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Impact of NOM Character on Copper Adsorption by Trace Ferric Hydroxide from Iron Corrosion in Water Supply System

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ABSTRACT

The fate of trace concentrations of cupric sulphate (< 0.4 mg/L) dosed into chloraminated distribution

systems to inhibit nitrification has been shown in this study to be controlled by at least two crucial

factors: the character of natural organic matter (NOM) and iron hydroxide corrosion products present at

low concentrations (< 2 mg/L). This research quantified the removal of Cu(II) ions added into waters

containing trace $Fe(OH)_3$ flocs and the effect of NOM of different character on this removal. The

dominant dissolved copper species in NOM-containing waters were found to be Cu(II)-NOM complexes.

Both intramolecular chelation and intermolecular complexation can occur, with the latter occurring

preferentially and resulting in the aggregation of smaller organic molecules to form larger molecules.

The presence of ferric hydroxide flocs when Cu(II) ions were added into NOM-containing waters was

shown to result in removal of Cu(II) ions, presumably as Cu(II)-NOM complexes. This removal was

through adsorption processes obeying Freundlich isotherms, although the presence of larger NOM

molecules and heterogeneous copper species (e.g. $Cu(OH)_{2(s)}$ and $CuO_{(s)}$) appeared to shield smaller

Cu(II)-NOM complexes from adsorption to some extent. For the strategy of inhibition of nitrification in

distribution systems by the addition of Cu(II) ions, complexation of Cu(II) ions by NOM and adsorption

of Cu(II)-NOM complexes by ferric hydroxide flocs released from pipe walls pose significant

operational challenges to maintaining the concentration of Cu(II) ions through the distribution system.

41 **Key Words:** Chloramine; Adsorption; Copper; Corrosion; Distribution system; Inhibition; Nitrification;

42 NOM

43 **1.   INTRODUCTION**

44   Maintaining an adequate disinfectant residual at water distribution extremities is required by the

45 guidelines of the environmental protection agency. Chloramine is chosen especially when challenging

46 conditions are encountered in distribution systems, including aging pipes, unexpected chlorine loss due

47 to inefficient organics removal in water treatment or other causes such as disinfectant by-products. The

48 Goldfields and Agricultural Water Supply Scheme (G&AWSS) in Western Australia is currently

49 applying chloramine mainly because the authorities met with incidences of *Naegleria fowleri* when

50 chlorine was used as disinfectant in their above ground pipe line system which is about 530 km end to

51 end with branches of pipeline totaling about 7000 km and experiences temperatures from 8 - 45°C [1].

52 *N. fowleri* is an amoeba and has been responsible for a number of fatal infections linked to public water

53 supplies. While chloramine provided a better alternative, it met with another challenge. Nitrification, a

54 microbial process serially converting ammonia to nitrite, has significantly reduced the stability of

55 disinfectant. Therefore, it is important to find solution to stabilize the chloramine.

56   More than 0.1 mg-Cu(II)/L was found to inhibit nitrifying bacteria [2]. The use of cupric sulphate

57 (CuSO$_4$) in lakes, reservoirs and other managed bodies remains the most effective algicidal treatment [3,

58 4, 5]. The World Health Organization (WHO) recommends a copper concentration of 1 mg/L as an

59 aesthetic standard for drinking water [6]. A novel method of dosing cupric sulphate (up to 400 µg-

60 Cu(II)/L) directly into drinking water distribution systems to inhibit the activity of nitrifying bacteria [7]

61 and protect chloramine residuals is being trialed in the G&AWSS. Effective inhibition and the desired

62 copper concentration were achieved when copper dosing was practiced in a pilot reservoir. However,

63 dissolved Cu(II) concentrations were found to decrease with distance along the cement-lined cast iron

64 pipeline, limiting the effectiveness of this approach. Therefore, it is important to understand the fate of

65 copper in the distribution system and devise approaches to maintain its concentration in the pipe line.

66 The likely species of copper in natural water bodies have been extensively studied. Wagemann and

67 Barica [8] claimed that only 5% of total copper could be found as free Cu^{2+} in natural water systems.

68 Snoeyink and Jenkins [9] summarized the status of various inorganic copper compounds being in

69 equilibrium with tenorite (CuO) in carbonate-buffered water, controlled by the partial pressure of CO_2.

70 The majority of copper existing in natural water bodies is believed to be in the form of Cu-NOM

71 complexes [10]. Edwards and Nicolle [11] reported the effects of NOM on copper corrosion by-product

72 release and found that NOM can interfere with the formation of a solid scale layer of $Cu(OH)_2$ and

73 dramatically increase the soluble copper concentration in water. Hullebusch et al. [12] suggested a

74 proportional relationship between organic copper compounds and dissolved organic carbon (DOC).

75 Gamble et al. [13] noted the aggregation mechanism adopted by Cu(II) when binding multiple

76 molecules.

77 The solubility of Cu(II) is reported to be controlled by an equilibrium between the soluble copper

78 complex and metastable solid phases, such as cupric hydroxide ($Cu(OH)_2$) and tenorite (CuO) [14]. The

79   size of $Cu(OH)_2$ particles varies with pH. At pH 8, the pH of water in the G&AWSS, the size of

80     $Cu(OH)_2$ particulates was reported to be about 400 nm [15]. Our laboratory experiments have also

81   shown that both $Cu(OH)_2$ and CuO particles can be removed by 0.2 μm membrane filters at pH >7.5

82   [16], such that these filters were chosen to remove particulate copper formed in the current research.

83   Our previous research using differential absorbance spectroscopy showed that NOM in Mundaring

84   Weir water (the feed water for the G&AWSS) was deficient in phenolic chromophores which are the

85   major constituents of the hydrophobic fraction of NOM [17]. Gamble et al. [18] suggested that phenolic

86   chromophores contribute to salicylic-acid type of bidentate chelating sites, which are believed to

87   preferentially chelate with Cu^{2+} and form relatively stable chelates. Controversially, one striking finding

88   revealed that the removal of the hydrophobic acid fraction from the surface water had little effect on Cu

89   binding, suggesting that the binding affinities of Cu to phenolic sites are weak [19].

90   When copper is dosed into an iron pipe distribution system, its fate could be affected by iron

91   corrosion. The vulnerability of a distribution system to corrosion depends on the chemical properties of

92   the water delivered (e.g. pH, alkalinity, dissolved oxygen, total dissolved solids) and its physical

93   characteristics (temperature, velocity), as well as the nature of pipe materials [20]. McNeill and

94   Edwards [21] did a comprehensive review of such various important factors, including dissolved oxygen

95   (DO), pipe age, biological activity, disinfectants, temperature, and dissolved copper, as they affect iron

96   pipe corrosion. Generally, the corrosion rate increases with the increased DO concentration [22]. Zhang

97   and Edwards [23] reported that cast iron can also reduce nitrite/nitrate to ammonia, indicating iron pipe

98 corrosion caused by the products of nitrification. Nitrification can also increase the growth of bacteria

99 that might stimulate microbiologically influenced corrosion (MIC) [24]. Disinfectant residuals in

100 general increase the corrosion rate [25]. Both chloramine and nitrification are present in the G&AWSS.

101 When copper sulphate is dosed into the G&AWSS to inhibit nitrification, a series of potential redox

102 reactions could be involved [9]. These reactions are listed in Table 1, arranged in order of oxidizing

103 capacity: $O_2 > NO_3^- > Cu^{2+} > Fe^{2+}$. Either in bulk water under aerating conditions or nitrification, both of

104 which are considered possible aquatic conditions in the distribution system, direct reaction between

105 Cu^{2+} and exposed iron, can be overruled by the presence of stronger oxidizing agents (O_2 and NO_3^-).

106 Chlorine and chloramine are also strong oxidizing agents which can compete with Cu^{2+} to react with

107 iron. Our earlier study [26] and studies by others [8, 10] found little dissolved copper existing in natural

108 water in the form of cupric ions, as most of the copper existed as Cu-NOM complexes. This finding

109 further excludes the possible reaction between free cupric ions and iron. Therefore, the effect of iron

110 pipe corrosion on dissolved Cu(II) in the context of natural waters literally refers to the interaction

111 between the dominant dissolved Cu(II)-NOM and trace iron corrosion products released through

112 corrosion.

113   Dissolved Cu(II) removal by iron salts has been extensively documented. Ridge and Sedlak [27]

114 reported that Cu^{2+} and Cu-EDTA complexes up to 13 mg-Cu(II)/L were noticeably removed by hydrous

115 ferric oxide (HFO) in wastewater treatment. Iron oxides have also been found to be good adsorbents to

116 remove high concentrations of cupric ions and ammonia-complexed copper in wastewater [28]. Since

6

117   dissolved copper of high concentrations can be efficiently removed by iron salts in wastewater treatment

118   processes, it raised a concern that the solubility of dosed copper salts could, on the other hand, be

119   jeopardized by iron salts released into distribution systems due to iron pipe corrosion, even if iron salts

120   are present at low concentrations.

121   Iron corrosion scales include goethite (a-FeOOH), lepidocrocite (g-FeOOH), magnetite (Fe_3O_4),

122   siderite ($FeCO_3$), ferrous hydroxide ($Fe(OH)_2$), ferric hydroxide ($Fe(OH)_3$), ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$),

123   green rusts (e.g. $Fe_4^{II}Fe_2^{III}(OH)_{12}CO_3$) and calcium carbonate ($CaCO_3$). A high concentration of readily

124   soluble Fe(II) content is reported to be present inside scales [28, 29]. On one hand, ferrous ions can be

125   released into bulk water during corrosion and oxidized to ferric particles. Sarin et al. [30] reported that

126   iron is released to bulk water primarily in the ferrous form. The ferrous ions are converted into ferrous

127   solids (e.g. $Fe(OH)_2$), which may then be converted to ferric solids (e.g. $Fe(OH)_3$) after reaction with

128   oxygen or other oxidising agents such as chloramine which are consistently present in the drinking

129   water [20]. On the other hand, NOM existing in the distribution system can form complexes with

130   released ferrous or ferric ions. Jones et al. [31] studied the dissociation kinetics of Fe(III)-NOM

131   complexes and reported the stability constant K for Fe(III)-NOM complexation at pH 8.0 within a range

132   of 9.90~10.34, which is significantly smaller than the stability constant K of $10^{2.4}$ for the formation of

133    $Fe(OH)^{2+}$ or $10^{2.3}$ for the formation of $Fe(OH)_{3(s)}$ [9]. The stability constant for Fe(II)-NOM

134   complexation is less than those for the Fe(III)-NOM complexation by two to four orders of magnitude

135   [32]. Therefore, the complexation between Fe(II) or Fe(III) and organic matter is insignificant or

136   negligible compared to the strong stability of $Fe(OH)_3$ formed in the drinking water at pH 8.0 short

137   after ferrous ions released into bulk water due to corrosion. Therefore, pre-formed ferric hydroxide flocs

138   were chosen to be the representative of the major corrosion products which are stable and available in a

139   relatively long period to react with dissolved Cu(II) in bulk water.

140   Based on these previous studies, Cu(II)-NOM complexes are unanimously acknowledged as the

141   major soluble copper forms in natural water, though the structure and preference of copper chelation

142   with certain fractions of specific organic matter remains unresolved. High concentrations of cupric ions

143   and complexed copper (up to 500 mg/L) in wastewater can be removed by adsorption to iron oxide

144   media and filtration. However, from the perspective of protecting low concentrations of dissolved Cu(II)

145   in distribution systems (e.g. as a nitrification inhibitor), little research has been conducted on dissolved

146   Cu(II) removal by low concentration (< 2 mg/L) iron pipe corrosion products released from corroded or

147   damaged pipes in distribution systems like the G&AWSS. Preliminary experiments using water from

148   Mundaring Weir showed adsorption of dissolved Cu(II) by $Fe(OH)_3$ flocs present at trace

149   concentrations, with the adsorption obeying Langmuir or Freundlich adsorption isotherms [26].

150   However, the relationships between NOM character and its distinct impact on copper-organic chelation

151   and dissolved Cu(II) removal by trace $Fe(OH)_3$ flocs remain unknown. Furthermore, the fate of

152   dissolved Cu(II) in water containing nitrifying bacteria is also of interest. This research aims to quantify

153   the removal of dosed Cu(II) in bulk water containing trace $Fe(OH)_3$ flocs and NOM of different

154 characters. The impact of NOM characteristics on dissolved Cu(II) removal was elucidated using

155 molecular weight distribution detected by UV_{254}.

156

157 **2.   MATERIALS AND METHODS**

158 **2.1 Selection, Sampling and Preparation of Water Samples**

159   Selected samples and the experimental protocol are given in Figure 1. To evaluate the effect of

160 NOM of different characters on Cu(II) removal, three different waters were selected. Mundaring raw

161 water (MRW) was selected as this is the source water for the G&AWSS. Pre-coagulated Mundaring raw

162 water (MCW) was prepared as comparison with MRW to evaluate how coagulable NOM and its

163 absence can affect the character of Cu-NOM complexes and thus their removal by $Fe(OH)_3$ flocs. As

164 coagulation preferentially removes hydrophobic fraction mainly containing aquatic humic material with

165 high MW [33], the majority of NOM contained in MCW would be uncoagulable and of small

166 molecular weight. The organic Cu(II) complexes formed between dissolved Cu(II) and these

167 uncoagulable NOM were also expected to be of smaller molecular size than those formed in MRW and

168 hence be protected from removal by ferric flocs. A synthetic water largely containing a hydrophobic

169 fraction was prepared with commercial humic acid and termed humic acid bulk water (HAW) in

170 comparison with MRW which is known to mainly contain hydrophilic organic compounds [17]. In order

171 to study the effect of nitrification observed in the distribution system on organic Cu(II) complexation

172 and its removal by ferric flocs, a severely nitrified water (NW) sample was collected from the laboratory

9

173   reactors fed with Mundaring water. Severe nitrification is defined as the condition when nitrite

174   concentration was more than 0.1 mg-N/L and chloramine decay is severely accelerated [34].

175   Depending on the copper dose, addition of copper was found to form particles in some experiments

176   and hence some sub-samples of MRW were filtered through a 0.2μm membrane filter to remove the

177   effect of preformed Cu(II)-containing particles. This filtration was not done for HAW and NW because

178   their preparation step already involved filtration.

179   <u>Mundaring Raw Water (MRW):</u> Regular sample collection from the outlet of Mundaring Weir, the

180   source water for the G&AWSS, has been conducted by our group from July 2008 to the present. The

181   quality of Mundaring water has been found to vary only slightly in terms of pH (7.6~8.1), DOC

182   (2.4~3.0 mg-C/L) and UV_{254} absorbance (0.031~0.038 cm^{-1}). A sample for this study was collected in

183   July 2009. The raw water was filtered through a 0.45 μm membrane to remove suspended solids or

184   particles before copper dosing.

185   <u>Post-Coagulated Mundaring Water (MCW):</u> Ferric chloride was employed as the coagulant to

186   remove coagulable NOM in MRW. Coagulation experiments showed that maximum DOC removal was

187   achieved by adding a coagulant dose (concentration in the jar) of 40 mg-FeCl$_3$/L at pH 5~5.5. Kastl et al.

188   [35] observed similar doses and pH resulting in maximum DOC removal in many waters. A jar tester

189   was used to control the coagulation process. The stirring speed was set at 200 rpm and ferric chloride

190   was dosed and the speed was continued for the next 2 minutes. The speed was set at 20 rpm and

191   continued for another 20 minutes. During coagulation, the pH of the bulk water was adjusted and

192   maintained at 5~5.5 using a HACH40d pH meter. HCl (1 N) and NaOH (1 N) were used to adjust pH.

193   After the coagulation, bulk water was kept intact for sedimentation and then filtered through 0.45 µm

194   and 0.2 µm polycarbonate membranes consecutively to remove flocs. NaOH (1 N) was titrated into the

195   filtrate to increase the pH to 7.8±0.2. The concentration of dissolved Fe(II) or Fe(III) in the filtrate was

196   determined using atomic absorption spectroscopy in SGS Pty. Ltd (WA) and found to be <0.05 mg/L.

197   <u>Humic Acid Water (HAW):</u> Humic acid water was prepared by diluting stock HA solution (3 g-C/L)

198   with MilliQ water (18 MΩ/cm, DOC<100 ppb). Humic acid was acquired from Sigma Aldrich[®],

199   containing 20% ash. HA solid was dissolved in MilliQ water first then centrifuged at 4000 rpm for 5

200   minutes to separate ash and other insoluble particles from the solution. The supernatant was withdrawn

201   and filtered through 0.45 µm membrane to further remove insoluble impurities. The final filtrate was

202   treated as the stock HA standard solution (3 g-C/L). This solution was diluted to give HAW the

203   following characteristics: 2.5±0.1 mg-C/L DOC and had UV Abs=0.248/cm (254 nm, 10 cm quartz cell).

204   This concentration of DOC was chosen to be as equal as possible to the DOC concentration in MRW.

205   <u>Nitrified Water (NW):</u> Two identical reactor systems, each assembled in series with five 20 L

206   reactors (R1 to R5), were set up in the laboratory. Automatic flow rate and temperature control were

207   installed for the reactors. Chloraminated Mundaring water was fed into the reactor, with mass ratio of

208   (Cl:NH_3-N) 4.5 to 1 maintained in the 25-litre feeding tank. In the start-up period, chlorine was

209   maintained at about 1mg/L. To expedite nitrification and to obtain the DS inoculums, chloraminated

210   water collected from G&AWSS was added into the reactors except R1. The chloramine concentration

211 was gradually increased up to 2.5 mg/L in the feeding tank. Water (20 L) was fed into the system

212 continuously every day to gain retention time of 20 ± 2 hrs. Water temperature was maintained at $20\pm2^{o}C$

213 in the reactors R1~R3 whereas $23\pm2^{o}C$ was maintained in R4 and R5 in order to achieve accelerated

214 microbial activities. By varying hydraulic conditions, temperature and chloramine residuals, nitrification

215 occurring in the distribution system can be simulated in the laboratory. In this research, NW was

216 collected from R4. NW contained 0.10 mg/L NH_3-N, 0.2 mg/L NO_2-N and 0.1 mg/L NO_3-N. The levels

217 of these inorganic nitrogen products indicated that severe nitrification occurred in NW [33].

218

219 **2.2 Analysis of Soluble Copper and Iron Species**

220 Soluble Cu(II), Fe(II) and Fe(III) concentrations in the source waters and bulk water samples

221 prepared in the laboratory were measured by Atomic Absorption Spectroscopy (AAS) by a commercial

222 laboratory before any experiment commenced. Total Cu(II) concentrations were found to be less than 20

223 µg/L before addition of copper and the dissolved Fe(II) and Fe(III) concentrations were below 0.05

224 mg/L before ferrous or ferric salt addition.

225 In the experiments, copper concentrations were analyzed after conversion of all forms of copper to

226 soluble copper(II) form and then by the bicinchoninate spectrophotometric method (Hach method 8506;

227 HACH DR2800). This method had a measuring range of 0.04~5 mg/L with ±20 µg/L accuracy. Samples

228 were digested using nitric acid (1:1) at pH 4~6 for total copper measurement. For measuring dissolved

229 copper concentrations, samples were filtered through a 0.2 µm PC (polycarbonate) membrane prior to

230 measuring total Cu concentration in the filtrate. In order to minimise interaction between the sample and

12

231   membrane and to prevent speciation changes, the volume of the filtrate was chosen to represent

232   approximately 50% of the volume of the raw sample [36]. For instance, to obtain 50 mL filtrate, 100

233   mL sample water was added and 50 mL was filtered through the filter paper.

234

235   **2.3 Dissolved Organic Carbon Measurement and Molecular Weight Distribution Analysis**

236   Water samples were filtered through a 0.45μm membrane before the analysis of UV_{254} absorbance

237   and dissolved organic carbon (DOC) concentration. UV_{254} absorbance was measured at 254 nm in a 10

238   cm quartz cell using a Helios UV/Vis Spectrophotometer. DOC concentrations were analysed using a

239   GE 5310C TOC analyser.

240   The apparent molecular weight distribution of the DOC detected by UV_{254} in the samples was

241   analysed by high performance size exclusion chromatography (HPSEC) according to the method of

242   Allpike et al. [37] and Warton et al. [38], except that an Agilent 1100 Series HPLC system was used and

243   that polystyrene sulfonate standards were used for molecular weight calibration. SEC was performed

244   using a TSK G3000SWxl (TOSOH Biosep, 5 μm resin) column and an Agilent 1100 HPLC instrument

245   with diode array detection at 254 nm. The column had an internal diameter of 7.8 mm and a length of 30

246   cm, with a void volume of 5.5 mL, determined with dextran blue. The eluent used was a 20 mM

247   phosphate buffer (1.36 g/L KH_2PO_4 and 3.58 g/L $Na_2HPO_4.12H2O$) at a pH of 6.85. The sample

248   volume was 100 μL and the flow rate was 1 mL/minute. Samples were first filtered through a 0.45 μm

249   nylon filter. The system was calibrated using a combination of polystyrene sulfonate standards (840 Da,

250   1290 Da, 3610 Da, 6520 Da, 15200 Da, 81800 Da). The calibration curve was linear ($R^2 = 0.991$) over

251   the apparent MW range tested.

252

253   **2.4: Preparation of Fe(OH)$_3$ flocs**

254   The method of preparing an Fe(OH)$_3$ suspension and its particle size distribution analysis are

255   presented in the Supplementary Information (SI).

256

257   **2.5 Cu(II) Solubility and Speciation**

258   Copper solubility was determined in bulk waters under various conditions: MilliQ water

259   (DOC<100 µg/L, 18 MΩ/cm), CaCO$_3$ buffered Milli-Q water (50 mg-CaCO$_3$/L) and MRW. Copper

260   solubility can be affected by the partial pressure of CO_2 contacting the water surface [9], and therefore

261   two experiments representing open and closed systems were conducted to investigate Cu(II) solubility

262   in each of these. In the open systems, the bulk water surface was open to the atmosphere (Log (P_{CO2}) = -

263   3.50) without capping the container during the course of the experiment. The closed system was

264   simulated by purging CO_2 from the bulk waters using nitrogen gas during the experiments and

265   excluding air from the samples during storage. An aliquot (1 mL) was withdrawn from the CuSO$_4$ stock

266   solution (1 g-Cu(II)/L) and added into the three types of bulk water (1 L), to attain a total Cu(II)

267   concentration of 1 mg-Cu(II)/L. The dissolved Cu(II) concentration was then measured at 2, 4, 24 and

268   48 hours. The experimental results were compared with the desktop results modelled using MINEQL+[®]

14

269 (Version 4.6, chemical equilibrium modeling system) to verify possible Cu(II) species and their

270 proportions.

271

272 **2.6 Dissolved Cu(II) Removal by Trace Ferric Hydroxide Flocs**

273 **2.6.1 General Experimental Procedure**

274 MRW, MCW, NW and HAW were used for the experiments. In each type of bulk water, different

275 initial Cu(II) concentrations (250, 400 and 1000 µg-Cu(II)/L) were made in duplicates, by dosing

276 appropriate stock solution of copper sulphate.

277 To investigate dissolved Cu(II) removal by $Fe(OH)_3$ flocs from each bulk water sample and their

278 duplicates, various amounts of $Fe(OH)_3$ suspension were added into each subsample containing a known

279 dissolved Cu(II) concentration. The appropriate Fe(III) concentration was achieved by adding aliquots

280 of $Fe(OH)_3$ stock suspension (1 g-Fe(III)/L). Tested Fe(III) concentrations were 0.1, 0.3 0.5, 1.0 and 2

281 mg-Fe(III)/L. A jar tester was used to stir (60 rpm for 30 mins) bulk water during and after the addition

282 of ferric salts. After the jar test, the samples were left for sedimentation for 4 hours (4 hours was

283 sufficient to reach equilibrium between dissolved Cu(II) species and $Fe(OH)_3$ flocs, see Figure 2S in

284 SI). During this time, the pH of each sample was monitored and adjusted to around pH 7.8-8.2, by

285 adding HCl solution (1 N) or NaOH solution (1 N), as necessary. Subsamples were then filtered through

286 0.2 µm polycarbonate membranes and the Cu(II) concentration remaining in the filtrate was measured.

287 The Cu(II) removal was calculated as the difference between the dissolved Cu(II) in the bulk water

288 before and after Fe(III) treatment.

289

290 **2.6.2 Method to Investigate the Effect of Pre-formed Cu(II) Particles on Dissolved Cu(II) Removal**

291   In order to evaluate the effect of the pre-formed Cu(II) particles (e.g. $Cu(OH)_2$, $CuO_{(s)}$) on dissolved

292 Cu(II) removal by $Fe(OH)_3$, the above post-Cu(II)-dosed samples were divided into two groups. In one

293 group (MRW and MCW), pre-formed particles were allowed to remain in bulk water during $Fe(OH)_3$

294 treatment. In the other (MWF, NW and HAW), pre-formed Cu(II) particles were removed by filtration

295 through a 0.2 µm polycarbonate membrane prior to $Fe(OH)_3$ addition.

296

297 **3.   RESULTS AND DISCUSSION**

298 **3.1 Water Quality Characteristics of the Water Samples**

299   The water quality characteristics of the four bulk water samples are presented in Table 2. The

300 apparent molecular weight (AMW) profiles detected by UV_{254} from size exclusion chromatographic

301 analysis (SEC-UV_{254}) of each sample are shown in Figure 2. The major NOM fraction(s) derived from

302 AMW analysis are described in Table 3.

303   The DOC concentration of MRW, HAW and NW were similar, and MCW had a relatively low DOC

304 concentration after removal of some of the DOC through coagulation. Despite having a slightly lower

305 DOC concentration than MRW, HAW had a much higher $SUVA_{254}$ than MRW (1.35 vs. 10.33 L mg^{-1}

306   m^{-1}, respectively (Table 2)), indicating substantially higher aromatic character in the HAW NOM [39].

307   MRW contained material with molecular weight less than 3000 Da (Figure 2) with majority of DOC

308   having an AMW distribution between 2000-3000 Da. For ease of discussion, NOM in Mundaring water

309   was classified as two fractions: coagulable (removed by coagulation, i.e. the NOM present in MRW but

310   not in MCW) and uncoagulable (NOM$_{uc}$; NOM remaining post-coagulation in MCW). The majority of

311   the 2000-3000 Da material in MRW was removed by coagulation, leaving DOC with AMW 1000-2000

312   Da being the predominant fraction in MCW (Table 3). This is consistent with previous reports of

313   coagulation removing predominantly higher MW NOM [37, 38, 40]. In the NW sample, representing

314   MRW subject to nitrification, there was a relative increase in one lower AMW fraction, centered on 500

315   Da (Figure 2). Two peaks between 900~1500 Da in MRW were not present in the chromatogram of

316   NW, possibly indicating microbiological use of this low-medium AMW material and production of

317   lower AMW material. This also supports our earlier observation that soluble microbial products are

318   formed in the nitrifying waters [41,42] The much higher UV$_{254}$ response for DOC in the HAW sample

319   compared to the MRW sample is consistent with the much higher SUVA$_{254}$ measured for the former

320   sample. The AMW profiles suggest that NOM in HAW was comprised of much higher MW

321   components (2-10 kDa) [43] than NOM in MRW (1-3 kDa) and clearly show that there is a substantial

322   difference in the character of these two NOM types.

323

324   **3.2 Cu(II) Solubility and Speciation in the Bulk Waters under Various Aqueous Conditions**

325   Table 4 summarizes the copper species (both particulate and dissolved forms) under different

326   aqueous conditions.

327   According to Table 4, free cupric ions (Cu^{2+}) are negligible in bulk water at pH>7.5. In equilibrium

328   with CuO(s) in an open system, Cu(II)-inorganic compounds can be neglected. Therefore, the dominant

329   dissolved copper species in NOM-containing bulk waters are Cu-NOM complexes. For instance, in

330   MRW, 840 μg/L dissolved Cu(II) was found to be in the form of Cu(II)-NOM complexes. The

331   remaining copper (160 μg/L) was presumably removed in the filtration step as copper particulates,

332   possibly comprised of $Cu(OH)_2$ and CuO.

333   Figure 3 shows the dissolved Cu(II) concentration measured in MRW and MCW 24 hours after

334   dosing with an aqueous copper sulphate solution to achieve an initial Cu concentration of 250, 400 and

335   1000 μg/L in the jar. The dissolved Cu(II) concentrations were almost equal in MRW and MCW when

336   the initial copper concentration was 250 μg/L and 400 μg/L, with only 20~30 μg/L and 50~80 μg/L,

337   respectively, found to be in the particulate form. However, when the initial Cu(II) concentration was

338   increased to 1000 μg/L, the different solubility of copper in these two waters became evident. In MRW,

339   the majority (840 μg/L) of the initial copper concentration was maintained as dissolved Cu-NOM, but in

340   MCW, only 340 μg/L existed as dissolved Cu(II)-NOM, with 660 μg/L Cu consisting of particulate

341   forms. This indicates that coagulable NOM (NOM_c) in MRW contributed significantly to increasing the

342   copper solubility by forming Cu(II)-NOM_c (Cu(II)-coagulable-NOM complex) when the initial copper

343   concentration was relatively higher. However, at lower initial copper concentrations (250 μg/L and 400

18

344 µg/L), uncoagulable NOM (NOM_{uc}) remaining in MCW was still capable of forming Cu-NOM_{uc} (Cu-

345 uncoagulable-NOM complexes) at similar concentrations to those found in MRW. In other words, dosed

346 copper preferentially complexed with NOM_{uc} in MRW until the uncoagulable fraction was saturated.

347 Further increased initial copper concentration up to 1 mg/L started binding with the coagulable fraction.

348

349 **3.3 Removal of Dissolved Cu(II) by Addition of $Fe(OH)_3$ Flocs at Low Concentrations**

350 Figure 4 (A, B, C, E and F) show the removal of dissolved Cu(II) by $Fe(OH)_3$ flocs in MRW, MWF,

351 NW, MCW and HAW respectively.

352 Addition of the flocs at a concentration of 2 mg-Fe/L effectively removed most of the dissolved

353 Cu(II) from Mundaring water samples (MRW and MWF) as well as NW when the initial copper(II)

354 concentrations were 250 or 400 µg/L. In the samples with initial Cu(II) concentration of 400 µg-

355 Cu(II)/L, the addition of ferric hydroxide flocs (2 mg-Fe/L) resulted in less than 100 µg/L dissolved

356 Cu(II) remaining (Figure 4A, B, C and E). Since the use of MINEQL® had established that the majority

357 of copper in these samples existed as Cu(II)-NOM complexes, it is likely that the $Fe(OH)_3$ floc was, in

358 fact, removing Cu(II)-NOM complexes.

359 The relative capacity of NOM to stabilize soluble Cu(II) was found to be stronger in HAW than in

360 NW or MRW with higher initial concentrations of dissolved Cu(II) and less removal of dissolved Cu(II)

361 by $Fe(OH)_3$ flocs observed in HAW (Figure 4F). For instance, only 20µg/L dissolved Cu(II) was

362 removed by 2 mg-Fe(III)/L flocs when initial copper concentration was at 250µg/L. These observations

363　can be attributed to the distinct character of HAW NOM which gave higher $SUVA_{254}$ (Table 2) and

364　contained more large MW components as evidenced in the AMW profile (Figure 2). Detailed discussion

365　is presented in 3.5.

366　　The laboratory results (Figure 4A, B, C and E) were tested against known adsorption isotherms,

367　Freundlich, Langmuir and BET. Freundlich isotherms ($\frac{Cu(II)removal}{Fe(III)Conc} = K_F \times FinalCu(II)^{1/n}$) were found to

368　be capable of representing the adsorption of dissolved Cu (II), presumably as Cu(II)-NOM, in MRW,

369　MCW (except 1 mg-Cu/L) and NW. Best fit parameters for the Freundlich isotherms are shown in Table

370　5. Adsorption phenomena generally occurred between dissolved Cu(II) and $Fe(OH)_3$ flocs, as shown by

371　the well-matched Freundlich isotherm curves in Figure 4. Considering that "K_F" and "n" reflect the

372　characteristics of adsorbent ($Fe(OH)_3$ flocs) and adsorbate (Cu(II)-NOM) [44], it is reasonable to see

373　similar K_F and n values for MRW (K_F=0.003, n=1.19) and MWF (K_F=0.003, n=1.16) due to their

374　common NOM composition. Higher initial Cu(II) concentrations were found in NW than in MRW or

375　MWF as more Cu(II) may have been complexed with NOM in NW (Figure 4C) than in MRW or MWF.

376　A direct comparison of Cu(II) removal between MWF and NW is given in Figure 4D. Slightly less

377　dissolved Cu(II) was removed from NW than MWF for the case of 250 and 400 µg-Cu(II)/L initial

378　Cu(II) concentration while Cu(II) removal was similar in both waters for the case of initial 1000 µg-

379　Cu(II)/L. Considering the measurement error of ±20 µg/L, the difference is not significant. However,

380　the same Freundlich isotherm parameters adopted for MRW or MWF could not be fit to NW data.

381　Instead, different "K_F" and "n" values were calculated for NW (K_F=0.0002, n=0.73). "K_F" and "n"

382　values are interpreted in Freundlich Adsorption Isotherm in terms of fundamental kinetics and diffusion

383　based properties [44]. Skopp [44] suggested that "K_F" is related to the diffusion coefficient of an

384　adsorption-desorption dynamics and "n" reflects the probability distribution for a molecule to access

385　adsorption sites. The different K_F and n values are believed to be related to soluble microbial products

386　from nitrification [41, 42], which were chelated with dissolved copper and had a different character

387　from Cu-NOM complexes formed in MRW or MWF.

388　　　　Figure 4E shows the removal of dissolved Cu(II) from MCW which contains only uncoagulable

389　NOM (NOM_{uc}). Therefore, Figure 4E can be regarded as the removal of Cu(II)-NOM_{uc}. Despite the

390　difference in DOC concentration between MRW (2.6 mg-C/L) and MCW (0.9 mg-C/L), similar trends

391　(MCW "n=1.17" and "K_F=0.0028") of Cu(II) removal were observed when initial Cu(II) concentration

392　was 250 or 400 µg-Cu(II)/L, indicating that the same type and number of Cu(II)-NOM complexes (i.e.

393　mostly Cu(II)-NOM_{uc}) may have formed. Much less removal found in MCW than MRW for 1000 µg-

394　Cu(II)/L initial copper case can be explained by the effect of pre-formed Cu(II) particles.

395

396　**3.4 Effect of Pre-formed Cu(II) Particles on Dissolved Cu(II) Removal**

397　　　　Some deviation of the experimental data from the Freundlich isotherm was observed in MRW

398　(Figure 4A). It shows the impact of pre-formed Cu-containing particles (CuO and Cu(OH)$_2$) on

399　dissolved Cu(II) removal.　When copper is added to bulk water it potentially forms either particulate or

400　stays as dissolved form. Particulate copper can be easily removed by filtering through 0.2 µm filter

401 paper. If the particulates are removed prior to $Fe(OH)_3$ flocs addition (MWF), in comparison with

402 MRW, one can easily find the impact of particulates on dissolved Cu(II) removal by ferric flocs. In the

403 case of MWF (Figure 4B), 160 µg-Cu(II)/L as Cu(II) particulates had been removed from the sample

404 with 1000 µg-Cu(II)/L initial Cu(II) concentration. In this experiment, 350 µg-Cu(II)/L remained in

405 MWF after 1 mg/L $Fe(OH)_3$ treatment, while 410 µg-Cu/L was measured in MRW in which these pre-

406 formed copper particulates remained. This indicates that the presence of these copper particulates

407 prevents removal of some of the dissolved Cu(II). However, one could note that the pre-filtration step

408 had little effect on dissolved Cu(II) removal at the two lower initial Cu(II) cases (250 and 400 µg-

409 Cu(II)/L) due to negligible Cu(II) particles formed at low initial copper cases.

410   This impact from the particles became obvious when initial copper concentration of 1000 µg-

411 Cu(II)/L was practiced in MCW (Figure 4E). Only around 350 µg-Cu/L remained in MCW at 0 mg-

412 Fe(III)/L addition. Reduced Cu(II) complexing sites on the lower concentration of NOM_{uc} must only

413 have been available to complex with around 350 µg-Cu(II)/L, with the remaining copper presumably

414 forming precipitates such as $Cu(OH)_2$ and $CuO_{(s)}$. When $Fe(OH)_3$ floc was added, the presence of this

415 large proportion of Cu-containing particles severely interfered with dissolved Cu(II) removal. With 2

416 mg-Fe/L, only 60 µg/L Cu-NOM_{uc} was removed. This dramatic change in the dissolved Cu(II) removal

417 could be due to preferential adsorption of the large copper-based precipitates on the $Fe(OH)_3$ flocs.

418

419 **3.5 Cu(II)-NOM Chelation and Its Impact on Cu(II)-NOM Removal by $Fe(OH)_3$ Flocs**

22

420   During the course of the experiments on dissolved Cu(II) removal by $Fe(OH)_3$ flocs, the analysis of

421   AMW distributions were undertaken on MRW and HAW. The samples were respective filtrates

422   collected 24 hours after the copper (400 µg-Cu(II)/L) addition, and 4 hours after the addition of $Fe(OH)_3$

423   floc (0.5 mg-Fe/L) (Figure 5A and B, respectively). The DOC concentration and UV_{254} absorbance

424   were also measured after copper dosing. The DOC concentration of MRW and HAW remained

425   unchanged before and after copper dosing. However, the UV_{254} absorbance increased in both MRW and

426   HAW after copper dosing (Figure 6A and B, respectively).

427   In the MRW samples, addition of copper did not change the DOC concentration of the water

428   samples (DOC concentration of 2.6±0.1 mg/L before and after copper addition). However, a

429   concentration of 400 µg/L copper increased the UV_{254} absorbance of MRW from 0.036 cm^{-1} to 0.046

430   cm^{-1} (Figure 6A), equivalent to a 28% increase in relative UV_{254} absorbance or $SUVA_{254}$ (since the

431   DOC remained unchanged) (Figure 6B). Apart from the $SUVA_{254}$ increase, the addition of copper

432   slightly shifted the distribution of MW to a higher range (2000-4000 Da) (Figure 5A). The change in

433   both $SUVA_{254}$ and AMW distribution reflected a restructuring of the DOC after complexing or chelating

434   with copper ions, perhaps indicating a change in the type of organic matter from hydrophilic to

435   hydrophobic through intermolecular bidentate chelation between smaller NOM molecules. The removal

436   of Cu-NOM by 0.5 mg-Fe/L $Fe(OH)_3$ was also concentrated on a narrow spectrum between 2500 Da

437   and 3500 Da. According to our previous work [17], the hydrophobic fraction of NOM, which is

438   generally rich in phenolic chromophores, is depleted in Mundaring water. Therefore, the change of

439 AMW distribution after $Fe(OH)_3$ adsorption provided another evidence showing that the dosed copper

440 in MRW chelated with hydrophilic fraction and converted them to hydrophobic molecules which were

441 readily removed by the flocs.

442   By contrast, only 4.7% increase in UV_{254} absorbance was measured in HAW when the initial copper

443 concentration was 400 µg/L (Figure 6B) and the DOC concentration remained unchanged. In addition,

444 little change in the AMW profile of DOC detected by UV_{254} in HAW was caused by copper dosing

445 (Figure 5B) since the DOC which was chelated with copper only accounted for a small proportion of the

446 whole UV_{254}-detected DOC in HAW. However, after the addition of $Fe(OH)_3$ flocs, compared with the

447 corresponding situation in MRW, the DOC detected by UV_{254} in HAW was considerably reduced over a

448 more extensive AMW range (2000-6000 Da), indicating that $Fe(OH)_3$ flocs removed the components of

449 large MW in HAW, since coagulation with ferric salts is believed to readily and preferentially remove

450 hydrophobic fraction mainly containing aquatic humic material with high MW [33]. In addition, little

451 dissolved Cu(II) removal by 0.5 mg/L $Fe(OH)_3$ as discussed previously (Figure 4F) again indicated that

452 dosed Cu(II) preferentially chelated with small MW components or the hydrophilic fraction in HAW

453 and consequently was shielded from $Fe(OH)_3$ adsorption by large MW components or the hydrophobic

454 fraction.

455   Gamble et al. [13] reported two general types of bidentate chelating sites for dissolved Cu(II): a

456 salicylate type and a dicarboxylate type (Figure 7). The dicarboxylate type could be both intramolecular

457 and intermolecular, depending on the functional groups available. According to the shift in UV_{254}-

24

458   detected DOC in MRW to higher AMW upon addition of copper(II), intermolecular dicarboxylate

459   chelation may be mainly responsible for copper binding in MRW, resulting in the aggregation of small

460   molecules, while salicylate chelation likely occurred in HAW in which the NOM may contain more

461   salicylate type binding sites. In either MRW or HAW, copper preferentially chelated with small organic

462   molecules or the hydrophilic fraction and converted them (or part of them) to hydrophobic complexes.

463

464   **4.   CONCLUSIONS**

465   Soluble Cu(II) ions used to inhibit nitrification in natural waters mainly exist in the form of various

466   organic Cu(II) complexes. Acting as a bridging ion, copper appears to have the capacity to aggregate

467   smaller organic molecules to form larger organic molecules via intermolecular complexation. Based on

468   the evidence provided by the changes in $SUVA_{254}$ and AMW distribution profiles of different NOM-

469   containing waters, Cu(II) ions are believed to preferentially form complexes with small molecules,

470   rather than large molecules. Trace ferric hydroxide flocs, which could be naturally present or released

471   from aging or corroded iron pipes, demonstrated varying capacity of removing Cu-NOM subject to

472   different aqueous conditions. Organic Cu(II) removal by ferric hydroxide flocs in Mundaring water was

473   found to be governed by an adsorption process obeying a Freundlich isotherm, while less organic Cu(II)

474   removal was observed in a solution of commercial humic acid due to the predominance of large MW

475   DOC in the humic acid, which shields small organic Cu(II) complexes from adsorption. Insoluble

476 copper species (e.g $CuO_{(s)}$ and $Cu(OH)_{2(s)}$) can affect adsorption of dissolved copper on ferric hydroxide

477 flocs to differing extents, depending on their relative proportion.

478   For the strategy of inhibition of nitrification in distribution systems by the addition of Cu(II) ions,

479 the impact of the character of NOM in the distributed water on the fate of dissolved copper ions is

480 therefore of crucial importance. Iron pipe corrosion offers a potential explanation for the significant loss

481 of Cu(II) in the distribution system, in comparison to the successful pilot-scale reservoir study where

482 release of ferric hydroxide flocs would have been minimal.

483

488

489 **SUPPORTING INFORMATION AVAILABLE**

490   Details of $Fe(OH)_3$ suspension preparation and dynamic process of Cu(II) removal by $Fe(OH)_3$ flocs.

491

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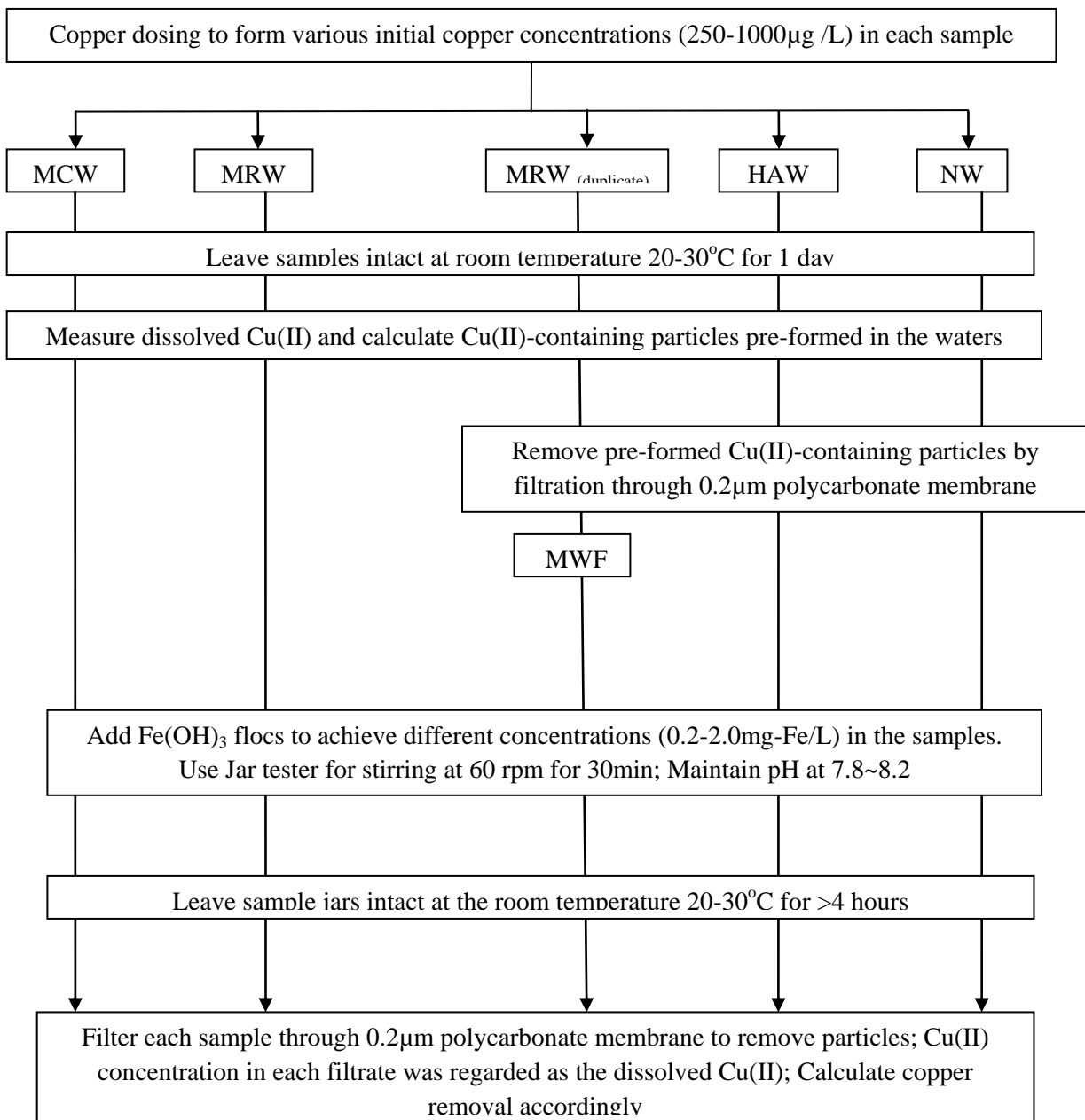
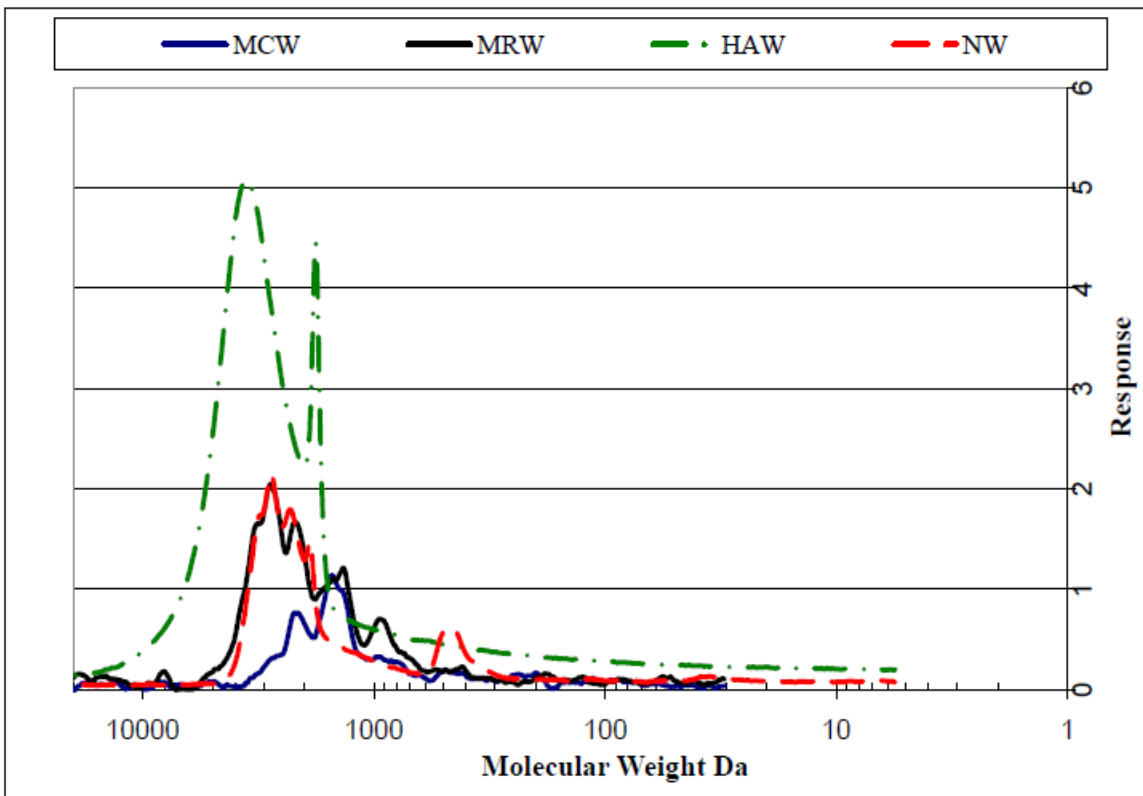**Figure 1: Flowchart of Cu(II) Removal Experiment Procedure**

Figure 2: Apparent Molecular Weight Distributions Detected by UV$_{254}$ in MRW, MCW, HAW and NW Bulk Water Samples
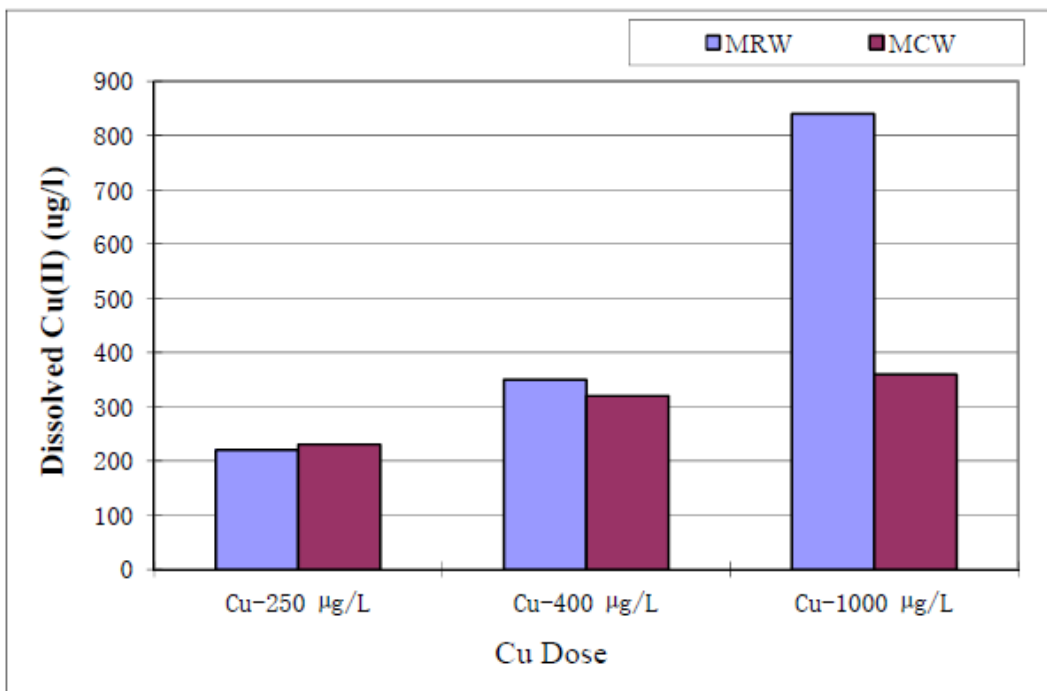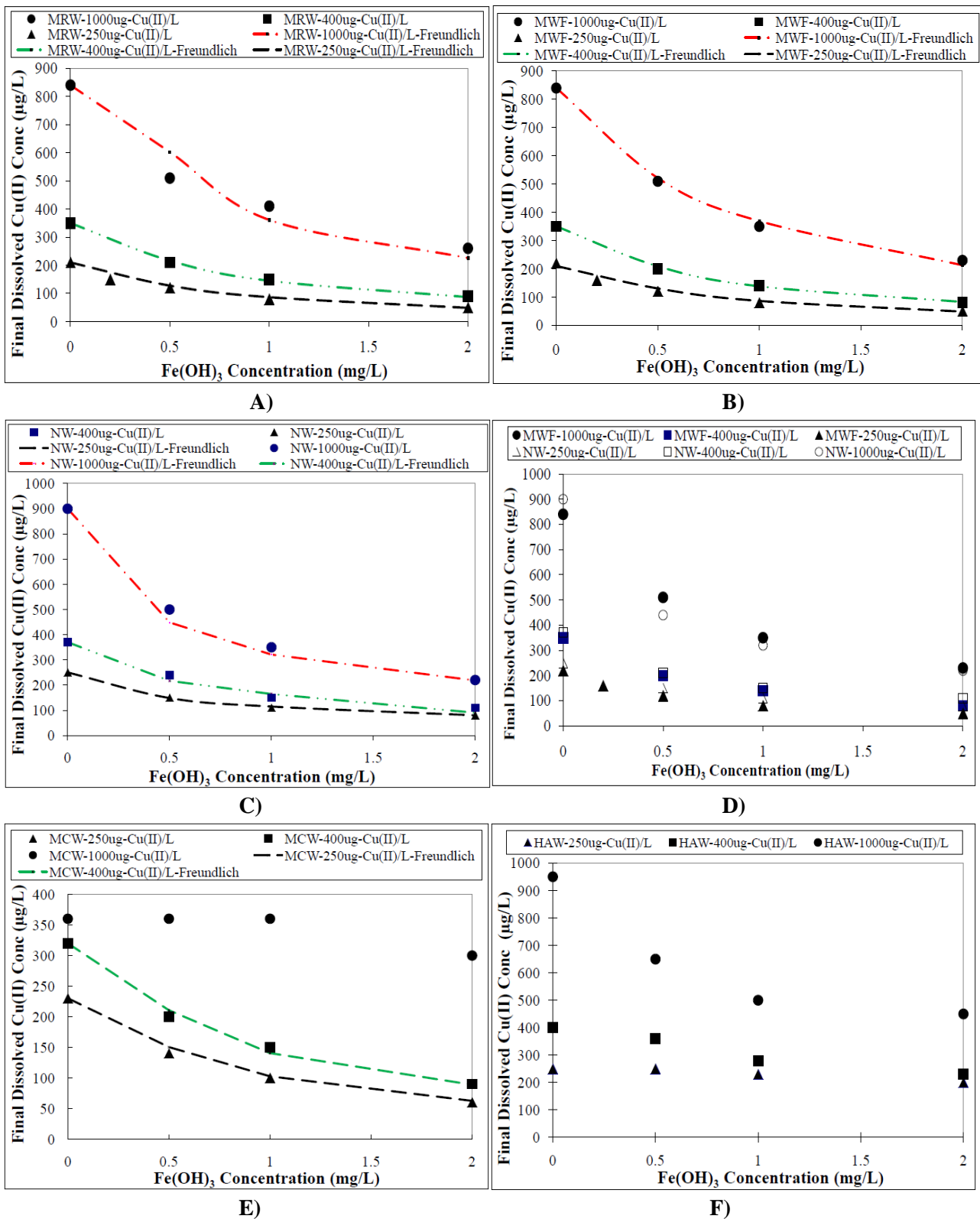

Figure 3: Copper(II) Solubility in MRW and MCW at Various Initial Copper Concentrations (Dissolved copper was measured 24 hours after copper dose) Measurement error in copper concentrations is ±20μg-Cu(II)/L.

Figure 4: Dissolved Cu(II) concentrations remaining in bulk waters 4 hours after addition of Fe(OH)₃ flocs dosed to reach concentrations as marked in x-axis. A) MRW; B) MWF; C) NW; D) Comparison of dissolved Cu(II) removal between MWF and NW; E) MCW; F) HAW; In MWF, NW and HAW Fe(OH)₃ was dosed after filtering particulates formed by copper addition in the previous step.

A)	B)
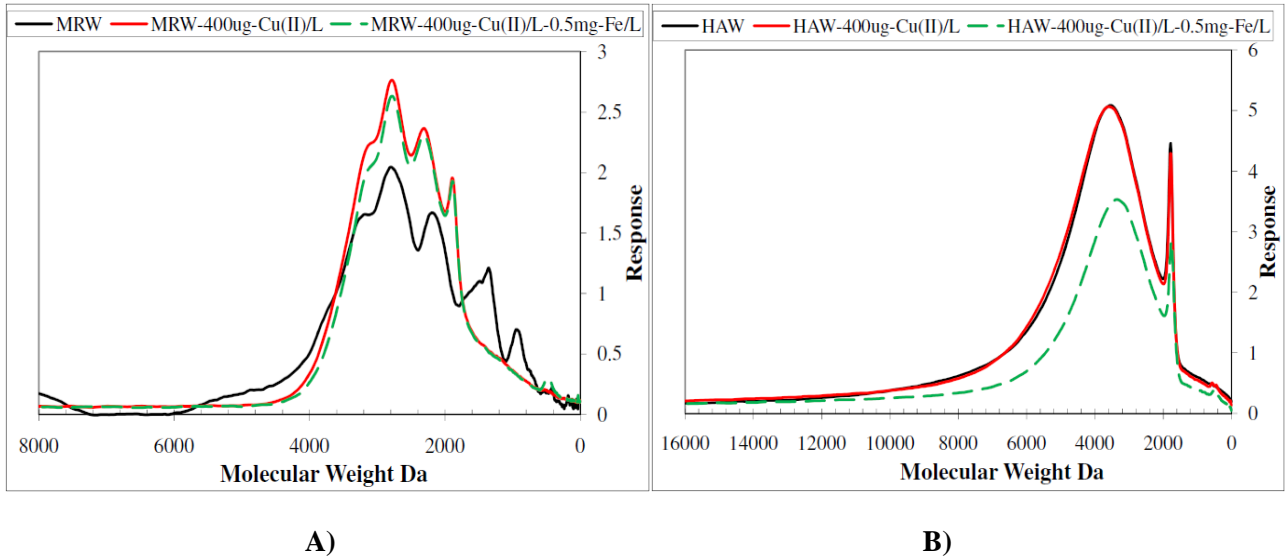
Figure 5: AMW distributions of UV$_{254}$-detected DOC in A) MRW, in the MRW filtrate 24 hours after addition of Cu(II) (400µg-Cu(II)/L) and in the MRW filtrate 4 hours following further addition of Fe(OH)$_3$ floc (0.5mg-Fe/L); and B) HAW, in the HAW filtrate 24 hours after addition of Cu(II) (400µg-Cu(II)/L) and in the HAW filtrate 4 hours following further addition of Fe(OH)$_3$ floc (0.5mg-Fe/L).
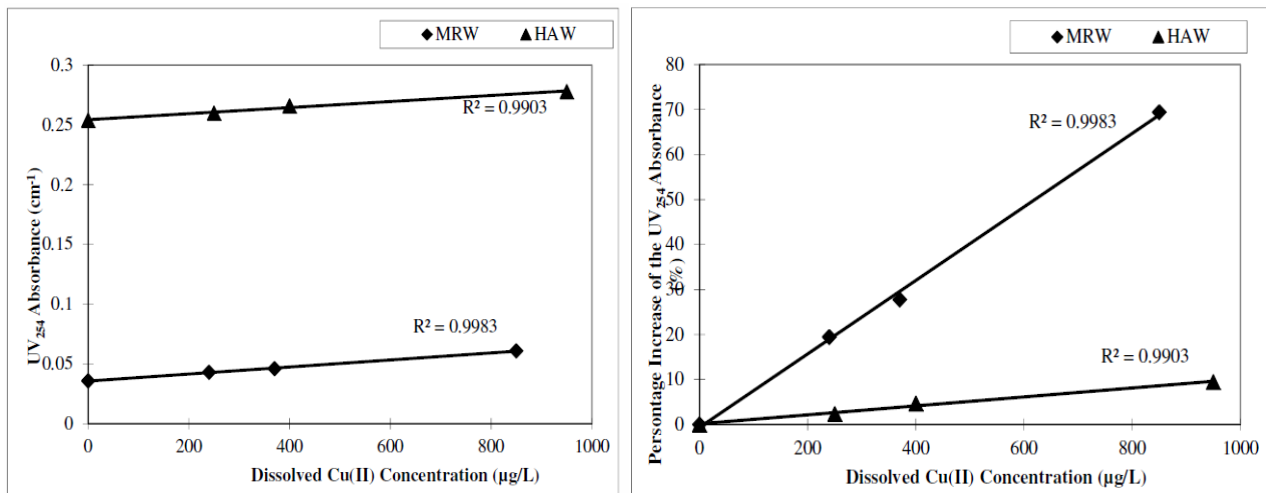
Figure 6: Change of UV$_{254}$ Absorbance Vs Copper Concentration A) Absolute UV$_{254}$ Abs Vs Copper concentration B) Relative Change (%) of UV$_{254}$ Absorbance Vs Copper Concentration
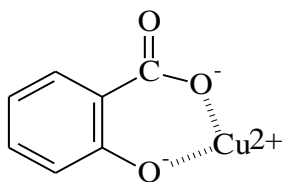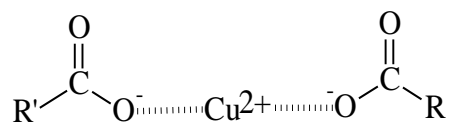
Salicylate chelation   Dicarboxylate chelation

Figure 7: Copper Chelation with Two Types of Bidentate Chelating Sites

Table 1: Potential Redox Reactions Considered in G&AWSS (Snoeyink and Jenkins, 1980)

Reaction	Standard Electrode Potentials at 25°C (Volt)
$O_2(ag) + 4H^+ + 4e^- = 2H_2O$	+1.27
$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O$	+0.84
$Cu^{2+} + 2e^- = Cu_{(s)}$	+0.34
$Fe^{2+} + 2e^- = Fe_{(s)}$	-0.44

Table 2: Water Quality Characteristics of the Bulk Water Samples

Water Samples	pH	UV_{254}	DOC	SUVA	Total concentration of dissolved Fe(II) or Fe(III)
	-	cm^{-1}	mg-C/L	L·mg^{-1}·m^{-1}	mg/L
MRW	7.9±0.2	0.035±0.002	2.6±0.1	1.35	<0.02
MCW	7.9±0.2	0.010±0.002	0.90±0.1	1.11	<0.05
HAW	7.9±0.2	0.248±0.002	2.4±0.1	10.33	<0.02
NW	7.9±0.2	0.026±0.002	2.5±0.1	1.04	<0.02

Table 3: The NOM Fraction(s) Dominating in Water Samples (Derived from Figure 1)

Water Samples	AMW Range (Da)	Major NOM Fraction
MCW	1000~2000	Uncoagulable
MRW	1000~3000	Coagulable + uncoagulable
HAW	2000~10000	More aromatic groups
NW	~500 + 2000~3000	Similar to MRW + smaller molecules produced through nitrification

Table 4: The Major Cu(II) Species under Various Aqueous Conditions after Dosing an Aqueous CuSO$_4$ Solution into Each Bulk Water to Achieve An Initial Concentration of 1000 µg-Cu(II)/L

Bulk Water Conditions	Intermediate[1] / Equilibrated[2] Copper Species	MINEQL® Calculation	Laboratory Data
Milli-Q water, pH=6.3±0.1, Open system	Cu^{2+}	Cu^{2+}=1 mg/L	Dissolved copper was measured at 0.98 mg/L 1 day after Cu dose
Milli-Q water, pH=7.5±0.1, Open system	Cu(OH)$_2$ / CuO	Cu^{2+}=3 µg/L + CuO$_{(s)}$	Dissolved copper (<20 µg/L) was measured both 2 hrs and 2 days after Cu dose
CaCO$_3$ buffered solution, pH=7.5±0.1, Open system	CuCO$_3$^{o}, CuOH$^+$ and Cu(OH)$_2$ / only CuO	Total soluble Cu=9 µg/L + CuO$_{(s)}$	100 µg/L and 10 µg/L dissolved Cu were found 2 hrs and 1 day after Cu dose respectively, the latter occurs when the system is in equilibrium with CuO
CaCO$_3$ buffered solution, pH=7.5±0.1, Closed system	Cu^{2+}, CuCO$_3$^{o}, CuOH$^+$ and Cu(OH)$_2$	Cu^{2+}=30 µg/L, CuOH$^+$=30 µg/L, CuCO$_3$^{o}= 48µg/L + Cu(OH)$_{2(s)}$	150 µg/L dissolved Cu was measured 4 hours after Cu dose. The system may be in equilibrium with Cu(OH)$_{2(s)}$
MRW pH=7.9±0.1, DOC=2.6 mg/L, Open system	CuCO$_3$^{o}, CuOH$^+$, Cu(OH)$_2$ and Cu-NOM / CuO and Cu-NOM	*Dependant on availability of binding ligands of MRW NOM	950 µg/L and 840 µg/L dissolved Cu was found 2 hrs and 1 day after Cu dose respectively. The latter occurs when the system reaches equilibrium with both CuO and Cu-NOM complexes

Note:

Intermediate[1] Copper Forms: possible Cu species existing in bulk water only 2 hours after dosing CuSO$_4$.

Equilibrated[2] Copper Forms: possible Cu species existing in bulk water 1 day after copper dose

*Cu-NOM chelation coefficient is dependent on a series of binding ligands varying in different NOM-containing water samples. They were not calculated by MINEQL in this study. Alternatively, the proportion of Cu-NOM was deducted from the difference between the total dissolved Cu(II) and the sum of inorganic copper compounds and free cupric ions.

Table 5: The Parameters Adapted in Freundlich Adsorption Isotherms

Variables and Constants	Valid Cu(II) Concentration	K$_F$	n	R^2

	Range			
Units	μg/L			
MRW	200~1000	0.003	1.19	0.98
MWF	200~1000	0.003	1.16	0.99
MCW	200~400	0.003	1.17	0.99
NW	200~1000	0.0002	0.73	0.98

Note: Cu_o: dissolved Cu(II) concentration at 0 mg-Fe(III)/L addition

C: Final dissolved Cu(II) concentration after ferric hydroxide flocs treatment

Freundlich isotherm: $Y = K_F C^{1/n}$

R^2: coefficient of determination