

1 **Coagulant recovery and reuse for drinking water treatment**

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9 **ABSTRACT**

10 Coagulant recovery and reuse from waterworks sludge has the potential to significantly
11 reduce waste disposal and chemicals usage for water treatment. Drinking water regulations
12 demand purification of recovered coagulant before they can be safely reused, due to the risk
13 of disinfection by-product precursors being recovered from waterworks sludge alongside
14 coagulant metals. While several full-scale separation technologies have proven effective for
15 coagulant purification, none have matched virgin coagulant treatment performance.

16
17 This study examines the individual and successive separation performance of several novel
18 and existing ferric coagulant recovery purification technologies to attain virgin coagulant
19 purity levels. The new suggested approach of alkali extraction of dissolved organic
20 compounds (DOC) from waterworks sludge prior to acidic solubilisation of ferric coagulants
21 provided the same 14:1 selectivity ratio (874 mg/L Fe vs. 61 mg/L DOC) to the more
22 established size separation using ultrafiltration (1285 mg/L Fe vs. 91 mg/L DOC). Cation
23 exchange Donnan membranes were also examined: while highly selective (2555 mg/L Fe vs.
24 29 mg/L DOC, 88:1 selectivity), the low pH of the recovered ferric solution impaired
25 subsequent treatment performance. The application of powdered activated carbon (PAC) to

26 ultrafiltration or alkali pre-treated sludge, dosed at 80 mg/mg DOC, reduced recovered ferric
27 DOC contamination to <1 mg/L but in practice, this option would incur significant costs.

28

29 The treatment performance of the purified recovered coagulants was compared to that of
30 virgin reagent with reference to key water quality parameters. Several PAC-polished
31 recovered coagulants provided the same or improved DOC and turbidity removal as virgin
32 coagulant, as well as demonstrating the potential to reduce disinfection byproducts and
33 regulated metals to levels comparable to that attained from virgin material.

34

35 *Keywords* Coagulant recovery and reuse; dissolution; ferric; membrane separation;
36 DOC

37

38 **1 INTRODUCTION**

39 Coagulation-flocculation is a key process in potable water treatment. While effective, its
40 application accounts for ~5% of operational expenditure (OPEX) at water treatment works
41 (Niquette et al., 2004). This is attributable to the combined costs of coagulant and pH
42 adjustment chemicals, as well as that of disposal of the resulting sludge or “water treatment
43 residuals” (WTR). Within the UK water industry, annual coagulant consumption exceeds
44 0.33m tonnes (Henderson et al., 2009) and WTR production exceeds 0.18 million (m) tonnes
45 (Pan et al., 2004), costing around £40m and £8m respectively at 2015 prices. The issue is
46 reflected globally: annual waterworks sludge production from alum dosing alone exceeds
47 730m tonnes in the US (Prakash and Sengupta, 2003) and in Japan, drinking water treatment
48 produces 0.3m tonnes of dry solids (Fujiwara, 2011).

49

50 Coagulant recovery can potentially reduce these costs by regenerating and reusing the
51 coagulant metals in the WTRs. This is usually achieved through acidification, commonly to
52 pH 2 (King et al., 1975; Parsons and Daniels, 1999; Keeley et al., 2014b). However, organic
53 compounds within the sludge have similar pH solubility behaviour (Prakash and Sengupta,
54 2003), contaminating the acidified recovered coagulant with suspended and dissolved organic
55 carbon (DOC). An early full-scale study of non-selective ferric recovery reported no
56 significant impact on treated water quality but the recovered ferric coagulant free acidity
57 increased lime demand and shortened filter run times (Saunders and Roeder, 1991).

58

59 When dosed into the potable treatment stream, elevated levels of residual DOC resulted at the
60 final chlorination stage yielding a commensurate increase in halogenated disinfection
61 byproducts (DBPs) in the final treated water (World Health Organization, 2000). Public
62 health protection and abidance with water quality regulations (USEPA, 2009; DWI, 2010)
63 demand the recovered coagulant (RC) to be appropriately purified to remove DOC and trace
64 metal contaminants.

65

66 Conventional, pressure-filtration membranes (Keeley et al., 2014a,b), adsorbents (Lindsey
67 and Tongkasame, 1975), chemical precipitation (Ulmert and Sarner, 2005), and ion exchange
68 (Prakash and Sengupta, 2003) have been tested for RC purification, but have failed to
69 combine adequate removal of organic contaminants with competitive process economics.
70 Reuse of impure RCs for phosphorus removal in wastewater treatment is a promising
71 circumvention to this problem (Babatunde and Zhao, 2007; Xu et al., 2009) but is less

72 ambitious than reuse in potable treatment which approaches the target of net chemical-free
73 treatment stipulated by some water-related research organisations ([UKWIR, 2007](#)).

74

75 Published research into coagulant reuse for potable water applications appears to have been
76 limited for the last decade. This study aims to provide a benchmark for the purity and
77 treatment performance of recovered ferric coagulant and to establish which RC
78 characteristics most affect treatment efficacy. The effect of augmenting existing RC
79 purification technologies (ultrafiltration, UF, and Donnan dialysis, DD) with pre- and post-
80 treatment stages was also studied by way of improving RC quality, particularly in terms of
81 minimising DOC contamination for which a lower level of 3.5 mg/L has been identified from
82 previous CR studies ([Prakash and Sengupta, 2003](#)). Of more practical importance is the
83 impact of this organic contamination on DBP formation, which pertains to the residual
84 organic compound levels from both the raw water and dosed RC and their reactivity with
85 chlorine.

86

87 **2 METHODOLOGY**

88 **2.1 Coagulant recovery and purification**

89 Dewatered WTR cake, measured as 14% dry solids (DS) containing ~25% Fe, was collected
90 from a 150,000 m³/d capacity water treatment works treating upland water with ferric sulfate
91 coagulant (13% as Fe) at a coagulation pH range of 4.7-5.1 (Derbyshire, UK). The raw water
92 had a pH of 6.26 with a zeta potential of -13.9mV. The character of the NOM within this raw
93 water has been determined to be predominantly hydrophobic (Keeley et al., 2014b). Slurries
94 containing 1 kg of sludge cake in 10L of deionised (DI) water were mixed for 24 h {1}

95 before subsequent coagulant recovery extraction using acid {3} or alkali {4} (Fig. 1; numbers
96 in parenthesis refer to sampling points shown in the figure).

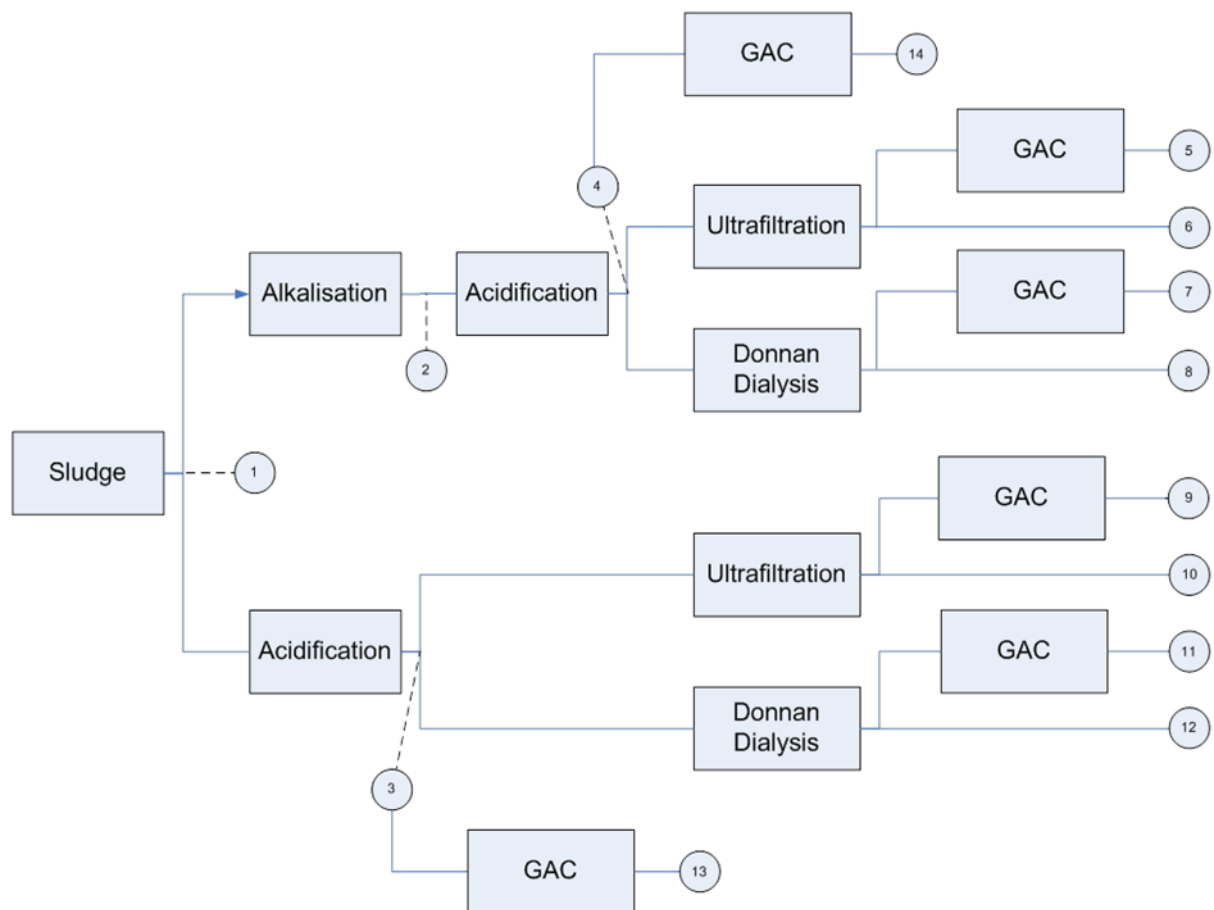
97

98 Alkali pre-treatment {2} comprised adjustment of the WTR slurry to pH 12 with reagent-
99 grade NaOH pellets, and mixing for 24 h, with periodic addition of NaOH to maintain the pH
100 at 12, prior to settlement. The solids fraction was retained on a 1.2 μ m pore size glass fibre
101 filter and washed with 1 L of DI water prior to digestion in 1 L of 5M H₂SO₄ for a further 24
102 h and dilution to 10 L with DI water. Direct solubilisation with acid was achieved by
103 adjusting the WTR slurry to pH 2 with 18M H₂SO₄ before mixing for 24 h {4}.

104

105 Both the alkali pre-treated and direct acid extractions were purified by pressure filtration {6;
106 10} or cation exchange extraction {8; 12}. Pressure filtration through a 2 kDa-rated
107 polyethersulfone membrane (Sterlitech Corporation, Kent, WA, USA) was conducted using a
108 flat-sheet crossflow cell of 0.007 m² membrane area (Keeley et al., 2014b). The membrane
109 cell was also adapted for use with a Nafion 115 cation exchange membrane, for which the
110 feed-side recirculated 2 L of acidified sludge and the strip-side 1 L of 1 M H₂SO₄. Membrane
111 specific surface area, time, feed:strip volumes and acid strength were selected according to a
112 previous study using similar materials (Prakash and Sengupta, 2003).

113



114
115

Figure 1. Recovered coagulant experimental processing scheme and sampling points:

- | | |
|--|----------------------------------|
| 1 Ferric sludge in water | 8 Alkali-purged, acidified, DD |
| 2 Ferric sludge in caustic | 9 Acidified, UF, PAC |
| 3 Acidified ferric sludge | 10 Acidified, UF |
| 4 Acidified, alkali purged | 11 Acidified, DD, PAC |
| 5 Alkali, acidified, UF (ultrafiltration), PAC (powdered activated carbon) | 12 Acidified, DD |
| 6 Alkali-purged, acidified, UF | 13 Acidified, PAC |
| 7 Alkali, acidified, DD (Donnan dialysis), PAC | 14 Alkali-purged, acidified, PAC |

116 Reference to these sampling points is made throughout the article, in parenthesis: {}.

117

118 A post-treatment adsorption stage was applied to all RCs to further reduce DOC
 119 concentrations {5; 7; 9; 11; 13; 14}. In addition to powdered activated carbon (PAC, Norit
 120 SA Super 94002-8), powdered graphite (PG, Fisher, UK) was also examined: previous
 121 studies had suggested PG to have a high organic acid adsorption capacity at pH values below
 122 3 (Xiao and Pignatello, 2014). Adsorption isotherms were produced using a batch method
 123 whereby 0-200 g/L of adsorbent (pre-wetted for 24 hours in 15 mL 0.005 M H₂SO₄) were

124 mixed for 48 hours with 25 mL of RC at pH 2 (UF permeate for the acidified RC sample
125 {10}). The aqueous phase was filtered through 0.45µm nylon filters (Fisher, UK) before
126 DOC analysis using a Shimadzu TOC-V analyser and soluble Fe determination using a
127 Perkin Elmer atomic absorption spectrometer (AAS). Other metals were extracted in nitric
128 acid and analysed using inductively coupled plasma mass spectroscopy. The resulting
129 isotherms were used to select the optimum adsorbent and dose (relative to RC DOC content)
130 which were then applied to RC from all preceding stages of purification {5; 7; 9; 11; 13; 14}.
131 RCs were then characterised in terms of pH, Fe and DOC content.

132

133 **2.2 Recovered coagulant treatment performance**

134 Jar tests were used to compare performance of RCs and virgin coagulant in terms of water
135 treatment. Raw water and virgin ferric sulfate coagulant (VFS; measured as 20% Fe) were
136 sampled from the same site as the WTRs. Jar tests (using a Phipps & Bird PB-700 jar tester)
137 were conducted at room temperature, based on an existing method (Sharp et al., 2006) with a
138 1.5min rapid mix at 200 rpm, a 15min flocculation mix at 50 rpm and a 20min settlement
139 stage. Treated water was analysed for DOC and turbidity, as well as zeta potential using a
140 Malvern Zetasizer Nano ZS.

141

142 A series of jar tests with VFS were used to determine the optimum coagulant Fe dose
143 (between 4 and 48 mg/L as Fe) and pH (between 3.5 and 5.5; corrected using dilute HCl and
144 NaOH) for DOC and turbidity removal. This dose and pH were then used for further jar tests
145 with RCs. Analyses comprised DOC, UV absorption at 254 nm (used to calculate specific
146 UV adsorption; SUVA), turbidity, and zeta potential. Residual metals (Cu, Pb, Ni, Cd, Cr

147 and Mn) were determined using inductively-coupled plasma spectroscopy, and
148 trihalomethane formation potential (THM-FP) measured using a protocol (Parsons et al.,
149 2004) adapted from standard methods (APHA, 1992). Size exclusion liquid chromatography
150 with 254 nm UV absorption detection was conducted using a Shimadzu VP series
151 chromatogram.

152

153 **3 RESULTS AND DISCUSSION**

154 **3.1 Recovered coagulant purity**

155 Three coagulant purification unit processes were studied: 1) alkali extraction of DOC prior to
156 acidification and solubilisation {4} of the retained solids; 2) membrane separation using UF
157 {6; 10} or DD {8; 12}; and 3) DOC adsorption with powdered carbon {5; 7; 9; 11; 13; 14}
158 (Fig. 1).

159

160 **Alkali pre-treatment.** A pH 12 NaOH solution was used to extract the bulk of the organic
161 compounds, as DOC, from WTRs {2} leaving the less soluble iron for subsequent dissolution
162 in H₂SO₄ {4}. The use of alkali to resolubilise and recover aluminium sludge has previously
163 been examined (Masschelein et al., 1985) but not for iron-DOC discrimination. This
164 combined alkali/acid process was effective in separating Fe from DOC by virtue of their
165 differing solubilities in alkali : an equal mass of WTR produced the same volume of acidified
166 sludge extract with 57% less DOC than extraction by acidification alone {3} (61 mg/L ±
167 1.4% DOC cf. 143 mg/L ± 2.8; Table 1). However, the corresponding Fe extracted was 47%
168 lower, such that the overall Fe:DOC ratio was only slightly higher at 14.3 cf. 12.9 for single-
169 step acidification. While solubility profiles suggest that only negligible amounts of Fe remain

170 in solution at pH 12 (King et al., 1976), loss of colloidal iron hydroxide and Fe-DOC through
171 the retaining glass-fibre filter may take place.

172

173 **Ultrafiltration (UF).** {6; 10} Size exclusion based purification of RCs has been thoroughly
174 investigated in previous studies (Lindsey and Tongkasame, 1975; Ulmert and Sarner, 2005;
175 Keeley et al., 2014a,b). These studies showed that within a range of <1-20 kDa MWCO UF
176 membranes, a 2 kDa MWCO gave the optimum balance of DOC rejection and trivalent metal
177 recovery. However, this MWCO nonetheless allowed significant DOC carryover, at 91 mg/L
178 DOC with 1285 mg/L Fe {10}, from a feed containing 143 and 1287 mg/L DOC and Fe
179 respectively {3} (Table 1). A similar Fe:DOC selectivity ratio before (12.9) {3} and after UF
180 (14.1) {10} would suggest a similarly low level of selectivity by size exclusion as with alkali
181 treatment {4}. Previous studies have highlighted the strength of Fe-DOC interactions as a
182 contributing factor for poor selectivity for Fe by UF purification, relative to the more weakly
183 interacting Al (Keeley et al., 2014a,b).

184

185 **Donnan dialysis (DD).** {8; 12} This method uses a cation exchange membrane to extract
186 coagulant metal ions from the acidified sludge, rather than filtering through a conventional
187 membrane. Since DD is a diffusive process and does not employ a transmembrane pressure, it
188 avoids the membrane fouling and energy usage of pressure-filtration and their associated
189 costs (Prakash and Sengupta, 2003). DD has additionally been reported to be the most
190 selective method for separating trivalent coagulant metals and DOC (Schneider, 2013) with
191 consistent Fe or Al recovery concentrations >5000 mg/L at yields of 70-75% with <5 mg/L
192 DOC contamination (Prakash and Sengupta, 2003). Similar performance was attained in this
193 study, with extraction from an acidified sludge feed yielding 82% Fe recovery at a

194 concentration of 2555 mg/L, with 29 mg/L DOC {12} (Table 1). The comparatively high
 195 yield and more dilute recovery solution are due to a lower volume ratio of feed sludge to
 196 recovery acid (2:1) than the 4:1 ratio used by Prakash and Sengupta (2003); the relative
 197 volumes affect the distribution of ions across the membrane at the point of Donnan
 198 equilibrium.

199

200 **Table 1: Fe and DOC levels, and Fe/DOC ratios in recovered coagulant sludge product (sample**
 201 **numbers relate to Fig. 1).**

Sam- ple	Recovered Coagulant	Fe (mg/L)		DOC (mg/L)		Fe/DOC	DOC added* (mg/L)
		Mean	S.D.	Mean	S.D.		
1	Ferric sludge in water	144	27	270	22	0.5	45
2	Ferric sludge in caustic	1094	448	1686	290	0.6	37
3	Acidified ferric sludge	1847	191	143	0.5	2.8	1.9
4	Acidified, alkali purged	874	17	61	0.1	14	1.7
5	Alkali, acidified, UF, PAC	823	26	2	0.2	341	0.06
6	Alkali-purged, acidified, UF	855	16	42	0.2	20	1.2
7	Alkali, acidified, DD, PAC	1072	19	2	0.1	597	0.04
8	Alkali-purged, acidified, DD	1056	28	4	0.3	261	0.09
9	Acidified, UF, PAC	1267	0	3	0.2	455	0.06
10	Acidified, UF	1285	34	91	0.2	14	1.7
11	Acidified, DD, PAC	2536	42	13	0.2	191	0.12
12	Acidified, DD	2555	75	29	0.2	88	0.27
13	Acidified, PAC	676	24	6	0.2	115	0.21
14	Alkali-purged, acidified, PAC	898	33	1	0.1	868	0.03

202 *refers to 24 mg/L Fe dosed in raw water

203

204 DD of the alkali pre-treated sludge {8} was less effective, with the same volume of sludge
 205 yielding 73% Fe at 1072 mg/L but with reduced DOC carryover of 4 mg/L (Table 1). The
 206 lower yield and concentration was due to a feed Fe concentration {4} less than half that of the
 207 single-step acidified feed {3}, due to the permeation of colloidal and solubilised Fe through
 208 the glass-fibre filter in the alkali pre-treatment process. Further reductions in process
 209 efficiency may have also been caused by the elevated levels of sodium in the RC, following

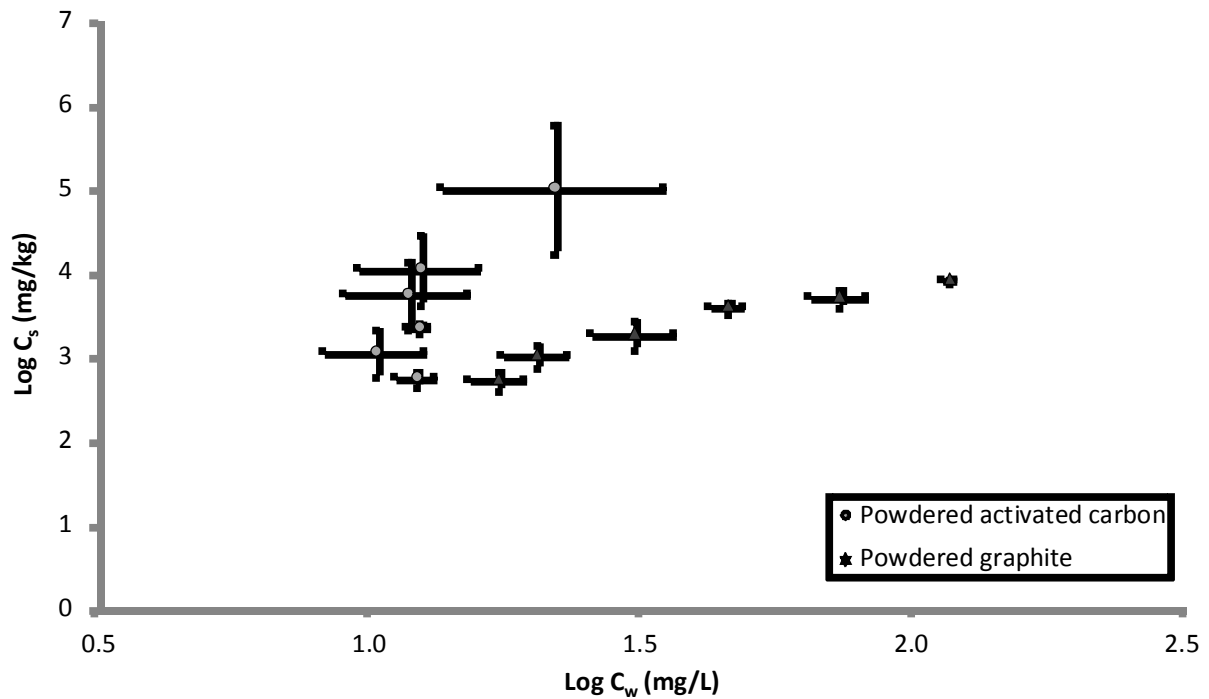
210 the preceding alkaline organics extraction step. These sodium ions are also extracted through
211 the cation membrane via the same ion exchange mechanism, competing with Fe and
212 establishing Donnan equilibrium at a lower net transfer of Fe ions (Pyrzynska, 2006).

213

214 **Adsorption.** Preliminary tests compared the adsorption of DOC by PG and PAC from an RC
215 sample containing 125 mg/L DOC and 1933 mg/L Fe. Adsorption isotherms at pH 2 showed
216 DOC removals of 90 and 86% by PAC and PG respectively at the highest adsorbent dose of
217 200 g/L. At lower doses PAC attained DOC removals 1.5-10 times more than those of PG
218 (Fig. 2). This corroborates previous results of applying granular activated carbon for DOC
219 removal from recovered alum sludge (Cornwell et al., 1981). The relative gradients of the
220 isotherm plot (Fig. 2) indicate PAC to have a greater DOC adsorption capacity than PG.

221

222 A PAC dose of 10 g/L was selected. Higher doses yielded marginal removal improvements: a
223 100 g/L dose reduced the DOC residual by only 2 mg/L less than the 10 g/L PAC dose
224 (yielding a residual DOC of 10.3 mg/L rather than 12.4 mg/L; both from a feed level of 125
225 mg/L). However, the 100 g/L PAC reduced the Fe yield by 330 mg/L compared with the 10
226 g/L PAC dose. At the dose of 10 g/L PAC removed 6 times more DOC than PG.
227 Accordingly, PG was excluded from further testing. Both adsorbents favoured DOC
228 adsorption over Fe adsorption, with only 9% and 15% reductions from the initial soluble Fe
229 concentration with 10 g/L of PAC and PG respectively. Evidence suggested that the small
230 improvement (10-15%) in Fe concentration at very high adsorbent doses (200 g/L) was
231 primarily by water uptake by the PAC, rather than organic carbon removal. Further details are
232 shown in Table S1 in Supporting Information.



233

234 Figure 2. Adsorption of DOC by PAC and powdered graphite at pH 2

235

236 The isotherms showed that a PAC dose of 80 mg/mg DOC was most effective at DOC
 237 removal from RCs, without significant uptake and loss of Fe. At this dose, removals of 94-
 238 98% were achieved from acidified {13}, alkali pre-treated {14}, and ultrafiltered RCs {5; 9}
 239 (Table 1). DD RCs were less effectively purified by PAC {7; 11}, with DOC removals of 54-
 240 56%, due to the low DOC concentrations of 4 and 29 mg/L, prior to PAC treatment {8; 12}.
 241 Low pH values make DOC and PAC more electropositive, increasing electrostatic repulsion
 242 to a point that adsorption is inhibited (Xiao and Pignatello, 2014). Additionally, the DD-
 243 treated RCs had significantly lower initial pH of ~0.5, compared to 1.5-2.8 for other PAC-
 244 treated RCs. The hydrophilic, low molecular weight/electronegativity nature of the residual
 245 DOC in DD-treated RCs may also negatively affect its ability to be adsorbed, although of all
 246 the purification methods evaluated in this study, DD RC {12} had the lowest DOC residual
 247 and may not require additional purification

248

249 The residual DOC concentrations for PAC-treated RCs {5; 7; 9; 11; 13; 14} were in the range
250 of 1-13 mg/L, comparable to the lowest reported DOC values in RCs of 3.5 mg/L (Prakash
251 and Sengupta, 2003) and 17 mg/L (Prakash et al., 2004). The lowest DOC concentrations for
252 PAC-treated RCs were from alkaline pre-treatment {5; 7; 14}, both with and without UF or
253 DD treatment. Alkaline pre-treatment thus removes DOC of different character to PAC, or
254 else chemically alters the residual DOC through hydrolysis and saponification (Randtke and
255 Jepsen, 1981; Schafer, 2001), such that enhanced overall DOC removal is attained from their
256 combination.

257

258 **Relative separation performance of individual processes.** All of the individual processes
259 were capable of recovering >70% of the feed Fe, other than alkali pre-treatment {4} and
260 direct PAC treatment of acidified sludge {13} which respectively recovered only 57% and
261 35% of the Fe. These yields do not take into account the yield from acidifying the base
262 sludge, which never exceeded 53% in this experiment. More importantly, in terms of their
263 impact on treated water quality, there was significant DOC rejection from each stage. UF {6;
264 10} gave the least effective DOC exclusion of 31-36% due to the comparable molecular
265 weight distributions of DOC compounds and Fe colloids. PAC treatment of DD-treated RCs
266 {8; 12} gave almost as poor DOC removals of 50-55%, due to low initial DOC levels (<29
267 mg/L) and the extensive electropositive repulsion between the DOC and PAC adsorption
268 sites at the low pH of the recovered DD solutions (Xiao and Pignatello, 2014). Alkali pre-
269 treatment gave similarly low levels of rejection, with incomplete alkali solubilisation of
270 organic compounds in the sludge {3} leading to carry-over into the recovered solid phase and
271 subsequent organic compound solubilisation upon acidification {4}. Far better DOC rejection

272 was provided by DD (80-93% {8; 12}) and PAC treatment at pH values of 2 and higher
273 initial DOC loadings (90-98% {5; 9; 13; 14}). These data indicate that charge or adsorptive
274 DOC removal is important in minimising DOC levels in the RC final product.

275

276 While individual CR process selectivity is an important consideration, the selectivity of
277 multiple processes in series has also been examined. A multistage RC purification train
278 would be a likely requirement to ensure reliable delivery of RCs with sufficient quality for
279 potable treatment by diversifying the modes and extent of DOC removal (Ulmert and Sarner,
280 2005; Cornwell et al., 1981). With the obvious practical constraints of a multistage recovery
281 process, more pragmatic water quality regulations may be prerequisite for full-scale potable
282 coagulant recycling.

283

284 **3.2 Coagulant recovery option assessment**

285 The combined performance of a number of CR treatment trains was evaluated in terms of RC
286 Fe concentration, DOC carryover and pH, as previously proposed by Cornwell et al (1981),
287 as well as Fe/DOC ratio (Table 1). These measures were then compared to coagulant
288 treatment performance and benchmarked against virgin ferric coagulant.

289

290 **Fe concentration.** For fully acidified and solubilised ferric RCs, soluble Fe concentration
291 could be indicative of RC ability to destabilise impurities, via surface charge neutralisation,
292 when dosed into raw water. By this measure, DD was the most effective treatment option:
293 DD without alkali pre-treatment {12} and DD followed by PAC polishing {11} gave the
294 highest Fe concentrations of 2555 and 2536 mg/L, respectively, although the incremental

295 reduction in DOC concentration was minor. The next highest was the unpurified sludge acid
296 extract with 1847 mg/L {3}. These results highlight the inevitable losses of Fe for alkaline
297 pre-treatment {4} or, to a lesser extent, UF {10}. The concentrations of Fe recovered using
298 UF {10} and DD {12} are comparable with previous studies using similar approaches
299 reporting RCs of 3500 mg/L Al with UF (Ulmert and Sarner, 2005) and 5400 mg/L Fe with
300 DD (Prakash and Sengupta, 2003), with feed concentration, pH and volume being key
301 determinants of RC concentration (King et al., 1975). More concentrated RCs (up to 30,000
302 mg/L Al) have been achieved through RC extraction from an ion exchange resin (Petruzzelli,
303 2000) or nanofiltration dewatering and precipitation of the RC salts (Ulmert and Sarner,
304 2005). These were not attempted in this study since the cost-benefit of producing RCs at
305 these high concentrations, whilst reducing transport volumes and allowing centralised
306 processing, is questionable.

307

308 **DOC concentration.** Since the principal concern of using RC in potable water treatment is
309 elevated DBP (disinfection by-product) formation from DOC, residual DOC provides a
310 useful indication of CR efficacy. Processes using PAC and alkali pre-treatment gave the
311 lowest DOC concentrations, viz: alkali pre-treatment coupled with PAC post-treatment (1
312 mg/L {14}); alkali pre-treatment with UF or DD and PAC post-treatment (2 mg/L {5; 7});
313 and non-pre-treated UF with PAC post-treatment (3 mg/L {3}). This suggests that PAC
314 treatment is integral to reaching the highest purity of RC and corroborates previous assertions
315 that an activated carbon polishing stage is required, although in these earlier studies the stage
316 was used to remove a synthetic organic extractant which has different characteristics to NOM
317 (Comwell et al., 1981). While PAC provides effective polishing, it nonetheless demands
318 reasonable DOC removal from preceding treatment processes, whether that is alkali pre-

319 treatment, membrane separation or a combination of both. Without such pre-treatment the
320 high DOC load in the RC and thus higher PAC dose relative to Fe, produces significantly
321 greater Fe adsorption and less complete DOC removal. Since UF and PAC utilize different
322 mechanisms of DOC removal (size and adsorption, respectively) they remove DOC different
323 fractions from RC and so maximize overall removal. Removal of the high molecular weight
324 DOC by UF reduces the load onto the PAC and ameliorates pore clogging, analogous to
325 coagulation and filtration prior to GAC in potable water treatment (Newcombe and Drikas,
326 1997).

327

328 **Fe/DOC ratios.** The efficacy of the RC increases with increasing Fe/DOC ratio due to the
329 associated reduced RC demand and DOC carryover. Because DOC concentrations are more
330 variable than Fe levels between the CR processes (between 1 and 143 mg/L in acidified RCs,
331 cf. 676-2555 mg/L for Fe) Fe/DOC ratios correlate more closely with DOC concentrations
332 than Fe (Table 1). Accordingly, the highest Fe/DOC ratios pertain to alkali-PAC {14} and
333 DD treatment {7} (868 and 597 respectively), both achieved primarily through extensive
334 DOC rejection. UF-PAC treatment {9} achieved a lower ratio of 455 due to the higher DOC
335 carryover (3 mg/L), albeit offset by a higher Fe concentration yield than the alkali pre-treated
336 RCs.

337

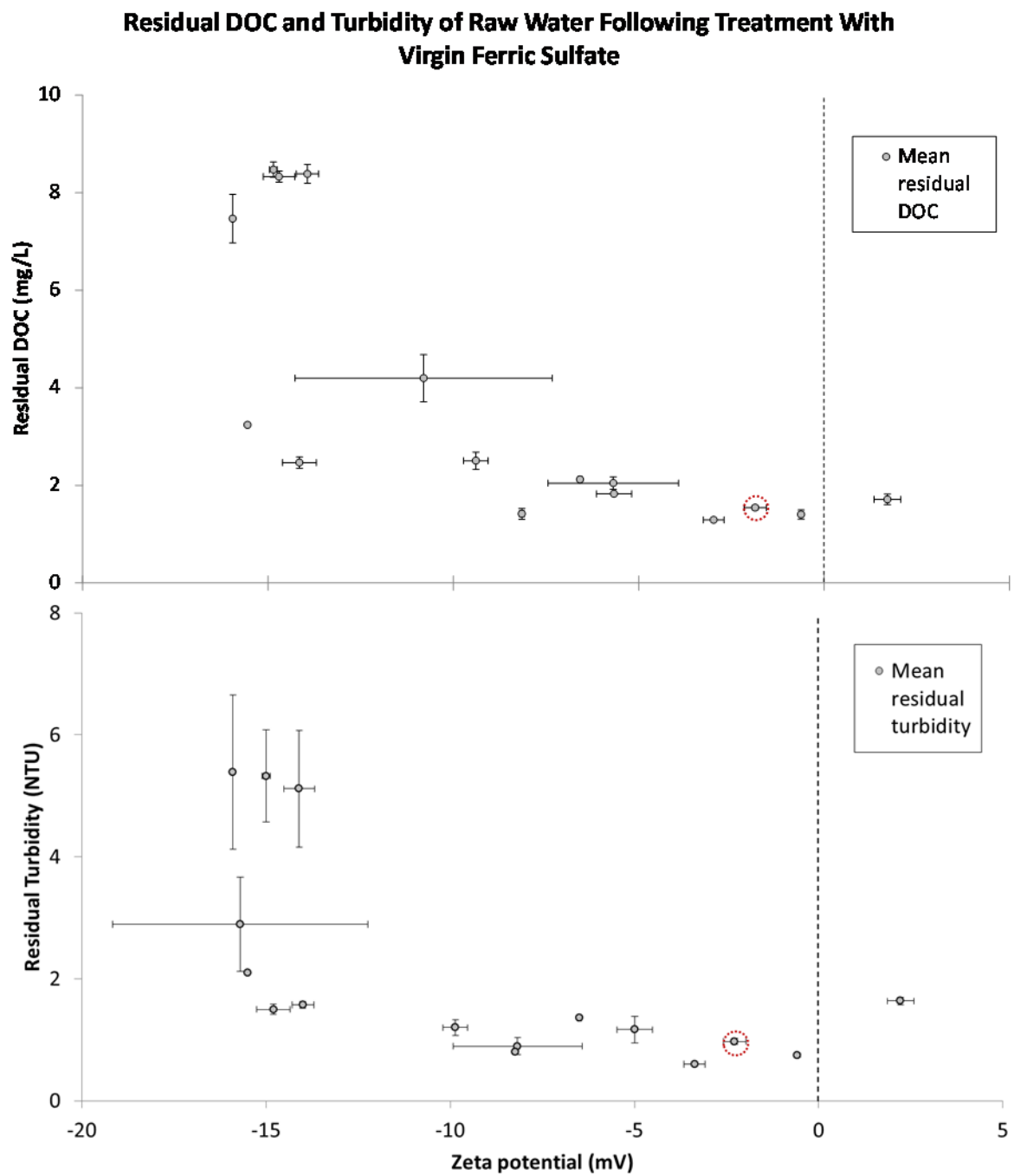
338 **3.3 Recovered coagulant treatment performance**

339 RC coagulant performance was benchmarked against virgin material (VFS). A VFS
340 coagulant dose of 24 mg/L as Fe and pH of 4.5 were selected from within the optimum
341 operating region with reference to zeta potential and DOC and turbidity removals (Fig. 3).

342 The relatively high dose was employed to ensure that coagulant performance was affected
343 only by coagulant quality, rather than external factors such as minor variations in raw water
344 character. This dose and pH combination was used for all subsequent jar tests using RCs.

345

346 RC treatment performance with PAC post-treatment, in terms of DOC and THM-FP removal
347 and treated water turbidity and Fe residual, revealed no significant trend with either RC Fe
348 dose, DOC concentration or Fe/DOC ratio. For alkali-pretreated coagulants % DOC removal
349 from the raw water was in the region of 66-77% {5; 6; 7; 8; 14} at Fe doses of 800-2600
350 mg/L with associated DOC concentrations of up to 91 mg/L and Fe/DOC ratios between 14
351 and 870 (Table 2). This compares with a value of 76% recorded for VFS dosed at a
352 concentration of 24 mg/L as Fe. The %THM-FP removal was within 18% of that determined
353 for VFS for all RCs, whilst residual turbidity was comparable (Table 2). In some cases {5; 9;
354 14} the %THM-FP removal with RCs was equal to the removal achieved with VFS. Residual
355 Fe concentrations were more variable, with generally higher concentrations than with VFS
356 but in some cases, including for the best DOC-removing RCs, residual Fe was comparable to
357 those for VFS.



359

360 Figure 3. Coagulation optimisation for DOC and turbidity removal using virgin ferric sulphate (VFS); circled

361

data point indicates dose selected for subsequent tests (24 mg/L Fe).

362

363 **Table 2 Mean percentage removals and residual treated water quality for recovered coagulants and virgin ferric sulfate.**

Sample	Recovered Coagulant	DOC removal	THM-FP removal	DOC (mg/L)	Specific DOC-THM-FP reactivity $\mu\text{g}/\text{mg}$	Turbidity (NTU)	Residual Fe (mg/L)
	Raw water	-	-	8.1	6.7	0.76	0.46
	Virgin ferric sulfate	76%	77%	2.0	6.5	0.6	0.2
3	Acidified ferric sludge	29%	<1%	5.8	9.4	9.2	12.0
4	Acidified, alkali purged	69%	64%	2.5	7.9	0.4	1.6
5	Alkali, acidified, UF, PAC	75%	73%	2.1	7.1	0.3	0.8
6	Alkali-purged, acidified, UF	72%	64%	2.2	8.8	0.3	0.3
7	Alkali, acidified, DD, PAC	66%	67%	2.7	6.7	0.6	0.4
8	Alkali-purged, acidified, DD	67%	64%	2.7	7.4	0.6	0.7
9	Acidified, UF, PAC	77%	74%	1.9	7.6	0.3	3.7
10	Acidified, UF	67%	58%	2.7	8.4	0.6	6.7
11	Acidified, DD, PAC	71%	65%	2.3	8.2	0.5	1.1
12	Acidified, DD	69%	67%	2.5	7.2	0.5	1.7
13	Acidified, PAC	74%	69%	2.1	7.9	0.4	0.2
14	Alkali-purged, acidified, PAC	77%	76%	1.9	6.9	0.4	0.2

364 Table 2 indicates that the best treatment performance is attained from PAC polishing
365 downstream of alkali pre-treatment. The related RCs {5; 14} provided 74-77% DOC
366 removal, comparable to VFS. For the DD RCs the amount of NaOH to maintain a
367 coagulation pH of 4.5 was 150 times (mol:mol) the Fe concentration for a dose of 24 mg/L
368 Fe. Aside from the additional cost this would incur at full-scale, the resulting concentration of
369 Na in the treated water (>1.4 g/L) would contravene most drinking water regulated limits
370 (DWI, 2010), though the use of lime would circumvent this issue. Acid recovery, already
371 proposed to improve the chemical efficiency of the feed side of the DD CR process
372 (Schneider, 2013), may reduce the acidity of the DD RC product and thus the requirement for
373 NaOH to achieve the pH window for coagulation. A further option is to use sodium ions on
374 the acidic strip side of the DD process to help drive the recovery of trivalent ferric ions
375 without imparting additional excess acidity to the end RC solution (Tor et al., 2004).

376
377 Reductions in THM-FP followed a similar pattern to DOC (Table 2), suggesting that the RCs
378 removed DOC of a similar reactivity. Based on previously determined DOC reactivity
379 (Keeley et al., 2014b) and DOC residuals, coagulants reducing THM-FP by ~75% would be
380 expected satisfy the THM limits of 80 and 100 µg/L for final treated water in the US and UK,
381 with THM-FPs of 65-70 µg/L (USEPA, 2009; DWI, 2010, respectively). These coagulants
382 comprised VFS (THM-FP reduction: 77%), alkali pre-treated with PAC polishing (76%
383 {14}), UF with PAC polishing (75% {9}), and alkali pre-treated with UF and PAC (72%
384 {5}).

385
386 The purest RCs appear able to match the THM precursor removal performance of
387 commercial VFS and may allow their use at full-scale to be reconsidered. Furthermore,

388 because THM-FP is a measure of the maximum possible THM levels, under more realistic
389 conditions with intermediate treatment (such as GAC or advanced oxidation) and less
390 complete chlorination, the absolute THM levels would be expected to be lower. Under these
391 circumstances the necessity and additional expensive of a two-stage RC purification approach
392 is questionable, particularly since they provide only minor improvements to THMFP ([Table](#)
393 [2](#)).

394

395 Trace metals determination in the treated waters revealed concentrations of Cu, Pb, Cd and
396 Cr to be well within the statutory potable water limits for both the US and UK ([Table S2](#);
397 Supporting Information). The slightly elevated levels for Ni recorded in some instances (up to
398 31 µg/L, cf. the UK regulatory limit of 20) were attributed to acid corrosion of the brass
399 fittings used. Mn levels were elevated above that for VFS-treated water for all RCs except
400 alkali pre-treated ones, suggesting Mn removal downstream of coagulation would be required
401 to meet the regulatory limit of 50 µg/L. However, this treatment stage is often required for
402 potable water treatment since commercial ferric coagulants can contain Mn concentrations of
403 up to 2% w/v. No work was performed to determine the phase of residual Mn in the treated
404 waters but given the low coagulation pH of the waters used in this study it is likely that pre-
405 oxidation would be required to destabilise Mn colloids for effective removal using filtration.
406 Similarly, the regulatory limit of 0.2 mg/L for Fe was exceeded for all coagulants – including
407 the virgin reagent; values ranged between 0.22 for VFS to 12 mg/L for acidified sludge.
408 However, residual iron would also be removed by the Mn removal.

409 **4 CONCLUSIONS**

410 The selectivity of a number of novel CR processes has been studied with respect to the Fe
411 and DOC concentration in the RC product, and the RC performance compared to virgin
412 reagent. PAC was found to be more effective than powdered graphite. A PAC dose of 80 mg
413 PAC/mg DOC consistently reduced RC DOC levels to below 15 mg/L with increased
414 removals to <6 mg/L at RC pH values above 1, with minimal loss of Fe. When used in
415 conjunction with alkali pre-treatment or ultrafiltration, PAC-treated RCs provided DOC and
416 turbidity removal from raw water equal to or greater than that attained by virgin coagulant.
417 UK and US regulatory limits for residual metals levels and THMs were sufficiently satisfied
418 by the purest of the RCs, albeit with some requirement for downstream removal of Mn and
419 Fe. The study outcomes suggest that a relatively simple, multistage RC purification
420 technology can be applied to recover coagulant from potable water sludge and reused for
421 potable water treatment.

422

423 Extraction through Donnan dialysis membranes yielded the highest selectivity for Fe and
424 rejection of DOC in a single process, corroborating previous research. However, the current
425 study determined that the potentially high ratio of acidity to Fe in the resulting RC demanded
426 excessive alkaline dosing to achieve the normal coagulation pH window for DOC removal, to
427 the detriment of both the process economics. In this respect, while a certain acidity level (pH
428 ~2) is required for Fe solubilisation, an excessive acid content is undesirable. The economic
429 burden of high PAC doses is also likely to be punitive.

430

431 The heterogeneous nature of organic and inorganic contaminants within raw RC dictates that
432 Fe RC of the appropriate purity is best achieved using a series of separation processes. The
433 efficacy of alkali extraction and UF appear to be similar in terms of DOC rejection per loss of
434 Fe, such that the inclusion of both in the same CR purification train is of marginal value.
435 Instead, either of these treatment method could be used upstream of a PAC polishing stage,
436 thereby reducing the DOC load on the PAC and commensurately reducing both the required
437 PAC dose and the loss of Fe by adsorption.

438

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442

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533 **SUPPORTING INFORMATION**

534 **Table S1 Sorption data used to determine the C_s and C_w values referred to in Fig. 2**

Adsorbent dose in recovered coagulant (g/L)	Powdered Activated Carbon		Powdered Graphite	
	End DOC (mg/L)	DOC removal per mass of adsorbent (mg/g)	End DOC (mg/L)	DOC removal per mass of adsorbent (mg/g)
200	12.2	0.6	17.2	0.5
100	10.3	1.1	20.3	1.0
50	12.4	2.2	30.6	1.9
20	11.8	5.6	45.6	4.0
10	12.4	11.2	73.0	5.2
1	21.9	102.8	116.4	8.3
0	124.7	0	124.7	0

535

536

537 **Table S2 Residual metal content in water treated with recovered coagulants.**

Sample		Zn		Cu		Pb		Ni		Cd		Cr		Mn		Fe	
		Value	SD	Value	S.D.	Value	S.D.	Value	S.D.	Value	S.D.	Value	S.D.	Value	S.D.	Value	S.D.
	Virgin ferric sulfate	261	41	2	1	N.D.		8	3	0.0	0.01	0.9	0.5	89	3	0.22	0.0
3	Acidified ferric sludge	235	11	3	1	N.D.		6	1	0.1	0.00	0.9	0.2	188	1	12.01	1.8
4	Acidified, alkali purged	206	38	2	0	N.D.		3	1	0.1	0.00	0.5	0.1	74	3	1.57	0.6
5	Alkali, acidified, UF, PAC	1070	10	174	5	1	0.1	24	1	0.1	0.01	1.1	0.1	82	2	0.75	0.1
6	Alkali-purged, acidified, UF	961	77	136	1	1	0.0	19	0	0.0	0.00	0.9	0.2	60	1	0.26	0.1
7	Alkali, acidified, DD, PAC	191	116	6	2	1	0.1	6	0	0.1	0.00	1.2	0.1	84	2	0.39	0.0
8	Alkali-purged, acidified, DD	131	48	6	2	N.D.		6	0	0.1	0.01	1.1	0.3	87	2	0.69	0.2
9	Acidified, UF, PAC	1360	87	215	11	N.D.		31	0	0.1	0.00	1.0	0.1	150	4	3.74	0.8
10	Acidified, UF	1407	59	240	9	0	1.1	30	1	0.1	0.00	1.4	0.1	138	4	6.72	0.5
11	Acidified, DD, PAC	293	166	4	2	N.D.		5	0	0.1	0.01	1.0	0.2	148	5	1.10	0.5
12	Acidified, DD	282	119	4	1	N.D.		5	0	0.1	0.01	0.9	0.2	152	4	1.70	1.0
13	Acidified, PAC	582	116	4	0	N.D.		15	0	0.3	0.02	0.8	0.1	582	3	0.23	0.1
14	Alkali-purged, acidified, PAC	285	126	3	1	N.D.		6	0	0.1	0.01	0.7	0.1	105	5	0.23	0.1
	Raw water	282	118	1	0	N.D.		1	0	0.0	0.00	1.2	0.0	6	1	0.46	0.1
Units		µg/L														mg/L	
DWI limit				2000		10		20		5		50		50		0.20	
USEPA limit				1300 (1000)		15				5		100		50		(0.30)	

538