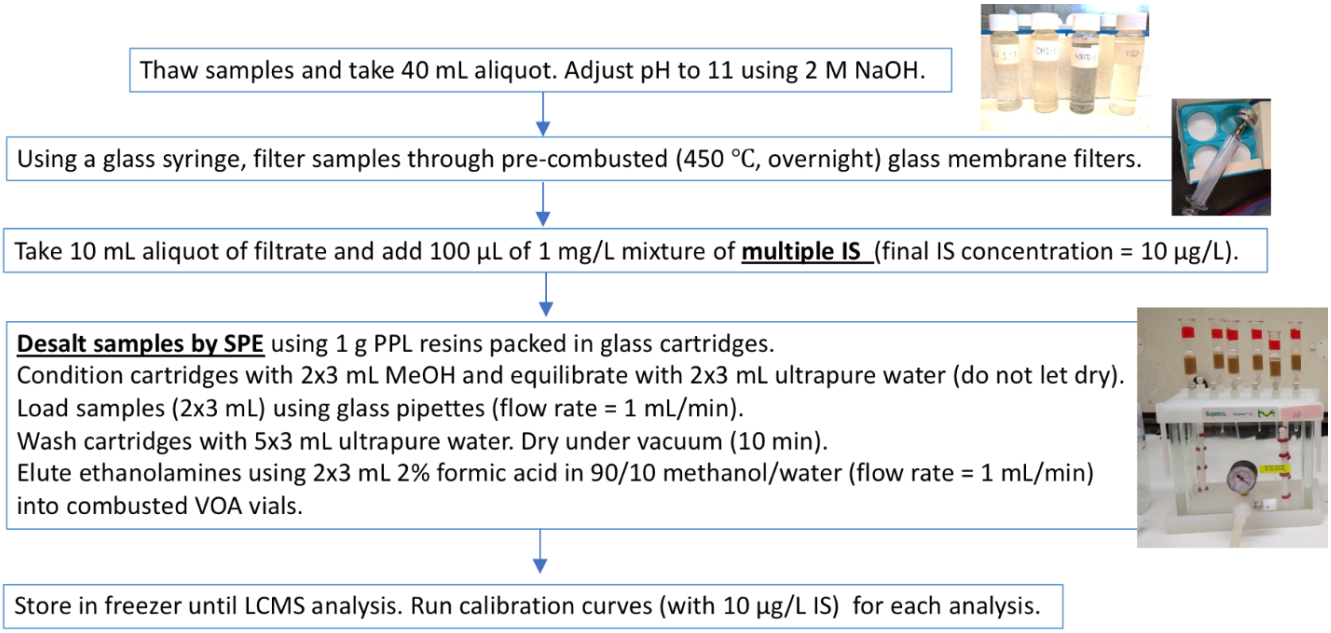

Figure S23. Summary of proposed procedure for accurate determination of ethanolamines in oil and gas wastewaters

Table S1. Characteristics of produced water (PW-Mar) samples measured by MIT and Eni SpA. Values in parentheses are absolute deviation (n=2, measurements from DIME VAL D'AGRI and LAAP SDONATO)

Parameter	Unit	PW1	PW2	PW3	PW4
MIT Plata Lab					
pH (20 °C)		7.24	6.9	7.35	7.16
chloride	mg/L	18577.7	14813.6	10353.5	8905
sulfate	mg/L	661.3	967.4	1436	1214.1
bromide	mg/L	394.6	326.8	204	168.1
nitrate	mg/L	<0.5	<0.5	<0.5	<0.5
phosphate	mg/L	<0.5	<0.5	<0.5	<0.5
Diesel range organic (DRO) compounds	mg/L	5.31	7.94	7.85	5.16
Eni SpA					
Relative gravity @60°F	g/L	1.016	1.009	1.017	1.012
pH (23°C)		6.51	6.55	6.58	6.56
Resistivity @20°C	Ohm*cm	32	44	63	65
Salinity (as NaCl)	mg/L	18100	13600	8110	8470
Total Suspended Solids	mg/L	<20	71	51	<20
S tot	mg/L	519	327	431	446
Sulfide	mg/L	76	26	64	82
Glycolate	mg/L	<10	<10	<10	<10
Formate	mg/L	<10	<10	<10	<10
Acetate	mg/L	63 (15)	61 (15)	47 (11)	39 (3)
Propionate	mg/L	<10	<10	11	<10
Carbonate	mg/L	1353	942	1200	1244
Butyrate	mg/L	<5	<5	<5	<5
Fluoride	mg/L	<25	<25	<10	<10
Chloride	mg/L	11743 (743)	8455 (225)	4981 (61)	5209 (69)
Nitrite	mg/L	<25	<25	<25	<25
Bromide	mg/L	235 (25)	168 (27)	109 (6)	112 (7)
Phosphate	mg/L	<25	<25	<25	<25
Sulfate	mg/L	499 (69)	659 (21)	835 (25)	875 (32)
Fe	mg/L	0.7	1.7	1.1	2.3
B	mg/L	97	75	52	51
Na	mg/L	5712 (668)	4410 (550)	2875 (216)	2929 (292)

K	mg/L	399 (62)	319 (44)	246 (28)	255 (28)
Ca	mg/L	857 (20)	697 (9)	634 (0)	624 (12)
Mg	mg/L	309 (2)	251 (1)	182 (1)	185 (0)
Al	mg/L	<0.5	<0.5	<0.5	0.54
Mn	mg/L	<0.5	<0.5	<0.5	<0.5
Zn	mg/L	<0.5	<0.5	<0.5	<0.5
Cd	mg/L	<0.5	<0.5	<0.5	<0.5
Cu	mg/L	<0.5	<0.5	<0.5	<0.5
Co	mg/L	<0.5	<0.5	<0.5	<0.5
Ni	mg/L	<0.5	<0.5	<0.5	<0.5
Pb	mg/L	<0.5	<0.5	<0.5	<0.5
Sr	mg/L	64	39	32	34
Cr	mg/L	<0.5	<0.5	<0.5	<0.5
Ba	mg/L	<0.5	<0.5	<0.5	<0.5
Tl	mg/L	<0.5	<0.5	<0.5	<0.5

Table S2. Composition of synthetic brine solutions

Contents	Brine 1	Brine 2	Brine 3	Brine 4
chloride, mg/L	5000	7000	10000	13000
bromide, mg/L	100	150	200	250
sulfate, mg/L	400	600	700	900
carbonate, mg/L	700	900	1100	1300
sodium, mg/L	3463	4870	6878	8933
calcium, mg/L	467	600	733	867
salinity, mg/L	10129	14120	19611	25250

Table S3. Experiments investigating interferences

Parameter	Sample matrix used to evaluate interferences
Effect of salts	Synthetic brine spiked with 20 µg/L MEA, DEA, TEA, MDEA, EDEA; Salinity[a] = 0 – 25,250 mg/L
Effect or natural organic matter	Humic acid solutions spiked with 20 µg/L MEA, DEA, TEA, MDEA, EDEA; Aldrich humic acid humic acid[b] = 0 – 295 mgC/L
Effect of co-extracted organic compounds	Bulk organic matter from each PW-Mar samples (SPE extract) spiked with 10 µg/L isotopically labelled ethanolamine mix.

[a]sum of Cl^-, Br^-, SO_4^{2-}, CO_3^{2-}, Na^+, Ca^{2+}; [b]measured using total organic carbon (TOC) analyzer

Table S4. Experiments investigating sample preparation and sample storage

Parameter	Conditions	Sample composition
Sample storage	Temperature ºC: -10, 4, 20 Preservative: pH 2 (HCl), 133 mg/L NaN_3 Storage time (day): 0, 7, 14, 28, 56	PW-Mar samples spiked with 20 µg/L MEA, DEA, TEA, MDEA, EDEA
Biodegradation potential	Temperature ºC: 20 Storage time: 0, 7, 14, 28, 56	Corrosion inhibitor (E-cori) + PW2-Mar sample
Type of filter for particle removal	EZ flow HP syringe filter (0.2 µm) Pre-combusted GF/F membrane filter (0.7 µm)	Ultrapure water with and without ethanolamines
Sample pH for solid-phase extraction	pH = 2.6, 5.7, 7.8, 11 (ultrapure water)	20 µg/L MEA, DEA, TEA, MDEA, EDEA in ultrapure water
Type of SPE material	Oasis HLB cartridge Bondesil PPL cartridge	20 µg/L MEA, DEA, TEA, MDEA, EDEA in ultrapure water
SPE elution solvent	Methanol 2% formic acid in 90/10 methanol water	20 µg/L MEA, DEA, TEA, MDEA, EDEA in ultrapure water

Table S5. Comparison of developed method to Dionex 271 and ASTM D7599

Parameter	**MIT – Acclaim**	**MIT – HILIC***	**Dionex 271**[1]	**ASTM D7599**[2]
Equipment	Agilent 6495 triple quadrupole LCMS	Agilent 6495 triple quadrupole LCMS	Dionex UltiMate. 3000 RSLC triple quadrupole MS	Waters Alliance LC – Quatro micro API MS
Column	Acclaim Trinity P1 (2.1 x 100 mm, 3 μm)	Waters Atlantis HILIC; Silica, 100 mm x 2.1 mm, 3 μm)	Acclaim Trinity P1 (2.1 x 100 mm, 3 μm)	Waters Atlantis HILIC; Silica, 100 mm x 2.1 mm, 3 μm)
Mobile phase	Isocratic, 90% acetonitrile; 10% 50 mM ammonium formate , pH 3.7	A: 15 mM ammonium acetate, B: 15 mM ammonium acetate in acetonitrile/water (95/5); Gradient (A/B): 0.6 min: 10/90; 1.2 min: 20/80; 2.4 min: 20/80; 8 min: 60/40	Isocratic, 90% Acetonitrile; 5% DI water; 5% Ammonium formate 100 mM, pH 3.7	A: acetonitrile, B: water, C: 200 mM ammonium acetate; Gradient (A/B/C) 0-1 min: 95/0/5; 2-4 min: 90/0/10; 10-13 min: 60/30/10; 15 min: 40/50/10; 18-20 min: 30/60/10; 25-27 min: 95/0/5
Injection volume	10	10	20	25
Flow rate, mL/min	0.5	0.3	0.6	0-2 min: 0.4; 2-27 min: 0.3
Linear range, ug/L	1-40	1-40	0.05 – 20	25-500
Stable isotope Internal standard	10 ug/L, multiple	10 ug/L, multiple	1 ug/L, d_8-DEA	200 ug/L, d_8-DEA
Sample prep	Filtration, SPE	Filtration	filtration as needed only	filtration
Ion source	ESI (+)	ESI (+)	ESI (+)	ESI (+)
Capillary voltage, V	2000	2000	4500	500
Ion transmission from ESI (V)	Ion funnel (150 V (high P RF, 50 V low P RF)	Ion funnel (150 V (high P RF, 50 V low P RF)	Cone	Cone (25 V)
Nebulizer P, psi	50	50	50 (GS1)	---
Nozzle voltage	0	0	---	---
Sheath gas temperature	330	330	---	120 (source temp)
Sheath gas flow, L/min	11	11	----	0.4 L/min (cone gas flow)
Drying gas temperature	150	150	700 (TEM)	300 (desolvation temp)
Drying gas flow	18	18	(20 psi GS2)	8.3 (desolvation gas flow)
Collision energy, eV	Variable	Variable	Variable	Variable
Scan mode	MRM	MRM	MRM	MRM
Dwell, ms	50	50	Variable (25-350)	100

**not recommended due to poor chromatographic separation.*

Table S6. Repeatability of ethanolamine concentrations in water analyzed by the LC/MS

Level, μg/L	Relative standard deviation (%)				
	MEA	DEA	TEA	MDEA	EDEA
1 (n=10)	2.9	4.0	8.8	3.2	5.2
5 (n=3)	2.0	3.6	3.0	2.3	1.7
10 (n=3)	2.4	4.3	2.7	1.6	2.2
15 (n=3)	2.5	1.2	3.0	2.5	4.4
20 (n=3)	2.1	1.5	6.0	6.3	0.2
40 (n=3)	0.5	8.7	3.6	3.2	1.9

Table S7. Comparison of ethanolamine concentrations (in ug/L) calculated using multiple isotopic standards (e.g., 1 internal standard per ethanolamine (EA)) versus using only D_8-DEA as internal standard for all ethanolamines. EDEA, MDEA, and TEA were overestimated while MEA was underestimated using only d_8-DEA. Concentrations were determined in SPE extracted PW-Sept samples (n=2, in parentheses are absolute deviation).

Samples	EDEA		MDEA		TEA		DEA		MEA	
	1 Int. Std/EA	d_8-DEA only	1 Int. Std/EA	d_8-DEA only	1 Int. Std/EA	d_8-DEA only	1 Int. Std/EA	d_8-DEA only	1 Int. Std/EA	d_8-DEA only
PW1	5.0 (0.3)	37.5 (6.1)	<1.0	1.5 (0.5)	12.5 (0.0)	77.2 (9.9)	17.8 (3.4)	17.9 (3.6)	41.4 (0.9)	5.4 (1.0)
PW2	<1.0	10.3 (0.6)	12.6 (0.4)	230.2 (10.9)	55.6 (0.7)	791.5 (21.4)	3830.1 (98.7)	3777.7 (19.7)	77.3 (9.4)	96.0 (8.3)
PW3	3.4 (0.1)	29.8 (0.2)	2.1 (0.0)	19.4 (0.6)	63.9 (0.3)	422.0 (8.7)	1158.6 (17.3)	1137.4 (0.4)	276.7 (0.9)	152.0 (10.3)
PW4	3.5 (0.0)	30.5 (0.1)	2.3 (0.1)	20 (0.1)	62.8 (0.1)	419.4 (20.9)	1078.2 (38.9)	1078.5 (31.4)	305.9 (5.7)	164.5 (4.7)

References

(1) Thermo Fisher Scientific. *Quantitative Analysis of Nitrogen Mustard Hydrolysis Products as Ethanolamines. Application Note 271.* https://assets.fishersci.com/TFS-Assets/CMD/Application-Notes/109792-AN271-IC-NitrogenMustard-Ethanolamines-19Jan2011-LPN2684.pdf.

(2) ASTM. *Standard Test Method for Determination of Diethanolamine, Triethanolamine, N-Methyldiethanolamine and N-Ethyldiethanolamine in Water by Single Reaction Monitoring Liquid Chromatography/Tandem Mass Spectrometry*. https://www.astm.org/d7599-16r17.html (accessed 2023-10-19).

(3) Gresham, G. L.; Groenewold, G. S.; Olson, J. E. Identification of the Nitrogen-Based Blister Agents Bis(2-Chloroethyl)Methylamine (HN-2) and Tris(2-Chloroethyl)Amine (HN-3) and Their Hydrolysis Products on Soil Using Ion Trap Secondary Ion Mass Spectrometry. *Journal of Mass Spectrometry* **2000**, *35* (12), 1460–1469. https://doi.org/10.1002/1096-9888(200012)35:12<1460::AID-JMS82>3.0.CO;2-J.

(4) Steckel, A.; Schlosser, G. An Organic Chemist's Guide to Electrospray Mass Spectrometric Structure Elucidation. *Molecules* **2019**, *24* (3), 611. https://doi.org/10.3390/molecules24030611.

(5) National Center for Biotechnology Information. PubChem Compound Summary. https://pubchem.ncbi.nlm.nih.gov.