

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, H₂S, NH₃ 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[®]) 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[®] AS23 ion exchange column (4 x 250 mm) and a carbonate eluent
172 (1.0 mM NaHCO₃ and 10.2 mM NaCO₃).

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⁻),
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⁻) (Krasner and Barrett, 1984). Studies have found
238 that the aroma threshold value for OCl⁻ 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_a 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⁻ (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 Gnamangara 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.

	Water Source			
	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 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 x 10 ⁻²	3.0 x 10 ⁻²	4.0 x 10 ⁻³	< 3 x 10 ⁻³	3.5 x 10 ⁻²	1.4 x 10 ⁻²	1.8 x 10 ⁻²	4.0 x 10 ⁻²
Manganese (mg/L)	1.4 x 10 ⁻²	6.0 x 10 ⁻³	2.0 x 10 ⁻³	nd	nd	< 2.0 x 10 ⁻³	1.4 x 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 (TKN) (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.