

# MONITORING OF NITROGENATED DBPs IN DRINKING WATER

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## **SUMMARY**

### **I OBJECTIVES**

The objectives of this project were to:

- i. Confirm nitrogen-containing disinfection by-product (N-DBP) compounds to monitor and select analytical methods.
- ii. Conduct appropriate performance testing for the selected analytes using the chosen methods.
- iii. Select water treatment works with due regard to the risk factors identified in previous reports.
- iv. Liaise with water companies to select and arrange access to appropriate sampling sites and locations.
- v. Conduct quarterly sampling of water leaving the selected water treatment works in accordance with best practice in terms of sampling and analysis, including appropriate analytical quality control.
- vi. Gather other relevant data such as water treatment performance information and water quality data to help interpret the results.
- vii. Report the findings of the survey, comparing levels found with established health based standards or with occurrence data from other countries.

### **II MOTIVATION**

Drinking water utility surveys in the US and other countries have reported the occurrence of a large number (i.e. hundreds) of disinfection by-products (DBPs) in treated drinking waters. These include a range of nitrogen-containing disinfection by-product compounds (N-DBPs) which have been reported to occur mostly in the low to sub-microgram per litre concentration range in treated drinking water. There is some evidence from non-regulatory studies that N-DBPs are more toxic than the trihalomethanes (THMs), which are regulated as DBPs in England and Wales currently. The source water characteristics and water treatment conditions that lead to the formation of N-DBPs have been studied but there remain gaps in understanding, and at the beginning of this project there were very limited or no occurrence data for most N-DBPs in drinking waters in England and Wales. A previous project (DWI/2/243) provided a review of the occurrence and toxicological information available on N-DBPs and recommended some priority N-DBPs for sampling in England and Wales. The N-DBPs studied in this project excluded the nitrosamines, which have been considered in previous Defra-sponsored projects (DWI 70/2/210 and DWI 70/2/239).

### III APPROACH

A sampling survey of 20 water supply systems in England and Wales was conducted to measure the concentrations of N-DBPs in drinking waters. Water supply systems were selected to include treatment works that have suspected risk factors for the formation of N-DBPs, such as certain source water characteristics or treatment processes in use; several supply systems with no risk factors were also included, to give a representative indication of typical N-DBP concentrations. The measured N-DBP groups were selected haloacetonitriles (HANs), haloacetamides (HAcAms), halonitromethanes (HNMs), and cyanogen chloride. Water samples were collected in four sampling rounds over a one-year period. Quality assured sample collection, storage and analytical methods using gas chromatography mass spectrometry were used for measuring the N-DBPs. Samples were collected from the pre-disinfection and final treated water stages at the treatment works as well as three locations in the distribution networks. The results of the survey were compared against existing health-based standards for selected N-DBPs and against the N-DBP concentrations that have been reported in other countries (e.g. the US). The N-DBP concentrations were also examined alongside other raw and treated water quality parameters (e.g. total organic carbon, trihalomethanes, haloacetic acids), the source water types, and the treatment processes in order to consider potential links to N-DBP occurrence.

### IV CONCLUSIONS

The N-DBPs occurred at broadly similar concentrations as have been reported in surveys in other countries, e.g. the US. As individual compounds, all the N-DBP compounds were typically only present at concentrations  $< 2 \mu\text{g/l}$ . HANs were detected at the highest group sum concentrations (mean =  $3.2 \mu\text{g/l}$ ), followed by HAcAms (mean =  $1.5 \mu\text{g/l}$ ), and HNMs (mean =  $0.4 \mu\text{g/l}$ ). All the measured N-DBPs occurred at levels below the current World Health Organisation (WHO) guidelines for dichloroacetonitrile ( $20 \mu\text{g/l}$ ) and dibromoacetonitrile ( $70 \mu\text{g/l}$ ). The lowland water sources that were included in this survey formed more N-DBPs than the upland and groundwater sources. The six treatment works that applied ozone were associated with higher concentrations of HANs and HAcAms than non-ozone treatment works, although this is potentially confounded because all the ozone works were treating lowland source waters which may have had higher N-DBP formation potential. The ozonated systems also produced higher cyanogen chloride concentrations, which agreed with the previous understanding of the formation of this compound. In general, supply systems applying chlorine formed slightly more HANs and HAcAms than those applying chloramines. Total chlorinated and brominated THMs were measured in rounds 1 and 4; none of the N-DBPs exhibited consistent correlations with total THMs. The nine chlorinated and brominated haloacetic acids ( $\text{HAA}_9$ ) were measured in round 4 only; HANs and HAcAms exhibited better linear correlations with  $\text{HAA}_9$  than with total THMs. However, there were no trends linking HNMs to either THMs or  $\text{HAA}_9$ . Total organic carbon alone was not a consistent predictor of N-DBP concentrations nor were there clear observed links with other individual measured water quality parameters. Possible correlations with total organic nitrogen could not be investigated because of

limitations in the sensitivity of the organic nitrogen measurement methods that were used. There were no significant consistent differences between the N-DBP concentrations measured in the different sampling rounds, nor were there consistent trends between N-DBP concentrations and water age in distribution (distance from the treatment works).

## 1. INTRODUCTION

Sampling surveys of drinking water utilities in the US and other countries have reported the occurrence of hundreds of disinfection by-products (DBPs) in treated drinking waters. These include a range of nitrogen-containing DBPs (N-DBPs). A recent review of N-DBP occurrence and toxicology information (DWI 70/2/243, Templeton *et al.* (2010)) summarised that N-DBPs have been reported in those countries to occur mostly in the low to sub-microgram per litre concentration range. The review described how there is some evidence that N-DBPs are more toxic than the trihalomethanes (THMs), which are regulated as DBPs in England and Wales; however, there is sparse toxicology information available for many N-DBPs, and specifically there have been very few *in vivo* toxicity studies, which are considered the most directly relevant type of toxicology data when considering probable human health effects. The review also highlighted that the source water characteristics and water treatment processes that lead to the formation of N-DBPs are moderately well understood; however there was either very limited or no occurrence data for most N-DBPs in England and Wales.

The N-DBPs studied in this project excluded the nitrosamines, which were considered in previous Defra-sponsored projects (DWI 70/2/210 and DWI 70/2/239).

## 2. OBJECTIVES

The objectives of this project were to:

- i. Confirm nitrogen-containing disinfection by-product (N-DBP) compounds to monitor and select analytical methods.
- ii. Conduct appropriate performance testing for the selected analytes using the chosen methods.
- iii. Select water treatment works with due regard to the risk factors identified in previous reports.
- iv. Liaise with water companies to select and arrange access to appropriate sampling sites and locations.
- v. Conduct quarterly sampling of water leaving the selected water treatment works in accordance with best practice in terms of sampling and analysis, including appropriate analytical quality control.
- vi. Gather other relevant data such as water treatment performance information and water quality data to help interpret the results.
- vii. Report the findings of the survey, comparing levels found with established health based standards or with occurrence data from other countries.

### 3. PROJECT APPROACH

#### 3.1 Selection of N-DBPs

The selection of N-DBPs for inclusion in this project considered the compounds that had been reported in earlier studies in other countries (e.g. Krasner *et al.*, 2006), to allow direct comparisons of N-DBP concentrations. The selection also sought to include those N-DBPs for which there were World Health Organisation (WHO) guideline values, namely dichloroacetonitrile (20 µg/l), dibromoacetonitrile (70 µg/l) and cyanogen chloride (70 µg/l), and those which had been ranked as being of 'moderate' concern for carcinogenicity based on structure-activity analysis, including certain haloacetonitriles and halonitromethanes (Woo *et al.*, 2002). Lastly, the selection of N-DBPs also took into account the analytical feasibility and whether quality assured methods existed.

The list of N-DBPs that were subsequently selected for consideration in this survey and their acronyms are given in Table 3.1.

**Table 3.1 List of N-DBPs originally included in this survey.**

<b>Haloacetamides (HAcAms)</b>
2-Chloroacetamide (CAcAm)
2-Bromoacetamide (BAcAm)
2,2-Dichloroacetamide (2,2-DCAcAm)
2,2-Dibromoacetamide (2,2-DBAcAm)
2,2,2-Trichloroacetamide (2,2,2-TCAcAm)
<b>Haloacetonitriles (HANs)</b>
Chloroacetonitrile (CAN)
Bromoacetonitrile (BAN)
Dichloroacetonitrile (DCAN)
Bromochloroacetonitrile (BCAN)
Dibromoacetonitrile (DBAN)
Trichloroacetonitrile (TCAN)
Dibromochloroacetonitrile (DBCAN)
<b>Halonitromethanes (HNMs)</b>
Chloronitromethane (CNM)
Bromonitromethane (BNM)
Dichloronitromethane (DCNM)
Bromochloronitromethane (BCNM)
Dibromonitromethane (DBNM)
Trichloronitromethane (TCNM)
Bromodichloronitromethane (BDCNM)
Dibromochloronitromethane (DBCNM)
<b>Cyanogen halides (CNXs)</b>
Cyanogen chloride (CNCl)
Cyanogen bromide (CNBr)

### **3.2 Selection of water supply systems**

Six water companies were contacted to recommend water supply systems for inclusion in the sampling survey. The intention was to include treatment works with a range of different treatment processes, including ozone, chlorine and UV disinfection as primary disinfectants within the treatment works, and chlorinated and chloraminated distribution networks. The intention was also to consider a range of different source water types, representative of those across England and Wales, and broadly classified as lowland and upland surface water, and groundwater. Also of interest were source waters with particular water quality characteristics which previous research suggested might be important in N-DBP formation, such as the presence of bromide and organic nitrogen (or believed to have elevated nitrogen content, such as in eutrophic waters).

A total of 20 water supply systems were selected for the sampling survey; summary information about these systems is provided in Appendix C. In brief, these included eight lowland, five upland, and seven groundwater source waters. Twelve of the source waters were characterised by the water companies as potentially being of elevated nitrogen content, e.g. because they were known eutrophic waters. Six systems applied chloramination in the distribution network while all others used chlorine. Six of the treatment works applied ozonation and one used low-pressure UV disinfection. Five had source waters with bromide > 150 µg/l, which was considered relatively high in the context of England and Wales. Five supply systems historically produced total trihalomethanes > 50 µg/l in distribution.

Samples were collected at pre- and post-disinfection points at the treatment works and from three distribution network locations, on the same day and all in duplicate, meaning that there were ten samples collected per sampling round per water supply system. Because of the large numbers of waters supply systems, samples, and parameters to be measured, and in an effort to work around the busy schedules of the water company personnel who volunteered to collect the samples, each sampling round was distributed over three or four months. The collection of samples in round 1 took place from July 2011 to October 2011, round 2 collection was from November 2011 to February 2012 (with one company submitting their round 2 samples late, in May 2012), round 3 was from May 2012 to July 2012, and round 4 was from August 2012 to October 2012.

No samples could be collected from water supply system G in round 1 and water supply system P in round 4 due to unforeseen problems at the treatment works. Also, the results of the volatile N-DBP method (refer to section 3.3 below) could not be reported for ten samples in round 3 and twenty samples in round 4 because of delays between the sample collection and analyses and no time remaining in the project to re-collect and re-analyse those samples.

### **3.3 Analytical methods and quality control**

The analytical methods for measuring the suite of N-DBP compounds are summarised in Appendices A and B. Method performance data is provided in the Supplementary Data Files accompanying this report. In brief, two methods were used, one to capture semi-volatile N-DBPs and the other for more volatile N-DBPs. The methods used liquid-liquid extraction with

methyl tert-butyl ether (MTBE) followed by gas chromatography mass spectrometry (GCMS) for detection of the compounds. All compounds were determined by the semi-volatiles method except the cyanogen halides, chloroacetonitrile and trichloroacetonitrile which were analysed using the volatiles method. All samples were extracted within 72 hours of collection and analysed within 15 days of collection. The limits of detection that were achieved are summarised in Table 4.1.

The recovery of haloacetonitriles, halonitromethanes was good however the recovery of haloacetamides was variable such that it was not possible to report data for 2-chloroacetamide, and 2-bromoacetamide, as they failed to meet analytical quality control standards on precision and recovery (which is why they are not included in Table 4.1). Also, the recovery of the two di-haloacetamides that were included in the project (dichloroacetamide and dibromoacetamide) was only approximately 20%, although this was a consistent recovery percentage; it was decided not to manipulate the data to account for this low recovery.

At the start of the survey, analytical standards of CNCl (SpecCert standard, from Fisher Scientific) and CNBr (from Sigma-Aldrich) were available however the CNCl analytical standard became commercially unavailable soon after the start of the survey. Therefore analytical standards were prepared using an *in situ* synthesis protocol based on a published procedure by Wu *et al.* (1998). The results generated for CNCl are therefore based on a non-certified analytical standard. Reported methods of analysis for CNCl in drinking water include purge-and-trap (P&T) GCMS, static headspace GCECD and micro liquid-liquid extraction (LLE) GCECD. USEPA Method 524.2 (P&T GCMS) has a reported quantification limit of 0.3 µg/l for CNCl, although this detection limit could not be achieved. An alternative USEPA method using a micro-LLE approach (USEPA Method 551.1) which uses MTBE and salting out has also been reported and this method was used for the extraction and analysis of CNCl and CNBr. Although providing a good recovery for CNCl, the analytical reproducibility and recovery for CNBr were low and therefore data for CNBr were not reported.

In addition to the N-DBPs, a range of other water quality parameters were measured using standard water analysis methods: pH, total organic carbon (TOC), UV absorbance at 254 nm, bromide, ammonia, nitrate, nitrite, total oxidised nitrogen, and total Kjeldahl nitrogen (TKN). Water temperature and disinfectant residual concentration were measured by the water company staff at the time of sample collection. The four chlorinated and brominated trihalomethanes (THMs) and the nine chlorinated and brominated haloacetic acids (HAAs) were also quantified in selected samples; THMs were quantified in the final treatment works and distribution system samples in sampling rounds 1 and 4 and HAAs were quantified in the same samples in round 4 only. Samples were analysed for THMs by a United Kingdom Accreditation Service (UKAS) accredited method. In summary, each sample was placed in a septum vial and allowed to equilibrate with its headspace vapour at 80 °C. A sample of the vapour was injected using an automatic headspace sampler into a capillary column GCECD. Analytes were quantified using procedural standard calibration. For HAAs, samples were analysed following extraction and derivatisation based on USEPA Method 552.3 and analysed using GCMS detection. In summary, a 400-mL volume of sample was adjusted to a pH of 0.5

or less and extracted with 40 mL of MTBE containing an internal standard. The haloacetic acids that were partitioned into the organic phase were then converted to their methyl esters by the addition of acidic methanol followed by heating for two hours. The solvent phase containing the methylated haloacetic acids was separated from the acidic methanol by adding 7 mL of a concentrated aqueous solution of sodium sulfate. The aqueous phase was discarded. The extract was then neutralized with a saturated solution of sodium bicarbonate and the solvent layer was removed for analysis. The target analytes were identified and quantified by capillary column GCMS. Analytes were quantified using procedural standard calibration.

It was attempted to measure total organic nitrogen (TON) by subtracting total inorganic nitrogen from total nitrogen, a method reported to be successful in a number of previous studies (e.g. Fang *et al.*, 2010; Chu *et al.*, 2011), however the TON contents of the source waters included in this survey were too low to calculate values using this subtraction method. TKN measurements were also attempted but were limited to a detection limit of 1 mg/l; none of the water samples produced organic nitrogen values above that concentration. Future studies of organic nitrogen in waters in England and Waters should employ methods capable of detecting lower concentrations, such as using dialysis pretreatment (Lee and Westerhoff, 2005). However, a recent study concluded that organic nitrogen removal does not correlate strongly with reductions in specific N-DBP formation potential or actual levels of N-DBP occurrence in full-scale treatment works, suggesting that only a small fraction of organic nitrogen is incorporated into N-DBPs and that bulk organic nitrogen measurements such as TON may not be as informative for N-DBP formation potential as dissolved organic carbon is for carbonaceous DBP formation (Krasner *et al.*, 2012).

## **4. FINDINGS AND DISCUSSION**

### **4.1 Summary of N-DBP concentration ranges**

The ranges of concentrations of the individual HANs, HAACs, and HNMs and cyanogen chloride over all four sampling rounds are summarised in Figure 4.1. Besides cyanogen chloride, which was detected less frequently and with large variability in concentration, dibromoacetonitrile (DBAN) was the commonly detected N-DBP compound that was detected at the highest mean value (1.4 µg/l) and also at the maximum concentration (8.1 µg/l). Table 4.1 summarises the number of samples in which each N-DBP compound was detected above its limit of detection (LOD), the total number of disinfected samples that were analysed for each compound (i.e. treatment works final water and distribution networks samples; almost all raw water / pre-disinfection samples exhibited N-DBP concentrations < LOD, as expected) and the overall mean concentration for each N-DBP compound over all four sampling rounds. It was most commonly the di-halogenated forms of the HANs that were detected, whereas both di-halogenated HAACs and trichloroacetamide (1,1,1-TCAcAm) were detected and chloropicrin (trichloronitromethane, TCNM) that was the most commonly detected HNM.

It is important to note that null values (i.e. samples with concentrations below the limits of detection) were not included in these mean calculations nor in any of the plots that are included in this report, therefore the N-DBP concentrations as reported here may be conservative over-estimates of the true typical occurrence levels.

The concentration ranges of the HANs, HNMs, and HAcAms expressed as sum detectable concentrations for the groups of compounds measured, for all water supply systems over the four sampling rounds, are summarised in Figure 4.2. It should be noted that not all the brominated and chlorinated species of each group were included in the analytical methods used in this survey.

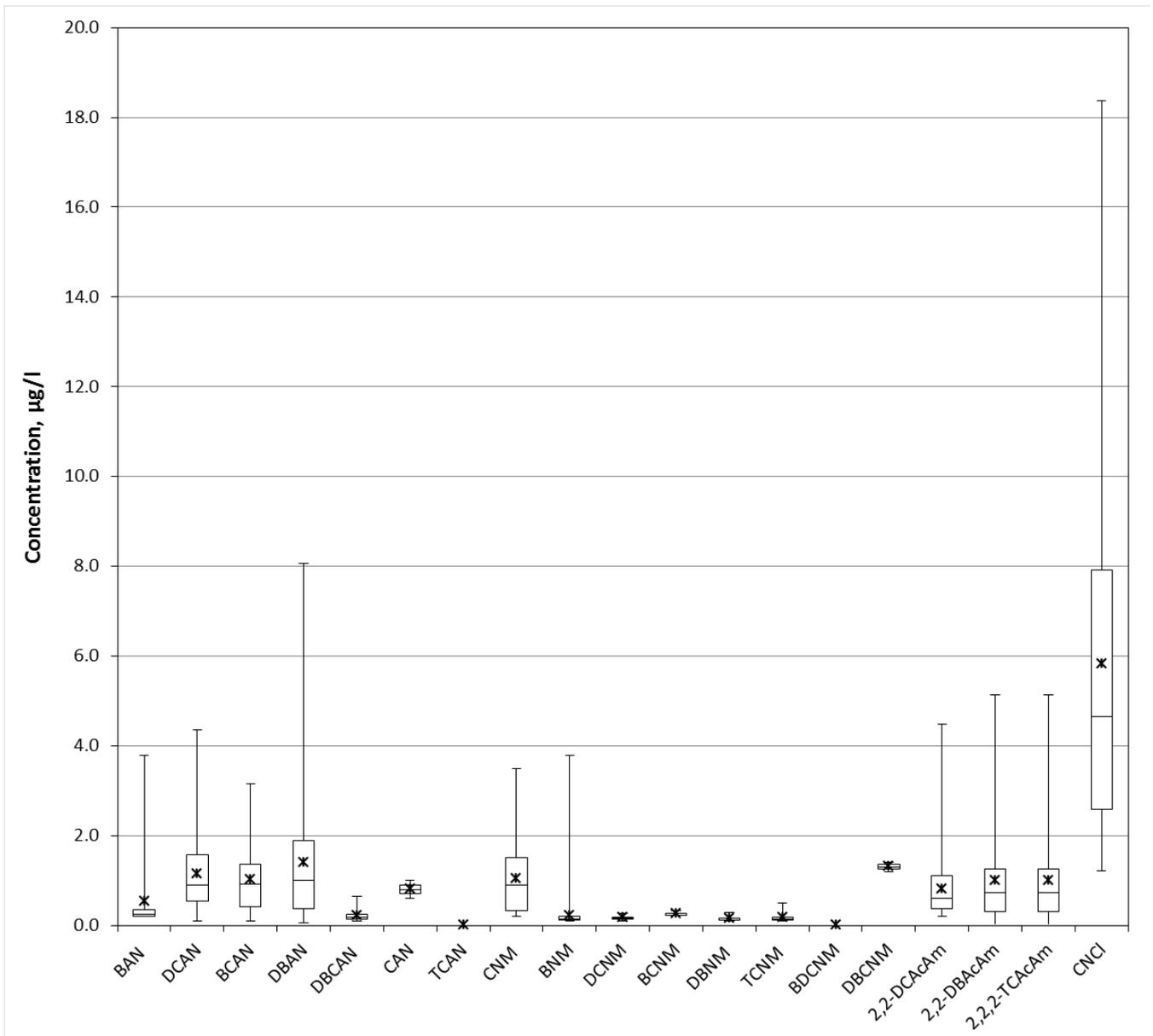
The HANs were found at the highest sum concentrations (mean concentration 3.2 µg/l), followed by HAcAms (mean 1.5 µg/l) and HNMs (mean 0.4 µg/l). The maximum total HAN concentration in any sample was 12.1 µg/l. Comparison of this value against the current WHO guidelines for DCAN (20 µg/l) and DBAN (70 µg/l) indicates that the water supply systems included in this survey produce water that is safely below these guideline values. The N-DBP concentration ranges detected in this survey also fall broadly within the ranges reported from previous surveys in other countries (refer to Appendix D for comparison).

The HAN results are broken down by sampling round, source water, and treatment type in Figure 4.3. The lowland waters using ozone and chlorine were associated with the highest HAN concentrations across all four sampling rounds. Lowland waters in general (i.e. all treatment types) produced higher HANs than the upland and groundwater sources, suggesting that the lowland waters have higher potential for HAN formation. For example, comparison of the lowland waters using chlorine only versus the upland and groundwater systems using chlorine only supports this hypothesis. Half of the lowland source waters included in this survey were eutrophic; algae have been suggested as an important source of amino acids which act as precursors for HANs and other DBPs (Trehy *et al.*, 1986). There were no clear differences in HAN concentrations in chlorinated versus chloraminated systems, suggesting that the nitrogen in the HANs may not originate from the chloramine.

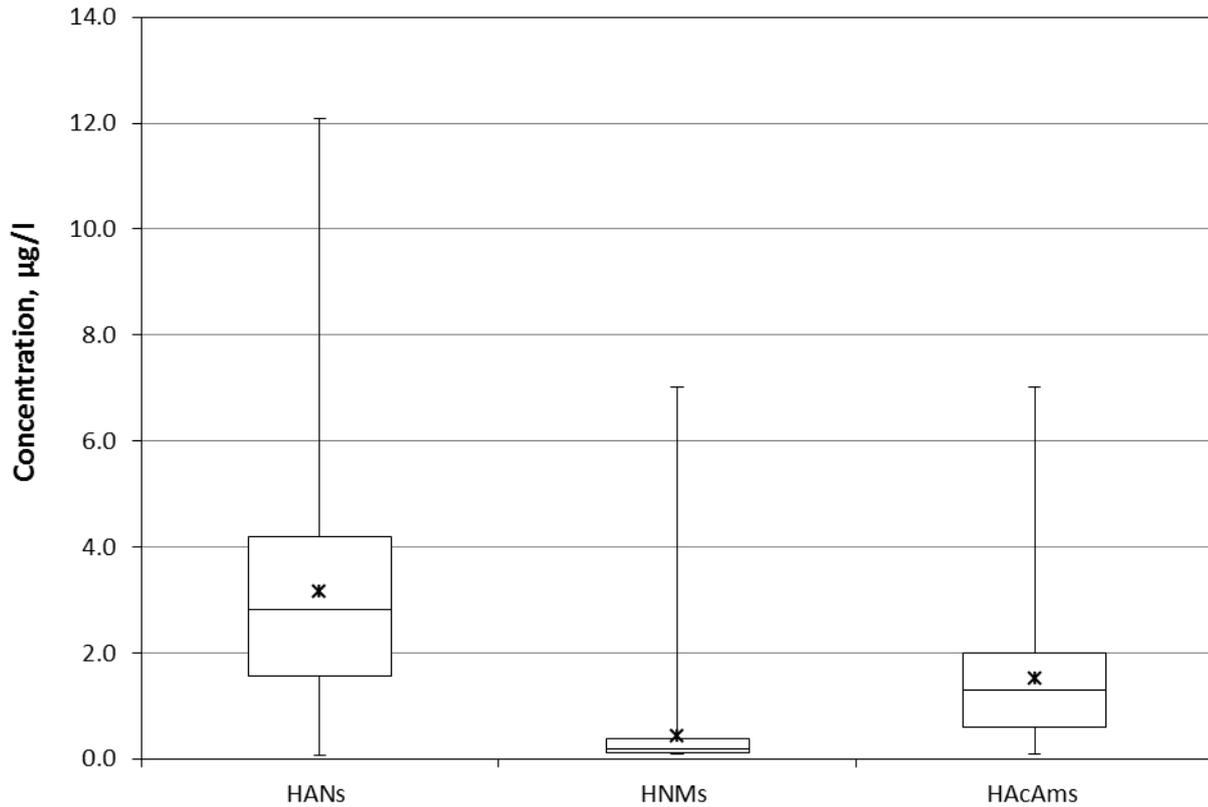
Analogous plots for HAcAms, HNMs, and cyanogen chloride are provided in Figures 4.4, 4.5, and 4.6, respectively. The HAcAms followed very similar trends to the HANs, though the concentrations were lower. The HNMs occurred at still lower concentrations but with greater variability between and within sampling rounds; no clear trends linked HNMs to the source or treatment types. Cyanogen chloride was detected less frequently than the other N-DBPs and with larger variability in the detected concentrations between and within sampling rounds.

**Table 4.1 The limit of detection (LOD) for each N-DBP, the number of samples for which each N-DBP was detected above its LOD, the total number of disinfected samples analysed for each N-DBP (i.e. excluding the raw water / pre-disinfection samples), and the overall mean concentrations in µg/l.**

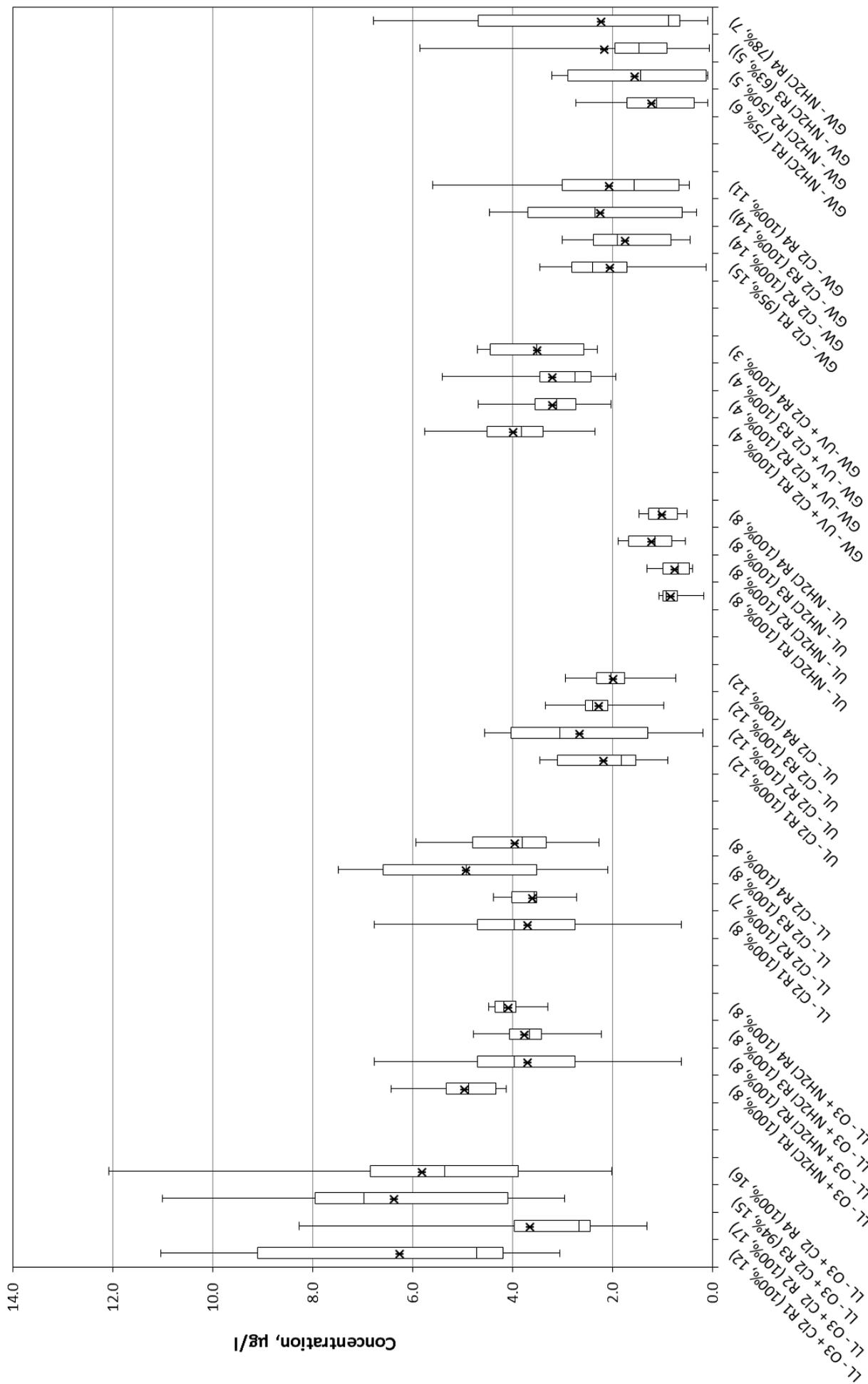
<b>N-DBP</b>	<b>LOD (µg/l)</b>	<b>Number of Samples Above LOD</b>	<b>Total Number of Disinfected Samples Analysed</b>	<b>Mean Concentration (µg/l)</b>
BAN	0.2	22	624	0.5
DCAN	0.2	497	624	1.1
BCAN	0.1	533	624	1.0
DBAN	0.1	510	624	1.4
DBCAN	0.1	46	624	0.2
CAN	0.5	2	600	0.8
TCAN	0.5	0	600	not detected
CNM	0.2	70	624	1.0
BNM	0.1	129	624	0.2
DCNM	0.1	30	624	0.2
BCNM	0.2	7	624	0.2
DBNM	0.1	56	624	0.1
TCNM	0.1	149	624	0.2
BDCNM	1.0	0	624	not detected
DBCNM	1.0	2	624	1.3
2,2-DCAcAm	0.2	401	624	0.8
2,2-DBAcAm	0.1	426	624	1.0
2,2,2-TCAcAm	0.3	426	624	1.0
CNCl	2.0	148	600	5.8



**Figure 4.1** The ranges of concentrations of individual N-DBPs measured over all four sampling rounds. The stars are the mean values, the lines within the boxes are the median values, the tops of the boxes are the 75<sup>th</sup> percentile values, the bottoms of the boxes are the 25<sup>th</sup> percentile values, and the whiskers extend to the maximum and minimum values. Samples for which no concentration was measured above the detection limit were excluded from the data sets.



**Figure 4.2** The ranges of of the sum of the concentrations for the haloacetonitriles (HANs), halonitromethanes (HNMs), and haloacetamides (HAcAms) measured in this survey over all four sampling rounds. The stars are the mean values, the lines within the boxes are the median values, the tops of the boxes are the 75<sup>th</sup> percentile values, the bottoms of the boxes are the 25<sup>th</sup> percentile values, and the whiskers extend to the maximum and minimum values. Samples for which no concentration was measured above the detection limit were excluded from the data sets.



**Figure 4.3 The ranges of the sum of the concentrations for the haloacetonitriles (HANs) measured in this survey. LL = lowland, UL = upland, GW = groundwater, O3 = ozone, Cl2 = chlorine, UV = ultraviolet disinfection, NH2Cl = chloramination, R1 = sampling round 1, R2 = round 2, R3 = round 3, R4 = round 4. The numbers in brackets represent the number of disinfected sampling locations (i.e. treatment works final water and distribution network) for which the concentration of at least one HAN was detected above the detection limit and therefore for which the sampling data was included in the data set and plotted here. The percentages in brackets represent the percentage of the sampling locations of that source water and treatment type for which at least one HAN was detected above the detection limit out of the total potential number of such locations. The stars are the mean values, the lines within the boxes are the median values, the tops of the boxes are the 75<sup>th</sup> percentile values, the bottoms of the boxes are the 25<sup>th</sup> percentile values, and the whiskers extend to the maximum and minimum values. Samples for which no concentration was measured above the detection limit were excluded from the data sets.**



**Figure 4.4** The ranges of the sum of the concentrations for the haloacetamides (HAcAms) measured in this survey. LL = lowland, UL = upland, GW = groundwater, O3 = ozone, Cl2 = chlorine, UV = ultraviolet disinfection, NH2Cl = chloramination, R1 = sampling round 1, R2 = round 2, R3 = round 3, R4 = round 4. The numbers in brackets represent the number of disinfected sampling locations (i.e. treatment works final water and distribution network) for which the concentration of at least one HAcAm was detected above the detection limit and therefore for which the sampling data was included in the data set and plotted here. The percentages in brackets represent the percentage of the sampling locations of that source water and treatment type for which at least one HAcAm was detected above the detection limit out of the total potential number of such locations. The stars are the mean values, the lines within the boxes are the median values, the tops of the boxes are the 75<sup>th</sup> percentile values, the bottoms of the boxes are the 25<sup>th</sup> percentile values, and the whiskers extend to the maximum and minimum values. Samples for which no concentration was measured above the detection limit were excluded from the data sets.



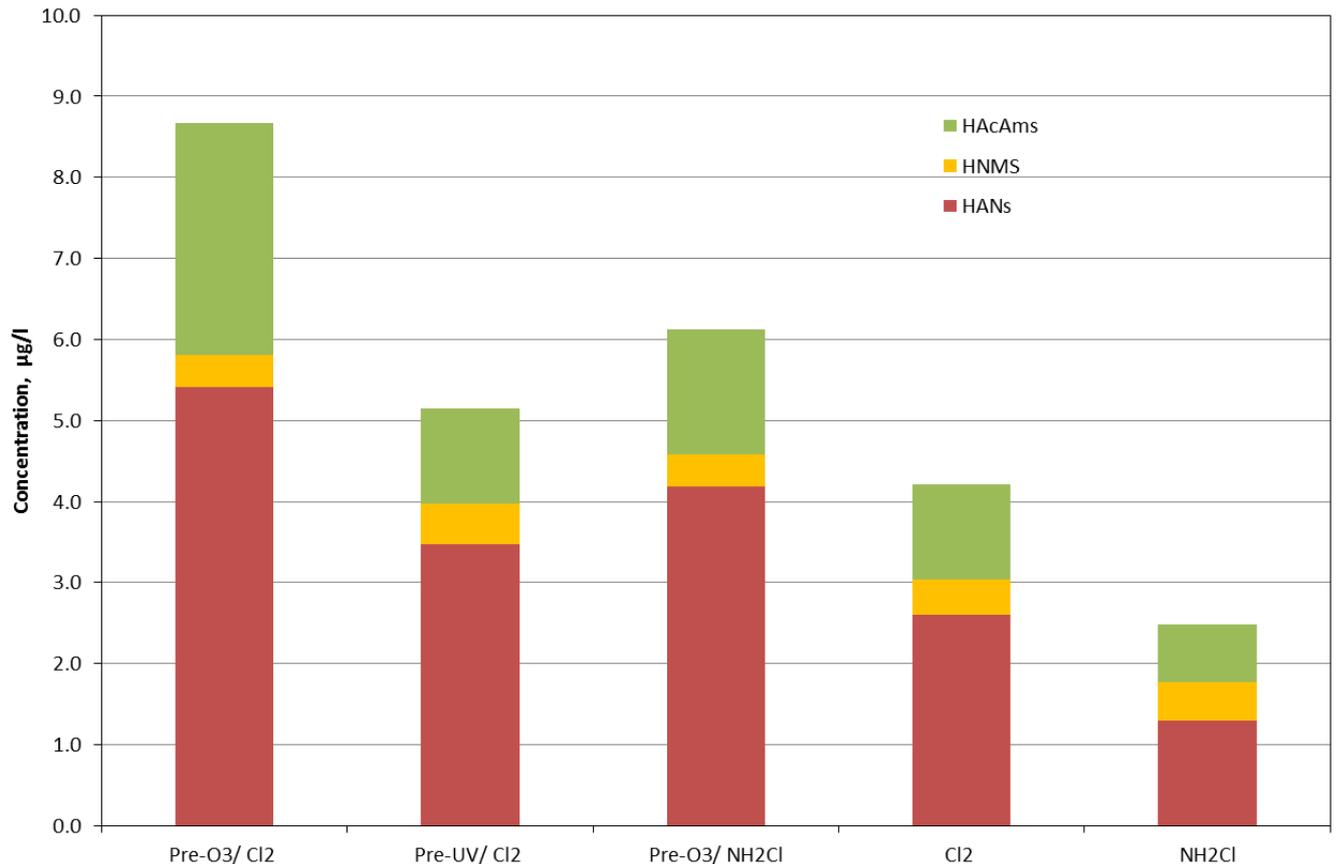
**Figure 4.5** The ranges of the sum of the concentrations for the halonitromethanes (HNMs) measured in this survey. LL = lowland, UL = upland, GW = groundwater, O3 = ozone, Cl2 = chlorine, UV = ultraviolet disinfection, NH2Cl = chloramination, R1 = sampling round 1, R2 = round 2, R3 = round 3, R4 = round 4. The numbers in brackets represent the number of disinfected sampling locations (i.e. treatment works final water and distribution network) for which the concentration of at least one HNM was detected above the detection limit and therefore for which the sampling data was included in the data set and plotted here. The percentages in brackets represent the percentage of the sampling locations of that source water and treatment type for which at least one HNM was detected above the detection limit out of the total potential number of such locations. The stars are the mean values, the lines within the boxes are the median values, the tops of the boxes are the 75<sup>th</sup> percentile values, the bottoms of the boxes are the 25<sup>th</sup> percentile values, and the whiskers extend to the maximum and minimum values. Samples for which no concentration was measured above the detection limit were excluded from the data sets.



**Figure 4.6 The ranges of concentrations of cyanogen chloride. LL = lowland, UL = upland, GW = groundwater, O3 = ozone, Cl2 = chlorine, UV = ultraviolet disinfection, NH2Cl = chloramination, R1 = sampling round 1, R2 = round 2, R3 = round 3, R4 = round 4. The numbers in brackets represent the number of disinfected sampling locations (i.e. treatment works final water and distribution network) for which the concentration of at least one HNM was above the detection limit and therefore for which the sampling data was included in the data set and plotted here. The percentages in brackets represent the percentage of the sampling locations of that source water and treatment type for which at least one HNM was detected above the detection limit out of the total potential number of such locations. The stars are the mean values, the lines within the boxes are the median values, the tops of the boxes are the 75<sup>th</sup> percentile values, the bottoms of the boxes are the 25<sup>th</sup> percentile values, and the whiskers extend to the maximum and minimum values. Samples for which no concentration was measured above the detection limit were excluded from the data sets.**

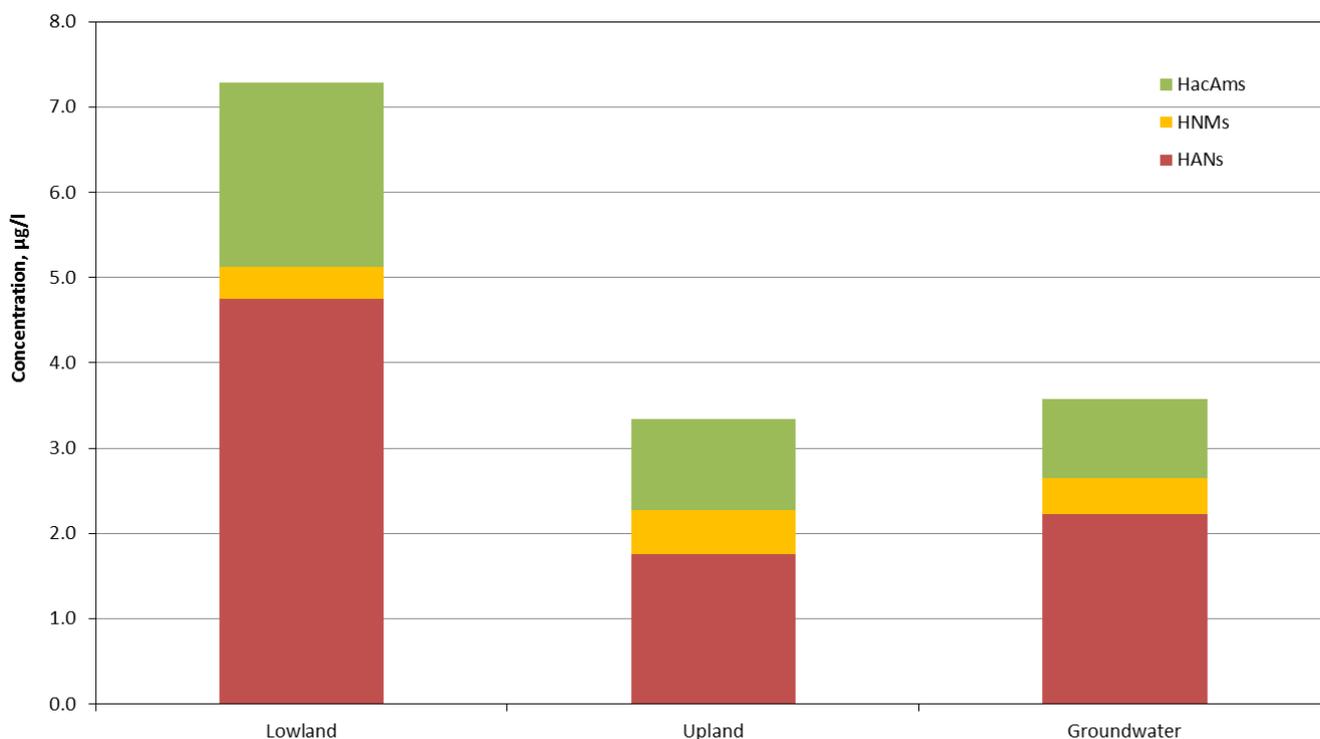
## 4.2 N-DBPs by treatment type and source water type

Figure 4.7 summarises the mean values of the HANs, HAcAms, and HNMs for the various treatment types, for all sampling rounds and source water types. Cyanogen chloride has been excluded from this plot because of its low frequency of detection compared to the other N-DBP groups and the large variability in the cyanogen chloride data; in general however, cyanogen chloride was measured at higher concentrations in the treatment works applying ozone (Figure 4.6), which agrees with previous findings (Krasner *et al.*, 2012).



**Figure 4.7 A comparison of the mean sum of the concentrations of the HANs, HAcAms, and HNMs measured in this survey for all rounds for different treatment types.**

Figure 4.8 summarises the mean values of these groups by source water type, with the lowland waters in this survey exhibiting higher total N-DBP concentrations, on average. As noted earlier, half of the lowland waters were eutrophic; algal organic matter (e.g. amino acids) is believed to be a significant precursor of several N-DBPs.



**Figure 4.8** A comparison of the mean sum of the concentrations of the HANs, HAcAms, and HNMs measured in this survey for all rounds for different source water types.

### 4.3 Links between N-DBPs and water quality parameters

A data analysis was conducted to consider whether any of these N-DBP groups could be related to total organic carbon (TOC) at the point of sampling, since TOC is a key precursor parameter for other DBPs, e.g. THMs. It can be seen in Figures 4.9-4.12 that of all the N-DBP groups, HANs had the best correlation with TOC, although with an  $R^2$  of only 0.36. Comparisons with UV absorbance at 254 nm, another common measure of organic content, produced even poorer correlations (Figures 4.13-4.16).

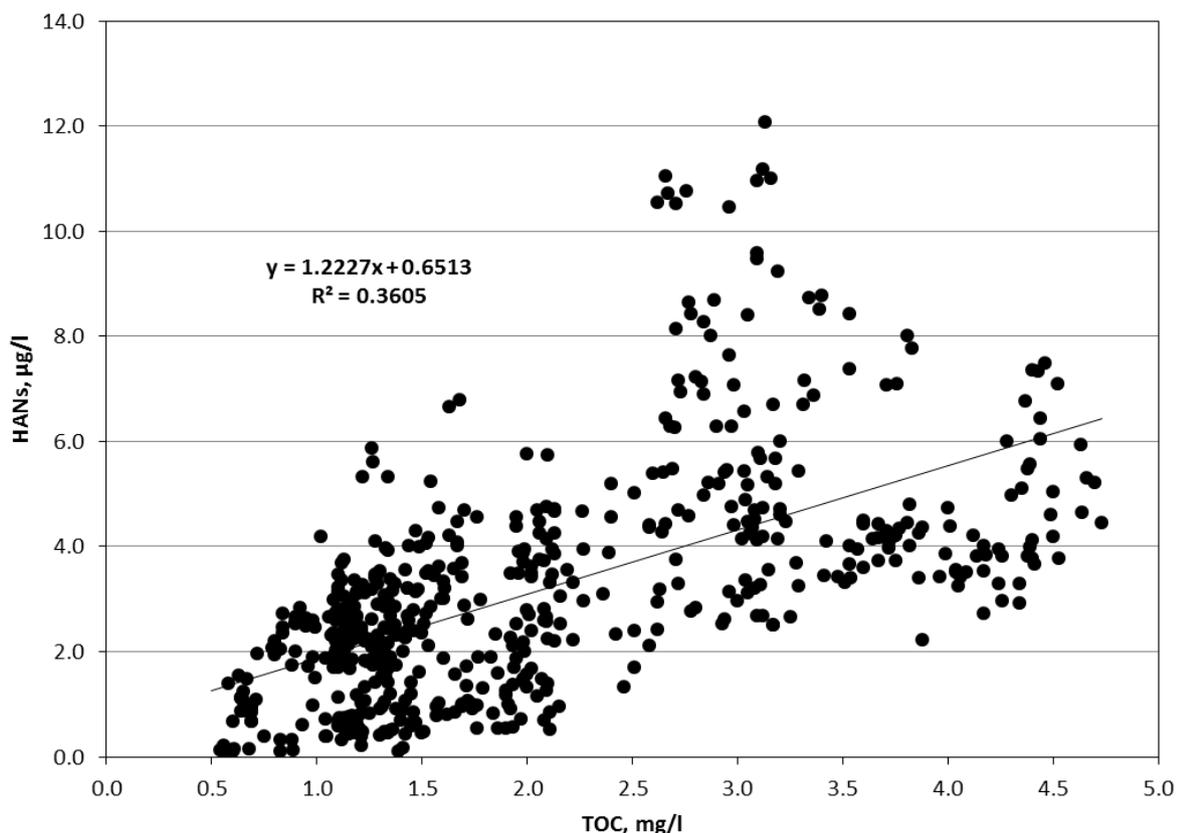
Similarly, the N-DBP group sum concentrations were compared against total THMs (Figures 4.17-4.20). Total THMs were found to be a poor predictor of the N-DBP concentrations (i.e. best  $R^2$  value of only 0.11).

Better correlations were observed between  $HAA_9$  and the HANs and HAcAms (Figures 4.21 and 4.22), with  $R^2$  values of 0.52 and 0.43, respectively. Previous research has highlighted reaction pathways between  $HAA_9$  and these N-DBP groups (e.g. Chu *et al.*, 2010), so a better relationship was expected than with THMs. No relationship between  $HAA_9$  and HNMs was discernible (Figure 4.23). It should be noted that unexpectedly high  $HAA_9$  values (i.e. above 100 µg/l) were detected in approximately a quarter of the samples that were analysed for  $HAA_9$  in round 4, which was because of an inexplicably high peak for chlorodibromoacetic acid

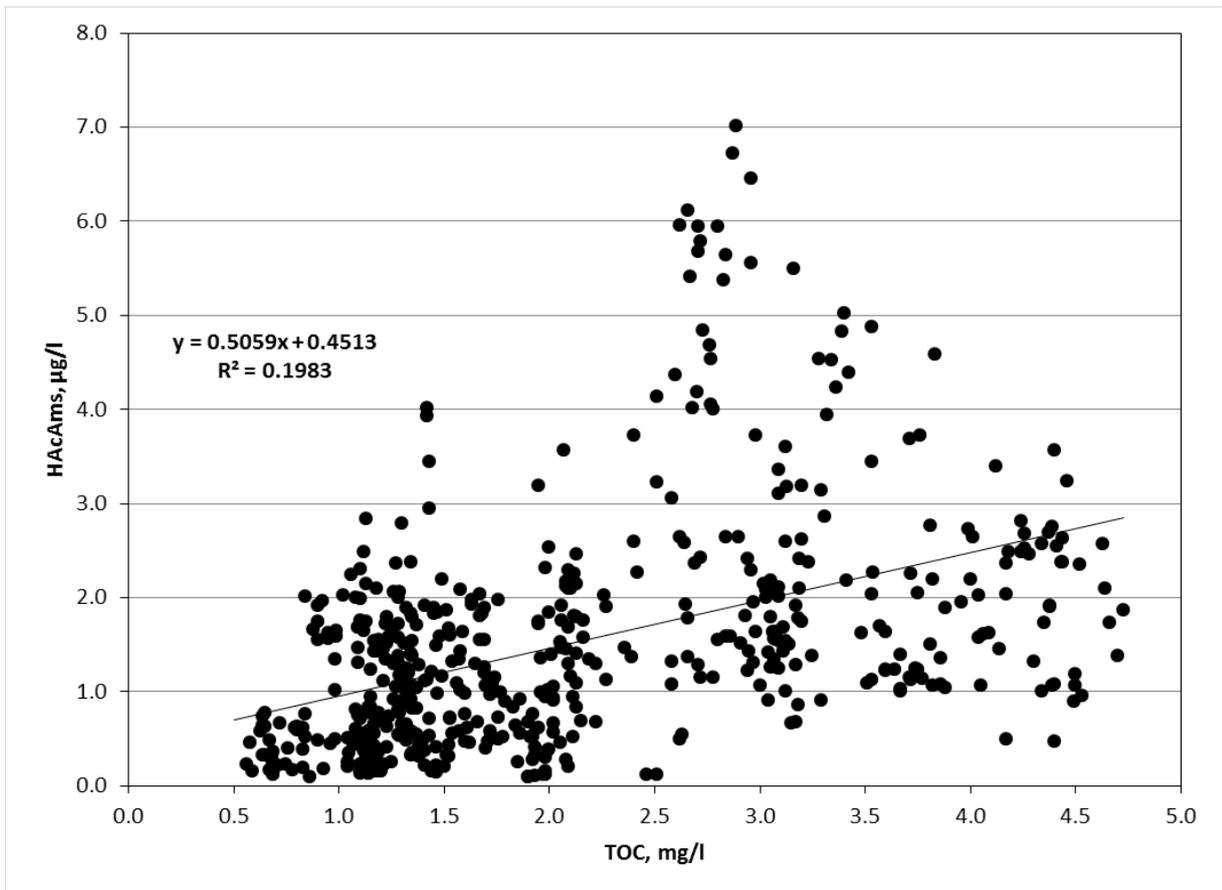
in those samples. The HAA<sub>9</sub> data for those samples are still reported here but should be considered questionable; for comparison, a previous survey of 20 UK water supply systems reported a maximum HAA<sub>9</sub> in distribution of 74.8 µg/l and a median in distribution of only 20.8 µg/l (Parsons and Goslan, 2011).

Figures 4.24-4.27 plot the N-DBP concentrations versus the pH of the samples. The maximum HAN, HAcAm, and cyanogen chloride concentrations were measured in samples with slightly basic pH in the range 7.5-8, while no discernible link was observed between pH and HNMs. This disagrees with previous research into the effect of pH on N-DBPs (Table 4.2), although this simple, straight comparison of pH versus N-DBP concentration neglects the confounding simultaneous effects of other potentially relevant water quality parameters and of different treatment types.

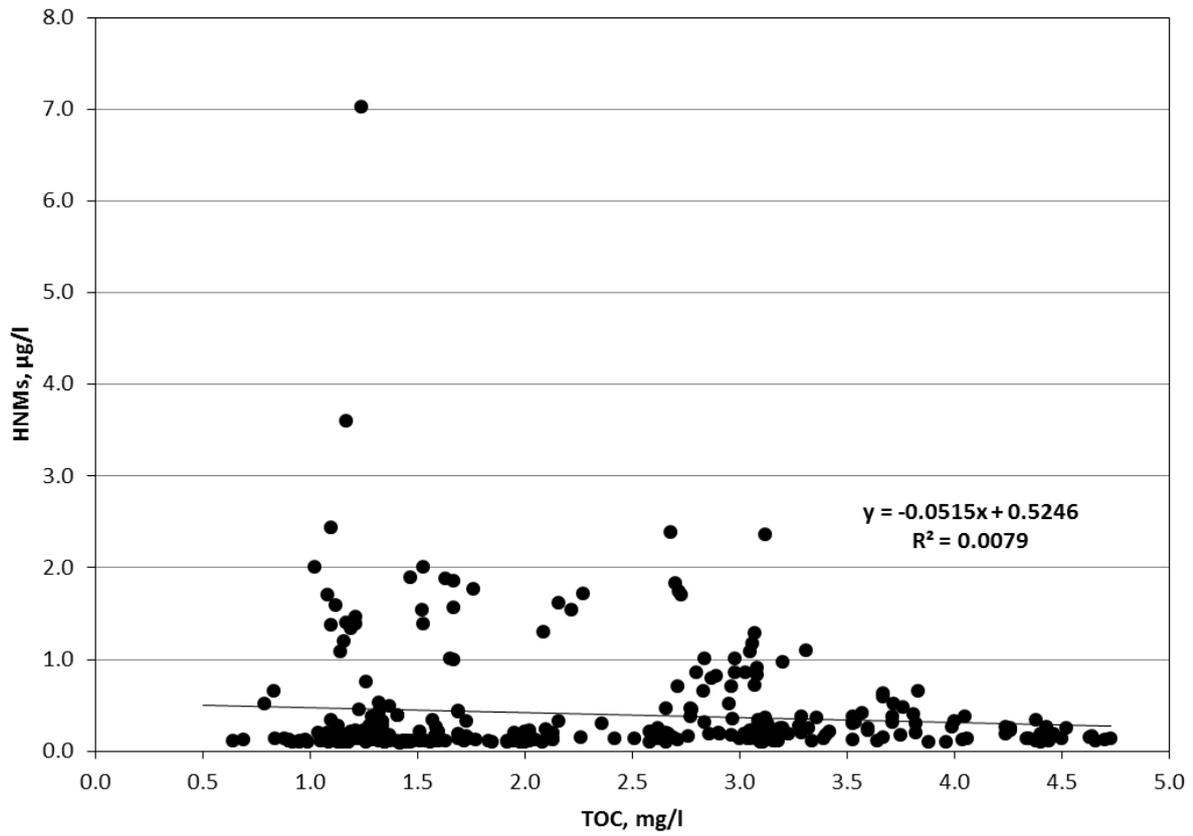
In the absence of total organic nitrogen data, total oxidised nitrogen as NO<sub>3</sub> was plotted versus the N-DBP concentrations (Figure 4.28-4.31). There was no discernible range of total oxidised nitrogen that appeared to be linked to N-DBP formation, confirming that inorganic forms of nitrogen are not useful predictors of N-DBP formation potential.



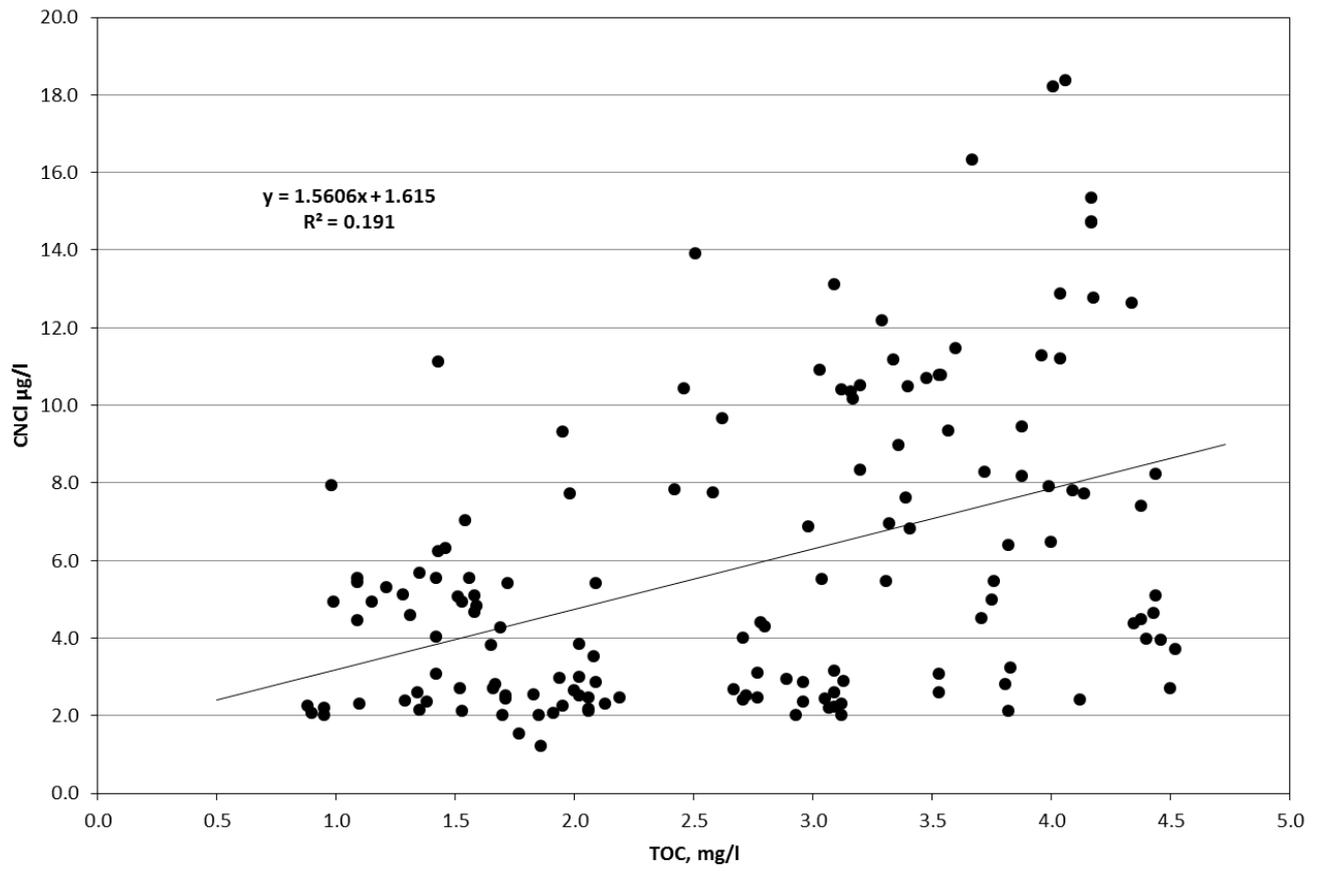
**Figure 4.9** A comparison of the sum of the concentrations of the haloacetonitriles (HAN<sub>5</sub>) measured in this survey versus total organic carbon (TOC) in the same sample.

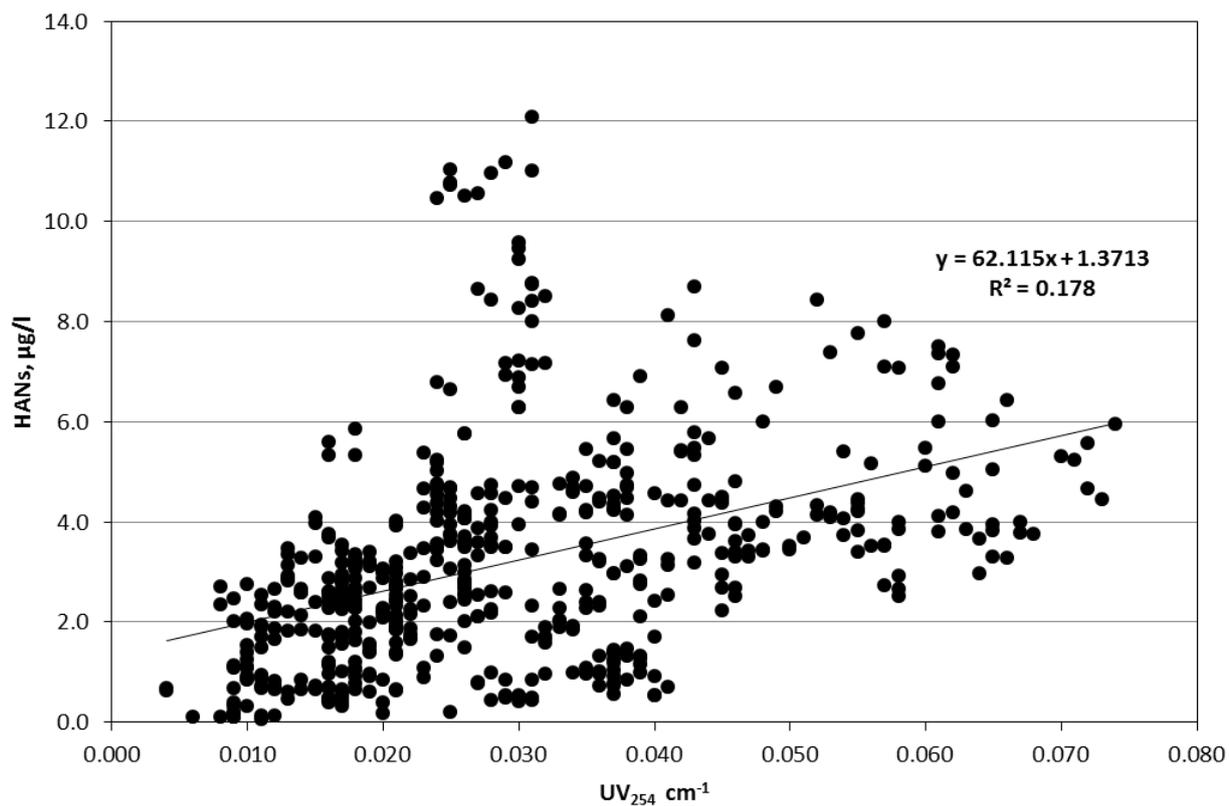


**Figure 4.10** A comparison of the sum of the concentrations of the haloacetamides (HAcAms) measured in this survey versus total organic carbon (TOC) in the same sample.

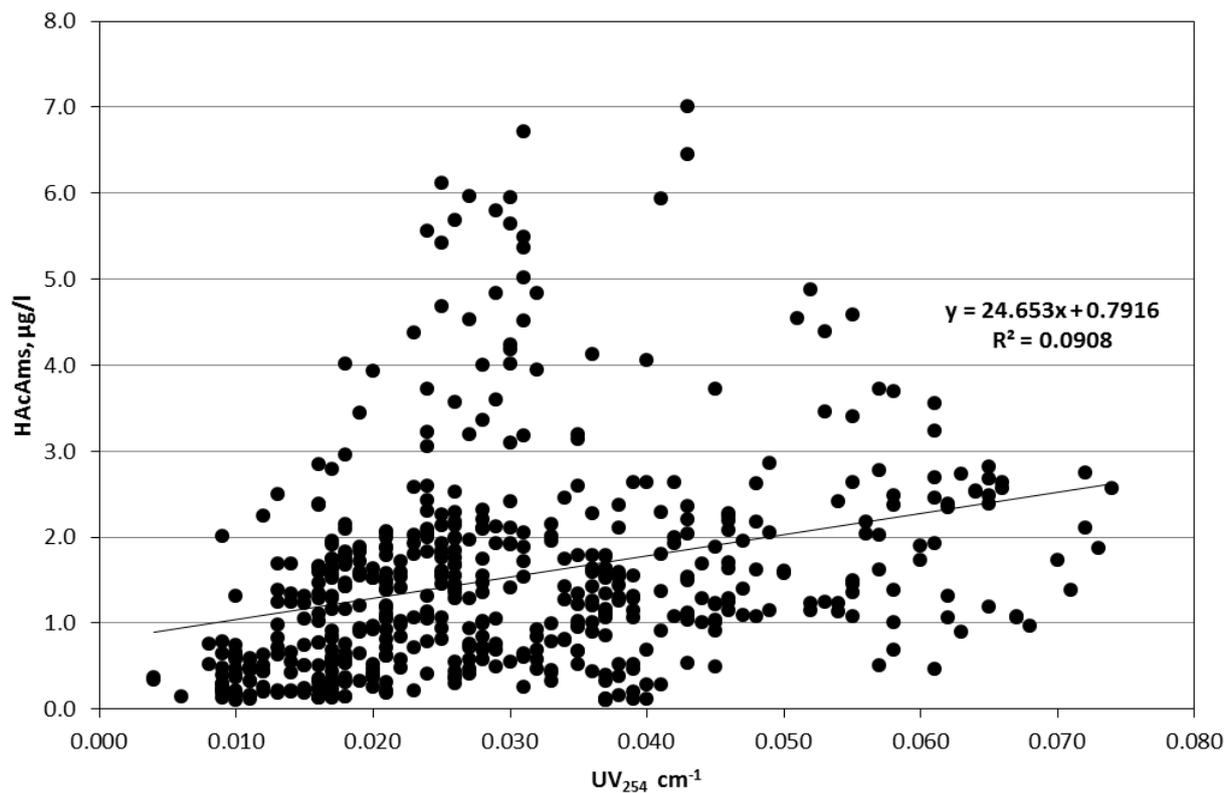


**Figure 4.11** A comparison of the sum of the concentrations of the halonitromethanes (HNMs) measured in this survey versus total organic carbon (TOC) in the same sample.

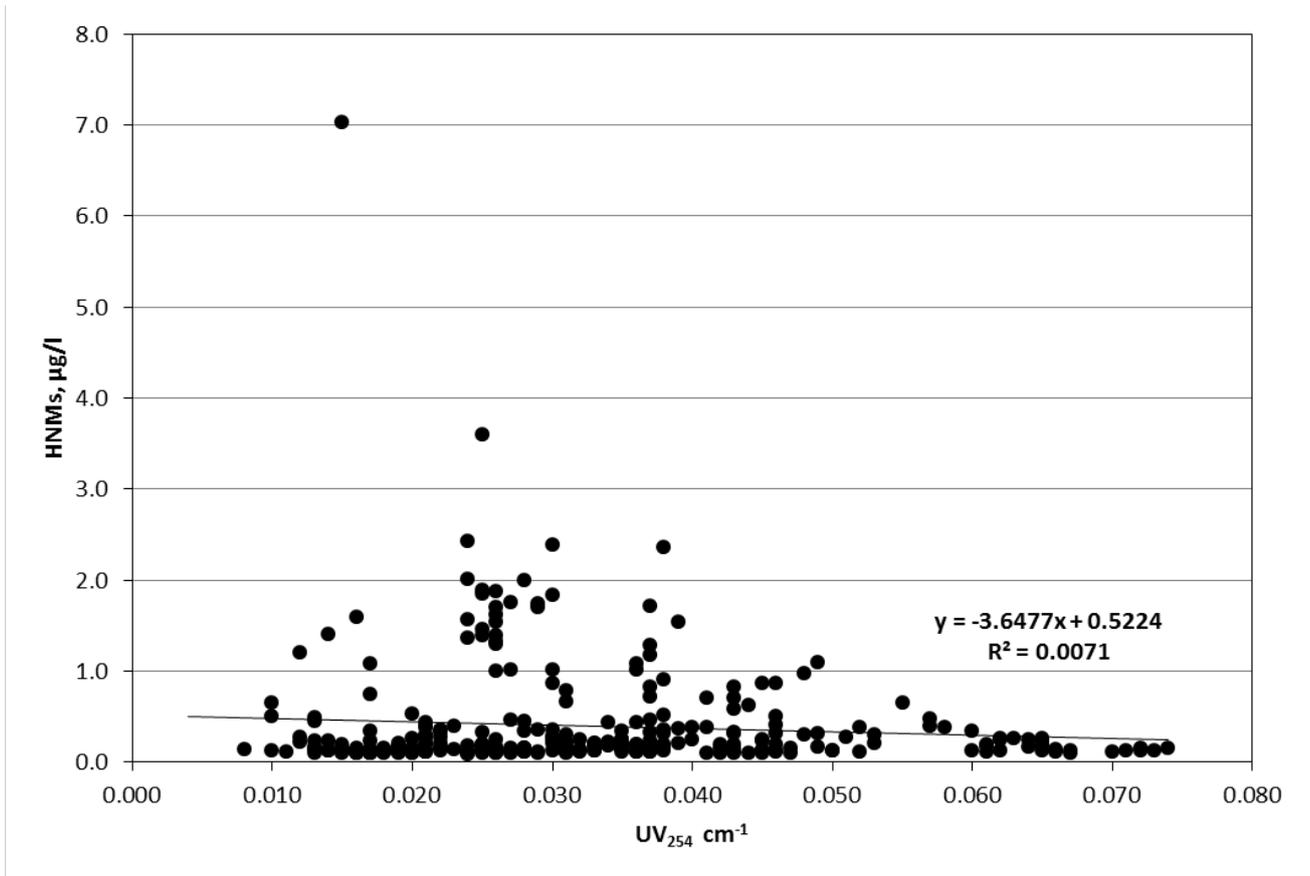




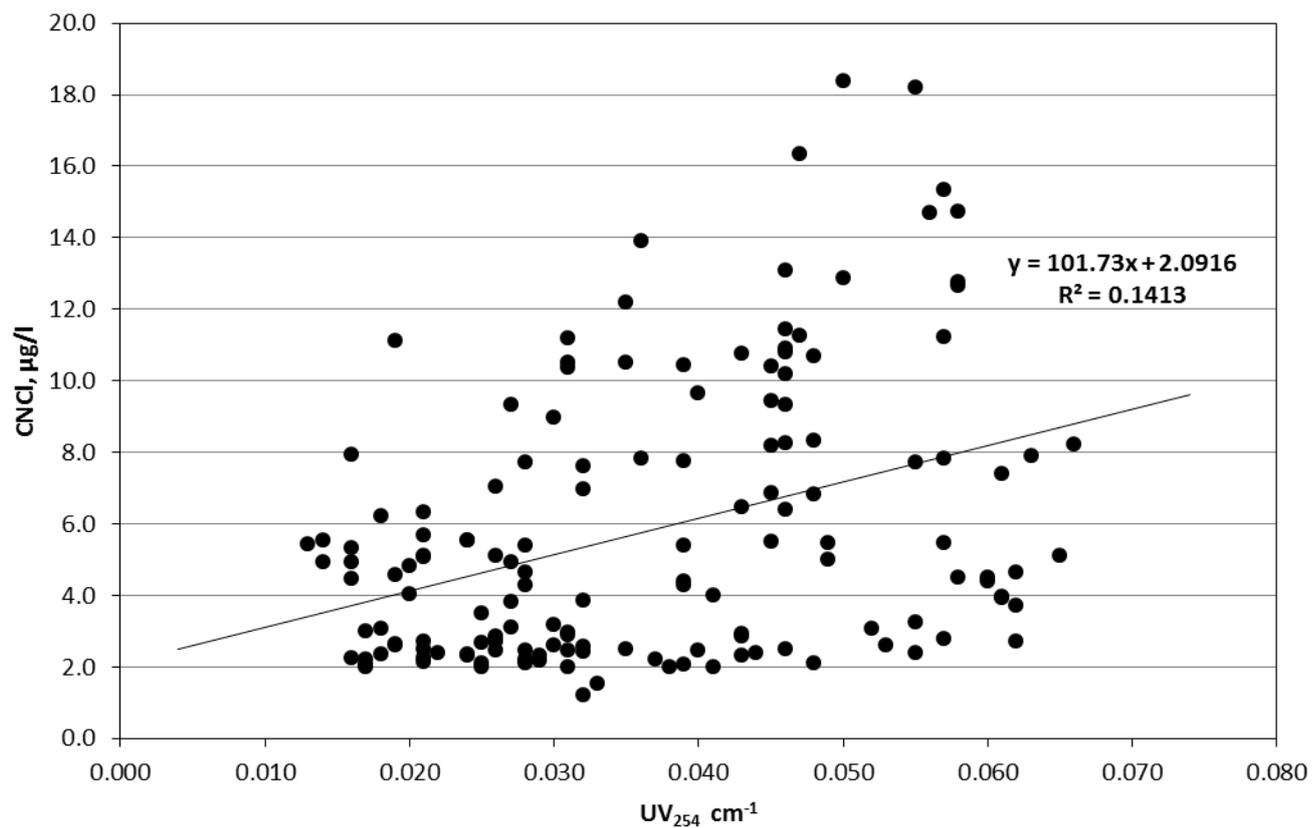
**Figure 4.13** A comparison of the sum of the concentrations of the haloacetonitriles (HANs) measured in this survey versus UV absorbance at 254 nm in the same sample.



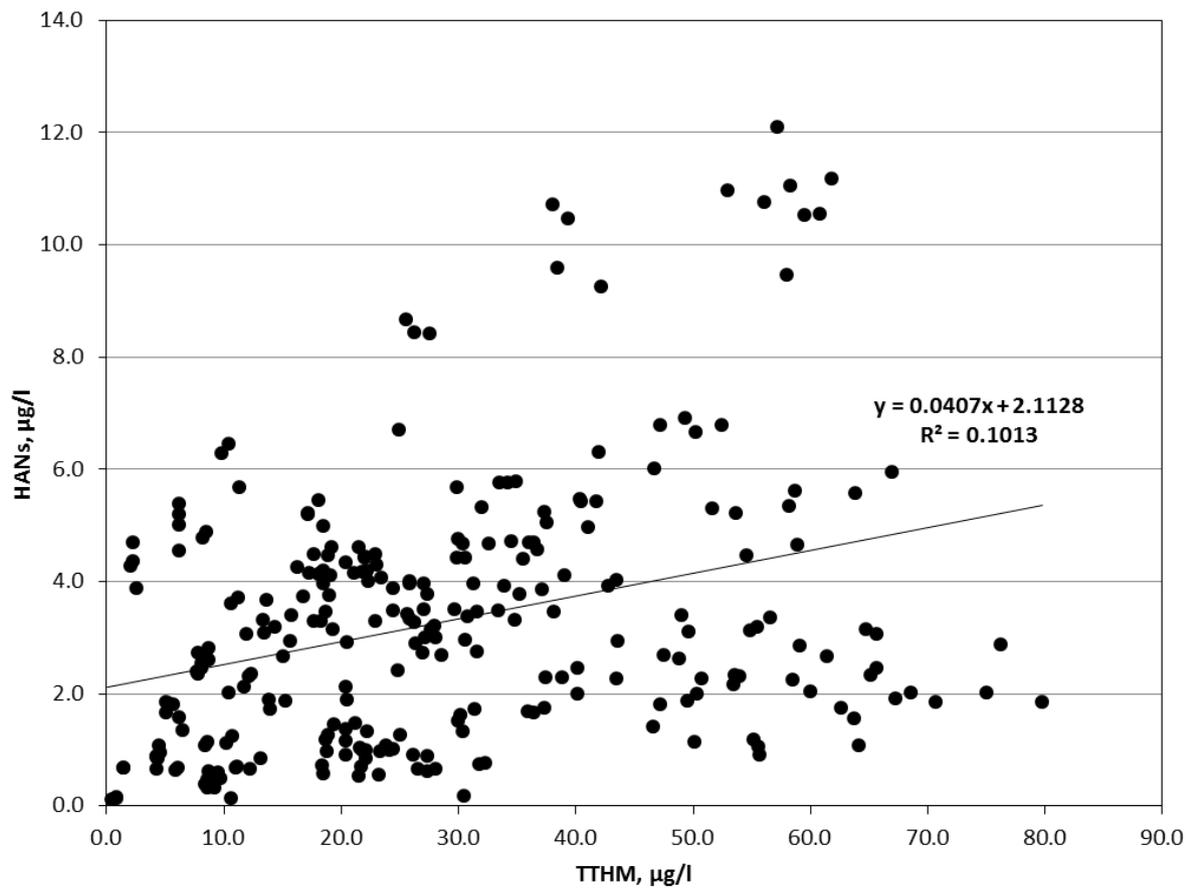
**Figure 4.14** A comparison of the sum of the concentrations of the haloacetamides (HAcAms) measured in this survey versus UV absorbance at 254 nm in the same sample.



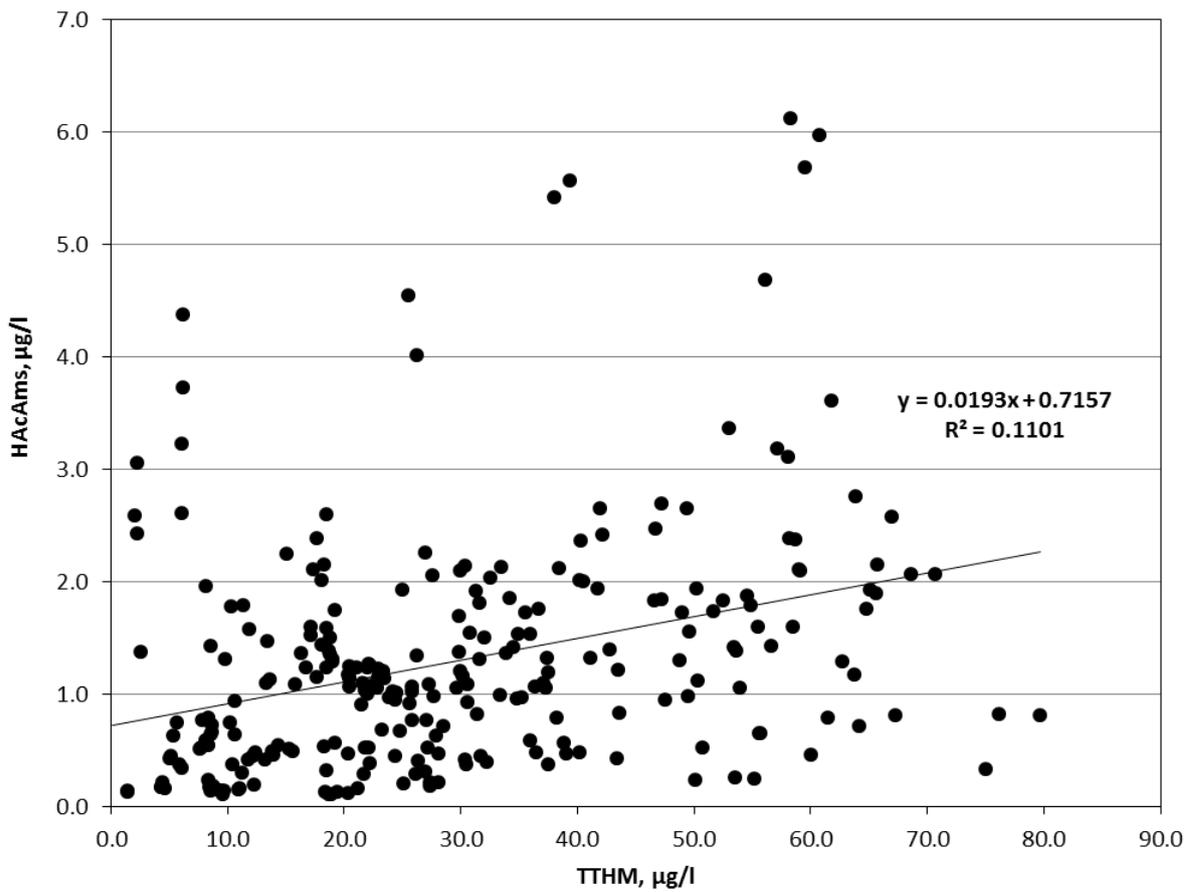
**Figure 4.15** A comparison of the sum of the concentrations of the halonitromethanes (HNMs) measured in this survey versus UV absorbance at 254 nm in the same sample.



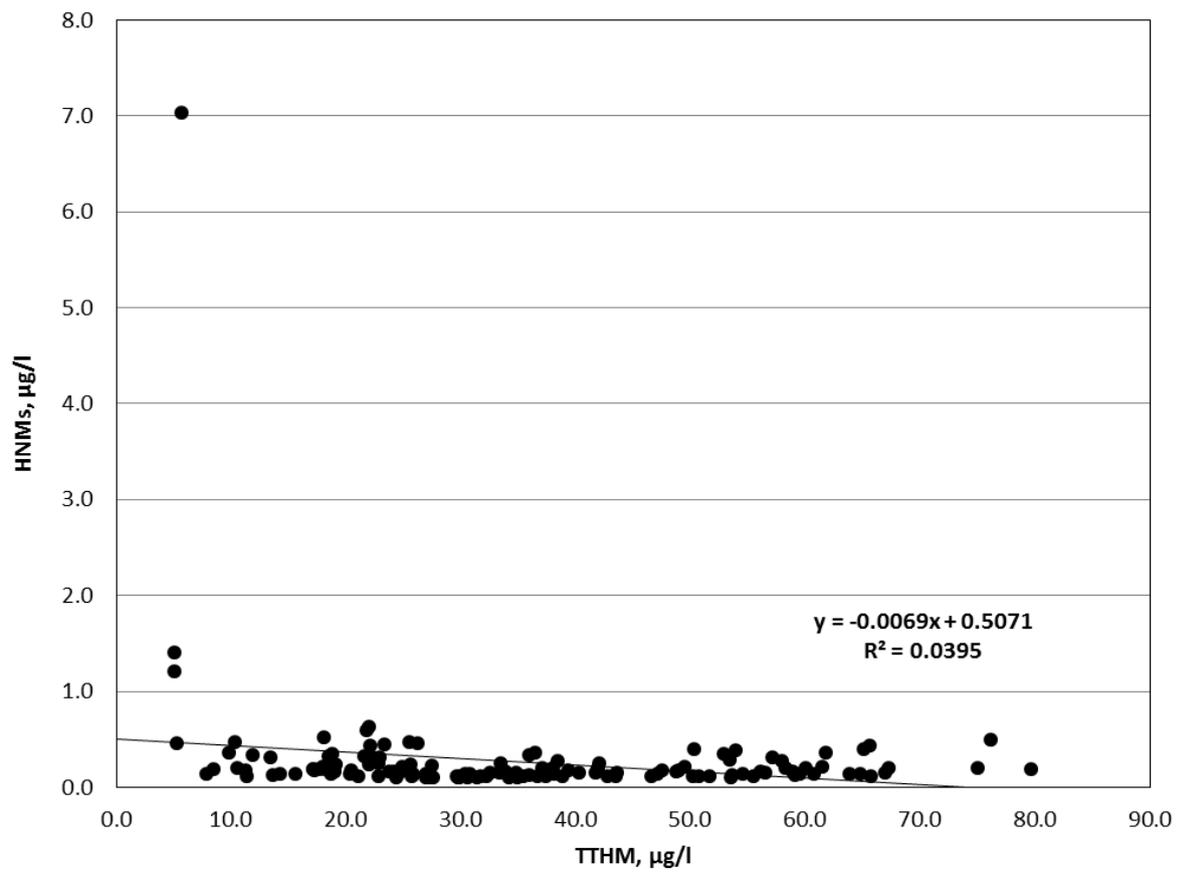
**Figure 4.16** A comparison of cyanogen chloride versus UV absorbance at 254 nm in the same sample.



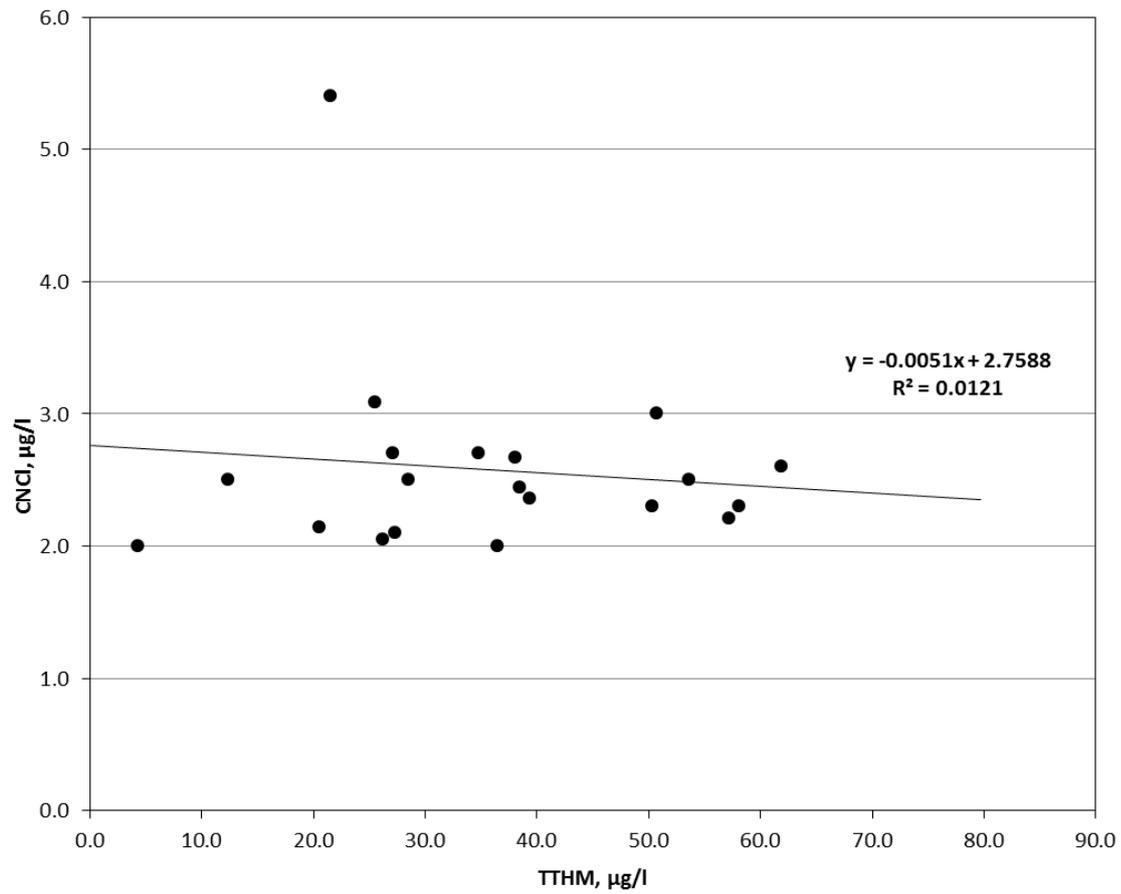
**Figure 4.17** A comparison of the sum of the concentrations of the haloacetonitriles (HANs) measured in this survey and total trihalomethanes (TTHMs) using data from sampling rounds 1 and 4 only. (THMs were only measured in those rounds.)



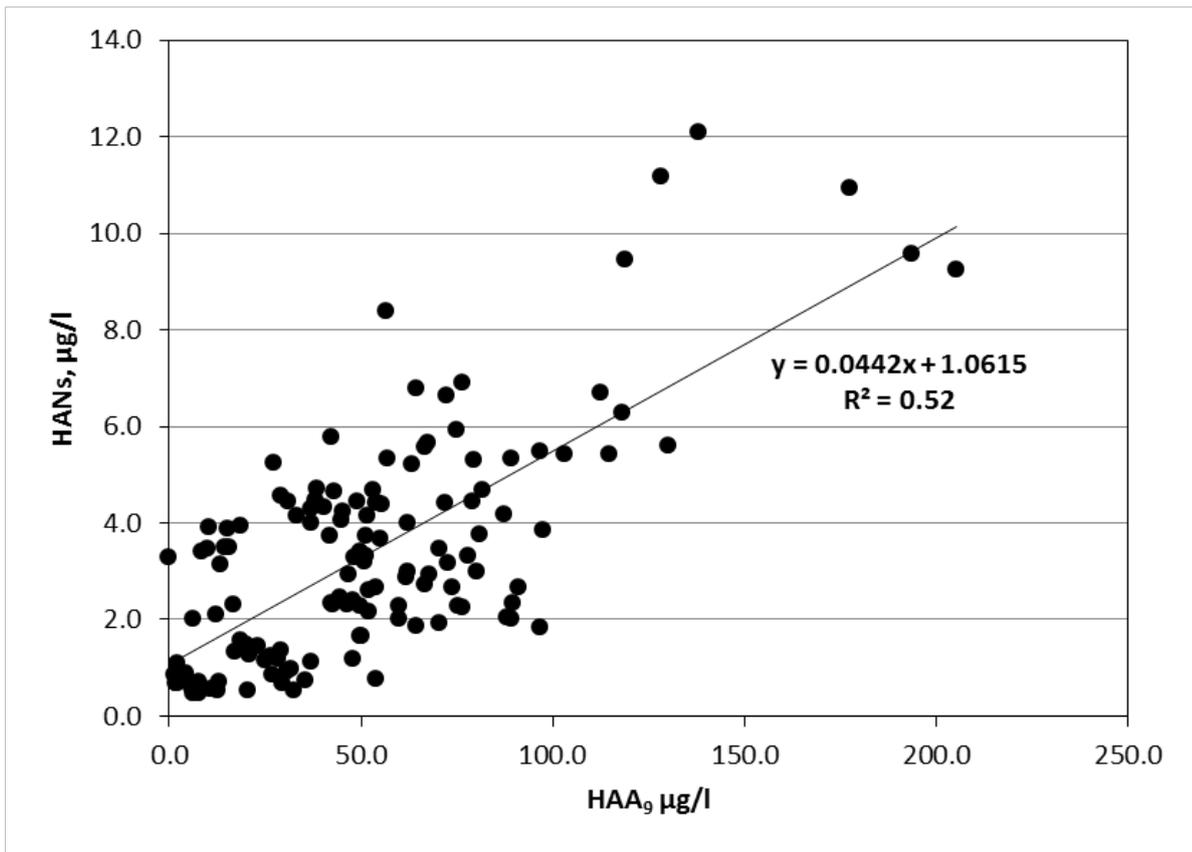
**Figure 4.18** A comparison of the sum of the concentrations of the haloacetamides (HAcAms) measured in this survey and total trihalomethanes (TTHMs) using data from sampling rounds 1 and 4 only. (THMs were only measured in those rounds.)



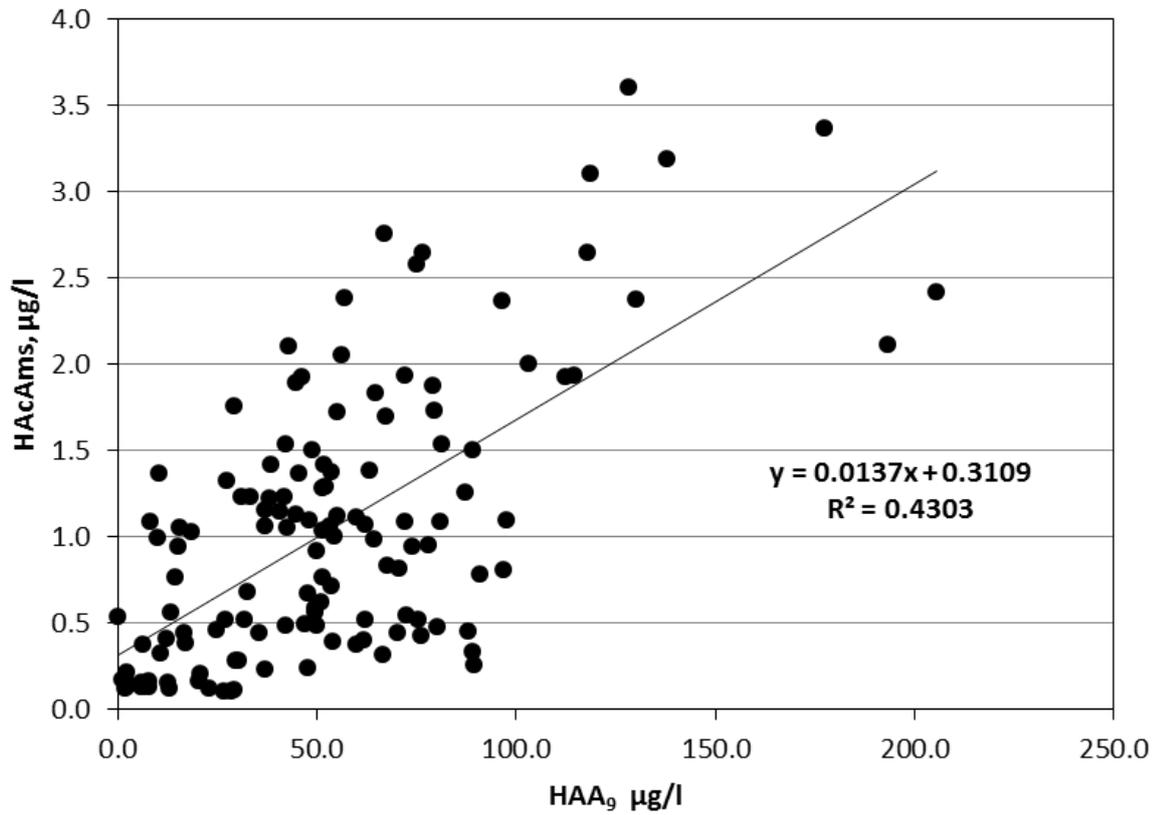
**Figure 4.19** A comparison of the sum of the concentrations of the halonitromethanes (HNMs) measured in this survey and total trihalomethanes (TTHM) using data from sampling rounds 1 and 4 only. (THMs were only measured in those rounds.)



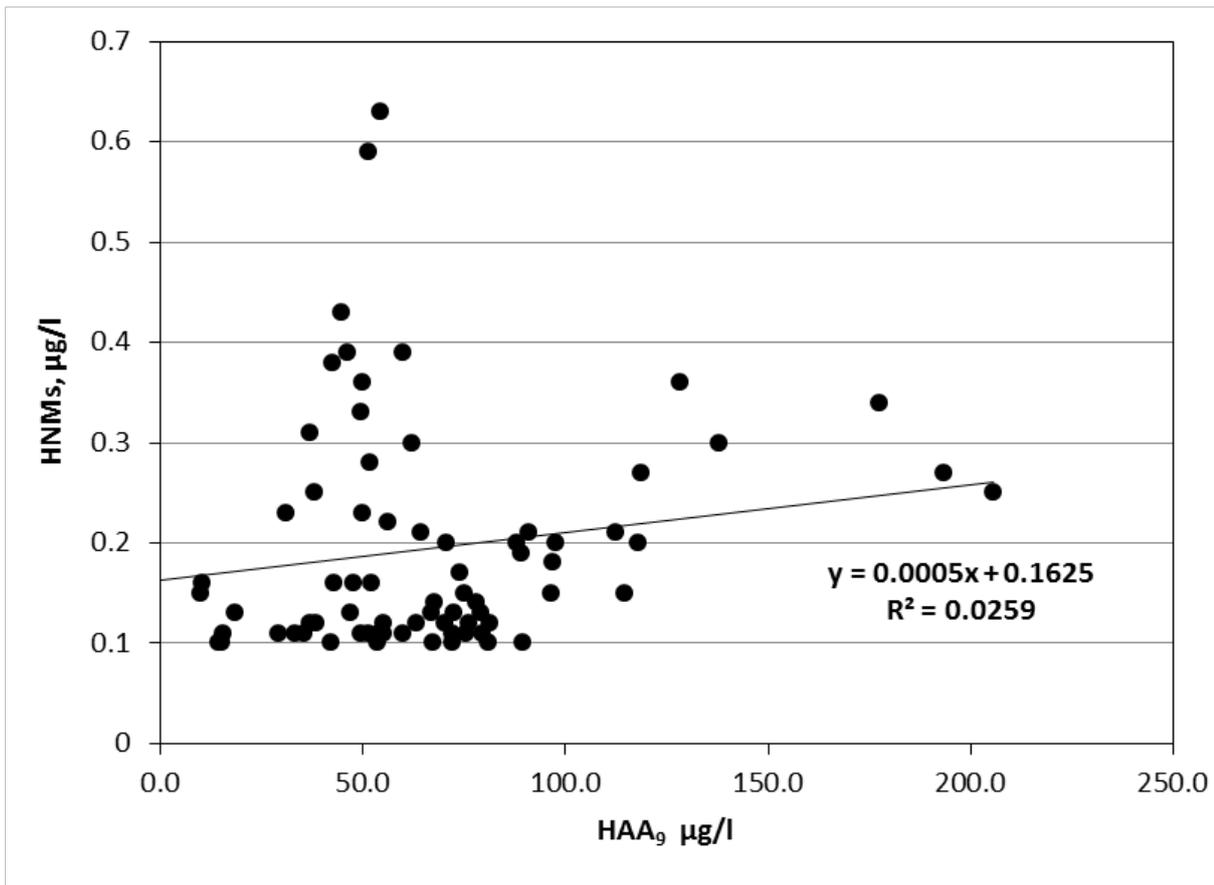
**Figure 4.20** A comparison of cyanogen chloride and total trihalomethanes (TTHM) using data from sampling rounds 1 and 4 only. (THMs were only measured in those rounds.)



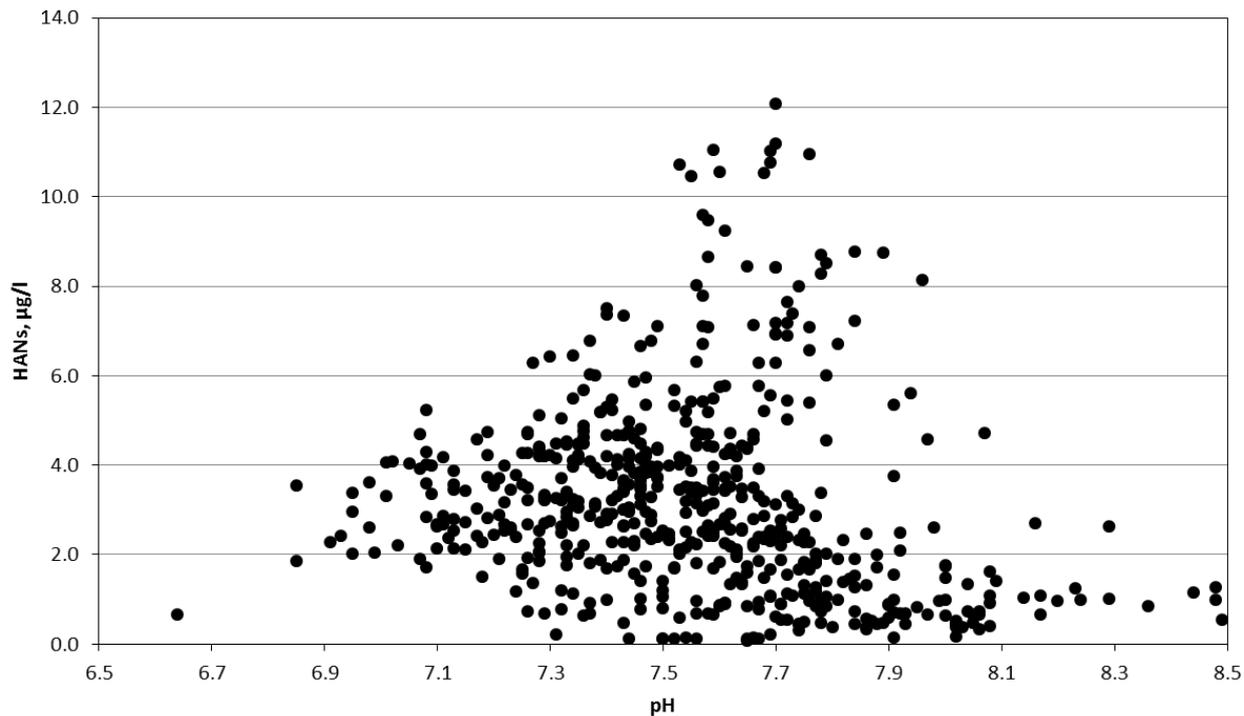
**Figure 4.21** A comparison of the sum of the concentrations of the haloacetonitriles (HANs) measured in this survey and the sum of the nine quantified haloacetic acids (HAA<sub>9</sub>) using data from sampling round 4 only. (HAAs were only measured in round 4.)



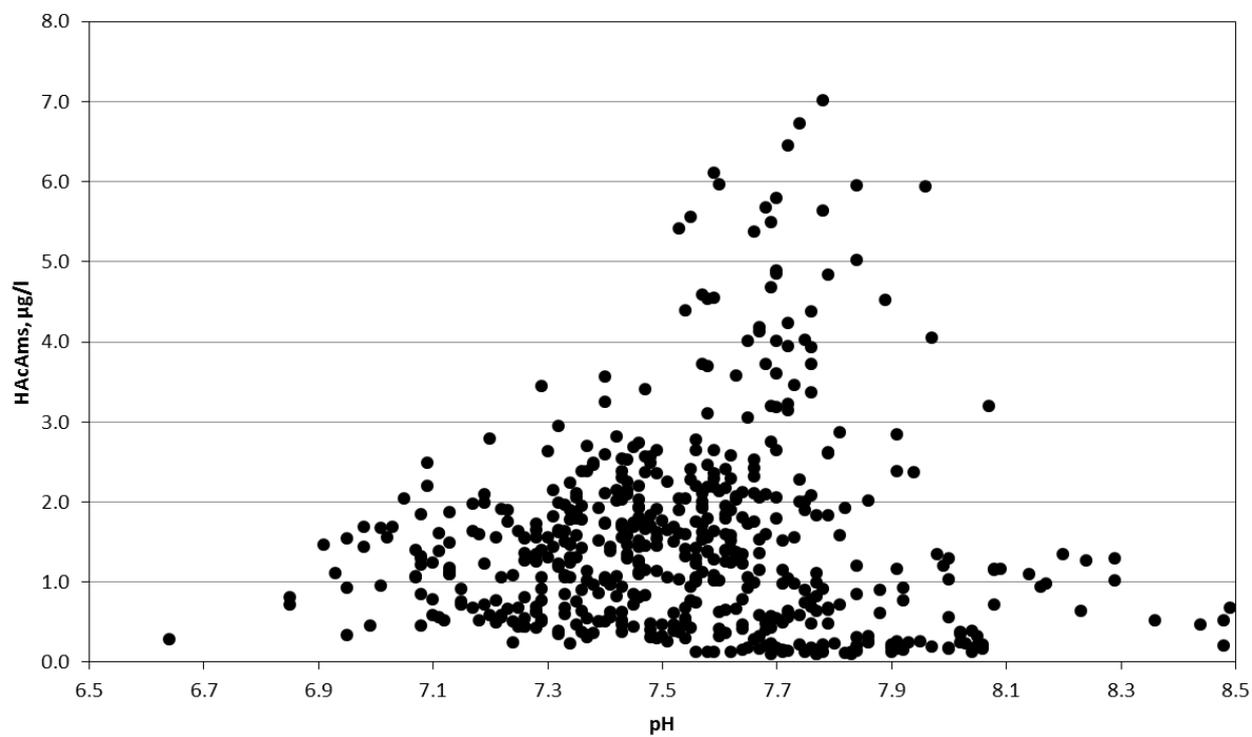
**Figure 4.22** A comparison of sum of the concentrations of the haloacetamides (HAcAms) measured in this survey and the sum of the nine quantified haloacetic acids (HAA<sub>9</sub>) using data from sampling round 4 only. (HAAs were only measured in round 4.)



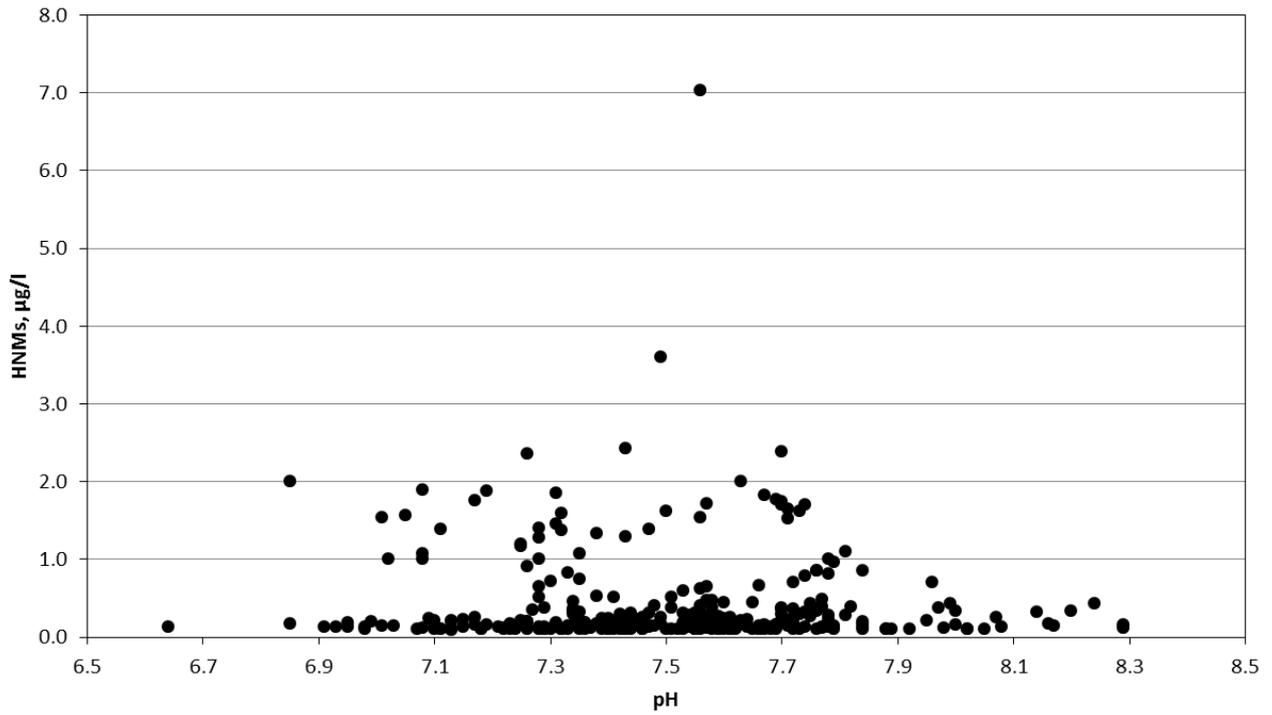
**Figure 4.23** A comparison of the sum of the concentrations of the halonitromethanes (HNMs) measured in this survey and the sum of the nine quantified haloacetic acids (HAA<sub>9</sub>) using data from sampling round 4 only. (HAAs were only measured in round 4.)



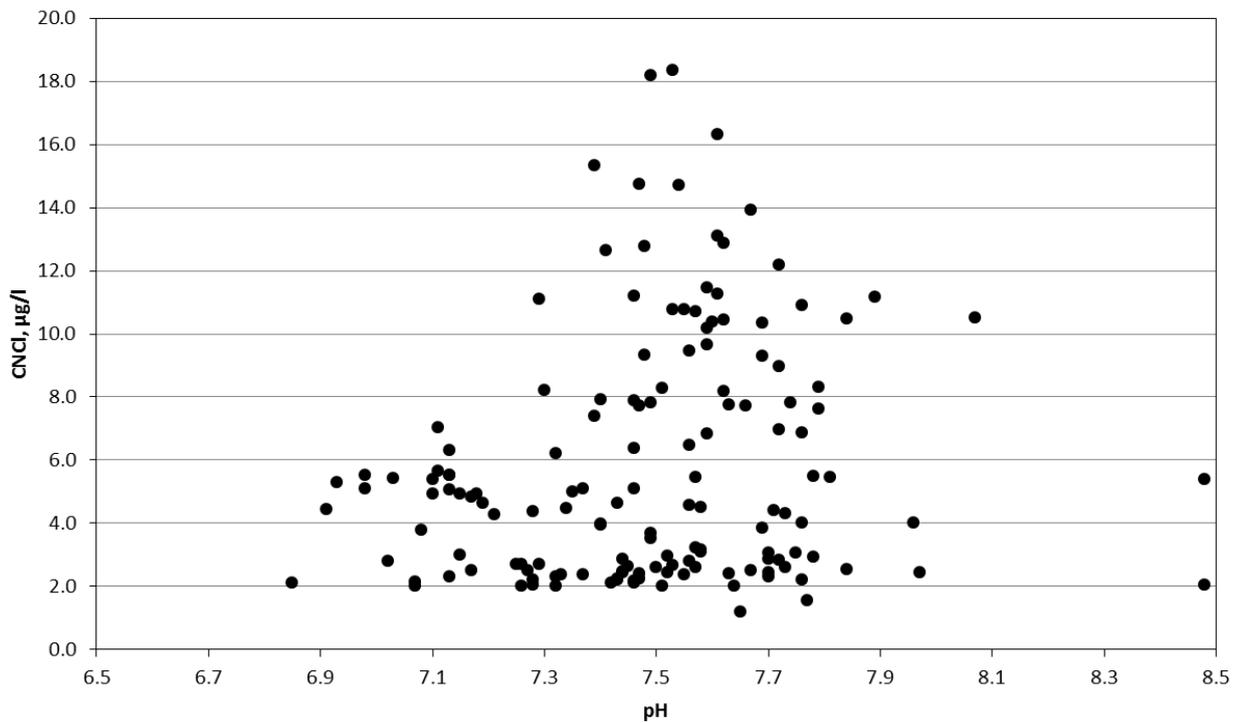
**Figure 4.24** A comparison of the sum of the concentrations of the haloacetonitriles (HANs) measured in this survey versus pH in the same sample.



**Figure 4.25** A comparison of the sum of the concentrations of the haloacetamides (HAcAms) measured in this survey versus pH in the same sample.



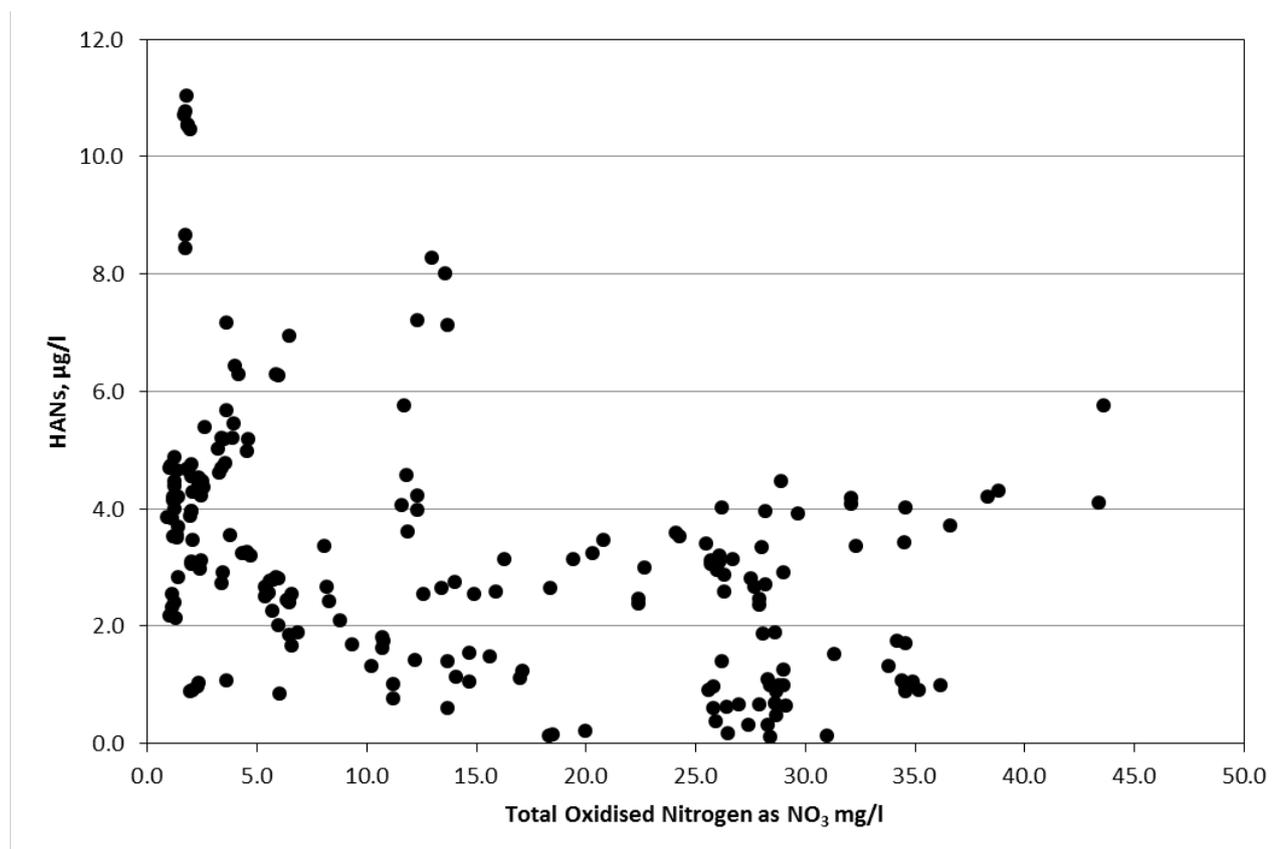
**Figure 4.26** A comparison of the sum of the concentrations of the halonitromethanes (HNMs) measured in this survey versus pH in the same sample.



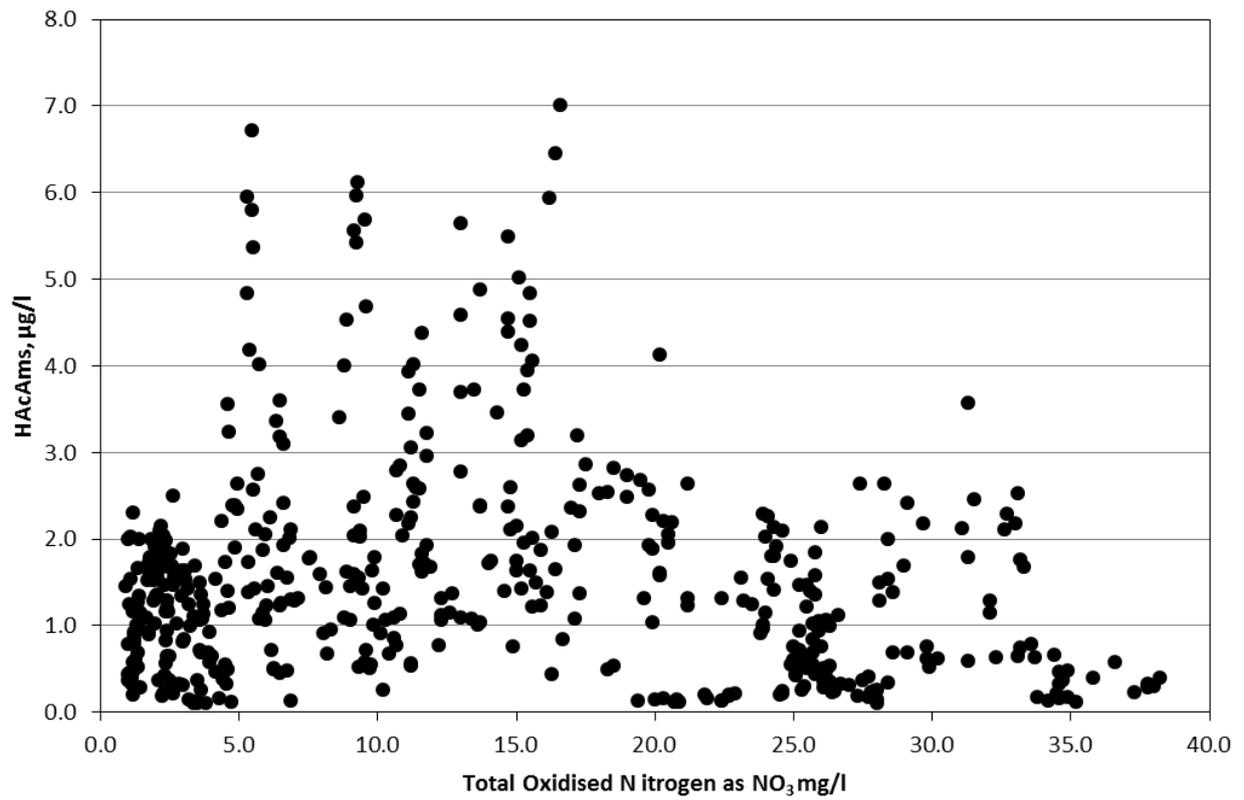
**Figure 4.27** A comparison of cyanogen chloride versus pH in the same sample.

**Table 4.2 Effect of pH on N-DBPs reported from previous research.**

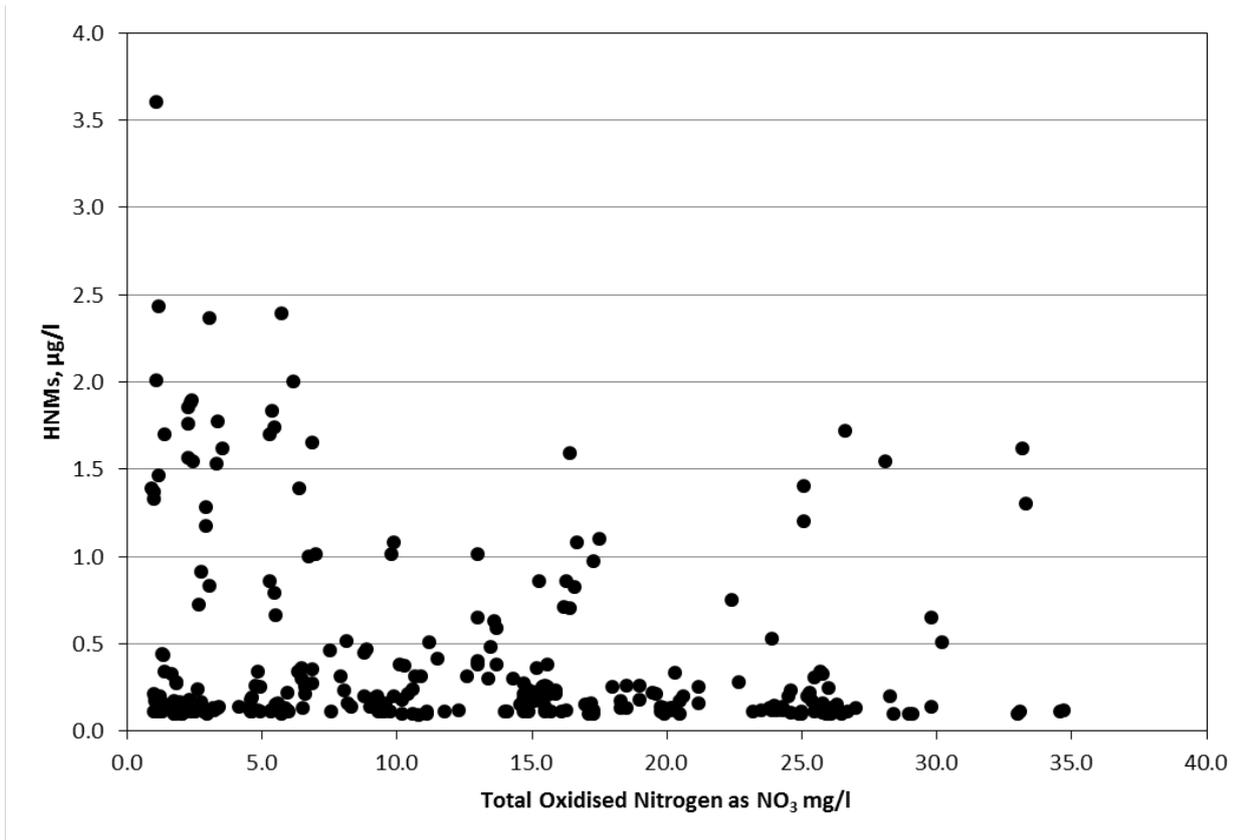
Group	pH effect	References
Haloacetonitriles	More stable at acidic pH, hydrolysed at alkaline pH	(Oliver, 1983; Stevens <i>et al.</i> , 1989; Glezer <i>et al.</i> , 1999)
Haloacetamides	Less stable at alkaline pH, probably more stable but lower concentrations at acidic pH	(Reckhow <i>et al.</i> , 2001; Krasner <i>et al.</i> , 2006; Chu <i>et al.</i> , 2010)
Halonitromethanes	TCNM formation increases with pH	(Merlet <i>et al.</i> , 1985; Joo and Mitch, 2007)
Cyanogen halides	Higher formation at acidic and neutral pH, unstable in presence of free chlorine	(Joo and Mitch, 2007; Mitch <i>et al.</i> , 2009)



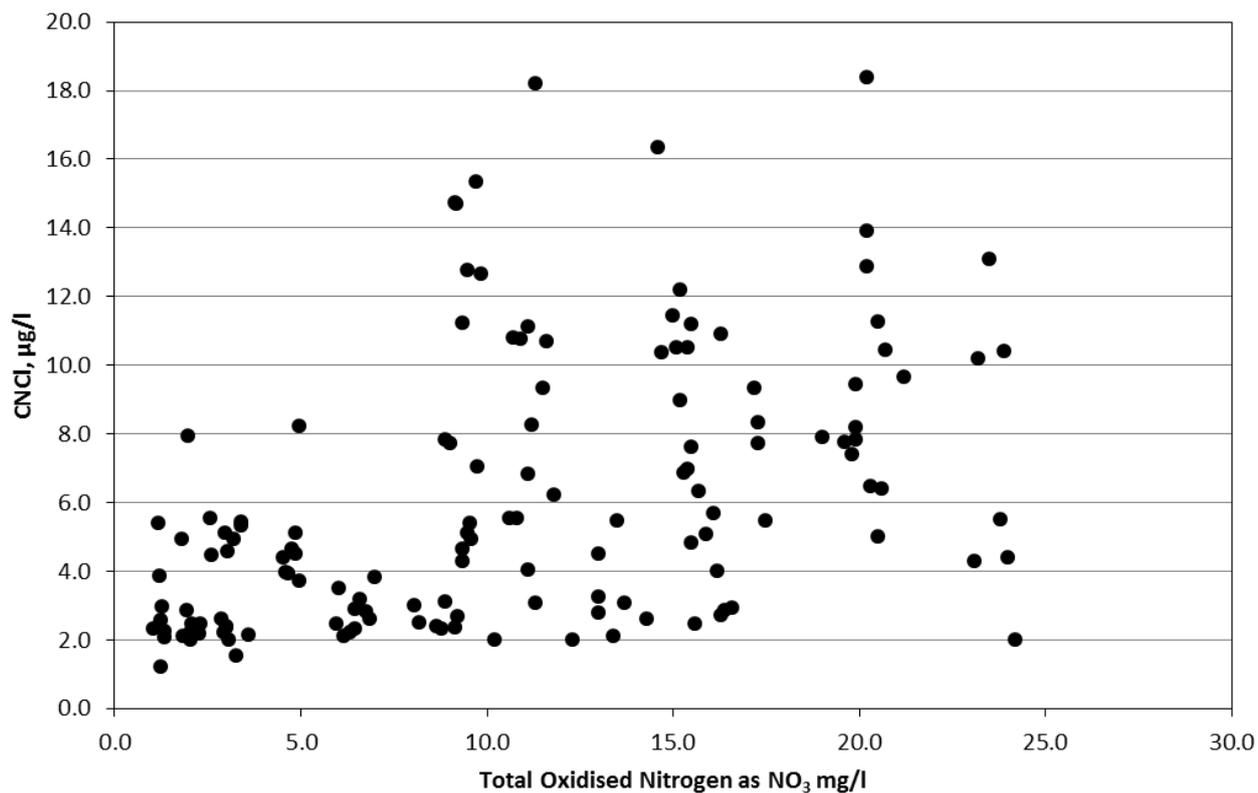
**Figure 4.28 A comparison of the sum of the concentrations of the haloacetonitriles (HANs) measured in this survey versus total oxidised nitrogen as NO<sub>3</sub> in the same sample.**



**Figure 4.29** A comparison of sum of the concentrations of the haloacetamides (HAcAms) measured in this survey versus total oxidised nitrogen as NO<sub>3</sub> in the same sample.

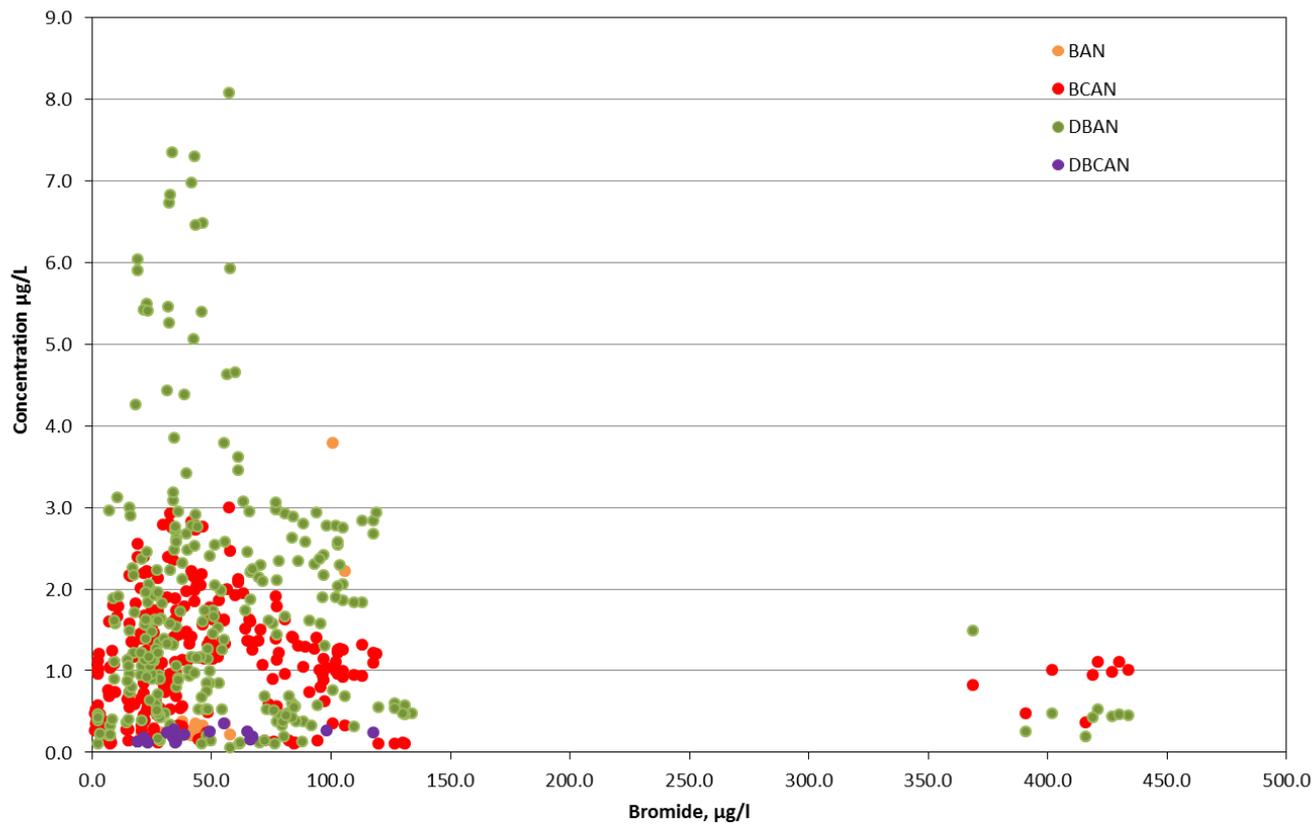


**Figure 4.30** A comparison of the sum of the concentrations of the halonitromethanes (HNMs) measured in this survey versus total oxidised nitrogen as NO<sub>3</sub> in the same sample.

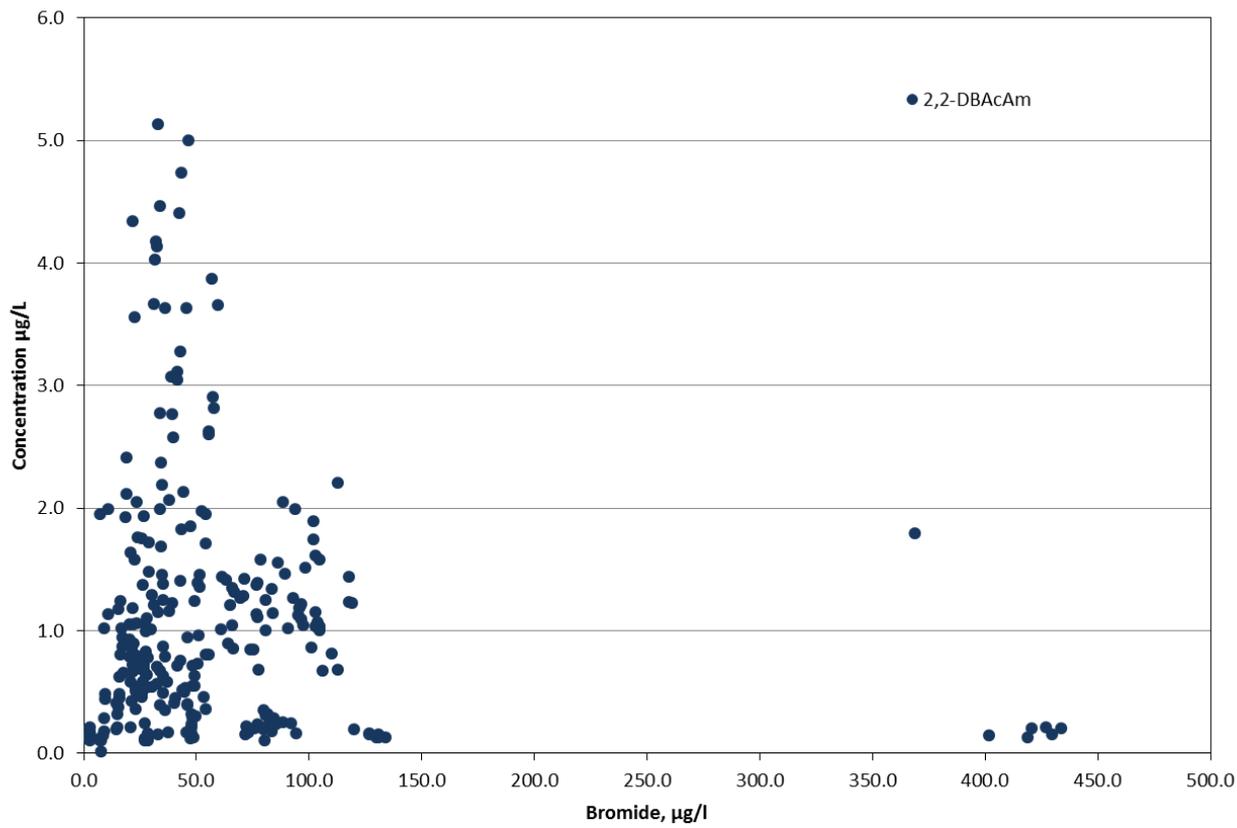


**Figure 4.31** A comparison of cyanogen chloride versus total oxidised nitrogen as  $\text{NO}_3$  in the same sample.

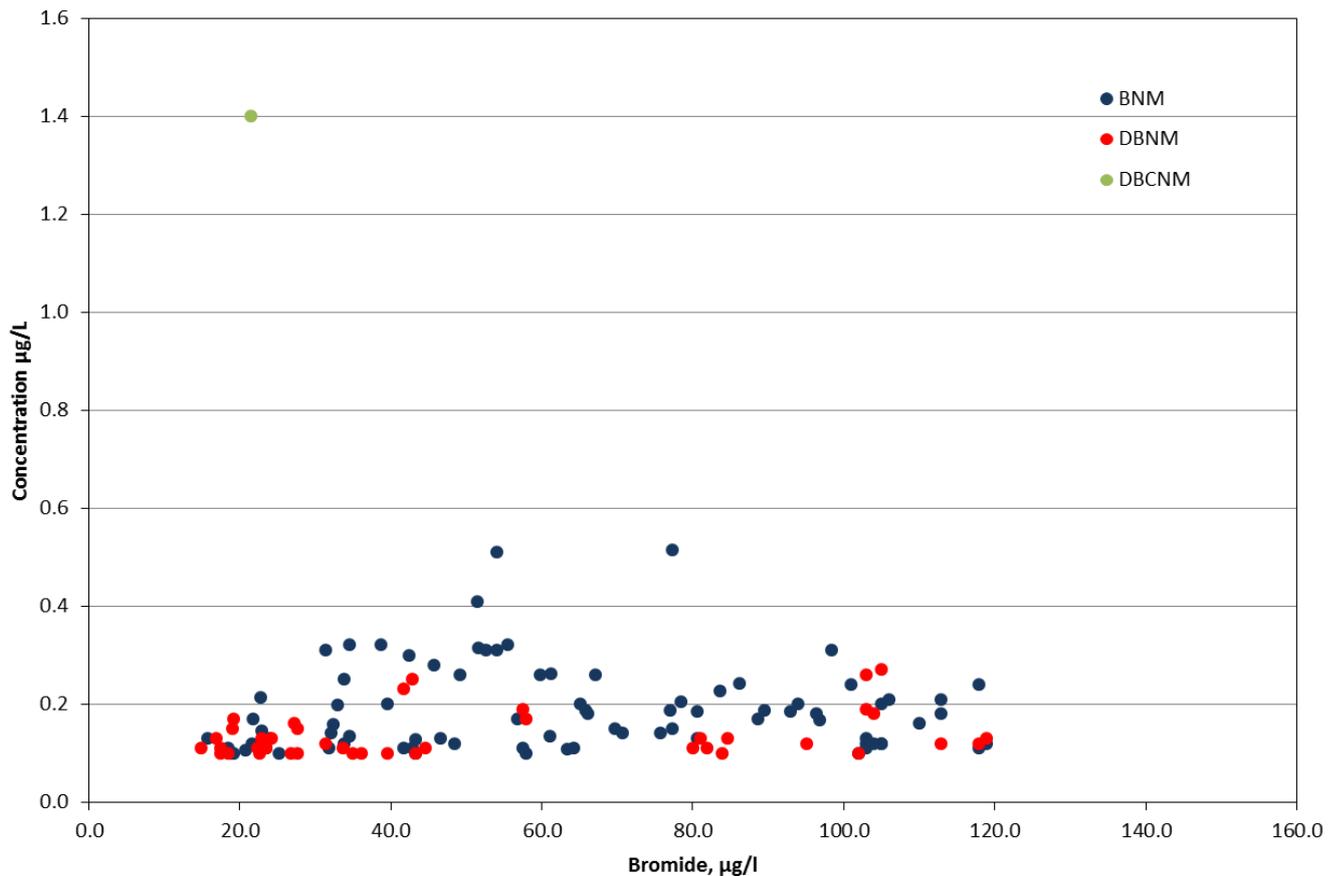
The link between bromide concentration and the formation of brominated N-DBPs was also considered (Figures 4.32-4.34), since brominated DBP analogues are reported to be more toxic than their chlorinated counterparts in *in vitro* toxicity tests (Plewa and Wagner, 2009). Bromide concentration on its own was not a consistent predictor of increased concentrations of brominated N-DBPs, suggesting that the treatment process types are likely more important in bromine incorporation than the bromide concentration, at least under the bromide concentration range included in this survey. For example, some of the highest concentrations of dibromoacetonitrile (DBAN) were in ozonated lowland systems, which had low to moderate concentrations of bromide in the source water compared to the bromide in some of the other source waters included in this survey. Also, the source waters with the highest bromide concentrations (approx. 400  $\mu\text{g/l}$ ) did not produce the highest concentrations of brominated N-DBPs.



**Figure 4.32 A comparison of the concentrations of individual brominated haloacetonitriles (HANs) versus bromide concentration for the same sample.**



**Figure 4.33 A comparison of the concentrations of 2,2-dibromoacetamide (2,2-DBAcAm) versus bromide concentration for the same sample. 2,2-DBAcAm was the only brominated HAcAm detected above its limit of detection.**

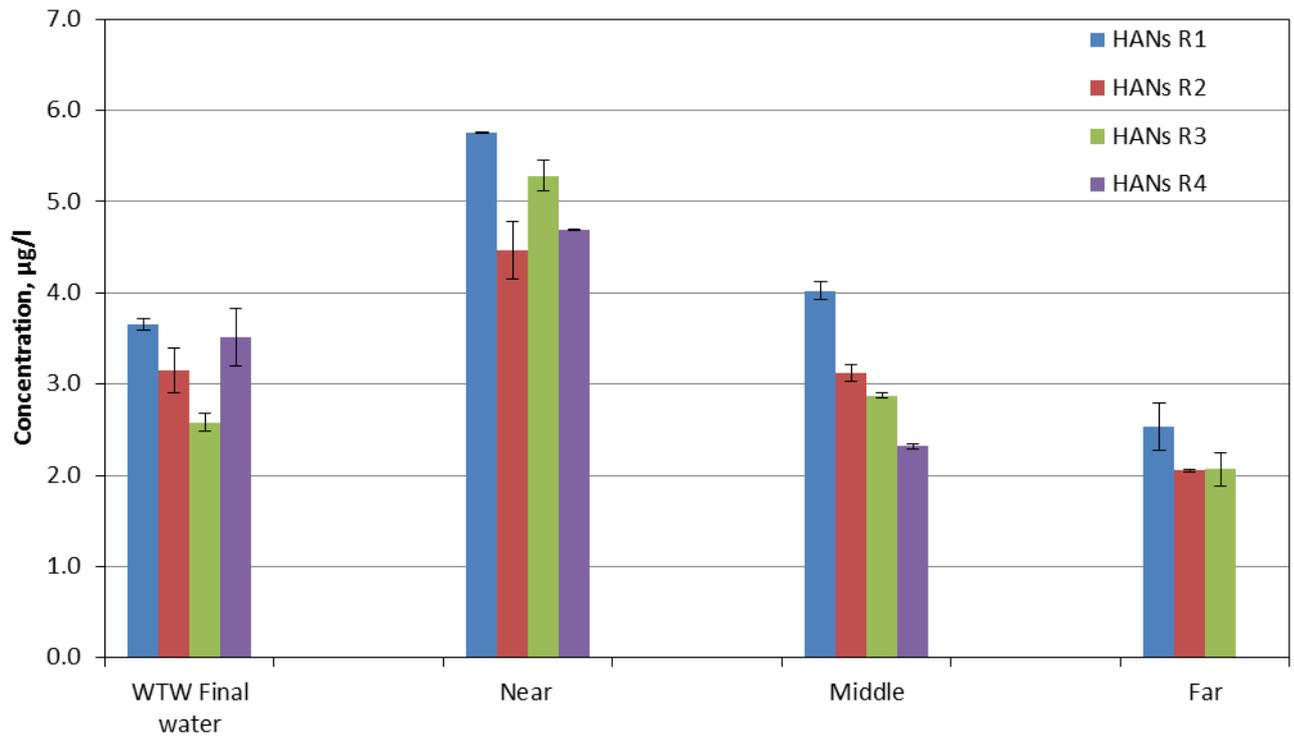


**Figure 4.34 A comparison of the concentrations of individual brominated halonitromethanes (HNMs) versus bromide concentration for the same sample.**

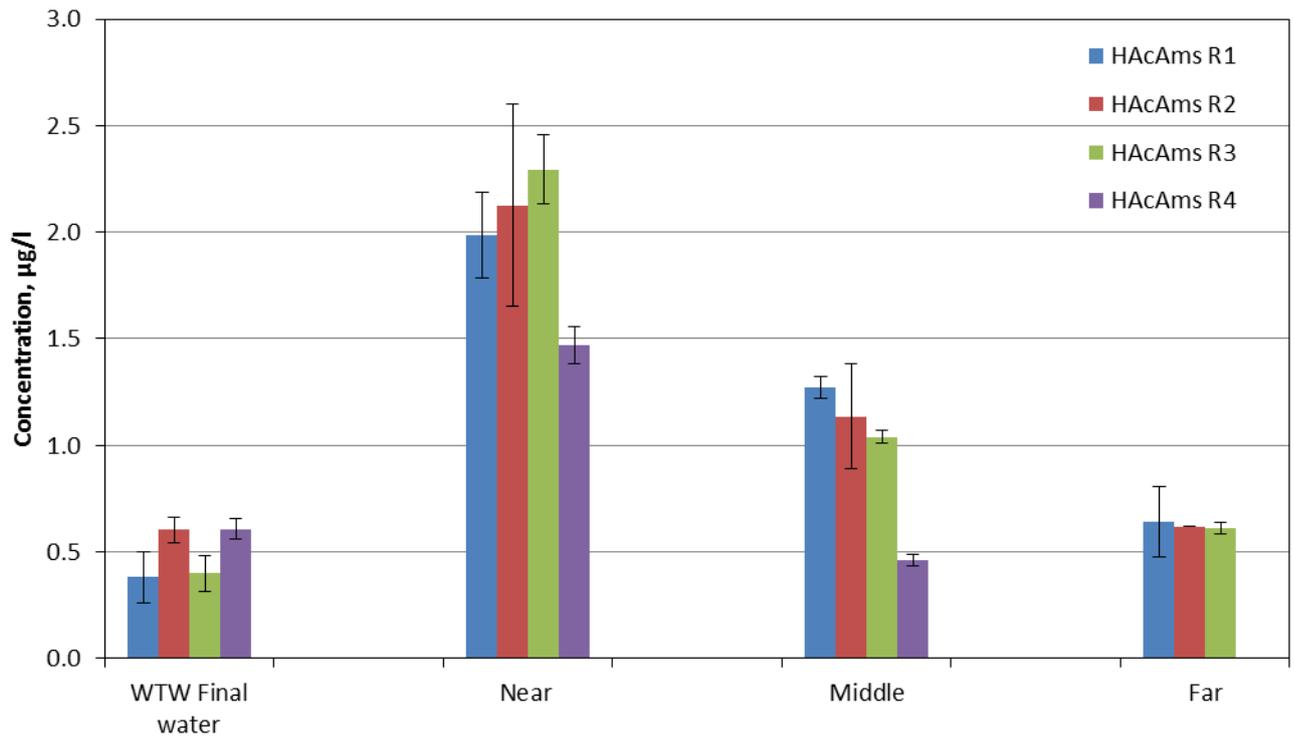
#### **4.4 N-DBPs in distribution networks**

Figures 4.35-4.41 summarise the differences in N-DBP concentrations between the final treatment works water and the water sampled from near, middle, and far sampling locations of the distribution networks for three of the water supply systems. None of these distribution networks employed booster chlorination. Typically the final treatment works concentrations and distribution network concentrations were within 1-2 µg/l of each other; both slight decreases (Figures 4.35-4.37) and slight increases (Figures 4.37-4.38) were observed. Figures 4.38-4.41 also illustrate that for some N-DBPs the concentrations between rounds at the same sampling location could vary by several µg/l, especially for cyanogen chloride (Figure 4.41).

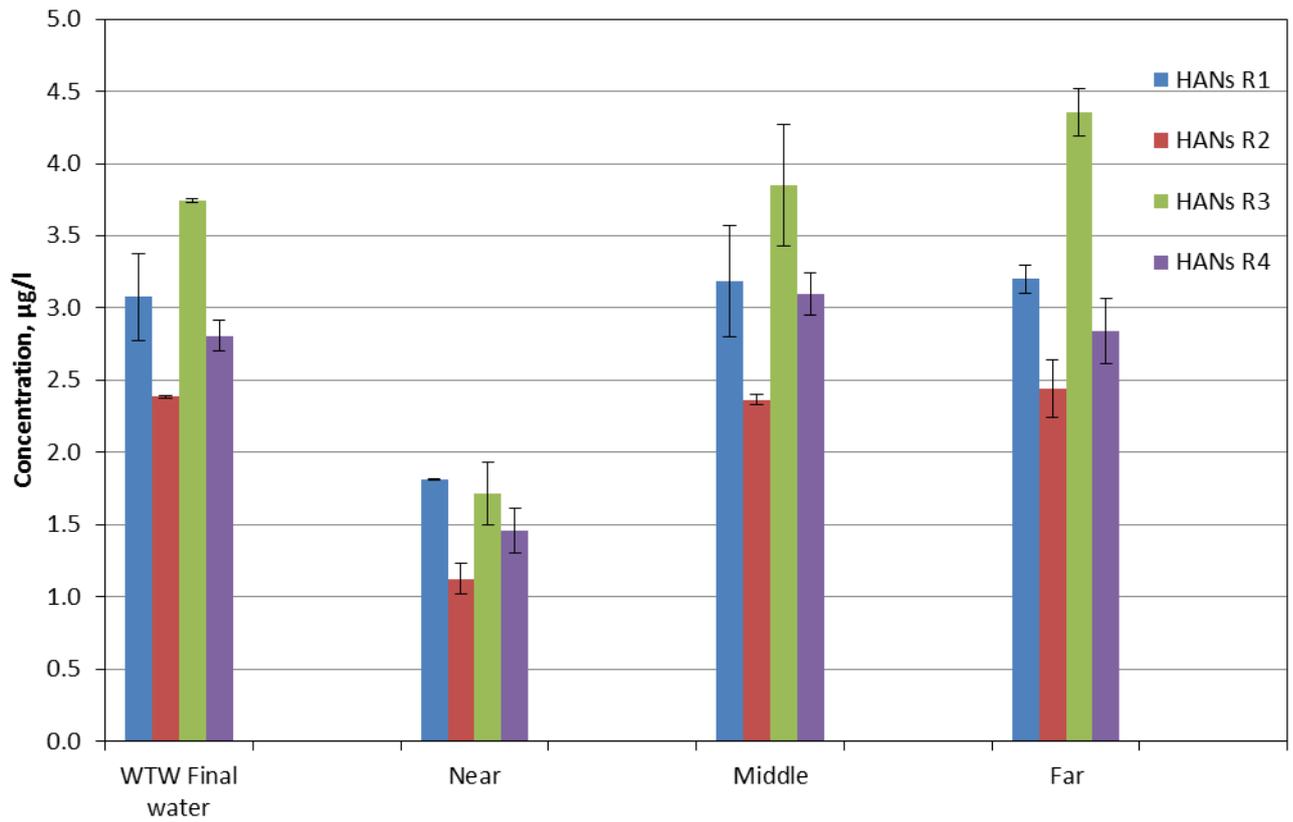
Similarly, in chloraminated distribution networks there were generally only small changes in the N-DBP concentrations and no consistent trends in terms of increases or decreases; data for HANs and HAChMs in distribution for chloraminated water supply systems A and C are shown as examples in Figures 4.42-4.45.



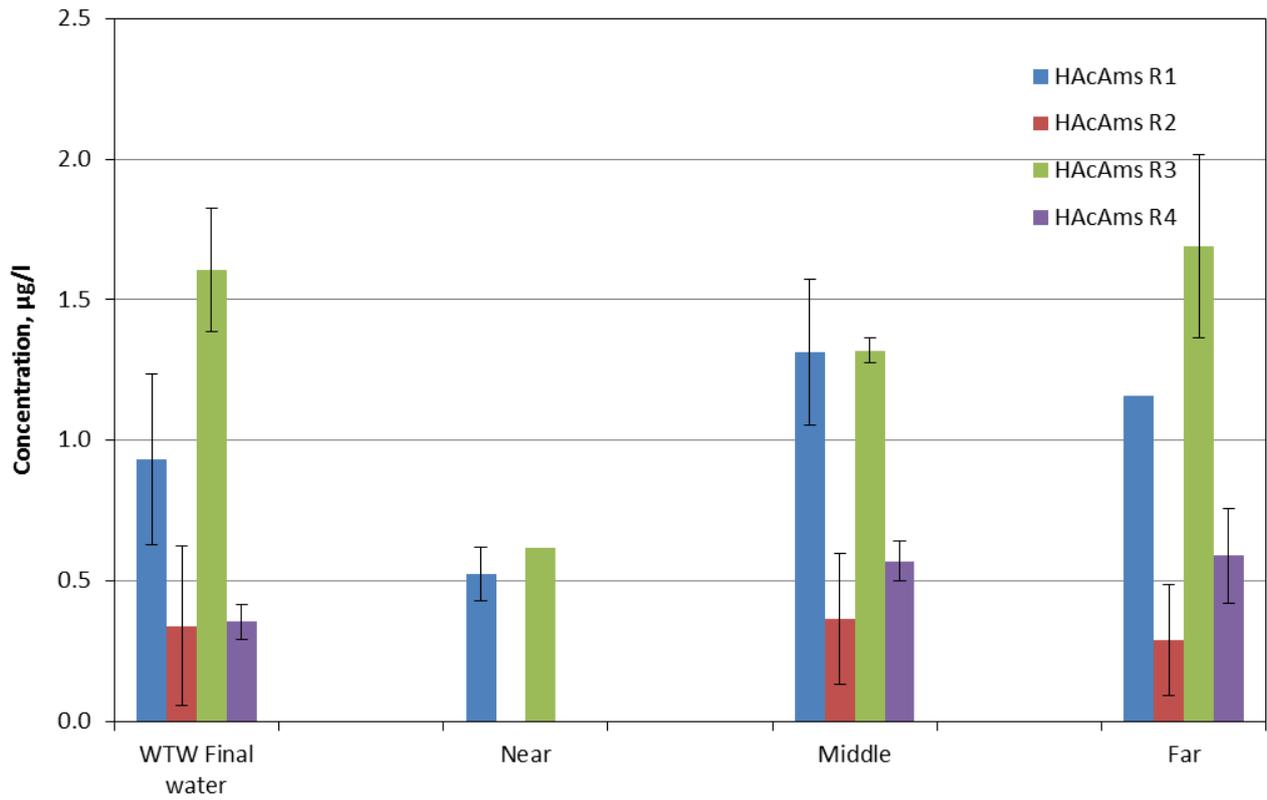
**Figure 4.35 A comparison of the sum of the concentrations of the haloacetonitriles (HANs) measured in this survey in the final water treatment works (WTW) samples and distribution location samples in the four rounds for water supply system D.**



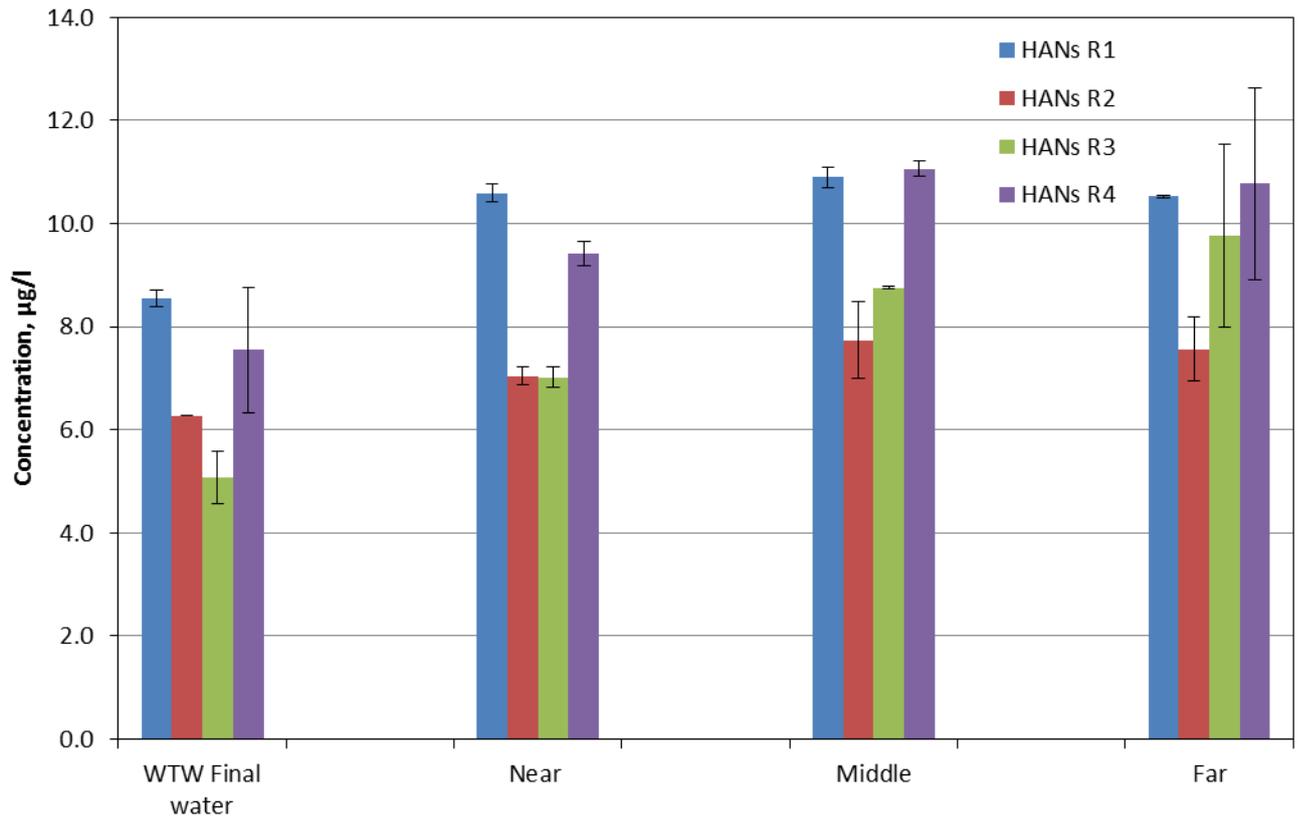
**Figure 4.36** A comparison of the sum of the concentrations of the haloacetamides (HAcAms) measured in this survey in the final water treatment works (WTW) samples and distribution location samples in the four rounds for water supply system D.



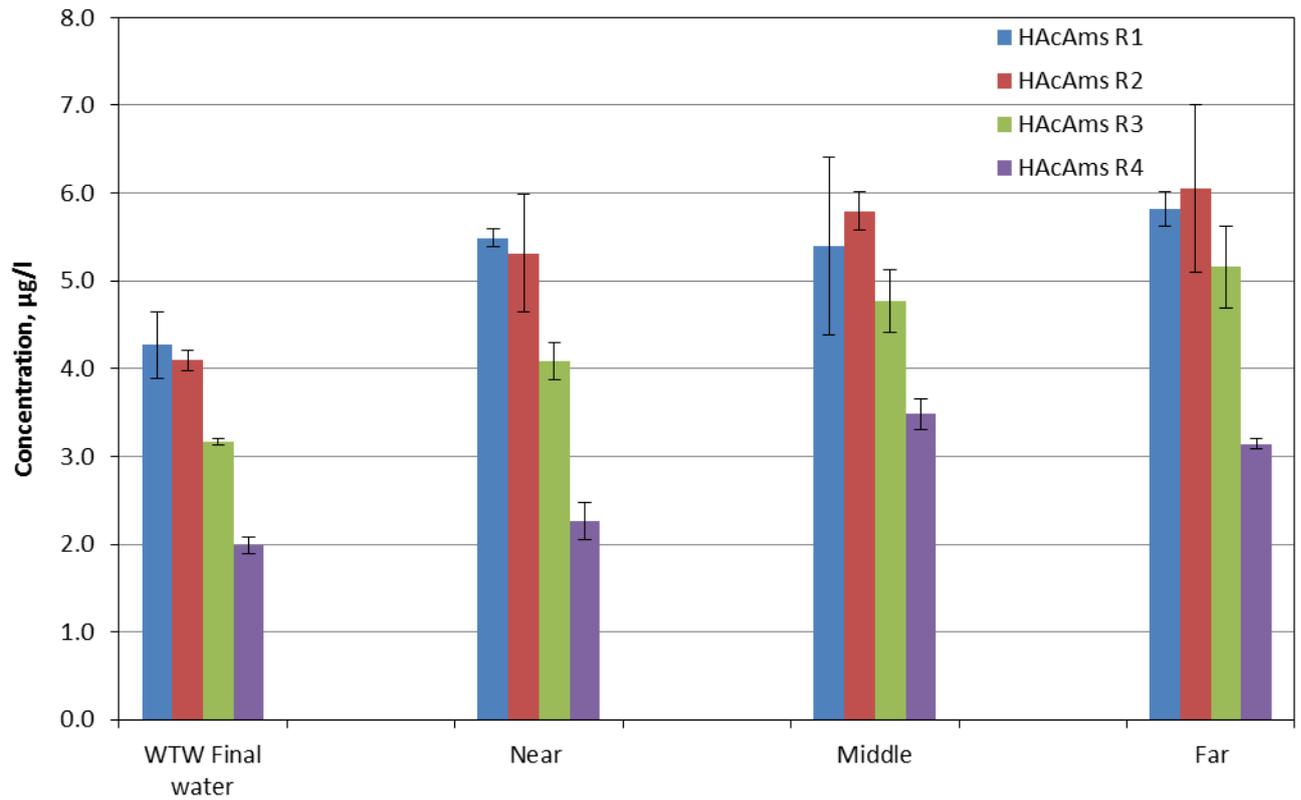
**Figure 4.37 A comparison of the sum of the concentrations of the haloacetonitriles (HANs) measured in this survey in the final water treatment works (WTW) samples and distribution location samples in the four rounds for water supply system T.**



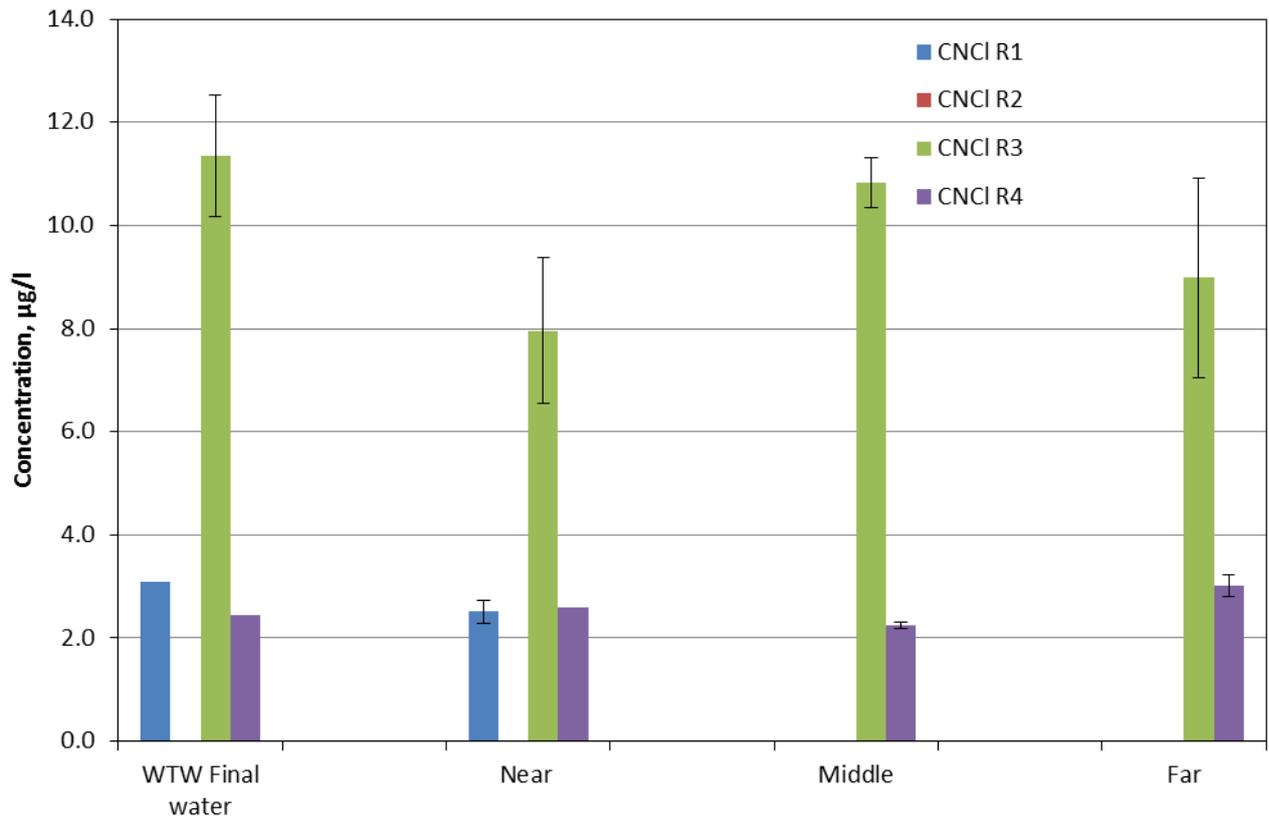
**Figure 4.38** A comparison of the sum of the concentrations of the haloacetamides (HAcAms) measured in this survey in the final water treatment works (WTW) samples and distribution location samples in the four rounds for water supply system T.



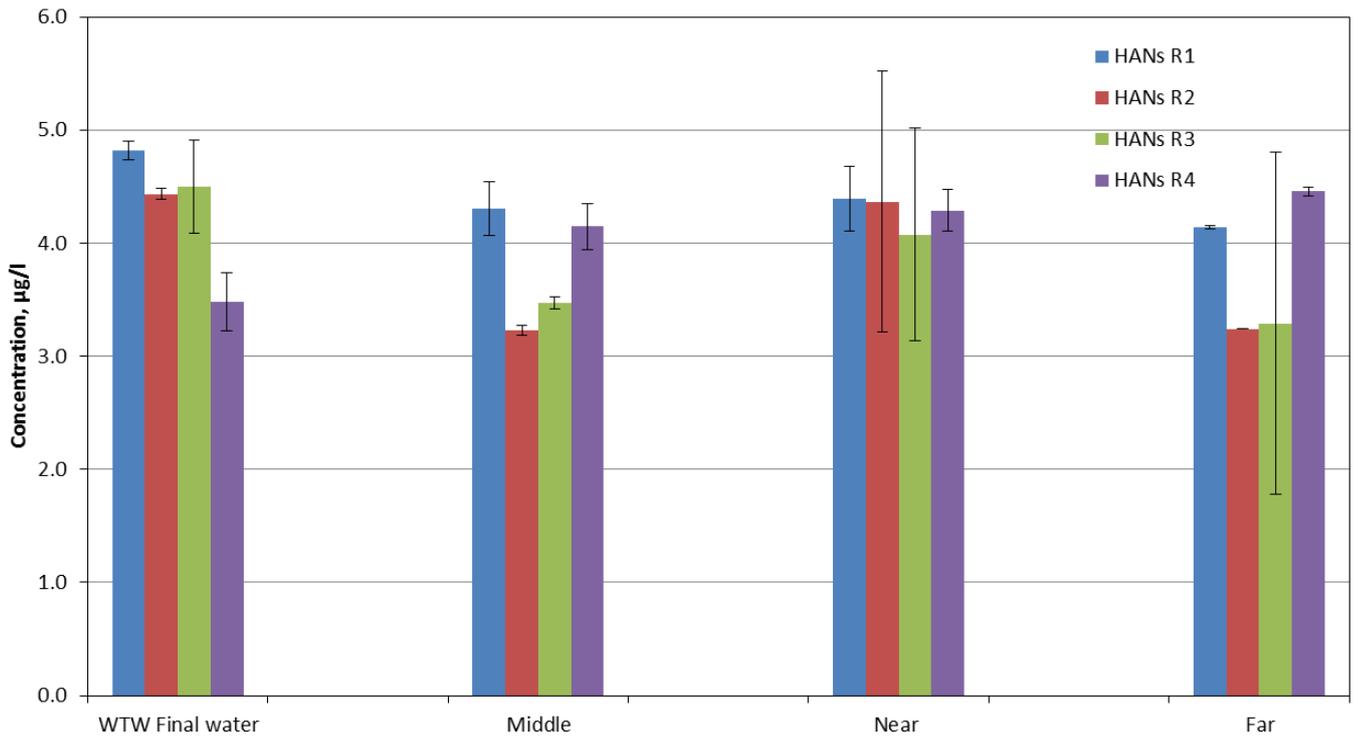
**Figure 4.39 A comparison of the sum of the concentrations of the haloacetonitriles (HANs) measured in this survey in the final water treatment works (WTW) samples and distribution location samples in the four rounds for water supply system B.**



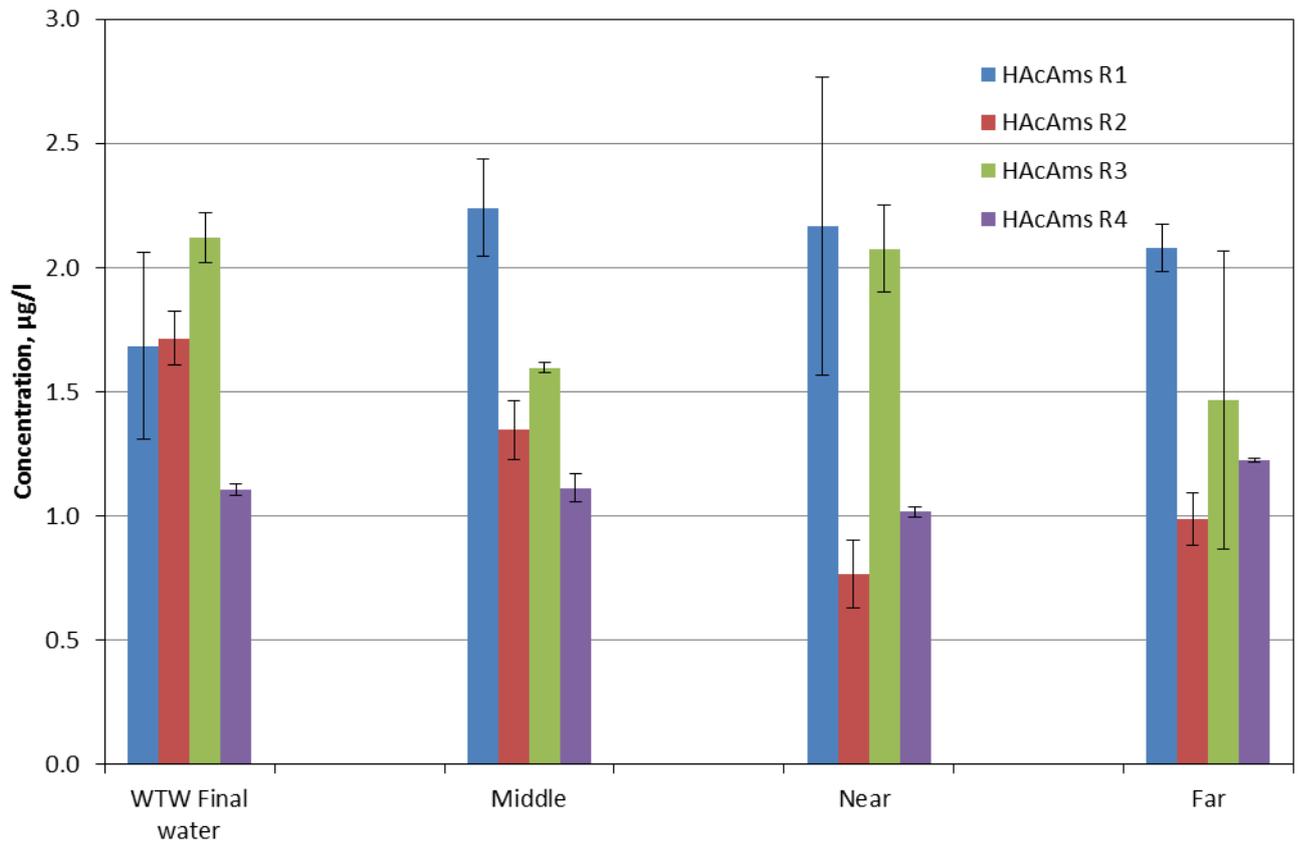
**Figure 4.40 A comparison of the sum of the concentrations of the haloacetamides (HAcAms) measured in this survey in the final water treatment works (WTW) samples and distribution location samples in the four rounds for water supply system B.**



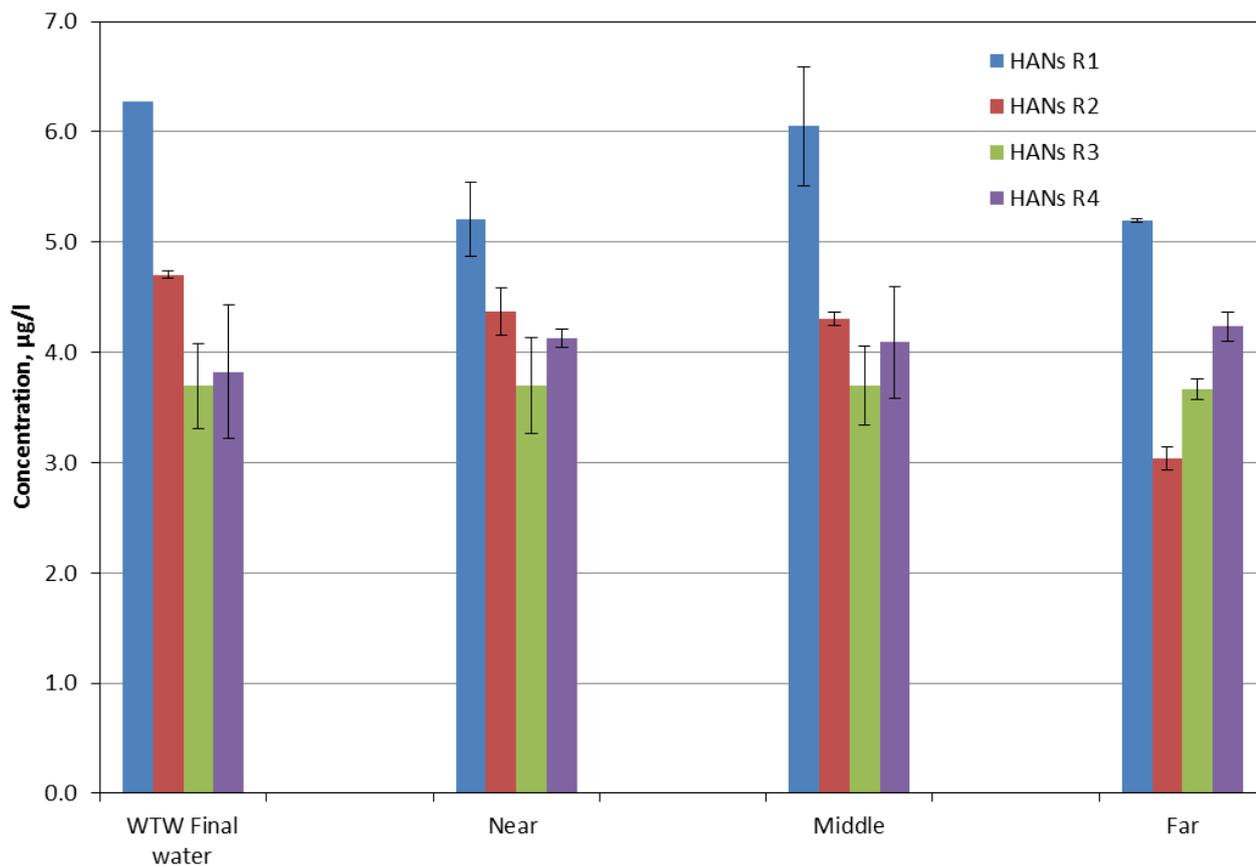
**Figure 4.41 A comparison of the cyanogen chloride concentrations in the final water treatment works (WTW) samples and distribution location samples in the four rounds for water supply system B.**



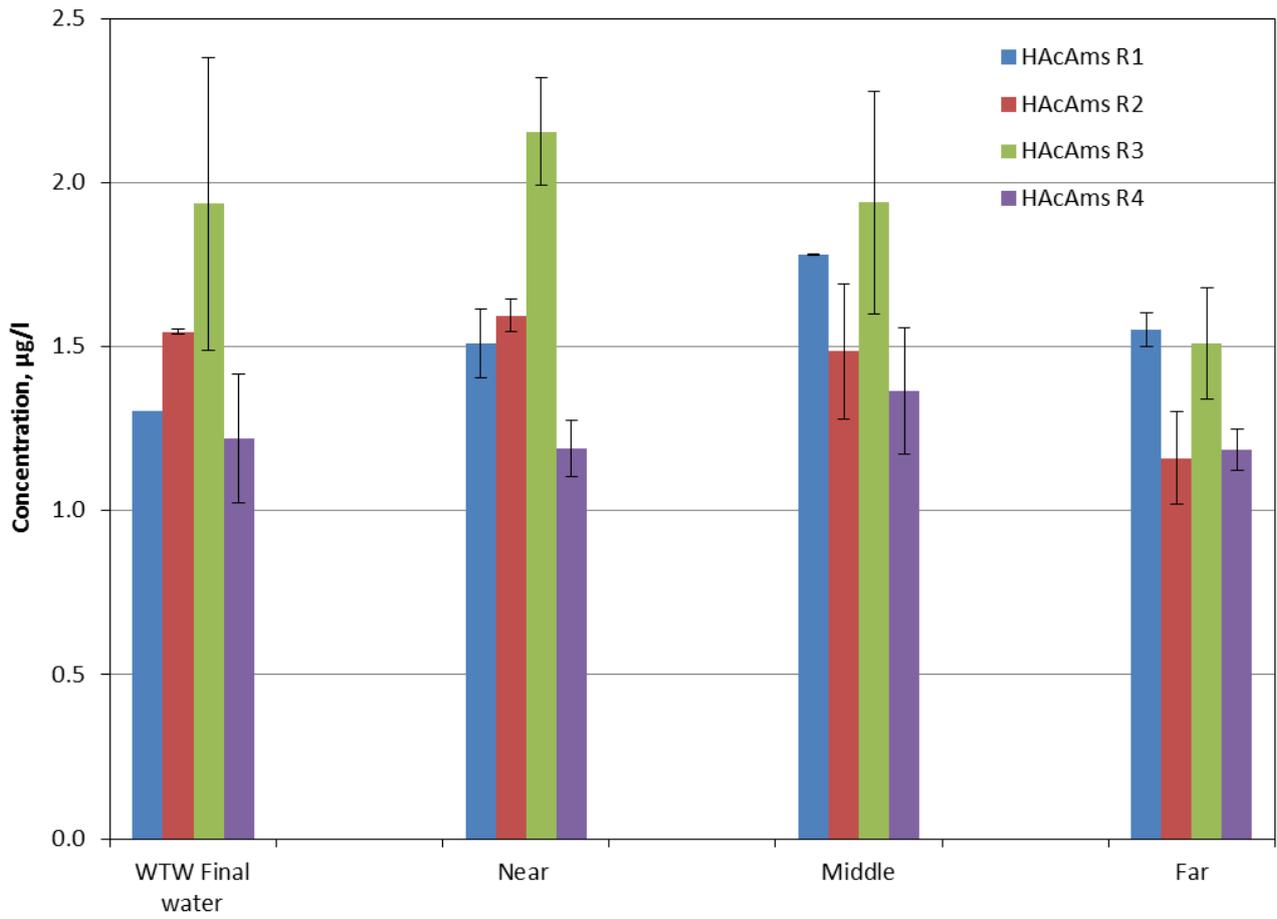
**Figure 4.42 A comparison of the sum of the concentrations of the haloacetonitriles (HANs) measured in this survey in the final water treatment works (WTW) samples and distribution location samples in the four rounds for water supply system A.**



**Figure 4.43 A comparison of the sum of the concentrations of the haloacetamides (HAcAms) measured in this survey in the final water treatment works (WTW) samples and distribution location samples in the four rounds for water supply system A.**

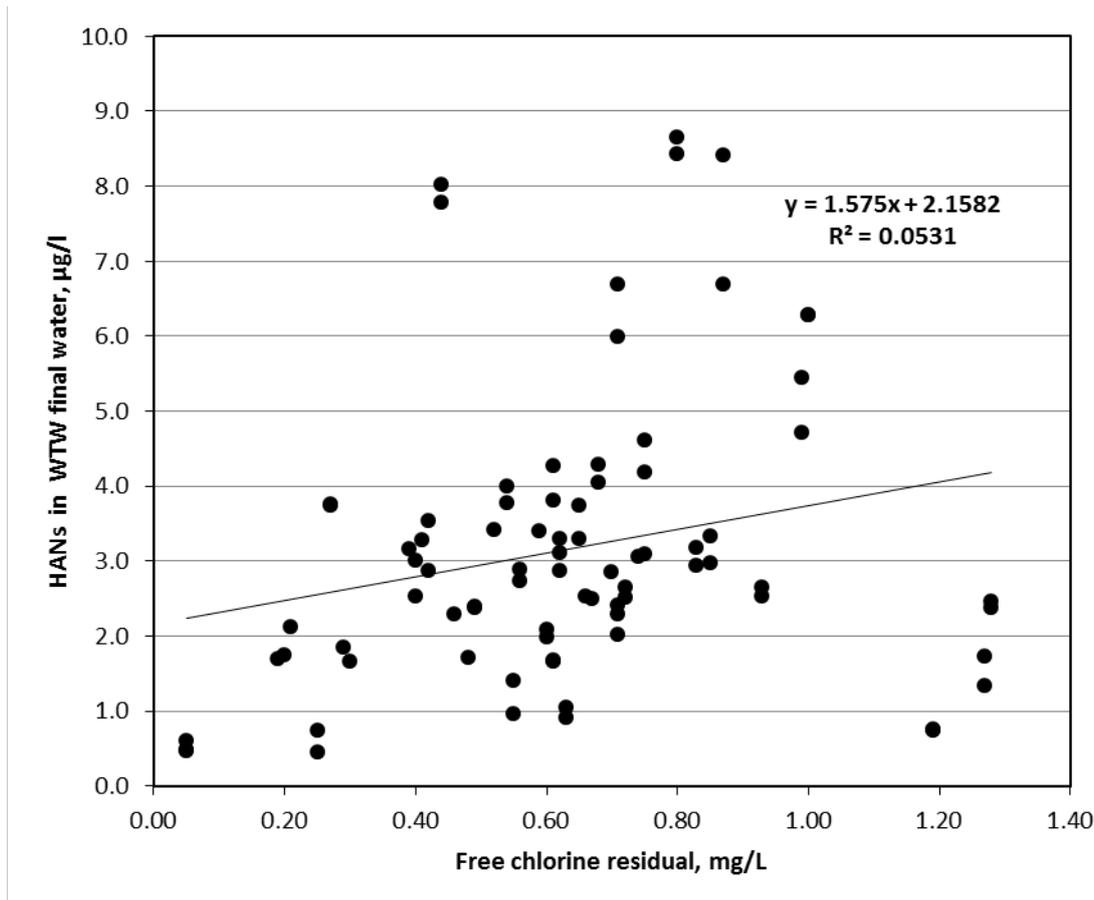


**Figure 4.44** A comparison of the sum of the concentrations of the haloacetonitriles (HANs) measured in this survey in the final water treatment works (WTW) samples and distribution location samples in the four rounds for water supply system C.



**Figure 4.45 A comparison of the sum of the concentrations of the haloacetamides (HAcAms) measured in this survey in the final water treatment works (WTW) samples and distribution location samples in the four rounds for water supply system C.**

Given that typically there were only relatively minor changes in N-DBP concentrations in distribution and that the majority of N-DBP formation therefore appeared to occur in the water treatment works, a comparison of the N-DBP concentrations in the final water treatment works samples versus the free chlorine residual in those samples was conducted. However, chlorine residual did not correlate well with HANs (Figure 4.46) nor with any of the other N-DBP groups; the best correlation of final water chlorine residual was with cyanogen chloride, but with an  $R^2$  value of only 0.22.



**Figure 4.46** A comparison of the sum of the concentrations of the haloacetonitriles (HANs) measured in this study in the final water treatment works (WTW) samples versus the free chlorine residual in those samples, for supply systems using chlorine in distribution.

## 5. CONCLUSIONS

The results of this survey suggest that haloacetonitriles (HANs), haloacetamides (HAcAms), and halonitromethanes (HNMs) occur at broadly similar concentrations in England and Wales as have been reported in surveys in other countries. All the measured nitrogen-containing disinfection by-products (N-DBPs) occurred at levels below the current World Health Organisation (WHO) guidelines for dichloroacetonitrile (20 µg/l) and dibromoacetonitrile (70 µg/l). As individual compounds, all the N-DBP compounds were typically only present at concentrations < 2 µg/l. HANs were detected at the highest group sum concentrations (mean = 3.2 µg/l), followed by HAcAms (mean = 1.5 µg/l), and HNMs (mean = 0.4 µg/l). It was most commonly the di-halogenated forms of the HANs that were detected, whereas both di-halogenated HAcAms and trichloroacetamide were commonly detected and trichloronitromethane was the most commonly detected HNM.

The lowland surface water sources that were included in this survey formed more N-DBPs than the upland surface water and groundwater sources.

The six treatment works that applied ozone were associated with higher concentrations of HANs and HAcAms than non-ozone treatment works, although this is potentially confounded because all the ozone works were treating lowland surface waters which may have had higher N-DBP formation potential.

Cyanogen chloride was also detected at the highest concentrations in the ozonated lowland systems, although with significant variation between and within sampling rounds. The cyanogen chloride concentrations were below WHO guidelines for this compound.

In general, supply systems applying chlorine formed slightly more HANs and HAcAms than those applying chloramines.

Total organic carbon and ultraviolet absorbance at 254 nm were poor predictors of N-DBP concentrations, nor were there clear observed links with other individual measured water quality parameters.

There were no significant consistent differences between the N-DBP concentrations that were measured in the different sampling rounds. This suggests there is no clear seasonal effect.

There were no consistent trends between N-DBP concentrations and distribution sampling distance from the treatment works. In general, N-DBP concentrations remained approximately the same in distribution or varied by only 1-2 µg/l between the works and the distribution sampling locations. Increased chlorine residual in the final water treatment works samples was not highly correlated to increased N-DBP concentrations either.

None of the N-DBPs exhibited consistent links with total trihalomethanes (THMs). HANs and HAcAms exhibited better linear correlations with total haloacetic acids (HAA<sub>9</sub>) than with total THMs. There were no trends linking HNMs to either THMs or HAA<sub>9</sub>.

## **6. ACKNOWLEDGEMENTS**

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## APPENDIX A Analytical method for the determination of semivolatile N-DBPs in drinking water using gas chromatography and mass spectrometry

This method describes a procedure for the determination of semi-volatile N-DBPs using liquid-liquid extraction and gas chromatography with mass spectrometry (GCMS) for detection and quantification.

### A1 Performance characteristics of the method

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A1.1	Substances determined	Bromoacetonitrile Dichloroacetonitrile Bromochloroacetonitrile Dibromoacetonitrile Dibromochloroacetonitrile Chloronitromethane Bromonitromethane Dichloronitromethane Bromochloronitromethane Dibromonitromethane Trichloronitromethane Bromodichloronitromethane Dibromochloronitromethane 1,1-Dichloroacetone 1,1,1-Trichloro-2-propanone 2,2-Dichloroacetamide 2,2-Dibromoacetamide 2,2,2-Trichloroacetamide
A1.2	Type of sample	Drinking water
A1.3	Basis of method	A 400 ml aliquot of the aqueous sample is adjusted to pH 4.5-5.0 and saturated with sodium chloride and extracted with 50 mL of methyl-tert-butyl ether (MTBE). Two $\mu\text{L}$ of the extract is then injected into a GCMS equipped with a fused silica capillary column.
A1.4	Range of application	Typically up to $40 \mu\text{g l}^{-1}$ for each N-DBP.
A1.5	Calibration curve	Calibrations are linear or curved dependent on the determinand, over the range of application of the method.
A1.6	Interferences	Any substance, which is co-extracted under the conditions used, exhibits similar chromatographic behaviour to any of the N-DBPs being determined and has the same mass spectral ions, will interfere. However, the method has high selectivity for the substances analysed.

A1.7	Standard deviation	Refer to Supplementary Data Files.
A1.8	Limit of detection	Refer to Supplementary Data Files.
A1.9	Sensitivity	This is instrument dependent.
A1.10	Bias	Refer to Supplementary Data Files.

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## **A2 Principle**

A 400 ml aliquot of the aqueous sample is spiked with deuterated internal standard, adjusted to pH 5.5-5.0 and saturated with sodium chloride and extracted with 50 mL of methyl-tert-butyl ether (MTBE). Two  $\mu\text{L}$  of the extract is then injected into a GCMS equipped with a fused silica capillary column.

## **A3 Hazards**

NDBPs are toxic substances which may be fatal if inhaled, harmful if swallowed or absorbed through the skin. In addition, methanol and acetone are toxic and flammable. Acetone is flammable. MTBE is highly flammable and a skin irritant.

## **A4 Reagents**

All reagents should be of sufficient purity that they do not give rise to significant interfering peaks in the analysis. Purity should be checked for each batch of materials by running procedural blanks with each batch of samples analysed. Solvents suitable for high performance liquid chromatography or pesticide analysis use and analytical grade materials are normally suitable unless otherwise stated and details of preparation are given where appropriate. To avoid potential evaporation of solvents, standard solutions should be stored in a refrigerator. However, prior to use, all solutions and solvents should be allowed to reach ambient room temperature before volumetric measurements are made.

A4.1 Water. This should be deionised or of similar quality.

A4.2 Acetone

A4.3 pH Paper -- Narrow ranges, pH = 3-5.5.

A4.4 Methyl-tert-butyl ether (MTBE).

A4.5 Sodium chloride

A4.6 Hydrochloric acid solution (10 v/v %). Add 10 ml of concentrated hydrochloric acid to approximately 60 ml of water (A4.1). Mix well. Make to 100 ml with water.

A4.7 Standard solutions

A4.7.1  $d_4$ -1,2- dichlorobenzene deuterated internal standard stock solutions ( $1 \text{ mg ml}^{-1}$ ). Into a 10-ml volumetric flask, dissolve an accurately weighed amount of approximately 10 mg of  $d_4$ -1,2- dichlorobenzene in approximately 9 ml of acetone (A4.2). Make to the mark with acetone and mix well. This solution should be stored at  $-18 \text{ }^\circ\text{C}$ .

A4.7.2 Intermediate deuterated internal standard stock solution ( $1 \text{ } \mu\text{g ml}^{-1}$ ). Add 50  $\mu\text{l}$  of the deuterated internal standard stock solution (A4.7.1) into a 50-ml volumetric flask containing approximately 45 ml of acetone (A4.2). Make to the mark with acetone and mix well. The concentration of the deuterated standard in this solution is nominally  $1 \text{ } \mu\text{g ml}^{-1}$ . This solution should be stored at  $-18 \text{ }^\circ\text{C}$ .

A4.7.3 Spiking deuterated internal standard stock solution ( $20 \text{ ng ml}^{-1}$ ). Add 400  $\mu\text{l}$  of intermediate deuterated internal standard stock solution (A4.7.2) into a 20-ml volumetric flask containing approximately 18 ml of acetone (A4.2). Make to the mark with acetone and mix well. The concentration of the deuterated standard in this solution is nominally  $20 \text{ ng ml}^{-1}$ . This solution should be stored at  $-18 \text{ }^\circ\text{C}$ .

A4.7.4 NDBP standard stock solutions ( $10 \text{ mg ml}^{-1}$ ). Into separate 10-ml volumetric flasks, dissolve an accurately weighed amount of approximately 100 mg of each NDBP solution (except those compounds in EPA551B mix) and add approximately 9 ml of acetone (A4.2). Make to the mark with acetone and mix well.

The concentration of each NDBP in these solutions is nominally  $10 \text{ mg ml}^{-1}$ . These solutions should be stored at  $-18 \text{ }^\circ\text{C}$ .

A4.7.5 Intermediate NDBP standard solution for calibration ( $50 \text{ } \mu\text{g ml}^{-1}$ ). Add 100  $\mu\text{l}$  of each NDBP standard stock solution (A4.7.4) and 0.5ml of EPA 551B halogenated volatiles mix into a 20-ml volumetric flask containing approximately 45 ml of MTBE (A4.4). Make to the mark with MTBE and mix well. The concentration of each NDBP in this solution is nominally  $50 \text{ } \mu\text{g ml}^{-1}$ . This solution should be stored at  $-18 \text{ }^\circ\text{C}$ .

A4.7.6 Spiking NDBP standard solution. Add 100  $\mu\text{l}$  of each NDBP standard stock solution (A4.7.4) and 0.5ml of EPA 551B halogenated volatiles mix into a 20-ml volumetric flask containing approximately 45 ml of acetone (A4.2). Make to the mark with acetone and mix well. The concentration of each NDBP in this solution is nominally  $50 \text{ } \mu\text{g ml}^{-1}$ . This solution may be stored at  $-18 \text{ }^\circ\text{C}$  for up to one year.

A4.7.7 Calibration standard solutions. Calibration standard solutions should be prepared. Each calibration solution should contain each NDBP and the deuterated internal standard. For example, each of the NDBP concentrations should be 40, 30, 20, 10, 5, 2.5, 0.5 and  $0 \text{ } \mu\text{g ml}^{-1}$  and the concentration of the deuterated internal standards should each be  $10 \text{ } \mu\text{g ml}^{-1}$ .

The following table shows the volumes of intermediate standard stock solution (A4.7.5) required to prepare 10 ml quantities of calibration standard solutions.

Standard Concentration (ug/ml)	NDBP solution in MtBE (ul)	Intermediate Standard (ul)	MtBE (ul)	Volume of Flask (ml)
40	1600	400	0	2
30	1200	400	400	2
20	800	400	800	2
10	400	400	1200	2
5	200	400	1400	2
2.5	100	400	1500	2
0.5	20	400	1580	2
0	0	400	1600	2

## A5 Apparatus

In addition to general laboratory glassware, the following are required.

A5.1 Analytical balance capable of weighing to 0.0001g.

A5.2 A horizontal shaker e.g. IKA Labortechnik HS501 digital.

A5.3 Extract concentration equipment. Any suitable proprietary concentrator with thermostatically controlled water bath or equivalent system.

A5.4 Nitrogen or air blow-down apparatus or equivalent system.

A5.5 GCMS/MS equipment

GC: Agilent 6890

Columns: Rtx5 Amine, 30 m x 0.25 mm diameter, 1 µm bonded film of polyphenylmethylsilicone deactivated pre-column, or equivalent.  
Restek base deactivated pre-column, 0.53 mm ID

Carrier gas: Helium, constant flow at 1.5 ml per minute.

Injection volume: 2 µl (Split split-less injection mode) with double gooseneck splitless liner, 4mm x 6.5 x 78.5 base deactivated.

Temperature programmes:

Oven: Initial temperature at 34 °C for 3 minutes, then 20 °C per minute to 300 °C and hold for 8 minutes.

Injector: 250 °C.

Mass Spectrometer: Agilent 5973

MS Quad Temperature: 150 °C

MS Quad Temperature: 230 °C

Target Compound	R.T.	Ions monitored m/z	
		Quan ion	Confirm Ion
d4 Dichlorobenzene (Internal Standard)	8.54	150	
Dichloroacetonitrile	4.91	74	82
Chloronitromethane	5.11	49	51
Dichloroacetone	5.12	83	43
Dichloronitromethane	5.36	83	85
Bromoacetonitrile	5.65	79	119
Trichloronitromethane	5.77	117	119
Bromonitromethane	6.17	95	93
Bromochloroacetonitrile	6.18	79	119
Bromochloronitromethane	6.53	129	127
Trichloroacetone	6.53	43	125
Chloroacetamide	7.16	44	93
Bromodichloronitromethane	7.06	163	161
Dibromoacetonitrile	7.29	118	93
Dibromochloroacetonitrile	7.2	154	152
Dibromonitromethane	7.54	173	171
Bromacetamide	8.07	44	137
Dibromochloronitromethane	8.53	207	209
Dichloroacetamide	8.44	44	76
Trichloroacetamide	9.53	44	82
Dibromoacetamide	9.97	44	217

## A6 Sample collection and storage

Samples should be collected in glass bottles of 1-litre capacity. Plastic screw tops may be suitable provided they are fitted with polytetrafluoroethylene or polytetrafluoroethylene-faced liners. Alternatively, ground-glass stoppers in glass bottles may be used. Prior to use, the bottles should be cleaned with a suitable cleaning agent (for example Decon 90). After

cleaning, the bottles should be rinsed with water and then allowed to drain, before being dried. Add 100 mg of ammonium chloride to each bottle prior to sampling. Samples should be analysed as soon as possible following collection and preservation. If storage of samples is unavoidable, samples should be stored in a refrigerator and kept at below 4°C. Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

## **A7 Analytical procedure**

A7.1 Remove samples from storage and allow them to equilibrate to room temperature and weigh 400 ±1 ml of sample into a 500ml glass bottle

A7.2 For each batch of samples weight out 400 ±1 ml of Rathburns water for a Analytical Quality Control blank and spike sample.

A7.3 Adjust the pH to 4.5-5 with 10% HCl acid

A7.4 Check pH using 3-5.5 pH papers

A7.5 Inject a 20ul aliquot of the internal standard spiking solution (A4.7.3).

A7.6. Add 64ul of NDBP spiking solution (A4.7.6) to the AQC spike sample.

A7.7 Add 50g of Sodium Chloride to each sample

A7.8 Add 50ml of MTBE to each sample.

A7.9 Put on shaker for 1 hour at 200rpm

A7.10 Remove the sample from the shaker, allow the water and MTBE phases to separate (approximately two minutes) and remove the upper solvent layer using a 50ml eppendorf pipette into a 60 ml vial. Ensure as little water as possible has carried over onto the bottom of the autosampler vial. If a dual phase appears in the vial, the bottom layer can be removed and discarded by using a Pasteur pipet.

A7.11 Place the vial in a freezer overnight to freeze out any water present in the extract.

A7.12 Filter the cold extract using MTBE prewashed glass wool to remove ice from the sample and concentrate the extract using a concentrator to approximately 1-2 ml.

A7.13 Further concentrate the extract to 100 ul using a nitrogen blow down apparatus.

A7.14 Sample Analysis and Identification

A7.15 GCMS conditions are described in Section A5.5. Tune the mass spectrometer and mass calibrate the system daily.

A7.16 Inject 2 µL of the sample extract and record the resulting peak areas using the data system. If the peak area exceeds the linear range of the calibration curve, the final extract should be diluted with MTBE and reanalyzed.

## A8 Calculation of results

A calibration graph of the ratio of the respective peak area or height of the NDBP of interest to the peak area or height of the corresponding deuterated internal standard should be constructed against the mass of deuterated internal standard injected. The original sample concentration should be calculated from the graph taking into account the volume of sample that is extracted (A7.2.1) and any dilutions that may have been used (for example, sections A7.4.1 and A7.7.1, note i).

The respective peak area or height of each specific NDBP should be measured. For each NDBP, the response ratio should then be calculated.

$$\text{Response ratio} = \frac{\text{peak area or height (SS)}}{\text{peak area or height (DIS)}}$$

where:

peak area or height (SS) is the peak area or height of the specific NDBP,  
peak area or height (DIS) is the peak area or height of the corresponding deuterated internal standard.

Plot the response ratio for the specific NDBP against the concentration of the specific NDBP in the calibration standards. From the plotted calibration curve, calculate the slope and intercept using linear regression.

Determining the corresponding response ratios in the unknown sample (RRu) and blank sample (RRb) enables the concentration of each NDBP,  $C_s$ , to be calculated.

$$C_s = ((RRu - RRb) - \text{intercept}) / \text{Slope}$$

## A9 Additional reading material

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## APPENDIX B Analytical method for volatile N-DBPs for the determination of volatile NDBPs in drinking water using using gas chromatography and mass spectrometry

This method describes a procedure for the determination of volatile N-DBPs using liquid-liquid extraction and gas chromatography with mass spectrometry (GCMS) for detection and quantification.

### B1 Performance characteristics of the method

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B1.1	Substances determined	Cyanogen Chloride Chloroacetonitrile Trichloroacetonitrile
B1.2	Type of sample	Drinking water
B1.3	Basis of method	A 50 ml aliquot of the aqueous sample is adjusted to pH 4.5-5.0 and saturated with sodium chloride and extracted with 2 mL of methyl-tert-butyl ether (MTBE). Two $\mu\text{L}$ of the extract is then injected into a GCMS equipped with a fused silica capillary column .
B1.4	Range of application	Typically up to $40 \mu\text{g l}^{-1}$ for each N-DBP.
B1.5	Calibration curve	Calibrations are linear or curved dependent on the determinand, over the range of application of the method.
B1.6	Interferences	Any substance, which is co-extracted under the conditions used, exhibits similar chromatographic behaviour to any of the N-DBPs being determined and has the same mass spectral ions, will interfere. However, the method has high selectivity for the substances analysed.
B1.7	Standard deviation	Refer to Supplementary Data Files.
B1.8	Limit of detection	Refer to Supplementary Data Files.
B1.9	Sensitivity	This is instrument dependent.
B1.10	Bias	Refer to Supplementary Data Files.

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## **B2 Principle**

A 50 ml aliquot of the aqueous sample is spiked with deuterated internal standard, adjusted to pH 4.5-5.0 and saturated with sodium chloride and extracted with 2 ml of methyl-tert-butyl ether (MTBE). Two  $\mu\text{L}$  of the extract is then injected into a GCMS equipped with a fused silica capillary column.

## **B3 Hazards**

NDBPs are toxic substances which may be fatal if inhaled, harmful if swallowed or absorbed through the skin. In addition, methanol and acetone are toxic and flammable. Acetone is flammable. MTBE is highly flammable and a skin irritant.

## **B4 Reagents**

All reagents should be of sufficient purity that they do not give rise to significant interfering peaks in the analysis. Purity should be checked for each batch of materials by running procedural blanks with each batch of samples analysed. Solvents suitable for high performance liquid chromatography or pesticide analysis use and analytical grade materials are normally suitable unless otherwise stated and details of preparation are given where appropriate. To avoid potential evaporation of solvents, standard solutions should be stored in a refrigerator. However, prior to use, all solutions and solvents should be allowed to reach ambient room temperature before volumetric measurements are made.

B4.1 Water. This should be deionised or of similar quality.

B4.2 Acetone

B4.3 pH Paper -- Narrow ranges, pH = 3-5.5.

B4.4 Methyl-tert-butyl ether (MTBE).

B4.5 Sodium chloride

B4.6 Hydrochloric acid solution (10 v/v %). Add 10 ml of concentrated hydrochloric acid to approximately 60 ml of water (B4.1). Mix well. Make to 100 ml with water.

B4.7 Standard solutions

B4.7.1 Fluorobenzene internal standard stock solutions ( $1 \text{ mg ml}^{-1}$ ). Into a 10-ml volumetric flask, dissolve an accurately weighed amount of approximately 10 mg of fluorobenzene in approximately 9 ml of acetone (B4.2). Make to the mark with acetone and mix well. This solution should be stored at  $-18 \text{ }^{\circ}\text{C}$ .

B4.7.2 Intermediate internal standard stock solution ( $1 \text{ } \mu\text{g ml}^{-1}$ ). Add 50  $\mu\text{L}$  of the internal standard stock solution (B4.7.1) into a 50-ml volumetric flask containing approximately 45 ml of acetone (B4.2). Make to the mark with acetone and mix well. The concentration of the

fluorobenzene standard in this solution is nominally  $1 \mu\text{g ml}^{-1}$ . This solution may be stored at  $-18 \text{ }^{\circ}\text{C}$  for up to 1 month.

B4.7.3 Spiking internal standard stock solution ( $20 \text{ ng ml}^{-1}$ ). Add  $400 \mu\text{l}$  of intermediate internal standard stock solution (B4.7.2) into a 20-ml volumetric flask containing approximately 18 ml of acetone (B4.2). Make to the mark with acetone and mix well. The concentration of the fluorobenzene standard in this solution is nominally  $20 \text{ ng ml}^{-1}$ . This solution should be stored at  $-18 \text{ }^{\circ}\text{C}$ .

B4.7.4 NDBP standard stock solutions ( $10 \text{ mg ml}^{-1}$ ). Into separate 10-ml volumetric flasks, dissolve an accurately weighed amount of approximately 100 mg of each NDBP solution and add approximately 9 ml of acetone (B4.2). Make to the mark with acetone and mix well.

The concentration of each NDBP in these solutions is nominally  $10 \text{ mg ml}^{-1}$ . These solutions should be stored at  $-18 \text{ }^{\circ}\text{C}$ .

B4.7.5 Spiking standard solution. Add  $100 \mu\text{l}$  of each NDBP standard stock solution (B4.7.4) and 0.5ml of EPA 551B halogenated volatiles mix into a 20-ml volumetric flask containing approximately 45 ml of acetone (B4.2). Make to the mark with acetone and mix well. The concentration of each NDBP in this solution is nominally  $50 \mu\text{g ml}^{-1}$ . This solution should be stored at  $-18 \text{ }^{\circ}\text{C}$ .

## B4.8 Preparation of Cyanogen Chloride

### B4.8.1 Preparation of Reagents for CNCl preparation

- a) Phosphate Buffer: Add 6g  $\text{NaH}_2\text{PO}_4$  in 100ml AQC (milli Q) water
- b) Free chlorine solution:  $\text{NaOCl}$  solution diluted to provide a concentration of 138mg/L chlorine
- c) Stock Cyanide standard: Add 0.212g  $\text{KCN}$  in 100ml milli Q water ( $1\text{ml} = 0.847 \text{ mg CN}^-$ )
- d) Intermediate Cyanide standard: Add 0.1ml of Stock Cyanogen in 100ml milli Q water ( $1\text{ml} = 0.847 \mu\text{g CN}^-$ )

### B4.8.2 Preparation of cyanogen chloride (200ug/L)

- a) Add 30ml milli Q water in 50ml volumetric flask
- b) Add 5ml  $\text{CNCl}$  intermediate ( $0.847 \mu\text{g/ml CN}^-$  solution)
- c) Add 4ml phosphate buffer
- d) Add 1.5ml of 138mg/L  $\text{NaOCl}$
- e) Invert twice and leave to sit for 2 mins
- f) Add approx 25mg ascorbic acid and gentle inversion for 30-40 seconds to quench residual chlorine

This is the primary Working Cyanogen Chloride solution at 200ug/L

### B4.8.3 Preparation of spiking solutions

- a) Cyanogen Chloride Spiking solution (CAN1) : Add 10ul of working CNCL solution(B4.8.2) in 10ml MeOH
- b) Cyanogen Chloride Spiking solution (CAN2) : Add 1 ml of working CNCL solution (B4.8.2 in 10ml MeOH
- c) EPA551B Spiking solution (Int 1): Add 100ul of 2000ug/ml EPA551B (Aldrich) in 10ml methanol
- d) EPA551B Spiking solution (Int 2): Add 1ml of EPA551B (Aldrich) Int 1 in 10ml Methanol

B4.9 Calibration standard solutions. Calibration standard solutions should be prepared. Each calibration solution should contain each NDBP and the deuterated internal standard. For example, each of the NDBP concentrations should be 100, 50, 20, 10, 5, 2.1, and 0 ng ml<sup>-1</sup> and the concentration of the deuterated internal standards should each be 10 ng ml<sup>-1</sup>. standards are prepared in distilled water and extracted using the same procedure used for samples.

The following table shows the volumes of spiking standard stock solution (B4.8.3) required to prepare 10 ml quantities of calibration standard solutions.

Standard (ng/ml)	CNCl wrk soln spiking (ml)	CAN Int 1 spiking (ul)	CAN Int 2 spiking (ul)	EPA551 Int 1 spiking (ul)	EPA551 Int 2 spiking (ul)
100	25	500		250	
50	12.5	250		125	
20	5	100		50	
10	2.5	50			250
5	1.25		250		125
2	0.5		100		50
1	0.25		50		25
0	0		0		0

## B5 Apparatus

In addition to general laboratory glassware, the following are required.

B5.1 Analytical balance capable of weighing to 0.0001g.

B5.2 A horizontal shaker e.g. IKA Labortechnik HS501 digital.

B5.3 GCMS/MS equipment

GC: Agilent 6890

Columns: J&W DB-624, 30 m x 0.25 mm diameter, 1.4 µm bonded

film of polyphenylmethylsilicone  
Supelco non-polar pre-column, 0.53 mm ID

Carrier gas: Helium, constant flow at 1.5 ml per minute.

Injection volume: 2 µl (Split split-less injection mode) with double gooseneck direct liner, 2mm ID deactivated.

Temperature programmes:

Oven: Initial temperature at 34 °C for 2.5 minutes, then 20 °C per minute to 220 °C and hold for 0 minutes.

Injector: 150 °C.

Mass Spectrometer: Agilent 5973

MS Quad Temperature: 150 °C

MS Quad Temperature: 230 °C

Target Compound	R.T.	Ions monitored m/z	
		Quan ion	Confirm Ion
Flurobenzene (Internal Standard)	5.6	96	
Cyanogen chloride	1.8	61	63
Chloroacetonitrile	6.3	48	75
Trichloroacetonitrile	5.6	108	110

## B6 Sample collection and storage

Samples should be collected in glass vials of 60 ml capacity with plastic screw tops fitted with polytetrafluoroethylene or polytetrafluoroethylene-faced liners. Prior to use, the bottles should be cleaned with a suitable cleaning agent (for example Decon 90). After cleaning, the bottles should be rinsed with water and then allowed to drain, before being dried. Add 6 mg of ammonium chloride to each bottle prior to sampling. Samples should be analysed as soon as possible following collection and preservation. If storage of samples is unavoidable, samples should be stored in a refrigerator and kept at below 4°C. Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

## B7 Analytical procedure

B7.1 Remove samples from storage and allow them to equilibrate to room temperature and adjust the volume in the vial to 50 ml.

B7.2 For each batch of samples weight out  $50 \pm 0.5$  ml of Rathburns water for a Analytical Quality Control blank and spike sample.

B7.3 Adjust the pH to 4.5-5 with 10% HCl acid

B7.4 Check pH using 3-5.5 pH papers

B4..5 Inject a 20ul aliquot of the internal standard spiking solution (B4.7.3).

B4..6. Add 64ul of NDBP spiking solution (B4.7.6) to the AQC spike sample.

B4..7. Add 15g of Sodium Chloride to each sample

B4..8. Add 2 ml of MTBE to each sample.

B4..9. Put on shaker for 1 hour at 200rpm

B4..10. Remove the sample from the shaker, allow the water and MTBE phases to separate (approximately two minutes) and remove the upper solvent layer using a glass Pasteur pipette into a 2 ml vial. Ensure as little water as possible has carried over onto the bottom of the autosampler vial. If a dual phase appears in the vial, the bottom layer can be removed and discarded by using a Pasteur pipet.

B4..11. Place the vial in a freezer overnight to freeze out any water present in the extract.

B4..12. Remove an aliquot of the extract and transfer to a vial with a 100 ul insert.

B4.14 Sample Analysis and Identification

B4.15 GCMS conditions are described in Section B5.3. Tune the mass spectrometer and mass calibrate the system daily.

B4.16 Inject 2  $\mu$ L of the sample extract and record the resulting peak areas using the data system. If the peak area exceeds the linear range of the calibration curve, the final extract (from the original frozen extract) should be diluted with MTBE and reanalyzed.

## **B8 Calculation of results**

A calibration graph of the ratio of the respective peak area or height of the NDBP of interest to the peak area or height of the corresponding deuterated internal standard should be constructed against the mass of deuterated internal standard injected. The original sample concentration should be calculated from the graph taking into account the volume of sample that is extracted (A7.2.1) and any dilutions that may have been used (for example, sections A7.4.1 and A7.7.1, note i).

The respective peak area or height of each specific NDBP should be measured. For each NDBP, the response ratio should then be calculated.

$$\text{Response ratio} = \frac{\text{peak area or height (SS)}}{\text{peak area or height (DIS)}}$$

where:

peak area or height (SS) is the peak area or height of the specific NDBP,  
 peak area or height (DIS) is the peak area or height of the corresponding deuterated internal standard.

Plot the response ratio for the specific NDBP against the concentration of the specific NDBP in the calibration standards. From the plotted calibration curve, calculate the slope and intercept using linear regression.

Determining the corresponding response ratios in the unknown sample (RRu) and blank sample (RRb) enables the concentration of each NDBP,  $C_s$ , to be calculated.

$$C_s = ((RRu - RRb) - \text{intercept}) / \text{Slope}$$

## **B9 Additional reading material**

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## APPENDIX C: Summary of the sampled water supply systems

**Table C.1 Summary of the characteristics of the 20 participating water supply systems. Elevated bromide was considered to be > 150 µg/l and elevated total THMs was considered to be > 50 µg/l historically. 'O3' indicated pre-ozonation. Non-chloraminated distribution networks all applied chlorine. For full raw water quality parameter data, refer to the Supplementary Data Files.**

Code	Source	Treatment Processes	Elevated Br?	O3?	Chloramination?	Elevated THMs?
A	Lowland eutrophic reservoir	Microstrainers, pre-ozonation, clarification, RGF, post-ozone, GAC adsorption, chlorination, ammoniation, plumbosolvency control	N	Y	Y	N
B	Lowland eutrophic reservoir	Micro-strainer, pre-ozonation, pH correction, Clarification (DAF), RGF, Post Ozonation, GAC adsorption, chlorination, plumbosolvency control	Y	Y	N	N
C	Lowland eutrophic reservoir	Pre-ozonation, clarification, RGF, post-ozone, GAC adsorption, chlorination, ammoniation, plumbosolvency control	N	Y	Y	N
D	Groundwater	UV irradiation, chlorination, plumbosolvency control	N	N	N	N
E	Lowland short retention reservoir (no algae)	pre-O3, pH adjustment, coagulant dosing, clarification, intermediate O3, RGF, GAC, chlorine, fluoride	Y	Y	N	Y
F	Lowland eutrophic reservoir	coagulation, flocculation, DAF, RGF, fluoride, GAC, chlorine	N	N	N	Y
G	Lowland source, no risk factors	biological filtration, polymer dosed, sedimentation, RGF, ozone, GAC, chlorine	N	Y	N	N
H	Groundwater	nitrate removal, disinfection, service reservoir	Y	N	Y	N

(the table continues on the following page)

I	Groundwater	disinfection, phosphoric acid, service reservoir	N	N	Y	N
J	Groundwater	two boreholes; filtration, iron and manganese removal, disinfection	Y	N	N	N
K	Upland source, no risk factors	ferric dosing, clarification, RGF, chlorine	N	N	N	Y
L	Upland	pH correction, pre-chlorination for Mn oxidation, RGF, membrane microfiltration, free chlorine, phosphate dosing	N	N	N	Y
M	Upland	Membrane microfiltration, free chlorine	N	N	N	N
N	Lowland river	pH correction, alum dosing, clarification, GAC-RGF, chlorine gas, RGF contactors for Mn removal, chlorine gas, de-chlorination with SO <sub>2</sub>	N	N	N	N
O	Lowland water body	pH correction, pre-oxidation with O <sub>3</sub> , coagulation, clarification, RGF, O <sub>3</sub> , GAC, superchlorination, dechlorination, phosphate dosing; some rechlorination in the network	N	Y	N	N
P	Groundwater	GAC, superchlorination, dechlorination, phosphate dosing	N	N	N	N
Q	Groundwater	pre-chlorination, RGF, sodium bisulfite, GAC, chlorination; long distribution network	Y	N	N	N
R	Upland river	pH correction, alum coagulation, clarification, RGF, GAC, chlorination, chloramination	N	N	Y	N
S	Upland reservoir	Clarification (2 streams - DAF and Centrifloc) with ferric sulphate, lime addition for Mn oxidation, RGF, lime for pH correction, ortho-P, chlorine gas, ammoniation in part of the network	N	N	Y	Y
T	Groundwater	Aeration, KMnO <sub>4</sub> , microfiltration, superchlorination with hypo, long storage, small network (< 1 km)	N	N	N	N

**APPENDIX D: Selected N-DBP survey data from other countries and regions**

**Table D.1 US N-DBP data from 16 water treatment works (Krasner *et al.*, 2006).**

N-DBPs (µg/L)			
	Minimum	Median	Maximum
Haloacetamides (HAcAms)			
Chloroacetamide	ND	ND	0.5
Bromoacetamide	ND	ND	1.1
Dichloroacetamide	ND	1.3	5.6
Dibromoacetamide	ND	0.6	2.8
Trichloroacetamide	ND	0.3	1.1
Haloacetonitriles (HANs)			
Chloroacetonitrile	ND	ND	0.9
Bromoacetonitrile	ND	ND	0.2
Dichloroacetonitrile	ND	1	12.0
Bromochloroacetonitrile	ND	0.6	3.0
Dibromoacetonitrile	ND	0.2	2.0
Trichloroacetonitrile	ND	ND	0.4
Dibromochloroacetonitrile	ND	ND	0.6
Halonitromethanes (HNMs)			
Chloronitromethane	ND	ND	0.8
Bromonitromethane	ND	ND	0.3
Dichloronitromethane	ND	ND	0.7
Bromochloronitromethane	ND	ND	<3.0
Dibromonitromethane	ND	ND	0.6
Trichloronitromethane	ND	0.2	2.0
Bromodichloronitromethane	ND	0.3	3.0
Dibromochloronitromethane	ND	ND	3.0
Bromopicrin	ND	ND	5.0

ND = not detected

**Table D.2 Canadian N-DBP data from Williams *et al.* (1995).**

Disinfectant	DCAN (µg/L)				TCNM (µg/L)			
	Winter		Summer		Winter		Summer	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Chlorine - Chlorine	2.1	0.1-12.6	2.7	<0.1-9.0	0.2	<0.1-1.2	0.3	<0.1-2.5
Chlorine - Chloramine	1.5	<0.1-0.7	2.6	0.4-11.2	0.2	<0.1-0.9	0.2	<0.1-0.9
Ozone – Chlorine/Chloramine	0.8	0.2-1.3	2.5	0.3-4.1	0.2	<0.1-0.3	1.2	<0.1-2.2

**Table D.3 Australian N-DBP data from Simpson and Hayes (1998).**

Location	Source	Treatment	Disinfectant	N-DBPs (µg/L)		
				HANs	TCNM	CNCI
Adelaide	3 Surface	Alum flocculation, sedimentation, DAF	Chlorine	3-36	<0.01-0.1	<0.8-6
Brisbane	2 Surface	Alum flocculation, sedimentation, sand filtration	Chloramines	3-16	0.3-1	3-8
Ballarat	3 Surface	No filtration	2 Chloramines and 1 Chlorine	1-29	<0.01-0.4	1-10
Newcastle	2 Surface	Alum flocculation, direct filtration	Chlorine	0.2-29	<0.01-1	<0.8-7
Melbourne	2 Surface	No filtration	Chlorine	2-7	0.1-0.3	1-3
Sydney	2 Surface	Alum flocculation, filtration	1 Chloramines and 1 Chlorine	3-11	0.1-0.3	<0.8-7
Perth	1 Surface and 1 Ground	Groundwater: pre-Cl <sub>2</sub> , alum flocculation/polyelectrolyte, filtration Surface water: no filtration	Chlorine	1-24	<0.01-0.3	2-6

**Table D.4 Scottish N-DBP data from Parsons *et al.* (2009).**

Source	Finished Water Quality			Treatment	Disinfection	N-DBPs (µg/L)				
	NPOC (mg/L)	SUVA (L/mg·m)	bromide (µg/L)			DCAN	BCAN	DBAN	TCAN	TCNM
Upland reservoir	2.1-2.4	0.8-1.6	0-36	Sand Filtration, activated carbon	Chlorine	0.2-0.4	0-0.2	0.1-1.0	ND	0-0.1
Reservoir	3.5-4.1	1.9-2.3	38-55	Coagulation, lime softening, pressure filtration	Chloramines	1.2-1.4	ND	0-0.2	ND	ND
River	2.3-3.5	1.3-1.6	41-130	Coagulation, lime softening, sedimentation, rapid gravity filtration	Chloramines	0.3-0.9	0.3-0.5	0.1-0.2	ND	0.1-0.2
River	1.5-3.3	1.2-1.9	152-222	Coagulation, lime softening, rapid gravity filtration	Chlorine	0.1-0.2	1.4-1.5	0.2-1.2	ND	0-0.1
River	1.5-3.3	0.7-1.6	33-74	Coagulation, lime softening, rapid gravity filtration	Chloramines	0.3-0.5	0.1-0.2	0.1-0.6	ND	0-0.1
Reservoir	2.7-4.0	1.9-2.2	25-49	Ozonation, rapid gravity filtration	Chloramines	1.4-2.1	0.1-0.2	0-0.2	0.1	0-0.2
Upland reservoir	3.1-4.3	1.5-1.9	24-54	Coagulation, lime softening, rapid gravity filtration	Chlorine	0.6-1.0	0.2-0.5	0.2-0.9	0.1	0.2-0.3