Chloroacetonitrile and *N,*2-Dichloroacetamide Formation from the Reaction of Chloroacetaldehyde and Monochloramine in Water

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- Figure S4. GC/EI/MS total ion chromatogram of reaction extracts by LLE and MTBE after 30 minutes of reaction where, chloroacetonitrile, 1-chloro-2-(chloroimino)ethane, and chloroacetamide were identified. Experimental conditions: $[NH_2Cl]_0$ = 1 mM, $[ClCH_2CHO]_{T,0}$ = 10 mM, $[CO_3]_{T,0}$ = 0.02 M, pH 9.00 ± 0.1, μ = 0.1 M, 18 ± 0.1^{o}C
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- K_1 and $\varepsilon_{\mathrm{ClCH_2CH(OH)NHCl}_\lambda}$calculation process
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- Table S3. First fitting results of experimental data (UV-1) for each wavelength ranging from 235 to 245 nm
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- Figure S13. Effect of monochloramine concentration on chloroacetonitrile, *N*,2-dichloroacetamide, and 2-chloro-1-(chloroamino)ethanol formation over time at drinking water conditions: $[NH_2Cl]_0$ = 1 & 4 mg/L as Cl_2, $[ClCH_2CHO]_{T,0}$ = 5 μg/L, pH=9.0, 18^{o}C
- Figure S14. Effect of chloroacetaldehyde concentration on chloroacetonitrile, *N*,2-dichloroacetamide, and 2-chloro-1-(chloroamino)ethanol formation over time at drinking water conditions: $[NH_2Cl]_0$ = 4 mg/L as Cl_2, $[ClCH_2CHO]_{T,0}$ = 5 & 10 μg/L, pH=9.0, 18^{o}C

<u>Calibration curve development for the quantification of chloroacetonitrile and chloroacetamide (as decomposition product of *N*,2-dichloroacetamide)</u>

Chloroacetonitrile stock solutions were freshly prepared by dissolving the compound in acetonitrile. 2-chloroacetamide stock solutions were freshly prepared by dissolving the compound in nanopure water. Increasing concentrations (5, 10, 40, 75, 100, 300, 500 μM) of chloroacetonitrile and 2-chloroacetamide were diluted in 10 ml of water with 20 mM phosphate buffer, ionic strength of 0.1 M, at pH 7.5. Standards were extracted with 1ml of ethyl acetate that contained 53.1 μM (6 mg/L) 1,2-dichloropropane as internal standard and 2.85 g of sodium sulfate. Chloroacetonitrile and chloroacetamide calibration curve correlation coefficient were > 0.98, and linear ranges were 5 – 75 μM and 10 – 500 μM, respectively. The effect of sodium thiosulfate on the stability of chloroacetamide and chloroacetonitrile was tested by adding 1.5 mM to the standards and found that the response did not change. Standards were ran at the beginning of each experiment to analyze 10-12 samples. Standards were prepared weekly and stored at 4°C.

Table S1. GC/MS methods used for the identification and/or quantification of reaction pathway intermediate and products

Compounds Analyzed	Chloroacetonitrile, Chloroacetamide 1-chloro-2-(chloroimino)ethane	*N*,2-dichloroacetamide
Method Name	GC/EI/MS	GC/NCI/MS
Instrument	Agilent 6850/5975C	Agilent 6890/5973
Column	DB-624 (Agilent J&W, Santa Clara, CA)	DB-624 (Agilent J&W, Santa Clara, CA)
Inlet Temperature	230 (LLE) / 240 ºC (SPME)	200 ºC
Injection Mode	Splitless	Split, Ratio 5:1 (5 mL/min)
Column Flow	1.0 mL/min	1.0 mL/min
Carrier Gas	Helium	Helium
GC Oven Program	35 ºC hold 3 min, ramp 10 ºC/min to 90 ºC, hold for 1 min, and ramp 10 ºC/min to 240 ºC	50 ºC hold 2 min, ramp 15 ºC/min to 250 ºC
Ionization Mode	Electron Impact	Negative Chemical Ionization (Methane)
Detector	Scan (35-300 amu) and SIM (Group 1 – 63, 41.1; Group 2 at 9.15 min 75, 48; Group 3 at 14 min – 93, 44.1)	SIM (128)

LLE Method for reaction compound identification

10 mL unquenched reaction samples were mixed with 1 mL MTBE and 2.85 g of sodium sulfate for 2 minutes followed by a phase separation of 3 minutes. Extracts were transferred to 200 μL inserts with no headspace for immediate analysis.

SPME Method for reaction compound identification

14 ml unquenched samples with minimum headspace were extracted with a 85μm Carboxen/PDMS (SPME) fiber and 3.85g of sodium sulfate for 15 minutes at 25ºC. Fibers where desorbed at 240 ºC for 1 minute in the GC/MS.

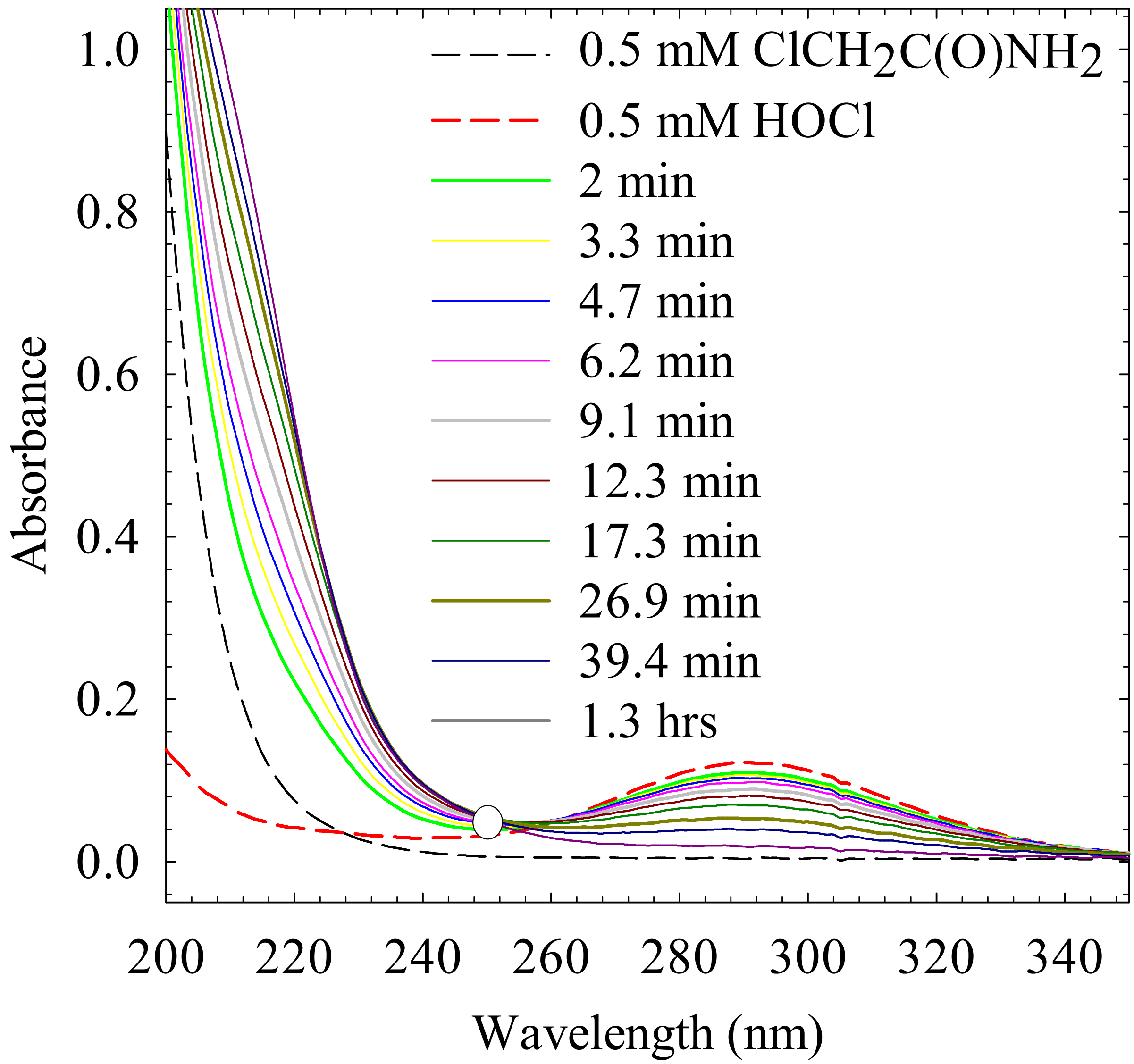


Figure S1. N,2-dichloroacetamide formation over time monitored with spectrophotometry from the reaction of chloroacetamide and hypochlorous acid, $[HOCl]_0$ = 0.5 mM, $[ClCH_2C(O)NH_2]_{T,0}$ = 0.5 mM, $[CO_3]_{T,0}$ = 0.02 M, pH 7.5 ± 0.1, μ = 0.1 M

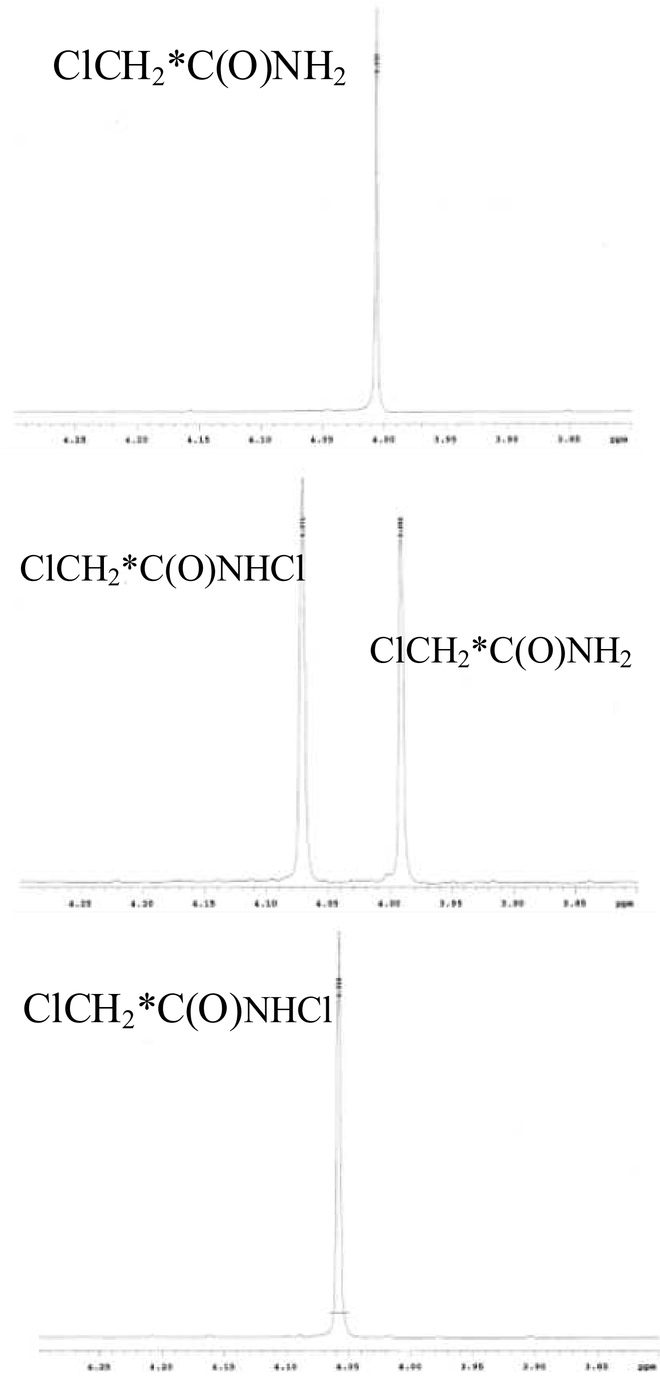


Figure S2. ^{1}H NMR spectra of chloroacetamide, the reaction of chloroacetamide and hypochlorous acid at 5 minutes, and *N*,2-dichloroacetamide at 15 days. Experimental conditions: $[HOCl]_0$ = 0.28 M, $[ClCH_2C(O)NH_2]_{T,0}$ = 0.28 M, 4°C

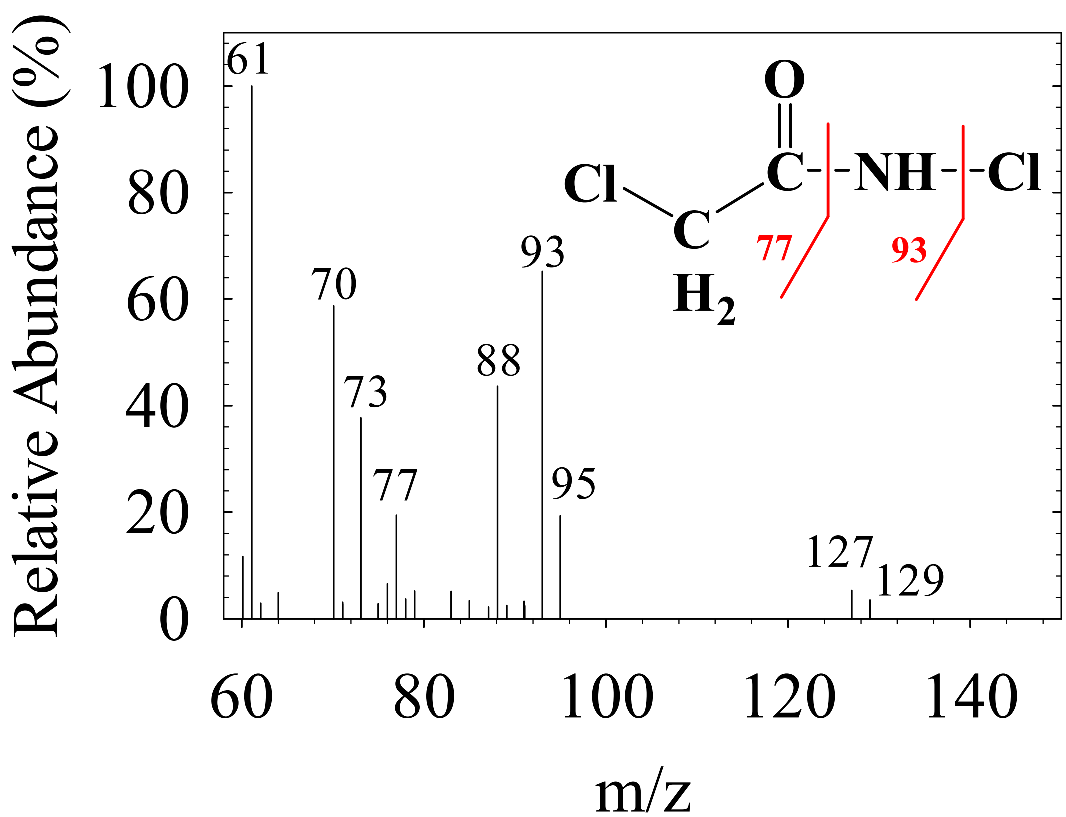
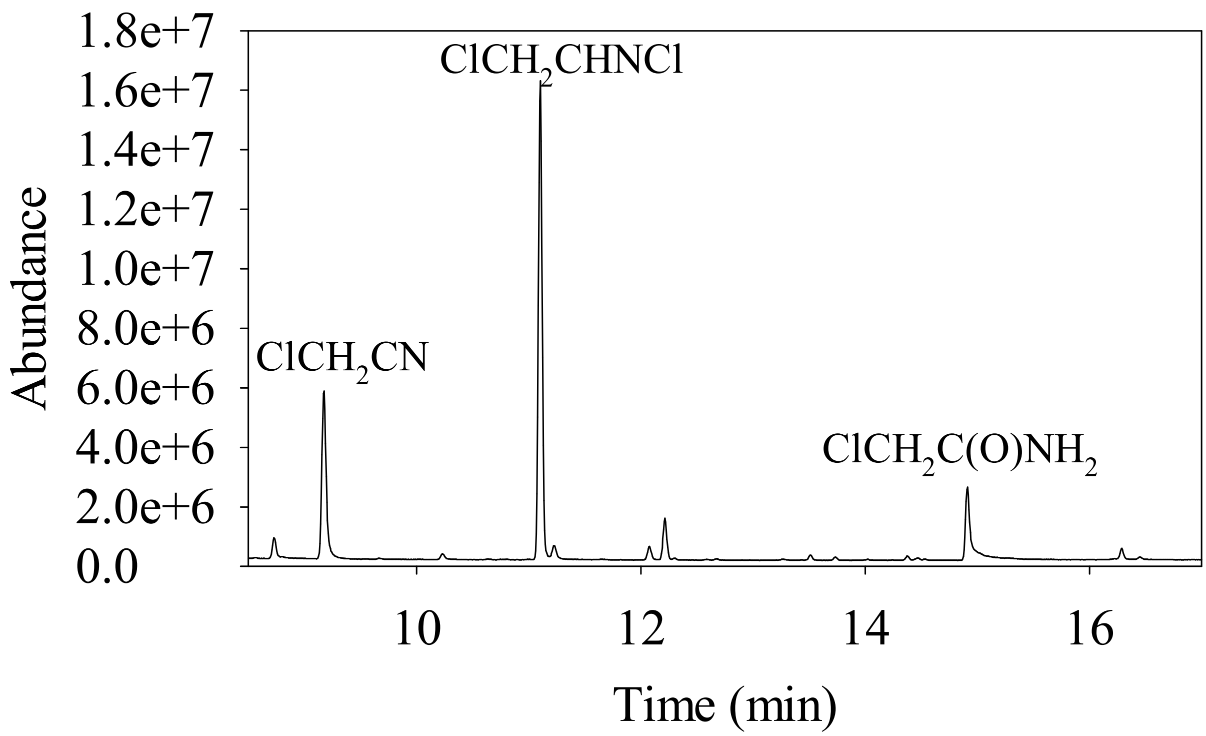


Figure S3. LRMS mass spectra of *N*,2-dichloroacetamide with traces of ethyl acetate used as an extraction solvent. *N*,2-dichloroacetamide m/z: 127(5.3%), 129(3.5%), 93 (65.2%), 95 (19.3%), 77 (19.4%). Ethyl Acetate m/z: 88 (43.6%), 73 (37.7%), 70 (58.7%), 61 (100%)



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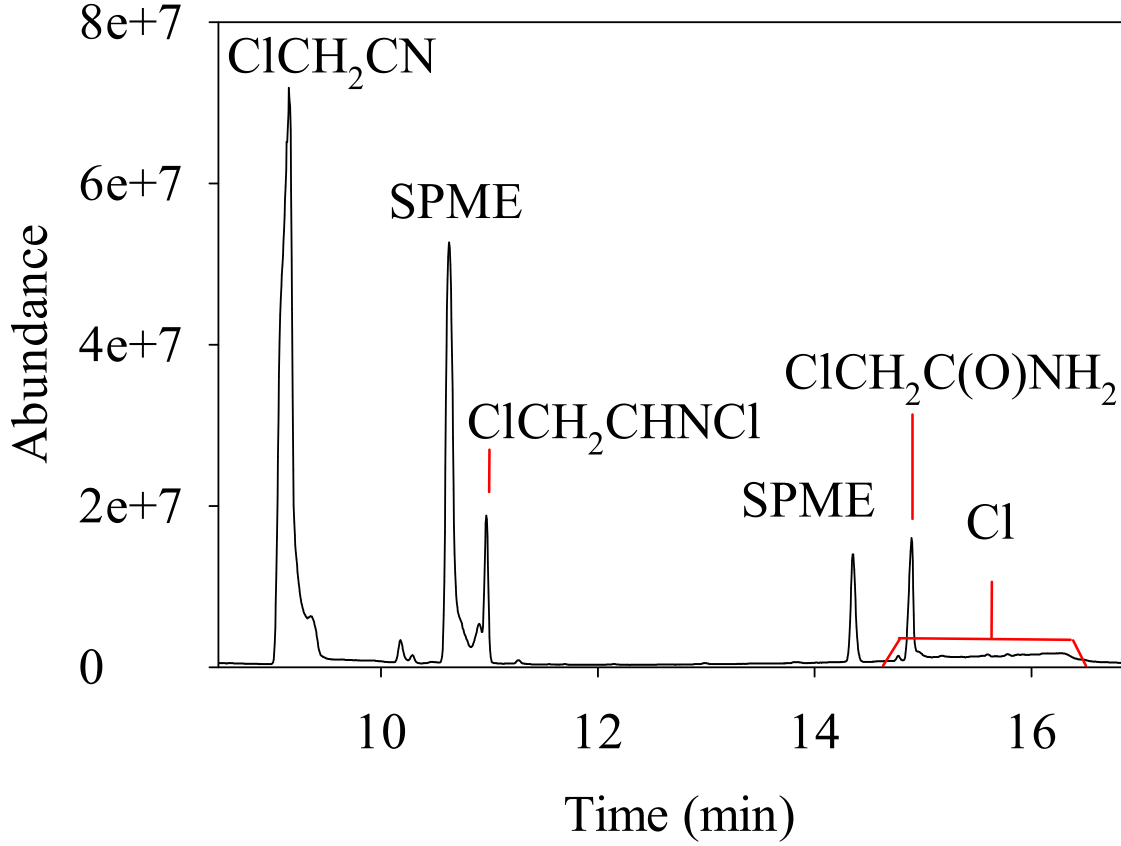

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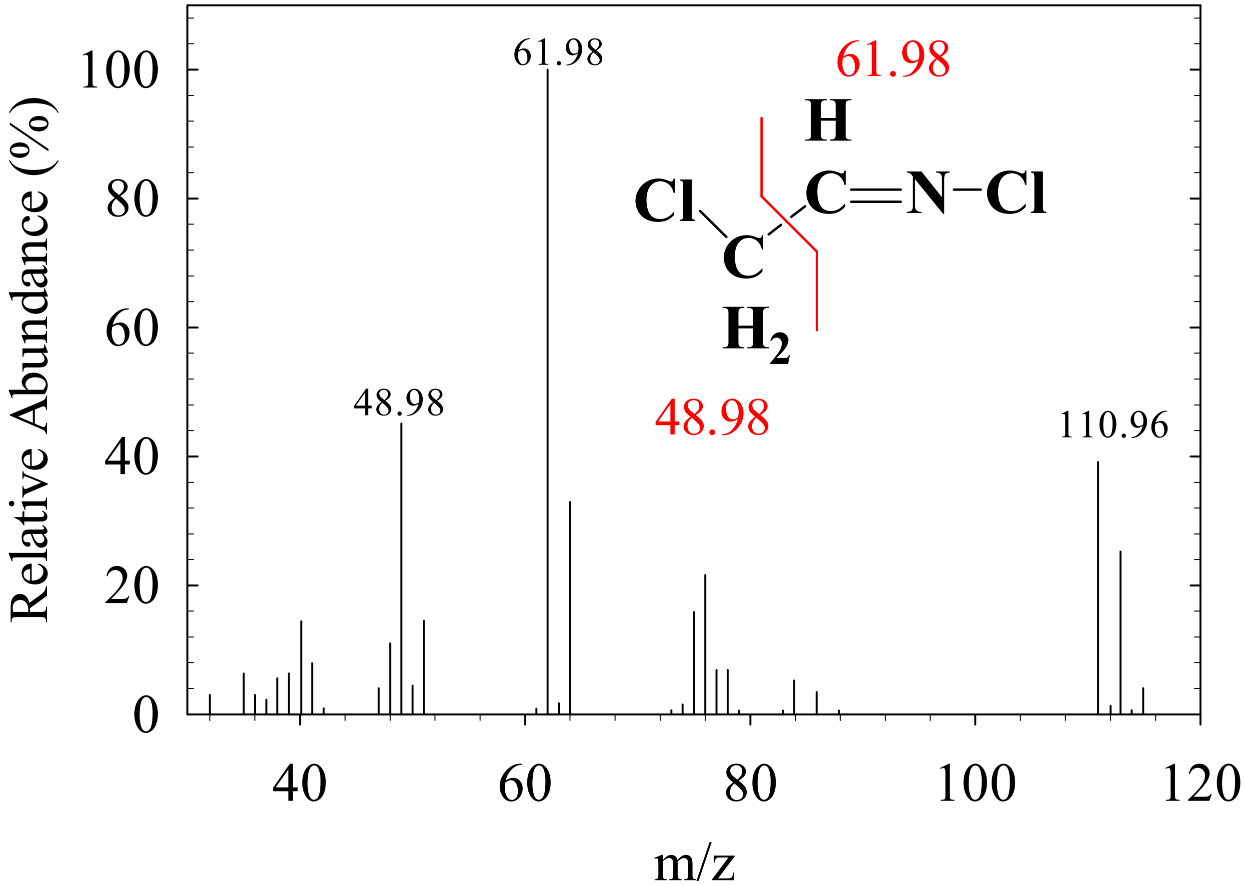

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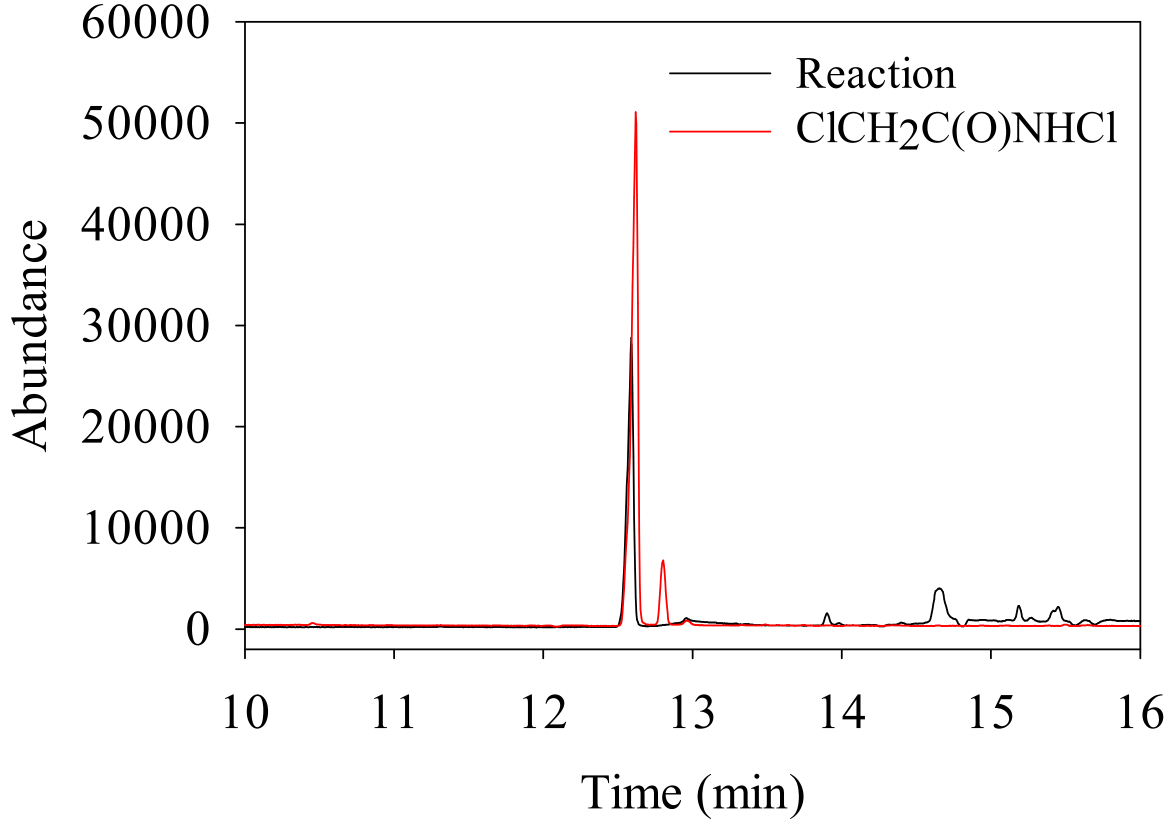

Figure S7. GC/NCI/MS select ion chromatogram (m/z:128) of N,2-dichloroacetamide standard and reaction extracts after 4 hrs. Experimental conditions: $[NH_2Cl]_0$ = 4.5 mM, $[ClCH_2CHO]_{T,0}$ = 20 mM, $[CO_3]_{T,0}$ = 0.02 M, pH 9.2 ± 0.3, μ = 0.1 M, 18 ± 0.1°C

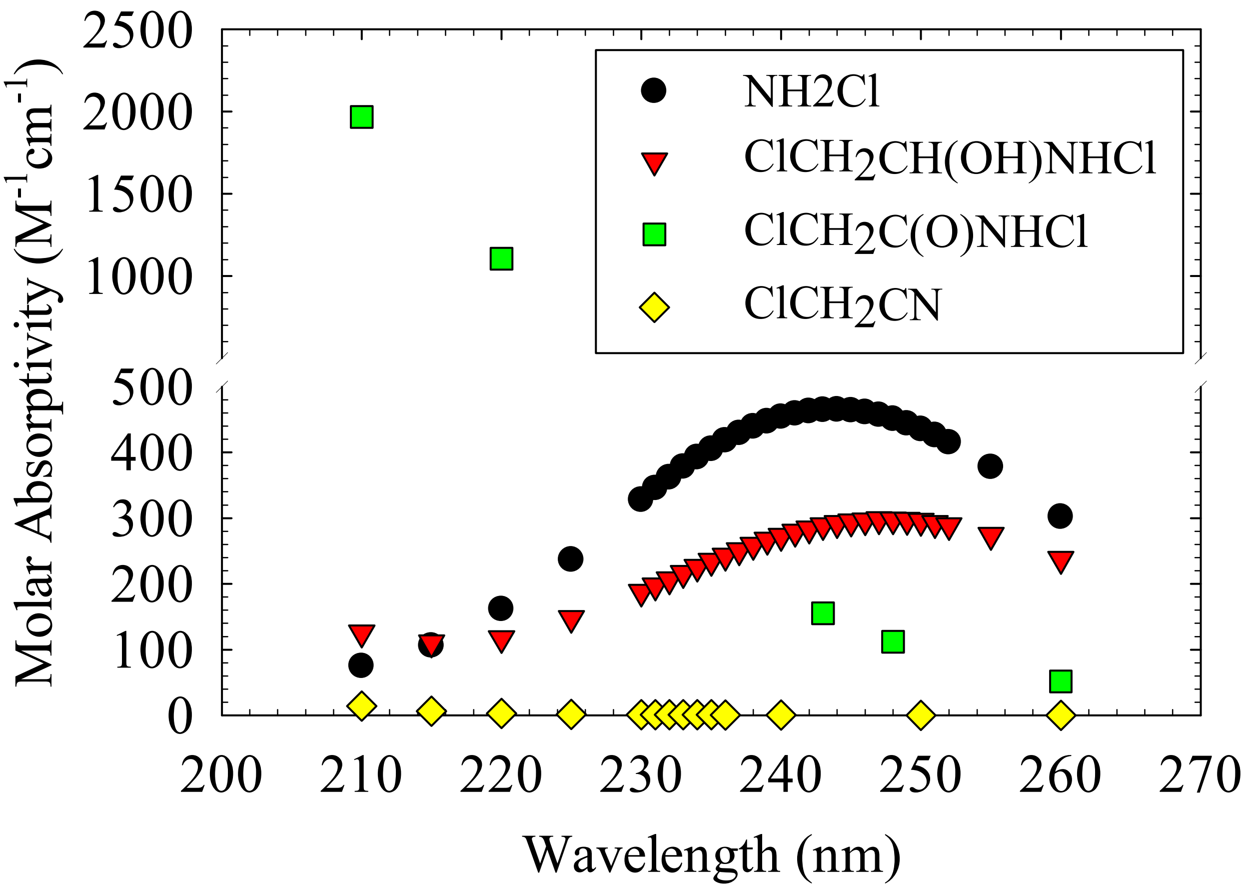

Figure S8. Molar extinction coefficients determined in this study for monochloramine, 2-chloro-1-(chloroamino)ethanol, *N*,2-dichloroacetamide, and chloroacetonitrile.

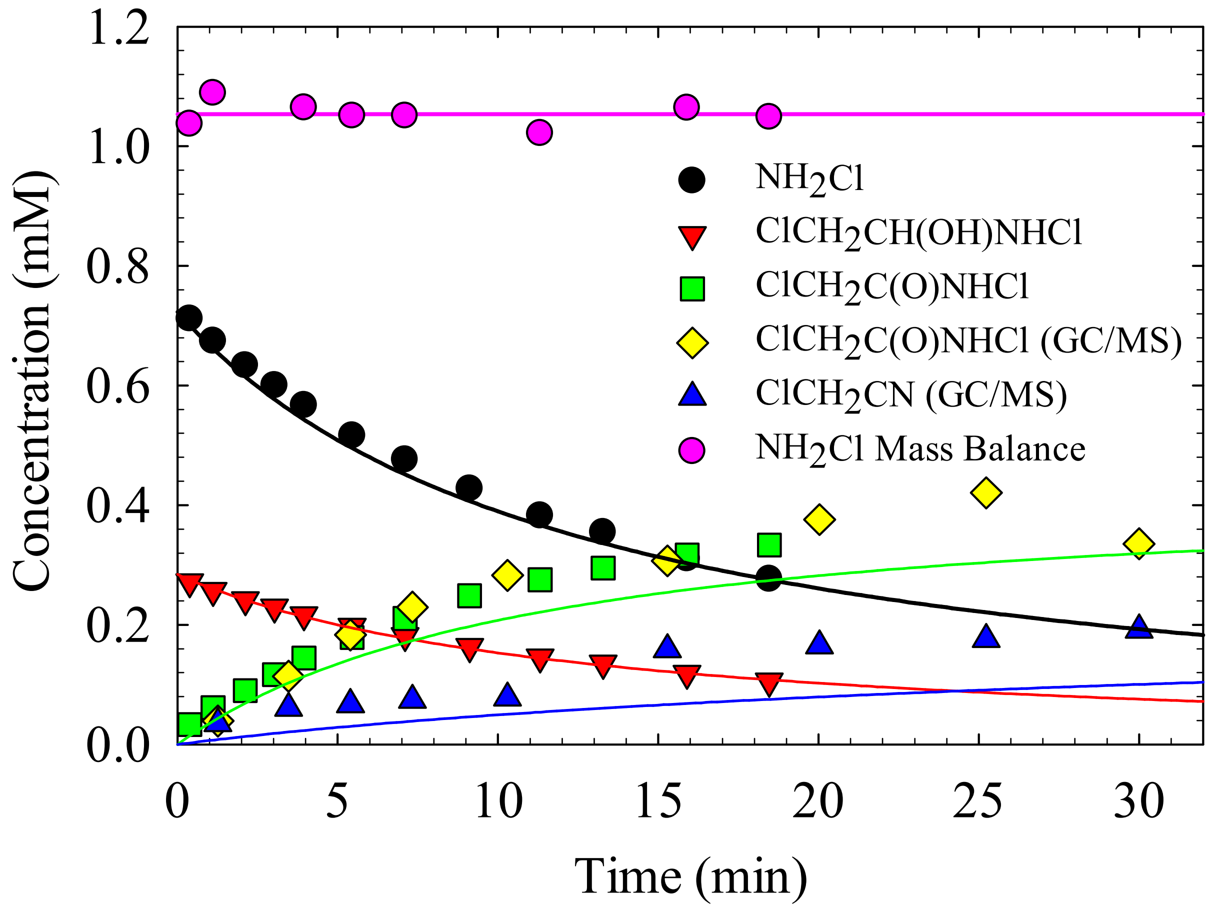

Figure S9. Monochloramine, 2-chloro-1-(chloroamino)ethanol, *N*,2-dichloroacetamide, and chloroacetonitrile concentrations over time (UV-2 and GC-2) and monochloramine mass balance. Symbols are experimental data points and lines are model fitting. Experimental conditions: $[NH_2Cl]_0$ = 1 mM, $[ClCH_2CHO]_{T,0}$ = 10 mM, $[CO_3]_{T,0}$ = 0.02 M, pH 9.83 ± 0.1, μ = 0.1 M, 18 ± 0.1°C

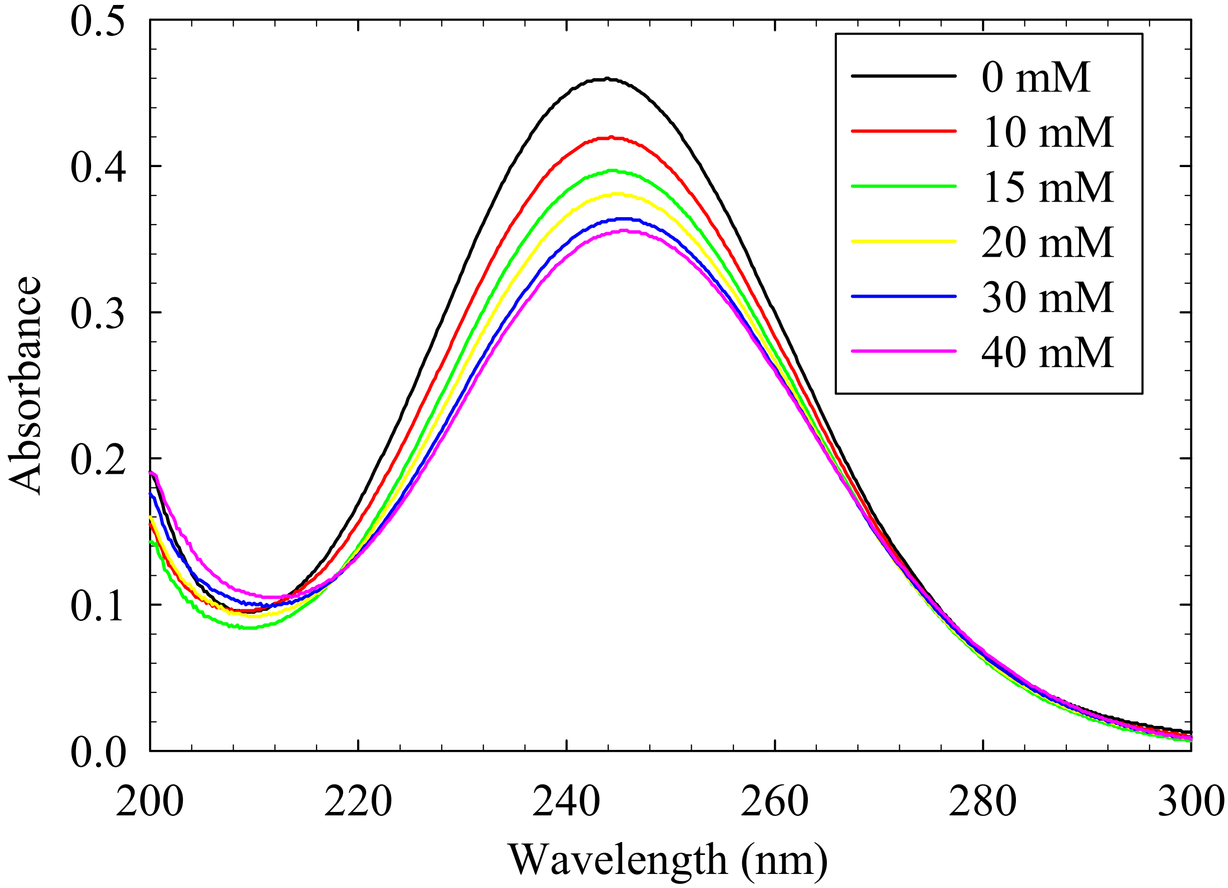

Figure S10. Effect of chloroacetaldehyde concentration on the equilibrium spectra for the reaction of chloroacetaldehyde and monochloramine at 1 to 3 min (UV-1) at experimental conditions: $[NH_2Cl]_0$ = 1 mM, $[ClCH_2CHO]_{T,0}$ = 10 - 40 mM, $[PO_4]_{T,0}$ = 0.02 M, pH 7.8 ± 0.1, μ = 0.1 M, 18 ± 0.1^{o}C

K_1 and $\varepsilon_{\mathrm{ClCH_2CH(OH)NHCl}_\lambda}$ calculation process

Table S2. Experimental data (UV-1) for a given wavelength (e.g. 243 nm) that was fitted to equation 7

$[\mathrm{NH_2Cl}]_0$ (mM)	$C_{T,\mathrm{ClCH2CHO}}$ (mM)	$[\mathrm{ClCH_2CHO}]_0$ (mM)	Absorbance at 243 nm	K_1 x10^3 (M^{-1})	1st $\varepsilon_{\mathrm{ClCH_2CH(OH)NHCl}_\lambda}$ ($M^{-1}cm^{-1}$)
0.99	10	0.206	0.419	1.95 ± 0.47	292 ± 21
0.99	15	0.309	0.395		
0.98	20	0.411	0.378		
0.98	30	0.617	0.361		
0.97	40	0.823	0.352		

Table S3. First fitting results of experimental data (UV-1) for each wavelength ranging from 235 to 245 nm

Wavelength (λ)	**K_1 x 10^3 (M^{-1})**	**1st $\varepsilon_{ClCH_2CH(OH)NHCl_\lambda}$ ($M^{-1}cm^{-1}$)**	**2nd $\varepsilon_{ClCH_2CH(OH)NHCl_\lambda}$ ($M^{-1}cm^{-1}$) (K_1 = 1.87 x10^3 M^{-1})**
210			126 ± 6
220			117 ± 5
230			188 ± 4
231			197 ± 4
232			206 ± 4
233			216 ± 4
234			226 ± 4
235	1.69 ± 0.45	225 ± 25	235 ± 4
236	1.77 ± 0.44	238 ± 23	243 ± 4
237	1.76 ± 0.42	245 ± 23	251 ± 4
238	1.82 ± 0.42	256 ± 22	259 ± 4
239	1.88 ± 0.47	267 ± 21	267 ± 4
240	1.86 ± 0.42	272 ± 20	273 ± 4
241	1.94 ± 0.44	282 ± 20	279 ± 4
242	1.91 ± 0.42	285 ± 23	284 ± 4
243	1.95 ± 0.47	292 ± 21	289 ± 4
244	1.99 ± 0.40	297 ± 17	292 ± 4
245	2.02 ± 0.44	301 ± 18	294 ± 3
246			296 ± 3
247			298 ± 3
248			298 ± 3
249			297 ± 3
250			295 ± 4
251			292 ± 3
252			289± 3
255			274 ± 3
260			237 ± 3
Average	1.87 ± 0.10		

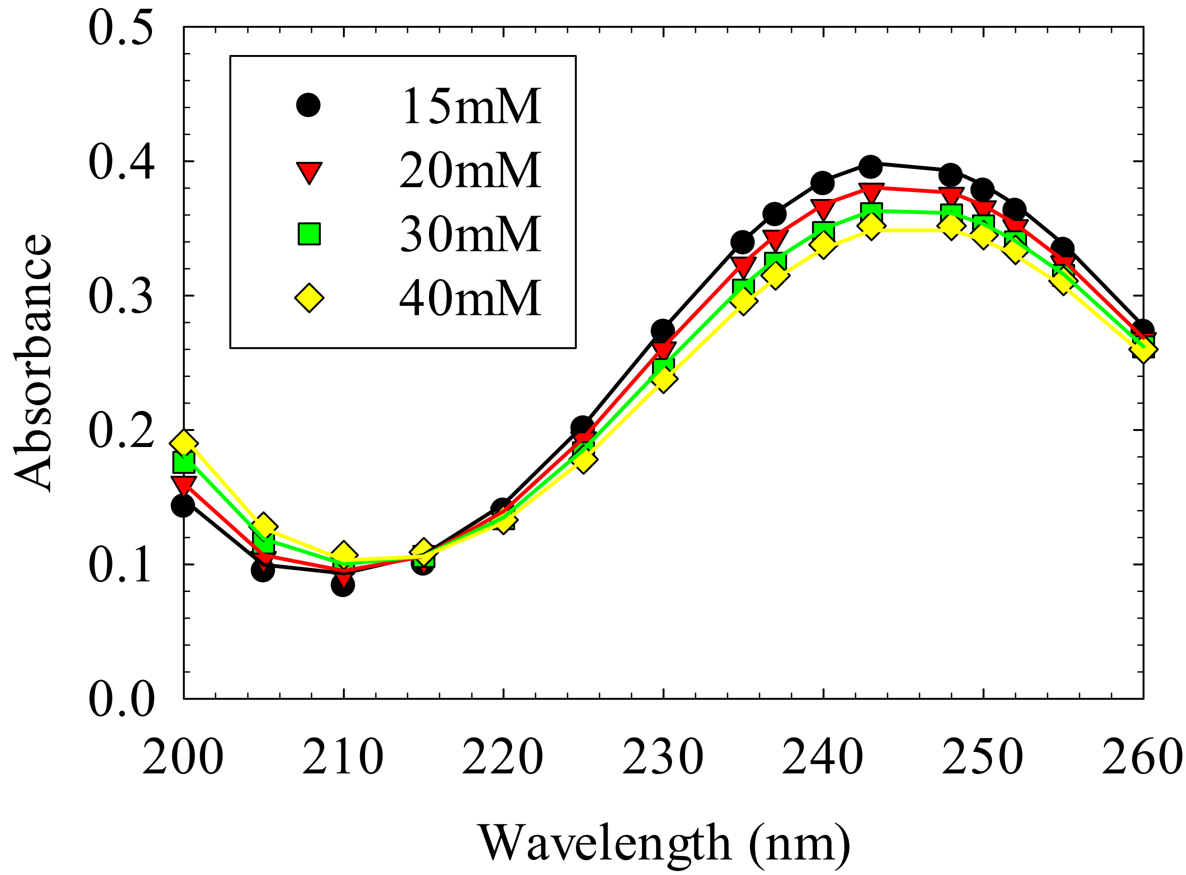

Figure S11. Comparison of experimentally measured (set UV-1, symbols) and calculated (lines) equilibrium absorbance at chloroacetaldehyde and monochloramine reaction time of 1-3 min.

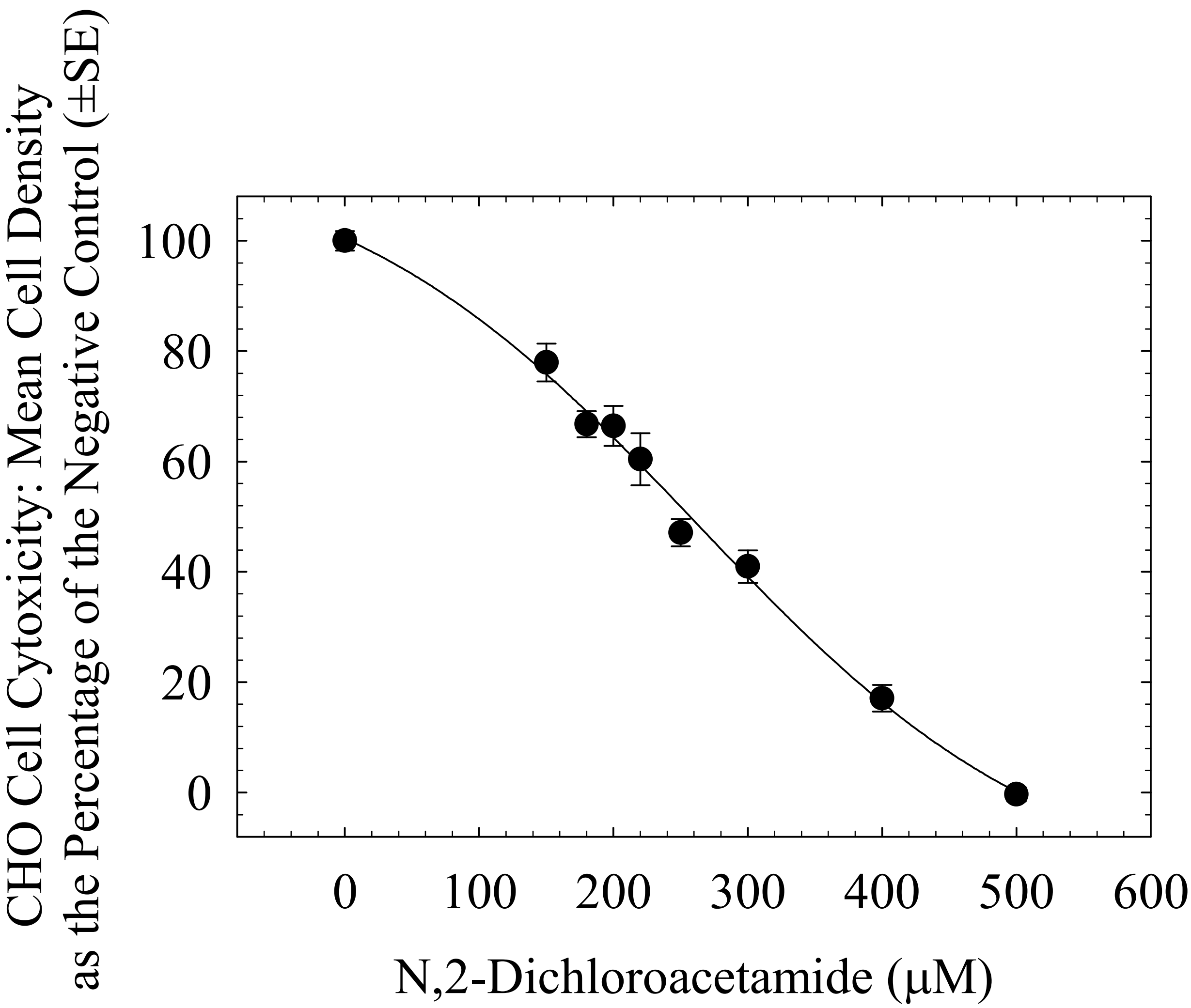

Figure S12. *N*,2-dichloroacetamide concentration-response curve and regression curve for chronic CHO cell cytotoxicity

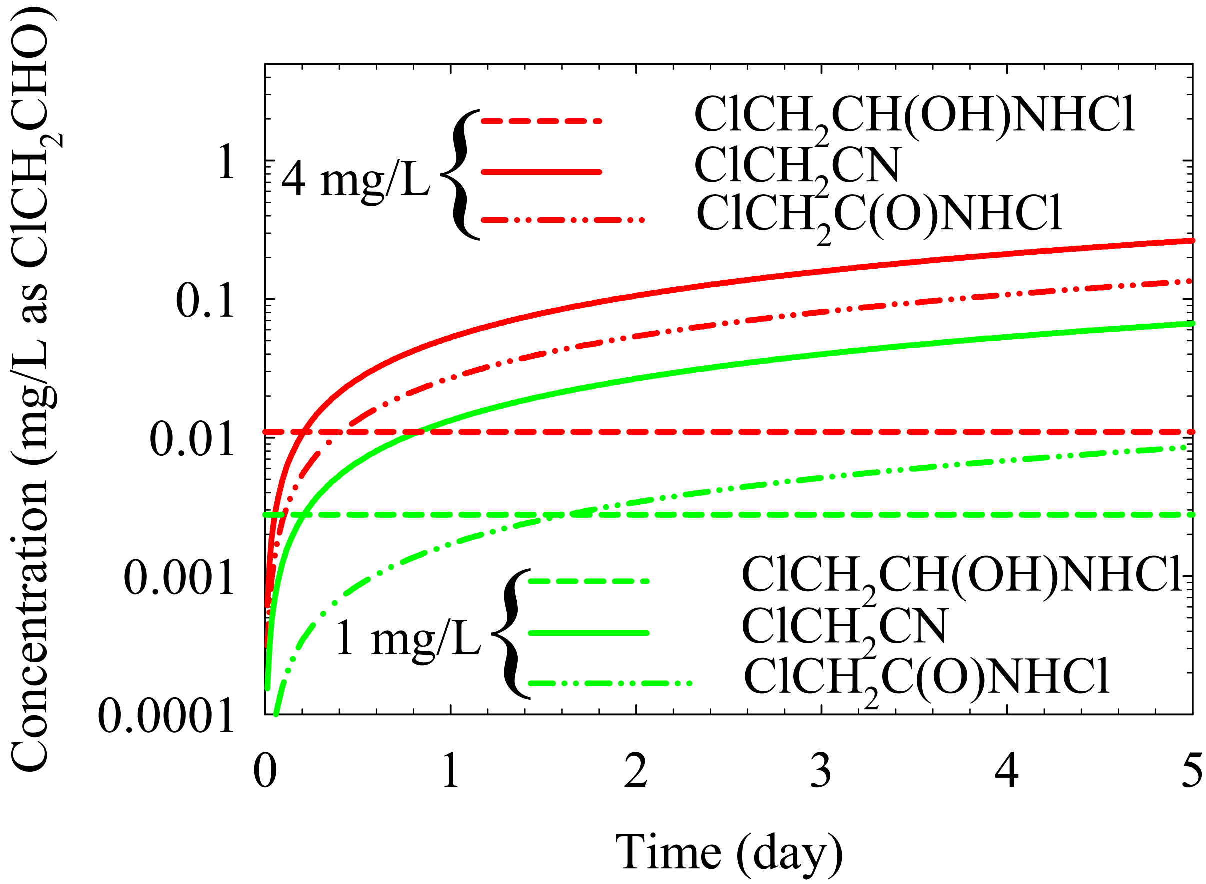

Figure S13. Effect of monochloramine concentration on chloroacetonitrile, *N*,2-dichloroacetamide, and 2-chloro-1-(chloroamino)ethanol formation over time at drinking water conditions: $[NH_2Cl]_0$ = 1 & 4 mg/L as Cl_2, $[ClCH_2CHO]_{T,0}$ = 5 μg/L, pH=9.0, 18ºC

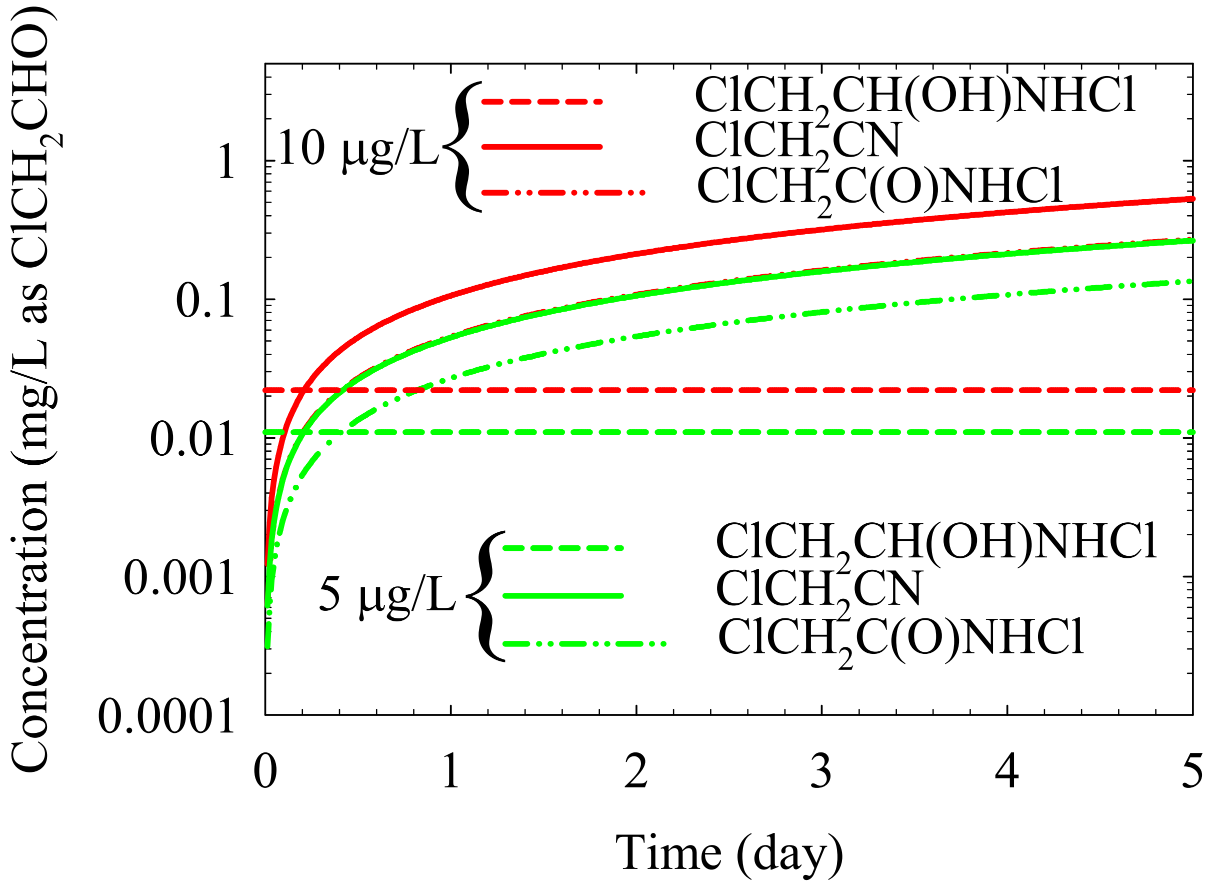

Figure S14. Effect of chloroacetaldehyde concentration on chloroacetonitrile, *N*,2-dichloroacetamide, and 2-chloro-1-(chloroamino)ethanol formation over time at drinking water conditions: $[NH_2Cl]_0$ = 4 mg/L as Cl_2, $[ClCH_2CHO]_{T,0}$ = 5 & 10 μg/L, pH=9.0, 18ºC