Supporting Information for

Degradation of Benzylamines During Chlorination and Chloramination

Chih-Hsien Lin,[2] Wei-Hsiang Chen,[2] and William A. Mitch[1*]

[1] Department of Civil and Environmental Engineering, Stanford University, 473 Via Ortega, Stanford, California 94305, United States

[2] Institute of Environmental Engineering, National Sun Yat-sen University, Kaohsiung, 804, Taiwan

* Corresponding author; email: wamitch@stanford.edu

Table S1. Sources and purities of reagents.

Chemical	Supplier	Purity
Methyl-tert-butyl ether (MtBE)	Sigma-Aldrich	99.5
Acetonitrile	Fisher	99.9
Methylene chloride	Fisher	99.9
Formaldehyde	Fisher	37% in water
9-Fluorenylmethoxycarbonyl chloride (FMOC-Cl)	Sigma-Aldrich	>99
2,4-Dinitrophenylhydrazine	Sigma-Aldrich	97
Methylamine hydrochloride	Sigma-Aldrich	>98
Dimethylamine hydrochloride	Sigma-Aldrich	99
N-Methylpropylamine	Acros	98
N-Nitrosodimethylamine	Accustandard	5 g/L in methanol
N-Nitrosodimethylamine-d6	Accustandard	0.1 g/L in methanol
N-Nitrosomethylbenzylamine	Toronto Research Chemicals	>98
Benzylamine hydrochloride	Acros	99
N-Methylbenzylamine	TCI	>98
N,N-Dimethylbenzylamine	TCI	98
3-Chloro-N-methylbenzylamine	AmBeed	99.35
4-Chloro-N-methylbenzylamine	AmBeed	95
2-Chlorobenzylamine	Sigma-Aldrich	95
4-Chlorobenzylamine	Sigma-Aldrich	98
3,5-Dichlorobenzylamine	AmBeed	99.77
Benzaldehyde	Acros	98+
2-Chlorobenzaldehyde	Sigma-Aldrich	99
3-Chlorobenzaldehyde	AmBeed	97
4-Chlorobenzaldehyde	AmBeed	99.86
2,4-Dichlorobenzaldehyde	AmBeed	99.66
3,5-Dichlorobenzaldehyde	AmBeed	98.34
Benzonitrile	Sigma-Aldrich	>99
3-Chlorobenzonitrile	AmBeed	99.92
4-Chlorobenzonitrile	AmBeed	99.28
2,4-Dichlorobenzonitrile	AmBeed	96
3,5-Dichlorobenzonitrile	AmBeed	97
2,4,6-Trichlorobenzonitrile	AmBeed	98

Text S1. Analytical method details.

Analysis of benzylamines: After quenching disinfectant residuals with ascorbic acid, benzylamines were analyzed by high performance liquid chromatography mass spectrometry (LC-MS) using an Agilent 1260 Infinity LC coupled with an Agilent 6460 triple quadrupole mass-spectrometer system with an electrospray ionization source (LC-ESI-QQQ-MS). Injections were 10 μL. Separation was achieved using an Agilent Poroshell 120 EC-C18 column (3 x 50 mm, 2.7 μm) column at 0.6 mL/min using 10 mM ammonium formate in deionized water (solvent A) and acetonitrile (solvent B) as mobile phases. The elution profile (10.5 min total) was 95% solvent A and 5% solvent B for 0.5 min; ramping to 30% B over 4 min; ramping to 80% B over 2 min and holding for 0.5 min; ramping to 30% B over 1 min; and ramping to 5% B over 1 min and holding for 1.5 min. ESI source parameters included a nebulizer gas flow rate of 7 L/min at 300 °C and 45 psi and a sheath gas flow rate of 9 L/min at 250 °C. The capillary voltage was 3500 V. All analyses were conducted in the positive ion mode with multiple-reaction monitoring (MRM); parameters included a 59 V fragmentor voltage, a collision energy of 10 V (except for 29 V for analysis of N-methylbenzylamine) and a 7 V cell accelerator voltage. Table S2 provides retention times, precursor ions and quantification ions for the eight compounds analyzed. Quantification limits were 5 μM.

Analysis of formaldehyde: After quenching disinfectant residuals with ascorbic acid, formaldehyde was measured after derivatization with 2,4-dinitrophenylhydrazine followed US EPA Method 8315A. Briefly 10 mL samples were supplemented with 0.4 mL of acetate buffer at pH 5 and 0.6 mL of 3 g/L dinitrophenylhydrazine in acetonitrile. The samples were placed in a rotating mixer within a 37 °C room for 1 h. Each sample was then extracted with 5 mL of methylene chloride for 2 min. The methylene chloride extract was dried with anhydrous sodium sulfate. Then, 200 μL of the methylene chloride extract was mixed with 800 μL of acetonitrile. The samples were analyzed using the same LC-MS system and column described above at a 0.6 mL/min flowrate (9 min total). Injections were 10 μL. Mobile phases were deionized water (solvent A) and acetonitrile (solvent B) starting at 5% B; ramping to 40% B over 0.5 min and holding for 4 min; ramping to 80% B over 2 min and holding for 0.5 min; ramping to 40% B over 1 min; and ramping to 5% B over 1 min. The derivative (formaldehyde-2,4-dinitrophenylhydrazone) was analyzed in the full-scan negative ion mode (m/z 150-220). Table S2 provides the retention time and quantification ion. The ESI source parameters were the same as described above with a 3500 V capillary voltage. The quantification limit was 10 μM.

Analysis of monomethylamine and dimethylamine: After quenching disinfectant residuals with ascorbic acid, samples were spiked with N-methylpropylamine as an internal standard. Amines were analyzed after derivatization with 9-fluorenylmethoxycarbonyl chloride (FMOC-Cl) according to the procedure of Teerlink et al. (1997). Briefly, 200 μL samples were mixed with 200 μL of 0.8 M borate buffer at pH 9.5 and 300 μL of 10 mM FMOC-Cl in acetonitrile. The samples were held at 37 °C for 30 min. Samples were treated with 100 μL of 100 mM glycine and then analyzed by LC-MS using the same LC-MS system and column described above at a 0.6 mL/min flowrate at a 10.5 min total elution time. Injections were 10 μL. Mobile phases were deionized water (solvent A) and acetonitrile (solvent B) starting at 50% B and holding for 4.5 min; ramping to 80% B over 2 min and holding for 1.5 min; ramping to 50% B over 1 min and holding for 1.5 min. The FMOC derivatives were

analyzed in the full-scan positive ion mode (m/z 100-390). Table S2 provides retention times and quantification ions. The ESI source parameters were the same as described above with a 3500 V capillary voltage. Quantification limits were 5 μM.

Analysis of benzaldehydes and benzonitriles: Benzaldehyde, benzonitrile and their chlorinated analogues were analyzed by gas chromatography mass spectrometry (GC-MS; Agilent 7890 GC coupled to an Agilent 240 ion trap MS system). Briefly, 50 mL samples were treated with 15 g of anhydrous sodium sulfate pre-heated to 100 °C and then extracted by shaking for 2 min with 3 mL MtBE containing 300 μg/L 1,2-dibromopropane as an internal standard. The MtBE extract was dried with anhydrous sodium sulfate and then analyzed by GC-MS. Separation was achieved using an Agilent DB-1701 column (60 m x 0.25 mm x 1 μm) with a 1 mL/min helium carrier gas flowrate. Samples (2 μL) were injected in splitless mode into the injection port at an initial temperature of 37 °C; the injection port temperature was ramped at 600°C/min to 230 °C. The oven was held at 37 °C for 2 min; ramped to 187 °C at 10 °C/min and held for 1 min; ramped to 221 °C at 4 °C/min and held for 1 min; and then ramped to 270 °C at 20 °C/min and held for 3 min. Analytes were detected in either the electron impact or chemical ionization modes using single ion monitoring. Table S3 provides the retention times, ionization modes and quantification ions. Quantification limits were 5 μM.

Analysis of N-nitrosamines: N-Nitrosodimethylamine (NDMA) and N-nitrosomethylbenzylamine also were analyzed using the same GC-MS system discussed above GC-MS. Briefly, 10 mL samples were extracted by shaking for 2 min with 10 mL methylene chloride. The methylene chloride extract was dried with anhydrous sodium sulfate and analyzed using the same GC-MS method described above for benzaldehydes and benzonitriles. However, methanol chemical ionization was used with tandem mass spectrometry. Table S3 provides the retention times, ionization modes and quantification ions. Quantification limits were 0.2 μM for NDMA and 1.25 μM for N-nitrosomethylbenzylamine. Wastewater samples (250 mL) were spiked with 40 ng/L deuterated d6-NDMA and then extracted by solid phase extraction (coconut shell activated carbon) and analyzed by GC-MS according to US EPA Method 521 with a 4 ng/L quantification limit for NDMA.

Analysis of benzyl alcohol: Benzyl alcohol was analyzed by high performance liquid chromatography with ultraviolet detection (HPLC-UV) at 254 nm. Separation was achieved using a ThermoFisher Scientific Ultimate3000, Hypersil Gold Vanquish C18 UHPLC Column. Mobile phases were 0.1% phosphoric acid (solvent A) and methanol (solvent B). At a total flowrate of 0.4 mL/min, the elution profile was 2% B for 2 min, ramping to 98% B over 3 min and holding for 2 min, ramping back to 2% B over 0.1 min and holding for 4 min.

Table S2. LC-MS analytical parameters.

Compound	Retention Time min	Mode	Precursor ion	Quantification ions
Benzylamine	1.4	MRM (+)	108	91.2
N-Methylbenzylamine	1.8	MRM (+)	122	65.2
N,N-Dimethylbenzylamine	2.4	MRM (+)	136	91.2
2-Chlorobenzylamine	2.7	MRM (+)	142	125
4-Chlorobenzylamine	3.8	MRM (+)	142	125
3-Chloro-N-methylbenzylamine	4.3	MRM (+)	156	125
4-Chloro-N-methylbenzylamine	4.5	MRM (+)	156	125
3,5-Dichlorobenzylamine	5.5	MRM (+)	176	159
Formaldehyde-2,4-dinitrophenylhydrazone	5.2	Full-scan (-)	NA	209
FMOC-monomethylamine	2.0	Full-scan (+)	NA	276
FMOC-dimethylamine	3.4	Full-scan (+)	NA	290
FMOC-N-methylpropylamine	6.8	Full-scan (+)	NA	318
FMOC-N-methylbenzylamine	7.9	Full-scan (+)	NA	366

Table S3. GC-MS analytical parameters.

Compound	Retention Time min	Ionization Mode	Precursor ion	Quantification ions
1,2-Dibromopropane	14.9	EI	NA	41, 121, 123
Benzaldehyde	17.8	EI	NA	77, 105, 106
2-Chlorobenzaldehyde	20	EI	NA	50, 111, 139
3-Chlorobenzaldehyde	21.3	EI	NA	50, 111, 139
4-Chlorobenzaldehyde	21.4	EI	NA	50, 111, 139
2,4-Dichlorobenzaldehyde[1]	24	EI	NA	173, 175
3,5-Dichlorobenzaldehyde[1]	24	EI	NA	173, 175
Benzonitrile	18.8	EI	NA	50, 76, 103
3-Chlorobenzonitrile	21.8	CI	NA	138
4-Chlorobenzonitrile	22.3	CI	NA	138
2,4-Dichlorobenzonitrile	23.8	CI	NA	172
3,5-Dichlorobenzonitrile	26	CI	NA	172
2,4,6-Trichlorobenzonitrile	29.2	CI	NA	208
N-Nitrosodimethylamine	14.4	CI	75	44, 47, 58
N-Nitrosodimethylamine-d6	14.4	CI	81	49, 50, 63, 64
N-Nitrosomethylbenzylamine	28.2	CI	151	91

[1] These compounds co-eluted

References

Teerlink, T.; Hennekes, M. W. T.; Mulder, C.; Brulez, H. F. H. Determination of dimethylamine in biological samples by high-performance liquid chromatography. J. Chromat. B 1997, 691, 269-276.