THM and HAA formation from NOM in raw and treated surface waters

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ARTICLE INFO

ABSTRACT

The disinfection by-product (DBP) formation potential (FP) of natural organic matter (NOM) in surface water sources has been studied with reference to the key water quality determinants (WQDs) of UV absorption (UV_{254}), colour, and dissolved organic carbon (DOC) concentration. The data set used encompassed raw and treated water sampled over a 30-month period from 30 water treatment works (WTWs) across Scotland, all employing conventional clarification. Both trihalomethane (THM) and haloacetic acid (HAA) FPs were considered. In addition to the standard bulk WQDs, the DOC content was fractionated and analysed for the hydrophobic (HPO) and hydrophilic (HPI) fractions. Results were quantified in terms of the yield (dDBPFP/dWQD) and the linear regression coefficient R^2 of the yield trend.

The NOM in the raw waters was found to comprise 30—84% (average 66%) of the more reactive HPO material, with this proportion falling to 18—63% (average 50%) in the treated water. Results suggested UV_{254} to be as good an indicator of DBPFP as DOC or HPO for the raw waters, with R^2 values ranging from 0.79 to 0.82 for THMs and from 0.71 to 0.73 for HAAs for these three determinants. For treated waters the corresponding values were significantly lower at 0.52—0.67 and 0.46—0.47 respectively, reflecting the lower HPO concentration and thus UV_{254} absorption and commensurately reduced precision due to the limit of detection of the analytical instrument.

It is concluded that fractionation offers little benefit in attempting to discern or predict chlorinated carbonaceous DBP yield for the waters across the geographical region studied. UV_{254} offered an adequate estimate of DBPFP based on a mean yield of ~2600 and ~2800 μg per cm^{-1} absorbance for THMFP for the raw and treated waters respectively and ~3800 and2900 μg cm^{-1} for HAAFP, albeit with reduced precision for the treated waters.

1. Introduction

It has long been recognised that natural organic matter (NOM) is the precursor for the key chlorinated carbonaceous disinfection by-products (DPBs) of trihalomethanes (THMs) and haloacetic acids (HAAs) following chlorine disinfection (Rook, 1977; Hua and Reckhow, 2007; Bond et al., 2011; Zeng and Arnold, 2014). Experimental investigations in this field have been based either on chemical analogues of NOM (Bond et al., 2012, 2016; Gao et al., 2013; Zeng and Arnold, 2014), intended to assess the relative reactivities of key organic molecular functional groups, or empirical/heuristic studies of real waters. In the latter case DBP formation can

be measured either in situ, i.e. in the treated water resulting from the site-based chlorination step (Sutherland et al., 2015), or more usually ex-situ using standard chlorination conditions to give the disinfection by-product formation potential (DBPFP). Normalising the DBPFP (THMFP and HAAFP for THM and HAA formation potential respectively) against the organic carbon (OC), or some other water quality determinant (WQD) provides the yield; if normalised against OC then this parameter is expressed in μg or μM DBP per mg or mM OC (or dissolved organic carbon, DOC).

Studies based on real waters (Table 1) have generally been limited to a small number (2—6) of water sources. Whilst other DBPs have been studied, and specifically nitrogenous species such as haloacetyl nitriles (HANs) and N-nitrosodimethylamine (NDMA), the focus has generally been on the carbonaceous species and on THMs in particular. However, nitrogenous DBPs (N-DBPs) such as haloacetonitriles (HAN) and halonitromethanes (HNM) are

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Table 1
Summary of recent carbonaceous DBP formation correlation studies, 2008 onwards.

DBP(s)	Water source	WQD(s)	Fractionation	Strongest correlation (R^2)	Reference
THMs	Raw/ultrafiltered surface water, Sd	UV_{254}, DOC	None	THMs vs DOC *(0.76/0.58 raw/ ultrafiltered)*	Sutherland et al., 2015
THMs, NDMA	Clarified surface waters, SC USA	UV_{254}, EEM−PARAFAC	None	THMs vs DOC *(0.95)*	Yang et al., 2015
THMs, HAAs, TOX, HAN, CP	Clarified surface waters, NA	SUVA	Chem + phys	THAAs yield vs SUVA[a] *(0.80)*	Hua et al., 2015
THMs, HAAs	Wastewater, Tu	UV_{272}, pH, Cl_2/DOC	None	THMs vs ΔUV_{272} *(0.91-0.99, pH dep.)*	Uyak and Demirbas, 2014
TCM	Surface water, WA USA	UV_{254}, DOC, EEM −PARAFAC	Chem	TCMFP vs $I_{278/506}$ *(0.88)*	Pifer et al., 2014
THMs	Surface water, WA USA	UV_{254}, DOC, EEM −PARAFAC		TTHMFP vs UV_{254} *(0.89)*	Pifer and Fairey, 2014
THMs, HAAs	Surface water, Tu	UV_{254}, DOC, EEM −PARAFAC	Chem + phys	No significant correlation	Karapinar et al., 2014
THMs	Surface water, WA USA	CD, SUVA, EEM −PARAFAC	None	TCM vs F_{MAX} *(0.84)*	Pifer and Fairey, 2012
THMs, HAAs, HAN, HKs,HAs, HNMs, i-THMs	Treated surface and borehole waters, England and Wales	NPOC, UV_{254}, SUVA,	None	Has vs UV_{254} *(0.86)*	Bougeard et al., 2010
THMs, HAAs	Raw/treated/surface waters, Italy, WA and DC, USA	UV_{272}, UV_{254}, TOC, DOC, SUVA	Chem	THM vs UV_{254} *(0.99)*	Roccaro and Vagliasindi, 2009
THMs	Surface waters, Ch	SUVA	Chem + phys	THM yield vs SUVA[a] *(0.39)*	Wei et al., 2008
THMs	Clarified surface waters, SC USA	BDOC	None	TTHMFP vs BDOC *(0.82)*	Teksoy et al., 2008
THMs, HAAs and TOX	Surface waters, Ko	SUVA	Chem	TCM yield vs SUVA[a] *(0.90)*	Jung and Son, 2008

BDOC Biodegradable DOC; NPOC non purgeable organic carbon; CD Chlorine demand; Ch China; CP Chloropicrin; DC District of Columbia; EEM−PARAFAC Fluorescence excitation−emission matrices and parallel factor analysis; F_{MAX} Maximum intensity of identified humic-like fluorophore in the fluorescence spectrum; HAN Haloacetylnitrile; HA haloaldehydes, HK haloketones; HNM halonitromethanes; i-HMs iodo-THMs $I_{278/506}$ Ratio of fluorescence absorption and emission; Ko Korea; nc No correlation; SC South Carolina; Sd Scotland; TCM Trichloromethane; TOX Total chlorinated organic carbon; Tu Turkey; WA Washington State; ΔUV_{272} Differential UV absorbance (Korshin et al., 1999).

[a] Yield vs SUVA is directly proportional to DBP concentration or FP vs. UV_{254}.

increasingly of health concern. These compounds have been shown to be more cytotoxic and genotoxic than the carbonaceous DBPs (Plewa et al., 2002) and with a greater impact on the overall toxicity from halogenated species in chlorinated waters (Zeng et al., 2016), such that some have been incorporated in the WHO drinking water guidelines (WHO, 2006).

A key aim of many reported studies has been to identify readily measurable water quality determinants (WQDs) which may provide a reliable indication of carbonaceous DBPFPs. As such, the linear correlation coefficient (R^2) is of key interest, since this indicates the legitimacy of employing the WQD as a surrogate for DBPFP. Reported DBPFP correlations have generally included either UV_{254} absorption or DOC as the benchmark. Some studies (Hua et al., 2015; Wei et al., 2008; Jung and Son, 2008) have correlated yield with SUVA, the equivalent of DBP concentration or formation potential vs. UV_{254}, since both yield and SUVA (UV_{254} absorbance per unit DOC concentration) are normalized against DOC concentration. In recent years WQDs using fluorescence spectroscopy, based on the 2D contours of excitation-emission fluorescence spectra, have been employed to try and improve the correlation (Yang et al., 2015; Pifer and Fairey, 2014, 2012; Pifer et al., 2014). Fluorescent components specific to molecular species recognised as DBP precursors are identified and quantified using PARAFAC analysis, employing methods originally proposed by Stedmon and co-workers (Stedmon et al., 2003; 2008).

There has also been a substantial body of work analysing the influence of individual chemical and/or physical fractions of the organic material on the DBPFP and/or yield. In such studies chemical fractionation is applied on the basis of the degree of hydrophobicity of the organic material and physical fractionation based on molecular size. Fractionation studies have pointed to the hydrophobic (HPO) fraction and high molecular weight (HMW) components as having the highest THMFP (Hua et al., 2015; Hu et al., 2014). However, other organic fractions, and specifically the transphilic (TPI) fraction, of the NOM can contribute significantly to the overall DBPFP (Li et al., 2014). The HPO content alone thus cannot reasonably be used as the basis for either informing the

appropriate chlorination process conditions or estimating the DBP levels in the treated chlorinated water. Moreover, fractionation methods do not lend themselves to on-line monitoring. Against this, since aromatic, humic compounds predominate in the HPO fraction (Weishaar et al., 2003; Bessiere et al., 2009), it may be expected for UV absorption (UV_{254}) to provide a reasonable indication of DBP formation potential (DBPFP) − as demonstrated in previous studies (Weishaar et al., 2003).

The current study assesses the validity of correlating THMFP and HAAFP against routinely-used water quality determinants of UV_{254}, colour and DOC, as well as the hydrophobic chemical fraction, based on a large data set (30 water treatment works, WTWs). The data set, encompassing a significant geographical region (Scotland) and time period (over two years) compares yield trends for raw and treated waters to assess the precision of the trends for both streams. The statistical significance of the yield correlations are quantified through classical linear correlation coefficient determination, allowing an appraisal of the actual practical viability of UV_{254} monitoring as a tool for predicting DBP formation.

2. Materials and methods

2.1. Sampling

The study was based on WTWs in Scotland employing conventional clarification with an alum coagulant. The 30 sites of interest (~15% of the total WTWs within Scotland) were selected based on high THMFP levels recorded for the treated waters (Valdivia-Garcia et al., 2016). All sites were fed with surface water, predominantly lowland (60%) or island (40%). 80% of the sites were located in the west of Scotland, the remaining 20% being evenly split between North and South (Fig. 1).

2.2. Sample analysis

Raw and treated water samples were collected over an 18−30 month period between January 2013 and June 2015 and analysed
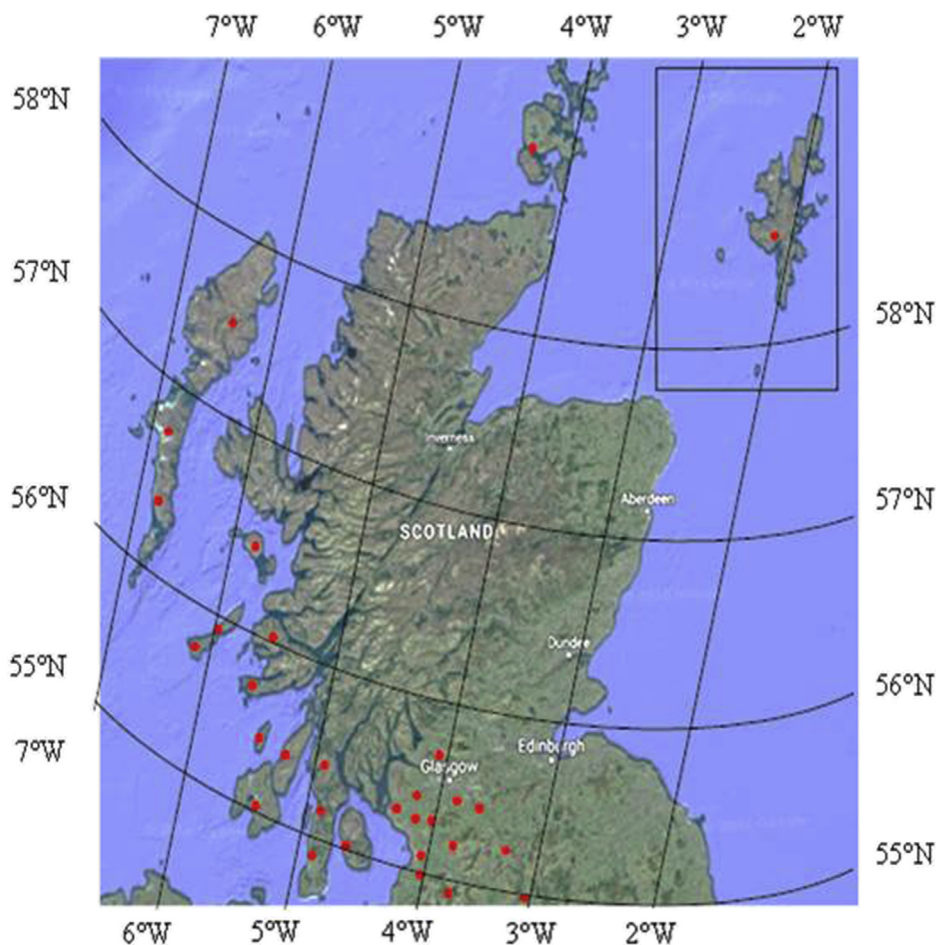
Fig. 1. Map of Scotland highlighting the locations and coordinates of the WTWs investigated.

at the Scottish Water UCAS-accredited Edinburgh laboratories. Colour, pH, zeta potential, turbidity, UV_{254} absorbance and DOC concentration were determined according to published methods (Goslan et al., 2009; APHA, 2012). Assured quality controls (AQCs) were used so to account for data anomalies relating to equipment malfunction or technical error; data for an AQC reading with a difference of more than 15% were repeated or removed. The complete data set comprised of 330 and 205 data points for raw and treated water respectively, ranging from 10 to 25 samples per site depending on the time period.

Chemical fractionation into HPO, TPI and HPI (hydrophilic) organic matter was according to previously published methods (Bessiere et al., 2009), with the sample pH adjusted to 2.5 from the standard pH of 2 to counter precipitation of sparingly soluble organic solutes. Chlorination conditions of 25 °C for 7 days were used throughout, and sample analysis for THMs and HAAs replicated at least seven times.

2.3. Statistical analysis

Data was analysed and correlations further investigated by simple linear regression using 95% confidence intervals. The results returned by box plots were confirmed statistically using Kruskal-Wallis analysis, appropriate for non-normally distributed data (Kruskal and Wallis, 1952). Analyses were undertaken using the *IBM SPSS Statistics version 22* software package and MS Excel.

3. Results and discussion

3.1. Water quality

The water quality range across all measured parameters (Table 2) indicate data for some parameters to be less scattered than others. Key parameters relating to NOM characterisation (% NOM recovery and %HPO) have standard deviation (SD) values below 15%. The SUVA SD value is similarly fairly consistent at 20% and the mean value of 4.72 L/(mgC.m) and 2.09 for raw and treated water respectively, comparable to those reported for other surface waters (Yang et al., 2015; Hua et al., 2015; Pifer et al., 2014; Pifer and Fairey, 2014; Bougeard et al., 2010). Other parameters, in particular the colour and tHAA concentration, were more highly scattered due to seasonal impacts. Higher and more variable DOC mean values of 7.74 mg/L ± 43% SD were recorded than those reported for previous studies (Yang et al., 2015; Karapinar et al., 2014; Bougeard et al., 2010; Roccaro and Vagliasindi, 2009), but are characteristic of upland Scottish waters (Sutherland et al., 2015; Valdivia-Garcia et al., 2016). The %HPO fraction was also higher, at 69% in raw water than the figure of 35% reported by Karapinar et al. (2014) (HPO = 35%), but comparable to values of 72–73% reported by Phetrak et al. (2016) and Bessiere et al., 2009 for moorland and sub-tropical waters.

3.2. Strength of yield correlations

Overall, the strength of linear correlation (the R^2 values) between DBPFP and the three WQDs studied for raw and treated

Table 2
Average, standard deviation (SD), min and max for raw and treated water samples measured at 30 sites over a period of 18–30 month; the equipment measuring range and lower reporting limit are also provided.

Parameter	Measurement range	LRL[a]	Water sample							
			Raw				Treated			
			Min	Max	Mean	%SD	Min	Max	Mean	SD
Calculated DOC(mgC/L)	0–20	<0.2	1.51	21.58	7.34	44%	0.85	3.45	1.80	29%
Measured DOC (mgC/L)	0–20	0–20	1.60	21.40	7.74	43%	0.80	3.70	1.92	31%
NOM fractionation recovery %	N/A	85–115	85	115	95	7%	85	115	95	8%
HPO (mgC/L)	0–20	<0.2	0.97	14.37	4.92	50%	0.40	1.68	0.89	29%
%HPO	N/A	N/A	30.21	83.23	65.90	14%	18.83	63.48	49.66	14%
TPI (mgC/L)	0–20	<0.2	0.24	4.42	1.26	48%	0.2	0.95	0.31	35%
%TPI	N/A	N/A	7.14	28.19	17.34	20%	7.10	34.30	17.48	18%
HPI (mgC/L)	0–20	<0.2	0.2	4.80	1.15	52%	0.22	2.40	0.60	43%
%HPI	N/A	N/A	3.13	48.83	16.76	46%	19.80	74.07	32.87	22%
THMFP yield (µg/mg C)	3.2–312.7**	<3.2	25.00	276.00	121.87	26%	24.00	169	77.80	21%
tTHM4 (µg/L)[b]	N/A	N/A	142.50	3723.6	972.10	58%	47.20	311	148.86	36%
HAAFP yield (µg/mg C)	5.3–200**	<5.3	27.00	336.00	154.27	36%	11.00	171	66.30	33%
tTHAA5 (µg/L)[c]	N/A	N/A	145.60	4729.4	1260.58	67%	21.60	410.4	128.86	49%
pH	N/A	N/A	4.63	9.20	6.86	11%	6.08	9.75	6.87	11%
Turbidity (NTU)xxx	0–250	<0.2	0.20	91.25	2.66	254%	<LRL	1.38	<LRL	–
SUVA (L/mg/m C)	N/A	N/A	0.53	9.17	4.72	23%	0.95	3.64	2.09	20%
UV 254 abs (/cm)	N/A	<0.01	0.03	0.96	0.37	51%	0.01	0.08	0.04	25%
Zeta potential (mV)[d]	N/A	N/A	−31.60	−8.80	−17.66	−18%	−26.30	4.00	−8.53	−53%
Colour (mg/L Pt/Co)	0-60 [e, f]	<2	6.58	190.78	59.14	62%	0.04	5.36	2.16	53%

*Over the range samples were diluted to fit range.
**According to Scottish Water UCAS approved methods the results for the drift standard are acceptable within 15% of the expected values.
  [a] Lower reporting limit.
  [b] The total THM is the sum of Chloroform, Dibromochloromethane, Bromodichloromethane and Bromoform.
  [c] The HAA5 Total is a total of monochloroacetic acetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid and dibromoacetic acid.
  [d] A Zeta potential Standard (DTS1235) is run with every batch of analysis. The result should be 42 + 4.2 mV.
  [e] Highly turbid samples were filtered through 0.45 µm before measurement.
  [f] Over the range samples were diluted to >10% of the range.

water followed the following trends:

  a) stronger correlations for THMFP (R^2 = 0.82 and 0.79 for UV_{254} and HPO respectively, Fig. 2a) than for HAAFP (R^2 = 0.77 and 0.74, Fig. 2c);
  b) similar strength of correlation of DBPFP with UV_{254}, HPO and DOC for raw water (R^2 = 0.79–0.82 for THMFP and 0.74–0.79 for HAAFP, Figs. 2–3 a,c)
  c) slightly weaker correlations with colour (R^2 = 0.77 for THMFP, Fig. 3ai, and 0.75 for HAAFP, Fig. 3ci, raw water);
  d) consistently stronger correlations for raw water (R^2 = 0.74–82) than for treated water (R^2 = 0.21–0.63) generally (Figs. 2–3, a vs. b, c vs. d).

The above observations reflect the higher conjugated molecular content of the raw water associated with aromatic compounds, which previous studies (Li et al., 2014; Weishaar et al., 2003) have associated with DBPFP. The almost identical trend in DBP yield when correlated with UV_{254} and HPO for both THMs and HAAs reflects the expected close correlation of UV_{254} with HPO (Fig. 3). Colour, on the other hand, correlated more poorly with HPO, particularly for the filtered waters. The increased data scatter in the treated water measurements results from the reduced DOC levels in these samples. These low concentrations are closer to the limit of detection (LoD) of the instruments compared with the higher concentrations of the raw waters, resulting in lower precision. The HPO fraction and overall concentration in the raw water is considerably higher than in the treated waters, and is thus more precisely measured. The chemical characteristics of the HPO in the treated water are also affected by the WTW treatment train.

3.3. Trends in yield

A comparison of the yield trends (d(DBPFP)/d(WQD)) for THM and HAA indicates them to be very similar. The ratio of the yields for the treated vs. raw water follows exactly the same pattern for both the THMs and HAAs (Fig. 4). The yield with reference to UV_{254} changes insignificantly between the raw and treated water for either DBP, whereas against DOC the yield is 2–3 times lower for the treated water compared to the feed. This reflects the removal of the more reactive organic carbon components by the water treatment process, in keeping with expectations based on the efficacy of clarification (Parsons et al., 2004). Whilst some of the gradient values relate to correlations of very low R^2 values, particularly for the treated water trends for HAA (Figs. 2d and 3d), the data nonetheless strongly indicate similar behaviour for the two DBPs.

The correlation gradient for UV_{254} vs. HPO is reduced only by 40% from feed to treated water, compared with >60% for UV_{254} vs. DOC. Colour is reduced to levels in the treated water which are too low to allow it to be reliably used as a DBPFP surrogate for this stream (R^2 = 2.1–2.8, Fig. 3bi and di).

Comparison with published yield values (Table 3) reveals the mean yield values vs UV_{254} from the current study to be broadly similar to those previously reported for raw waters, though the range of reported values is extremely broad (from 1100 to 5300 µg per cm^{-1} for the THM data). The current study raw water THM yield R^2 values are also amongst the highest of those reported (Li et al., 2014; Pifer and Fairey, 2014; Jung and Son, 2008), but lower for the treated waters. Yields are higher for the HAA species cf. THMs, as observed by previous authors (Delpla and Rodriguez, 2016; Zeng and Arnold, 2014; Nguyen et al., 2013; Roccaro et al., 2009), with the absolute raw water yield values vs. mg DOC in the current study
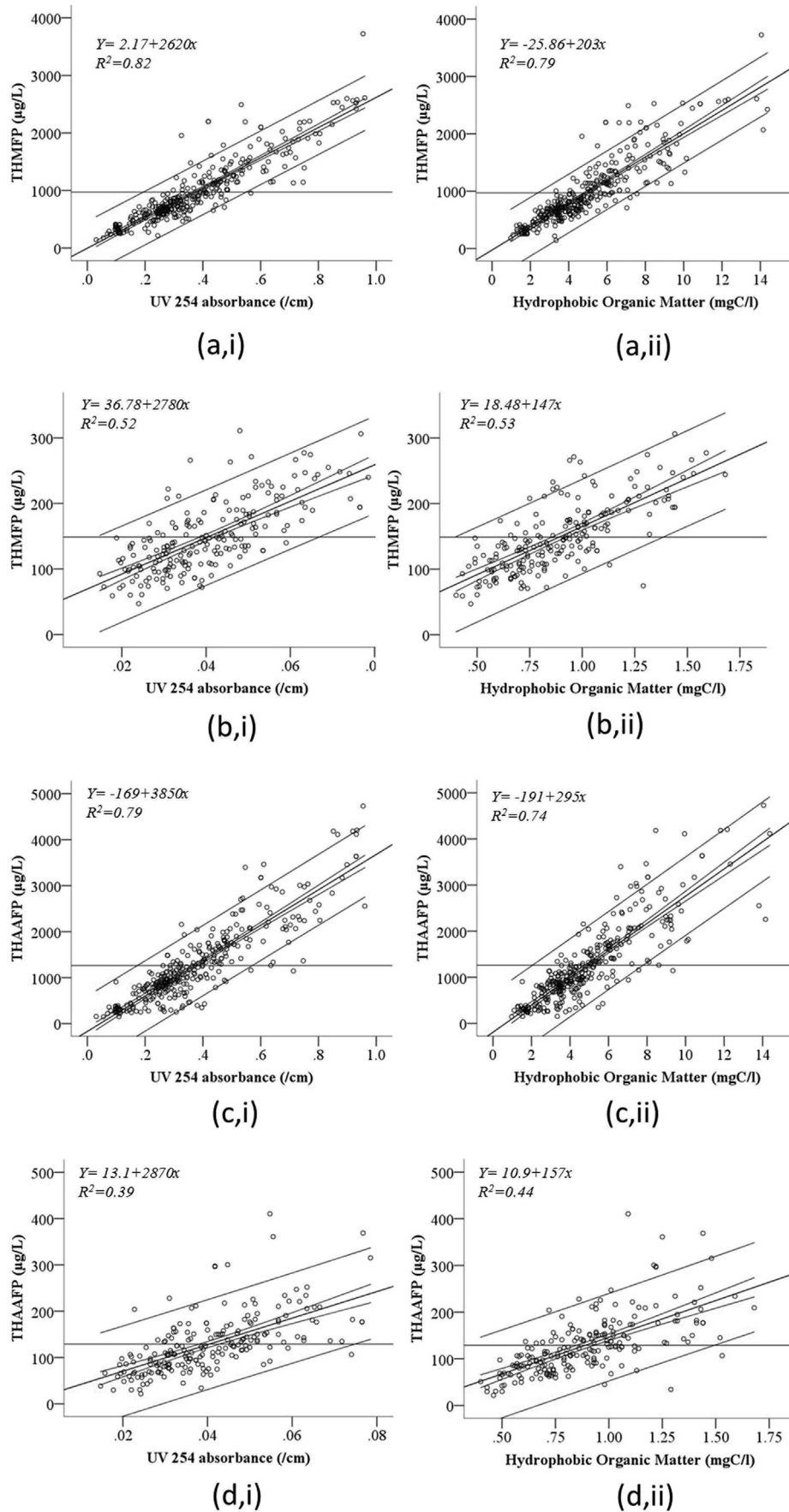
Fig. 2. Examples of (a, c) raw and (b, d) treated water, for (a–b) THMFP and (c–d) HAAFP vs WQDs of (i) UV_{254}, and (ii) HPO, with 95% confidence intervals, confidence intervals to the mean, and mean DBP (µg/L) indicated.
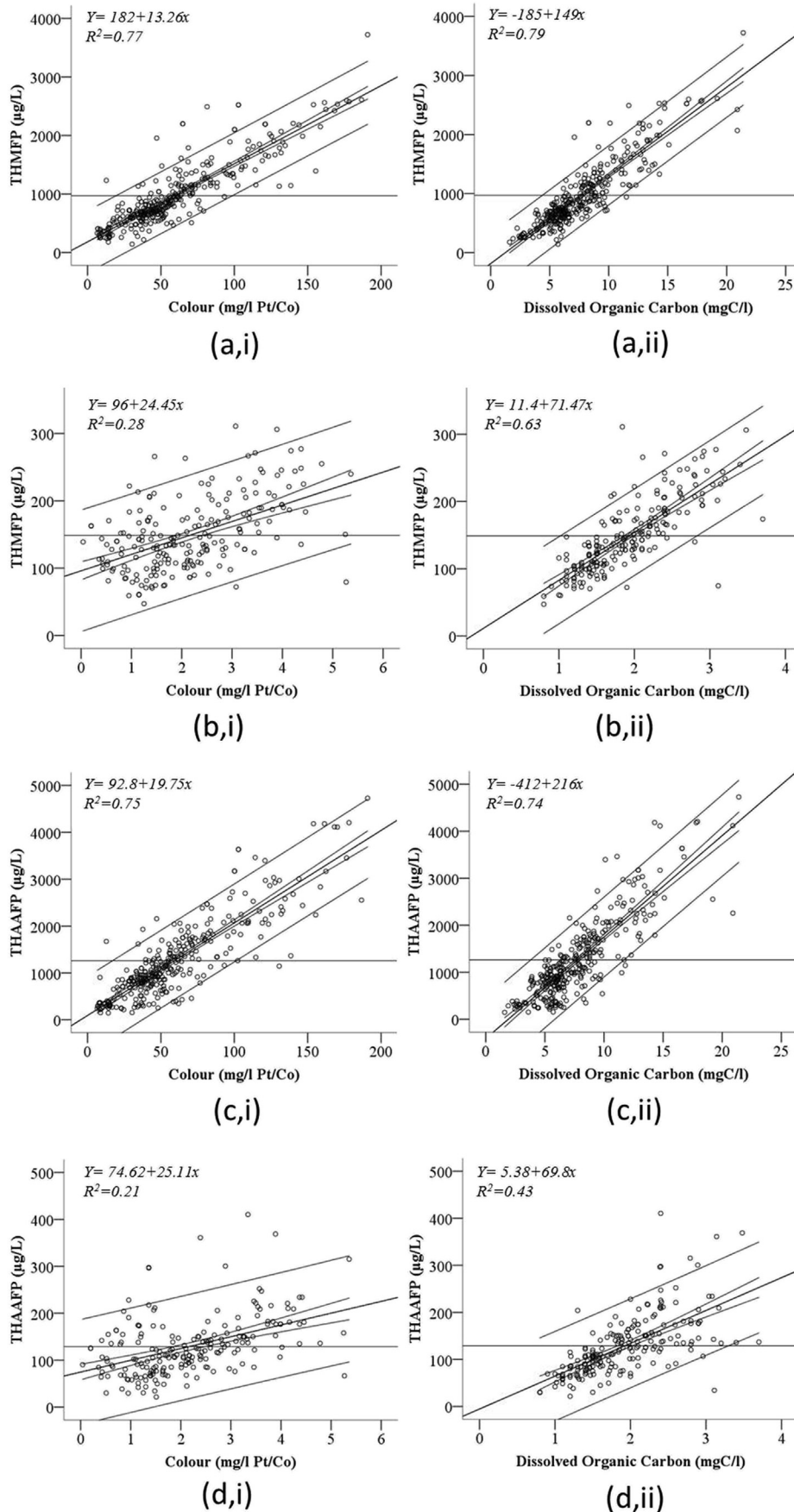
Fig. 3. Examples of (a, c) raw and (b, d) treated water, for (a–b) THMFP and (c–d) HAAFP vs WQDs of (i) Colour and (ii) DOC, with 95% confidence intervals, confidence intervals to the mean, and mean DBP (μg/L) indicated.
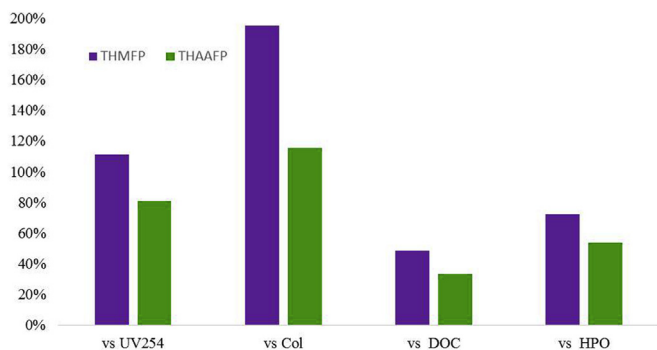
Fig. 4. Ratio of gradient values, treated vs. raw, for the DBPFP correlations referred to in Figs. 1—2.

being somewhat higher than those reported previously (Delpla and Rodriguez, 2016; Pifer and Fairey, 2014; Teksoy et al., 2008). The R^2 values for the raw water trends are not substantially lower than those reported for correlation with the fluorescence-based parameter of 0.88 (Table 1, Pifer and Fairey, 2014), suggesting that the benefit offered by more extensive EEM−PARAFAC analysis over that of UV_{254} monitoring is perhaps water quality-dependent.

3.4. HPO trends

Figs. 2−3 indicate generally the same strength in the correlation of DBPFP with UV_{254}, DOC and HPO for both raw and filtered water. R^2 values are consistently lower for the treated water samples due to their generally lower yield values and imprecision associated with the previously-mentioned closeness of the DOC measurement

to the LoD of the analytical instrument.

The distribution of the chemical fractions across the >500 water samples taken indicate higher proportions of HPO in the feed than treated waters, but with nonetheless a relatively high proportion of this fraction (50% ± 7.5) in the treated water (Fig. 5). Since the HPO fraction is generally considered to be conducive to removal by conventional clarification (Parsons et al., 2004), this outcome suggests that some clarification performance improvement could be attained at many of the sites to reduce this fraction and the subsequent DBPFP.

Whilst there was reasonable consistency in the proportion TPI across all samples, making up approximately 15% of the total OC, the HPI and HPO fractions varied according to the site-based clarification efficacy. Since yield always decreased from feed to treated waters (Fig. 4) and this can be associated with the change in HPO, a relationship can be discerned between the THM yield %HPO. Clustering of feed and treated water data is evident (Fig. 6). For these two clusters there exists a threshold %HPO value (%HPO-threshold) at which the proportion of the treated water data points above threshold ($X_{treated}$) is the same as the proportion of raw water data below it (X_{raw}):

$$X_{treated} = X_{raw} \text{ at } \%HPO = \%HPO_{threshold}$$

Analysis of these data clusters indicates that $\%HPO_{threshold} = 57.5\%$ at $X = 12.5\%$. Correlation of mean DBP yield against mean DOC for samples having an HPO content above and below the 57.5% threshold, indicate the raw water samples have an 83% higher overall mean DOC level and generate a 37% higher yield of THMs (Fig. 7a). Applying the same process to the HAA data indicates a similar threshold value (60%), and a 64% higher yield of HAAs (Fig. 7b). Against this, for the treated waters the absolute

Table 3
DBPFP yield values vs. DOC and UV_{254}, respectively.

DBP	μg/mg		μg per cm^{-1}		Reference
	Y	R^2	Y	R^2	
THM	43−145	−	−	−	Depla and Rodriguez, 2016
THM	124	0.90	−	−	Yang et al., 2015
THM	−	−	5278[a]	0.5	Hua et al., 2015
THM	−	−	1220	0.91	Li et al., 2014
THM	91	0.75	3602[a,b]	0.89	Pifer and Fairey, 2014
THM	−	−	2156	0.6	Karapinar et al., 2014
THM	−	−	1299	0.39	Wei et al., 2008
THM	61	0.81	−	−	Teksoy et al., 2008
THM	−	−	2405	0.88	Jung and Son, 2008
THM	−	−	1102	0.65	Jung and Son, 2008
THM	−	−	1630	0.51	Weishaar et al., 2003
THM	−	0.69−0.76	−	0.85−0.98	White et al., 2003
THM	18−35[c]	−	−	−	Roccaro et al., 2015
THM	15−55[c]	0.45[d], 0.90[e]	−	0.73[d], 0.94[e]	Roccaro and Vagliasindi, 2009
THM	−	0.63	−	0.49	Bougeard et al., 2010
THM	**149**	**0.79**	**2620**	**0.82**	**Current study, raw**
THM	**71**	**0.63**	**2780**	**0.52**	**Current study, treated**
HAA	117−174	−	−	−	Depla and Rodriguez, 2016
HAA	−	−	7743[a]	0.80	Hua et al., 2015
HAA	−	−	1630	0.94	Li et al., 2014
HAA	−	−	2365	0.65	Jung and Son, 2008
HAA	−	−	1991	0.69	Jung and Son, 2008
HAA	−	0.53−0.74	−	0.35−0.98	White et al., 2003
HAA	25−65[c]	−	−	−	Roccaro et al., 2015
HAA	38−88[c]	0.75[d], 0.84[e]	−	0.79[d], 0.95[e]	Roccaro and Vagliasindi, 2009
HAA	**216**	**0.74**	**3850**	**0.79**	**Current study, raw**
HAA	**70**	**0.43**	**2870**	**0.39**	**Current study, treated**

[a] Converted from molar yields assuming fully chlorinated species to predominate.
[b] Average of 11 water sources.
[c] Increases linearly with SUVA.
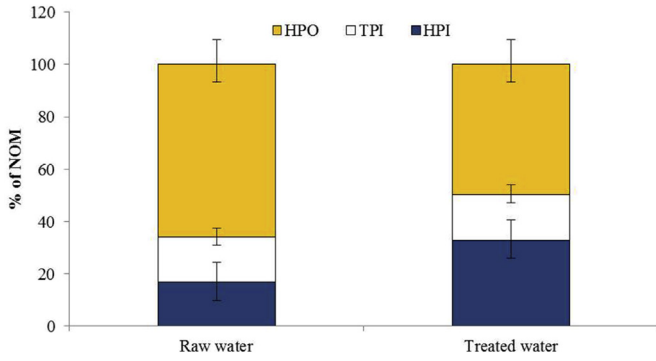[d] Single water source.
[e] Dual water source.

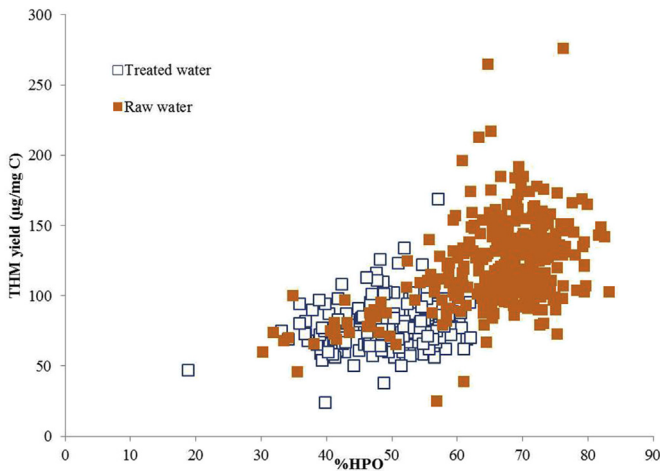**Fig. 5.** Distribution of organic fractions for raw and treated water, respectively.

Fig. 6. Correlations between yield THM vs %HPO, for raw and treated water samples.

the analytical instrument.

3.5. Seasonal and geographical trends

Seasonal and geographical data were analysed on a similar basis to a previous study (Sutherland et al., 2015) of regional THM trends, where the same three seasons were identified largely based on anecdotal trends in DBPFP. The outcomes for concentrations of feed UV_{254} (Fig. 8a) and treated water THMFP (Fig. 8b) and THAAFP (Fig. 8c) over the three seasons illustrate a declining trend in both UV_{254} and treated water DBPFP from the Jul–Oct season to the Nov–Feb and Mar–Jun seasons. This result was confirmed as being statistically significant ($p < 0.05$) according to the Kruskal-Wallis (K-W) non-parametric test of differences (Kruskal and Wallis, 1952). It also corroborates the outcomes of the Sutherland et al. study, which was based on membrane filtration WTWs, as well as those of previous studies of the impact of seasonal temperatures on THMFP (Karapinar et al., 2014; Wei et al., 2010; Goslan et al., 2002). Accordingly, changes in DBP levels can be attributed to the concentration of reactive NOM, rather than changes in NOM reactivity.

Analysis of locational trends, based on geographical region ("North", "South", "East" and "West") revealed no clear trends. However, as with previous studies of the region (Valdivia-Garcia et al., 2016; Sutherland et al., 2015), a small but statistically significant (confirmed by the K-W analysis) increase in reactivity (i.e. increased DBPFP without a corresponding increase in the DOC level) was evident for the Scottish islands installations (Fig. 9).

4. Conclusions

A study of trends in disinfection byproduct (DBP) yield against the water quality determinants (WQDs) of UV_{254} absorption, dissolved organic carbon (DOC) concentration and the hydrophobic (HPO) fraction of the DOC has been conducted across the Scottish region. Raw and treated waters from 30 water treatment works (WTWs) were sampled over a 30 month period and trends in trihalomethanes and trihaloacetic acids (THMs and THAAs) determined.

Statistical analysis of the data trends has revealed:

- Linear regression correlation coefficient (R^2) values of DBP yield vs the various WQDs follow the same pattern for both THM and HAA, with slightly weaker correlations for HAAs.

different in both the DOC concentration and the yield between the high and low HPO waters is small, as indicated by the almost co-incident open data points at a DOC below 1 mg/L in Fig. 7a and b. However, such interpretation should be treated with caution, given the limitations of the NOM resin fractionation method (such as carry-over of material between fractions) and the closeness of the low DOC concentrations in the treated water fractions to the LoD of
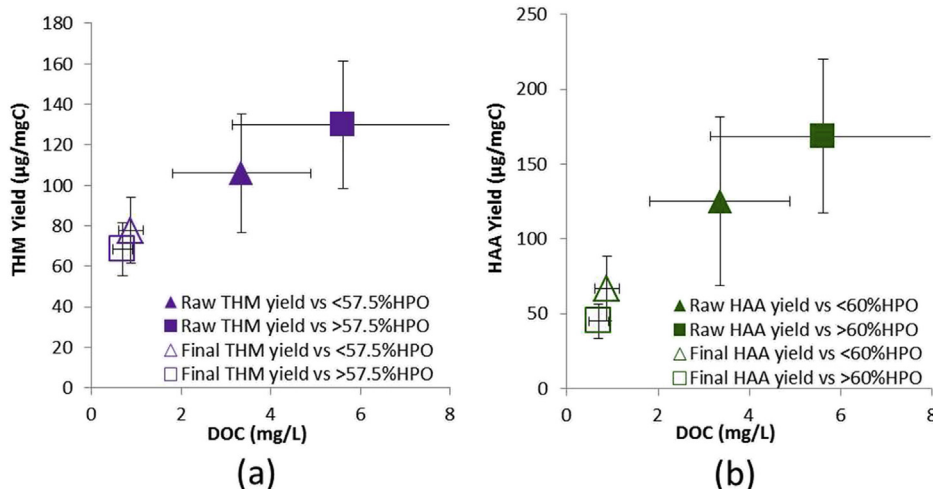

Fig. 7. DBP yield for (a) THMs and (b) HAAs vs DOC concentration for raw and treated waters, including standard error intervals: influence of HPO content.
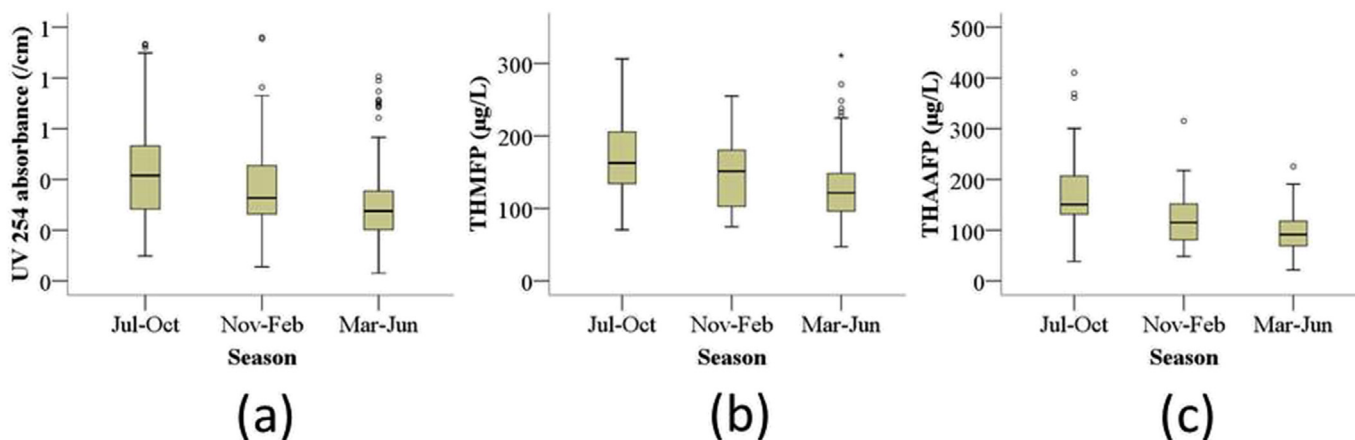
Fig. 8. Box plots-and-whiskers plots for a) raw water UV254 (/cm), b) treated water THMFP (μg/L), and (c) treated water THAAFP for the three seasons.

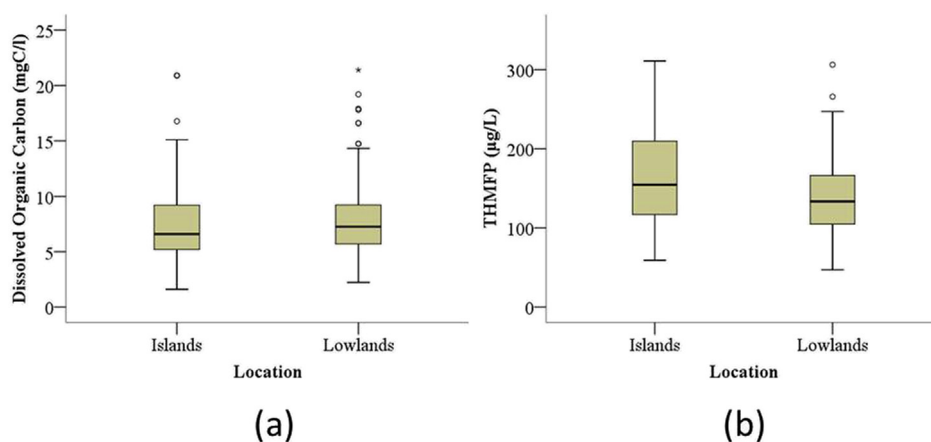**Fig. 9.** Box plots-and-whiskers representing the a) DOC (mg/L) and THMP (μg/L) for the two locations in raw and treated water, respectively.

- All WQDs are reasonable indicators of DBPFP in the raw waters sampled in the study, with only colour correlating slightly more weakly ($R^2 = 0.77$) with THMFP than the other surrogates UV_{254}, DOC and HPO ($R^2 = 0.79-0.82$); equivalent values for THAAFP were 0.63 for colour and 0.71–0.74 for the other three WQDs. Both UV_{254} and DOC thus appear to be as good an indicator of DBPFP as HPO for both THMs and HAAs, such that chemical fractionation offers little additional benefit in determining DBPFP for the waters studied;
- R^2 values for the corresponding correlations for treated waters were <0.56 for THMFP and <0.48 for THAAFP, apart from THMFP vs DOC ($R^2 = 0.67$), reflecting the reduced HPO content which represents the most reactive organic carbon component;
- Seasonal trends in DBPFP followed that of UV254, with no apparent impact on yield, whereas as a slight increase in yield was evident with location specifically for island-based installations.

It is concluded that UV_{254} offers a reasonable surrogate for DBPFP across the geographical region studied, particularly with reference to THMs for which the measured correlation coefficient was 0.82 for the raw waters. Evidence suggests that this relates to the commensurately close correlation ($R^2 = 0.91$) between UV_{254} and the hydrophobic content of the DOC. However, the correlation is weaker for the treated waters due to the reduced HPO content

and prevalence of other less reactive organics which nonetheless contribute to DBPFP.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2017.01.051.

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