

Drinking water: the problem of chlorinous odours

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ABSTRACT

Chlorinous off-flavours in drinking water are a leading cause of complaints to Australian water utilities and other utilities worldwide. The occurrence and causes of chlorinous odours in drinking water were investigated with the use of an odour panel, trained using a modified flavour profile analysis technique. A new system for classifying water types according to the causes of chlorinous odours was developed in order to enable improved management strategies for the reduction of these off-flavours. Waters of 'Type 1' exhibit a chlorinous odour only when the free chlorine equivalent concentration is equal to or above the odour threshold concentration (OTC) for free chlorine. Waters exhibiting a chlorinous odour both above and below the OTC of free chlorine are designated 'Type 2'. 'Type 3' waters are those in which the possible presence of a chlorinous odour is masked by another odour. Although causative compounds of the chlorinous off-flavours were not determined, bromine was proposed to play an important role in distribution systems where source waters have high concentrations of bromide that may not be removed by the available treatment processes. Management strategies for improvements in aesthetic water quality for each water type are proposed.

Key words | bromine, chlorine, drinking water, natural organic matter, off-flavours, water treatment

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INTRODUCTION

Chlorinous off-flavours in drinking water are a leading cause of taste and odour complaints to water utilities in Australia (Joll *et al.* 2007), and are also commonly reported worldwide (Mackey *et al.* 2004a). Aesthetic quality of drinking water is usually the only measure of quality available to most consumers, and is therefore the basis by which consumers judge the safety of drinking water (McGuire 1995). The end result may be reduced confidence in water utilities, increased consumption of bottled water (McGuire 1995) and a shift towards point of use or point of entry treatment devices (Mackey *et al.* 2004a).

Despite obvious concern by water authorities (Khiari *et al.* 1999; Welte & Montiel 1999; Marchesan & Morran 2004), identification of the causes of chlorinous off-flavours is often difficult. Chlorinous off-flavours can be transient, and may diminish by the time a field officer arrives to inspect the problem (Willmore 2005). In addition, consumers often do not accurately identify chlorinous off-flavours (Mackey *et al.* 2004b). The presence of any

objectionable odour may be misidentified as chlorinous because of widespread awareness of chlorine as a key drinking water chemical (Mackey *et al.* 2004b).

Many Australian treated waters, particularly in Western Australia, require relatively high chlorine doses (up to 7 mg/L for pre-chlorination and up to 4 mg/L for chlorination post-treatment) due to high levels of dissolved organic carbon (DOC) remaining after treatment. Additionally, some above ground pipelines are exposed to frequent high temperatures, causing greater chlorine decay rates (Joll *et al.* 2007). Elevated chlorine doses are essential to ensure adequate disinfection throughout the distribution system, but can make management of chlorinous off-flavour incidents difficult.

A number of chlorinous off-flavour complaints are received each year by the Water Corporation of Western Australia, the water utility supplying the majority of drinking water in the state of Western Australia. Complaints are typically widespread across the Metropolitan Region of Perth,

the capital city of Western Australia. In the Perth Metropolitan Region, approximately 46% of the distributed drinking water is derived from groundwater extraction, 15–23% from seawater desalination (introduced in November 2006) and the remaining 31–39% from surface water storages located in the Darling Range (Water Corporation 2011, 2012). Perth's groundwater for drinking purposes is obtained from the Jandakot Mound and the Gngangara Groundwater System. The latter system includes a surficial aquifer (the Gngangara Mound), the underlying semi-confined Mirrabooka aquifer and the deeper confined Leederville and Yarragadee aquifers. While the local surface water typically requires minimal treatment, the quality of the groundwater varies widely and groundwater sources commonly require a number of treatment steps to reduce the concentrations of DOC, hydrogen sulphide, ammonia and iron, and to reduce colour and turbidity.

Consumer complaints of chlorinous off-flavours are a serious problem for many utilities that use chlorine-based disinfectants worldwide, since these taints adversely affect consumer perceptions of water safety and quality. It is therefore of significant interest to further investigate chlorinous off-flavours. The aims of this study were to identify and classify the causes of chlorinous off-flavours, using the Perth distribution system. Since elevated bromide concentrations occur frequently in southern Australian source waters and since brominated compounds are generally more organoleptically potent than their chlorinated analogues (Acero *et al.* 2005), the role of bromide in chlorinous off-flavours was also investigated. This is the first study of the role of bromide in the formation of chlorinous off-flavours in drinking water. A new system for classifying water types according to the causes of chlorinous odours was proposed. Improved water quality management practices to reduce these off-flavours in distributed waters were developed.

MATERIALS AND METHODS

Preparation of glassware

All glassware was carefully prepared to remove odours and contaminants. Preparation included final rinsing with ultra-pure water (Milli-Q) several times, and annealing the glassware in an oven set at 550 °C overnight, with the

annealed glassware being stored in a room without background odour. Just prior to use, glassware was rinsed at least three times with sample water.

Sample sites and collection

Samples were collected from drinking water treatment plant outlets in amber bottles, filled to the top to minimise headspace and immediately transported in a cooler to the laboratory. The primary samples were taken from two surface water treatment plant outlets (SW1 and SW 2) and six groundwater treatment plant outlets (GW 1, GW 2, GW 3, GW 4, GW 5 and GW 6) in the Perth Metropolitan Region, forming the foundational study sites for this research.

The water quality of the surface water sources is relatively good, with no treatment other than disinfection and fluoridation currently employed (Allpike 2008). The groundwater treatment plants source groundwater from a number of different aquifers in the Gngangara Groundwater System, as shown in Table 1.

The water treatment processes employed at the different groundwater treatment plants were as follows: GW 1 (GW 1 extracts water from a limestone formation rather than interbedded sandstone, siltstone and shale (Salama 2005)): aeration, lime softening, pH adjustment, filtration, chlorination and fluoridation; GW 2: pre-chlorination and aeration, enhanced alum coagulation, rapid sand filtration, lime softening, chlorination and fluoridation; GW 3: aeration, pre-chlorination, a magnetic ion exchange (MIEX[®]) resin process, alum coagulation, chlorination for manganese removal and filtration, before final chlorination and

Table 1 | Water sources for the groundwater treatment plants

Groundwater treatment plant sample	Water source			
	Superficial aquifer	Mirrabooka aquifer	Leederville aquifer	Yarragadee aquifer
GW 1	✓		✓	✓
GW 2		✓	✓	
GW 3	✓		✓	✓
GW 4	✓	✓	✓	
GW 5	✓	✓		
GW 6				✓

fluoridation; GW 4: pre-chlorination, coagulation, rapid sand filtration, post-chlorination and fluoridation; GW 5: aeration, pre-chlorination, alum coagulation, rapid sand filtration, final chlorination and fluoridation; GW 6: chlorination and fluoridation only.

Additional study sites (SW 3, GW 7, GW 8 and GW 9) were included to provide a larger sample size for examination of the role of bromide in the causes of chlorinous odours in treatment plant outlet waters. SW 3 was located in tropical North Western Australia and GW 7, GW 8 and GW 9 were in the Perth Metropolitan Region. The treatment processes were as follows: SW 3: polyaluminium chloride coagulation, membrane filtration, chlorination and fluoridation; GW 9: chlorination and fluoridation. GW 7 and GW 8 were storage supplies in Perth's Integrated Water Supply System.

Chlorine concentrations of treatment plant outlet water samples

Treatment plant outlet water samples were temperature controlled (25 °C) upon arrival in the laboratory. Free and total chlorine equivalent concentrations in the samples were measured immediately, and periodically over time until the free and total chlorine equivalent concentrations were not detectable (<0.02 mg/L). Free and total chlorine equivalent concentrations were measured in duplicate using a DPD-based method with a pocket colorimeter (HACH, Loveland, CO, USA).

Odour assessment of treatment plant outlet water samples

After temperature-control (25 °C) for 30 min, the treatment plant outlet samples were poured into wide-necked conical flasks (250 mL) fitted with watch glass lids just prior to assessment of odours by the odour panel, who had been trained to use the modified flavour profile analysis technique, described by McDonald and co-workers (McDonald *et al.* 2009). All odours, including chlorinous odours, were recorded by the panellists. Previously, the odour threshold concentration (OTC) for free chlorine was found to be 0.1 ± 0.05 mg/L by this odour panel (McDonald *et al.* 2009). Further odour panel events were conducted on the equilibrated water samples when the free and total chlorine

equivalent concentrations were above and below the OTC for free chlorine.

Organic and inorganic water quality parameters

The free chlorine in a subsample of each water sample was quenched by the addition of aqueous sodium sulphite solution (4.25 mL; 12 g/L) and the quenched samples were analysed by a commercial laboratory (SGS Australia Pty Ltd) for a number of water quality parameters (Table 2). Bromide was analysed in our laboratory by ion chromatography with UV detection (Dionex ICS90; Dionex Corporation, Sunnyvale, CA) using a DionexIonPac[®] AS23 ion exchange column (4 × 250 mm) and a carbonate eluent (1.0 mM NaHCO₃ and 10.2 mM NaCO₃).

RESULTS AND DISCUSSION

Water samples were collected from eight treatment plant outlets in the Perth Metropolitan Region. These samples were analysed for general water quality parameters and the chlorine concentrations and odour characteristics were monitored over time (25 °C).

Water quality characteristics of treatment plant outlet samples

Typically, surface water samples had lower alkalinity, total alkalinity and hardness than the water exiting the groundwater treatment plants (Table 2), as a result of the greater exposure of the groundwater to carbonate-containing rocks.

Groundwater samples generally had higher chloride and bromide concentrations than the surface water samples, except for GW 5 (chloride 42 mg/L; bromide 0.18 mg/L) where the lower bromide and chloride content was consistent with its up-gradient location in the Gngangara Mound (Davidson 1995). The highest bromide concentrations were found in GW 1 and GW 3 (both 0.43 mg/L).

The bromide concentrations in these water samples would be considered as moderate to high in comparison to those in previous reports for natural waters used for drinking water (e.g. <0.25–0.54 mg/L) (Boyer & Singer 2005; Singer *et al.* 2007), with moderate concentrations reported

Table 2 | Water quality parameters of treatment plant outlet samples

	Water sample							
	SW 1	SW 2	GW 1	GW 2	GW 3	GW 4	GW 5	GW 6
Alkalinity as HCO ₃ (mg/L)	11.3	15.3	142	58	130	126	122	173
Bromide (mg/L)	0.05	0.24	0.43	0.38	0.43	0.27	0.18	0.42
Chloride (mg/L)	79	16	115	100	305	130	42	<0.5
Dissolved organic carbon (mg C/L)	2.6	2.0	2.2	2.8	2.8	1.8	3.6	2
Hardness as CaCO ₃ (mg/L)	35	31	132	138	102	162	197	97
Iron (mg/L)	5.0×10^{-2}	3.0×10^{-2}	4.0×10^{-3}	$<3 \times 10^{-3}$	3.5×10^{-2}	1.4×10^{-2}	1.8×10^{-2}	4.0×10^{-2}
Manganese (mg/L)	1.4×10^{-2}	6.0×10^{-3}	2.0×10^{-3}	nd	nd	$<2.0 \times 10^{-3}$	1.4×10^{-2}	nd
pH	6.7	7.4	8.0	7.9	8.7	7.5	7.8	8.3
Total alkalinity as CaCO ₃ (mg/L)	9	13	120	50	110	100	100	140
Ammonia as nitrogen (mg/L)	0.03	0.03	0.03	0.04	0.09	0.01	nd	0.01
Total Kjeldahl nitrogen (mg/L)	0.145	0.19	0.15	0.079	0.165	0.105	nd	0.079
^a Free chlorine equivalent concentration (mg/L)	1.03	0.67	0.40	0.50	0.56	0.31	0.39	0.62
^a Total chlorine equivalent concentration (mg/L)	1.12	0.74	0.55	0.51	0.67	0.48	0.48	0.72

nd = no data because it was not measured.

^aMeasured at 1.5 hours after sampling.

as around 0.11 mg/L (Ates *et al.* 2007), and very high concentrations around 0.70 mg/L (Hansson *et al.* 1987). The current water samples were quenched with a reducing agent to reconvert any aqueous bromine (HOBr and OBr⁻), which would have formed from reaction of naturally occurring bromide with chlorine, to bromide. Some of this bromine may have already reacted with other species, e.g. DOC, to produce brominated disinfection by-products (DBPs). The bromide concentrations in the source waters and treated waters prior to addition of chlorine may therefore have been higher than those measured in the quenched treatment plant outlet waters. The bromide concentrations in GW 1, GW 2, GW 3 and GW 6 were around 0.4 mg/L or greater and could be considered as moderately high in the worldwide perspective.

DOC concentrations were relatively high for all treatment plant outlet waters, ranging from 1.8 mg/L for GW 4 to as high as 3.6 mg/L for GW 5. With the exception of GW 1 and GW 6, the groundwater treatment plants had a DOC removal step. The relatively high DOC concentrations in the treatment plant outlet waters indicate that removal of DOC is difficult and that there remains a refractory component of the DOC which is not effectively removed.

Odour assessment and chlorine concentrations of treatment plant outlet samples

Free and total chlorine equivalent concentrations of the treatment plant outlet samples were measured over time (Figure 1). Odours were assessed by the odour panel, at

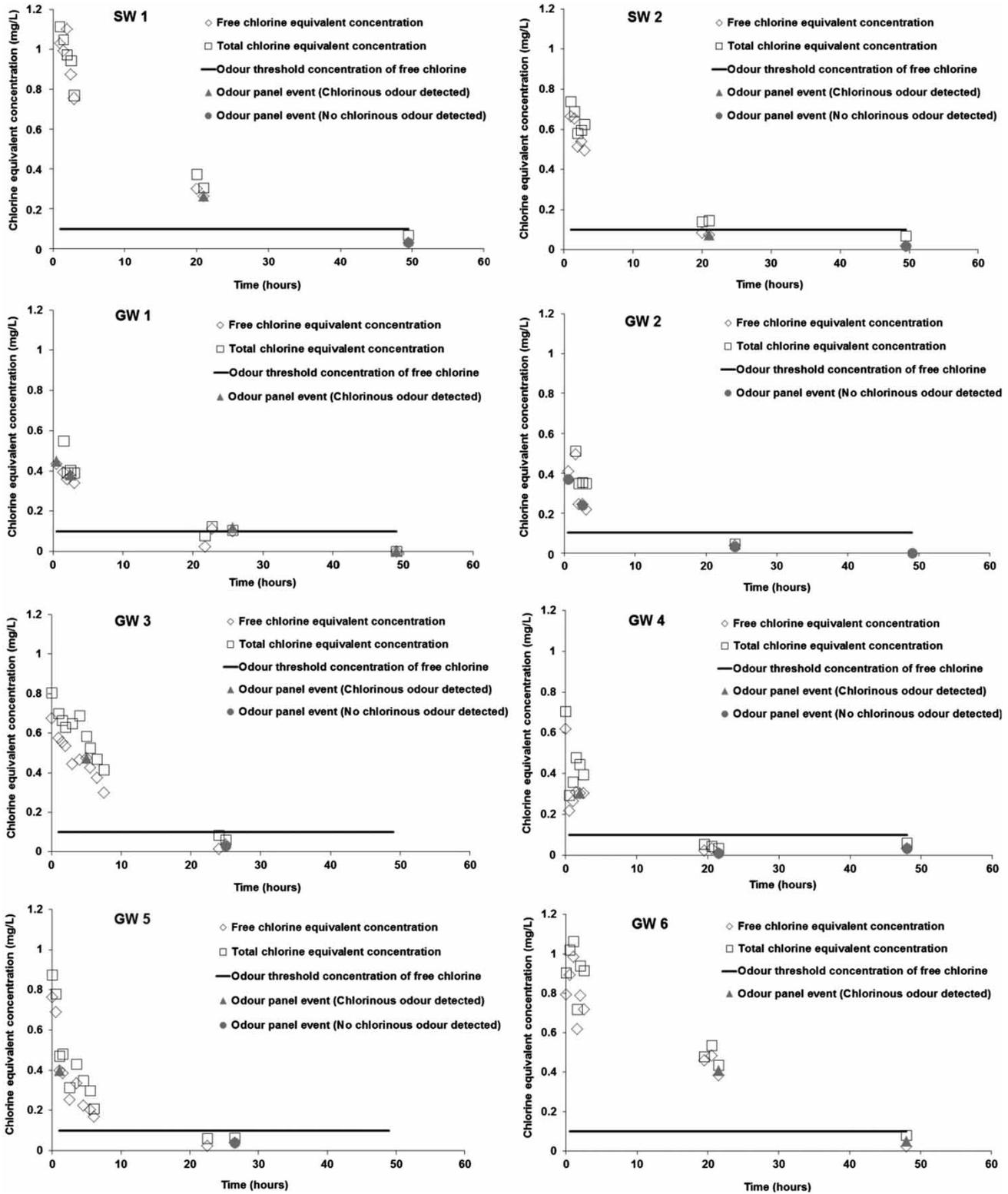


Figure 1 | Concentration of free and total chlorine equivalents over time for treatment plant outlet samples. Odour panel events in which panellists detected a chlorinous odour are indicated by a solid grey triangle. Odour panel events in which panellists did not detect a chlorinous odour are indicated by a solid grey circle. The odour threshold concentration for free chlorine for the panel is indicated as a line on the graph at 0.1 mg/L.

least once when the free chlorine equivalent concentration was above the free chlorine OTC, and at least once when the free chlorine equivalent concentration was below the OTC for free chlorine, as shown in Figure 1. The odour panel assessments (events) were plotted as the corresponding free chlorine equivalent concentration measured at the time of the event.

The odour panel detected a chlorinous odour as the predominant odour in SW 1, SW 2, GW 1, GW 3, GW 4, GW 5 and GW 6 samples when the free chlorine equivalent concentration was at or above the OTC for free chlorine, but not below the OTC for free chlorine. GW 3 had different odour characteristics to the other four samples (SW 1, SW2, GW 4 and GW 5), exhibiting an additional odour, which will be discussed later. Samples SW 1, SW 2, GW 4 and GW 5 were therefore classified as 'Type 1', where a chlorinous odour is only detected when the free chlorine equivalent concentration is at or above the OTC for free chlorine and where the chlorinous odour is therefore likely due to the presence of free chlorine.

Not all water treatment plant outlet samples behaved in this manner: for samples GW 1 and GW 6, a chlorinous odour was detected not only when the free chlorine equivalent concentration was above the OTC for free chlorine, but also consistently when the free chlorine equivalent residual was lower than the OTC for free chlorine, and even when there was no detectable free chlorine equivalent residual (limit of detection of 0.02 mg/L). For GW 1, there was a chlorinous odour detected by the panel when neither free nor total chlorine equivalent residual were detectable. These samples were classified as 'Type 2'.

The off-flavour associated with free chlorine is due to the species hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-) (Krasner & Barrett 1984). Studies have found that the aroma threshold value for OCl^- is higher than for HOCl, indicating that a lower pH could result in a more easily detected chlorinous odour (Krasner & Barrett 1984). The major species present depends upon pH, with the pK_a of HOCl being 7.53. The Australian Drinking Water Guidelines specify a pH of finished water between 6.5 and 8.5 (ADWG 2004). At pH 6, 95% of the hypochlorite will be in the HOCl form and, at pH 9, the predominant species present will be OCl^- (Clark & Sivaganesan 2002). Type 1 water samples exhibited a range of pH (Table 2): SW 1

(pH 6.7), SW 2 (pH 7.5), GW 3 (pH 8.7), GW 4 (7.5) and GW 5 (pH 7.8), indicating that some samples contained predominantly hypochlorous acid and some samples predominantly hypochlorite, but presumably the lower the pH, the more easily detected the odour due to chlorine.

The presence of a chlorinous odour without the presence of any free chlorine equivalent concentration suggest that the odour is due to compounds that are not free chlorine nor other compounds capable of the DPD oxidation reaction required for the measurement of free chlorine. Most taste and odour problems not due to excess chlorine are thought to be due to compounds formed upon the reaction of the oxidising disinfectant with natural organic matter, i.e. DBPs (Freuze *et al.* 2004).

In the Type 2 waters, when there was no free chlorine equivalent residual remaining, the chlorinous odour was likely due to one or more DBPs. When the free chlorine equivalent concentration was present but below the free chlorine OTC, again the chlorinous odour may have been due to these one or more DBPs and, possibly, oxidants other than chlorine. When the free chlorine equivalent concentration was above the free chlorine OTC, the chlorinous odour may have been due to some or all of these factors, as well as free chlorine itself.

Occurrence of chlorinous off-flavours due to compounds other than free chlorine has previously been reported in South Australian (Morran & Marchesan 2004) and French (Welte & Montiel 1999) distribution systems. Morran & Marchesan (2004) suggested that the chlorinous off-flavour was due to combined chlorine compounds, such as complex chloramines or other chlorinated compounds. Welte & Montiel (1999) proposed that the cause of the chlorinous off-flavour may have been trichloramine which formed during chlorination of some organic nitrogen compounds. The taste and odour episode in France (Welte & Montiel 1999) provoked further research into the possible origins of chlorinous off-flavours (Freuze *et al.* 2004, 2005) where *N*-chloroaldimines were found to form from reactions between chlorine and amino acids, and to exhibit chlorinous odours, with OTCs as low as 1 $\mu\text{g/L}$. Earlier studies also linked chlorinous odours to the presence of chloramines formed during chlorination of amino acids and peptides (Bruchet *et al.* 1992). Other potential chlorinous off-flavour compounds include monochloramine (Krasner & Barrett

1984; Piriou & Perelle 1999), dichloramine (Krasner & Barrett 1984), aldehydes (Froese *et al.* 1999) and bromine (McDonald *et al.* 2009). Potentially, bromamines could also impart a chlorinous odour; however, the OTCs or descriptors for bromamines have not previously been reported.

In addition, untrained panellists (the majority of drinking water consumers) are not always able to determine the difference between chlorinous, medicinal and chemical odours (Mackey *et al.* 2004b). 'Chlorinous' off-flavours may therefore also include other compounds found in drinking water. A range of compounds reported to be present in water and associated with having a chlorinous off-flavour by consumers (but not typically described as such by trained panellists) were reported by Mackey *et al.* (2004b), and broadly include trihalomethanes, halophenols and miscellaneous phenol-based compounds. In the current study, it is unlikely that the chlorinous odours in Type 2 waters were due to combined chlorine compounds, such as chloramines. Some Type 1 waters had higher ammonia or total Kjeldahl nitrogen concentrations than Type 2 water (Table 2), and it would be expected that these waters would contain higher concentrations of chloramines than the Type 2 waters, but they did not exhibit chlorinous odours. There was no observed link between ammonia or total Kjeldahl nitrogen concentrations and chlorinous odours, or indeed, between combined chlorine and chlorinous odours. Additionally, at least one of the study sites (GW 1) exhibited a distinct and persistent chlorinous odour when total chlorine residual was not detectable. Other odorous compounds were therefore indicated, although the odorous compounds may well be organic bromamines (or chloramines) that are present below the detectable limit for total chlorine.

The GW 2 sample exhibited different odour characteristics to the other samples (Figure 1). GW 2 did not exhibit a chlorinous odour even when the free chlorine equivalent concentration was above the OTC for free chlorine. At all odour panel events, this sample was described as having a strong 'sulphurous' odour. This odour presumably masked the odour of chlorine when the free chlorine equivalent concentration was above the OTC of free chlorine. Groundwater from the Gngangara Mound contains significant concentrations of sulphide which is oxidised using aeration and pre-chlorination during treatment. Oxidation of sulphides using this method is often incomplete and the

partially oxidised sulphur compounds that are formed may impart the sulphurous odour (Heitz *et al.* 2000; Heitz 2002). Up to ~100 µg/L residual partially oxidised sulphur compounds remain after treatment of these sulphidic groundwaters (Wilmot & Wajon 1997). It has been suggested that this fraction of sulphur would be limited to compounds such as elemental sulphur sols, possibly associated with organic matter, refractory organosulphur compounds or particulate iron-sulphides (Heitz 2002). Possible sources of sulphurous odours in drinking water may be due to one or more heterocyclic organosulphur compounds of the formula C₃H₆S₃, C₄H₈S₂, and C₅H₁₀S₂ (dithiolanes and trithiolanes) (Heitz 2002). Dithiolanes and trithiolanes are known to have strong sulphurous or sulphidic odours (Fors 1983). However, it was not possible to directly attribute the sulphurous odour in the water samples in this study to any of these substances.

If any chlorinous odours were present when the free chlorine equivalent concentration was below the free chlorine OTC, they would also have been masked by this odour. This sample was therefore designated as 'Type 3', where chlorinous odours that may be present are masked by another stronger odour. The concept of masking is well known, e.g. for free chlorine masking earthy and musty odours in drinking waters (Suffet *et al.* 1995), but this is the first report of a sulphurous odour masking a chlorinous odour in a drinking water.

The odour panellists (60%) also detected a sulphurous odour in the GW 3 sample when the free chlorine equivalent concentration was below the OTC for free chlorine. The sulphurous odour was present (detected by 20% of panellists), but not strong enough to mask the chlorinous odour, when the free chlorine equivalent concentration was above the OTC of free chlorine, but became important when the free chlorine equivalent concentrations were low, masking any possible chlorinous off-flavours present. This water was therefore also designated as being of Type 3, as it contained an additional odour that could mask chlorinous odours, albeit over a lower chlorine equivalent concentration range.

Role of bromide in the formation of chlorinous odours

Bromide occurs naturally in many drinking water sources, with concentrations commonly ranging from around

0.05–0.80 mg/L in Western Australian source waters (Heitz *et al.* 2004), but can reach up to 2.8 mg/L and higher if the water is affected by saltwater intrusion or other phenomena (Gruchlik *et al.* 2011). Bromide is difficult to remove with conventional water treatment practices and is readily oxidised by chlorine during water treatment to form bromine (Westerhoff *et al.* 2004). This has a number of implications for studies of chlorinous odours. First, during the analysis of chlorine concentrations, the bromine can also react with the DPD reagent and be measured as its free chlorine equivalent concentration, and secondly, the presence of bromine must be considered when assessing off-flavours, as bromine has been described as having a chlorinous odour (McDonald *et al.* 2009).

The composition of the initial free chlorine equivalent concentrations in a series of treated water samples, including the treatment plant outlet waters and four additional water samples (SW 3, GW 7, GW 8, GW 9), is given in Table 3. Since chlorine was present in excess in these samples, and oxidation of bromide by chlorine is relatively rapid ($k_{\text{Br}^- + \text{HOCl} \rightarrow \text{HOBr} + \text{Cl}^-} = 1.55 \times 10^5 \text{ M s}^{-1} \text{ s}^{-1}$) (Kumar & Margerum 1987), it can be assumed that all of the bromide measured in the quenched samples would have been present

as bromine in the samples when collected. In this case, up to 34% of the free chlorine equivalent concentrations would have been due to bromine in these samples (Table 3). It is therefore likely that the measured chlorine residual in many parts of the distribution system comprises at least some portion of bromine. This understanding of the importance of bromine as a residual disinfectant in distribution systems where the source water is high in bromide concentration and the treatment processes do not significantly remove bromide fills a key knowledge gap for water utilities. McDonald *et al.* (2009) determined the OTC for bromine to be 0.04 mg/L free chlorine equivalents (odour described as chlorinous), while the free chlorine OTC was 0.1 mg/L. Therefore, at free chlorine equivalent concentrations below 0.1 and above 0.04 mg/L, a chlorinous odour cannot be due to the presence of chlorine but could well be due to the presence of bromine.

For Type 1 and 2 waters, the relationships between water type and bromide concentration in the quenched samples is shown in Figure 2. A significant correlation was observed between bromide concentration and water type ($p = 0.0095$, Spearman's rank correlation). The probability of drinking water exhibiting a chlorinous odour when the

Table 3 | Composition of the initial free chlorine equivalent concentration for the treatment plant outlet and storage reservoir water samples

	Measured initial free chlorine equivalent concentration (mg/L)	Initial bromine concentration (as bromine; mg/L) ^a	Initial bromine concentration (as free chlorine equivalent concentration; mg/L) ^b	Bromine as % of measured initial free chlorine equivalent concentration ^c	Type
SW 1	1.39	0.05	0.02	2	1
SW 2	1.42	0.24	0.11	7	1
GW 4	0.71	0.27	0.12	17	1
GW 5	0.77	0.18	0.08	11	1
GW 8	0.42	0.22	0.10	24	1
GW 1	0.66	0.43	0.19	29	2
GW 6	0.80	0.42	0.19	23	2
SW 3	0.99	0.35	0.16	16	2
GW 7	0.76	0.28	0.12	16	2
GW 9	0.60	0.29	0.13	22	2
GW 3	0.68	0.43	0.19	29	3
GW 2	0.50	0.38	0.17	34	3

^aCalculations based on the concentration of bromide measured in the quenched sample, assuming that all of this bromide was in the form of bromine in the sample prior to quenching.

^bCalculations based on the molar concentration of bromine having equivalent DPD-oxidising capacity as the same molar concentration of chlorine, with this concentration of chlorine then being expressed as a mass concentration.

^cCalculations based on the free chlorine equivalent concentrations.

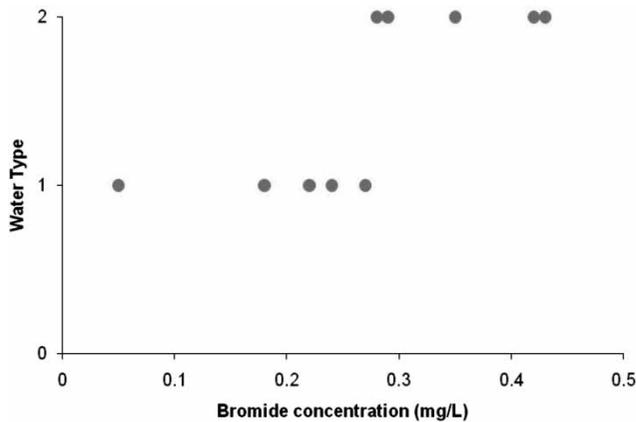


Figure 2 | Relationships between water type (1 and 2) and bromide concentration for the treatment plant outlet and storage reservoir outlet samples.

free chlorine equivalent concentration is below the OTC for free chlorine appeared to increase with higher bromide concentrations in the quenched samples.

While bromine itself may be contributing to chlorinous odours at low equivalent free chlorine concentration (0.04–0.1 mg/L), in the cases of GW 1 and GW 6, chlorinous odours were detected at concentrations even lower than the OTC of bromine. These samples exhibited chlorinous odours when the free chlorine equivalent concentration was below the method detection limit of 0.02 mg/L, well below the published OTC of bromine. In these cases, other compounds must have contributed to the odour, and in light of the relationship between bromide and Type 2 waters, it is probable that these compounds are bromine-containing, either brominated DBPs or inorganic bromamines. The speciation of DBPs will be influenced by the bromide ion concentration in the water source, since bromine can react with natural organic matter preferentially to chlorine to produce more brominated, rather than chlorinated, DBPs (Clark *et al.* 2001).

Implications for drinking water management strategies

For Type 1 sites, chlorinous off-flavour complaints are likely to be caused by the free chlorine equivalent concentration, comprised predominantly of free chlorine, and will most likely occur closer to the treatment plant. Management options for these waters could include a reduction in chlorine dose, while still ensuring sufficient residual throughout the distribution system. The ability to do this would

depend upon the chlorine demand and residence time of the water in the distribution system.

In these studies, high concentrations of bromine (>0.3 mg/L) appeared to have a large influence on the formation of the chlorinous off-flavours. Management strategies to improve the aesthetic quality of Type 2 waters would include reduction of bromide concentration during the treatment process. Bromide removal would aid in the reduction of chlorinous off-flavours due solely to bromine (measured as a chlorine equivalent), and also in reduction of the formation of any other odorous brominated DBPs that could contribute to chlorinous off-flavours. For Type 3 waters, off-flavour issues are significant and removal of groundwater-derived sulphurous compounds, or more complete oxidation of these compounds to sulphate, in water treatment processes would improve the aesthetic water quality.

Currently, there are no economically feasible methods to remove bromide from source waters such as those in the current study where high concentrations of bromide are accompanied by high concentrations of natural organic matter. New cost-effective methods for selective removal of bromide from drinking waters are our current focus and may provide significant benefits in terms of mitigation of chlorinous off-flavours.

CONCLUSIONS

A new system for classifying water types according to the cause of chlorinous off-flavours was developed. Type 1 waters exhibited a chlorinous odour only when the free chlorine equivalent concentration was equal to or above the OTC for free chlorine. Type 2 waters exhibited a chlorinous odour both above and below the OTC for free chlorine. Type 3 waters had the presence of another odour that masked any chlorinous off-flavours.

Up to 34% of the free chlorine equivalent concentration in these samples was found to be due to bromine. Water type classifications were found to be related to the concentration of bromide in the quenched samples. Bromine was proposed to play an important role in disinfectant residual and chlorinous odours in waters in distribution systems where source waters have high

concentrations of bromide which is not removed by the available treatment processes.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge assistance from Alan Maus, Dr Rino Trolio and other staff of the Western Australian Water Corporation. This research was funded by the Water Corporation, the Cooperative Research Centre for Water Quality and Treatment (now Water Quality Research Australia) and the Australian Research Council.

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First received 1 July 2012; accepted in revised form 10 January 2013