

1 **Drinking water: the problem of chlorinous odors**

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34 **ABSTRACT**

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

50

51 **Keywords:** Drinking water, off-flavours, chlorine, bromine, natural organic matter, water  
52 treatment

53

54 **INTRODUCTION**

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

62

63 Despite obvious concern by water authorities (Khiari et al., 1999; Welte and Montiel, 1999;  
64 Marchesan and Morran, 2004), identification of the causes of chlorinous off-flavours is  
65 often difficult. Chlorinous off-flavours can be transient, and may diminish by the time a field  
66 officer can arrive to inspect the problem (Willmore, 2005). In addition, consumers often do  
67 not accurately identify chlorinous off-flavours (Mackey et al., 2004b). The presence of any  
68 objectionable odor may be misidentified as chlorinous because of widespread awareness  
69 of chlorine as a key drinking water chemical (Mackey et al., 2004b).

70

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

78

79 A number of chlorinous off-flavour complaints are received each year by the Water  
80 Corporation of Western Australia, the water utility supplying the majority of drinking water  
81 in the state of Western Australia. Complaints are typically widespread across the  
82 Metropolitan Region of Perth, the capital city of Western Australia. In the Perth  
83 Metropolitan Region, approximately 50-60% of the distributed drinking water is derived  
84 from groundwater extraction, 15-20% from seawater desalination (introduced in November  
85 2006), and the remaining 20-35% from surface water storages located in the Darling  
86 Range (Water Corporation, 2009). Perth's groundwater for drinking purposes is obtained  
87 from the Jandakot Mound and the Gnangara Groundwater System. The latter system  
88 includes a surficial aquifer (the Gnangara Mound), the underlying semi-confined  
89 Mirrabooka aquifer, and the deeper confined Leederville and Yarragadee aquifers. While  
90 the local surface water typically requires minimal treatment, the quality of the groundwater  
91 varies widely and groundwater sources commonly require a number of treatment steps to  
92 reduce the concentrations of DOC, H<sub>2</sub>S, NH<sub>3</sub> and iron, and to reduce colour and turbidity.  
93

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

104 according to the causes of chlorinous odors was proposed. Improved water quality  
105 management practices to reduce these off-flavours in distributed waters were developed.

106

## 107 **MATERIALS AND METHODS**

### 108 **Preparation of glassware**

109 All glassware was carefully prepared to remove odors and contaminants. Preparation  
110 included final rinsing with ultrapure water (Milli-Q) several times, and annealing the  
111 glassware in an oven set at 550°C overnight, with the annealed glassware being stored in  
112 a room without background odor. Just prior to use, glassware was rinsed at least three  
113 times with sample water.

114

### 115 **Sample sites and collection**

116 Samples were collected from drinking water treatment plant outlets in amber bottles, filled  
117 to the top to minimise headspace, and immediately transported in a cooler to the  
118 laboratory. The primary samples were taken from two surface water treatment plant outlets  
119 (SW 1 and SW 2), and six groundwater treatment plant outlets (GW 1, GW 2, GW 3, GW  
120 4, GW 5, and GW 6) in the Perth Metropolitan Region, forming the foundational study sites  
121 for this research.

122

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

127

128 The water treatment processes employed at the different groundwater treatment plants  
129 were as follows: GW 1 (GW1 extracts water from a limestone formation rather than

130 interbedded sandstone, siltstone and shale (Salama, 2005)): aeration, lime softening, pH  
131 adjustment, filtration, chlorination and fluoridation; GW 2: pre-chlorination and aeration,  
132 enhanced alum coagulation, rapid sand filtration, lime softening, chlorination and  
133 fluoridation; GW 3: aeration, pre-chlorination, a magnetic ion exchange (MIEX<sup>®</sup>) resin  
134 process, alum coagulation, chlorination for manganese removal and filtration, before final  
135 chlorination and fluoridation; GW 4: pre-chlorination, coagulation, rapid sand filtration,  
136 post-chlorination and fluoridation; GW 5: aeration, pre-chlorination, alum coagulation, rapid  
137 sand filtration, final chlorination and fluoridation; GW 6: chlorination and fluoridation only.

138

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

146

#### 147 **Chlorine concentrations of treatment plant outlet water samples**

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

154

#### 155 **Odor assessment of treatment plant outlet water samples**

156 After temperature-control (25°C) for half an hour, the treatment plant outlet samples were  
157 poured into wide-necked conical flasks (250 mL) fitted with watch glass lids just prior to  
158 assessment of odors by the odor panel, according to the method described by McDonald  
159 and co-workers (McDonald et al., 2009). All odors, including chlorinous odors, were  
160 recorded by the panellists. Previously, the OTC for free chlorine was found to be  $0.1 \pm$   
161  $0.05$  mg/L by this odor panel (McDonald et al., 2009). Further odor panel events were  
162 conducted on the equilibrated water samples when the free and total chlorine equivalent  
163 concentrations were above and below the OTC for free chlorine.

164

### 165 **Organic and inorganic water quality parameters**

166 The free chlorine in a subsample of each water sample was quenched by the addition of  
167 aqueous sodium sulphite solution (4.25 mL; 12 g/L) and the quenched samples were  
168 analysed by a commercial laboratory (SGS Australia Pty. Ltd.) for a number of water  
169 quality parameters (Table 2). Bromide was analysed in our laboratory by ion  
170 chromatography with UV detection (Dionex ICS90; Dionex Corporation, Sunnyvale, CA)  
171 using a Dionex IonPac<sup>®</sup> AS23 ion exchange column (4 x 250 mm) and a carbonate eluent  
172 (1.0 mM NaHCO<sub>3</sub> and 10.2 mM NaCO<sub>3</sub>).

173

## 174 **RESULTS AND DISCUSSION**

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

178

### 179 **Water quality characteristics of treatment plant outlet samples**

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

183

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

189

190 The bromide concentrations in these water samples would be considered as moderate to  
191 high in comparison to those in previous reports for natural waters used for drinking water  
192 (e.g. < 0.25 – 0.54 mg/L) (Boyer and Singer, 2005; Singer et al., 2007), with moderate  
193 concentrations reported as around 0.11 mg/L (Ates et al., 2007), and very high  
194 concentrations around 0.70 mg/L (Hansson et al., 1987). The current water samples were  
195 quenched with a reducing agent to reconvert any aqueous bromine (HOBr and OBr<sup>-</sup>),  
196 which would have formed from reaction of naturally occurring bromide with chlorine, to  
197 bromide. Some of this bromine may have already reacted with other species, e.g. DOC, to  
198 produce brominated disinfection by-products (DBPs). The bromide concentrations in the  
199 source waters and treated waters prior to addition of chlorine may therefore have been  
200 higher than those measured in the quenched treatment plant outlet waters. The bromide  
201 concentrations in GW 1, GW 2, GW 3, and GW 6 were around 0.4 mg/L or greater, and  
202 could be considered as moderately high in the worldwide perspective.

203

204 DOC concentrations were relatively high for all treatment plant outlet waters, ranging from  
205 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



206 6, the groundwater treatment plants had a DOC removal step. The relatively high DOC  
207 concentrations in the treatment plant outlet waters indicate that removal of DOC is difficult  
208 and that there remains a refractory component of the DOC which is not well-removed.

209

#### 210 **Odor assessment and chlorine concentrations of treatment plant outlet samples**

211 Free and total chlorine equivalent concentrations of the treatment plant outlet samples  
212 were measured over time (Figure 1). Odors were assessed by the odor panel, at least  
213 once when the free chlorine equivalent concentration was above the free chlorine OTC,  
214 and at least once when the free chlorine equivalent concentration was below the OTC for  
215 free chlorine, as shown in Figure 1. The odor panel assessments (events) were plotted as  
216 the corresponding free chlorine equivalent concentration measured at the time of the  
217 event.

218

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

227

228 Not all water treatment plant outlet samples behaved in this manner: for samples GW 1  
229 and GW 6, a chlorinous odor was detected not only when the free chlorine equivalent  
230 concentration was above the OTC for free chlorine, but also consistently when the free  
231 chlorine equivalent residual was lower than the OTC for free chlorine, and even when

232 there was no detectable free chlorine equivalent residual (limit of detection of 0.02 mg/L).  
233 For GW 1, there was a chlorinous odor detected by the panel when neither free nor total  
234 chlorine equivalent residual were detectable. These samples were classified as 'Type 2'.

235

236 The off-flavour associated with free chlorine is due to the species, hypochlorous acid  
237 (HOCl) and the hypochlorite ion (OCl<sup>-</sup>) (Krasner and Barrett, 1984). Studies have found  
238 that the aroma threshold value for OCl<sup>-</sup> is higher than for HOCl, indicating that a lower pH  
239 could result in a more easily detected chlorinous odor (Krasner and Barrett, 1984). The  
240 major species present depends upon pH, with the pK<sub>a</sub> of HOCl being 7.53. The Australian  
241 Drinking Water Guidelines specify a pH of finished water between 6.5 and 8.5 (ADWG,  
242 2004). At pH 6, 95% of the hypochlorite will be in the HOCl form and, at pH 9, the  
243 predominant species present will be OCl<sup>-</sup> (Clark and Sivaganesan, 2002). Type 1 water  
244 samples exhibited a range of pH (Table 2): SW 1 (pH 6.7), SW 2 (pH 7.5), GW 3 (pH 8.7),  
245 GW 4 (7.5) and GW 5 (pH 7.8), indicating that some samples contained predominantly  
246 hypochlorous acid and some samples predominantly hypochlorite, but presumably the  
247 lower the pH, the more easily detected the odor due to chlorine.

248

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

255

256 In the Type 2 waters, when there was no free chlorine equivalent residual remaining, the  
257 chlorinous odor was likely due to one or more DBPs. When the free chlorine equivalent

258 concentration was present but below the free chlorine OTC, the chlorinous odor may have  
259 been due to these one or more DBPs and, possibly, oxidants other than chlorine. When  
260 the free chlorine equivalent concentration was above the free chlorine OTC, the chlorinous  
261 odor may have been due to some or all of these factors, as well as free chlorine itself.

262

263 Reports of chlorinous off-flavours due to compounds other than free chlorine have  
264 previously been reported in South Australian (Morran and Marchesan, 2004) and French  
265 (Welte and Montiel, 1999) distribution systems. Morran and Marchesan (2004) suggested  
266 that the chlorinous off-flavour was due to combined chlorine compounds, such as complex  
267 chloramines or other chlorinated compounds. Welte and Montiel (1999) proposed that the  
268 cause of the chlorinous off-flavour may have been trichloramine which formed during  
269 chlorination of some organic nitrogen compounds. The taste and odor episode in France  
270 (Welte and Montiel, 1999) provoked further research into the possible origins of chlorinous  
271 off-flavours (Freuze et al., 2004; Freuze et al., 2005) where *N*-chloroaldimines were found  
272 to form from reactions between chlorine and amino acids, and to exhibit chlorinous odors,  
273 with OTCs as low as 1 µg/L. Earlier studies also linked chlorinous odors to the presence of  
274 chloramines formed during chlorination of amino acids and peptides (Bruchet et al., 1992).  
275 Other potential chlorinous off-flavour compounds include monochloramine (Krasner and  
276 Barrett, 1984; Piriou and Perelle, 1999), dichloramine (Krasner and Barrett, 1984),  
277 aldehydes (Froese et al., 1999), and bromine (McDonald et al., 2009). Potentially,  
278 bromamines could also impart a chlorinous odor, however, the OTCs or descriptors for  
279 bromamines have not previously been reported.

280

281 In addition, untrained panellists (the majority of drinking water consumers) are not always  
282 able to determine the difference between chlorinous, medicinal, and chemical odors  
283 (Mackey et al., 2004b). 'Chlorinous' off-flavours may therefore also include other

284 compounds found in drinking water. A range of compounds reported to be present in water  
285 and associated with having a chlorinous off-flavour by consumers (but not typically  
286 described as such by trained panellists) were reported by Mackey and co-workers (2004b),  
287 and broadly include trihalomethanes (THMs), halophenols, and miscellaneous phenol-  
288 based compounds. In the current study, it is unlikely that the chlorinous odors in Type 2  
289 waters were due to combined chlorine compounds such as chloramines. Some Type 1  
290 waters had higher ammonia or Total KN concentrations than Type 2 water (Table 2), and it  
291 would be expected that these waters would contain higher concentrations of chloramines  
292 than the Type 2 waters, but they did not exhibit chlorinous odors. There was no observed  
293 link between ammonia or total Kjeldahl nitrogen (TKN) concentrations and chlorinous  
294 odors, or indeed, between combined chlorine and chlorinous odors. Additionally, at least  
295 one of the study sites (GW 1) exhibited a distinct and persistent chlorinous odor when total  
296 chlorine residual was not detectable. Other odorous compounds were therefore indicated,  
297 although the odorous compounds may well be organic bromamines (or chloramines) that  
298 are present below the detectable limit for total chlorine.

299

300 The GW 2 sample exhibited different odor characteristics to the other samples (Figure 1).  
301 GW 2 did not exhibit a chlorinous odor even when the free chlorine equivalent  
302 concentration was above the OTC for free chlorine. At all odor panel events, this sample  
303 was described as having a strong 'sulphurous' odor. This odor presumably masked the  
304 odor of chlorine when the free chlorine equivalent concentration was above the OTC of  
305 free chlorine. Groundwater from the Gngara Mound contains significant concentrations  
306 of sulphide which is oxidised using aeration and pre-chlorination during treatment.  
307 Oxidation of sulphides using this method is often incomplete and the partially oxidised  
308 sulphur compounds that are formed may impart the sulphurous odor (Heitz et al., 2000;  
309 Heitz, 2002). Up to ~100 µg/L residual partially oxidised sulphur compounds remain after

310 treatment of these sulfidic groundwaters (Wilmot and Wajon, 1997). It has been suggested  
311 that this fraction of sulphur would be limited to compounds such as elemental sulphur sols,  
312 possibly associated with organic matter, refractory organosulphur compounds, or  
313 particulate iron-sulphides (Heitz, 2002). Possible sources of sulphurous odors in drinking  
314 water may be due to one or more heterocyclic organosulphur compounds of the formula  
315  $C_3H_6S_3$ ,  $C_4H_8S_2$ , and  $C_5H_{10}S_2$  (dithiolanes and trithiolanes) (Heitz, 2002). Dithiolanes and  
316 trithiolanes are known to have strong sulphurous or sulfidic odors (Fors, 1983). However, it  
317 was not possible to directly attribute the sulphurous odor in the water samples in this study  
318 to any of these substances.

319

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

326

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

335

336 **Role of bromide in the formation of chlorinous odors**

337 Bromide occurs naturally in many drinking water sources, with concentrations commonly  
338 ranging from around 0.05 to 0.80 mg/L in Western Australian source waters (Heitz et al.,  
339 2004), but can reach up to 2.8 mg/L and higher if the water is affected by saltwater  
340 intrusion or other phenomena (Gruchlik et al., 2011). Bromide is difficult to remove with  
341 conventional water treatment practices and is readily oxidised by chlorine during water  
342 treatment to form bromine (Westerhoff et al., 2004). This has a number of implications for  
343 studies of chlorinous odors. First, during the analysis of chlorine concentrations, the  
344 bromine can also react with the DPD reagent and be measured as its free chlorine  
345 equivalent concentration, and secondly, the presence of bromine must be considered  
346 when assessing off-flavours, as bromine has been described as having a chlorinous odor  
347 (McDonald et al., 2009).

348

349 The composition of the initial free chlorine equivalent concentrations in a series of treated  
350 water samples, including the treatment plant outlet waters and four additional water  
351 samples (SW 3, GW 7, GW 8, GW 9), is given in Table 3. Since chlorine was present in  
352 excess in these samples, and oxidation of bromide by chlorine is relatively rapid ( $k_{\text{Br}^- + \text{HOCl}} \rightarrow \text{HOBr} + \text{Cl}^- = 1.55 \times 10^3 \text{ M s}^{-1} \text{ s}^{-1}$ ) (Kumar and Margerum, 1987), it can be assumed that all of  
353 the bromide measured in the quenched samples would have been present as bromine in  
354 the samples collected. In this case, up to 34% of the free chlorine equivalent  
355 concentrations would have been due to bromine in these samples (Table 3). It is therefore  
356 likely that the measured chlorine residual in many parts of the distribution system  
357 comprises at least some portion of bromine. This understanding of the importance of  
358 bromine as a residual disinfectant in distribution systems where the source water is high in  
359 bromide concentration and the treatment processes do not significantly remove bromide,  
360 fills a key knowledge gap for water utilities. McDonald and co-workers (2009) determined  
361

362 the OTC for bromine to be 0.04 mg/L free chlorine equivalents (odor described as  
363 chlorinous), while the free chlorine OTC was 0.1 mg/L. Therefore, at free chlorine  
364 equivalent concentrations below 0.1 and above 0.04 mg/L, a chlorinous odor cannot be  
365 due to the presence of chlorine but could well be due to the presence of bromine.

366

367 For Type 1 and 2 waters, the relationships between water type and bromide concentration  
368 in the quenched samples is shown in Figure 2. A significant correlation was observed  
369 between bromide concentration and water type ( $p = 0.0095$ , Spearman's rank correlation).  
370 The probability of drinking water exhibiting a chlorinous odor when the free chlorine  
371 equivalent concentration is below the OTC for free chlorine appeared to increase with  
372 higher bromide concentrations in the quenched samples.

373

374 While bromine itself may be contributing to chlorinous odors at low equivalent free chlorine  
375 concentration (0.04 – 0.1 mg/L), in the cases of GW1 and GW6, chlorinous odors were  
376 detected at concentrations even lower than the OTC of bromine. These samples exhibited  
377 chlorinous odors when the free chlorine equivalent concentration was below the method  
378 detection limit of 0.02 mg/L, well below the published OTC of bromine. In these cases,  
379 other compounds must have contributed to the odor, and in light of the relationship  
380 between bromide and Type 2 waters, it is probable that these compounds are bromine-  
381 containing, either brominated DBPs or inorganic bromamines. The speciation of DBPs will  
382 be influenced by the bromide ion concentration in the water source, since bromine can  
383 react with NOM preferentially to chlorine to produce more brominated, rather than  
384 chlorinated, DBPs (Clark et al., 2001).

385

386 **Implications for drinking water management strategies**

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

393

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

404

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

410

411 **Conclusions**



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

417

418 Up to 34% of the free chlorine equivalent concentration in these samples was found to be  
419 due to bromine. Water Type classifications were found to be related to the concentration of  
420 bromide in the quenched samples. Bromine was proposed to play an important role in  
421 disinfectant residual and chlorinous odors in waters in distribution systems where source  
422 waters have high concentrations of bromide which is not removed by the available  
423 treatment processes.

424

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**Table 1.** Water sources for the groundwater treatment plants.

	<b>Water Source</b>			
	Superficial Aquifer	Mirrabooka Aquifer	Leederville Aquifer	Yarragadee Aquifer
Groundwater Treatment Plant Sample				
GW 1	✓		✓	✓
GW 2		✓	✓	
GW 3	✓		✓	✓
GW 4	✓	✓	✓	
GW 5	✓	✓		
GW 6				✓



**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 <sub>3</sub> (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 <sub>3</sub> (mg/L)	35	31	132	138	102	162	197	97
Iron (mg/L)	5.0 x 10 <sup>-2</sup>	3.0 x 10 <sup>-2</sup>	4.0 x 10 <sup>-3</sup>	< 3 x 10 <sup>-3</sup>	3.5 x 10 <sup>-2</sup>	1.4 x 10 <sup>-2</sup>	1.8 x 10 <sup>-2</sup>	4.0 x 10 <sup>-2</sup>
Manganese (mg/L)	1.4 x 10 <sup>-2</sup>	6.0 x 10 <sup>-3</sup>	2.0 x 10 <sup>-3</sup>	nd	nd	< 2.0 x 10 <sup>-3</sup>	1.4 x 10 <sup>-2</sup>	nd
pH	6.7	7.4	8.0	7.9	8.7	7.5	7.8	8.3
Total alkalinity as CaCO <sub>3</sub> (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 (TKN) (mg/L)	0.145	0.19	0.15	0.079	0.165	0.105	nd	0.079
<sup>a</sup> Free chlorine equivalent concentration (mg/L)	1.03	0.67	0.40	0.50	0.56	0.31	0.39	0.62
<sup>a</sup> 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.

<sup>a</sup>Measured at 1.5 hours after sampling.