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Formation of halogenated disinfection by-products during microfiltration and reverse osmosis treatment: Implications for water recycling

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Abstract

A suite of 34 disinfection by-products (DBPs), including 8 halomethanes, 9 haloacetic acids, 6 haloacetonitriles, 6 haloaldehydes, 4 haloketones and the halonitromethane chloropicrin, were monitored in two microfiltration (MF) and reverse osmosis (RO) treatment plants as part of a larger study of chemical removal by MF/RO treatment for water recycling purposes. Both DBP detection frequency and concentration increased during treatment, and this was attributed to a chloramination step used to minimize RO membrane fouling. The degree of DBP formation was particularly related to plant residence time, with DBPs falling into two distinct groups; the first group in which DBP concentration increased with increasing residence time (e.g. chloroform and bromochloroacetaldehyde) and a second group in which increased residence time did not affect the concentration (e.g. dichloroacetic acid and 1,1-dichloropropanone). These results indicate that MF/RO plant design and wastewater quality are both important factors in minimising DBP formation within MF/RO treatment. RO rejection was influenced by several chemical-specific

properties, including pKa, log Kow and DBP class. Rejection of haloacetic acids, present as charged molecules, was consistently better than 90% and did not alter with log Kow. For all other DBPs, present as neutral molecules, rejection was much more variable, and decreased with decreasing log Kow, although the effect of MW and log Kow on rejection could not be separated. The DBP formation described in this study lead to variable estimations of DBP removal by RO and thus it is recommended that DBPs are used as indicators of RO removal efficiency with caution, and only after DBP formation within RO treatment has been studied.

Key words

indirect potable reuse, chloramination, disinfection by-product formation

1. Introduction

Water scarcity is driving the increased use of recycled water, and removal of contaminants from treated wastewater is now an important research issue, particularly for potable reuse [1, 2]. Typically, a combination of advanced treatments, such as ultrafiltration, microfiltration (MF) or reverse osmosis (RO) membranes, ultraviolet irradiation, or advanced oxidation processes, are applied prior to potable reuse [1, 2]. However, the formation of additional chemicals during advanced treatment has not yet been rigorously studied.

One class of chemicals extensively studied in drinking water, but less so in wastewater, is disinfection by-products (DBPs), which result from reactions between precursors such as natural organic matter (NOM) and disinfectants such as chlorine, monochloramine or ozone. More than 600 DBPs, representing a variety of chemical classes, and produced under a wide range of disinfection conditions and in different drinking waters have been identified [3]. While some DBPs are of little health concern, long-term DBP exposure has been associated with increased bladder cancer risk [4] and some growth-related birth outcomes [5]. Evidence remains inconclusive for association of DBP exposure with other cancers [6], or with other adverse reproductive or developmental outcomes [7, 8].

Several studies have already measured DBPs and DBP precursors in secondary wastewater [9-11] and their presence may be related to DBPs originally present in drinking water, the use of

household products that contain chlorine such as bleach [12], or due to chlorine dosed during wastewater treatment. More recently, DBPS have been found be amongst the most frequently detected chemicals in RO-treated wastewater [13]. Wastewater may also be disinfected before release to the environment [9, 11]. Ammonia is often present in secondary wastewater, meaning that disinfection may occur after the formation of chloramine species (chloramination), rather than *via* free chlorine [9, 11].

Compared to chlorination, chloramination of drinking water significantly reduces the formation of commonly regulated DBPs such as the trihalomethanes (THMs) and haloacetic acids (HAAs) [14, 15]. However, formation of other emerging DBPs may increase [16], particularly nitrogen containing DBPs [17, 18]. Chloramination has also been shown to increase the proportion of dihalogenated DBPs that form compared to trihalogenated DBPs, particularly for HAAs [18-22], but also for haloacetonitriles (HANs) [21], haloaldehydes (HALs) [11, 21] and haloketones (HAKs) [21, 23]. The difference in formation between dihalogenated HAAs (DHAAs) and trihalogenated HAAs (THAAs) has been attributed to different precursors and reaction pathways in chloramination [24, 25] than those occurring during chlorination. For other classes of DBPs, it has been suggested that trihalogenated species require the production of a dihalogenated intermediate [26] and that these intermediates are stable in chloraminated systems and therefore do not undergo further halogen substitution [23].

Chloramination has been considered a special case of chlorination, where DBP formation is still controlled by the small quantities of free chlorine released through disassociation of monochloramine [9, 19, 22]. However, DBP formation by direct action of chloramine species rather than free chlorine has been proposed for THMs [19], HAAs [9, 27, 28] and HANs [23, 29].

As part of a larger study of the removal of 396 compounds in MF/RO treatment [1], a suite of 34 DBPs were monitored throughout 2 MF/RO treatment plants. This paper describes the formation and removal of several DBPs within MF/RO treatment. The DBP classes studied included 8 halomethanes (HMs), including 4 THMs and 4 other HMs, the latter of which are not typically

studied in drinking water (chloromethane, bromomethane, dibromomethane and bromochloromethane), 9 HAAs, 6 HANs, 6 HALs, 4 HAKs, and the halonitromethane chloropicrin. In MF/RO treatment, it is standard practice to chloraminate wastewater before MF to minimize RO membrane fouling [30]. The chlorine dosed before MF rapidly reacts with ammonia present in wastewater to form monochloramine. Here, we consider the effect of MF/RO treatment and specifically the chloramination step in formation of DBPs during advanced water treatment, particularly focusing on reaction time, DBPs speciation, and bromine incorporation. DBPs concentration data is also used to calculate RO rejection efficiency, and differences in rejection efficiency are discussed with respect to compound-specific properties such as charge and hydrophobicity. This study increases the number of DBPs that have been characterized in MF/RO water recycling systems, and provides evidence that DBP formation within MF/RO plants can lead to an underestimation of RO treatment performance.

2. Experimental Methods

2.1. Water Recycling Plants.

Samples were collected from 2 MF/RO treatment plants operating in Perth, Australia: the full-scale Kwinana Water Recycling Plant (KWRP) and the pilot-scale Beenyup Pilot Plant (BPP). At KWRP, secondary treated wastewater from Woodman Point wastewater treatment plant (WWTP) is subjected to MF/RO to produce approximately 17 ML/day of recycled water for use by neighbouring industry. The BPP treats secondary wastewater from Beenyup WWTP, Perth's major northern metropolitan WWTP. While most secondary wastewater from Beenyup WWTP is discharged to the Indian Ocean, a small volume (~100 kL/day) is treated by MF/RO in the BPP, with the recycled water used for research purposes only. Further details of each plant have been previously published [1, 31].

While the MF/RO treatment process is slightly different at each plant, both consist of initial coarse screening filter, chloramination and pH adjustment, continuous MF, and RO membrane treatment, as depicted in Figure 1.

2.2. Sample Collection.

Sampling was carried out from December 2006 to October 2008 [1]. Typically sampling focused on secondary wastewater and post-RO water. However, on a number of occasions, sampling of post-MF water was also undertaken and the results reported in this paper are from the sampling events which had at least 1 set of samples that included wastewater, post-MF and post-RO, matched for date and plant. This occurred on 5 occasions at KWRP (Event 2: 30th May 2007, 4th June 2007, 7th June 2007, Event 3: 21st September 2007, and Event 6: 6th June 2008) and on 3 occasions at BPP (Event 3: 26th September 2007, Event 4: 1st April 2008 and Event 6: 5th June 2008), providing 8 paired samples in total. Field and trip blanks were also collected on each day of sampling and analysed in the same manner as samples.

To avoid DBP formation and degradation after sampling, grab samples were taken for DBP measurements and preservation agents were added to all sampling bottles prior to sample collection, as described in the supporting information in Table S1. Samples were analyzed as soon as practicably possible and were processed in an order based on analyte stability. Generally HAAs samples were analyzed first, followed by other halogenated DBPs, and then halomethanes. All samples were stored at 4 °C in the dark until analysis.

2.3. Analytical Methods.

All DBPs were measured by gas chromatography mass spectrometry (GC-MS), although different sample preparation methods were used for different groups [1]. Halomethanes were separated and concentrated using on-line purge and trap and measured by GC-MS; HAAs were preconcentrated by liquid-liquid extraction (LLE) and derivatized to their corresponding methyl esters by the addition of acidic methanol before GC-MS analysis; HANs, HALs, HAKs and chloropicrin were all measured in a single method incorporating preconcentration by LLE before GC-MS analysis. Further details of the analytical methods are presented in the supporting information.

3. Results and Discussion

3.1. DBP Detection Frequency and Concentration.

Analysis of both detection frequency (Table 1) and median concentration data (Table 2) demonstrates that there is an increased detection frequency and concentration for several DBPs in post-MF water compared to secondary wastewater for both KWRP and BPP. For KWRP, the highest median concentrations for 23 of 34 DBPs (68%) were found in post-MF water samples. Moreover, 9 DBPs detected in post-MF water were not detected in either wastewater or post-RO water, while 4 DBPs were detected in post-MF and post-RO water but not in wastewater. At BPP, 9 DBPs (26%) showed the highest median concentration in post-MF water samples, with 3 DBPs detected in post-MF water but not in either wastewater or post-RO water, and 1 DBP was detected in post-MF and post-RO water but not in wastewater.

Whilst there was significant variation in concentrations, as illustrated by the 95% confidence interval (CI) error bars in Figures S1 and S2 (see supporting information), post-MF concentrations were statistically greater than wastewater concentrations for several DBPs. At KWRP, post-MF concentrations were statistically greater than concentrations in wastewater for 8 DBPs: 2 THMs (chloroform, bromodichloromethane), 2 HAAs (dichloroacetic acid and bromochloroacetic acid), 1 HAN (dichloroacetonitrile), and 3 HALs (trichloroacetaldehyde, dibromoacetaldehyde, bromochloroacetaldehyde). At BPP, post-MF concentrations were statistically greater for 2 DBPs: bromochloroacetic acid and 1,1-dichloropropanone.

At both BPP and KWRP, wastewater undergoes chloramination before MF to minimize RO membrane fouling. Chlorine dosing occurs after secondary wastewater has been adjusted to a target pH value of 6, to avoid RO membrane scaling. The chlorine rapidly reacts with ammonia present in the secondary wastewater to form monochloramine. Thus, the increase in both DBP detection frequency and concentrations measured post-MF is attributed to this chloramination step. Furthermore, the increased DBP detection frequency measured at KWRP compared to BPP is probably influenced by differences in the chloramination process used at each plant. At KWRP, sodium hypochlorite (NaOCl) is added to achieve a final chloramine concentration of 1.65 mg/L.

Aqueous ammonia is only added when the ammonia concentration in the secondary wastewater is less than 1 mg/L. The average ammonia concentration at KWRP during this study was 6.8 ± 5.0 mg/L [1] and additional ammonia was never required. The residence time between the NaOCl dosing point and the post-MF sampling point is about 25 minutes when KWRP is operating at full capacity and longer if the plant is operating at less than full capacity. At BPP, aqueous ammonia and sodium hypochlorite (NaOCl) are dosed constantly to maintain consistent chloramine concentrations of 1-1.5 mg/L (winter) and 1.5-2 mg/L (summer) and an oxidation reduction potential reading between 470-510 mV. The residence time between the dosing point and the post-MF sample point is about 20 seconds, plus several additional minutes in storage prior to RO treatment. Therefore the time available for DBP formation is relatively short. Therefore, it is likely that the elevated concentrations of DBPs observed post-MF at KWRP are related to the longer plant residence times compared to at BPP. A similar impact of residence time was seen in a Queensland MF/RO plant, where decreased contact times of chloramine before MF/RO also resulted in lower bromodichloromethane concentrations [32].

3.2. Effect of Flow Rate on DBP Formation.

The effect of plant residence time on DBP formation at KWRP was further investigated by comparing plant flow to the increase in DBP concentrations between secondary wastewater and post-MF sampling points. The net increase in DBP concentration for each sampling day at KWRP for the 8 DBPs with significantly greater post-MF concentrations was plotted against average daily plant flow (Figure 2), excluding trichloroacetaldehyde, which was only detected in 1 post-MF sample. Pearson correlations indicated that DBPs can be classified into 2 distinct groups. For 5 DBPs (chloroform, bromodichloromethane, bromochloroacetaldehyde, dibromoacetaldehyde, dichloroacetonitrile), DBP formation was negatively correlated with flow rate ($R < -0.5$) suggesting that these DBPs continue to form with increased residence time within the plant. For chloroform and bromochloroacetaldehyde the correlation between flow rate and their formation was significant at $p < 0.05$, while for dichloroacetonitrile, the correlation was significant at $p < 0.1$. For the second

group of 3 DBPs (bromochloroacetic acid, dichloroacetic acid and 1,1-dichloropropanone), a higher flow rate apparently either increased or had no effect on formation ($R > -0.5$). It is noted that the positive correlation for the 2 HAAs is particularly influenced by 1 data point, in which the highest formation was measured at the highest flow rate, and this may have skewed data that otherwise show no significant positive correlation. In any case, formation of these 3 DBPs did not increase with increased reaction time (i.e. decreasing flow rate) after an apparent initial rapid rate of formation. Bromochloroacetic acid and 1,1-dichloropropanone were the only DBPs to show a statistically significant increase at BPP, where reaction time is in the order of minutes and this would also support the hypothesis that these DBPs formed faster than the other studied DBPs. However, the difference in behavior between the 2 groups cannot be explained by reaction rate alone. Other factors that may affect DBP concentrations over time include limited precursor concentrations and the nature of those precursors, the role of free chlorine or other chloramine species such as dichloramine, and competing degradation reactions [19, 26, 33, 34].

Reaction rates for DHAA formation have previously been found to be faster than for THM formation in chloramination studies of humic matter [15]. In addition DHAA formation has been postulated to occur from functional groups that reacted quickly with chlorine [25, 26], as opposed to other DBPs that form from slower reacting sites that arose after depletion of the fast reacting functional groups. Thus the formation pattern of bromochloroacetic acid and dichloroacetic acid at KWRP could be attributed to reactions with fast reacting functional groups that are rapidly depleted, suggesting that concentrations of these DHAA are more influenced by precursor concentration or nature than plant residence time. Formation of 1,1-dichloropropanone has also been found to be more influenced by precursor concentration than chloramine concentration [23], suggesting again that precursor concentration is more important than plant residence time.

Neither of the DBP formation patterns described can be explained by reactions with species other than monochloramine, such as free chlorine (HOCl), which is present before monochloramine formation and released after monochloramine disassociation, or dichloramine. The reaction of

HOCl with ammonia is extremely rapid [33], and there is significant excess ammonia in both MF/RO plants (molecular ratio of Cl:N in KWRP is 0.07 and in BPP is 0.7). Therefore the initial free HOCl concentration would not have been significant in these systems. Dichloramine formation is similarly minimized in low Cl:N systems [19, 35], particularly at pH = 6-7, when degradation of dichloramine is rapid compared to monochloramine decomposition [35].

While it could be hypothesized that the rapid formation observed for bromochloroacetic acid, dichloroacetic acid and 1,1-dichloropropanone is controlled by the depletion of free HOCl rather than limited by precursor concentrations, DHAA formation in the presence of preformed monochloramine at concentrations comparable to those measured in this study has been demonstrated for raw drinking waters [28]. Monochloramine decomposition will be limited in the presence of excess ammonia, and DBP formation after monochloramine decomposition has been shown to be delayed by up to 4 hours [27], which is a much longer time than the residence time in either MF/RO plant.

Finally, competing degradation reactions are also unlikely to contribute significantly to the formation pattern seen for bromochloroacetic acid, dichloroacetic acid and 1,1-dichloropropanone. Degradation pathways for HAAs rely on the presence of free chlorine for transformation and low reaction rates means that significant changes to HAA concentrations occur on daily or weekly timescales [34]. 1,1-dichloropropanone is also known to be stable in chloramine solutions below pH 7 [23], again suggesting 1,1-dichloropropanone degradation is not favoured in the studied systems.

3.3. Degree of Halogenation and Bromine Incorporation.

Most (6 out of 9) DBPs found at highest concentration in post-MF water were dihalogenated rather than trihalogenated. The THMs were the only trihalogenated species formed. There is a significant body of evidence supporting the preferential formation of dihalogenated DBPs over trihalogenated DBPs in chloraminated wastewater and drinking water systems for HAAs, HANs, HALs and HAKs [11, 18-23]. This is usually attributed to differences in reaction pathways for dihalogenated and trihalogenated species [24, 25] or because monochloramine does not have

sufficient halogen substitution power to produce trichlorinated species from dichlorinated intermediates [23, 26]. This pattern has not been observed for HMs, however mono and dihalogenated HMs are rarely studied. While only THMs showed significant increases in post-MF water in this study, it should be noted that the 2 most frequently detected analytes were the DHMs bromochloromethane and dibromomethane, which were found in all samples including post-RO water. In comparison, the percentage detection of all other DBPs in post-RO water was much lower. Little is known about DHM formation in either drinking water or wastewater. While bromochloromethane and dibromomethane were not detected in the EPA Nationwide Occurrence Survey [16, 36], detection limits in that study (0.1-0.5 μg/L) were an order of magnitude poorer than those achieved here. Bromochloromethane and dibromomethane have been noted in other studies discussing DBP toxicity, and prioritization of emerging and regulated DBPs, although these DBPs are largely discounted because their concentrations are rarely above LOD [3, 37]. Given that previously devised benchmark values assigned to DHMs [1] are lower than those of regulated THMs, further investigation of DHMs and potential DHM precursors would enable a better understanding of the high frequency of detection observed in this study.

While bromide oxidation to HOBr is not favoured in the absence of free chlorine, Br incorporation into DBPs in chloraminated systems is still possible through production of bromochloramine and other Br-substituted amines [28, 33]. The proportion of Br-DBPs was evaluated using the Bromine Incorporation Factor (BIF) [10, 18, 20, 38]. As described by Obolensky and Singer [38], BIF is calculated as the ratio of the molar contribution of all brominated species compared to the total molar contribution of all DBP species and enables comparison of Br incorporation across DBP classes (Table S3, supporting information). Generally BIFs were < 0.1 except for BIF (THM4) in BPP (0.37 and 0.44 for secondary wastewater and post-MF water respectively), and there were no statistically significant trends in BIF for secondary wastewater and post-MF water for any DBP class. Bromide concentrations in the secondary wastewater entering BPP (0.28 ± 0.05 mg/L) and KWRP (0.27 ± 0.1 mg/L) were relatively stable during the study [1]

and high compared to many international drinking water sources [18, 21, 38]. However, DOC in secondary wastewater is also high compared to many drinking water sources (BPP average 8.1 ± 0.6 mg/L; KWRP average 10.1 ± 1.1 mg/L) and the resulting Br:DOC ratios (BPP ~ 35 μg Br/mg DOC, and KWRP ~ 26 μg Br/mg DOC) are much lower than used in studies testing Br incorporation into DBPs in chloraminated systems [9, 25], or in drinking water systems that show significant formation of Br-THMS [21]. The lack of correlations found for the BIFs is consistent with other studies [20].

3.4. RO Rejection Efficiency and Treatment Performance.

While RO rejection of chloroform has been measured in a number of studies [2, 39], there is relatively little data concerning rejection of other halogenated DBPs. This study presents new RO rejection data for HALs, HAKs and HANs. The efficiency of RO to remove DBPs is important as it is the only barrier for DBP removal in MF/RO treatment. However, given the potential for formation of DBPs after chloramination, RO rejection efficiency cannot be determined using the DBPs concentrations in secondary wastewater. Thus, RO rejection efficiency was calculated using paired post-MF and post-RO samples. This approach has previously been demonstrated to produce higher treatment efficiency values than using paired secondary wastewater and post-RO samples for DBPs and VOCs that increase in concentration after chloramination or exposure to the atmosphere [1, 40], and also enabled calculation of RO rejection for 9 additional DBPs not originally detected in secondary wastewater. For those DBPs whose concentration was below LOD after RO, the efficiency was calculated assuming a concentration equal to half the LOD as a worst-case scenario, but this approach was only used when the post-MF concentration was at least 5 times higher than the LOD [2, 41]. Rejection efficiencies calculated from KWRP data are plotted in Figure 3. Very high variability is seen in rejection efficiency for some DBPs, as indicated by large standard deviations. Membrane rejection can be influenced by compound-specific properties (e.g. molecular size, solubility, diffusivity, polarity, hydrophobicity, and charge), membrane properties (e.g., permeability, pore size, hydrophobicity, and charge), as well as membrane operating conditions

(e.g., flux, transmembrane pressure, and regeneration). Based on a comprehensive literature review, Bellona *et al*. [42] have proposed a scheme for qualitative prediction of rejection of organic micropollutants which considers molecular weight (MW), pKa, log Kow and molecular width. The most important solute-membrane interaction important for chemicals removal are steric exclusion, charge interaction and solute-membrane affinity (e.g. hydrophobic attraction or hydrogen bonding) [43]. The MW range (50-250 Da) of the DBPs considered in this work spans the nominal MW cut-off (MWCO) of the RO membrane (approx. 100–150 Da), and thus solute membrane affinity is likely to be important in determining rejection rates. Controlled studies using compounds of comparable MW (~ 150 Da), but varying log Kow (–2.56 to 2.45) has shown that increasing hydrophobicity decreases rejection for 'tight' nanofiltration membranes (MWCO ~ 150-300 Da), which results from increased attraction of hydrophobic molecules to the membranes, and also potentially because the effective diameter of hydrophilic compounds is increased due to hydration [44]. However, neutral hydrophobic compounds also have the highest adsorption onto the (typically) hydrophobic membranes, meaning that apparent rejection can appear to be higher for hydrophobic compounds if the membrane has not yet reach steady state with respect to adsorption [45].

In this study, only 1 class of DBPs (HAAs) have pKa values that are lower than the typical operating pH of KWRP (pH 6) and are therefore expected to be present as negatively charged molecules that will be electrostatically repulsed from the negatively charged membrane [46]. Rejection of HAAs was consistently better than 90% and did not alter with either log Kow or MW. For all other DBPs, which are expected to be present as neutrally molecules, RO rejection was much more variable, as evidenced by larger standard deviation bars in Figure 3. Rejection was not statistically correlated with MW ($R= 0.058$ $p = 0.724$), but decreased with decreasing log Kow ($R = 0.604$ significant at $p <0.01$). This was particularly evident for HMs with log Kow < 2, which showed lower median rejections and much greater variability in rejection compared to HMs with log Kow > 2. Rejection data for HAN and HAK also followed this trend, however it is noted that

rejection of the single HAL measured (bromochloroacetaldehye) was consistently high, despite log Kow = 1.11. It is possible that the aldehyde functional group aided membrane adsorption, an important factor in membrane rejection, and therefore rejection was underpredicted by log Kow [42, 47]. The observed positive correlation between rejection and hydrophobicity (log Kow) appears to contradict laboratory studies [44], unless the membranes have not yet reached steady state with respect to adsorption of hydrophobic compounds. However, this seems unlikely given KWRP had been in operation for over 30 months at the first sampling event. It is noted, however, that there is a better statistical correlation between MW and log Kow for these DBPs (R = 0.713), than the correlation of either parameter with rejection, suggesting that it is not possible to separate the influence of MW and log Kow on rejection for the DBPs studied. This is particularly likely, given the large MW range (50-250 Da), particularly in relation to the membrane MWCO, and the relatively low range of log Kow (0.43-2.22).

The median chloroform RO rejection efficiency was greater than 95%, which is significantly higher than the removal estimates of 25-50% seen in other studies [2, 41]. Removal efficiency of chloroform is highly dependent on the fouling stage of the membrane with higher removal by more fouled membranes [39]. The general trend of RO rejection of chloroform (i.e. post-MF to post-RO treatment efficiency) in this project was for greater removal by the KWRP (median RO removal 99%, n=5) than the BPP (median RO removal 60%, n=2). This may be due to the improved rejection of older, more fouled membranes at KWRP compared to the nine-month old BPP membranes and RO rejection of chloroform at BPP was more similar to previously reported values [2, 41]. Results for HANs and HAAs are comparable to those measured in seawater desalination [41]

The use of chemical indicators in recycled water has been proposed for monitoring and for assessing the performance of treatment processes [2, 40, 48, 49]. Ideally, treatment performance is monitored with a set of chemicals that represent a broad range of physico-chemical properties, in particular size, charge, and hydrophobicity to give confidence that the indicators chosen also

account for unknown and new chemicals with varying properties. The majority of DBPs are typically small, neutral compounds, with hydrophobic properties that lead to intermediate or poor RO rejection; chloroform in particular has been suggested as a treatment performance indicator for membrane treatment efficiency [2]. However, DBP formation as described in this study can lead to very variable estimations of treatment performance and thus it is recommended that DBPs are used as treatment performance indications with caution and only after DBP formation within the RO treatment process has been tested. This is particularly the case for chloroform, given the strong relationship between plant retention time and formation (e.g. Figure 2).

3.5. Significance of Results.

The formation of DBPs within MF/RO treatment lead to the detection of DBPs in post-RO water that were not otherwise present in the source secondary wastewater, and affected the overall removal efficiency of MF/RO treatment. As anticipated, plant residence time was a significant factor in DBP formation, directly affecting the percentage detection of DBPs in post-RO water, and resulting in a greater frequency of detections in the full-scale KWRP as compared to the pilot-scale BPP. Plant design minimizing chlorine contact time before RO is therefore critical in minimizing DBP concentrations in RO treated water. However, these results also demonstrate that reduction of contact time does not reduce all DBP formation, with some DBPs apparently controlled by precursor concentration. While further investigation is required, it is anticipated that WWTP processes also require optimization to minimise DBP precursors in secondary wastewater, such as through implementation of advanced biological treatment upstream of MF/RO treatment. Despite uncertainties over DBPs formation and RO removal, median concentrations in post-RO water remained lower than health values (Table S2), indicating that there was no human health concern from DBPs in the MF/RO systems studied in this project.

This study increases the number of DBPs that have been characterized in MF/RO water recycling systems. In particular, the consistent detection of 2 DHMs, dibromomethane and bromochloromethane, is unusual. Given that previously devised benchmark values assigned to

DHMs are lower than those of regulated THMs, further investigation of DHMs and potential DHM precursors would enable a better understanding of the significance of the high frequency of detection observed in this study.

Reverse osmosis is the only barrier in the MF/RO treatment process for chemical removal and thus is essential for removal of DBPs from recycled water. However, it is apparent that calculation of DBP removal by comparing DBP concentrations in secondary wastewater and post-RO samples can be confounded by potential impacts from chloramination. The use of DBPs as treatment performance indicators is attractive because they represent small, poorly rejected compounds, can be measured routinely, and are typically detected at frequency and concentration appropriate for treatment performance indicators. However, as described in this study, DBP formation within MF/RO plants can lead to variable treatment performance and thus it is recommended that DBPs are used as treatment performance indicators with caution, and only after DBP formation within the MF/RO treatment process has been studied. Despite this, DBPs remain excellent indicators of recycled water quality for regular monitoring of final product water because of their widespread occurrence and drinking water health significance.

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Figure Captions

Figure 1. Schematic diagram showing the location of secondary wastewater, post-microfiltration (MF) and post-reverse osmosis (RO) sampling points at Kwinana Water Recycling Plant and Beenyup Pilot Plant. At both plants, wastewater undergoes chloramination before MF to minimize RO membrane fouling. Chlorine dosing occurs after secondary wastewater has been adjusted to a target pH value of 6, to avoid RO membrane scaling. The chlorine reacts with ammonia, either present in secondary wastewater or added, to form monochloramine.

Figure 2. Comparison of the net increase in concentration for DBPs with post-MF concentrations that were statistically greater than concentrations in secondary wastewater plotted against average daily plant flow rate for all samples from Kwinana Water Recycling Plant.

Figure 3. Percentage RO rejection calculated using paired post-MF and post-RO samples from Kwinana Water Reclamation Plant. Rejection was calculated using half the LOD for those DBPs reported below LOD after RO, but only when the concentration in the post-MF sample was at least 5 times greater than LOD. Error bars represent the standard deviation, although those points with an asterisk represent one paired data point only. Log Kow data was calculated using ACD ChemSketch (ACD/Labs, Toronto, Canada).

Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2012.11.031.

References

[1] P. Van Buynder, R. Lugg, C. Rodriguez, M. Bromley, J. Filmer, P. Blair, M. Handyside, S. Higginson, N. Turner, O. Lord, P. Taylor, K. Courtney, C. Newby, A. Heitz, K. Linge, J. Blythe, F. Busetti, S. Toze, Premier's Collaborative Research Program (2005-2008): Characterising Treated Wastewater For Drinking Purposes Following Reverse Osmosis Treatment. Technical Report, Department of Health, Western Australia, 2009.

[2] J.E. Drewes, D. Sedlak, S. Snyder, E. Dickenson, Development of Indicators and Surrogate for Chemical Contaminant Removal during Wastewater Treatment and Reclamation, WateReuse Foundation, Alexandria, VA, 2008.

[3] S.D. Richardson, M.J. Plewa, E.D. Wagner, R. Schoeny, D.M. Demarini, Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research, Mutat. Res., 636 (2007) 178-242.

[4] C.M. Villanueva, K.P. Cantor, J.O. Grimalt, N. Malats, D. Silverman, A. Tardon, R. Garcia-Closas, C. Serra, A. Carrato, G. Castaño-Vinyals, R. Marcos, N. Rothman, F.X. Real, M. Dosemeci, M. Kogevinas, Bladder cancer and exposure to water disinfection by-products through ingestion, bathing, showering, and swimming in pools, Am. J. Epidemiol., 165 (2007) 148-156.

[5] R.G. Tardiff, M.L. Carson, M.E. Ginevan, Updated weight of evidence for an association between adverse reproductive and developmental effects and exposure to disinfection by-products, Regul. Toxicol. Pharm., 45 (2006) 185-205.

[6] M.J. Nieuwenhuijsen, R. Smith, S. Golfinopoulos, N. Best, J. Bennett, G. Aggazzotti, E. Righi, G. Fantuzzi, L. Bucchini, S. Cordier, C.M. Villanueva, V. Moreno, C. La Vecchia, C. Bosetti, T. Vartiainen, R. Rautiu, M. Toledano, N. Iszatt, R. Grazuleviciene, M. Kogevinas, Health impacts of long-term exposure to disinfection by-products in drinking water in Europe: HIWATE, J. Water Health, 7 (2009) 185-207.

[7] T.J. Luben, A.F. Olshan, A.H. Herring, S. Jeffay, L. Strader, R.M. Buus, R.L. Chan, D.A. Savitz, P.C. Singer, H.S. Weinberg, S.D. Perreault, The healthy men study: an evaluation of exposure to disinfection by-products in tap water and sperm quality, Environ. Health Perspect., 115 (2007) 1169-1176.

[8] M.J. Nieuwenhuijsen, D. Martinez, J. Grellier, J. Bennett, N. Best, N. Iszatt, M. Vrijheid, M.B. Toledano, Chlorination Disinfection By-Products in Drinking Water and Congenital Anomalies: Review and Meta-Analyses, Environ. Health Perspect., 117 (2009) 1486-1493.

[9] Y.N. Qi, C. Shang, I.M.C. Lo, Formation of haloacetic acids during monochloramination, Water Res., 38 (2004) 2375-2383.

[10] S.W. Krasner, P. Westerhoff, B.Y. Chen, B.E. Rittmann, G. Amy, Occurrence of Disinfection Byproducts in United States Wastewater Treatment Plant Effluents, Environ. Sci. Technol., 43 (2009) 8320-8325.

[11] S.W. Krasner, P. Westerhoff, B. Chen, G. Amy, S.N. Nam, Z.K. Chowdhury, S. Sinha, B.E. Rittmann, Contribution of Wastewater to DBP Formation, AWWA Research Foundation, Denver, CO, 2008.

[12] European Communities, Pollutants in urban waste water and sewage sludge, in, Office for Official Publications of the European Communities, Luxembourg, 2001, pp. 273.

[13] K.L. Linge, P. Blair, F. Busetti, C. Rodriguez, A. Heitz, Chemicals in Reverse Osmosis-treated Wastewater: Occurrence, Health Risk, and Contribution to Residual Dissolved Organic Carbon, Journal of Water Supply: Research and Technology - AQUA, (in press).

[14] J.F. Lu, T. Zhang, J. Ma, Z.L. Chen, Evaluation of disinfection by-products formation during chlorination and chloramination of dissolved natural organic matter fractions isolated from a filtered river water, J. Hazard. Mater., 162 (2009) 140-145.

[15] W. Liu, L.M. Cheung, X. Yang, C. Shang, THM, HAA and CNCl formation from UV irradiation and chlor(am)ination of selected organic waters, Water Res., 40 (2006) 2033-2043.

[16] S.W. Krasner, H.S. Weinberg, S.D. Richardson, S.J. Pastor, R. Chinn, M.J. Sclimenti, G.D. Onstad, A.D. Thruston, Occurrence of a new generation of disinfection byproducts, Environ. Sci. Technol., 40 (2006) 7175-7185.

[17] M.J. McGuire, J.L. McLain, A. Obolensky, Information Collection Rule Data Analysis, AWWA Research Foundation, Denver, CO, 2002.

[18] I. Kristiana, Disinfection By-Products in Chlorinated and Chloraminated Potable Water Systems: Effects of Precursors and Environmental Factors, in: Department of Chemistry, Curtin University, Perth, 2007, pp. 363.

[19] A.C. Diehl, G.E. Speitel, J.M. Symons, S.W. Krasner, S.J. Hwang, S.E. Barrett, DBP formation during chloramination, J. Am. Water Work Assoc., 92 (2000) 76-90.

[20] E.H. Goslan, S.W. Krasner, M. Bower, S.A. Rocks, P. Holmes, L.S. Levy, S.A. Parsons, A comparison of disinfection by-products found in chlorinated and chloraminated drinking waters in Scotland, Water Res., 43 (2009) 4698-4706.

[21] C.M.M. Bougeard, E.H. Goslan, B. Jefferson, S.A. Parsons, Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine, Water Res., 44 (2010) 729-740.

[22] G.A. Cowman, P.C. Singer, Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances, Environ. Sci. Technol., 30 (1996) 16-24.

[23] X. Yang, C. Shang, P. Westerhoff, Factors affecting formation of haloacetonitriles, haloketones, chloropicrin and cyanogen halides during chloramination, Water Res., 41 (2007) 1193-1200.

[24] L. Liang, P.C. Singer, Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water, Environ. Sci. Technol., 37 (2003) 2920-2928.

[25] S.E. Duirk, R.L. Valentine, Bromide oxidation and formation of dihaloacetic acids in chloraminated water, Environ. Sci. Technol., 41 (2007) 7047-7053.

[26] G.V. Korshin, M.M. Benjamin, H.S. Chang, H. Gallard, Examination of NOM chlorination reactions by conventional and stop-flow differential absorbance spectroscopy, Environ. Sci. Technol., 41 (2007) 2776-2781.

[27] Y. Hong, S.B. Liu, H. Song, T. Karanfil, HAA formation during chloramination - significance of monochloramine's direct reaction with DOM, J. Am. Water Work Assoc., 99 (2007) 57-69.

[28] P.G. Pope, G.E. Speitel, M.R. Collins, Kinetics of dihaloacetic acid formation during chloramination, J. Am. Water Work Assoc., 98 (2006) 107-120.

[29] X. Yang, C. Fan, C. Shang, Q. Zhao, Nitrogenous disinfection byproducts formation and nitrogen origin exploration during chloramination of nitrogenous organic compounds, Water Res., 44 (2010) 2691-2702.

[30] C.R. Bartels, M. Wilf, K. Andes, J. Iong, Design considerations for wastewater treatment by reverse osmosis, Water Sci. Technol., 51 (2005) 473-482.

[31] F. Busetti, A. Heitz, Determination of human and veterinary antibiotics in indirect potable reuse systems, Int. J. Environ. Anal. Chem., 91 (2011) 989-1012.

[32] Y. Kumar, T. Walker, Y. Poussade, C. Robillot, Towards the effective management of disinfection by-products in water recycling plants: the example of Bundamba Advanced Water Treatment Plant., in: Ozwater 2010, Brisbane, Australia, 2010.

[33] P.J. Vikesland, K. Ozekin, R.L. Valentine, Monochloramine decay in model and distribution system waters, Water Res., 35 (2001) 1766-1776.

[34] X.R. Zhang, R.A. Minear, Decomposition of trihaloacetic acids and formation of the corresponding trihalomethanes in drinking water, Water Res., 36 (2002) 3665-3673.

[35] C.T. Jafvert, R.L. Valentine, Reaction scheme for the chlorination of ammoniacal water, Environ. Sci. Technol., 26 (1992) 577-586.

[36] H.S. Weinberg, S.W. Krasner, S.D. Richardson, A.D. Thruston, The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a National DBP Occurence Study, Environmental Protection Agency, Athens, GA, 2002.

[37] A. Hebert, D. Forestier, D. Lenes, D. Benanou, S. Jacob, C. Arfi, L. Lambolez, Y. Levi, Innovative method for prioritizing emerging disinfection by-products (DBPs) in drinking water on the basis of their potential impact on public health, Water Res., 44 (2010) 3147-3165.

[38] A. Obolensky, P.C. Singer, Halogen substitution patterns among disinfection byproducts in the Information Collection Rule database, Environ. Sci. Technol., 39 (2005) 2719-2730.

[39] J.E. Drewes, C. Bellona, M. Oedekoven, P. Xu, T.U. Kim, G. Amy, Rejection of wastewater-derived micropollutants in high-pressure membrane applications leading to indirect potable reuse, Environ. Prog., 24 (2005) 400-409.

[40] C. Rodriguez, K. Linge, P. Blair, F. Busetti, B. Devine, P. Van Buynder, P. Weinstein, A. Cook, Recycled water: potential health risks from volatile compounds and the use of 1,4-dichlorobenzene as a treatment performance indicator, Water Res., 46 (2012) 93-106.

[41] E. Agus, D.L. Sedlak, Formation and fate of chlorination by-products in reverse osmosis desalination systems, Water Res., 44 (2010) 1616-1626.

[42] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment - a literature review, Water Res., 38 (2004) 2795-2809.

[43] A.R.D. Verliefde, E.R. Cornelissen, S.G.J. Heijman, E.M.V. Hoek, G.L. Amy, B. Van Der Bruggen, J.C. Van Dijk, Influence of Solute-Membrane Affinity on Rejection of Uncharged Organic Solutes by Nanofiltration Membranes, Environ. Sci. Technol., 43 (2009) 2400-2406.

[44] L. Braeken, R. Ramaekers, Y. Zhang, G. Maes, B. Van der Bruggen, C. Vandecasteele, Influence of hydrophobicity on retention in nanofiltration of aqueous solutions containing organic compounds, J. Membr. Sci., 252 (2005) 195-203.

[45] B. Van der Bruggen, L. Braeken, C. Vandecasteele, Evaluation of parameters describing flux decline in nanofiltration of aqueous solutions containing organic compounds, Desalination, 147 (2002) 281-288.

[46] A.R.D. Verliefde, E.R. Cornelissen, S.G.J. Heijman, J. Verberk, G.L. Amy, B. Van der Bruggen, J.C. van Dijk, The role of electrostatic interactions on the rejection of organic solutes in aqueous solutions with nanofiltration, J. Membr. Sci., 322 (2008) 52-66.

[47] Y. Kiso, Factors affecting adsorption of organic solutes on cellulose acetate in an aqueous solution system, Chromatographia, 22 (1986) 55-58.

[48] M. Benotti, R. Trenholm, B. Vanderford, J. Holady, B. Stanford, S. Snyder, Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water., Environ. Sci. Technol., 43 (2009) 597-603.

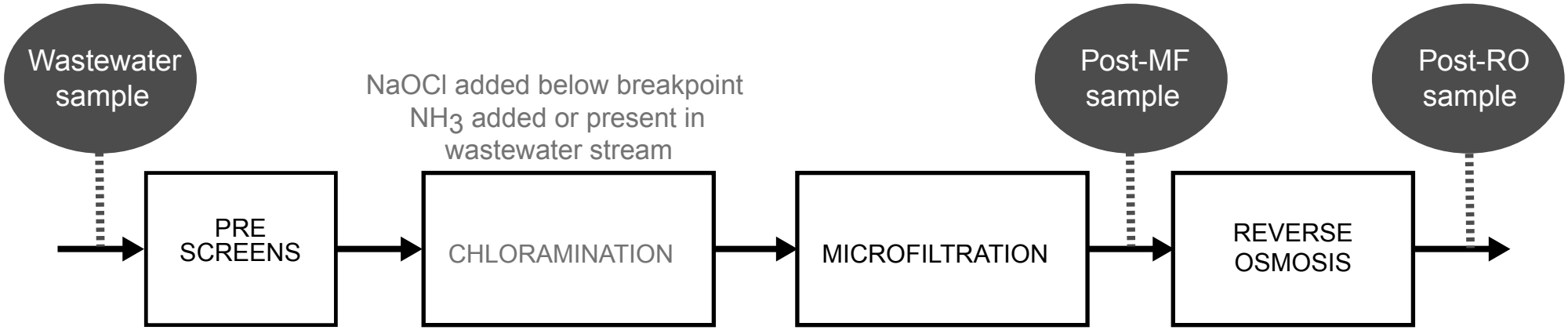
[49] E.R.V. Dickenson, S.A. Snyder, D.L. Sedlak, J.E. Drewes, Indicator compounds for assessment of wastewater effluent contributions to flow and water quality, Water Res., 45 (2011) 1199-1212.

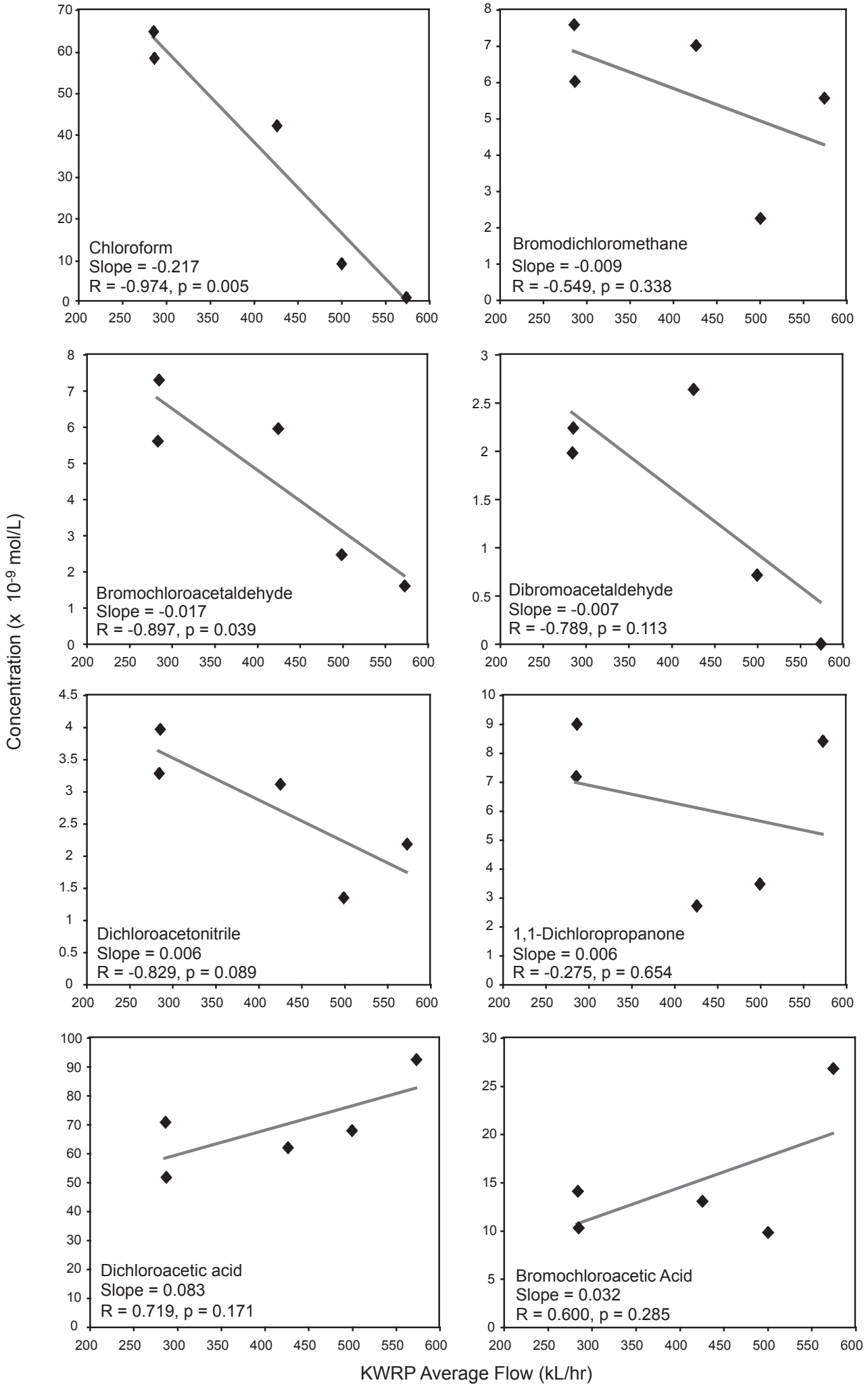
Table 1. Percentage detections of each DBP in secondary wastewater (n=8), post-MF water (n=8) and post-RO water (n=8); nd: not detected.

Analyte	**Secondary wastewater**	**Post-MF water**	**Post-RO water**
Bromochloromethane	100%	100%	100%
Bromomethane	nd	nd	nd
Chloromethane	37.5%	87.5%	37.5%
Chloroform	75.0%	100%	37.5%
Dibromomethane	100%	100%	100%
Bromodichloromethane	87.5%	100%	37.5%
Dibromochloromethane	75.0%	87.5%	12.5%
Bromoform	87.5%	87.5%	12.5%
Chloroacetic acid	12.5%	37.5%	nd
Bromoacetic acid	nd	25.0%	nd
Dichloroacetic acid	62.5%	100%	12.5%
Trichloroacetic acid	62.5%	87.5%	nd
Bromochloroacetic acid	nd	75.0%	nd
Dibromoacetic acid	nd	37.5%	nd
Dichlorobromoacetic acid	nd	25.0%	nd
Dibromochloroacetic acid	25.0%	25.0%	nd
Tribromoacetic acid	nd	nd	nd
Trichloroacetonitrile	nd	nd	nd
Chloroacetonitrile	nd	nd	nd
Dichloroacetonitrile	nd	75.0%	62.5%
Bromoacetonitrile	nd	nd	nd
Bromochloroacetonitrile	nd	50.0%	37.5%
Dibromoacetonitrile	nd	nd	nd
Trichloroacetaldehyde	nd	12.5%	nd
Bromochloroacetaldehyde	nd	62.5%	nd
Bromodichloroacetaldehyde	25.0%	12.5%	nd
Dibromoacetaldehyde	nd	50.0%	nd
Chlorodibromoacetaldehyde	nd	nd	nd
Tribromoacetaldehyde	nd	nd	nd
Chloroacetone	nd	37.5%	12.5%
1,1-Dichloropropanone	37.5%	68.8%	12.5%
1,1,1-Trichloropropanone	nd	62.5%	nd
1,3-Dichloropropanone	nd	37.5%	12.5%
Chloropicrin	nd	nd	nd

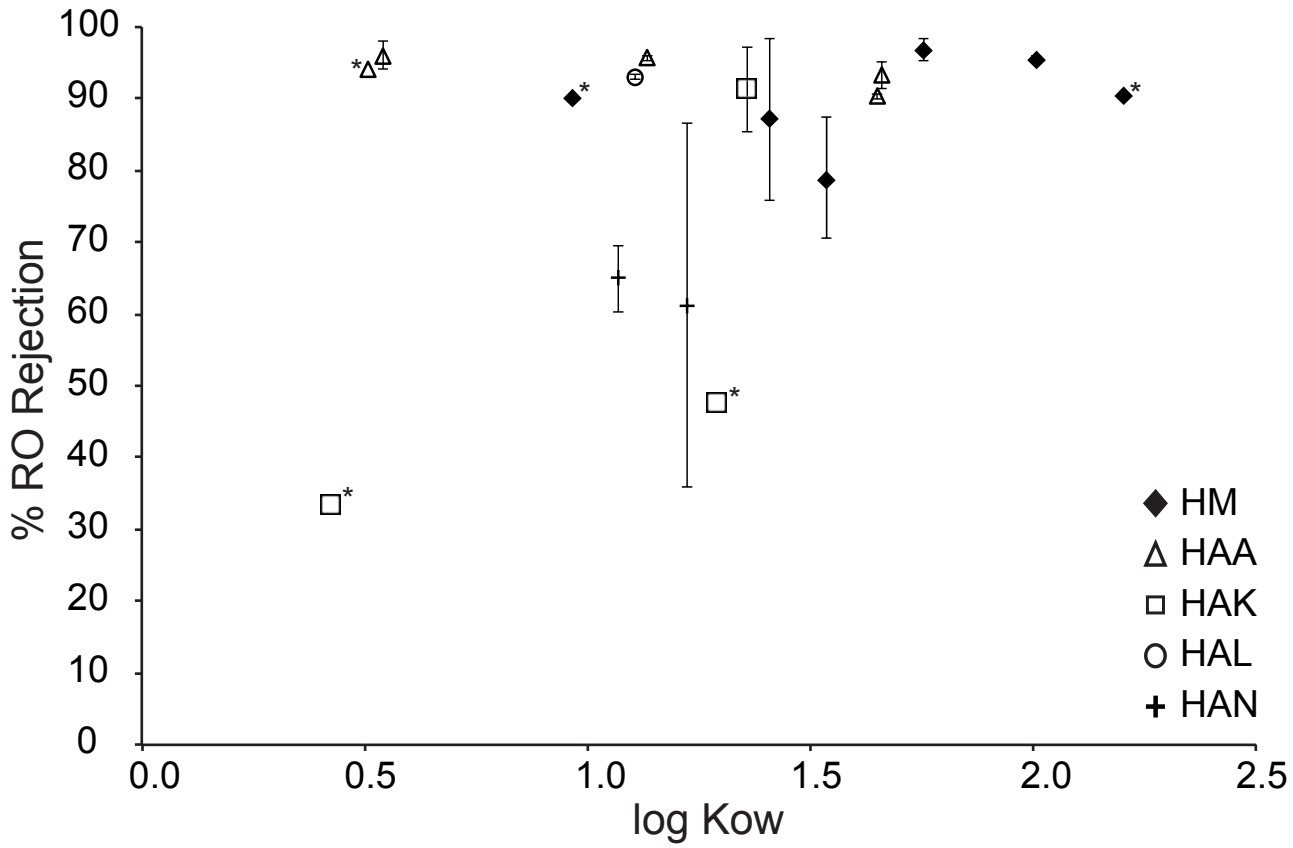
Table 2: Median concentrations of DBPs in paired secondary wastewater, post-MF water and post-RO water samples for both Kwinana Water Reclamation Plant (n=5) and Beenyup Pilot Plant (n=3). The range of detected concentrations is also included in parentheses. Data for bromomethane, tribromoacetic acid, trichloroacetonitrile, chloroacetonitrile, bromoacetonitrile, dibromoaceotnitrile, chlorodibromoacetaldehyde, tribromoacetaldehyde, and chloropicrin is not included as these DBPs were never detected above detection limits (LOD).

	Kwinana Water Recycling Plant			**Beenyup Pilot Plant**		
	Secondary wastewater	**Post-MF water**	**Post-RO water**	**Secondary wastewater**	**Post-MF water**	**Post-RO water**
Bromochloromethane	0.35 (0.25-1.2)	1.00 (0.40- 1.40)	0.10 (0.06- 0.35)	0.10 (0.06-0.22)	0.15 (0.05-0.18)	0.15 (0.06-0.23)
Chloromethane	0.51	0.20 (0.18-0.59)	0.06	0.05 (0.03-0.07)	0.06 (0.04-0.08)	0.07 (0.05-0.08)
Chloroform	1.35 (0.85-2.10)	7.00 (1.60-8.90)	0.06	0.27 (0.24-0.29)	0.30 (0.15-0.32)	0.12 (0.10-0.14)
Dibromomethane	0.56 (0.27-1.2)	0.98 (0.50-1.40)	0.17 (0.12-0.23)	0.07 (0.05-0.33)	0.10 (0.06-0.37)	0.10 (0.08-0.48)
Bromodichloromethane	0.07 (0.03-0.16)	0.61 (0.24-0.75)	<LOD	0.06 (0.03-0.07)	0.08 (0.07-0.42)	0.04 (0.04-0.06)
Dibromochloromethane	0.16 (0.14-0.28)	0.31 (0.25-0.42)	<LOD	0.30 (0.16-0.50)	0.41 (0.39-0.43)	0.24
Bromoform	0.16 (0.14-0.27)	0.18 (0.08-0.19)	<LOD	0.17 (0.08-1.01)	0.31 (0.04-1.14)	0.01
Chloroacetic Acid	<LOD	0.88	<LOD	1.98	0.50 (0.43-0.58)	<LOD
Bromoacetic Acid	<LOD	0.18	<LOD	<LOD	0.05	<LOD
Dichloroacetic acid	0.45 (0.41-1.29)	9.18 (7.09-13.12)	0.16	0.99	2.46 (1.53-8.91)	<LOD
Trichloroacetic Acid	2.79 (2.23-19.51)	3.43 (2.80-19.20)	<LOD	5.22	2.47 (0.31-4.63)	<LOD
Bromochloroacetic Acid	<LOD	2.47 (1.82-5.22)	<LOD	<LOD	3.28	<LOD
Dibromoacetic Acid	<LOD	0.53 (0.40-0.53)	<LOD	<LOD	<LOD	<LOD
Dichlorobromoacetic Acid	<LOD	0.28 (0.27-0.28)	<LOD	<LOD	<LOD	<LOD
Dibromochloroacetic Acid	0.45 (0.43-0.47)	0.49 (0.42-0.56)	<LOD	<LOD	<LOD	<LOD
Dichloroacetonitrile	<LOD	0.35 (0.16-0.44)	0.12 (0.05-0.12)	<LOD	0.03 (0.02-0.04)	0.02
Bromochloroacetonitrile	<LOD	0.06 (0.05-0.07)	0.03 (0.02-0.04)	<LOD	<LOD	<LOD
Trichloroacetaldehyde	<LOD	0.17	<LOD	<LOD	<LOD	<LOD
Bromochloroacetaldehyde	<LOD	0.96 (0.35-1.22)	<LOD	<LOD	<LOD	<LOD
Bromodichloroacetaldehyde	1.79 (1.17-2.40)	1.41	<LOD	<LOD	<LOD	<LOD
Dibromoacetaldehyde	<LOD	0.52 (0.17-0.62)	<LOD	<LOD	<LOD	<LOD
Chloroacetone	<LOD	0.32 (0.12-0.35)	0.21	<LOD	<LOD	<LOD
1,1-Dichloro-2-propanone	0.25 (0.22-0.98)	1.06 (0.41-1.29)	0.23	<LOD	0.30	<LOD
Trichloropropanone	<LOD	0.06 (0.04-0.25)	<LOD	<LOD	<LOD	<LOD
1,3-Dichloropropanone	<LOD	0.11	0.06	<LOD	<LOD	<LOD


Wastewater sample
NaOCl added below breakpoint
NH_3 added or present in wastewater stream
Post-MF sample
Post-RO sample
PRE SCREENS
CHLORAMINATION
MICROFILTRATION
REVERSE OSMOSIS



Linge et al. Figure 2



Linge *et al*. Figure 3