



Evaluation of the implications and efficacy of proposed changes to haloacetic acid drinking water regulation

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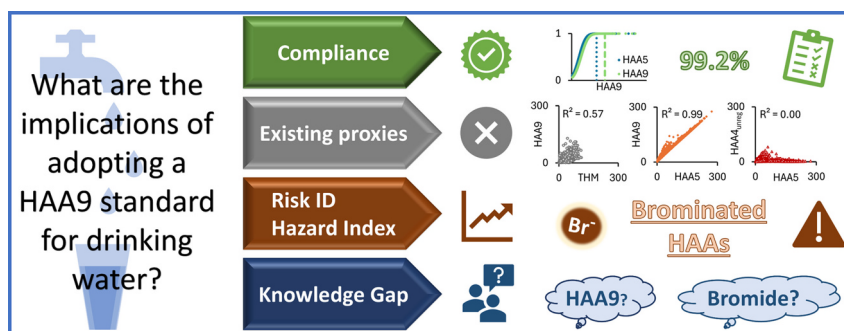
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HIGHLIGHTS

- Collation of UK haloacetic acid data demonstrates likely compliance with HAA9.
- Use of THMs and HAA5 as proxies for unregulated HAA4 requires reassessment.
- Bromine substitution of THMs does not map to that of HAAs, restricting predictions.
- Increasing ratio of bromide to organic matter at chlorination enhances risk.
- Brominated HAAs dominate the relative hazard index in drinking waters.

GRAPHICAL ABSTRACT



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ABSTRACT

As an increasing number of countries move towards regulatory control of haloacetic acids (HAAs) in drinking water, there is a need to better understand the current levels, and areas where compliance will be more challenging. This study collated the available UK data and assessed the implications of adopting a standard for five HAAs (HAA5, as implemented in regions including the EU, the US and Scotland) or expanding regulation to include all nine chlorinated and brominated HAAs (HAA9, not yet implemented but proposed for England and Wales and considered in the US). In treated water samples, high levels of compliance were reported, with 99.7% of samples below the proposed standard of 80 µg/L for HAA9 and 99.2% within that of 60 µg/L for HAA5. The suitability of HAA5 as a surrogate for HAA9 was assessed and a good linear correlation between them observed in treated water ($R^2 = 0.94$). However, correlation between HAA5 and the unregulated brominated HAAs was poor ($R^2 = 0.03$), and consequently only information about the currently unregulated HAAs can identify where HAA9 compliance will diverge from that of regulated DBPs. Notably, while within this study compliance with proposed legislation was determined primarily by the formation of chlorinated HAAs, when a risk-based approach was taken brominated HAAs were the dominant influence. Consequently, this work highlighted that the ratio between bromide and carbon is key for the controlling the DBP risk from chlorinated water, and an improved understanding of the levels of brominated HAAs is crucial for identifying this risk.

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1. Introduction

Disinfection by-products (DBPs) are formed during the chlorination of drinking water and are concerning because of their potential adverse effects on health. DBPs can incorporate bromide from source waters as well as chlorine used for disinfection, with the resulting brominated DBPs (Br-DBPs) being more toxic than their chlorinated equivalents (Richardson et al., 2007). To minimise the exposure of drinking water consumers to this risk, DBPs are regulated in many jurisdictions, and the World Health Organisation (WHO) provides Guideline Values (GVs) for some individual DBPs (WHO, 2022). Most DBP regulations cover four brominated and chlorinated trihalomethanes (THM4) to a level of 100 µg/L (EU, UK) or 80 µg/L (US, Singapore), but increasingly haloacetic acids (HAAs) are also included (Table 1). For example, China, Japan and Australia regulate only the chlorinated HAAs while the US, EU and Scotland have extended this to include two brominated HAAs. These jurisdictions set a combined limit of 60 µg/L for five of the nine chlorinated and brominated HAAs - monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), and trichloroacetic acid (TCAA) - collectively referred to as HAA5. Notably, the four higher molecular weight brominated species - bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA) - are currently excluded from any regulatory control. In this paper, these are referred to as unregulated HAA4, acknowledging that additional non-regulated iodo-HAAs also exist. Originally, the exclusion of the unregulated HAA4 was due to analytical challenges and the supposition that HAA5 is a good enough proxy for the HAA9 (Furst, 2025; Samson et al., 2017), but improvements in analytical methodology have now made HAA9 testing more widely available and such assumptions are less acceptable (Grundy et al., 2024).

However, the exclusion of the larger brominated HAAs from standards is under review. New regulations for all nine brominated and chlorinated HAAs are now being considered in countries like England and Wales, which currently have no HAA regulation (DWI, 2024a), and

the potential for existing HAA5 legislation to move to HAA9 is under consideration in the US (Samson and Seidel, 2022). The proposal to measure HAA9 and move away from HAA5 raises questions about how such a change may impact current thinking. In particular, the inclusion of additional brominated HAAs raises the question of whether these species are important, especially in bromide rich waters. The WHO currently provide guideline values for only three of the chlorinated HAAs (MCAA = 20 µg/L, DCAA = 50 µg/L and TCAA = 200 µg/L), limiting the ability to assess the impact of the change to HAA9. However, recent work (Bull and Bevan, 2024) has proposed levels for the other HAAs with values of 333 µg/L for MBAA and 3 µg/L for DBAA within the currently regulated HAA5 as well as 100 µg/L for BCAA, 73 µg/L for BDCAA, 50 µg/L for DBCAA and 1 µg/L for TBAA for the unregulated HAA4 (Table 1). This data can be utilised to consider the risk associated with each individual HAA using the concept of Relative Hazard Index, where the ratio of the actual concentration to the guideline value is calculated (Rosenblum et al., 2024; WHO, 2022). Previous use of the concept has shown that the risk associated with DBPs comes predominantly through the Br-HAAs (Losty, 2019) and provides a useful lens to assess the potential risk due to the unregulated HAA4. While the values proposed by Bull and Bevan (2024) need further investigation before potential adoption, they do indicate that relatively low mass concentrations of these species could pose an increased risk.

Previous surveys concerning HAAs have presented mixed views, with the earliest reported survey in the UK identifying relatively high mean HAA concentrations ranging from 35 µg/L to 95 µg/L across three water supply zones (Malliarou et al., 2005). Importantly, this study only included MBAA, DCAA, BCAA, DBAA, TCAA and BDCAA as analytical challenges meant MCAA, DBCAA and TBAA were not included. Even given this exclusion, six samples had levels above 200 µg/L. Significantly, this omission highlights the problems associated with the analytical technology available at the time, which is still used worldwide to monitor HAA5. It has been demonstrated to consistently underestimate the larger brominated HAAs (Grundy et al., 2024), contributing to the current knowledge gap regarding levels of the unregulated HAA4. A

Table 1
Summary of carbonaceous DBPs, guideline values and regulations.

Compound name	Acronym	WHO GV, µg/ L ^a	Proposed GV, Bull et al., µg/L ^b	Regulation China, µg/L ^c	Regulation Japan, µg/L ^d	Guidelines Australia, µg/ L ^e	Guidelines Canada, µg/ L ^f	Regulations Scotland, EU ^g , US ^h , Singapore ⁱ	Regulation/ Proposed England and Wales, µg/L ^j
Monochloroacetic acid	MCAA	20	–	–	20	150	HAA5	HAA5	Proposed HAA9
Dichloroacetic acid	DCAA	50	–	50	30	100	<80 µg/L	<60 µg/L	<80 µg/L
Trichloroacetic acid	TCAA	200	–	100	30	100			
Monobromoacetic acid	MBAA	–	333	–	–	–			
Dibromoacetic acid	DBAA	–	3	–	–	–			
Bromochloroacetic acid	BCAA	–	100	–	–	–	–	–	
Bromodichloroacetic acid	BDCAA	–	73	–	–	–	–	–	
Dibromochloroacetic acid	DBCAA	–	50	–	–	–	–	–	
Tribromoacetic acid	TBAA	–	1	–	–	–	–	–	
Chloroform (Trichloromethane)	TCM	300	–	THM4 <1000 µg/L	THM4 <100 µg/L	THM4 <250 µg/L	THM4 <100 µg/L	THM4 <100 µg/L	THM4 <100 µg/L
Bromodichloromethane	BDCM	60	–					Scotland, EU <80 µg/L	
Dibromochloromethane	DBCM	100	–					US, Singapore	
Bromoform (Tribromomethane)	TBM	100	–						

^a WHO (2022).

^b Bull and Bevan (2024).

^c USDA (2023).

^d He et al. (2018).

^e NHMRC (2025).

^f Health Canada (2014).

^g Directive (EU) 2020/2184 (2020).

^h US EPA (2016).

ⁱ NAVFAC (2016).

^j DWI (2024b).

need therefore exists for a more recent survey of HAA9, utilising the improved analytical techniques now available, to ensure that an accurate picture of current levels is available for decision makers.

Further surveys in the UK reported HAA9 levels that were substantially lower, with a median of 12.5 µg/L across 20 sites (DWI, 2011) and a median value of 0.3 µg/L reported in a groundwater and 20.6 µg/L in an upland water source (Zhang et al., 2010). Nationwide survey data from the USA revealed median levels of 16 µg/L for HAA5 and 22 µg/L for HAA9 (Samson and Seidel, 2022). Occurrence studies from Poland and France indicate that high levels of compliance with the limit of 60 µg/L for HAA5 will be achieved with average values of 0.9–14.5 µg/L and 1.1–4.0 µg/L respectively (Louyer et al., 2025; Ochmańska et al., 2025). Overall, these surveys provide reassurance that HAA9 levels are likely to be predominantly within the proposed mass concentration targets. However, brominated HAAs remain of concern given they have historically been under-reported (due to analytical challenges) and the available data remains limited. This gap may be consequential as changes in climate and population increase within the UK are proposed to increase bromide levels in source waters (Leri et al., 2024).

In part, this historic paucity of HAA9 data reflects the belief that THM4 and/or HAA5 act as an effective proxy for the unregulated four Br-HAAs, and prior research has attempted to predict the concentration of the four unregulated species from THM4 and HAA5 data (Roberts et al., 2002; Samson et al., 2017). However, as HAAs and THMs are reported to form from different precursor organic matter and reaction pathways, and correlations between their formation levels are highly source dependent, employing THM4 data to predict HAA9 is often unreliable (Liang and Singer, 2003; Uyak et al., 2014). Similarly, bromine incorporation into DBPs, which disproportionately influences formation of the unregulated HAA4, is known to depend on the specific nature of the organic matter present as well as bromide levels (Liang and Singer, 2003; Zhang et al., 2011). Consequently, as much existing data worldwide has been for HAA5 and employed older analytical techniques lacking robustness for Br-HAAs, it is an improved understanding of the formation of the unregulated HAA4 which is most pressing.

Therefore the aim of this study was to elucidate how the adoption of an HAA9 standard changes our thinking about DBP compliance compared to that established based on levels of THM4 and HAA5. To achieve this, a survey of HAA9 data from drinking water systems was compiled from sources across the UK and correlations were drawn between the levels of HAA9, HAA5 and the unregulated HAA4. The data was analysed to identify where formation of the unregulated HAA4 diverges from HAA5 and whether proposals to identify these high-risk scenarios can be made. In addition, the study provides an assessment of how HAA data could be used for monitoring potential increases in risk or to improve water treatment decisions.

2. Methodological approach

2.1. Data classification

Data values were classified in terms of the source water types, treatment type, treatment stage and disinfection process. Source waters were classified as groundwaters (GW) (fed by boreholes, wells, and springs), surface waters (SW) (from rivers and reservoirs) and mixed waters (MX = GW + SW). Further classification was assigned by catchment type as either upland (UL) or lowland (LL) waters to reflect known difference in the organic make up and background water characteristics (Bougeard et al., 2010; Valdivia-Garcia et al., 2019).

The data provided covered a range of organic removal technologies and was labelled accordingly as either coagulation, ion exchange, nanofiltration (NF) membrane, or minimal treatment. In addition, different disinfection approaches were covered and sub-categorised based on where chlorination was used: Chlorine (Cl Cl – both primary and residual disinfection), Chlorine/chloramine (Cl ClAm – primary disinfection by chlorination – followed by stabilisation to chloramine),

UV/chlorine (UV Cl – residual disinfection by chlorination) and Membrane/chlorine (NF Cl – residual disinfection by chlorination). The data also covered several stages within the water treatment process and, to ensure comparability, sub-categories were created to isolate different formation patterns:

Raw – untreated source water, prior to treatment or chlorination
Raw Formation Potential (FP) – raw water where the potential for formation of DBPs is assessed by adding chlorine in laboratory conditions, generally with a significant excess of chlorine to assess the potential maximum DBP formation
Water Treatment Works (WTW) Internal – samples from within the treatment plant, at different stages within the process, which had been exposed to chlorine
WTW Miscellaneous – samples where the treatment stage within the WTW is unclear, and includes pilot plants and investigations, and as such is unlikely to be representative

Treated Water – combined from WTW final, distribution and tap:

WTW Final – samples from the outlet of the plant
Distribution – samples from the distribution zone, including storage reservoirs or tanks
Tap – samples taken at customer tap

Bromide data were only available for a limited subset of the samples with HAA9 data (Supplementary material Table S2), but where available the source types with over 100 µg/L bromide were classified for the purposes of this study as high bromide. This level is within the normal range of bromide in freshwater (10 to 500 µg/L) and is considered to be the level above which Br-DBPs present a significant risk (Leri et al., 2024; Zhang et al., 2011). Importantly, the bromide levels reported for treated waters were from samples taken after disinfection and so the reported bromide concentrations represented the unreacted bromide levels, hence under-reporting the levels at the point of chlorination. The bromide analysis was performed on samples in separate containers (different preservatives) to those used for the measurement of HAA9, but samples had the same sample identifier assigned and were taken concurrently and at the same stage of the treatment process in each case.

2.2. Data analysis

2.2.1. Bromine Substitution Factor

Bromine Substitution Factor (BSF) was calculated as moles of bromine per mole of halogen present in DBPs formed, with values therefore ranging from 0 to 1 (fully chlorinated to fully brominated).

2.2.2. Box and whisker plots

The box represents the quartile range, with the whiskers extending to the data point equal to 1.5 times the interquartile range. The median is marked by a horizontal line across the box and the mean by a cross.

2.2.3. Model for unregulated HAA4

Models were evaluated which predicted the molar concentration of the unregulated HAA4 from THM4 and HAA5 (Roberts et al., 2002; Samson et al., 2017; US EPA, 2016):

$$[BCAA] = 0.5 \frac{DCAA([BDCM] + [DBC])}{[TCM]} \quad (1)$$

$$[BDCAA] = \frac{[TCAA][BDCM]}{[TCM]} \quad (2)$$

$$[DBC] = \frac{[TCAA][DBC]}{[TCM]} \quad (3)$$

$$[TBAA] = \frac{[TCAA][TBM]}{[TCM]} \quad (4)$$

2.2.4. Relative Hazard Index

The potential for harm from the DBPs formed was assessed using the Relative Hazard Index (RHI):

$$\text{Relative Hazard Index} = \sum \frac{\text{Concentration DBP } (\mu\text{g/L})}{\text{Guideline Value for DBP } (\mu\text{g/L})} \quad (5)$$

Guideline Values used are those published by the WHO (WHO, 2022) or derived from toxicological data from several sources and collated to determine a health-based guidance value (Bull and Bevan, 2024).

2.3. DBP analytical methodology

For the data utilised in this study, all HAA9 samples were preserved with ammonium chloride and analyses were reported to have been conducted using Liquid Chromatography Mass Spectrometry (LC-MS/MS) based analytical methods. The majority (93%) of samples were analysed at a UKAS (ISO:17025) accredited laboratory, with the remainder reported from laboratories where the method had been validated in-house. Consequently, the analytical methods used will have been assessed for precision, accuracy and reportable range and ongoing quality will have been appropriately assured, in line with the requirements of UKAS accreditation and UK Drinking Water Testing Standards (DWTS) (UKAS, 2023). The analytical methods utilised for THM or bromide analysis were not reported but it was determined that the samples were collected concurrently to those for HAA9, in other words taken at the same time and treatment stage, but with different sample containers and preservatives, as appropriate.

3. Results and discussion

3.1. HAA9 prevalence

3.1.1. All sample types

Raw water samples have very low HAA9 concentrations (median 1.8 $\mu\text{g/L}$), while raw water FP samples formed much higher levels (median 147.5 $\mu\text{g/L}$), reflecting the absence and excess of chlorine respectively. Note that the low levels of HAAs within raw waters is likely to be an artefact of the statistical treatment of results below the reporting limit, which are reported at half the limit of detection of the method. Within the treatment works, HAA9 levels decreased prior to the final outlet with median levels of 49.4, 22.6, 22.1 and 13.2 $\mu\text{g/L}$ for the WTW internal, WTW final, distribution and tap sampling points respectively (Fig. 1a). The levels observed in the treated samples (WTW Final, distribution, tap) demonstrate a decrease in HAA levels over time, after the storage tanks and reservoirs where most of the distribution samples were collected. This is congruent with previous studies, where decreases in HAA levels during distribution were observed and attributed to the degradation of the HAAs (Dong et al., 2023).

3.1.2. Treated samples by source type

The median values of HAA9 in treated waters were 9.9, 13.7, 17.3, 34.6 and 24.0 $\mu\text{g/L}$ for GW, MX LL, MX UL, SW LL and SW UL respectively (Fig. 1b). While the HAA9 levels were lower than other water types, groundwater derived samples had a larger range of values than the mixed lowland and upland sources, with standard deviations 13.5 and 5.1 and 9.7 $\mu\text{g/L}$ respectively. This was attributed to the minimal treatment of many groundwaters which reduced consistency in the levels of organic matter present for these water sources. The surface water data reported the greatest variation in HAA9 with standard deviations of 15.1 and 13.1 $\mu\text{g/L}$ for lowland and upland sources.

The reported data is consistent with previous surveys in both the UK and US (DWI, 2009; Samson et al., 2017) and is aligned to the fact that

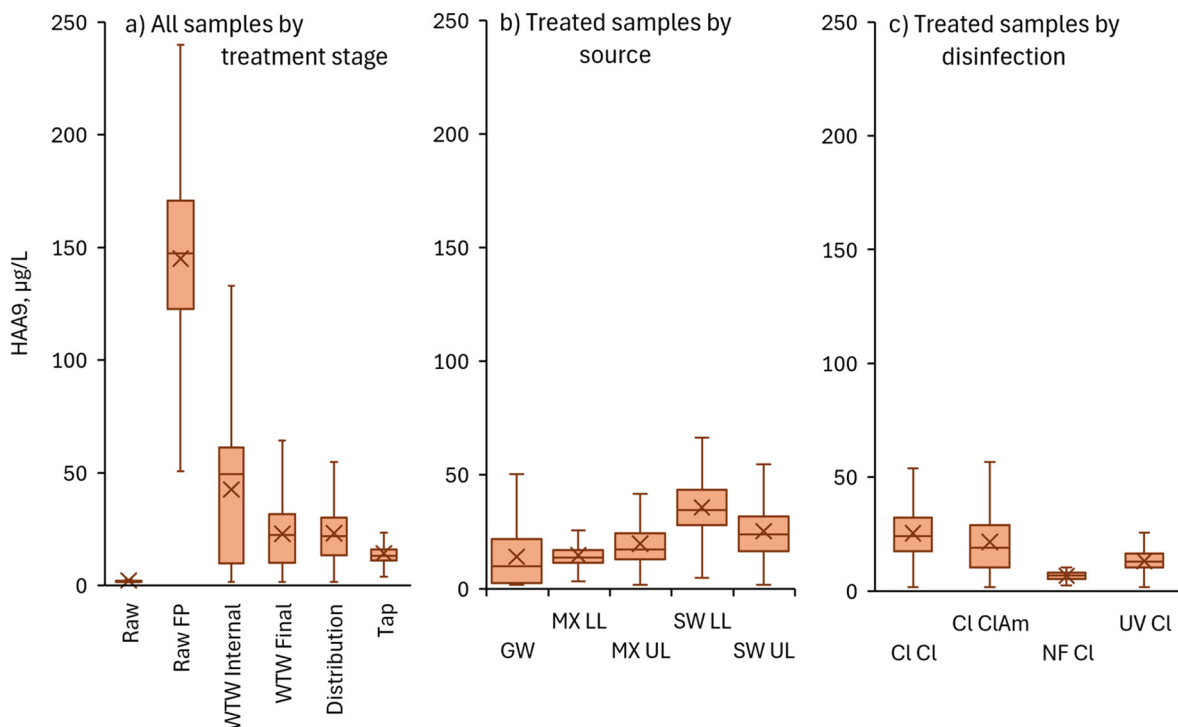


Fig. 1. Distribution of measured HAA9 by a) all samples by treatment stage b) treated samples by source type c) treated samples by disinfection process (FP – formation potential, WTW – water treatment works, GW – groundwater, MX – mixed, LL - lowland, UL - upland, SW – surface water, Cl Cl – primary and residual chlorine, Cl ClAm, primary chlorination, residual chloramination, NF Cl – nanofiltration membrane, residual chlorine, UV Cl – ultraviolet disinfection, residual chlorine).

surface waters typically have higher organic matter concentrations than other water types. In contrast to the previous UK study, the upland surface source waters showed similar HAA9 average values to those in the lowland equivalent, despite upland sources generally containing higher levels of organic matter in the raw water (Metcalf et al., 2015). However, a survey of fourteen UK waters revealed similar findings and showed that the recalcitrant nature of the organic matter in lowland sites meant that the final water dissolved organic carbon (DOC) was often higher than the equivalent in upland waters (Losty, 2019). To illustrate, they reported final non-purgeable organic carbon (NPOC) of less than 2 mg/L for the upland sites but values between 1 and 4 mg/L for the lowland sites. However, the average chlorine reactivity of the organic compounds in the lowland sites was 30.9 $\mu\text{g}/\text{mg}$ compared to 76.9 $\mu\text{g}/\text{mg}$ for the upland sites, such that the two features balanced out to form roughly similar levels of DBPs.

3.1.3. Treated samples by disinfection approach

Comparison of the data as a function of disinfection practice revealed similar median HAA9 levels of 24.2 $\mu\text{g}/\text{L}$ and 19.1 $\mu\text{g}/\text{L}$ respectively for water sources where chlorine or chloramine was used as the residual disinfectant, with chlorine as the primary disinfectant in both cases (Fig. 1c). This links to prior research demonstrating that cytotoxicity is not influenced by using residual chloramine (Lau et al., 2024). Consequently, replacing the residual disinfectant with chloramine will not be a reliable solution to reduce HAA levels, despite the evidence that when used as a primary disinfectant chloramine significantly reduces HAA formation (Pan et al., 2023). By contrast, in sites where chlorine was only used for residual disinfection (UV Cl and NF Cl), the HAA9 concentrations had median values of 13.0 and 6.8 $\mu\text{g}/\text{L}$, reflecting the lower levels of chlorine applied and the low levels of organic matter in the water prior to disinfection (Neale et al., 2025).

3.1.4. Assessment against proposed regulation

Plotting cumulative probability of the HAA9 concentrations in treated water data (WTW final, distribution, tap) demonstrated that high levels of compliance with proposed HAA regulations is expected (Fig. 2a). For a limit of 60 $\mu\text{g}/\text{L}$ for HAA5, only 0.8% of treated samples exceeded that level with the 99th percentile at 58.1 $\mu\text{g}/\text{L}$. Likewise, for HAA9, if a proposed target of 80 $\mu\text{g}/\text{L}$ was envisaged, then the proportion of samples meeting this was higher, with 0.3% exceeding the target and the 99th percentile at 65.6 $\mu\text{g}/\text{L}$. When solely customer tap samples

were considered, only two samples (0.2%) exceeded the target for HAA5 and no exceedances (0%) were observed for HAA9 (from a smaller data set of 1319 compared to 13,079 treated samples). However, reported regulatory monitoring data for THM4 in 2024 showed there were no failures among the 18,798 samples in England, Wales and Scotland (DWI, 2024b; DWQR, 2024). This indicates that HAAs are a higher risk of non-compliance than existing DBPs. This is consistent with the Drinking Water Quality Regulators (DWQR) report on HAA compliance in Scotland which identified 12 HAA5 samples over the standard of 60 $\mu\text{g}/\text{L}$ and a compliance rate of 99.74%, compared to 100% compliance for THM4 (DWQR, 2024).

Comparison to similar data from the United States, which utilised the Unregulated Contaminant Monitoring Rule 4 (UCMR4) and state managed compliance data (Samson and Seidel, 2022), showed a shallower increase was observed in US data demonstrating that levels are generally higher in the US (Fig. 2b). This is reflected in higher levels of non-compliance in US water, with estimates that 1.7% of Public Water Systems have a HAA5 compliance value greater than the 60 $\mu\text{g}/\text{L}$ maximum contaminant level (MCL) (Samson and Seidel, 2022). It is proposed that the variation in HAA9 between the US and UK is due to the combination of higher chlorine concentrations used in the US, as seen in higher average residual chlorine in US drinking water, and the greater use of surface water sources in the US (Karim et al., 2020; Turner et al., 2021). Such surface sources often have higher organic content and therefore DBP formation, with both these factors reflected in the higher average THM4 levels of 33.6 $\mu\text{g}/\text{L}$ in the US compared to 24.2 $\mu\text{g}/\text{L}$ in the UK (Villanueva et al., 2023).

3.2. The use of HAA5 as a proxy for HAA9

The overall correlation between HAA5 and HAA9 had a linear regression coefficient (R^2) of over 0.99 and appears to offer the potential to use HAA5 as a proxy of HAA9 (Fig. 3a). However, HAA5 contributed 84% by weight of HAA9 for the samples here, and consequently the correlation is self-fulfilling. Analysis across the water types revealed that HAA5 represents more than 75% of the HAA9 value in 40% of the results related to groundwaters but 80% for surface waters, demonstrating the relationship is source dependent and HAA5 is less representative of HAA9 in groundwaters. Further, when HAA5 is used to correlate with solely the unregulated HAA4, no correlation is apparent (Fig. 3b), which demonstrates that HAA5 is not a suitable proxy for understanding levels

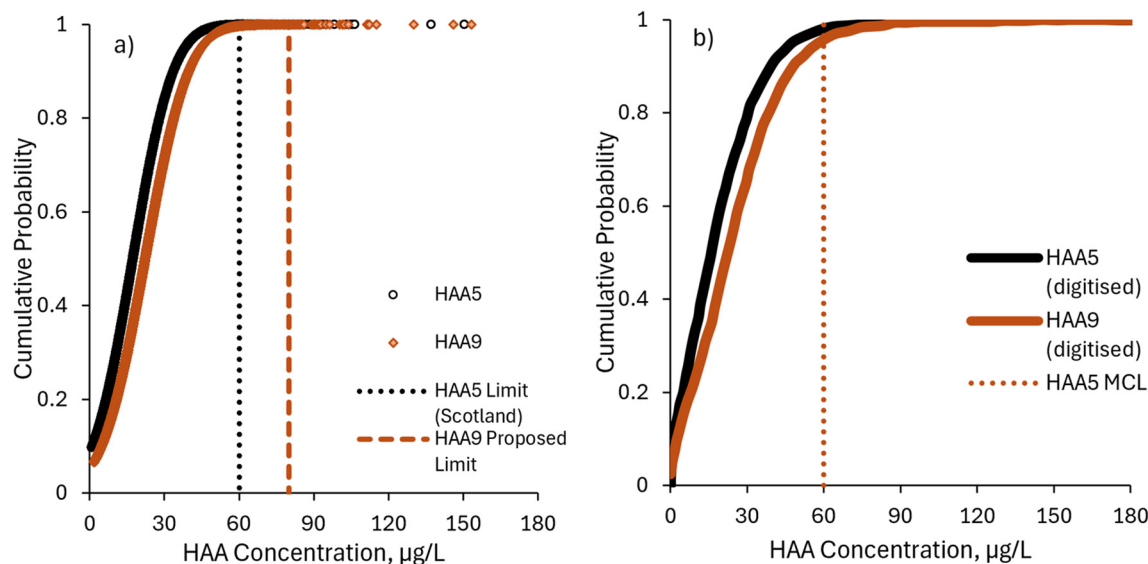


Fig. 2. Cumulative probability plot of HAA5 and HAA9 data from a) UK data from treated water b) digitised US UCMR4 data (reproduced from Samson and Seidel (2022) with permission), with vertical lines indicating current or proposed limits.

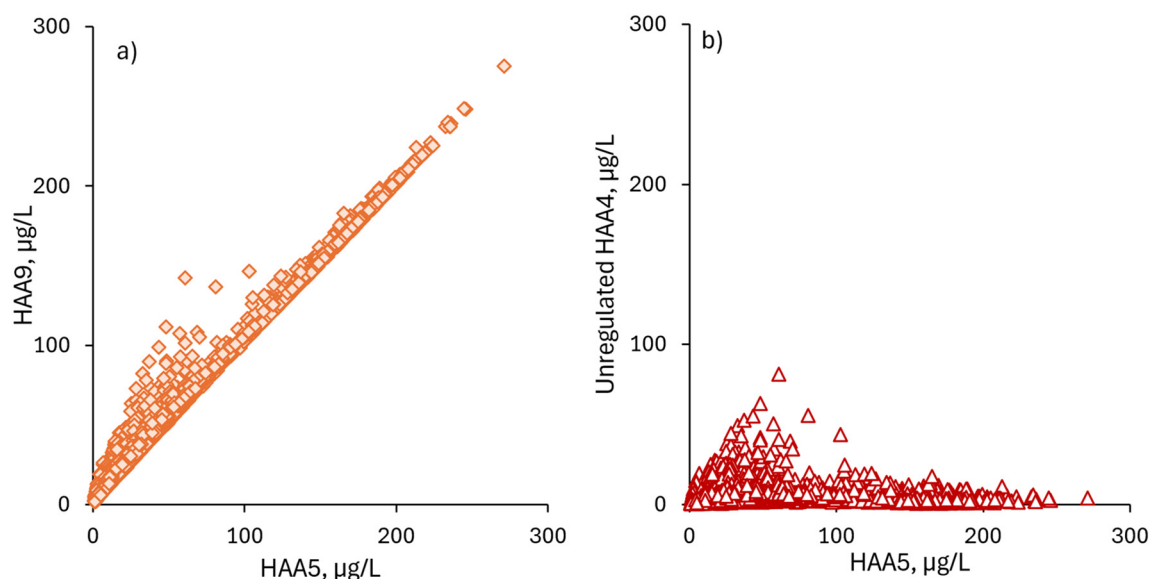


Fig. 3. Scatterplot comparison for all samples of a) HAA5 to HAA9 b) HAA5 to unregulated HAA4.

of the unregulated brominated HAA4.

Further analysis of the results in treated water established that the treatment type influenced the correlation (Fig. 4a–d). For waters treated by ion exchange, low levels of HAA4 were observed, consistent with the ability of ion exchange to remove some bromide from the water hence lowering levels of brominated HAAs formed (Soyluoglu et al., 2020). Supporting evidence is provided by comparing the high and low

bromide water data sets (Fig. 4e–f). Better correlations were observed between HAA5 and HAA4 for the higher as opposed to the lower bromide source water data, with linear correlation coefficients (R^2) of 0.72 and 0.00 respectively. No relationships were apparent for the other treatment categories (Fig. 4b–d) although clear divergence into two distinct categories of high and low HAA4 formation was observed for the minimal treatment group (Fig. 4b). This was proposed to be due to

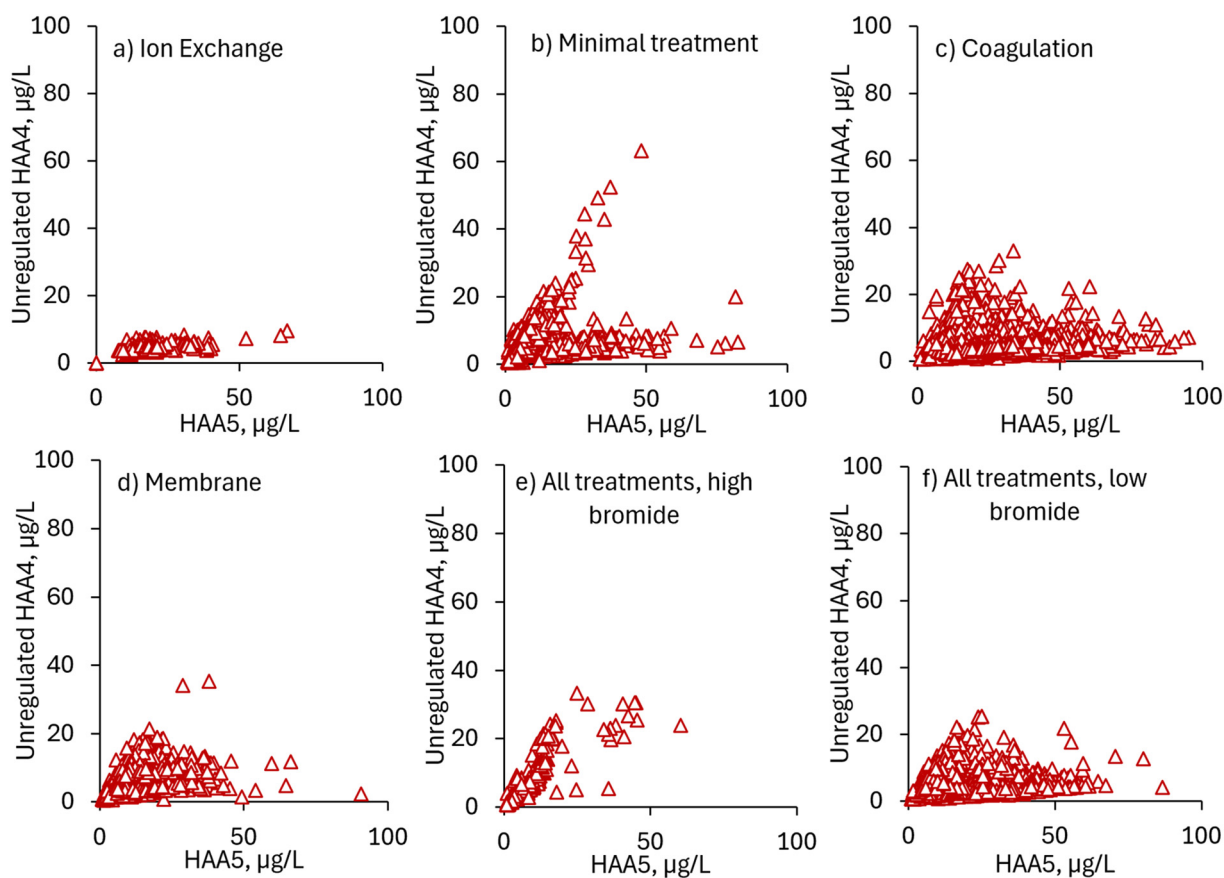


Fig. 4. Correlation between HAA5 and the unregulated HAA4 a) Ion exchange b) Minimal treatment c) Coagulation d) Membrane e) High bromide f) Low bromide (e and f all treatments, where bromide level available).

inconsistency in composition of the minimally treated source waters, both in organic matter and bromide levels, which are linked to local geology (Leri et al., 2024).

Organic matter has been demonstrated to preferentially incorporate bromine over chlorine, with this dependent on the molecular structure of the organic compounds and the relative concentration of bromide and chlorine (Westerhoff et al., 2004). Analysis of the individual HAA species formed at different parts of the treatment cycle reveal a gradual increase in the concentration of the unregulated Br-HAAs from 2.1% of total HAAs in raw FP waters to 33.4% in tap waters (Fig. 5). Raw water formation potentials were almost exclusively chlorinated HAAs and therefore were contained in the HAA5, congruent with the high levels of chlorine applied. Samples from the later treatment stages showed an increasing proportion of brominated HAA from 2.3% of total HAAs in the raw water FP to 24.5% in the WTW final samples and 65.9% in the tap samples. This occurs as the levels of chlorine decrease, resulting in a higher ratio of bromide to chlorine. However, when viewed through the lens of regulated versus unregulated species, the proportion of the Br-HAAs associated to the unregulated species decreased from 92.4% of Br-HAAs in the raw water FP to 80.9% in the distribution and 50.7% in the tap samples. This reflects the increasing proportion of the regulated DBAA within the brominated HAAs, posited to be due to the increasing proportion of hydrophilic content within the organic matter after treatment. This hydrophilic content has been associated with higher formation of di-halogenated HAAs in individual real-world sources and surrogates (Dejaeger et al., 2022), hence increased relative formation of DBAA occurs as the ratios of bromide to chlorine increase.

3.3. THMs as a guide for HAAs

Historically it had been hoped, but not proven, that THM levels could

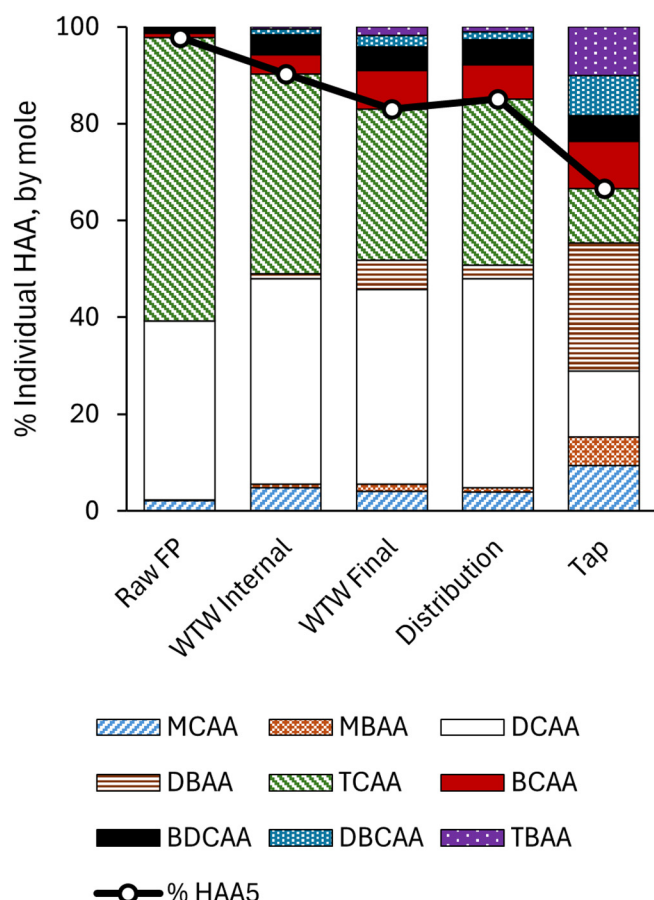


Fig. 5. Individual HAA percentages by mole for each treatment stage.

act as a suitable indicator of the overall risk from DBP formation, including HAAs (Roberts et al., 2002). Assessment of the efficacy of THMs as a proxy for HAAs in the current study showed a coarse correlation between THM4 and HAA9, with a linear correlation coefficient $R^2 = 0.57$ (Fig. 6a). However, the data was scattered with a breadth that made the correlation of no practical use. To illustrate, in the case of HAA9 (Fig. 6a) a THM4 value of $50 \pm 1 \mu\text{g/L}$ correlates to a value of HAA9 between 2 and $84 \mu\text{g/L}$. A similar pattern was observed for HAA5 (Fig. 6b, $R^2 = 0.50$), with not even a loose trend observed for the unregulated species (Fig. 6c, $R^2 = 0.17$). Previous data analysis has shown that although correlations can exist for specific sites (Malliarou et al., 2005), they need regular reassessment and overall there is not a consistent relationship between THM4 and HAA9 due to changes in the organic matter make up. This breakdown in correlation has been observed in both real-world studies (Bougeard et al., 2010; Uyak et al., 2014) and when using surrogate compounds (Grundy et al., 2026).

However, modelling studies have proposed that the prediction capability of THMs for HAA9 can be improved by accounting for the levels of bromination of the THMs and extrapolating this to the HAAs (Eqs. (1)–(4), Roberts et al., 2002; US EPA, 2016). Applying the predictive tool to all samples within the current data generates a correlation coefficient of $R^2 = 0.91$ for HAA9 (Fig. 7a). However, this reflects the percentage contribution of HAA5 (discussed above) and the data is split into two groups – one with a very strong correlation and the other significantly over-predicting HAAs - indicating caution is required. The observed correlation deteriorated when only the unregulated HAA4 were included, with a regression coefficient $R^2 = 0.43$ (Fig. 7b). This compares to previous reports that utilised the US UCMR4 dataset and showed a linear correlation coefficient $R^2 = 0.95$ for HAA9 but a reduced correlation with $R^2 = 0.69$ for HAA4 (Samson et al., 2017). The prediction of TBAA in the current dataset was particularly poor, with the 95th percentile of predicted values at $21.4 \mu\text{g/L}$ (range 0–113.4 $\mu\text{g/L}$) comparing to 95th percentile at $3.0 \mu\text{g/L}$ (range 0–15.5 $\mu\text{g/L}$) for the observed values (Fig. 7f). Consequently, in waters with high bromoform formation, the model notably over-predicts the levels of TBAA and the unregulated HAA4. This is consistent with work on model compounds that shows that lower levels of TBAA form at high ratios of bromide to chlorine (median BSF 0.43 and 0.3% of HAAs as TBAA at higher bromide), unlike bromoform where complete bromination is more frequently observed (BSF 0.64 and 22% of THM4 as bromoform at higher bromide) (Grundy et al., 2026). This demonstrates the complexity of using THMs to predict HAAs, where source waters vary in bromide and, importantly, reveals how thinking will likely change when an HAA9 standard is introduced and the significance of the currently unregulated Br-HAAs is increased.

Further analysis of bromine incorporation revealed a general relationship between the Bromine Substitution Factor (BSF) of the THMs and HAAs (Fig. 8a). However, a distinct subset was observed for highly brominated THMs, where the HAA BSF does not increase at the same rate as the THM BSF but instead tails off to a maximum of between 0.6 and 0.8. Interestingly, a recent model compound study revealed that this behaviour was not differentiated by aliphatic or aromatic characteristics and so will not be traceable to specific source water types or hydrophilicities (Grundy et al., 2026). This trend in BSF is significant because it implies some water types will favour the formation of the unregulated HAA4, and THM bromination is not a good indicator for this.

The BSF of the DBPs is also shown to be linked to the disinfection practice, with far higher BSF observed where chlorination was applied as a residual as opposed to the primary disinfectant (Fig. 8b). To illustrate, the median BSF was 0.70 and 0.70 for NF Cl and UV Cl compared to 0.06 and 0.07 for Cl Cl and Cl ClAm respectively. The difference reflects the higher chlorine concentration applied when used as a primary disinfectant, which then translates to a higher chlorine to bromide ratio and promotes chlorination over bromination. To illustrate, where primary chlorination was used an average HAA9 of $34.4 \mu\text{g/L}$ was formed of which 14% by mass is the unregulated HAA4. In contrast, where

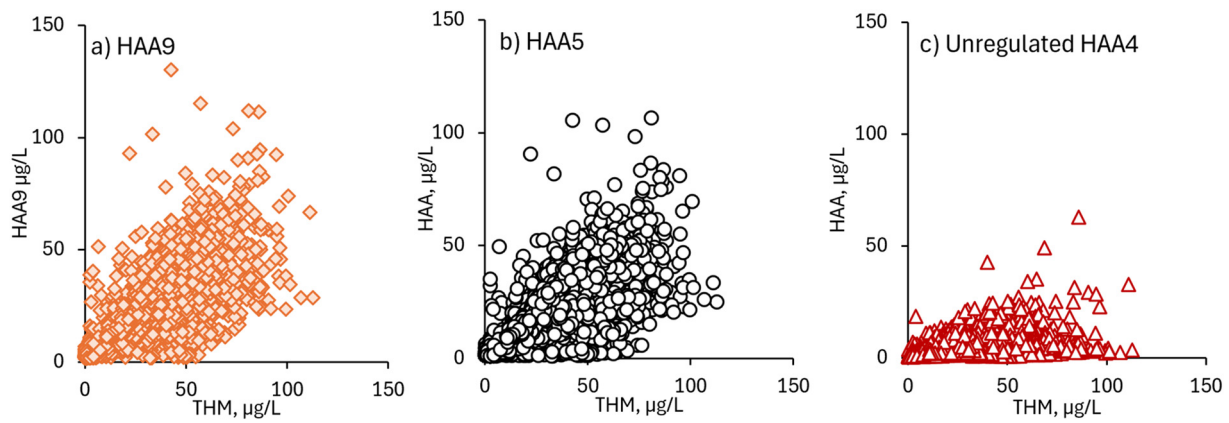


Fig. 6. Correlation between THM4 and a) unregulated HAA4 b) HAA5 c) HAA9 in treated waters.

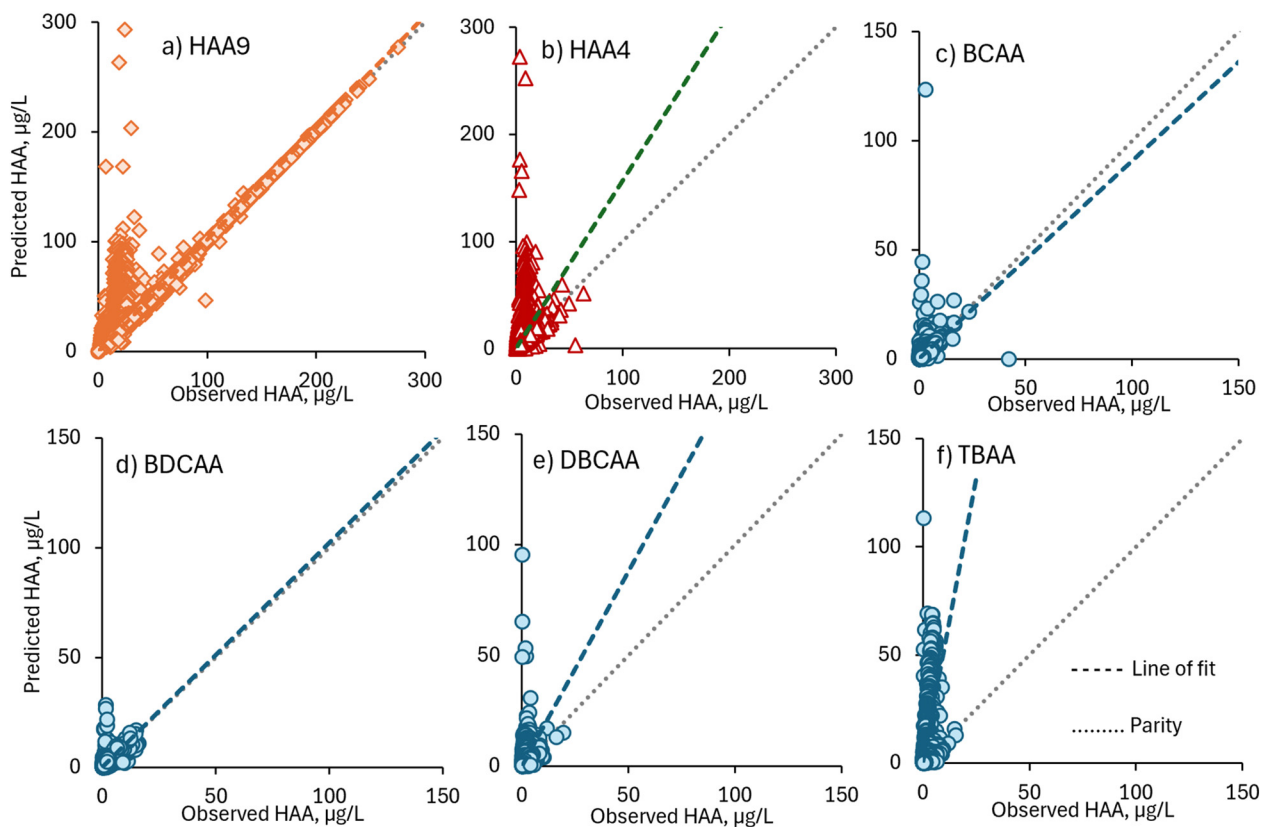


Fig. 7. Correlation between observed and predicted HAAs a) HAA9 b) Unregulated HAA4 c) BCAA d) BDCAA e) DBCAA f) TBAA.

chlorine was not used as the primary disinfectant, an average HAA9 of 12.7 µg/L was formed of which 44% was HAA4. Therefore, for sites which use chlorine as a residual disinfectant and where bromide is present, a larger proportion of HAA9 will be made up of the unregulated HAA4 and consequently HAA5 will be an even less effective proxy for HAA9.

3.4. HAAs viewed through hazard index

The impact of adopting an HAA9 standard as opposed to HAA5 can be further explored through the lens of Relative Hazard Index (RHI – Eq. (5)) to incorporate both the concentration and the relative toxicity of the different species (Rosenblum et al., 2024; WHO, 2022). Overall, in treated waters HAAs made the dominant contribution to RHI, with THM4 making a minor contribution in all cases (Fig. 9). To illustrate, the

overall average RHI was 0.17 from THM4 and 1.48 from HAA9 including 0.71 from HAA5 and 0.77 from HAA4. This contrasts markedly with the yield, where THMs are the largest group formed in treated water and the unregulated HAA4 the least with average concentrations of 28.7 µg/L for THMs and 4.9 µg/L for HAA4, from an average 22.3 µg/L for HAA9. This supports previous analysis highlighting the significance of the relative toxicity of the brominated HAAs when taking a risk-based rather than total mass-based approach (Peterson et al., 2023).

Comparison of the different source water types highlighted the higher RHI for mixed lowland sources and the importance of the contribution from the unregulated HAA4 species (Fig. 9a). To illustrate, the average RHI from treated HAA9 in MX LL sources was 4.35, with contributions from HAA5 and HAA4 of 1.85 and 2.50 respectively. These sources were dominated by sites with high bromide levels using UV disinfection and residual chlorine, and consequently formed

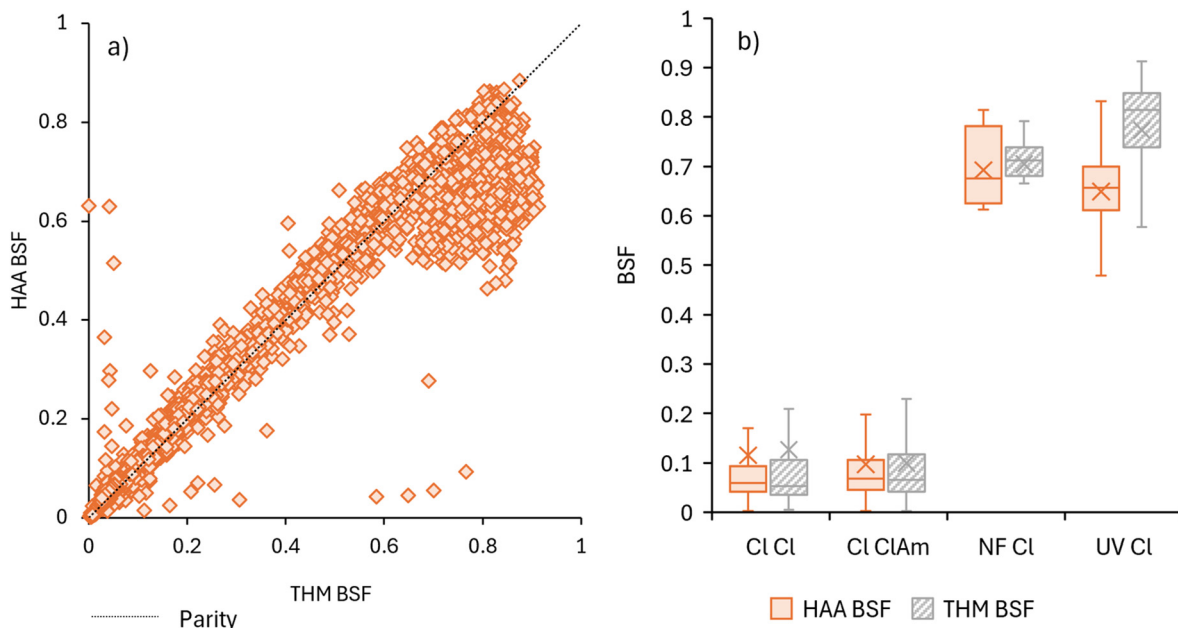


Fig. 8. BSF as (a) a comparison between THM and HAA and (b) as a function of disinfection practice.

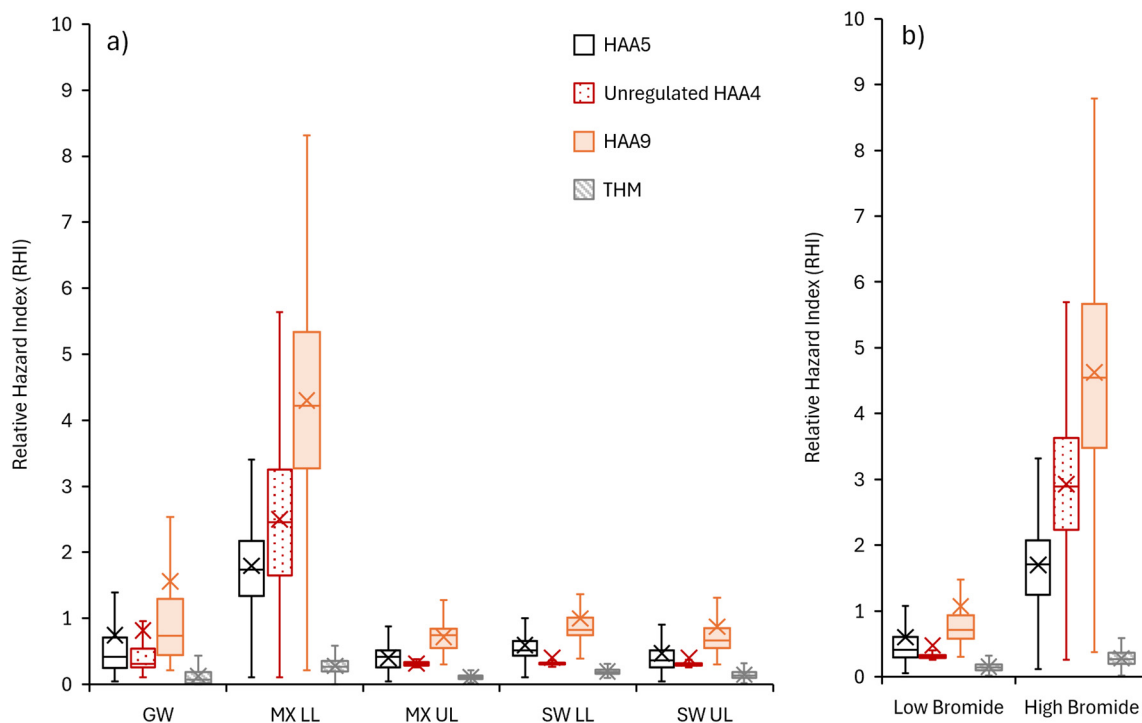


Fig. 9. Relative Hazard Index (RHI) in treated water a) by different source types b) by low and high bromide.

relatively high levels of TBAA, which has a significantly lower guideline value of $1 \mu\text{g/L}$ (Bull and Bevan, 2024). Consequently, when considering risk, particular care should be taken where the ratio between chlorine and bromide may drive the formation of the more toxic TBAA over the less concerning chlorinated HAAs (Furst, 2025).

The importance of bromide was further explored by separating the data between low ($<100 \mu\text{g/L}$) and high ($>100 \mu\text{g/L}$) bromide samples (Fig. 9b), noting that high bromide in treated water had levels sufficient to react with chlorine to form brominated DBPs and retain levels over $100 \mu\text{g/L}$ at the sampling point. The RHI associated with HAA9 increased from 1.07 to 4.74 between low and high bromide waters.

Furthermore, the overall RHI increased to 4.99 in treated water with high bromide, with 60% of this attributed to the unregulated HAA4 and only 5.6% from THM4. This demonstrates that understanding the levels of bromide is crucial for understanding the levels of risk, a finding reflected in the link between bromide and the geno- and cyto-toxicity of disinfected waters (Yang et al., 2014) and the increase in toxicity observed for water sources that experience seawater intrusion (Chowdhury, 2023). However, it is important to note that in this study bromide is measured concurrently with the HAAs and consequently inevitably under-reports the levels present at the point of disinfection, because it does not account for the bromide incorporated into DBPs.

Correlation analysis between bromide concentration and DBP mass concentration of HAA5, HAA4 or THM4 revealed no trend with linear correlation coefficients (R^2) of 0.05, 0.15 and 0.00 for unregulated HAA4, HAA5 and THM4 respectively (Fig. 10a–c). Furthermore, despite the increased toxicity of brominated HAAs, only limited correlation was observed between the bromide and the RHI for each DBP group, with linear correlation coefficients (R^2) of 0.57, 0.33 and 0.22 for unregulated HAA4, HAA5 and THM4 respectively (Fig. 10d–e). This demonstrates that existing bromide measurements in treated water, after chlorination, will not enable understanding of the risk from brominated HAA formation. Therefore as regulations move towards inclusion of brominated HAAs, and an improved understanding of the hazard associated with Br-DBPs is required, assessment of the risk from Br-DBPs can only utilise bromide data obtained prior to the addition of chlorine.

4. Conclusions

This survey of HAA9 in UK waters suggests good overall compliance with a future proposed standard of $<80 \mu\text{g/L}$ for England and Wales, with average levels of $14.3 \mu\text{g/L}$ in samples of consumer's tap waters and $22.3 \mu\text{g/L}$ in treated, chlorinated waters. Analysis of the data revealed key learnings when considering the future use of an HAA9 over an HAA5 standard. Importantly, THM4, HAA5 and bromide post-chlorination concentrations were poor proxy measures to predict the likely levels of formation of the currently unregulated HAA4. Furthermore, correlations with HAA9 are misleading, as a large proportion of the HAA levels in the HAA9 are associated with the HAA5 and so give a false sense of confidence in understanding formation of the unregulated HAA4. Consequently, where HAA9 data are not available, it is inadvisable to rely on THM data or a combination of HAA5 and THM data to fill this knowledge gap.

Increased formation of the unregulated HAA4 occurred when the bromide to chlorine ratio increased, either through a high bromide

concentration relative to a lower organic matter level and/or where chlorine is only used as a residual disinfectant. The importance of Br-HAAs is most notably observed when viewed through the lens of hazard index, where the contribution from HAA4 can become dominant.

Overall, the work shows that thinking associated with DBPs needs to change if considered from the perspective of HAA9 over HAA5, with much greater consideration needed concerning bromide incorporation and the relative ratio between chlorine and bromide. Further, existing measurements and proxies need to be re-examined, as they currently provide minimal insight into the formation of the additional four brominated HAAs when switching from HAA5 to HAA9. In terms of treatment, this means the residual DOC will need to be low enough to prevent DBP formation becoming concerning, or that consideration will be required to ensure practice does not excessively favour formation of Br-HAAs.

CRediT authorship contribution statement

Polly Grundy: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Peter Jarvis:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **John Fawell:** Writing – review & editing. **Emma Goslan:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **John Haley:** Writing – review & editing, Supervision. **Bruce Jefferson:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Polly Grundy reports financial support was provided by EPSRC Centre for Doctoral Training in Water Infrastructure and Resilience. Polly

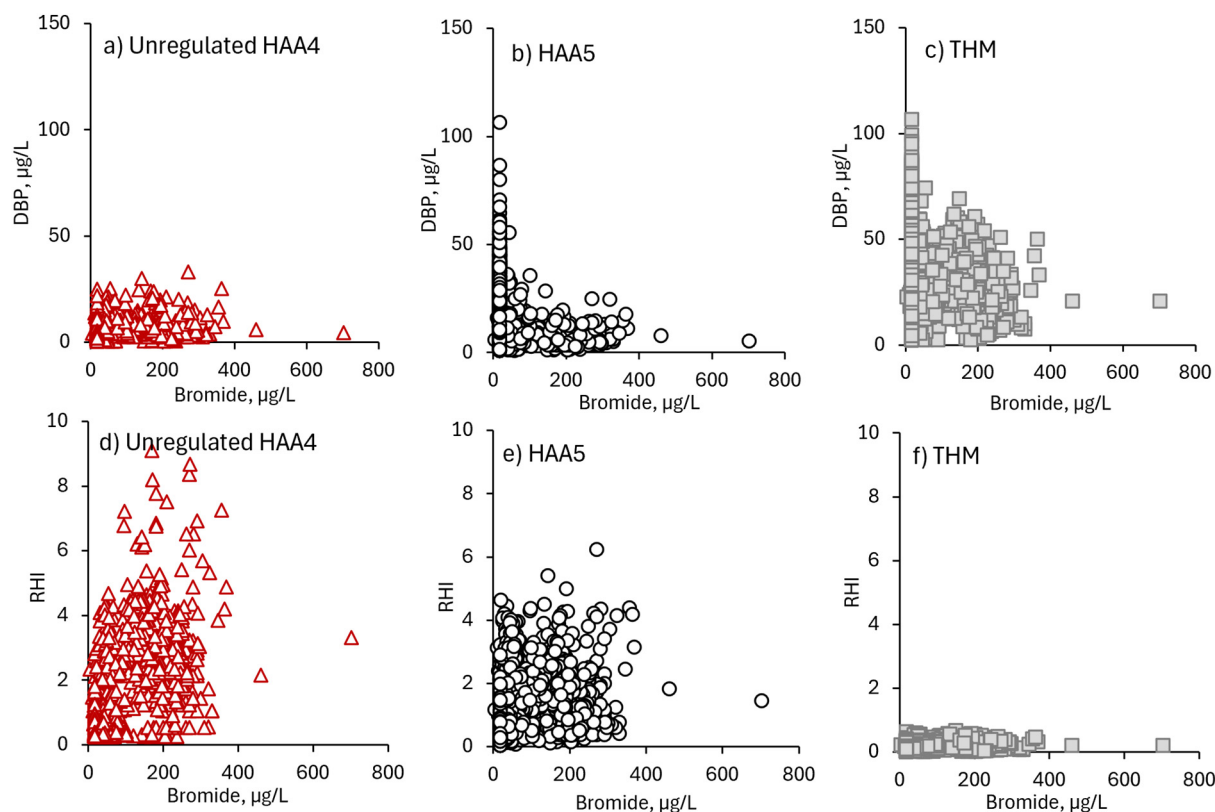


Fig. 10. Correlation between bromide and DBP yield for a) unregulated HAA4 b) HAA5 c) THM4 and between bromide and RHI for d) unregulated HAA4 e) HAA5 f) THM4.

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Fig. 2b was reproduced by digitiser with consent from Samson and Seidel (2022) using PlotDigitizer, 3.1.6, 2025, <https://plotdigitizer.com>.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2026.181741>.

Data availability

Summarised data supporting this study are openly available from CORD at [doi:10.57996/cran-ceres-2807](https://doi.org/10.57996/cran-ceres-2807). The raw data cannot be shared at this time due to data-sharing restrictions.

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Evaluation of the implications and efficacy of proposed changes to haloacetic acid drinking water regulation

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