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Determination of halonitromethanes and haloacetamides: an evaluation of sample preservation and analyte stability in drinking water

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1. Abstract

Simultaneous quantitation of 6 halonitromethanes (HNMs) and 5 haloacetamides (HAAms) was achieved with a simplified liquid-liquid extraction (LLE) method, followed by gas chromatography-mass spectrometry. Stability tests showed that brominated tri-HNMs immediately degraded in the presence of ascorbic acid, sodium sulphite and sodium borohydride, and also reduced in samples treated with ammonium chloride, or with no preservation. Both ammonium chloride and ascorbic acid were suitable for the preservation of HAAms. Ammonium chloride was most suitable for preserving both HNMs and HAAms, although it is recommended that samples be analysed as soon as possible after collection. While groundwater samples exhibited a greater analytical bias compared to other waters, the good recoveries (>90%) of most analytes in tap water suggest that the method is very appropriate for determining these analytes in treated drinking waters. Application of the method to water from three drinking water treatment plants in Western Australia indicating N-DBP formation did occur, with

32 increased detections after chlorination. The method is recommended for low-cost, rapid
33 screening of both HNMs and HAAms in drinking water.

34 ## 2. Introduction

35 Nitrogenous disinfection by-products (N-DBPs) are a group of organic by-products that can be
36 formed during the disinfection of water sources rich in organic nitrogen [1,2]. Halonitromethanes
37 (HNMs) and haloacetamides (HAAms) are 2 classes of N-DBPs that are unregulated, but raise
38 questions for public heath protection because they are more toxic than the regulated disinfection by-
39 products (DBPs) [3-5]. The HNMs have been identified as extremely cytotoxic and genotoxic [4],
40 with the brominated HNMs ranked among the DBPs with the highest potential toxicities [5,6].
41 Haloacetamides have also been found to be more genotoxic and cytotoxic than currently regulated
42 haloacetic acids [3]. Nine bromine- and chlorine-substituted HNMs, and five bromine- and
43 chlorine-substituted HAAms have been identified in drinking waters to date [6-9], however neither
44 class has been comprehensively studied.

45 A lack of routine or well-validated analytical methods to measure these N-DBPs is one factor that is
46 hindering studies of the formation and occurrence of HNMs and HAAms in drinking waters .
47 Analytical methods for HNMs and HAAms have recently been reviewed [1,10]. Reported methods
48 generally employ a liquid-liquid extraction (LLE) procedure based on the USEPA method 551.1
49 [11], with or without modification, followed by gas chromatography with electron-capture detection
50 (GC–ECD) [9,12,13] and/or gas chromatography with mass spectrometry (GC–MS) [3,14,15].
51 More recently, two analytical methods employing headspace sampling have been reported for the
52 determination of nine HNMs in tap and swimming pool water [16,17], which are more sensitive
53 than LLE but also require specialized headspace sampling equipment. Sample preservation is also
54 critical for maintaining sample integrity in finished drinking water samples where a disinfectant
55 residual may exist. However, it is equally important that the added preservative does not affect
56 analyte concentrations during sample storage. Various preservatives have been recommended [18],
57 including sodium sulphite, ammonium chloride and ascorbic acid. Some studies, however, have
58 demonstrated that these preservatives can interact with certain DBPs, altering apparent
59 concentrations [9,19,20]. In particular, HNMs are known to undergo rapid degradation when
60 exposed to certain preservatives [9,12,20].

61 Here we report the validation of a single analytical method developed for the quantitation of 6
62 HNMs and 5 HAAms in drinking water samples, using LLE followed by GC-MS. Extraction by
63 LLE was employed because of its demonstrated suitability for both HNMs and HAAms. To our
64 knowledge, this is the first report of an analytical method for the simultaneous determination of
65 both HNMs and HAAms. In addition, the effect of four commonly used preservatives, ammonium

chloride, ascorbic acid, sodium sulphite and sodium borohydride,, were evaluated for their suitability in the determination of both HNMs and HAAms. Finally, the proposed method was used to characterize HNMs and HAAms in selected drinking water treatment plants in Western Australia.

3. Experimental

3.1. Reagents and standards

Trichloronitromethane (TCNM, chloropicrin, 5000 μg/mL in acetone) was obtained from AccuStandard Inc. (New Haven, USA). All other target analytes were purchased as neat compounds with purities between 85 and 99.5%; bromochloronitromethane (BCNM), dichloronitromethane (DCNM) bromodichloronitromethane (BDCNM), dibromochloronitromethane (DBCNM), tribromonitromethane (TBNM, bromopicrin,) and dibromoacetamide (DBAAm) from Orchid Cellmark (New Westminister, Canada), bromoacetamide (BAAm), dichloroacetamide (DCAAm) and trichloroacetamide (TCAAm) from Sigma-Aldrich (Castle Hill, Australia), and chloroacetamide (CAAm) from ChemService (Westchester, USA). Deuterated compounds, [^{2}H6] 1,2-dibromopropane (1,2-dibromopropane-d_6, 99.7%) and [^{2}H2] 1,1,2,2-tetrachloroethane (1,1,2,2-tetrachloroethane-d_2, 99.5%), were from CDN Isotopes (Pointe-Claire, Canada) and Sigma Aldrich (Castle Hill, Australia), respectively. Stock solutions (1 mg/mL in acetone) were stored at -14°C.

Acetone (>99.5%, HPLC grade) was from Mallinckrodt Baker (Phillipsburg, USA) and methyl-*tert*-butyl-ether (MTBE) (>99%, ACS reagent) was from Sigma-Aldrich (Castle Hill, Australia). Sodium sulphate, magnesium sulphate and hydrochloric acid (analytical grade or better) were from Ajax Finechem (Taren Point, Australia). Reagents used in preservation and stability studies included ammonium chloride (99.5%, Biolab (Aust) Clayton, Australia), L-Ascorbic acid (>99%, Sigma-Aldrich, Castle Hill, Australia), sodium sulfite and sodium borohydride (98% and 97%, respectively, Ajax Finechem, Taren Point, Australia).

3.2. Analysis of HNMs and HAAms

The LLE method employed was adapted from USEPA Method 551.1 [11], and optimised for solvent extraction volume, extraction pH and salt addition. Full details of the LLE optimisation and final procedure are provided in the Supporting Information (SI).

GC-MS determination was undertaken using an Agilent-6890N Gas Chromatograph coupled with a 5975 mass selective detector (MSD), operating in the electron impact ionization (EI) mode. Chromatographic peaks for target analytes were identified based on retention time and the presence of qualifying ions (SI Table S1). Generally the ion that had the highest intensity was chosen as the quantifying ion. The HAAms exhibit characteristic “tailing” peak shapes, which have been attributed to interactions with the EI ion source [3], which aided in peak identification.

99 ### 3.3. Sample preservation and analyte stability

100 Ultrapure water and tap water samples were fortified with 10 or 20 μg/L of the target N-DBPs.
101 Preservation agents (ascorbic acid, 20 mg/L; ammonium chloride, 100 mg/L; sodium borohydride,
102 40 mg/L; sodium sulphite, 25 mg/L) were added in excess to simulate quenching a residual of at
103 least 5 mg/L free chlorine. Preliminary tests using ultrapure water tested the immediate effects of
104 each preservative on target N-DBPs. Following these, ammonium chloride and ascorbic acid were
105 selected for further study over 14 days. The effect of pH (4-8) was also evaluated using unpreserved
106 ultrapure water samples adjusted with dilute hydrochloric acid or sodium hydroxide. Samples were
107 stored in the dark at 4°C during each test, and analysed at 1, 2, 3, 4, 7, 10 and 14 days.

108 ### 3.4. Sample collection

109 Raw and treated drinking waters were sampled from selected water treatment plants in Western
110 Australia between June 2010 and December 2010. Sample sites included two groundwater
111 treatment plants in metropolitan Perth and one surface water treatment plant in the northwest of
112 Western Australia, all utilising conventional treatment and chlorine disinfection. Raw source water
113 ranged in dissolved organic carbon (3-12 mg/L) and total nitrogen content (0.2-0.7 mg/L), and
114 treatment processes varied. Each site was sampled for raw water, treated water (post-disinfection)
115 and distribution system water (reticulation). Sampling procedures are detailed in the SI.

116 ## 4. Results & Discussion

117 ### 4.1. Analyte stability

118 #### *4.1.1. Sample preservation*

119 Preliminary analyte degradation tests using spiked (20 μg/L) ultrapure water treated with
120 ammonium chloride (100 mg/L), ascorbic acid (20 mg/L), sodium sulphite (25 mg/L) or sodium
121 borohydride (40 mg/L) demonstrated that the response ratios (equal to the ratio of the peak area of
122 the analyte to the peak area of the surrogate standard, 1,2-dibromopropane-d_6) of the brominated tri-
123 HNMs (BDCNM, DBCNM and TBNM) all decreased in the presence of ascorbic acid, sodium
124 sulphite and sodium borohydride, compared to samples with no preservation (SI Figure S1). Only
125 ammonium chloride treatment resulted in brominated tri-HNMs response ratios comparable to those
126 in unpreserved samples. Sodium sulphite and sodium borohydride also produced a decrease in the
127 response ratio for TCNM. Response ratios for some HAAm increased in the presence of ascorbic
128 acid, although this was not investigated further. The decrease in HNM concetrations observed in the
129 presence of sodium borohydride and sodium sulphite is attributed their strong reducing nature and
130 longer-term (14-day) stability tests were undertaken with ascorbic acid and ammonium chloride
131 only.

132 *4.1.2. 14-day stability study*

133 The effect of either ascorbic acid or ammonium chloride were tested over 14 days using spiked (20
134 μg/L) ultrapure water (Figure 1), and spiked (20 μg/L) tap water samples, with and without chlorine
135 addition after preservation (Figure 2). Results of BAAm and CAAm are not shown due to their poor
136 response in early studies, which meant that these analytes could not be conclusively determined
137 throughout the stability test period. In ultrapure water the stabilities of DBAAm, DCAAm, TCAAm,
138 TCNM, BCNM and DCNM were comparable for three preservation scenarios (i.e., no preservation,
139 ascorbic acid, and ammonium chloride). However, the brominated tri-HNMs were never detected in
140 ascorbic acid treated samples, and rapidly decreased within the first 3 days for samples with no
141 preservation, or when treated with ammonium chloride (Figure 1). The results confirmed that
142 treatment with ascorbic acid quickly degraded the brominated tri-HNMs, but did not affect other
143 analytes. The findings were similar in tap water without chlorine addition (Figure 2), however the
144 degradation of HNM species in unpreserved and ammonium chloride-quenched samples was
145 noticeably greater for tap water than for ultrapure water. There were no clear indications of
146 instability of HAAms during the period of testing, regardless of water type or preservative, although
147 there were slight fluctuations in the responses of these analytes.

148 High concentrations of chlorine resulted in the rapid destruction of HAAms, presumably due to
149 their conversion to haloacetic acids in the presence of free chlorine [8]. The concentrations of some
150 HAAms (DCAAm, TCAAm and DBAAm) decreased immediately upon the addition of further
151 chlorine (3 mg/L) to (already chlorinated) tap water without preservation or when treated with
152 ammonium chloride (Figure 2). Treatment with ascorbic acid preserved the concentrations of these
153 HAAms in chlorinated tap water. While treatment with ammonium chloride did not preserve
154 HAAm concentrations, no further degradation was detected after the initial chlorination, and levels
155 of HAAms were similar to that in unpreserved chlorinated tap water. Thus the use of ammonium
156 chloride as a preservative for HAAms is still applicable to chlorinated samples.

157 Interestingly, the initial responses of the brominated tri-HNMs were significantly higher when tap
158 water was treated with 3 mg/L free chlorine after preservation, for both unpreserved and ammonium
159 chloride-quenched samples. All 3 brominated tri-HNMs behaved similarly and responses for
160 TCNM were also notably higher in tap water with 3 mg/L free chorine. Furthermore, TCNM
161 increased in the unpreserved chlorinated tap water after day 4, suggesting there was additional
162 formation of TCNM in the water in the presence of free chlorine. TCNM is formed during
163 chlorination [21,22], but there is little information in the literature to determine whether significant
164 levels of HNMs are expected to form at the free chlorine concentration added in our experiments.

165 Overall, it is clear that many HNMs are unstable and serve as the limiting factor in the application
166 of this method for the analysis of HNMs and HAAms. Therefore, it is recommended that samples
167 be kept at 4ºC and analysed as soon as possible upon laboratory receipt, to minimize loss of
168 analytes. Ammonium chloride has previously been recommended over ascorbic acid for the
169 preservation of brominated HNMs [9] and results from this study confirm that ammonium chloride
170 is the most suitable preservation agent for both HNMs and HAAms over short periods of time.
171 However, it is important to note that the dechlorinating mechanism of ammonium chloride involves
172 the conversion of free chlorine to combined chlorine (i.e. monochloramine) [11]; therefore, it does
173 not act as a quenching agent in chloraminated samples. A more effective quenching agent for
174 chloramination that does not affect HNMs and HAAms has yet to be proposed. In these cases, we
175 recommend samples remain unpreserved but analysed as soon as possible.

176 *4.1.3. The effect of pH*

177 HNMs and HAAms are generally susceptible to base-catalysed degradation [14,23], however
178 DCAAm is also known to undergo hydrolysis under strongly acidic conditions [23]. The influence
179 of pH on the stability of target analytes was studied in ultrapure water containing 20 μg/L of target
180 analytes at pHs 4, 5, 6, 7 and 8, over 14 days (SI Figure S2). No significant differences were
181 observed in samples between pH 4-7. However, all three brominated tri-HNMs decreased at a
182 significantly faster rate at pH 8, and reduced to below detection by day 2. This faster degradation is
183 attributed to base-catalysed hydrolysis occurring at alkaline pH. Overall, these results emphasize
184 that samples should be analysed as soon as possible and should not be stored under alkaline pH
185 conditions. The use of ammonium chloride as a preservative is advantageous in this respect as it is
186 likely to reduce the pH of the sample to below pH 7, due to its acidic nature.

187 **4.2. Method validation**

188 Table 1 lists calibration and validation data for the analytical method. Method detection limits
189 (MDLs) were calculated according to the USEPA method [24], using the 95% confidence level of
190 the standard deviation of nine replicate measurements of a low concentration standard. MDLs
191 ranged from 0.08μg/L for TCNM and DCAAm, to 6 μg/L for TBNM. These are comparable with
192 previously reported limits (i.e. <1 μg/L) [9,16] for most of these analytes, other than the brominated
193 tri-HNMs (BDCNM, DBCNM, TBNM) and mono-HAAms (BAAm, CAAm), which presented the
194 least sensitivity. Most analytes showed linear calibration curves ($R^2 > 0.99$), except for the
195 brominated tri-HNMs as well as the mono-HAAms. For these analytes, linearity was generally
196 better over the high (1-100 μg/L) concentration range than the low (1-20 μg/L), which may be
197 explained by a lack of sensitivity and responses at low concentrations. Bias of the analytical method
198 was evaluated by measuring untreated surface water, groundwater and tap water, each spiked with

20 μg/L of analytes (in triplicate). Overall, the good recoveries of analytes other than the brominated tri-HNMs in tap water show that the method is appropriate for determining the presence of these analytes in treated drinking waters. Relative standard uncertainties were calculated for after identifying relevant uncertainty sources via a cause and effect diagram [25]. The uncertainty budget incorporated precision calculated as the relative standard deviation of triplicate spiked samples, calibration standard preparation, sample volume, and linear regression of the calibration curve. Generally the greatest source of uncertainty was precision (precision ranged from 4-31%), although linear regression of the calibration curve was also a significant source of error, particularly for the brominated tri-HNMs .

4.3. Analysis of drinking water samples

Concentrations of HNMs and HAAms were quantified in raw and treated drinking waters from two groundwater treatment plants in metropolitan Perth, and one surface water treatment plant in the northwest of Western Australia (Table 2), quantified via external calibration. Field and trip blank sample results were always below detection limits. None of the analytes were detected in any of the raw source waters, but were detected after disinfection with chlorine. The frequency of detections immediately post-chlorination was similar to the frequency of detections in the distribution system and there were no clear trends of either increasing or decreasing concentration with incresing residence time in the distribution system.

Only one HNM (DCNM), and three HAAms (CAAm, DCAAm and DBAAm) were measured at quantifiable concentrations. Dihalogenated species were the most frequently detected. The detected concentrations were similar to previously reported values (low μg/L) of these compounds in drinking waters from North America [9]. Further application of this method will provide an opportunity to prioritise these N-DBPs, potentially leading to further investigation of their toxicity, and understanding of their formation in drinking water sources.

5. Conclusions

Stability and validation studies indicate that HNMs are unstable, extremely sensitive to degradation from many common preservatives, and the limiting factor when applying LLE-GC-MS for the combined analysis of HNMs and HAAms. While ammonium chloride was the most suitable for preserving both HNMs and HAAms, it is important to note that ammonium chloride does not act as a quenching agent in chloraminated samples. An alternative quenching agent for waters from chloraminated systems that does not affect HNMs has yet to be proposed. Ascorbic acid is appropriate for chloraminated samples for preserving HAAms only.

231 Despite the higher detection limits for the brominated tri-HNMs and the mono-HAAms achieved in
232 this study, compared to previous studies [9,16], this is the first reported method using GC-MS for
233 the simultaneous determination of HNMs and HAAms. Occurrences of HNMs and HAAms in
234 drinking waters are typically in the low μg/L range, but drinking water guidelines have not yet been
235 established for these N-DBPs. This method, which can simultaneously measure HNM and HAAm,
236 will be very useful for generating drinking water occurrence data, as well as facilitating future work
237 on the formation and control of these N-DBPs.

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243 7. Figure Captions

244 Figure 1. Stability of HNMs and HAAms in ultrapure water fortified with 20 μg/L target analytes,
245 containing no preservative (●),100 mg/L ammonium chloride (△) or 20mg/L ascorbic acid (□).
246 See Table 1 for definition of analyte acronyms.

247 Figure 2. Stability of HNMs and HAAms in tap water fortified with 20 μg/L target analytes,
248 without chlorine addition, containing no preservative (●), 100 mg/L ammonium chloride (▲) or 20
249 mg/L ascorbic acid (■); and in tap water fortified with 20 μg/L target analytes, with chlorine
250 addition (3mg/L free Cl_2), containing no preservative (○), 100 mg/L ammonium chloride (△) or 20
251 mg/L ascorbic acid (□). See Table 1 for definition of analyte acronyms.

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303

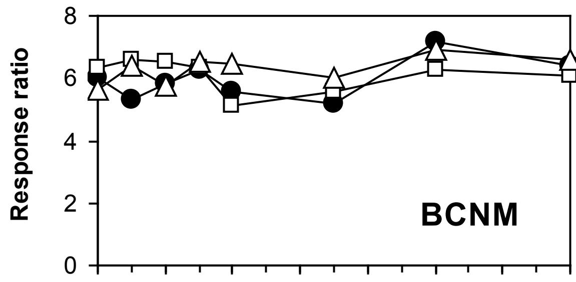
304

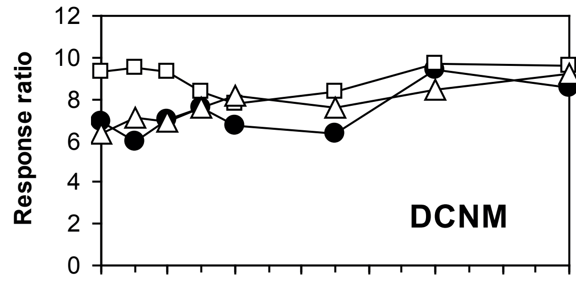
Table 1. Calibration and validation data for the analytical method. Method detection limit (MDL) calculated as per the USEPA method [24] based on 9 measurements (n=9) of low concentration standards (0.5-10 µg/L). R^2 values are from calibration curves with intercept forced through zero. Bias was determined using untreated surface water, groundwater, and tap water (n=3 of each water type), all spiked with 20 µg/L of each analyte, and is expressed as the mean percentage of spiked recoveries over all samples. Relative standard uncertainties were calculated employing an uncertainty budget that incorporated precision of replicate spiked samples, calibration standard preparation, sample volume and linear regression of the calibration curve. All errors are reported as standard deviation. All quantification was via external calibration.

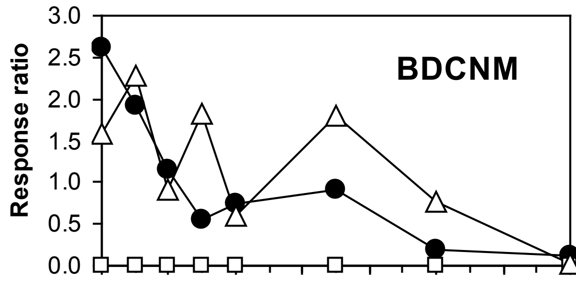
Analyte	**R^2 (1-20 µg/L)**	**R^2 (1-100 µg/L)**	**MDL (µg/L)**	**Bias (%)**			**Standard relative uncertainty (%)**
				Tap Water	**Source Water A**	**Source Water B**	
Bromochloronitromethane (BCNM)	0.997	0.997	0.09	89±3	110±10	99±4	11%
Dichloronitromethane (DCNM)	0.999	0.995	0.2	100±5	110±15	140±1	7%
Bromodichloronitromethane (BDCNM)	0.958	0.982	1	45±3	50±4	0	8%
Dibromochloronitromethane (DBCNM)	0.915	0.967	2	27±5	30±4	0	29%
Tribromonitromethane (TBNM, bromopicrin)	0.873	0.928	6	13±4	13±4	0	26%
Trichloronitromethane (TCNM, chloropicrin)	0.998	0.993	0.08	93±2	94±0.4	87±5	25%
Bromoacetamide (BAAm)	0.978	0.959	2	95±21	160±28	49±38	34%
Chloroacetamide (CAAm)	0.974	0.977	1	99±9	180±40	98±19	13%
Dibromoacetamide (DBAAm)	0.994	0.992	0.1	100±12	150±4	100±9	43%
Dichloroacetamide (DCAAm)	0.992	0.990	0.08	100±9	160±4	96±15	6%
Trichloroacetamide (TCAAm)	0.996	0.996	0.1	97±4	110±4	94±3	12%

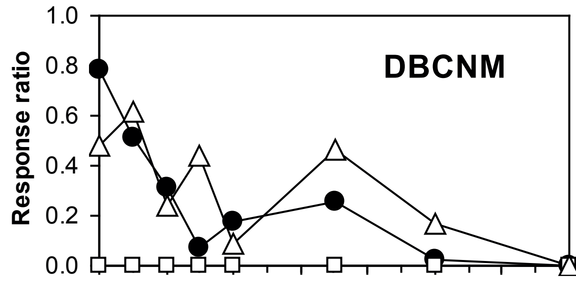
Table 2. Concentrations of halonitromethanes (HNMs) and haloacetamides (HAAms) from select water treatment plants in Western Australia. Results from field blanks (n=5) and trip blanks (n=3) are not reported because they were all below detection. See Table 1 for definition of analyte acronyms.

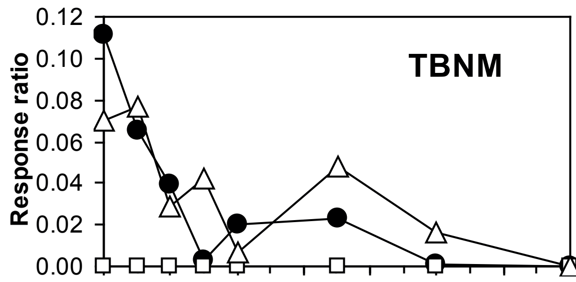
	HNMs (µg/L)						HAAms (µg/L)				
	BCNM	DCNM	BDCNM	DBCNM	TBNM	TCNM	BAAm	CAAm	DBAAm	DCAAm	TCAAm
Groundwater WTP 1											
Raw source water	<0.09	<0.2	<1	<2	<6	<0.08	<2	<1	<0.1	<0.08	<0.1
Post-Cl	<0.09	0.97	<1	<2	<6	<0.08	<2	<1	0.48	0.19	<0.1
Reticulation	<0.09	<0.2	<1	<2	<6	<0.08	<2	<1	0.37	0.08	<0.1
Groundwater WTP 2											
Raw source water	<0.09	<0.2	<1	<2	<6	<0.08	<2	<1	<0.1	<0.08	<0.1
Post-Cl	<0.09	0.41	<1	<2	<6	<0.08	<2	9.2	0.86	0.21	<0.1
Storage Reservoir	<0.09	0.83	<1	<2	<6	<0.08	<2	7.6	<0.1	<0.08	<0.1
Reticulation	<0.09	0.29	<1	<2	<6	<0.08	<2	<1	<0.1	<0.08	<0.1
Surface WTP 3											
Raw source water	<0.09	<0.2	<1	<2	<6	<0.08	<2	<1	<0.1	<0.08	<0.1
Post-Cl	<0.09	<0.2	<1	<2	<6	<0.08	<2	<1	0.82	0.16	<0.1
Reticulation	<0.09	<0.2	<1	<2	<6	<0.08	<2	<1	1.7	0.58	<0.1

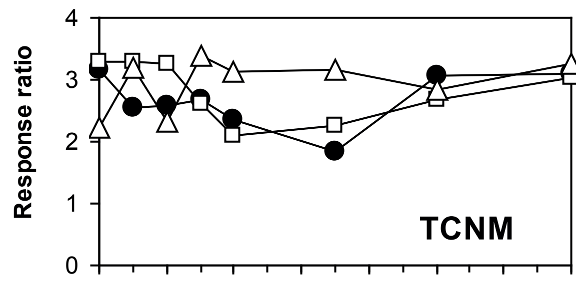

Response ratio
BCNM
0
2
4
6
8

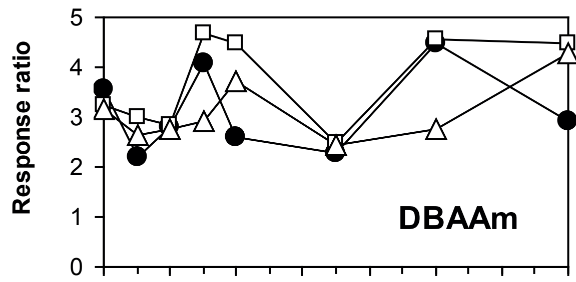

Response ratio
DCNM
0
2
4
6
8
10
12

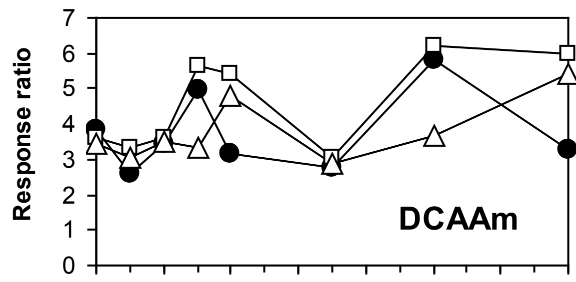

Response ratio
BDCNM
0.0
0.5
1.0
1.5
2.0
2.5
3.0

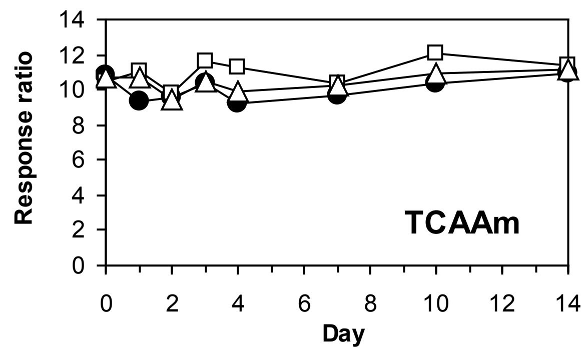

Response ratio
DBCNM
0.0
0.2
0.4
0.6
0.8
1.0

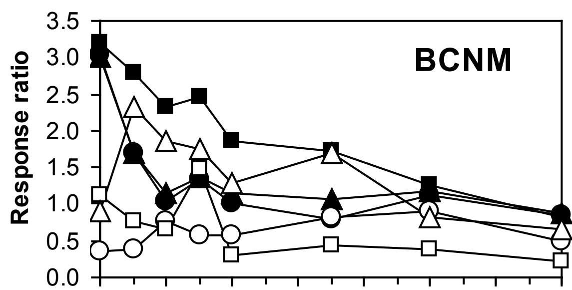

Response ratio
TBNM
0.00
0.02
0.04
0.06
0.08
0.10
0.12

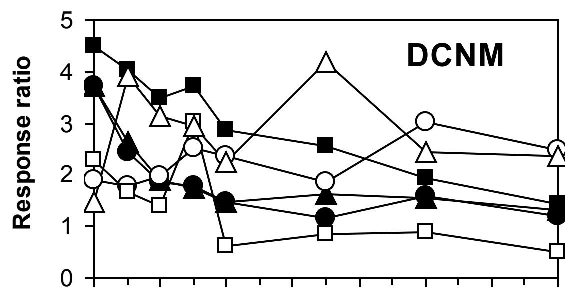

Response ratio
TCNM
0
1
2
3
4

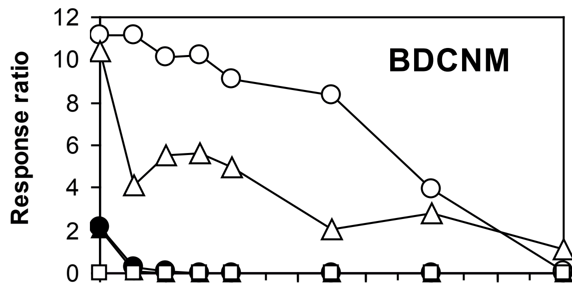

Response ratio
DBAAm
0
1
2
3
4
5

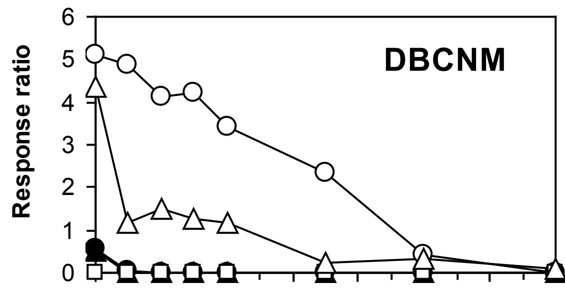

Response ratio
DCAAm
0
1
2
3
4
5
6
7
0
2
4
6
8
10
12
14
Day

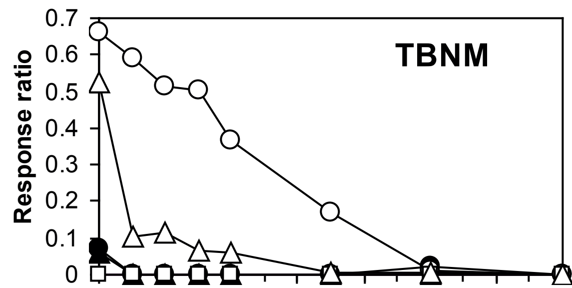

Response ratio
TCAAm
0
2
4
6
8
10
12
14
0
2
4
6
8
10
12
14
Day

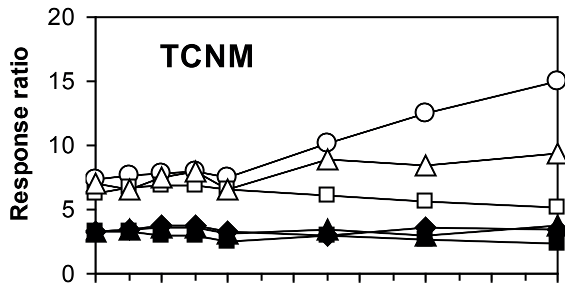

BCNM
Response ratio
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

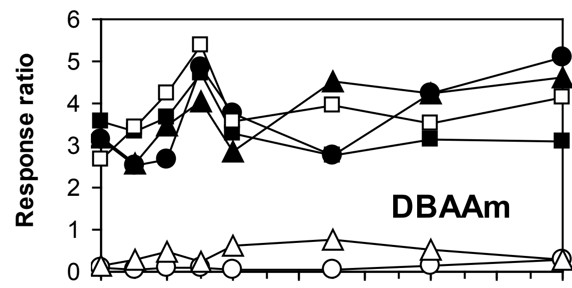

DCNM
Response ratio
5
4
3
2
1
0

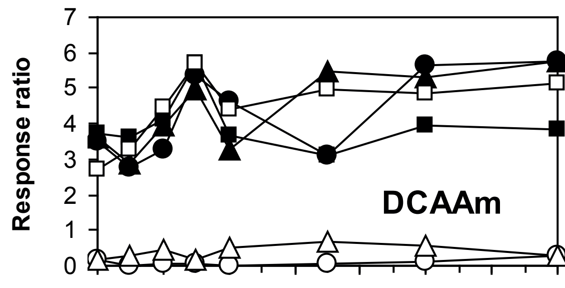

BDCNM
Response ratio
12
10
8
6
4
2
0

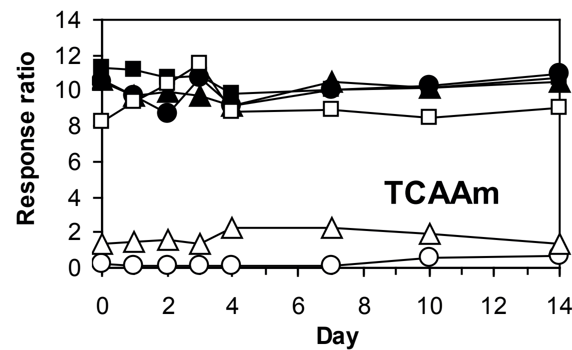

DBCNM
Response ratio
6
5
4
3
2
1
0


TBNM
Response ratio
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0


TCNM
Response ratio
20
15
10
5
0


DBAAm
Response ratio
6
5
4
3
2
1
0


DCAAm
Response ratio
7
6
5
4
3
2
1
0
0
2
4
6
8
10
12
14
Day


TCAAm
Response ratio
14
12
10
8
6
4
2
0
0
2
4
6
8
10
12
14
Day